



Ammonia leaching as a pre-treatment for the processing of oxidised PGM ores

By Research Candidate:

Kabwe Musonda

Supervisors:

Professor Jochen Petersen



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Department of Chemical Engineering,

University of Cape Town

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Dedicated to my Mother,

Gertrude Chembe Ndashye Musonda,

With all my love

ABSTRACT

The exploitation of near-surface deposits has resulted in the need to adjust current conventional mineral processing technologies for the treatment of low grade oxidised PGM ores. The exposure of the ore to the atmosphere leads to the formation of an oxidation layer (consisting of base metal oxides) which inhibits the flotation process that requires a clean mineral surface to be effective.

Previous studies have shown that an acid pre-treatment could lead to a 20% PGM recovery increase. Due to the corrosive nature of acid, such treatment would require additional equipment and a pre-wash. Therefore, this project investigates the use of ammonia as a pre-treatment of oxidised low grade PGM ores. Ammonia leaching has shown success in the extraction of base metals (94% and 91% Cu and Ni extraction) and is used as a wash reagent in an attempt to dissolve the oxidation layer and expose a cleaner mineral surface.

Both column leaching of whole ore and batch stirred tank reactor leaching of milled ore were investigated as pre-treatment methods for varying length of process times, and the material was subsequently tested for its flotation behaviour. The total solids, base metal and PGM recoveries were monitored in order to determine the effect of the treatment.

Due to the low extraction of base metals, less than 10%, the ammonia column treatment was unsuccessful at dissolving the oxidation layer and hence had only modest impact on the flotation process, with an indication that leaching treatment rather depresses gangue flotation than enhancing valuable recovery. In comparison, the samples treated in batch stirred tank reactors showed an actual decrease in PGM and base metal upgrade and recovery, and flotation appeared to become entirely unselective. It is suspected this was caused by significant residual ammonia interfering with the flotation reagents.

Complete extraction of valuable metals (base metals and PGMs) was also investigated using a long-term ammonia and cyanide column leach of whole ore material. This resulted in 3%, 40% and 73% total extraction of Ni, Pt and Pd, respectively.

It was postulated that Fe oxides/hydroxides (10% wt. of the ore), which were not leached by the ammonia, inhibit effective leaching and bubble attachment in both the extraction and pre-treatment tests. Further, the presence of naturally floating gangue such as talc resulted in low base metal and PGM grades. Overall, this project has

shown that ammonia is not a viable option as a chemical pre-treatment for the flotation of the low grade oxidised PGM ore investigated in this study

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'I aimed high, I was ambitious, I seized opportunities, I made opportunities, embraced successes and failures but most importantly, I leaned in'

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GLOSSARY

Acronym	Definition
AAS	Atomic Absorption Spectroscopy
BIC	Bushveld Igneous Complex
BM	Base Metal
ICP	Inductive Coupled Plasma
MSDS	Material safety data sheet
MSZ	Main Sulphide Zone
NFG	Naturally floating gangue
PGE	Platinum Group Element
PGM	Precious Group Metal
PPM	Pilanesburg Platinum Mines
SIBX	Sodium Isobutyl Xanthate
UCT	University of Cape Town
UG2	Upper Group 2

1 INTRODUCTION

Platinum group metals (PGMs) have physical and chemical properties that make them invaluable to our society today. Platinum and palladium are the focus of this study and play an important role in auto catalysts, industrial catalyst applications and the glass industry (Aspola, et al., 2012).

South Africa (SA) holds the majority of the world's PGM reserves (Liddell & Adams, 2012). PGMs are situated in several types of deposits; namely stratiform deposits, Norite intrusions, Ni-Cu bearing sill and Placer deposits (Vermaak, 1995). PGMs in SA are located in the Bushveld Igneous Complex (BIC), which falls under the stratiform deposits. Table 1 below summarises the world's leading PGM regions including SA's share.

Table 1: Summary of the world's PGM reserves in 2011, adapted from (Polinares, 2012)

Country/Region	PGM [t]	Share [%]
South Africa	62 000	95.3
Russia	1100	1.7
USA	900	1.4
Canada	310	0.5
Others	800	1.2

In the BIC, PGMs are found in the Merensky Reef, Upper Group 2-chromite Reef (UG2) and Platreef. In addition, PGMs associated with igneous deposits often contain significant quantities of base metal sulphides, in particular, iron, nickel and copper sulphide minerals.

Down to a depth of 1200m, the BIC has approximately 204 and 116 million ounces of provable and probable reserves of platinum and palladium, respectively (Cawthorn, 1999). Ore bodies are processed using conventional mining, processing, smelting and refining route (Crundwell *et al.*, 1995). The process is as follows:

- a) The mined ore is crushed, screened and is subsequently milled to liberate the PGM minerals before physical concentration is achieved by flotation.
- b) The mineral concentrate is then sent to the smelter to be further concentrated to form a matte.

- c) The matte is sent to a base metal refinery where nickel, copper and cobalt are separated and refined to obtain a PGM concentrate. This PGM concentrate is refined and the PGMs are separated (Royal Bafokeng Platinum, 2014; Crundwell *et al.*, 1995).

A summary of the conventional processing flow sheet is presented in Figure 1.

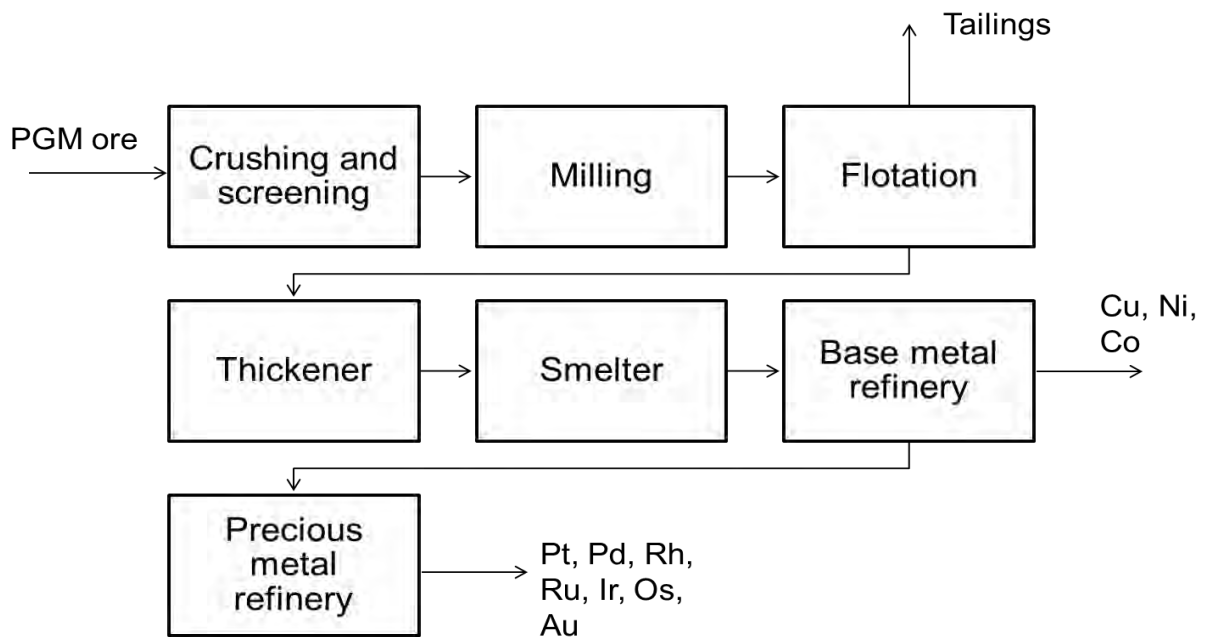


Figure 1: Summary of the conventional PGM and base metal processing routes

An increase in the depth of mining leads to higher operating costs and capital expenditure costs and also significant safety considerations. This leads to a growing need to exploit near-surface ores which maybe of a lower economic value. These deposits include low grade and oxidised ores which may not be economically viable using the conventional mineral processing methods. Additionally, an increase in labour and energy costs over the last couple of years has necessitated the development of innovative technologies to recover from otherwise uneconomical deposits (Liu & Tang, 2010)

For the processing of weathered ores, the oxidised nature of the mineral surface has been shown to affect metallurgical performance (Ramonotsi, 2011). In particular, oxidation of the mineral surface affects the recoveries of PGM in the flotation process, which relies on the surface chemical difference between hydrophobic and hydrophilic minerals (Kawatra, 2001). As a consequence of mineral oxidation during weathering, the hydrophobicity of the mineral surface may be altered due to the formation of an oxidation layer which consists of oxidation products such as base metal

oxides/hydroxides. This surface alteration results in a decrease in PGM mineral recovery. In order to improve PGM recovery during the flotation of weathered ores, Ramonotsi (2011) has suggested a chemical pre-treatment to dissolve this oxidation layer prior to flotation. Here, the acid pre-treatment improved PGM flotation recoveries and achieved a 20% improvement. However an acid pre-treatment requires a water wash prior to the flotation process which operates at a high pH levels ($\text{pH} > 9$).

Previously, a 2-stage process was investigated that included a primary acid heap bioleach of base metals, followed by a secondary direct cyanide leach of PGMs and achieved a high extraction of PGMs from low grade ore. This process included multiple stages of caustic washing between the acid leach and the cyanide leach to prevent the formation of the toxic hydrogen cyanide gas (Mwase, Petersen & Eksteen, 2012). In an attempt to eliminate the use of caustic washing and to work in an alkaline environment, Muzawazi (2013) explored the use of an ammonia heap leach to extract base metals from Platreef concentrate.

Muzawazi (2013) studied the chemical feasibility and dissolution kinetics of ammonia leaching in order to extract base metals from low grade PGMs. A successful extraction rate ($> 90\%$) was achieved for both nickel and copper. The ability of ammonia to dissolve base metals in solutions suggests that it could be used to dissolve base metals oxides in the oxidation layer and therefore dissolving this layer to create a cleaner surface for the flotation stage. This can be viewed as an alternative to Ramonotsi's (2011) acid treatment.

The aim of this study was to investigate the use of ammonia to enhance the recovery of PGMs from weathered ores. To achieve this aim, ammonia was used as a chemical pre-treatment agent for weathered PGM ores to improve flotation efficiencies. This ammonia pre-treatment was used on both coarse ore (whole ore) and milled ore in order to determine the most effective mode of treatment.

2 LITERATURE REVIEW

2.1 Platinum Group Metal Mining in South Africa

South Africa has the World's largest known resources of platinum group metals (South African government, 2014). Platinum group metals are mined near Rustenburg in the BIC, in the North West Province. The BIC extends for approximately 300-400 kilometres and contains the world's largest known deposits of platinum group metals such as platinum, palladium, rhodium, ruthenium, iridium and osmium (Jones, 1999; Cawthorn, 1999). The BIC contains approximately 62 816 tons of PGM reserves which is approximately 94% of the world total (Polinares, 2012). Figure 2 shows the location of the BIC in Africa and more specifically in South Africa. The BIC can be divided into 3 main regions, the northern limb, the western limb and the eastern limb (Schouwstra *et al.*, 2000; Voordouw & Buekes, 2000).

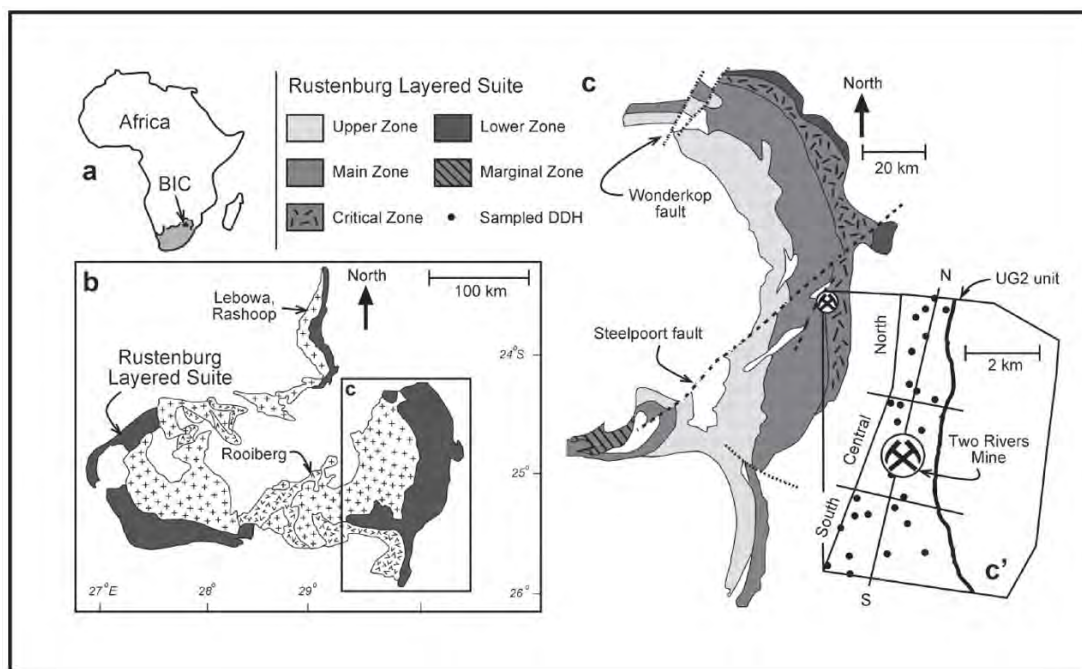


Figure 2: The location of the Bushveld Igneous Complex in Africa and South Africa (Voordouw & Buekes, 2000)

There are three major reefs that are located in the BIC; Platreef, Merensky reef and Upper Group 2 (UG 2). These ores predominantly contain platinum and palladium. Most minerals in the BIC that are of economic importance can be divided into either chromite containing minerals or sulphide containing minerals (Cawthorn, 2010).

Merensky

Until the 1970's, Merensky reef was the only source of platinum in South Africa (Cawthorn, 1999). This ore is situated between two chromite layers and is located in both the western and eastern limbs of the BIC (Cawthorn *et al.*, 2002). In comparison to the other ores, it contains a high PGM grade (80% of the platinum mined in South Africa) and also higher platinum to palladium ratio (Africa, 2008). The PGM content ranges from 4-10 g/t (Jones, 1999). Merensky ore also contains 3% base metal sulphides which are distributed as follows: pyrrhotite (Fe_{1-x}S , 45%), pentlandite ($(\text{Fe}, \text{Ni})_9\text{S}_8$, 32%), chalcopyrite (CuFeS_2 , 16%) and pyrite (FeS_2 , 2-4%) (Shamaila & O'Connor, 2008).

UG 2

The UG 2 reef group is located consistently throughout the BIC region and is rich in chromite containing minerals (Schouwstra *et al.*, 2000) The UG 2 reef is approximately 0.15 – 2.5 meters thick (Jones, 1999) and lies 200m below the Merensky reef. The UG 2 reef contains 4.4 – 10.6g/t of PGMs (Jones, 1999), which makes it the reef with the highest PGM concentration. The UG 2 ore has much lower base metal sulphides (<1%) content than the Merensky and Platreef (Solomon, 2010).

Platreef

Platreef is located in the northern limb of the BIC and relative to the Merensky and UG 2 reef; it has low platinum to palladium ratio. Platreef contains 2-5g/t of PGMs, which is considerably lower than Merensky and UG 2 (Fuerstenau *et al.*, 2007). Platreef base metal sulphides concentrations are found to be irregular in both value and distribution. The PGMs in Platreef ores occur as Pd and Pt bismuth-telluride and arsenides, which are slow-floating in comparison to PGM sulphides (Vermaak, 1995). Furthermore, there is a high association of PGMs to silicate minerals in some areas, which do not easily float. This creates a problem with using the conventional PGM extraction methods (Schouwstra *et al.*, 2000). Mining of this reef was discontinued in the early 1930s due to ore treatment issues; however extensive test work has been done since to improve the use of this ore to mine platinum (Africa, 2008).

Due to the differences in mineralogical content as shown in Table 2, they have different processing techniques. Merensky and UG 2 reefs which lie in close proximity to each other have similar metallurgical processing routes (Dunne, 2011). The Platreef ore is

geologically more complex than the other two reefs and requires innovative design to process it (Vermaak, 2005).

Table 2: Summary of the bulk mineralogy and PGM distribution in Platreef, Merensky and UG2 (Shamaila & O'Connor, 2008).

	Platreef	Merensky	UG2
Bulk mineralogy	Pyroxene	Pyroxene	Pyroxene
	Serpentine	Feldspar	Chromite
	Calc silicates		Feldspar
	Base metal sulphides	Base metal sulphides	Base metal sulphides
Base Metal distribution (mass %)	Ni ~ 67%	Ni ~ 62%	Ni ~ 80%
	Cu ~ 33%	Cu ~ 38%	Cu ~ 20%
PGM distribution	Tellurides ~ 30%	Tellurides ~ 30%	Tellurides < 5%
	Arsenides ~ 21%	Arsenides ~ 7%	Arsenides < 5%
	Alloys ~ 26%	Alloys ~ 7%	Alloys ~ 20%
	Sulphides ~ 3%	Sulphides ~ 36%	Sulphides ~ 70%
	Rest ~ 20%	Rest ~ 20%	Rest < 5%

2.1.1 Association of PGMs

PGM deposits can be divided into discrete PGMs and PGMs that are associated with other minerals. PGMs may exist in the following forms:

1. mainly sperrylite, cooperite, and braggite (relict PGMs);
2. in solid solution as relict sulphides;
3. as secondary PGM neoformations;
4. as PGE oxides/hydroxides that replace primary PGMs;
5. hosted in secondary oxides/hydroxides and silicates like iron oxides/hydroxides, manganese oxides/hydroxides and phyllosilicates;
6. hosted in sulpharsenides, arsenides and tellurides;
7. PGMs which deport to base sulphide minerals such as pyrrhotite (Fe_{1-x}S), Pyrite (FeS_2) and chalcopyrite (CuFeS_2).

Figure 3 is an example of PGM association of an oxidised ore (Becker *et al.*, 2014),

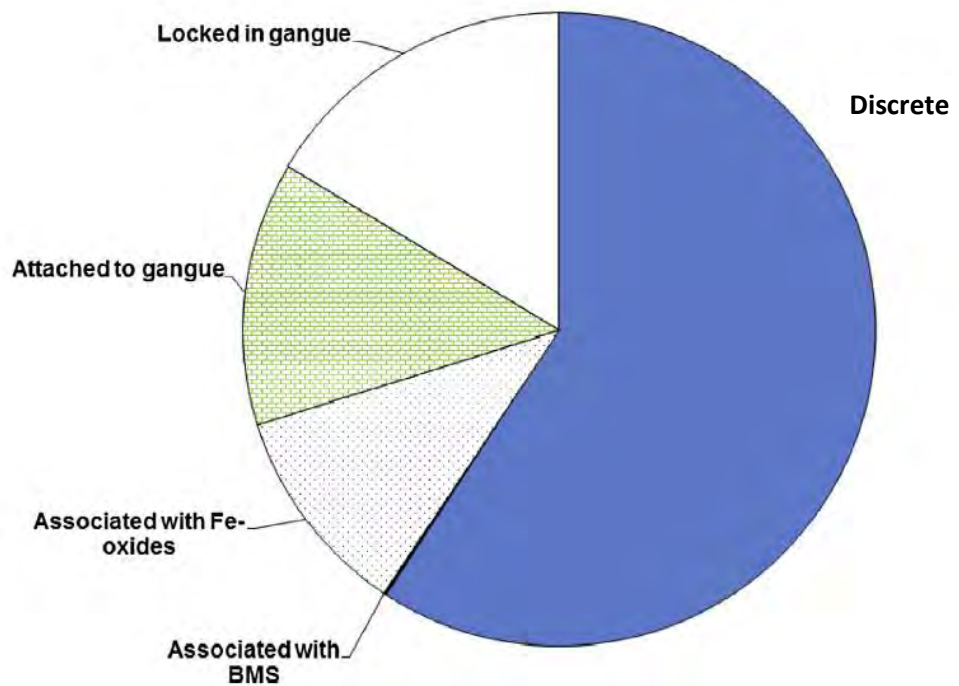


Figure 3: Association of PGMs in feed of oxidised ore adapted from Becker *et al.* (2014)

2.2 Conventional Extraction Methods

As shown in Figure 4 the conventional extraction process includes 3 main stages: comminution (crushing and screening; milling); concentration (flotation; thickening; smelter; base metal refinery; and precious metal refinery); and separation of base metals and PGMs.

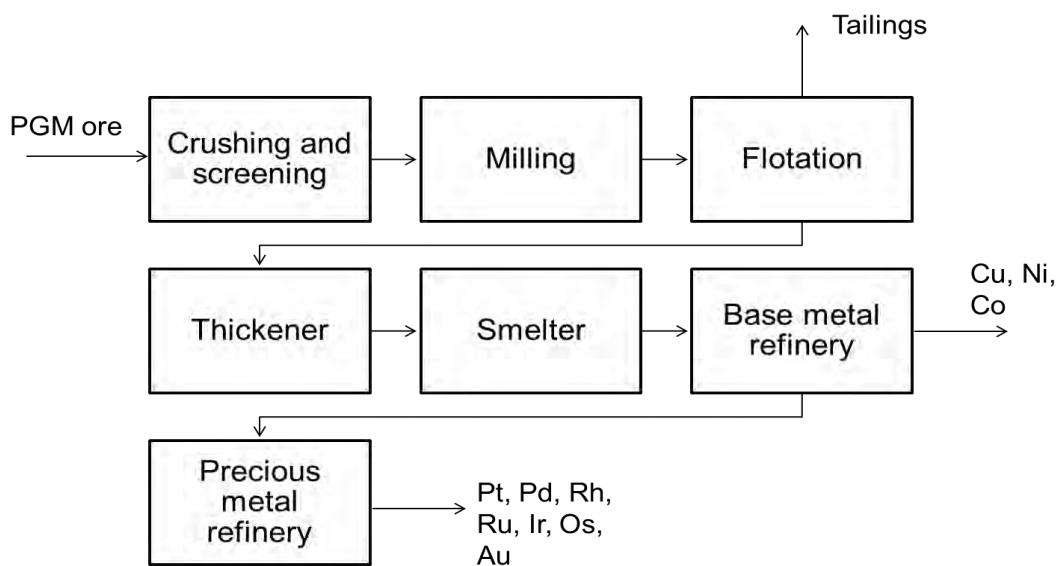


Figure 4: Summary of the conventional PGM and base metal processing routes

However, Figure 5 gives a more detailed look at the PGM processing route in South Africa.

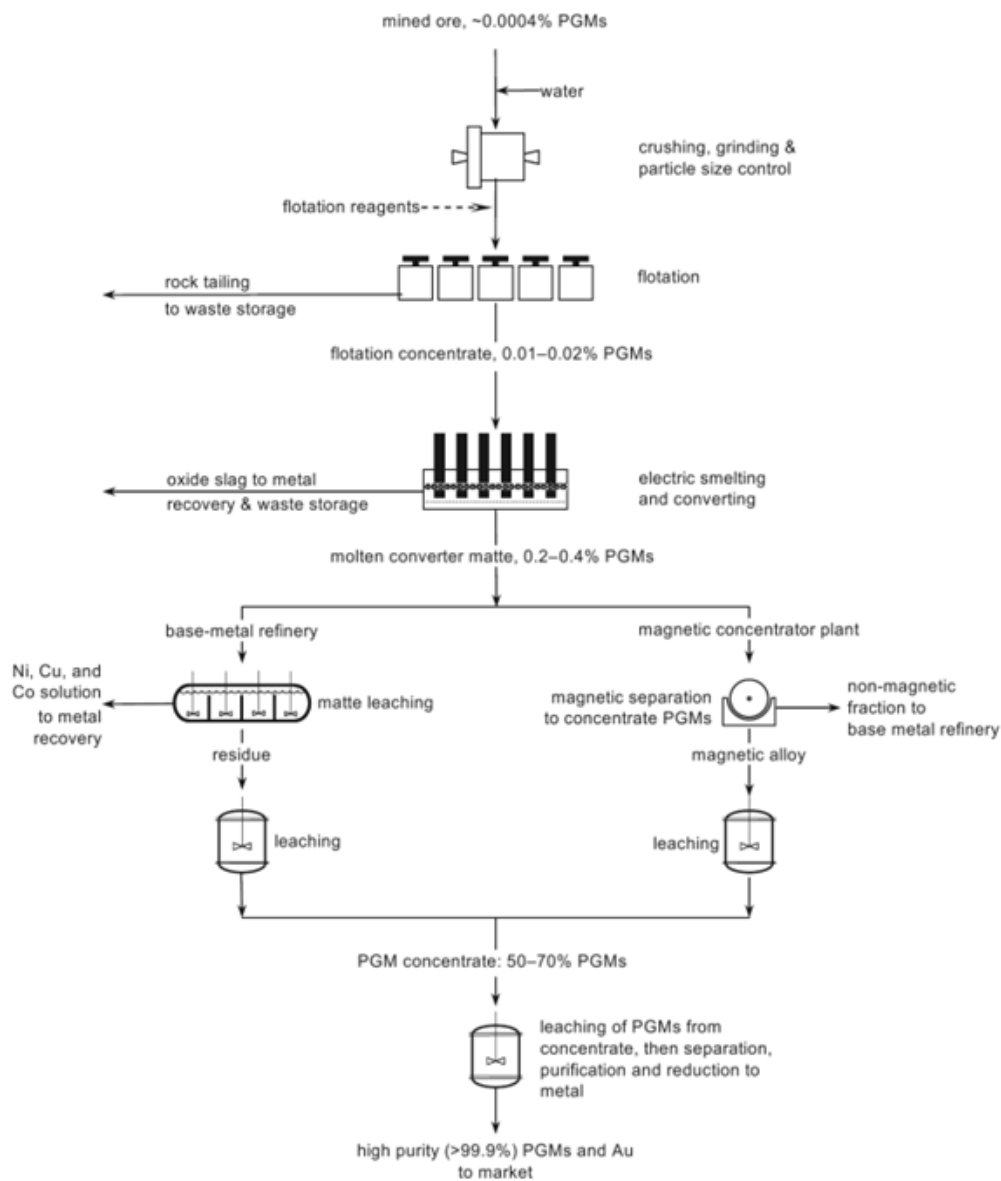


Figure 5: General flow sheet for the production of PGMs and gold in South Africa (Crundwell, et al., 1995)

Blasting and the use of explosives are used in order to remove ores from their natural beds. Blasting can also be regarded as the first stage of comminution. Comminution is a process that occurs as a sequence of crushing and grinding. Crushing reduces the particle size to such a level that grinding may occur in order to liberate /unlock the minerals. Crushing is a dry process which involves the collision of the ore with a rigid surface and grinding is usually a wet process that involves the abrasion of the ore with free motion media such as steel balls or rods (Wills, 1997).

The PGM ore is then sent to the flotation stage. Flotation is a selective process that can be used to obtain specific separations from various ores. Flotation, which was patented in 1906, permitted the mining of low grade and complex ores (Wills, 1997). Flotation yields a concentrate that contains approximately 100-200g/tonne PGMs (this is a 20 times upgrade of the ore) (Crundwell *et al.*, 1995; Cramer, 2008). This upgrading is as a result of isolating the minerals that contain PGMs in a small amount of flotation concentrate and discarding the gangue that contains little to no PGMs.

The flotation concentrates are then smelted and converted to produce a PGM rich matte. This matte has a PGM concentration of 1000-2000g/tonne, which is 10-20 times upgrade from the flotation concentrate. The smelting process is energy intensive and is not economical for low grade ore (Crundwell *et al.*, 1995).

The matte is slow cooled to allow the formation of Ni alloys that collect PGMs. The PGMs are concentrated in the Ni alloys (the PGM concentrate of the metallic alloy is approximately 60-70%) which are then magnetically separated from the non-magnetic matte. The non-magnetic matte is then leached and refined to recover Cu, Ni and Co products. The magnetic separation stage is specific to the Anglo American Platinum process, other processes leach the entire matte to recover base metals and then recover PGMs from the residue. The base metal refinery step upgrades the ore 400 times. The base metals are then separated out.

The PGM refinery step involves primary separation which separates individual PGMs from impurities and other PGMs. This is followed by secondary purification and the reduction step which reduces metal salts to pure metals (>99.9% purity) (Crundwell *et al.*, 1995).

The flotation process described in this section is one of the most important, versatile and complex mineral processing techniques. Manipulation of this process has led to treatment of ores that may have been previously considered uneconomical (low grade ores/weathered ores) (Wills, 1997). The next section will take a closer look at this flotation process.

2.3 Flotation

Froth flotation is a method of physically separating particles based on the ability of air bubbles to be attached to particles of a specific mineral surface in water slurry (Crozier, 1992).

2.3.1 Mechanics of flotation

The ore that is milled is mixed with water to form a slurry/pulp. Chemicals that assist with the flotation process such as collectors, frothers and depressants are added to the slurry and conditioned over specific times. The slurry is then introduced to the flotation cell and aerated to produce bubbles. The hydrophobic particles attach to the bubbles which then float to the surface to form a froth layer which is then mechanically collected. The hydrophilic particles remain in the pulp and form part of the tailings. These tailings may go through several flotation scavenging stages before they are discarded as waste. Figure 6 shows the set-up of a flotation cell.

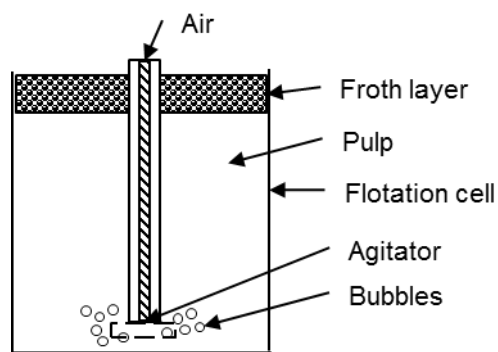


Figure 6: Schematic that shows the set-up of a flotation cell

The flotation process utilises the wettability of various minerals in order to achieve effective flotation. This means that flotation uses the hydrophobic (water repellent) and hydrophilic (wettable by water) nature of particles to determine which particles will be attached to the air bubbles and which particles will remain in the slurry (Cottrell, 1967). Figure 7 is an illustration of the selective bubble attachment in the slurry.

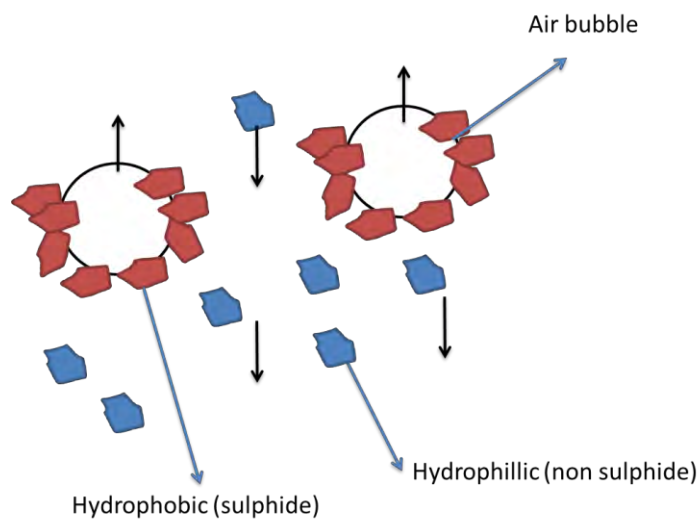


Figure 7: Selective attachment of bubbles to hydrophobic particles

This segregation is based on the surface bonding properties of the minerals. Non-polar minerals have weak molecular bonds and are difficult to hydrate (hydrophobic), Examples of these minerals include sulphur, molybdenite, diamond, coal and talc, which are all naturally floatable (Crozier, 1992). In the case of the flotation of sulphide minerals, the difference lies between sulphide minerals (hydrophobic) and non-sulphide minerals (hydrophilic). It is important to note that, any process that alters the surface properties of the minerals affects the hydrophobic or hydrophilic nature of the mineral and hence affects the flotation efficiency (Ross, 1997; Crozier, 1992).

2.3.2 Bubble attachment

In this process, the particles that are attached to air bubbles are carried to the surface, whilst particles that are not attached to air bubbles remain in the water slurry (Kawatra, 1989).

The success of bubble attachment is dependent of several physical properties. The particle and the bubble must successfully *collide*. Thereafter, the bubble can only stick to the particle if it is able to displace the water surrounding the particle, this is possible if the particle is water repellent (hydrophobic). The particle must then *adhere* to the bubble surface and be *stable* in order to be floated to the top. In order to achieve this, the use of flotation reagents is necessary (Crozier, 1992). However a combination of turbulence and gravitational forces may lead to the particle being detached from the bubble before it reaches the surface (King, 1982; Wills, 1997). In order to understand the forces involved in this system, a closer look at bubble, particle and water interface is necessary.

The contact angle (θ) is the angle between the liquid-gas and the liquid-solid interfaces. At equilibrium, the contact angle (θ) is expressed in Young's equation as,

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta$$

Equation 1

Where, γ_{SG} , γ_{SL} , and γ_{LG} are the tensions of the solid-gas, solid-liquid and liquid-gas interfaces. Figure 8 is an illustration to show the three-phase contact between the gas (bubble), liquid (water) and solid (particle) surface.

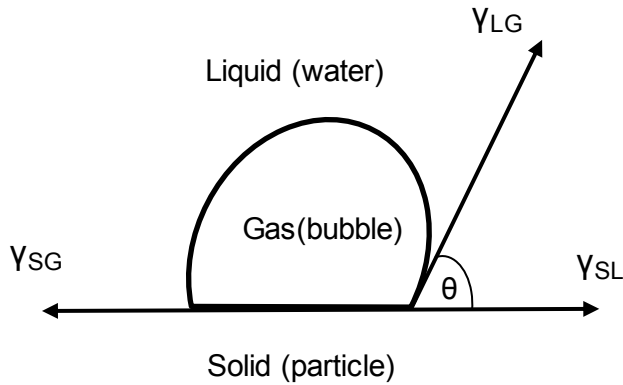


Figure 8: Illustration of the equilibrium contact angle between air, water and solid

The work of adhesion is defined as the force required to break the solid-gas interface. This force is equal to the work required to separate the solid-gas interface and produce separate liquid-gas and solid-liquid interfaces. This is shown in Equation 2

$$W_{SG} = \gamma_{SL} + \gamma_{LG} - \gamma_{SG}$$

Equation 2

Combining Equation 1 and Equation 2 gives:

$$W_{SG} = \gamma_{LG}(1 - \cos \theta)$$

Equation 3

The larger the contact angle (θ) the greater the work of adhesion between the particle and the bubble (according to Equation 3). This means that the attachment is more stable and hence the floatability of mineral increases as the contact angle increases.

This process can only be applied to relatively fine particles as they are light enough to be carried upwards by the bubbles. The bubble and particle must remain attached and float to the froth layer which overflows or is mechanically collected as concentrate (Wills, 1997). However, very fine particles may lead operational problems such as high froth stabilisation, high reagent consumption, non-specific collector adsorption and rapid oxidation, all of which may affect the grade and/or recovery of the minerals (King, 1982).

The flotation process is dependent on three parameters that are highly interrelated. These are the equipment used, the chemicals (reagents) and the entire operation (which includes feed rate, mineralogy, particle size, pulp density and temperature) (Kawatra, 1989; Fuerstenau, 1999). Most minerals are not naturally hydrophobic and therefore need the addition of flotation reagents in order to improve their hydrophobicity (Wills, 1997; Gaudin, 1939; Pryor, 1965; King, 1982).

2.3.3 Flotation reagents

Several processes make use of chemical reagents in order to alter certain particles to make them more amenable to flotation. Flotation relies on the difference of surface properties between various minerals in order to separate, the addition of reagents enables these differences to become more apparent (Wills, 1997). These chemicals include frothers, collectors, depressants, modifiers and activators (Crozier, 1992).

Collectors

Most minerals need surfactants such as collectors in order to make them more hydrophobic. Collectors are chemicals that form a hydrophobic mono-layer on certain surface of minerals which reduces the stability of the hydrated layer and therefore enables the attachment of the particle to the bubble and also increases the bubble contact angle.

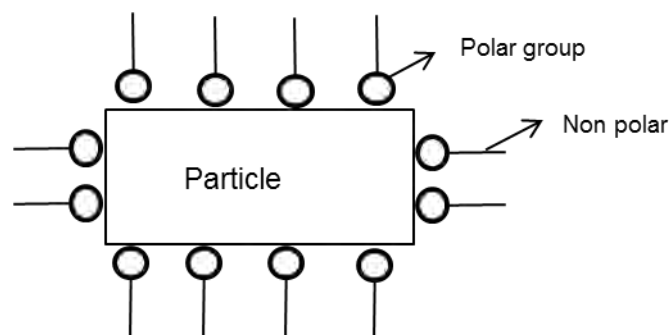


Figure 9: Collector adsorption on a particle surface

An excessive concentration of collector may lead to collector multilayers being formed on the surface and reducing the amount of hydrocarbons in the flotation pulp (Wills, 1997).

Collectors can be non-ionic, anionic or cationic (Crozier, 1992; Kawatra, 1989). Examples of anionic collectors include carboxylic, sulphates, sulfonates, xanthates and dithiophosphates (Kawatra, 1989). Depressants are chemicals that prevent the absorption of collectors on certain minerals, by doing this they allow certain minerals to float and prevent certain other minerals from floating (Cottrell, 1967).

Frothers

Frothers are compounds that prevent bubbles from bursting and the formation of a stable froth layer that allows for the effective mechanical collection of the concentrate (Kawatra, 1989). Frothers come in the form of alcohol or water soluble polymers such as propylene glycols.

Frothers are hetero-polar surface-active molecules that are adsorbed onto the gas-liquid interface of the bubble. The polar structure of the frother reacts with the water dipoles and the non-polar (hydrocarbon) group is forced into the gas phase. Frothers surround the air bubble as shown by Figure 10, and hence reduce the surface tension, hence making the bubbles more stable.

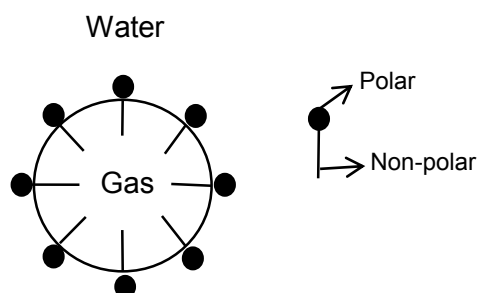


Figure 10: Schematic showing action of the frothers (right) and bubble (left) in flotation pulp (Wills, 1997)

Most flotation processes employ the use of at least two frothers in order to stabilise the froth and to control the dynamics of the flotation process (Wills, 1997).

Effect of pH

The selectivity and therefore separation of minerals is dependent on a balance between reagents and pH. Due to the stability of collectors in an alkaline medium, successful flotation occurs in an alkaline medium. In mining operations, the pH is controlled by the addition of various chemicals. In order to increase the pH, lime, sodium hydroxide and ammonia are added to the pulp and acids such as sulphuric acid are added to reduce the pH. Work done by Mezunda (2011) showed that in terms of the flotation of PGMs, the highest grade was achieved at a pH of 6 and the highest recovery was achieved at a pH of 9. This was due to the stability of the xanthate collector in alkali conditions. However, at a pH of 11 (as shown in Figure 11), xanthate collectors become highly stable and this reduces their collecting ability. Given these pH ranges, balance between reagent usage and pH is vital (Muzendu *et al.*, 2011; Wills, 1997).

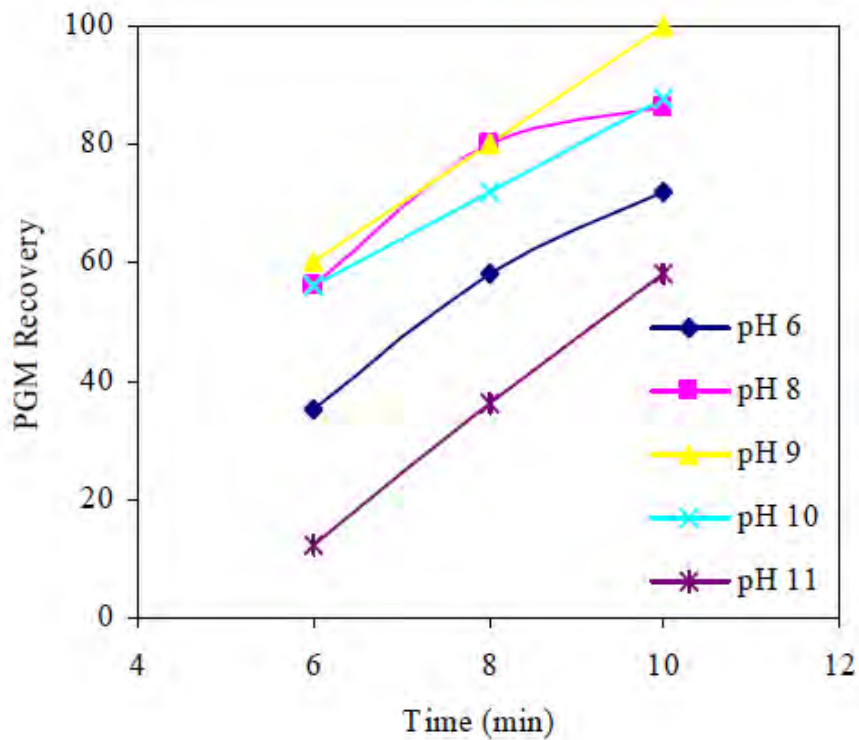


Figure 11: Graph shows the recovery of PGMs over time for various pH values (Muzendu, et al., 2011)

Further, the recovery of copper and nickel was monitored at various pH levels. Figure 11 shows the relationship between pH of the pulp and the recovery of copper and nickel. The highest and lowest copper and nickel recovery was achieved at pH 6 and 11 respectively.

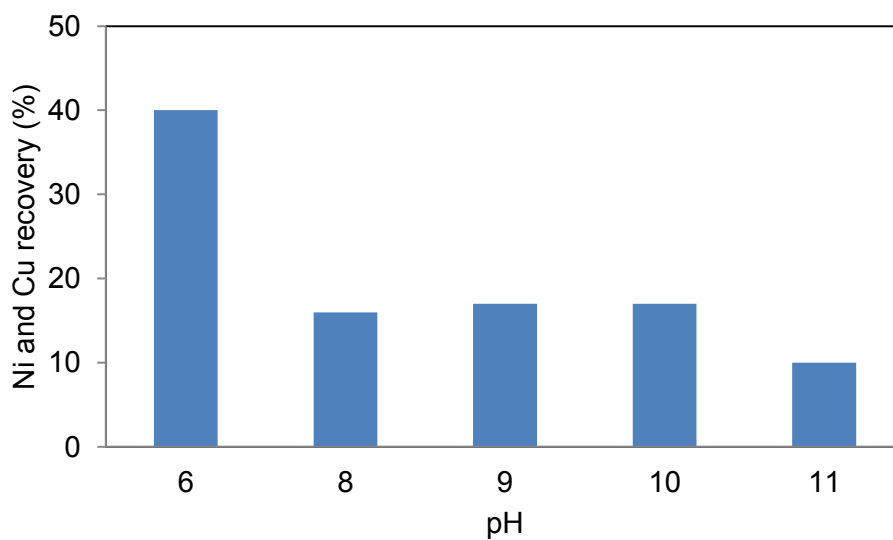


Figure 12: Graphs shows the recovery of base metals and varying pH levels (Muzendu, et al., 2011)

2.3.4 Determining success of flotation tests

There are various methods that are used to determine the success of the flotation process; these are all directly linked to the effectiveness of the physical separation. These include the ratio of concentration (F/C), %metal recovery ($((cC/fF)*100)$), %metal loss ($1-\text{metal recovery}$), enrichment ratio (c/f) and %weight recovery ($1/(\text{ratio of concentration})$) (Kawatra, 1989), where;

c = total weight of specific element in concentrate

f = total weight of specific element in feed

C = total weight of concentrate

F = total weight of feed

However, what is more useful to note is the grade and recovery of each of the valuable metals in the flotation process. In this case the grade and recoveries are determined by the following equations;

$$\text{Grade} = \frac{\text{Mass of specific element in feed/concentrate}(g)}{\text{Total mass of feed/concentrate}(g)} \%$$

Equation 4

$$\text{Recovery} = \frac{\text{Mass of specific element in concentrate}(g)}{\text{Mass of specific element in feed}(g)} \%$$

Equation 5

2.4 Weathered/Oxidised Ores

Figure 13 shows that the BIC outcrops in some regions and is exposed to the surface (Black, 2000). This proximity to the surface (Merensky and UG 2 reefs) suggests that these ores are exposed to air and are susceptible to weathering/oxidation. Weathered ores are defined as ores that contain minerals that have been oxidised.

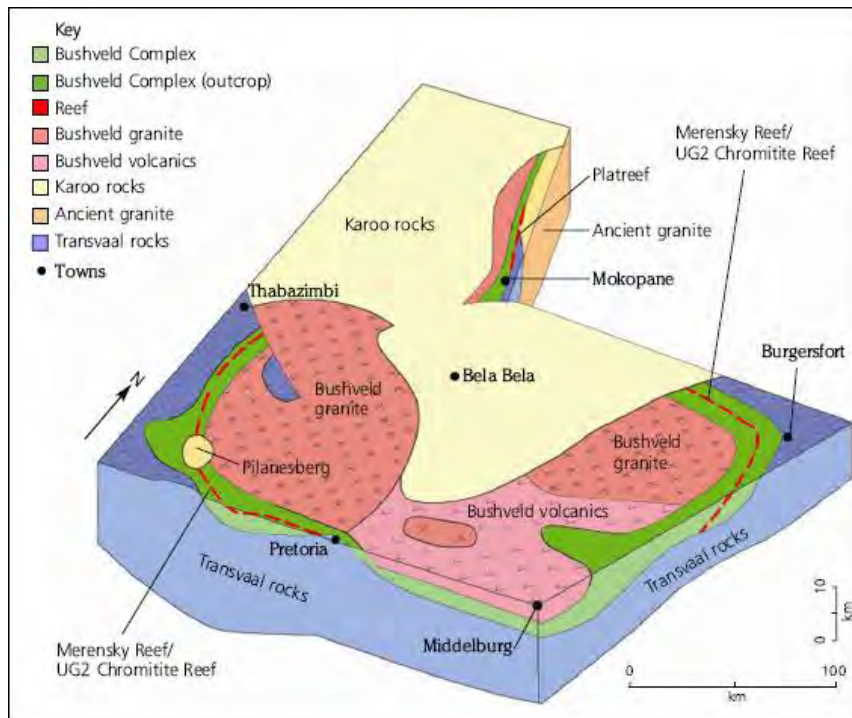


Figure 13: Schematic of the Bushveld complex showing the location and depth of the Merensky, UG 2 and Platreef ore (Cawthorn, 2010).

Figure 14 below shows how, due to atmospheric conditions, material near the surface has been altered and oxidised in comparison to ores that are found deeper beneath the surface. The upper layer shows the oxidised/weathered zone where sulphide minerals have been oxidised. The water flooding which excludes any air (oxygen) prevents the extension of the oxidised zone below the water table. The oxidised zones are usually depleted (leached) by percolating supergene water which subsequently results in a mineral enriched zone (Bartlett, 1998).

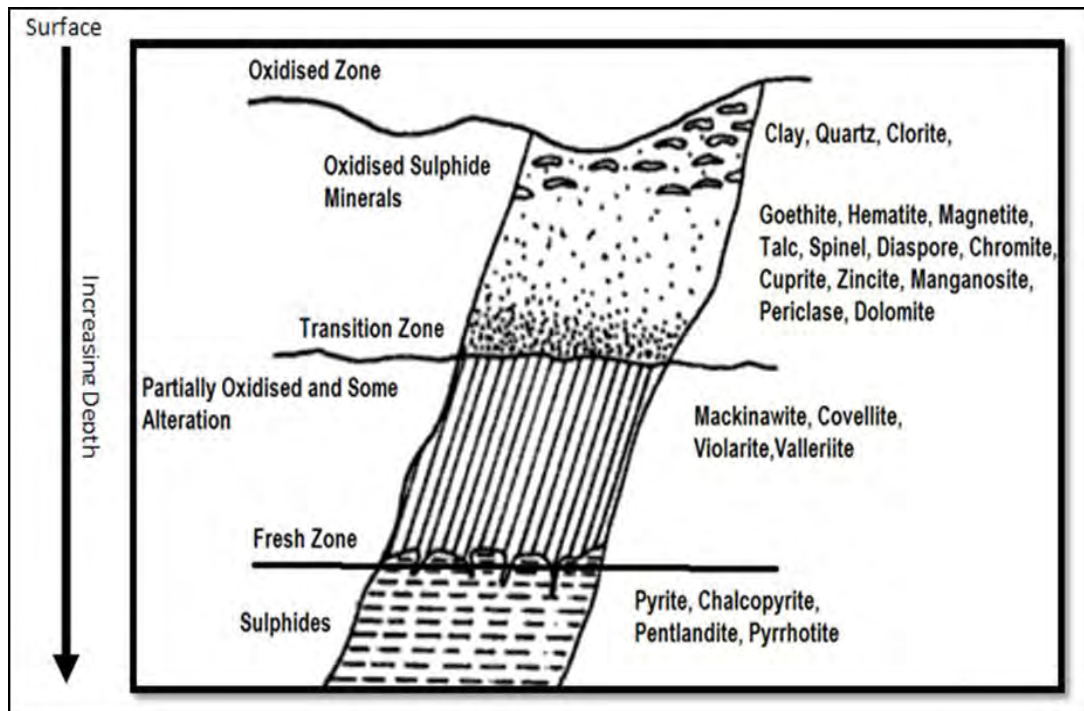
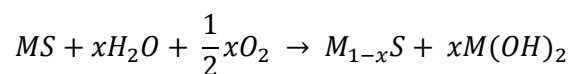


Figure 14: Model of ore deposit showing the oxidation of sulphide minerals near the surface to the sulphide deeper beneath the surface (Bartlett, 1998)

Weathering weakens the structure of the ore, and may occur as an oxidation layer or alternatively occur within the ore's cracks/crevices (pervasive oxidation).

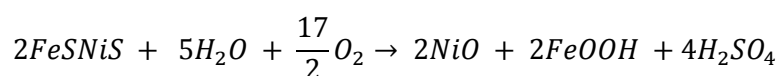
On a smaller scale, weathering occurs as a result of anodic oxidation of the sulphide minerals by the cathodic reduction of oxygen. Here, the process of oxygen reduction uses up electrons released in the oxidation of sulphide minerals. The oxidation mechanisms of sulphides are dependent of the type of sulphides and are influenced by pH, Eh and gas atmosphere (Clarke *et al.*, 1995). The basic oxidation mechanism is represented by Equation 6, where;



Equation 6

MS represents the metal sulphide.

In particular, the oxidation of pentlandite has been suggested by Equation 7 where;



Equation 7

However, Smart *et al.* (1996) recognise that the actual oxidation process is more complex. The mechanisms of surface oxidation and the subsequent formation of oxidation products can be summarised as:

1. metal deficient (sulphur rich), oxide surfaces, polysulphides and elemental sulphur;
2. oxidised fine particles attached to larger sulphide particles;
3. colloidal metal hydroxides particles and flocs;
4. layers of hydroxides and oxides;
5. formation of sulphate and carbonate species;
6. non-uniform spatial distribution with different oxidation rates.

Several investigations into the nature and composition of the oxidation process have been summarised in the following section.

2.4.1 Oxidation layer

Smart (1991) showed that the surfaces of oxidised sulphur minerals contained a thick carbonaceous layer which is hydrophilic, particularly on pyrite and chalcopyrite ores. This reduces their floatability. This study concluded that effective flotation was dependent on the amount of clean surface of particle that was able to attach to air bubbles.

Research conducted on the oxidation of pyrrhotite and pentlandite showed that pyrrhotite oxidises more rapidly than other sulphide minerals such as pentlandite (Legrand, Bancroft & Nesbitt, 2005; Koski *et al.*, 2008). In the case of both pentlandite and pyrrhotite, the study alludes to the formation of FeOOH on the mineral surface. During oxidation the iron species migrate from the bulk of the mineral to the surface and are oxidised there. Further, Ni(OH)₂ and NiSO₄ were found on the pentlandite surface. This layer hinders the flotation performance of these minerals (Legrand, Bancroft & Nesbitt, 2005).

In terms of specific minerals, Becker (2009) shows that pyrrhotite is more susceptible to oxidation in comparison to other sulphide minerals such as pentlandite ((Fe, Ni)₉S₈), pyrite (FeS₂) and chalcopyrite (CuFeS). This leads to the poor flotation of the pyrrhotite mineral. Therefore any ore body that is dominated by pyrrhotite would be more difficult to float.

Newell *et al.* (2006) showed that oxidation had more of an impact on finer size fractions (especially for pyrrhotite), and therefore lower flotation recoveries of oxidised PGM are expected with finer size particles.

2.4.2 Case study: Main Sulphide Zone (MSZ), Great Dyke

Another region in Southern Africa with an abundance of weathered/oxidised ore is the Great Dyke region in Zimbabwe. The Great Dyke consists of the world's second largest PGE reserves (160-250Mt) after the South African BIC (Obethur *et al.*, 2013). In an attempt to compare the PGE grades of the two regions, the Merensky and UG2 grades are typically 7-9 g/t and the Platreef generally has a grade of 3-4 g/t (Cawthorn, 2010; Kinnaird, 2005). This is in comparison to a grade of 3.5-3.9 g/t in the MSZ region (Obethur, *et al.*, 2013). The Main Sulphide Zone (MSZ) of the Great Dyke Zimbabwe is approximately 1.5-4 m wide and linearly extends over 550km NNE.

The MSZ is characterised by vertical patterns of base metal sulphides and PGE distribution. The MSZ is further divided into a lower PGE subzone (which is further subdivided into lower Pd>Pt zones and upper Pd<Pt zones) and an upper BMS subzone. Pervasive oxidation is often deeper than 30m below the surface

During oxidation/weathering, the metal sulphides partly release their metals and are replaced by iron oxides/hydroxides. This is particularly true for base metal sulphides. In terms of PGMs, approximately 50% of Pd is lost/ transported by acidic surface waters. Pd is evidently more mobile than Pt. PGMs are redistributed and are found as secondary PGMs in ill-defined PGM oxides/hydroxides, Fe/Mn/Co hydroxides and secondary silicates. These forms make it difficult to recover PGMs using the conventional processes.

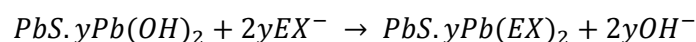
The near surface oxidised MSZ ores have large PGE potential and are a resource worth tapping into. The early attempts to mine this ore were the Old Wedza mine and the Hartley mine in the 1920's and 1990's respectively. However due to low PGE (<<50%) recoveries achieved by conventional metallurgical methods such as gravitational concentration and flotation, these attempts were uneconomical. Therefore studies have been focussed on using bulk leaching (hydrometallurgical methods) in order to recover PGMs. Success has been achieved with lixiviants such as acid and organic complexing ligands. Higher PGM recoveries (>50%) have been observed with single stage and multi-step hydrometallurgical processes. This work is closely linked to the chemical and mineralogical behaviour of weathered BIC ores (focussing on Platreef ores) (Obethur *et al.*, 2013).

2.5 Flotation of Oxidised Ores

2.5.1 Effect of oxidation on flotation

Flotation recovery rapidly decreases with increasing oxidation of mineral surfaces and leads to low PGM ore recoveries (<50%) via the conventional metallurgical method (Obethur, et al., 2013). The efficiency of the flotation process is highly dependent on the mineral surface and the addition of collector molecules that create a hydrophobic effect for successful bubble-particle attachment. On a surface level, oxidised sulphide minerals are surrounded by a surface of base metal oxides/hydroxides that inhibit collector adsorption (Boulton, 2002; Clarke *et al.*, 1995). However, it can also be noted that in some cases, the role of collectors is to counteract the hydrophilic effect of metal hydroxides rather than improve the hydrophobic nature of floating minerals (Smart *et al.*, 1996)

Smart *et al.* (1996) studied the effect of ethyl xanthate collector on an oxidised surface layer and shed some light on the concentrations of ethyl xanthate required to achieve effective removal of oxidative products and the surface layer. The authors work shows that a collector such as xanthate or EDTA can function as a surface cleaning agent. This is facilitated by the formation of iron, copper or lead hydroxyl xanthate species and demonstrated by Equation 8



Equation 8

Where the collector EX is seen to replace the OH group of the metal hydroxide group of the metal hydroxide. Prestidge *et al.* (1995) discovered that xanthate concentrations higher than the conventional flotation required concentrations were needed in order to dissolve the surface oxidation layer.

In order to completely understand the effect of oxidation on flotation, a closer look at the various techniques that have been established in an attempt to remove or counteract the effect of this oxidation layer is formed on the surface.

2.5.2 Improvement techniques

There are several techniques that have been investigated in an attempt to improve the efficiency of the flotation of oxidised ores. These include sulfidisation, ultrasonic treatments, the use of hydroxamate collectors and an acid pre-treatment.

Sulfidisation of oxidised pentlandite

In general, sulfidisation involves an aqueous conversion of a non-sulphide mineral surface to a sulphide-like mineral surface. The sulfidisation mechanism involves the formation of base metal sulphides on the oxidised mineral surface from their corresponding base metal species either through a conversion of base metal hydroxides or a precipitation process (Newell & Bradshaw, 2007).

The conversion of base metals includes the adsorption of hydrosulphide ions onto the mineral followed by the anionic exchange to create a sulphide surface (Newell & Bradshaw, 2007). Another school of thought is that the precipitation of base metal sulphides on the surface of the oxidised ore occurs particularly at low hydrosulphide concentrations (Zhou & Chander, 1993). The sulfidisation process subsequently renders the ore more amenable to flotation (Newell & Bradshaw, 2007).

The sulfidisation mechanism is dependent on the type of oxidised sulphide mineral. As an example, oxidised chalcopyrite and pentlandite ores were sulfurized by an anionic exchange which led to the formation of chalcocite-like surfaces. Alternatively, oxidised pyrrhotite appeared to be sulfurized via both an anionic exchange and the precipitation of base metals. In the case where sulfidisation of pentlandite was investigated, it was found that the flotation of oxidised pentlandite was successfully restored, largely due to the formation of copper and iron sulphides on the oxidised surface. In general, the addition of base metal ions during sulfidisation provides a viable technique for the flotation recovery of oxidised base metal and precious metal minerals (Newell & Bradshaw, 2007).

One of the main disadvantages of sulfidisation is that in a plant scenario an optimum result for this technique is highly dependent on reagent conditioning time, mixing properties and other variables which lead to poor reproducibility (Castro *et al.*, 1974).

Ultrasonic treatment

Ultrasonic treatment involves the intense shaking of mineral particles to remove the surface oxidation layer in order to expose a cleaner surface for the flotation process. A mineral that responds positively to the ultrasonic treatment has mainly undergone surface level oxidation. Figure 15 shows the effect of an ultrasonic treatment on the flotation recoveries of an oxidised Merensky type ore (Newell *et al.*, 2006).

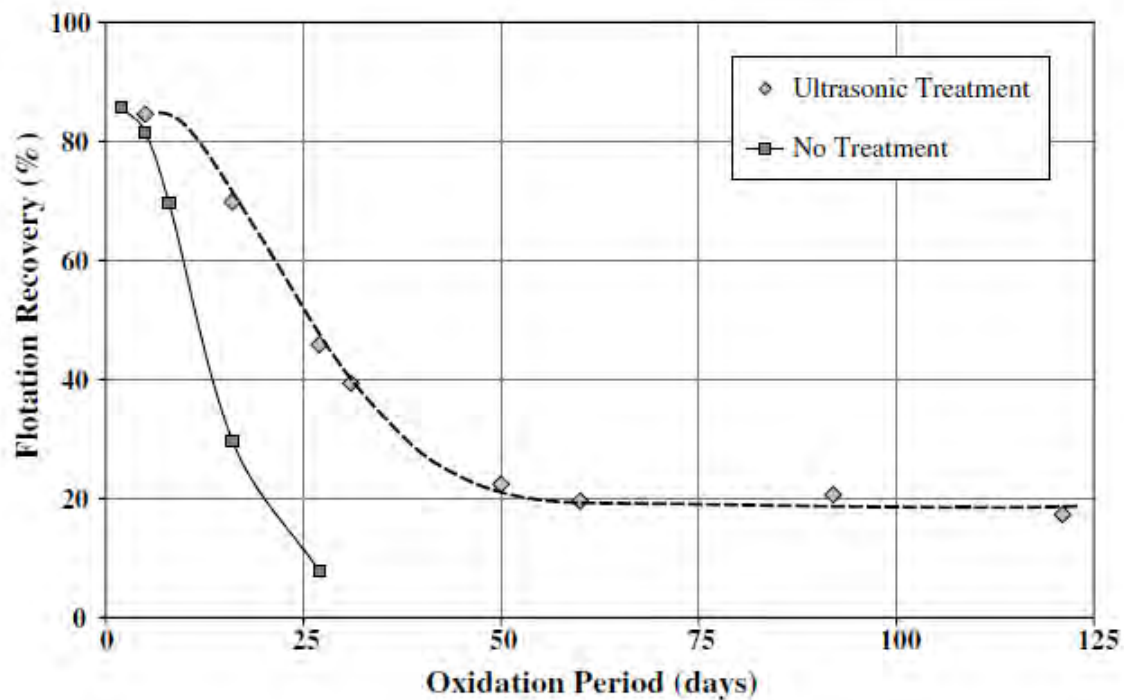


Figure 15: The effect of the ultrasonic treatment on the flotation of oxidised ores (Newell *et al.*, 2006).

Figure 15 shows that the removal of the surface oxidation layer by an ultrasonic treatment improves the flotation recoveries of the ore, when comparing the ultrasonic treatment recovery curve to the no treatment recovery curve. Further, what is important to note is that for longer oxidation periods, the surface alteration results in a significant drop in the recovery for both treatments. Ultrasonic treatment would work well with surface oxidation but would be less effective in cases where oxidation is pervasive and occurs in cracks and crevices. However, little work has been done in terms of commercialising this process.

Hydroxamate collector

In the case of copper ores, various collectors such as organic complexing agents, fatty acids, fatty amines and petroleum sulphonates are used in the flotation of oxidised ores. Even though these chemicals showed promising results in the laboratory, their lack of selectivity over carbonate gangue minerals such as dolomite and calcite makes them unsuitable (Deng & Chen, 1991).

Copper oxide ores do not respond favourably to traditional collectors, therefore require alternative processing techniques. The use of alkyl hydroxamate as a metal oxide mineral collector has been in use since the early 1940s (Lee, Nagaraj & Coe, 1998).

Today, several operations are currently using alkyl hydroxamates synthesized by Ausmelt is supplied as an alkaline chemical. The hydroxamate collector is potassium hydrogen n-octano hydroxamate (AM28 made by Ausmelt Limited). It is a non-hazardous product that works best at a pH above 6. It forms a relatively thick hydrophobic layer on mineral surfaces (Lee *et al.*, 2009)

An investigation by Lee *et al.* (2009) has showed that using AM28 in conjunction with traditional sulphide collectors such as Xanthate can successfully simultaneously recover copper sulphides and oxides by flotation from a blend of sulphide and oxide ores. An improvement in the recovery of base metals such as copper, would result in an improvement in the PGMs that are associated with base metals.

However, in an investigation of the use of alkyl hydroxamate (AM28) co-collector in the treatment of oxidised ores, Becker Wiese & Ramonotsi (2014) discovered that a 39% improvement in PGE recoveries was due to increased froth stability and water recovery rather than the selective action of the collector.

Acid pre-treatment

Another way of improving the flotation of oxidised sulphide mineral is to use a chemical to dissolve the oxy/hydroxide layer, exposing a clean sulphide layer for effective collector adsorption. The technique of using low concentrations of sulphuric acid to digest and dissolve the layer was investigated by Ramonotsi (2011). This process, which is called pre-leaching or non-oxidative leaching, requires the treatment of the ore using a less-than stoichiometric amount of H₂SO₄. Stoichiometric amounts were used to maintain the appropriate pH level for the flotation cell.

Results of the investigation show that the acid pre-leach improved flotation recoveries by over 20%. However, these treatments also led to poor grade-recovery curves as the acid was non-selective and was suspected to activate gangue minerals (Ramonotsi, 2011). Further, due to its corrosive nature, new infrastructure would have to be established to make this a viable option and a neutralising stage would have to be introduced in order to raise the pH of the slurry (flotation cells are operated at a pH of 9).

2.6 Ammonia Leaching

Leaching is defined by the process of extracting soluble minerals from a solid (ore) by means of a solvent. This can be by either opening up of the ores to solubilize the metal

values or leaching easily soluble constituents such as gangue in order to obtain a more concentrated ore (Habashi, 1999; Gupta, 2003).

According to Habashi (1999), the choice of a leaching reagent is dependent on several factors. The solubility of a reagent is its ability to dissolve the required mineral. For economical purposes, not only must a lixiviant be able to dissolve the required mineral but also be moderately selective, as this minimizes reagent usage. Another important aspect of regeneration of a reagent is the ability to regenerate and possibly reuse a solvent that reduces both operating costs and any environmental impacts that maybe associated with reagent disposal.

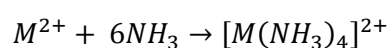
In most cases sulphuric acid is the most common choice, however its ability to dissolve gangue material increases the amount of acid consumption, thus a more selective reagent is needed for such deposits (Liu & Tang, 2010).

2.6.1 Dissolution mechanism

Ammonia leaching is based on its ability of aqueous ammonia to form amine complexes which stabilise metals in solution at alkaline pH. With the exception of molybdenum, ammonia forms water-soluble complexes with transition metals. This forms the chemical core of the use of ammonia in metallurgy. (Milbourne, et al., 2003; Welham, et al., 2010; D & Madigan, 1975).

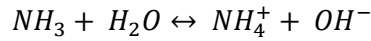
Ammonia leaching requires an oxidant to oxidize sulphide minerals. Several oxidants such as bromates, chlorates, oxygen, peroxides and persulfates have been utilised in the leaching of copper sulphides. Oxygen (which can be supplied as compressed air), being the least expensive, has been widely used in the dissolution of base metal sulphides (Bell, et al., 1995).

Ammonia can exist in several forms, and these include free ammonia (NH₃), ammonium ions (NH₄⁺) and metal amines. For the leaching of base metals, free ammonia can be considered as the active complexing agent and reacts with metal ions (Habashi, 1993). Equation 9 shows this reaction.



Equation 9

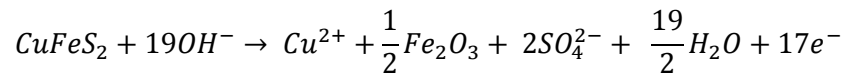
Ammonia is very soluble in water and the equilibrium in Equation 10 demonstrates the solubility of ammonia in water (Osseo-Asare *et al.*, 1983).



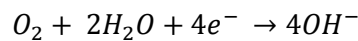
Equation 10

In order to fully understand the dissolution process of base metals sulphides by ammoniacal solutions, the dissolution of chalcopyrite will be used as an example to better illustrate the process. The leaching of chalcopyrite can be illustrated as a redox reaction with the oxidation of the chalcopyrite by the reduction of oxygen (oxidant).

Equation 11 and Equation 12 show the anodic and cathodic half reactions (half-cell reactions) are used to demonstrate the redox reaction that occurs in order to form the metal ion and is facilitated by the oxidant (oxygen in this case).

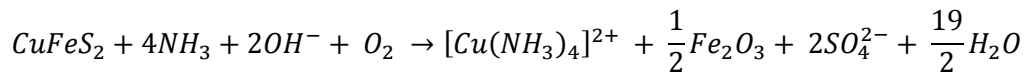


Equation 11



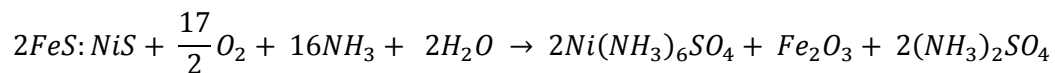
Equation 12

The overall reaction is given as:



Equation 13

Another example of the dissolution of base metal sulphides is the extraction of nickel from pentlandite which is shown by Equation 14



Equation 14

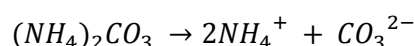
(Beckstead & Miller, 1977; Bell, et al., 1995; Gupta & Mukherjee, 1990; Muzawazi, 2013)

Most sulphide reactions are known to occur at relatively slow rates; however, these reactions can be catalysed by the presence of a metal catalytic ion. In order for a metal ion to act as a catalyst, it must be incorporated in the surface layer of the metal sulphide lattice and must also be able to form a redox couple to catalyse the reaction between

the sulphide and the oxidant (such as Equation 13). A study of the oxidative ammonia leaching of sphalerite (ZnS), indicates that the catalytic activity of Cu(II) is due to the redox couple Cu(II)/Cu(I), where the copper-amine complex oxidises the ZnS and is oxidised by oxygen (Ghosh, et al., 2003).

Other base sulphides such as covelite, bornite and chalcocite have better extraction rates than chalcopyrite due to the passivation caused by the formation of hematite (iron oxide) on chalcopyrite surface. Iron is superficially dissolved by the formation of a ferrous ammonium complex which rapidly precipitates as ferric oxides/hydroxides. These hydroxides are known to affect the kinetics of the base metal sulphides (Gupta & Mukherjee, 1990). More on the passivation layer will be discussed in section 2.6.5.

Further, in order to obtain higher extraction rates, a combination of NH₃ and NH₄⁺ salts is known to strengthen the buffering ability (maintain a desirable pH) of the solution by the addition of ammonium ions (Tozowa, et al., 1976; Gupta & Mukherjee, 1990). This is facilitated by the dissolution of ammonium salts shown in Equation 15



Equation 15

The dissolution of the salt in Equation 15, results in an increase in the ammonium ion concentration, which according to Le Chatelier's principle will drive to the left and increase the free ammonia concentration. An increase in free ammonia would increase the chances of the formation of metal-amine complexes and an increase in OH⁻ would maintain an alkali environment and suitable pH. Figure 16 shows that a specific NH₃/NH₄⁺ ratio is required in order to maintain a certain pH and therefore favourable leaching results.

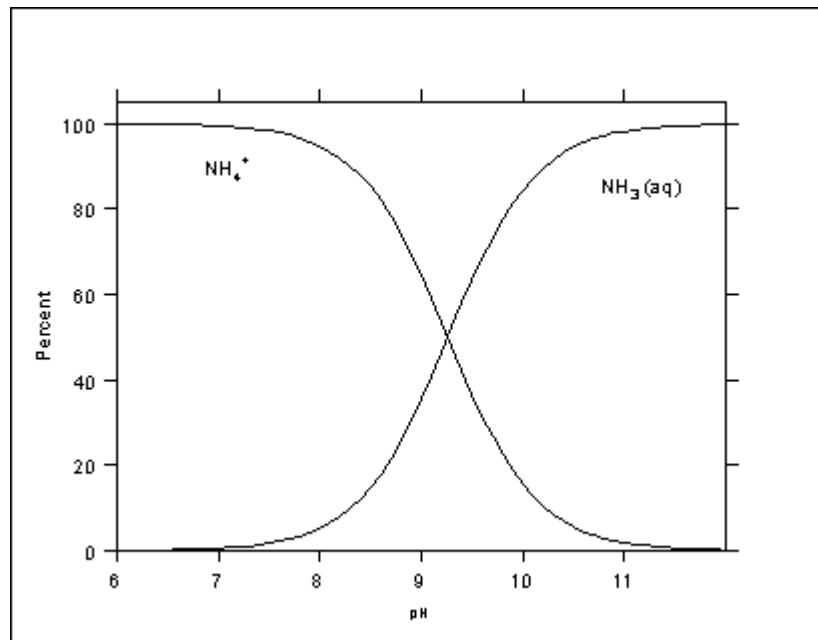


Figure 16: Percentage of NH₃ and NH₄⁺ as a function of pH (Illinois State Water Survey, n.d.)

Therefore the ratio of NH₃/NH₄⁺ has an important role to play in achieving higher extraction rates. According to Figure 16 and Figure 17, in order to facilitate the formation of the stable copper-amine complex, [Cu(NH₃)₄]²⁺, a pH of approximately 9.4 is required, this corresponds to a NH₃/NH₄⁺ ratio of approximately 1 (Muzawazi, 2013).

2.6.2 Thermodynamics of ammonia leaching

The chemistry of ammonia leaching in hydrometallurgy is not only defined by Equation 9 to Equation 13, but also by the behaviour and stability of the metal-NH₃-H₂O complex at different pH, which is depicted by the various Eh-pH diagrams (Takeno, 2005). Eh-pH diagrams provide useful information with regards to the stability of the various metal phases at various oxidation potentials and pH's. The behaviour of the copper and nickel complex will be looked at in greater detail (Meng & Han, 1996).

In the Cu-NH₃-H₂O system, the species present are NH₃, NH₄⁺, H⁺, Cu²⁺, Cu⁺, Cu(OH)₃⁻, Cu(OH)₄²⁻, Cu(OH)₂²⁺, CuNH₃⁺, Cu(NH₃)₂²⁺, Cu(NH₃)₂⁺, Cu(NH₃)₂²⁺, Cu(NH₃)₃²⁺ and Cu(NH₃)₄²⁺. The stability of these complexes is dependent on the pH and Eh values. Figure 17 shows that at a pH of 9-11, the dominant soluble copper complexes are Cu(NH₃)₄²⁺ and Cu(NH₃)₂⁺. Work by Caron (1950) and Peters (1976) indicate that the Cu(NH₃)₄²⁺ is stable in the pH range of 8-11.

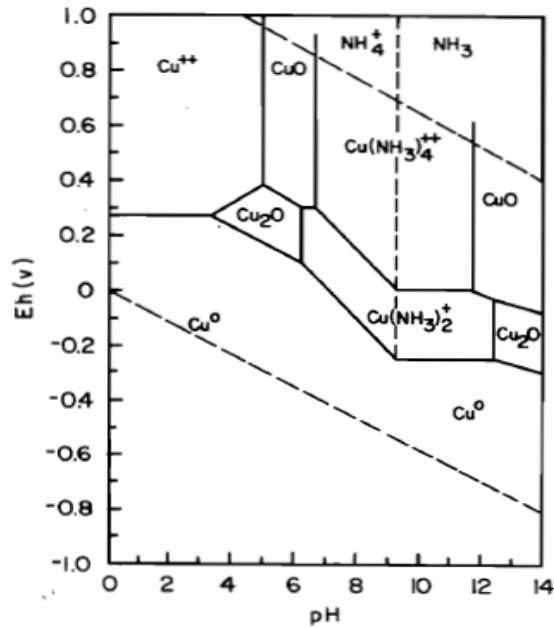


Figure 17: Eh-pH diagram for the copper-ammonia-water system at 25°C and 101.3 kPa (Takeno, 2005)

According to Meng & Han (1996), the ratio of these two species is related to the oxidation potential of the system and is described as:

$$Eh = 0.074 - 0.1182 \log[NH_3] + 0.0591 \log \frac{[Cu^{2+}]}{[Cu^+]}$$

Equation 16

The Ni-NH-H₂O chemistry is slightly different from the chemistry of other base metals such as copper and cobalt in terms of the solubility of certain species and position in the respective Eh-pH diagram. The predominant species in the Eh-pH diagram is the Ni (NH₃)₅²⁺ in the pH range of 8.5-10.5.

Deviation from these pH ranges will result in the oxidation and therefore precipitation of nickel and copper oxides in solution. However, the formation of a stable ferrous amine complex occurs between a pH of 9.2 and 9.7. This short window indicates that in the ranges that stable copper and nickel amine complexes are formed, the ferrous amine complex is quickly oxidised and precipitated (contributing to the passivation layer).

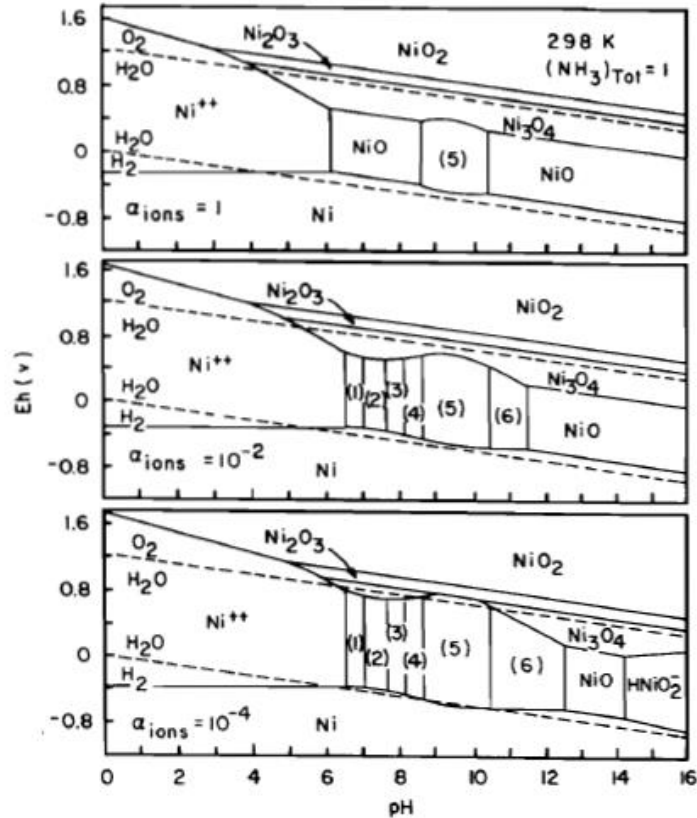


Figure 18: Eh-pH diagram for the Nickel-ammonia-water system at 25°C and 101.3 kPa. 1. Ni (NH₃)²⁺ 2. Ni (NH₃)₂³⁺ 3. Ni (NH₃)₃²⁺ 4. Ni (NH₃)₄²⁺ 5. Ni (NH₃)₅²⁺ 6. Ni (NH₃)₆²⁺ (Takeno, 2005)

2.6.3 Leaching kinetics

The dissolution of metals in ammoniacal solutions is electrochemical in nature, the oxidising agents take electrons from the metal (cathode side) and the metal emits electrons. According to Meng and Han (1996), the overall reaction is controlled by the oxygen diffusion through the mass transfer boundary layer to the cathodic sites.

The concentrations of both ammonia and oxygen play an important role in determining the overall rate. Here, the rate expression was observed as (Sohn & Wadsworth, 1979) as:

$$rate = \frac{2AD_{O_2}[O_2](k_{NH_4}[NH_4^+] + k_{NH_3}[NH_3])}{8AD_{O_2}[O_2] + \delta k_{NH_4}[NH_4^+] + \delta k_{NH_3}[NH_3]}$$

Equation 17

Where k_{NH_3} and $k_{NH_4^+}$ are the rate constant and δ is the thickness of the diffusion layer. The effect of various kinetic variables such as temperature, ammonia concentration,

pulp density, leaching time and particle size has been widely investigated and will be further discussed.

Effect of temperature

Studies have shown that copper extraction is highly dependent on temperature. As temperature increases, the rate of the reaction and hence the rate of copper extraction increases (Bell, et al., 1995). An increased temperature leads to an increase in kinetic energy of the particles, which leads to more collisions and hence more reactions.

Work done by Muzawazi (2013) showed an increase of Cu and Ni extractions by 19% and 30% respectively after a 20°C increase in operating temperatures. Temperature variable experiments were used to calculate initial rates and therefore activation energies in work done by Beckstead and Miller (1977), Bell *et al.* (1995) and Muzawazi (2013). Beckstead and Miller (1977) and Bell *et al.* (1995) both concluded that this electrochemical reaction was limited by surface reaction mechanisms. However, Muzawazi (2013) concluded that Ni extraction was diffusion controlled and Cu extraction was both surface kinetics and diffusion controlled. Precautions must be taken when dealing with temperatures above 50°C as ammonia losses and hydrolysis may occur (see section 2.6.5)

Effect of ammonia concentration

An increase in ammonia concentration results in an increase in the amount of metal extracted. Work by Lui & Tang (2010) shows an increase in Cu extracted from 20 – 65% when the total ammonia concentration was increased from 1M-3M. However, what is interesting to note is that an increase above 3M had no impact on the extraction rate. Muzawazi (2013) showed that below 3M, the dissolution reaction (for both Cu and Ni) was first order with respect to ammonia concentration. However, above 3M, the dissolution reaction was independent of the ammonia concentration. Beckstead and Miller (1977) reported that rate of extraction was independent of the ammonia concentration.

Effect of pulp density

The pulp density can be described as the solid/liquid ratio. A lower pulp density means that there is more reactant available for the leaching process, therefore higher extraction rates (Bingol, et al., 2005). Muzawazi investigated the effect of pulp density in the ammoniacal leaching and found a marginal increase in total extraction with an increase in pulp density from 1-5%. This was due to an increase in the $[Cu(NH_3)_4]^{2+}$

concentration as it acts as a catalyst. A marginal decrease in the extraction was noted when the pulp density was increased to 20%. Overall, the effect of pulp density (1-20%) over a 5 day leaching period between was negligible.

Effect of leaching time

Leaching investigations show that for a period of up to 4 hours, copper recoveries increase with increasing leaching times. Initial leaching and dissolution of the ore is very fast, approximately 40% within the first 5 minutes and after 30 minutes of leaching, copper recovery increases at a slower rate. What is interesting to note is that under low oxygen pressure, the dissolution of copper is a linear function of the leaching time (Bingol *et al.*, 2005).

Effect of oxygen partial pressure

Other factors such as partial pressure of oxidant which would be oxygen in this case have been examined in literature. Earlier investigators found that because rate was proportional to the stirring velocity (batch stirred tank reactors), this indicated that the rate was partly controlled by the diffusion of oxygen through the solution. Alternatively it was observed that due to the formation of a coating layer around the copper surface, the rate may be determined by the diffusion of oxygen through this surface layer.

In order to investigate the role of oxygen in the chemical reaction, Halpern (1953) maintained a high oxygen partial pressure above the solution to ensure that no coat around the surface was formed and ensured the rapid transport of oxygen through the solution. The results showed no dissolution occurred in the absence of oxygen. Further, the rate was directly proportional to oxygen pressure, at low oxygen pressures and was independent of oxygen pressures at higher oxygen pressures (>3atm). This was illustrated by Figure 19.

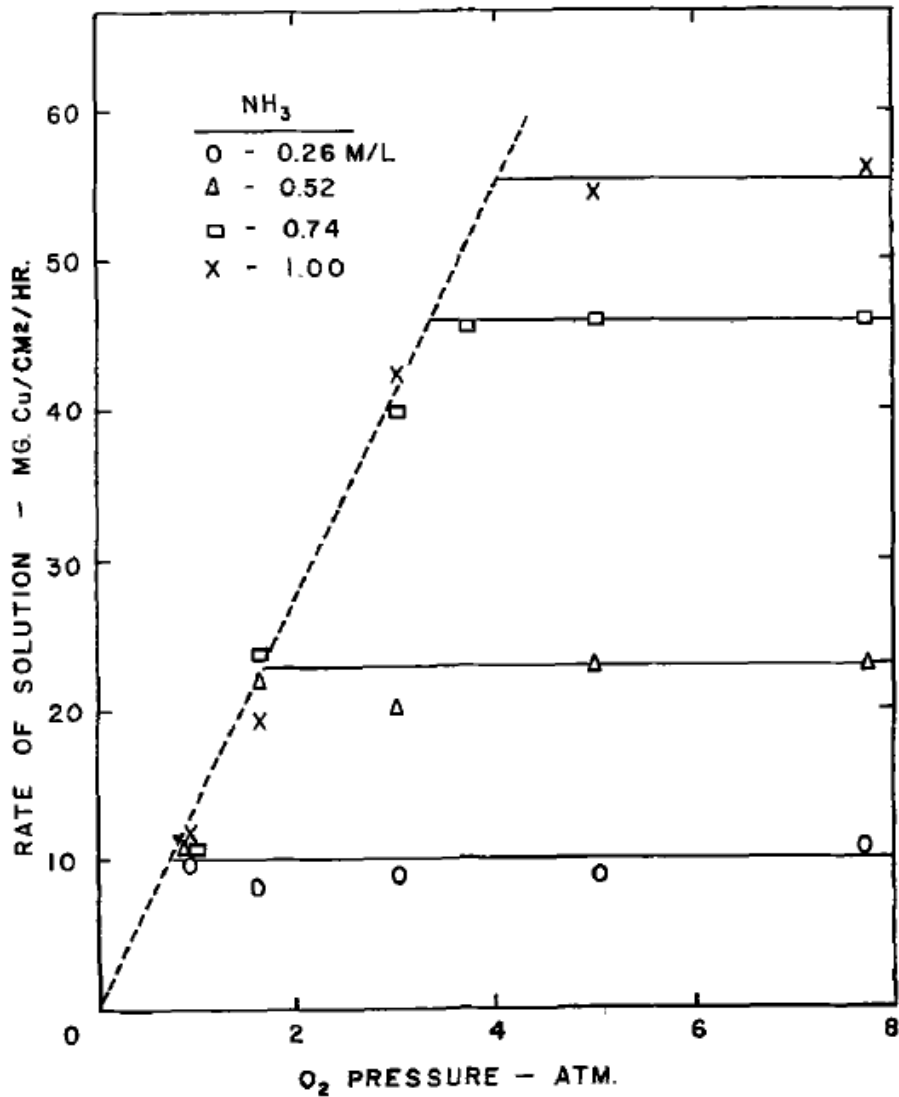


Figure 19: The effect of oxygen pressure on the rate of copper extraction (Halpern, 1953).

Similarly, Bell, Welch & Bennett (1995) concluded that the extraction process would not proceed without oxygen and the effect of oxygen after the initial extraction phases is minimal. This was explained by an adsorption process that leads to an oxygen saturated layer surrounding the particles.

In a comparison between the gas-liquid mass transfer in columns and tanks tests, Muzawazi (2013) discovered that the rate of leaching was limited by the oxygen mass transfer in the columns however this was not conclusive in the tank reactors.

Effect of particle size

The rate of dissolution of a solid is determined by one or more of the following steps: mass transfer of the lixiviant from the solution to the surface of the particle, mass transfer of the products from the particle surface and mass transfer within the pore of

the particle (if dealing with a porous particle). Therefore the dissolution rate and the leaching mechanism depend highly on the size of the particle (R , the radius of the particle).

Table 3: Shows the effect of particle size on the rate and model of dissolution (University of Cape Town, 2008)

Model	Rate controlling process	Variation of τ
Shrinking particle without product layer	Chemical reaction	R
	Aqueous phase diffusion	R
Shrinking particle with product layer	Chemical reaction	R
	Aqueous phase diffusion	R
	Product layer diffusion	R^2

Where τ represents the time taken to completely dissolve a particle with radius, R (University of Cape Town, 2008).

Higher copper extraction rates are expected when dealing with samples of a smaller particle diameter. This is simply explained by an increase in surface area and hence diffusion of the lixiviant through the sample (Liu & Tang, 2010).

According to results from Bell *et al.*, (2005), the most significant leaching parameters for the ammonia leaching are temperature, oxygen partial pressure and ammonia concentration.

2.6.4 Advantages of ammonia leaching

Ammonia leaching alleviates corrosive problems that are usually caused by other leaching reagents such as acidic solutions (Bell *et al.*, 1995). Ammonia solutions are highly selective (do not dissolve gangue materials) and hence in terms of usage for the dissolution of specific base metals, it is an economical choice. Lastly, the availability and price of ammonia is low in comparison to most of the other solvents (Gos & Rubo, 2001). Another advantage of using ammonia arises when dealing with PGM lixiviant such as cyanide, thiosulphate. The optimum operating conditions are based in an alkali environment and hence using ammonia (as a first stage base metal lixiviant) is ideal (Mwase, 2009). In general, it has been indicated that ammonia's low cost, availability and selectivity makes it attractive (Chang & Liu, 1998).

2.6.5 Limitations of Ammonia leaching

Loss of solvent

The volatility of a liquid is the tendency of molecules to escape from the liquid phase into the gas phase (the ease with which it can be vaporised). Vaporisation occurs when the temperature of a liquid is high enough that the vapour pressure of the liquid is equal to the atmospheric pressure. This point is defined as the normal boiling point and the temperature is known as the boiling point temperature. This dependency on temperature and pressure is defined by the Clapeyron equation:

$$\frac{dP}{dT} = P \cdot \frac{\Delta_{vap}H}{RT_{vap}^2}$$

Equation 18

Where P is the pressure, T is the temperature, $\Delta_{vap}H$ is the enthalpy of vaporisation, and R is the gas constant (Atkins & Paula, 2010).

Ammonia is highly volatile and has a low boiling point and hence evaporates easily. This leads to ammonia losses in the extraction process and hence impacts the rate of extraction. Therefore in order for the effective extraction of base metal at elevated temperatures, a closed system (where pressure is controlled) would be required to prevent ammonia losses via evaporation. High temperature experiments would need to be operated at higher pressures to reduce the chances of ammonia losses (Kuhn *et al.*, 2009).

Muzawazi (2013) found that ammonia losses increased as the temperature and concentration of ammonia in both the columns and batch stirred tank reactors. The rate of ammonia loss was 0.18mol/L/day and 0.55mol/L/day of ammonia for the stirred tank reactors and the column reactors respectively (8M ammonia concentration at ambient temperatures).

In terms of the environmental impact, effluent limits are dependent on various locations, for instance the city of Cape Town has a limit of 10mgN of ammonia per litre of effluent disposed (City of Cape town, 2008). Ammonia would need to be regenerated and reused as it cannot be easily disposed of (Gos & Rubo, 2001).

Passivation layer

One of the major problems identified with the development of ammonia solution for leaching of copper is the build-up of a ferric oxide reaction product layer at the mineral

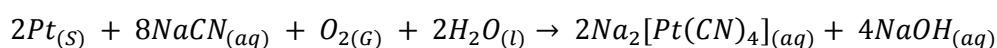
surface (Bell, et al., 1995). Due to the fact that the dissolution is an electrochemical process, passivation is likely to occur especially when high or low pH is used (Meng & Han, 1996). According to Dutrizac (1981), a ferric oxide product layer was shown to inhibit the reaction and reduce the rate of the reaction.

One possible solution may lie in the addition of saccharides or other organic compounds (such as DEPTA, EDTA) to the ammonia solution. These compounds have the ability to dissolve iron oxides in solution. OH groups attached to long chain molecules may act as sequestration agents which keep the iron in solution and hence prevent the formation of ferric oxide and iron can be recovered from the leachate (Kneil & Kroll, 1954). However more research needs to be done in terms of the impact of addition of organic compounds on the extraction rates and subsequent separation processes.

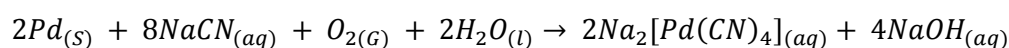
2.7 Cyanide Leaching of PGMs

Cyanide is a general term that refers to any chemical that contains the cyano group (a triple bond between carbon and nitrogen). Cyanide solutions have been used in the mining industry for the past 120 years, more specifically in the gold refining industry. Cyanide, in its dilute form (100-500ppm) is used to dilute gold and separate gold from its ore (Fraiser Institute, 2012).

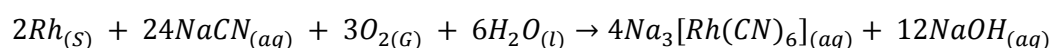
Cyanidation has been long used in the gold industry for the direct extraction of gold at ambient conditions (Chamberlain & Pojar, 1984). In terms of PGM extraction, work by McInnes *et al.* (1994) showed that process occurs in the same manner as the gold extraction process. Further, the process proceeds via the following chemical reactions (Chen & Huang, 2006) for the Pt, Pd and Rh:



Equation 19



Equation 20



Equation 21

According to work by Chen and Huang (2006), the reaction between sodium cyanide and PGMs doesn't occur at appreciable rates when operated at room temperatures

and pressures (as is the case in gold extraction). The reaction rates of the above reactions are proposed to be controlled by the surface chemical reactions.

Further an oxidising agent is required to oxidise the Pt, Pd and Rh metal to soluble Pt^+ , Pd^+ and Rh^+ ions in solution, hence forming aurocyanide complex ions (Grosse, et al., 2003) dependant on the most stable form of the cations. The choice of oxidising agents varies from pure oxygen to air.

Work by Mwase (2009) showed the successful use of sodium cyanide in the extraction of PGMs. In his investigations, Mwase (2009) compared sodium cyanide to other chemicals such as organic acids, sodium bisulphide and thiosulphate solutions, and found that sodium cyanide had significantly higher PGM extractions. Cyanide was successful in extracting 20% Pt, 87% Pd and 46% Rh in a packed bed reactor over a period of 21 days.

In terms of Platreef, PGMs may occur as Pd and Pt bismuth-tellurides and arsenides (Platreef) which are slow-floating in comparison to PGM sulphides minerals (Shamaila & O'Connor, 2008; Vermaak, 1995), and further the complex PGM mineralisation (van Wyk, 2014) renders these PGMs difficult to fully recover via the conventional concentrate (via flotation)-smelt-refine process. Using conventional methods may lead to an increase in smelter operating costs (low-grade), reduce smelter integrity (due to the chromite), increase converting costs that may be associated with gas handling and treatment of acid plants and may lead to a negative environmental impact due to the production of SO_2 gas and Fe-bearing slag (Mwase, Petersen & Eksteen, 2012).

2.7.1 Base metal extraction prior to PGM extraction

In the case of ores that contain copper, it is common practice to keep copper levels in solution below 300-500 ppm and may note problems with gold recovery and cyanide consumption when copper concentrations exceed this amount (Stewart & Kappes, 2012). This theory can be extended to other PGMs ores.

When copper is dissolved with adequate free cyanide, a $Cu(CN)_3^{2-}$ complex is formed and results in the consumption of cyanide (Mwase, 2009). Further, $Cu(CN)_3^{2-}$ complex in a heap may cause environmental issues as these complexes end up in tailings dams and waste material (Alymore, 2001) and will require treatment. These issues would affect the economics of the process (Stewart & Kappes, 2012). In addition, separation of the base metals and PGM prior to leach operations provides flexibility in designing

the operating conditions for both base metal and PGM dissolution stages (Adams *et al.*, 2011).

Further, batch tests done by Chen and Huang (2006) proved that pressure oxygen pre-treatment was vital to obtain high PGM extractions. This is because in the pressure oxygen pre-treatment, all the sulphides are converted to sulphates and oxides therefore exposing any encapsulated PGMs.

Laboratory scale tests indicate extraction rates and trends during the leaching process. Column tests and batch stirred tank reactor tests simulate heap leaching dumps and agitation tank leaching respectively. The next section gives a closer look at large scale leaching practices.

2.8 Leaching techniques

At present, leaching is the most essential front-end operation in hydrometallurgy. The leaching process is grouped into 2 main categories: percolation leaching and agitation leaching.

Percolation leaching

Percolation leaching involves the percolation of the lixiviant through a stationary ore body. Lean lixiviant trickles through the ore by gravity and is collected at the bottom as rich/pregnant solution. The main types of percolation leaching are in situ, heap and dump leaching. In situ leaching involves the leaching of ore that has not been mined or has been blasted to allow for lixiviant percolation and also uses natural oxidants such as air. Heap leaching is similar to in situ leaching but requires the construction of a heap to allow for optimum extractions. The heap must be constructed on a slope to allow for easier drainage of the lixiviant. The bottom of the heap is made as waterproof as possible to reduce the chances of ground water contamination. The lixiviant is sprayed evenly over the heap and is allowed to drain through to the bottom as shown in Figure 20

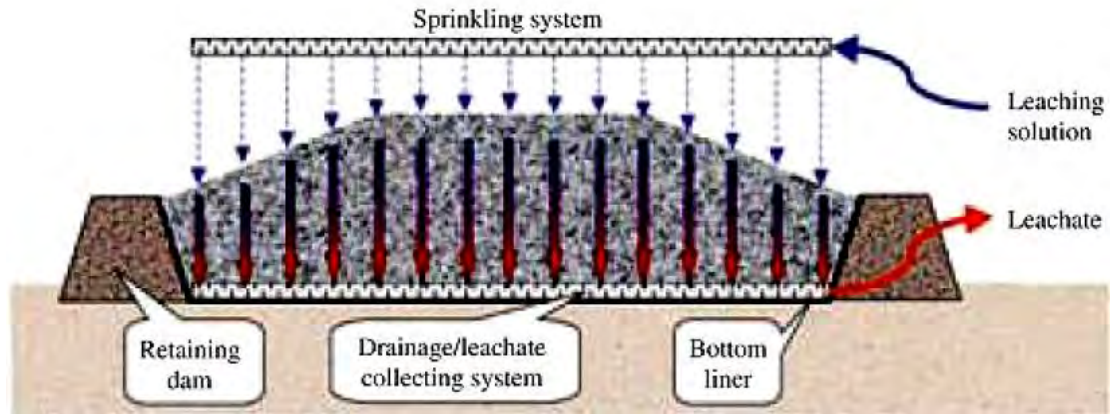


Figure 20 : A typical heap leaching system (Environmental Radiation Survey and Site Execution, 2009)

Agitation leaching

Agitation leaching requires the treatment of finely ground ore which is kept in suspension by the agitation of slurry, mechanically or pneumatically. This process is performed in specifically designed vessels that can be operated as batch, concurrent, counter current systems below or above atmospheric pressure and temperatures. In this process, a cylindrical tank with a cone shaped bottom which is opened on both ends is used as a reactor. Compressed air is let in through a pipe that lies coaxial to the leaching tank. The presence of air bubbles lowers the density of the pulp in the pipe and the density differential causes an airlift and overflow of the pulp. This tank is called a Pachuca and is shown in Figure 21. In terms of pressure leaching operations, an autoclave is used. Pressure leaching is useful when dealing with reactions that need higher temperatures to proceed and also when dealing with volatile liquids such as ammonia. Agitators and baffles are also used to improve the mixing and to prevent the formation of vortices in the solution.

Figure 22 shows a summary of the two main types of leaching and the specific leaching operations that fall under these two types.

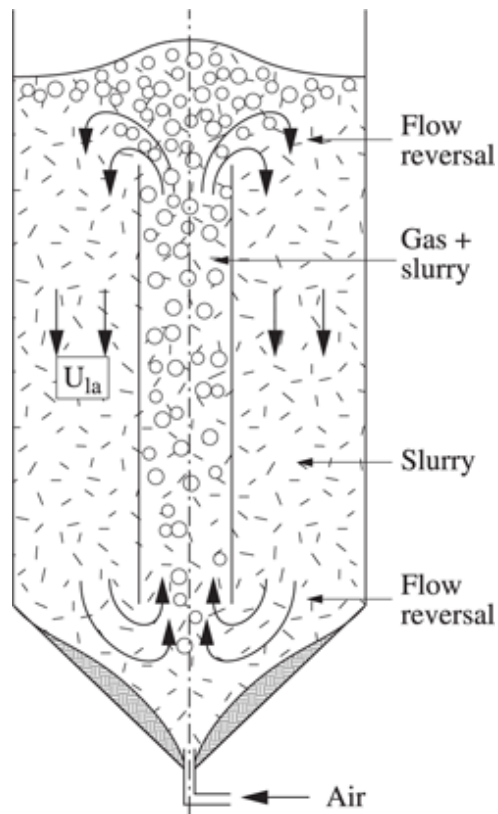


Figure 21: Pachuca tank used for agitated leaching (Vignes, 2011)

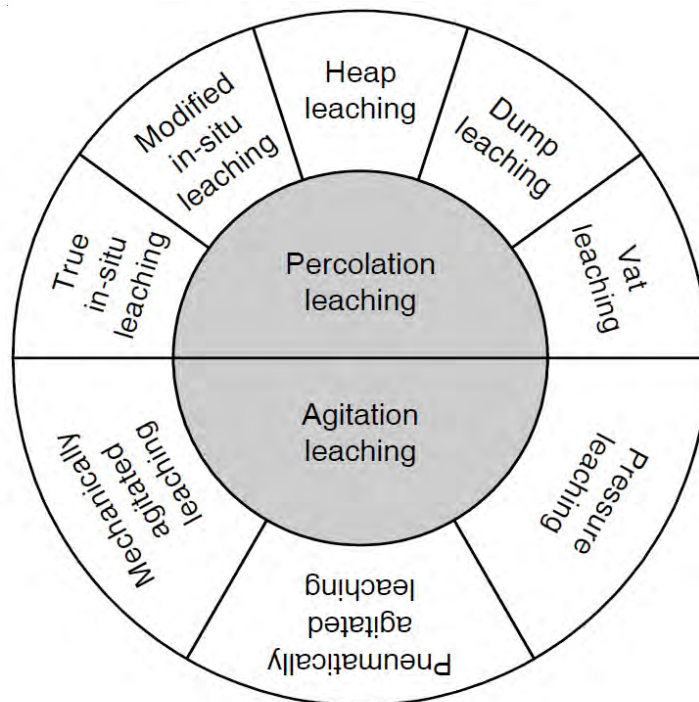


Figure 22: Classification of the different leaching techniques (Gupta, 2003)

The main advantages and disadvantages of percolation and agitated leaching are presented in Table 4

Table 4: Advantages and disadvantages of percolated and agitated leaching (U.S. Environmental Protection Agency, 1994; Kappes, 1998; Gupta & Mukherjee, 1990; Gupta, 2003; Bartlett, 1992)

	Percolation leaching	Agitation leaching
Advantages	<ul style="list-style-type: none"> • Economically suitable for treating low-grade ores. • Generally low capital and operating costs • Shorter start-up times • Large tonnages 	<ul style="list-style-type: none"> • In terms of ammonia leaching, due to its high volatility, the ammonia lost can be captured and recirculated. • It is easier to achieve design targets in tank leaching as operating conditions are better controlled, also have higher recovery efficiencies. • Allows for the operations at controlled conditions such as pressures and temperatures • Faster rate of dissolution
Disadvantages	<ul style="list-style-type: none"> • High recoveries require longer leaching periods • May result in the contamination of ground water 	<ul style="list-style-type: none"> • High capital investments required. • High maintenance costs

In order to determine the efficiency of a particular process, it is beneficial to investigate both percolation leaching (columns) and agitated tank leaching (batch stirred tank) routes.

2.8.1 Different ammonia leaching techniques

In 1903, Malzoc proposed the use of ammonia solutions for leaching copper, nickel and cobalt sulphides in France (Habashi, 2005). Several processes developed after that and these are described by Meng and Han (1996). Here, the various processes

are discussed, namely, Kennecott, Caron, Sherritt Gordon, INCO and Arbiter (Meng & Han, 1996).

Kennecott process

This was one of the earliest commercial applications of the ammonia leaching technique of copper extraction and was established in 1916. Two separate plants were set up by Kennecott in Alaska and Calumet in the United States of America (Hawley, 2008). This process involved the extraction of copper from copper oxides and native copper. Due to the fact that copper oxides are very soluble in ammoniacal solutions, copper sulphides are converted to copper oxides under high temperature oxidation (Gupta & Mukherjee, 1990).

Caron process

The Caron process includes the extraction of nickel and cobalt from low grade oxide ores such as lateritic ores and has been used for the production of nickel since 1944 (Rhamadhani, et al., 2009). It has been mostly used for the recovery of nickel and cobalt in commercial scales in Australia and Cuba. During this process, finely ground ore is roasted in a reducing environment and subsequently leached with ammoniacal carbonate solutions under aerobic conditions (Valix & Cheung, 2002).

Sherritt-Gordon process

In the 1950's, direct ammonia leaching process (Sherritt-Gordan) of copper, nickel and cobalt sulphide ores under high pressures and temperatures was established. The Sherritt Gordon process uses ammonia leaching in an autoclave in order to recover base metals and was established in Alberta, Canada (Habashi, 2005).

INCO process

The INCO process was established in Canada in the early 1950's and used ammonia solutions to extract nickel, copper and cobalt from pyrrhotite. This extraction process is preceded by oxidative roasting of sulphur concentrates and quenching of the calcine by under reducing conditions. In the late 1960's a semi-commercial plant was set up for treating low grade pentlandite-pyrrhotite concentrate (Habashi, 2005).

Arbiter process

According Habashi (2009), the Arbiter process was established in the 1970's and is an ammoniacal high pressure leach. The process is carried out at 5psig, 75-80°C in the

presence of oxygen and uses ammonia to leach copper from chalcocite, covellite, bornite and precipitated copper. The copper in solution is concentrated and purified to marketable cathodes. After the extraction of copper, the lean solution was boiled to evaporate and distil ammonia; however this step was technically difficult and uneconomical hence unsuccessful (Arbiter & Milligan, 1976).

Escondida process

The Escondida process was established in 1998 in Chile. This includes the partial oxidation of Copper in ammonia. Due to the fact that partial leaching is achieved, the sulphur is not oxidised and hence the reagent is preserved can be easily reused. However, this process has been discontinued and to the author's knowledge it is unknown why this process has been discontinued due to poor economics.

2.9 Research Approach

The exposure of the ore body to the surface leads to the formation of an oxidation layer. This oxidation layer inhibits the flotation recovery of the ore. The extent of the oxidation determines the nature of the treatment required. Figure 23 illustrates the differences between surface layer oxidation and oxidation that is more invasive (oxidation along crevices and cracks). Further, this justifies the need of investigating both coarse ore and milled ore.

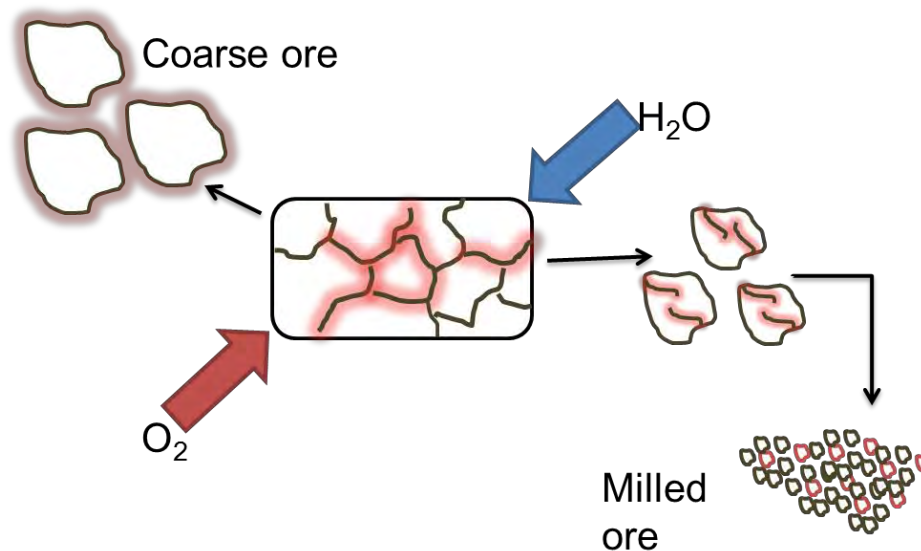


Figure 23: Diagrammatic representation of the extent of ore oxidation

Work has been done by Newell (2006), Newell & Bradshaw (2007) and most recently an acid pre-treatment by Ramonotsi (2011) in an attempt to remove this oxidation layer.

In particular, the metallurgical performance of Pilanesberg Platinum Mines (PPM) has been dominated by low flotation recoveries due to the predominance of weathered/oxidised minerals present in the ore. It is suspected that this is due to the fact that the mine is extracting ore near the surface and better recoveries are achieved from ores mined from a deeper source (Ramonotsi, 2011)

Previously, Mwase *et al.* (2012) investigated a 2-stage process that included a primary acid heap bioleach of base metals followed by a secondary direct cyanide leach of PGMs and achieved a high extraction of PGMs from low grade ore. This process included multiple stages of caustic washing between the acid leach and the cyanide leach and also included thermophilic micro-organisms. In an attempt to eliminate the use of caustic washing and to work in an alkaline environment, Muzawazi (2013) explored the use of an ammonia heap leach to extract base metals from Platreef concentrate.

A 2-stage process was developed to first extract base metals and then PGMs from low grade Platreef (Mwase *et al.*, 2012). The need to have an alkali environment for both steps, led to work by Muzawazi (2013), who investigated the use of an ammonia treatment to extract base metals from Platreef ore.

The ammoniacal leaching process has proven to be technically feasible for the treatment of Platreef flotation concentrate and base metal extraction of approximately 94% Cu and 91% nickel (Chang & Liu, 1998; Muzawazi, 2013). The leaching of base metals such as Cu, Ni and Co in alkali conditions is an established technique and is currently applied in processes such as the Kennecott, Caron, Sherritt Gordon, Arbitor and Inco. Muzawazi demonstrated the possibility of using ammoniacal solutions to extract Ni and Cu from low grade PGM ores and concentrates on a laboratory scale.

This project investigates the use of ammonia as a pre-treatment of PGM ores prior to the flotation process. Ammonia is used as a wash in an attempt to dissolve the oxidation layer by the dissolution of base metal oxides found in the oxidation layer. The dissolution of the oxidation layer facilitates the increased exposure of the mineral surface, hence making it more amenable to the flotation reagents. Ammonia is highly selective and has a favourable pH for the flotation stage. These are some of the

advantages over alternative treatments such as the acid pre-treatment (Ramonotsi, 2011).

In this project, both percolation leaching and agitation leaching will be investigated. Column tests and batch stirred tank reactor tests are performed to simulate heap (percolation) and tank reactors respectively. This also allows the determination of the extent of oxidation as coarse ore will be treated in the columns and milled ore will be treated in batch stirred tank reactors, see Figure 23

In this project, ammonia leaching is explored as a possible improvement technique as a chemical pre-treatment for the flotation of oxidised ores. Further, ammonia leaching is also used as first step to extract base metals and followed by the extraction of PGMs by cyanide in an attempt to recover valuable metals from oxidised ores (Mwase, 2009; Muzawazi, 2013).

2.9.1 Objectives of study

The principal aim of this study is to investigate the use of ammonia leaching as a chemical pre-treatment method for oxidised PGM ores to improve flotation or alternatively as a lixiviant for the extraction of valuable metals from oxidised ores. The following key questions will be answered in the study:

- Can an ammonia treatment of PGM oxidised/weathered ores make the PGM ores more amenable to flotation?
- What are the optimal reactor configurations (columns or batch stirred tank reactors) and the optimal operating conditions in which to conduct this process?
- As alternative to the conventional processing route, can ammonia be used as a lixiviant to treat PGM oxidised/weathered ores in the extraction of base metals prior to the sodium cyanide leaching of PGMs?

A summary of the research approach is illustrated in Figure 24. Route 1 shows the ammonia column pre-treatment of coarse ore and subsequent milling of the ore prior to the flotation of the treated ore. Route 2, shows the milling of the ore prior to the batch stirred tank reactor treatment and flotation of the treated ore. Route 3 shows the column leaching (coarse ore) of base metals and PGM metals with an ammonia and cyanide leach respectively.

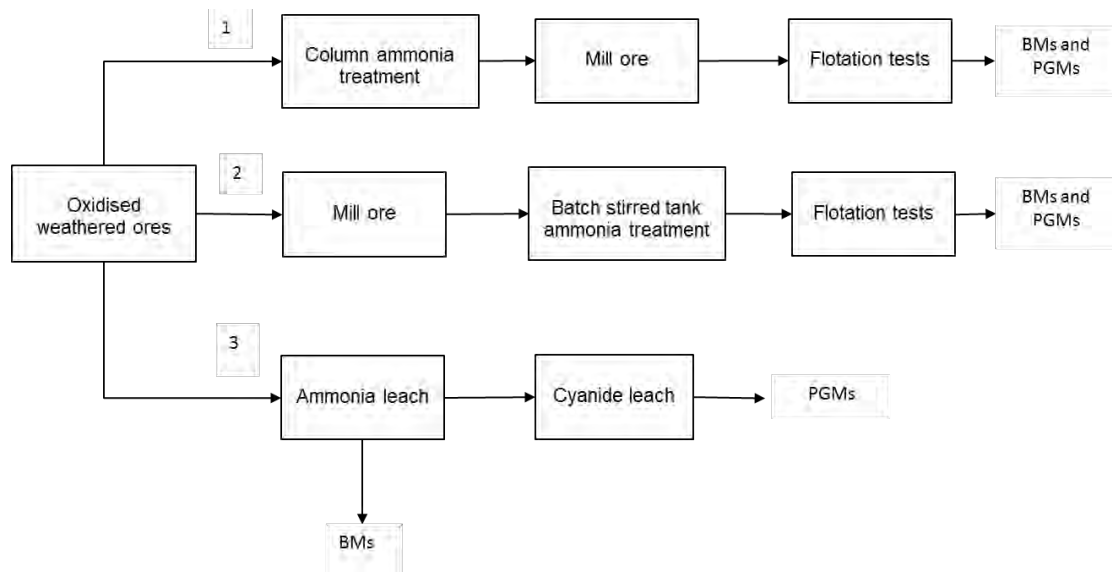


Figure 24: Schematic of overall experimental procedure

3 EXPERIMENTAL PROCEDURE

This chapter consists of: A materials section (which describes sample preparation); ammonia leaching methodology; flotation methodology and a description of the analytical techniques used. The experimental procedure is summarised in Figure 24.

The ammonia pre-treatment was conducted in both column reactors (route 1) and batch stirred tank reactors (route 2) to simulate a heap leach and an agitated tank reactor respectively.

An ammonia-cyanide leach was also be investigated as an alternative route (route 3) to the use of ammonia and the conventional route. These tests were done to determine the feasibility of using ammonia leach to extract base metals followed by a cyanide leach to extract PGMs.

3.1 Materials

The sample was sourced from the Pilanesburg Platinum Mines (PPM) operation in South Africa. PPM primarily treats ore from an open pit mine. This ore is exposed to the surface and has undergone low temperature weathering and surface alteration (Becker *et al.*, 2014). This ore was sourced from a stock pile of oxidised ores with a top size of 80mm.

3.1.1 Sample bulk mineralogy and elemental analysis

An elemental assay of the sample was carried out in order to determine the concentration of the base metals and PGMs in the sample. Table 5 shows the base metal and PGM elemental analysis for the coarse (columns) and milled (batch stirred tank) ore treatments.

Table 5: Total base metal and PGM elemental analysis on ore sample

Al	Ca	Cu	Fe	Mg	Ni	S	Pt	Pd	Ag
%	%	%	%	%	%	%	ppm	ppm	ppm
2.58	3.51	0.024	10.3	14.6	0.174	0.02	0.756	0.333	0.13

Table 6: Mineralogy data of sample adapted from Becker, Wiese & Ramonotsi (2013).

Mineral	Wt.% in feed
Base metal sulphides	0.2
Olivine	3.8
Orthopyroxene	24.6
Clinopyroxene	10.3
Serpentine	10.6
Talc	18
Chlorite	5.1
Amphibole	6.8
Plagioclase	4.4
Epidote	1.2
K-feldspar	0.1
Mica	0.9
Calcite	1.0
Quartz	0.3
Chromite	0.8
Fe oxides/ hydroxides	11
Other	0.9

Table 6 shows the lack of base metals (0.2%) in comparison to Merensky and UG 2 ores (typically 1-3%). This is in accordance with the oxidation/weathering of Merensky ores (Obethur *et al.*, 2013). The low sulphur concentration shown in Table 5 and Table 6 also indicates that most of the sulphides and subsequently elemental sulphur have been oxidized. Further, the high percentage of Fe oxides/hydroxides (11% wt.) alludes to the presence of an oxidation layer that is dominated by Fe oxides/hydroxides, this is line with work done by Smart (1991).

3.1.2 Sample preparation

The samples used in both the column tests (coarse) and the batch stirred tank reactor (milled ore) tests were obtained from the same bulk sample analysed in section 3.1.1. This bulk sample was analysed and split into 20kg samples. The splitting was done by a Rotary 1×10 kg splitter, as shown by Figure 25.

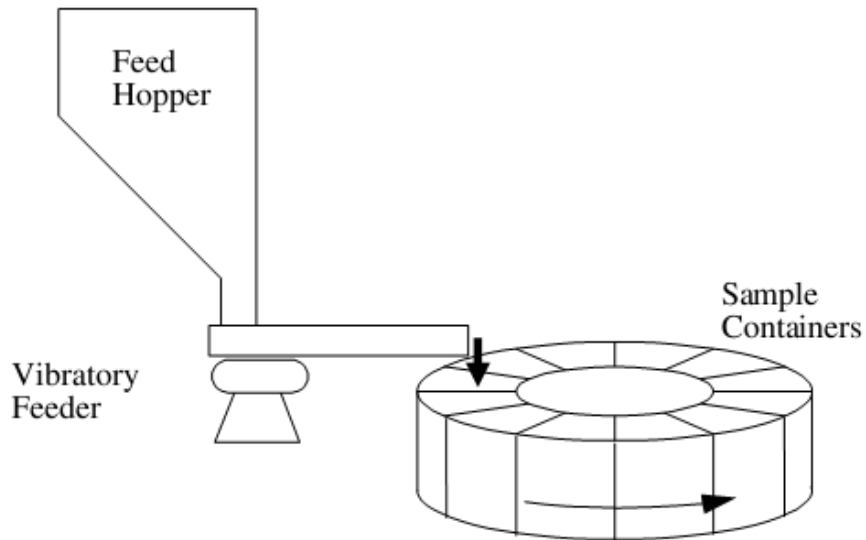


Figure 25: Schematic of the 1 x 10kg splitter used to split ore in order to obtain representative sample. (Anon., 2009)

For the column tests, in order to obtain a representative population of the ore, a 20kg sample was split by the same Rotary 1x10 kg splitter into five 4kg samples. The 4kg samples were further split into two 2kg sub-samples. Each 2 kg sub-sample was used to represent a specific column treatment. This is represented by Figure 26

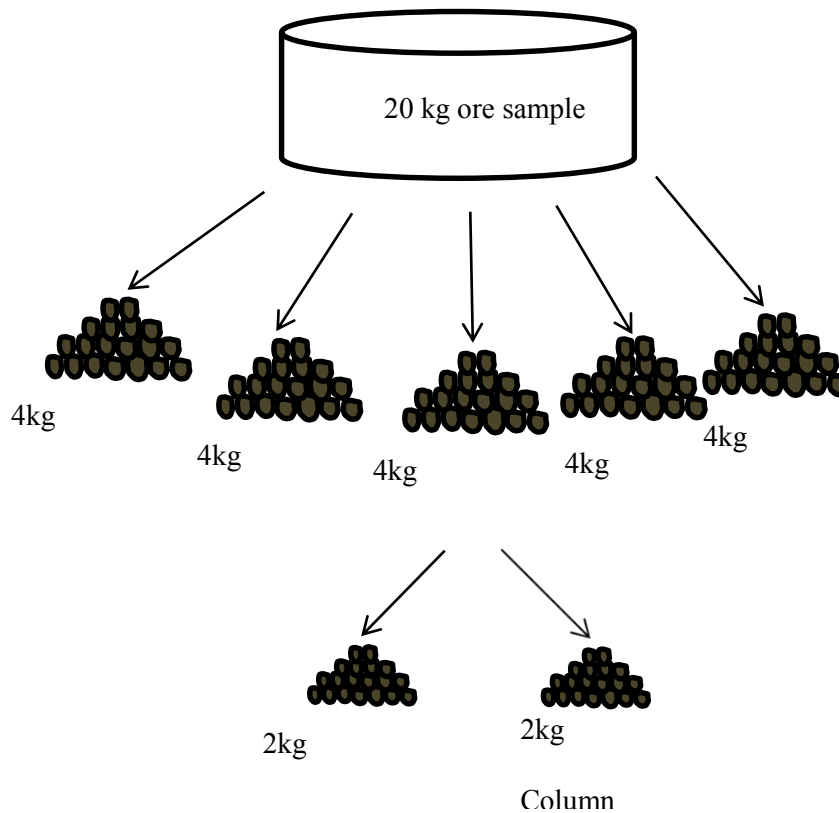


Figure 26: Schematic of splitting procedure for ammonia column leaching

For the batch stirred tank reactor tests, in order to obtain a representative population, a 20kg sample was split into five 4kg ore samples. These 4kg sample were further split by the same Rotary 1x10 kg splitter into two 2kg sub samples. The 2 kg sample was further split into three 660g sub-samples.

3.1.3 Sample milling

As shown in Figure 24, the coarse ore that was treated in the columns was milled prior to the flotation tests. The milled ore that was treated in the batch stirred tank reactors was milled prior to treatment. The particle size distribution presented by Figure 27 shows the particle size distribution of the ore prior to the milling process.

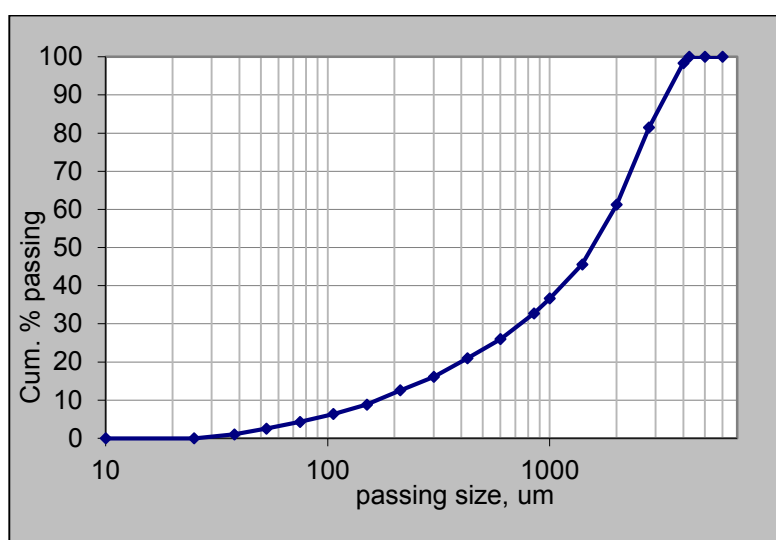


Figure 27: Particle size distribution graph of head sample

In terms of the column treatments, the ore was used to simulate coarse ore (whole ore) in a heap leach. However, a comparison to the standard particle top size used in heap leaching found that this ore was much smaller (Ghorbani, et al., 2011). Further, this ore also had a high fines content (>30% cum passing).

In order to determine the correct milling time and curve, research conducted by Ramonotsi's (2011) was used as a benchmark, as he had done prior work with the same material. For this project, the ore was milled to a particle size of 75 μm , 80% passing. This particle size distribution was achieved by milling the ore using a 1kg mill as shown by Figure 28.

A stainless steel 1kg rod mill was used in the milling process (diameter 200 mm). 20 rods were used with 50% water content. The rod sizes used are summarised by Table 7. The mill was operated at 90mph

Table 7: Details of rods used in mill

Number of rods	Rod sizes (radius × length) mm
6	16 × 285
8	20 × 285
6	25 × 285



Figure 28: 1kg mill used to mill head sample for flotation

The milling time was determined by the milling curve for this particular ore. The milling curve was calculated by milling the ore for different set times and these times were plotted against the 75 μ m percentage passing to determine the length of milling time required to achieve a particle size of 75 μ m, 80% passing. For this particular ore and mill, a milling time of 32 minutes was required to mill to the specified size.

Figure 29 represents the milling curve used to determine the milling time required to obtain the correct particle size distribution.

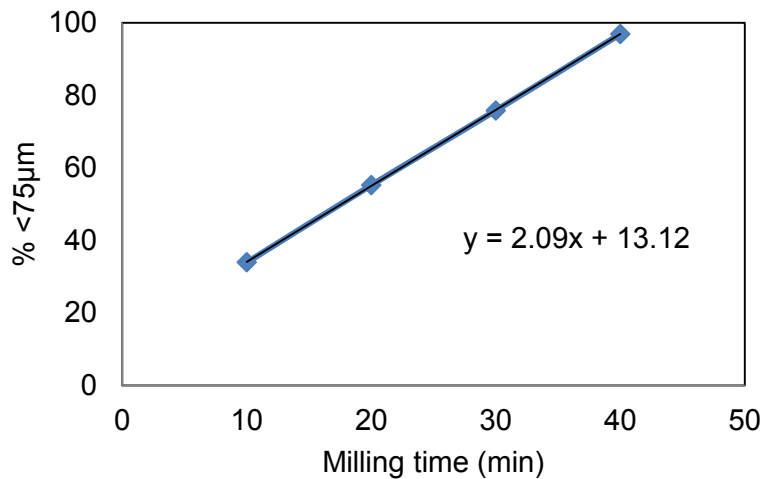


Figure 29: Milling curve used to obtain milling time for required size fraction.

The particle size distribution presented by Figure 30 shows the particle size distribution of the ore after the milling process. As shown in the graph, the treatment did not affect the particle size distribution of the ore. The plot of the different treatments shown in Figure 30, indicate that the particle size was kept consistent throughout the flotation process.

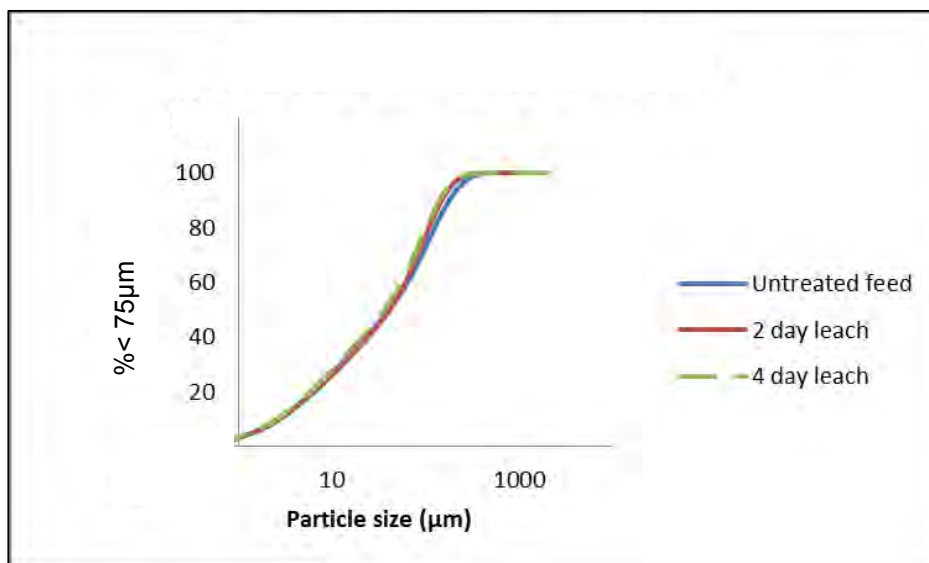


Figure 30: Particle size distribution of milled ore which shows that consistency was kept throughout the leaching process

3.2 Methods: Ammonia pre-treatment tests

The general procedure consisted of an ammonia wash in order to dissolve the oxidation layer (products) formed during the weathering of the ore.

3.2.1 Column reactor leaching (coarse ore)

In order to treat the coarse ore, 2kg samples of ore (from the splitter) was mixed with 160ml (8%v/w) of water in order to form a suitable agglomerate mixture for the column leaching tests. This agglomerate was then packed in the vertical column. Figure 31 shows the column setup. The columns used were 0.5m long and had a diameter of 0.09m. The column comprised of a feed pipe, gas inlet and outlet pipes, a heating element and a thermocouple. The solution was pumped (via a peristaltic pump) from the fresh solution containers to the top of the column and subsequently trickled down through the column. The glass marbles ensured even distribution of the solution. The 7M total ammonia solution consisted of a 3M 25% aqueous ammonia solution and a 2M ammonium carbonate solution. Muzawazi (2013) showed extractions above 60% for both Cu and Ni with a 7M total ammonia concentration.

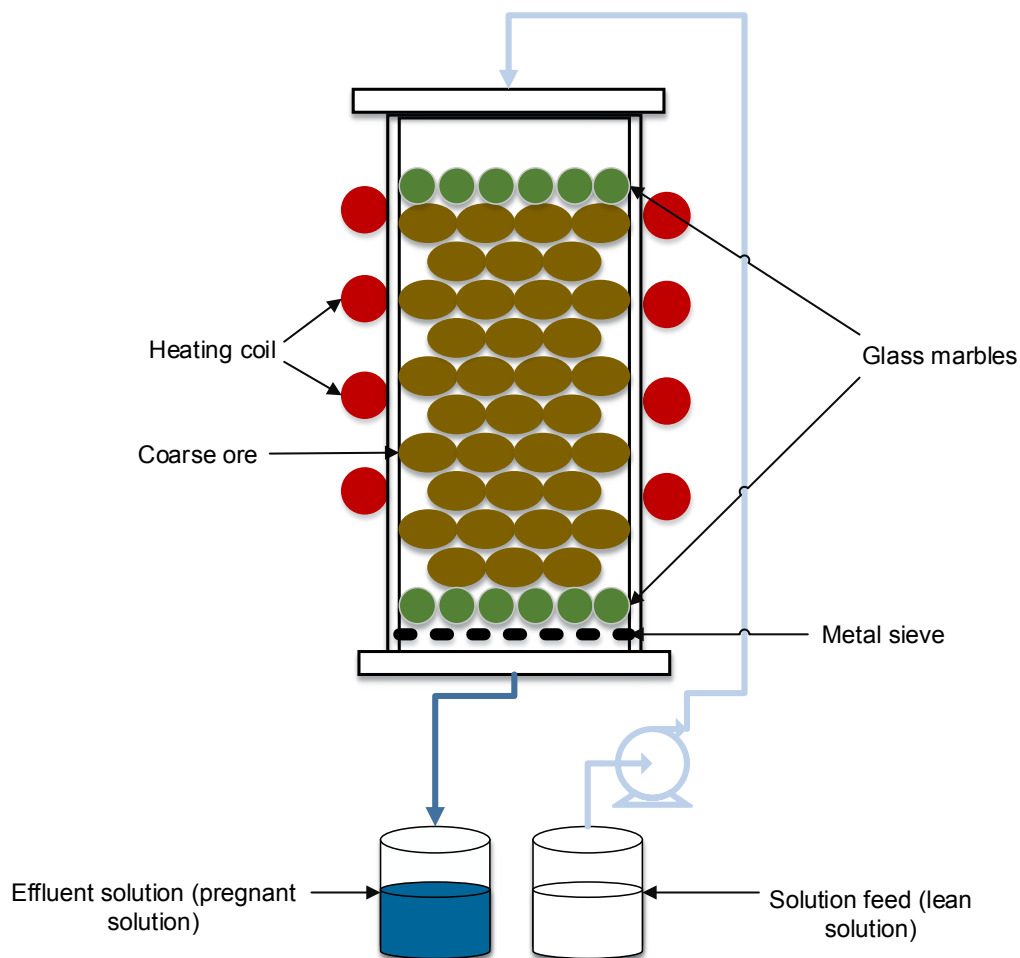


Figure 31: Schematic of the column reactors used to simulate a heap leach

The solution was pumped at a rate of 1000ml/day. Three columns were set-up and each column represented a different length of treatment. Column 1 ore was treated to a period of 2 days; while column 2 ore was treated for 5 days and column 3 was treated for a total of 10 days. All three (3) columns were treated with the same lixiviant and operated at ambient temperature conditions. Table 8 shows a summary of the column operating conditions.

Table 8: Summary of column leaching operating conditions

	1	2	3
NH₃(as)	3M	3M	3M
(NH₄)₂CO₃	2M	2M	2M
Temperature	ambient	ambient	ambient
Water added	8%	8%	8%
Leaching time (days)	2	5	10

For the ammonia leach tests, (NH₄)₂CO₃ was used as a suitable buffering salt and contributed to the total ammonia concentration. Results by Muzawazi (2013) show that (NH₄)₂CO₃ was the best option for a buffering salt as it showed the highest Cu and Ni extractions and also maintained the most stable pH readings. (NH₄)₂CO₃ was compared to NH₄Cl and (NH₄)₂SO₄ (Muzawazi, 2013).

In terms of the sampling of the columns, 50ml of the column solution effluent was obtained for every sample. The sampling of the solution effluent was done every 12 hours for the first 2 days for column 1, 2 and 3. Thereafter, sampling was done daily for columns 2 and 3. The samples were drawn in duplicate in order to determine any error associated with the analysis.

The treated ore was then dried and milled (see section 3.1.3) in preparation for the 3L flotation tests.

3.2.2 Batch stirred tanks (milled ore)

The three 660g sub-samples were milled (see section 3.1.3) and used for the untreated, 1 hour treatment and 3 hour treatments, respectively. Each of these 660g heaps were then split into 400g for repeat tests and 200g for individual head sample analysis.

For the tank leaching reactions, 2L Applikon reactors were used. These tank reactors consisted of a 2 blade mechanical stirrer and Pyrex baffles. Figure 32 shows a picture and schematic of the batch stirred tank reactors used.

In terms of the batch stirred tank reactors, a typical arrangement of an agitator and baffles was used. Turbulent mixing is vital for systems where mass transfer plays an important role in the reaction. An impeller to tank diameter ratio of 0.6 was used for this particular system.

Batch 1

Batch 2

For this treatment, 200g of milled ore was treated in a 2L ammonia solution thus a 10%

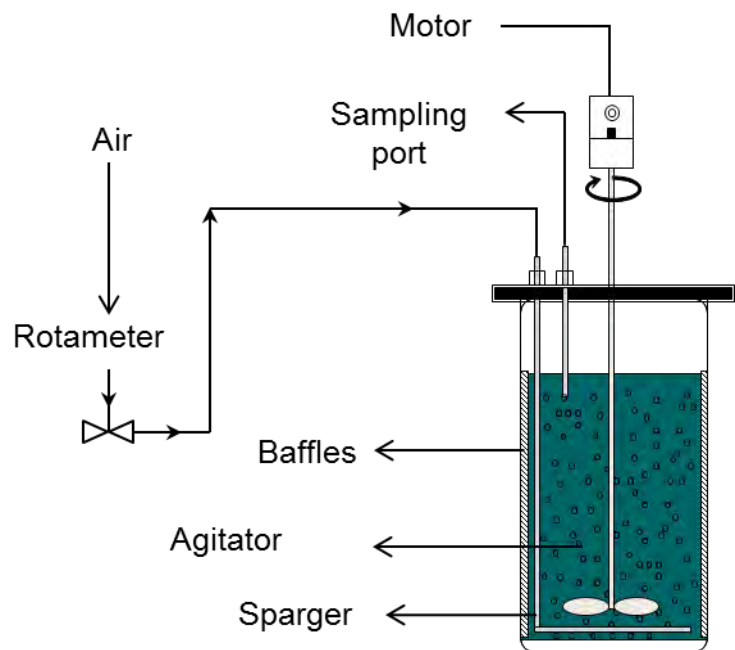


Figure 32: Batch stirred tank reactors used to treat milled ore (picture and schematic)

pulp density was used. The solution used to treat/wash the milled ore was a 5M total ammonia solution. The 5M total ammonia solution consisted of a 3M 25% aqueous ammonia solution and a 2M ammonium carbonate solution. Batch 1 and batch 2 stirred tank reactors were run for 1 hour and 3 hours respectively. Batch 3 was used to represent the untreated milled ore. Table 9 illustrates a summary of the batch stirred tank operating conditions.

Table 9: Summary of Batch stirred tank leaching conditions

	1	2
NH₃(aq)	3M	3M
(NH₄)₂CO₃	2M	2M
Temperature	ambient	ambient

Pulp density (w/v)	10%	10%
Leaching time (hour)	1	3

The sampling was conducted by extracting 10ml of the solution with a syringe and filtering out the ore using a vacuum pump filter. The solution was sampled every 20 minutes, and as in the columns, duplicate samples were analysed to determine the error associated with the analytical technique. After the treatment time, the ammonia was decanted and the solids were taken to the 1L flotation cell to be floated.

3.3 Ammonia Leaching: Extraction of Valuable Metals

A possible alternative route to the conventional method described is a hydrometallurgical process that involves the complete chemical extraction of valuable metals which was investigated. This route consists of the extraction of base metals and PGM's in order to recover the total economic value of the ore. The experimental route suggested was adapted from research conducted by Mwase (2009) and Muzawazi (2013). Base metal extraction will be done with the use of ammonia as a lixiviant and PGM extraction with the use of cyanide as a lixiviant (Mwase, 2009).

3.3.1 Ammonia column leach

For the ammonia leach, two coarse ore columns were set-up for each run to enable reproducibility and the determination of error associated with the experimental procedure. The 2 columns were packed with 3kg of the sample

Table 10 describes the operating conditions of the 2 ammonia columns. For these long term column tests, a lower total ammonia concentration was used than the pre-treatment tests, by reducing the amount of ammonium carbonate. This was done to minimise reagent costs and a high extraction was still expected over a leaching period of 30 days.

For the sample preparation, splitting procedure and column packing was similar to the procedure described in the ammonia leaching a pre-treatment (column) section and as illustrated in Figure 26

Table 10: Summary of Ammonia column leaching conditions

Columns		
	1	2
NH₃(aq)	3M	3M
(NH₄)₂CO₃	1M	1M
Temperature	ambient	ambient
Water added	8%	8%
Leaching time (days)	28	28
Aeration(ml/min)	80	80

Sampling of the column effluent occurred every 12 hours for the first 3 days, and then daily for the next 7 days and finally sampling occurred every second day for the remaining 20 days of the treatment.

3.3.2 Cyanide column leach

In order to conduct a sodium cyanide leach, special attention had to be paid to the safety precautions taken when dealing with a sodium cyanide solution. Details of the Safety, Health and Environment (SHE) impact will be discussed in section 3.6.2.

The extraction of PGMs, would start with the extraction of base metals using ammonia and be followed by the extraction of PGMs using cyanide as a lixiviant. The effect of ammonia pre-leach was investigated by the running of two ambient columns: column 1 was a direct sodium cyanide leach to extract both base metals and PGMs and column 2 was an ammonia leach to extract base metals followed by a sodium cyanide leach to extract PGMs.

Two sodium cyanide columns were set up and operated under identical conditions. However, column 1 had fresh ore and column 2 used ore that was previously leached with ammonia in order to investigate the effect of an ammonia leach to extract base metals prior to a sodium cyanide leach. The sodium cyanide solution columns were set-up in the same way as the ammonia columns described in section 3.3.1. Table 11 summarises the operating conditions;

Table 11: Summary of cyanide column leaching conditions

	Columns	
	1	2
NaCN	0.5M	0.5M
Temperature	40°C	40°C
Water added	8%	8%
Leaching time (days)	30	30
Ammonia leach	4M	4M
Aeration (ml/min)	80	80

3.3.3 Ammonia batch stirred tank leach

Due to the low extraction rates of base metals achieved in the ammonia column tests, a closer look at the operating conditions such as:

- the effect of initial copper concentration;
- ammonia concentration;
- acid pre-treatment (0.54M);
- pulp density.

Table 12 describes the various batch reactors run and their operating conditions;

Table 12: Summary of the batch stirred tank reactor operating conditions

	Batch reactors				
	1	2	3	4	5 (base case)
NH₃(aq)	2.7M	5.4M	2.7M	2.7M	2.7M
(NH₄)₂CO₃	1.3M	2.6M	1.3M	1.3M	1.3M
Pulp density (%)	5%	5%	15%	5%	5%
Initial [Cu]	500ppm	50ppm	50ppm	50ppm	50ppm
Acid pre-treatment	No	No	No	Yes	No
Temperature	Ambient temperatures				
Aeration (ml/min)	80				

In terms of the ammonia leaching batch tests for the extraction of base metals, the sample preparation, splitting procedure and batch stirred tank set-up was similar to the procedure described by section 3.2.2 (Batch stirred tanks). However, to facilitate the maximum extraction of base metals, the reactors were run for 2 days. For each of the operating conditions, duplicate batch tank reactors were set-up for each run to enable reproducibility and the determination of error associated with the experimental set-up. Due to the numerous tests being conducted, the total ammonia concentration was reduced to minimise reagent costs, however, the $\text{NH}_3/(\text{NH}_4)_2\text{CO}_3$ was kept high enough for optimum extractions.

3.4 Methods: Flotation Tests

These treatments were followed by batch flotation tests on the treated and untreated oxidised. Flotation rate tests were conducted in order to determine the effect of the each of the treatments. Flotation rate tests include the collection of concentrates over various time periods in order to generate recovery-time, grade-time and mass-time curves (Eurus Mineral Consultants, 2012).

Due to the constraint of the reactor size (2L) in the batch stirred tank tests, two different flotation cells were used, for the column treated ore and the batch stirred tank treated ore. The different flotation cells would require different reagent dosages, impeller speeds and air flow rates. These were scaled down on the basis of the mass of the material being floated.

3.4.1 Flotation batch tests

Column leach flotation tests (coarse ore)

The flotation tests on the column treated ore were conducted on a 3L flotation cell (UCT standard flotation cell) with an impeller speed of 1200rpm and the air flow rate of 7l/min. Figure 33 shows the flotation cell used.



Figure 33: A 3L flotation cell used in batch flotation tests

The ore was added and the volume was made up using synthetic plant water (30% solids). The composition of the plant water is shown in Table 13.

Table 13: Composition of plant synthetic water

Ingredient	Amount (g)/ 40L
Magnesium sulphate	24.50
Magnesium nitrate	4.28
Calcium nitrate	9.44
Calcium chloride	5.88
Sodium chloride	14.24
Sodium carbonate	1.20

The flotation process started with the addition of various reagents in a particular order. Firstly, 15ml of SIBX solution (Sodium Isobutyl Xanthate) was added as a collector and left to condition for 2 minutes. Subsequently 10ml of Sendep solution (depressant) was added and allowed to condition for a further 2 minutes. Then, 40µml of Senfroth (frother) was added and allowed to condition for 1minute

Table 14: Summary of flotation reagent sequence and addition times

Reagent addition	Reagent	Dosage (mg/kg)	Condition time
1	SIBX	150	5
2	Sendep	100	3
3	Senfroth	40	1

An air flow rate of 7L/min. was maintained throughout the flotation test. The agitation rate was set to 1200rpm for all the flotation tests. Concentrates were collected mechanically over the froth layer. During the first 5 minutes, the reagents are added and conditioned (as shown in Table 14). After these initial 5 minutes, the aeration was switched on and the first concentrate (C1) was collected over the next minute of aeration (after 1 minute of aeration); the second concentrate (C2) was collected over the next 3 minutes (after 4 minutes of aeration); the third concentrate (C3) was collected over the next 3 minutes (after 7 minutes of aeration); and finally the fourth concentrate (C4) was collected over the next 8 minutes (after 15 minutes of aeration). The whole flotation process lasted a total of 20 minutes. This flotation procedure was set according to the standard outlined by Wiese, Harris & Bradshaw (2005). The concentrate collection procedure is summarised in Table 15:

Table 15: Summary of the concentrate collection times

Time (min)	Concentrates
1	C1
4	C2
7	C3
15	C4

Batch stirred tank flotation tests (milled ore)

Due to the size and the appropriate pulp density of the batch stirred tank reactors (that were used to treat the milled ore); each batch reactor could only treat at 200g at a time. Therefore, a smaller flotation cell was used to determine the effect of the batch stirred tank treatment of the ore. The flotation tests on the column treated ore were conducted on a 1L flotation cell (UCT standard flotation cell).

Table 16: Summary of flotation reagent sequence and the addition times

Reagent addition	Reagent	Dosage (mg/kg)	Condition time
1	SIBX	30	5
2	Sendep	25	3
3	Senfroth	8	1

The flotation tests on the milled ore were conducted on a 600ml Denver flotation cell. Similar to the coarse ore flotation tests, the process started with the addition of various reagents in a particular order. Firstly, 3ml of SIBX (Sodium Isobutyl Xanthate) was added as a collector and left to condition for 2 minutes. Subsequently, 2.5ml of Sendep (depressant) was added and allowed to condition for a further 2 minutes. Next, 8µml of Senfroth (frother) was added and allowed to condition for 1minute.

An air flow rate of 3L/min. was maintained throughout the flotation test. The agitation rate was set to 250rpm for all the flotation tests. The same flotation method described in the *Column leach flotation tests (coarse ore)* section.

Table 17: Summary of the concentrate collection times

Time (min)	Concentrates
1	C1
4	C2
7	C3
15	C4

3.5 Analytical Techniques

Head sample analysis was conducted at ALS Geochemistry in Johannesburg, South Africa. The tests conducted were the PGM-ICP27 to determine the concentration of the PGMs and ME-ICP81 for the base metals. For the PGM-ICP27, a 30g nominal weight sample is analysed and Pt, Pd and Au are determined by a lead oxide collection fire assay. For the ME-ICP81 test, the sample is digested by the 'Four acid' digestion method and a 30g nominal weight sample is analysed for the base metals (ALS Geochemistry, 2013).

To determine the base metal content in the lixiviant effluent, Atomic Absorption Spectroscopy (AAS) was used at the UCT. AAS is a spectro-analytical test that was used to qualitatively and quantitatively determine the elemental make up of a solution

(The Royal Society of Chemistry, 2010). However, the AAS test could only determine elemental concentrations above 5ppm.

For samples with base metal or PGM concentrations less than 5ppm, the Inductive Coupled Plasma Mass Spectrometer (ICP-MS) test was used. ICP-MS is an analytical technique used to determine concentration of various elements (Wolf, 2005). It has a particularly low detection limit which makes it ideal for low grade ores or samples with low concentrations

3.6 Safety, health and environment

3.6.1 Ammonia (NH₃)

Ammonia is a highly volatile compound and ammonia gas is lighter than air. Therefore, the leaching process must occur in a closed system or alternatively in a highly ventilated area or an area where a forced-draft has been implemented. Ammonia has an atmospheric lifetime of a couple of days and disintegrates into nitrogen which forms a major part of the natural environment (78% of air). However, due to the solubility of ammonia in water, it forms an alkaline solution which causes an imbalance in pH of surface water (ammonia solution).

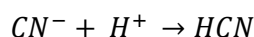
The health and safety precautions in the laboratory are adapted from a recently conducted experiment in the laboratory (Muzawazi, 2013) and information gathered from the MSDS's that are attached in the appendices. The following guidelines were followed during the duration of the experiments.

- Emergency shutdown procedures that are stipulated in the laboratory safety forms in the appendix must be followed. Furthermore, these forms are located above the reactor to ensure the safe operation of the various reactors.
- Any open experiments that include ammonia such as the periodic preparation of the ammoniacal solution must be conducted in fume hood cupboard.
- Any leaks and spills can be mopped and neutralised with water or dilute acetic acid solutions.
- Personal Protective Equipment (PPE) such as gloves, safety glasses, safety shoes and laboratory coats must be worn at all times.
- Any skin and eyes contact must be dealt with the emergency shower and eyewash respectively which are located close to the nearest exit.

- The Material Safety Data Sheets (MSDS) for ammonia and ammonium carbonate are provided in Section 8.5 (appendices).

3.6.2 Cyanide

Cyanide salts and solutions can be hazardous and toxic if consumed through the known points of entry, being the skin (absorbed), the eyes, inhalation of powder or hydrogen cyanide gas and ingestion of salts and solution. The warning signs of cyanide poisoning include dizziness, numbness, headache, rapid pulse, nausea, reddened skin, and bloodshot eyes. Prolonged exposure results in vomiting, laboured breathing, followed by unconsciousness; cessation of breathing, rapid weak heart beat and death. Severe exposure by inhalation can cause immediate unconsciousness. Further details are available in the MSDS in the appendix (Musonda & Mwase, 2009). The release of hydrogen cyanide gas is facilitated by the reaction below,



Equation 22

Hydrogen cyanide gas poses a level 3 health risk (highest level) and Table 18 summarises the threats to the human entry points:

Table 18: Dangers of HCN gas to human body

Entry point	Limits
Nose/inhalation	<ul style="list-style-type: none"> • At 20 ppm, exposure for several hours causes slight warning signs • At 50 ppm, exposure for an hour causes disturbances • At 100 ppm exposure for 30 to 60 minutes is dangerous and exposure to 300 ppm can be rapidly fatal
Skin/absorption	<ul style="list-style-type: none"> • 2% HCN in air may cause poisoning(3 minutes) • 1% is dangerous (10 minutes) • 0.05% may produce symptoms(30 minutes)

Mouth/ingestion

- 1 mg of cyanide salt per 1 kg of body weight is fatal

Symptoms of contamination include dizziness, numbness, headache, nausea, laboured breath and death. The following precautions were taken by the investigator when dealing with cyanide solutions in the laboratory:

When preparing a CN solution:

- Always wear correct PPE (safety glasses, gas mask and lab coat, safety shoes) when dealing with CN solutions
- Always verify your calculations
- Ensure and check enough alkalinity of receiving solution (pH>10)
- Weigh out and immediately close solid CN bottle
- Make leaching solution with buffered water (as per Mintek standard method)
- Make sure that equipment is rinsed with EDTA and bicarbonate solution before use
- Familiarise myself with cyanide anti-dote kit

When analysing CN samples:

- Any beakers/containers used must be rinsed in EDTA and bicarbonate solution to remove metal ions and any acidic residues
- Cleaning equipment used to clean up spills must be disposed of immediately after use
- Keep solution refrigerated
- Store in secondary containment barrier
- Label correctly with adequate warning
- Always have alkali solution available to counter any drops in pH
- Be sure to decontaminate any vessels used during experiment by placing them in FeSO₄

For people working in close proximity with cyanide experiments:

- Inform people in research group or who share lab space
- Have MSDS readily available/accessible

- Cyanide anti-dote kit available close to workspace
- First Aid instructions written out and accessible close to work space

In terms of waste disposal, approximately 60 litres of sodium cyanide was produced as waste over the experimental run. This was stored in 25L containers and disposed of appropriately. The Enviroserv waste management company was hired to transport the waste to the Vissershok landfill where it is treated with HTH before dumping.

4 AMMONIA LEACHING RESULTS AND DISCUSSION

This chapter focuses on presenting the results of the ammonia leaching as a pre-treatment and long term ammonia leaching. Figure 34 shows the experimental procedure and the results (ammonia and cyanide leaching) presented in this section have been highlighted.

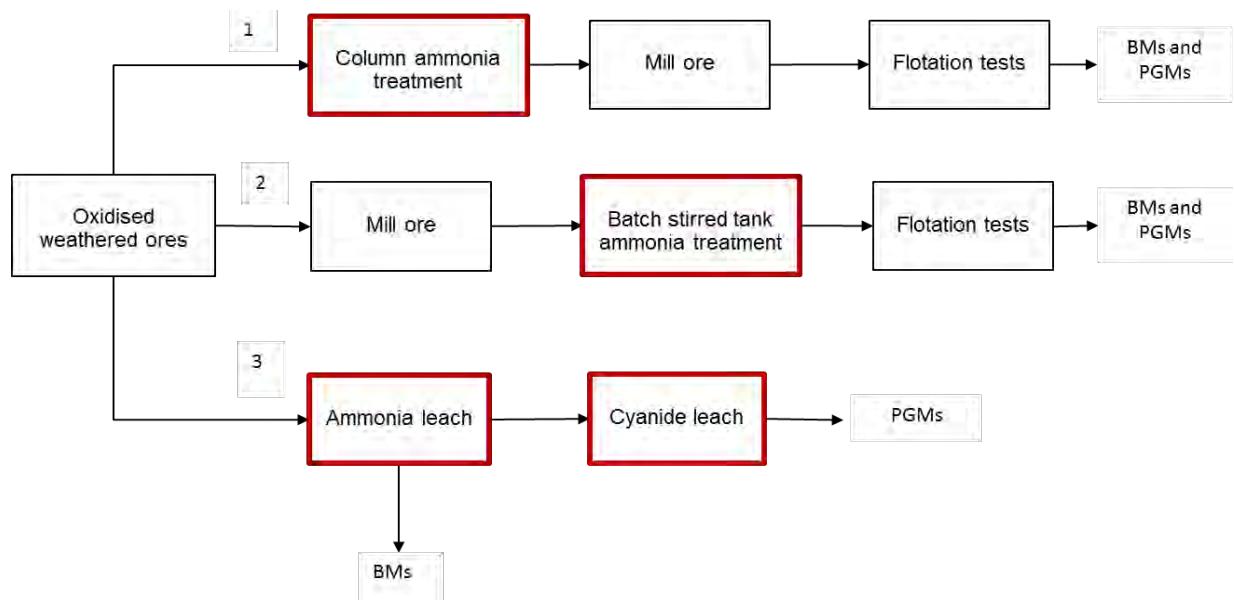


Figure 34: Schematic of the experimental procedure with the ammonia and cyanide leaching results highlighted

4.1 Ammonia leaching: Pre-treatment

This section shows the results of the ammonia pre-treatment in both the column tests and the batch stirred tank reactor tests. This section provides the results of the head sample analysis for each column and the progress of the ammonia pre-treatment will be shown by the extraction of Cu, Fe and Ni (base metals). Further, this section also contains result discussions on the extraction of each of the base metals in both the column treatment tests and the batch stirred tank reactors.

4.1.1 Column treatment tests

In order to monitor the coarse ore (column) treatment, the extraction of copper (Cu), nickel (Ni) and Iron (Fe) were monitored over a period of the various treatment times which were column 0 (no treatment), column 1 (2 days), column 2 (5 days) and column 3 (10 days) as explained in section 3.2.1. The aim of this treatment was to dissolve the oxidation layer that consisted of base metal oxides and therefore the extraction of base metals was monitored. To accurately determine the extraction of base metals, a head

sample analysis was performed on the ore used in each column. Table 19 shows the results of the head sample analyses.

Table 19: Elemental analysis results for ammonia columns head sample

Column	Type of treatment	Cu (%)	Fe (%)	Ni (%)
0	untreated	0.027	9.4	0.18
1	2 day treatment	0.028	9.6	0.18
2	5 day treatment	0.027	9.5	0.17
3	10 day treatment	0.027	9.3	0.18

The results in Table 19 show consistency in the initial Cu, Fe and Ni concentrations for all 4 columns.

4.1.2 Column treatment: Base metal extractions

The extraction of the Cu, Ni and Fe are all shown in Figure 35. The Cu extraction curves show a total extraction of 55%, 24% and 58% after 2, 5 and 10 days of treatment respectively. The Ni extraction curves show a total extraction of 0.6%, 0.8% and 1.1% after 2 and 5 days and 10 days of treatment respectively. The Fe extraction curves show a total extraction less than 0.01% for both the 2 and 5 day treatments and 0.02% after the 10 day treatments.

One of the tools used to confirm the presence of metal ammonia complexes formed in solution are the pH and ORP readings which were taken and plotted in Figure 36. For all three of the column treatments, the pH readings were within the range of 9.5-10, and the ORP readings were within the range 182-212 mV. These values indicate the formation (Muzawazi, 2013) of the $\text{Cu}(\text{NH}_3)_4^{2+}$ ion and the $\text{Ni}(\text{NH}_3)_5^{2+}$ ion that form the metal-amine complex as shown in work done by Muzawazi (2013).

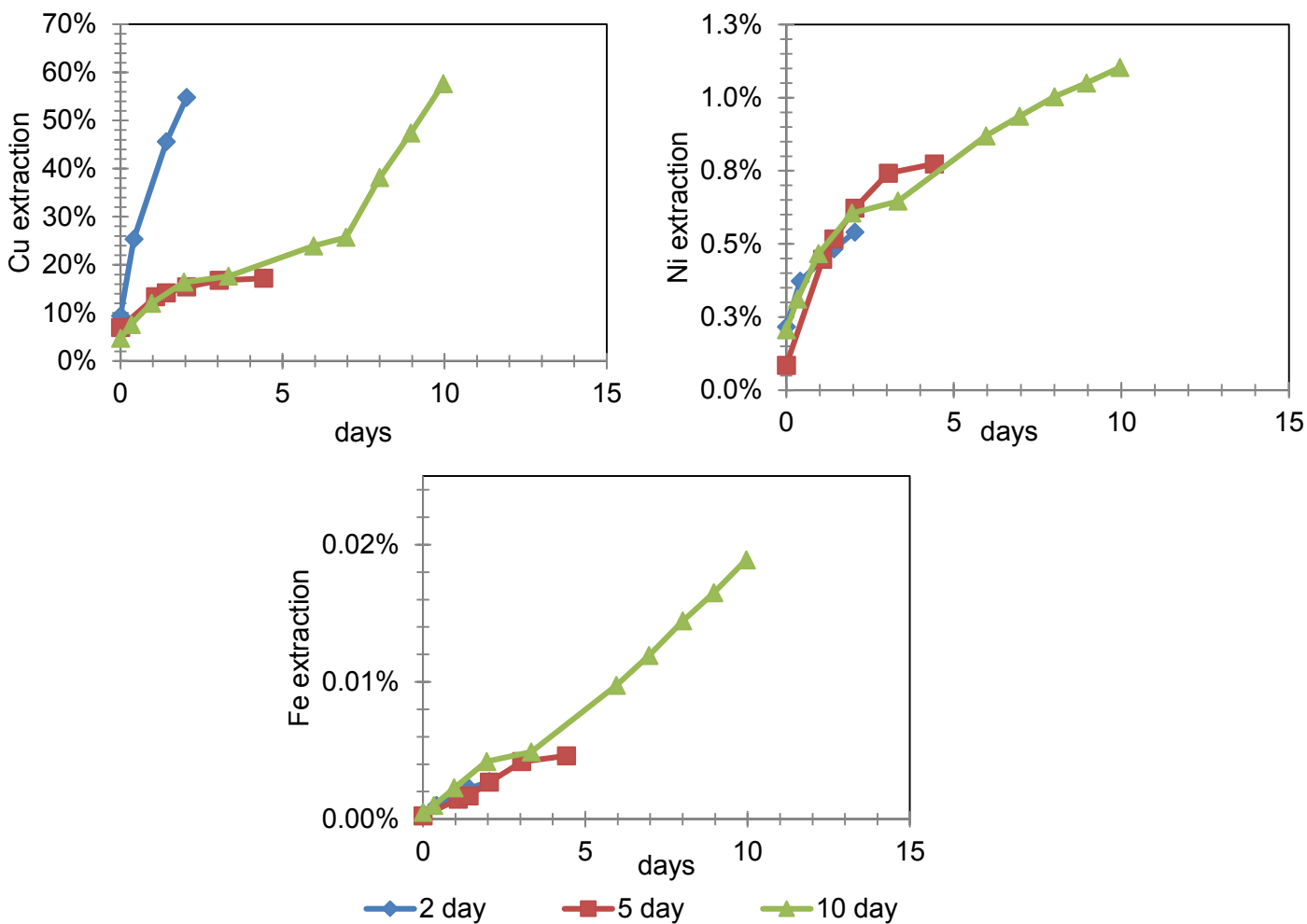


Figure 35: Extraction rates of Cu, Ni and Fe in column treatments with 7M total ammonia, ambient temperatures.

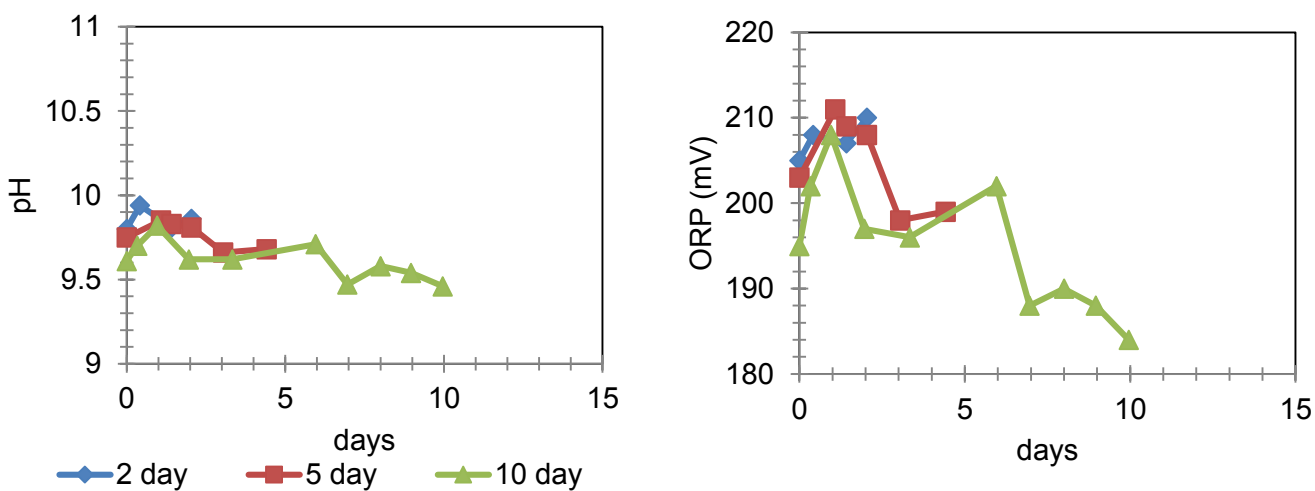


Figure 36: pH and ORP readings for ammonia column treatments with 7M total ammonia, ambient temperatures.

4.1.3 Batch stirred tank treatment

Batch stirred tank reactors were used to treat milled ore with ammonia. For the same reason as in the column treatments, the extraction of copper (Cu), nickel (Ni) and Iron (Fe) were monitored over a period of the various treatment times which were batch 0 (untreated), batch 1(1 hour), batch 2 (3 hour), was monitored. The 1 hour batch was repeated as batch 1a and batch 1b to ensure reproducibility. To accurately determine the extraction of base metals, a head sample analysis was performed on the ore used in each batch. Table 20, shows the results of the head sample analyses.

Table 20: Elemental analysis results for ammonia batch head sample

Batch	Type of treatment	Cu (%)	Fe (%)	Ni (%)
0	untreated	0.04	9.8	0.16
1	1 hour treatment	0.03	8.8	0.16
2	3 hour treatment	0.03	8.8	0.17

The results in Table 20 show consistency in the initial Cu, Fe and Ni concentrations for all 3 batch stirred tanks.

4.1.4 Batch stirred tank treatment: Base metal extraction

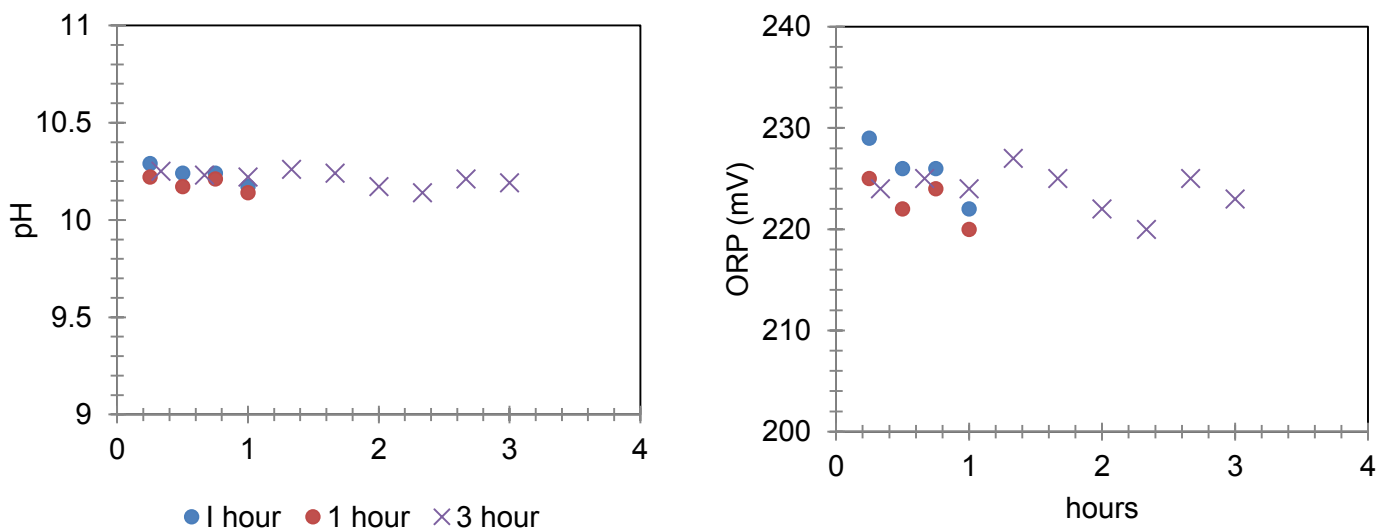


Figure 37: pH and ORP readings for batch stirred tank reactors with 7M total ammonia, ambient temperatures.

For the batch stirred tank treatments (see Figure 37), the pH readings were within the range of 10-10.5, and the ORP readings were within the range 220-230 mV. These values, like in

the column treatment tests, indicate the formation of the $\text{Cu}(\text{NH}_3)_4^{2+}$ ion and the $\text{Ni}(\text{NH}_3)_5^{2+}$ ion that form the metal- amine complex (Takeno, 2005; Muzawazi, 2013).

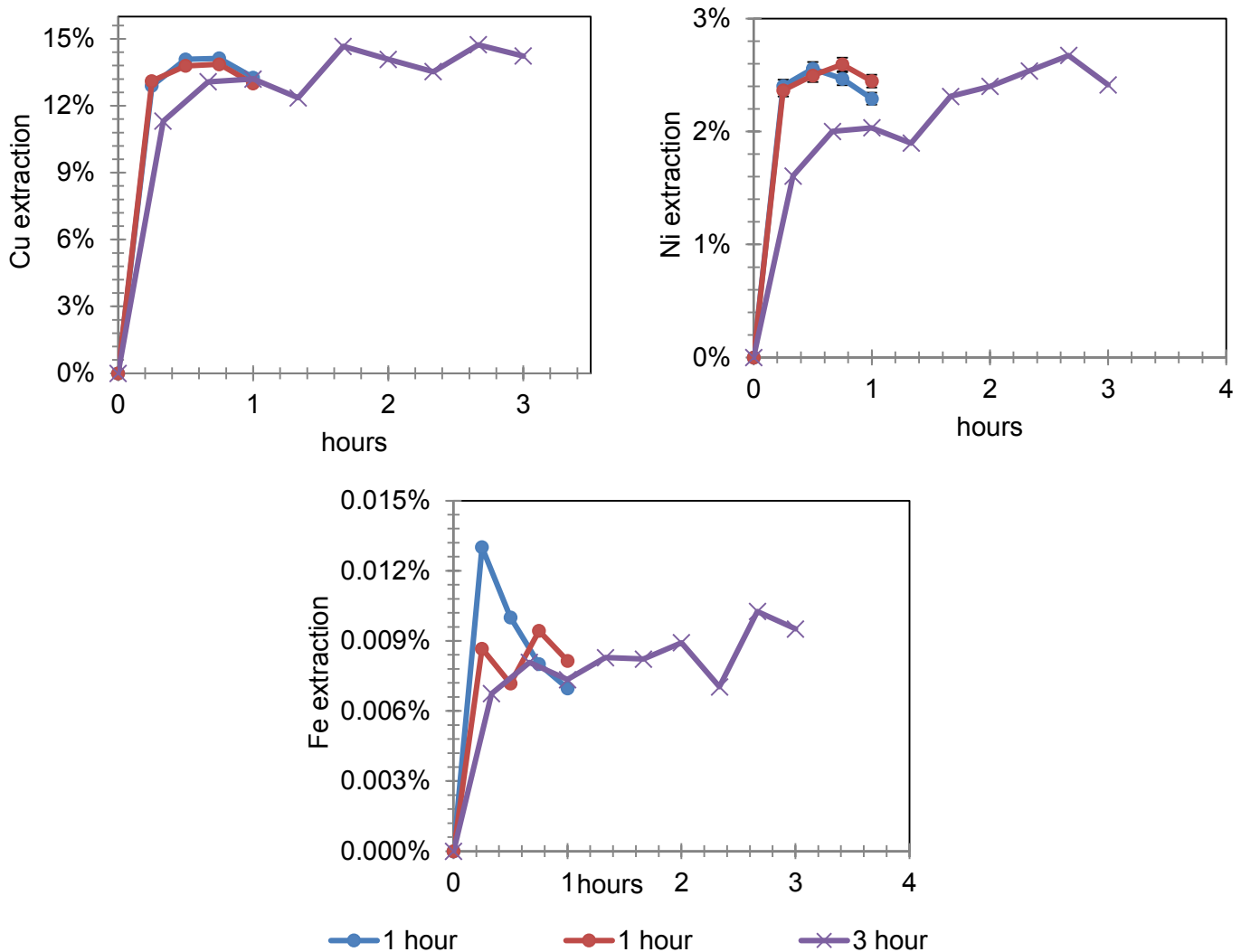


Figure 38: Extraction rates for Cu, Ni and Fe in batch stirred tank reactors with 7M total ammonia and ambient temperatures.

The extraction of the Cu, Ni and Fe are all shown in Figure 38. The Cu extraction curves show a total extraction of 13% and 14% after 1 and 3 hours of treatment, respectively. The Ni extraction curves show a total extraction of 2% after 1 and 3 hours of treatment. The Fe extraction curves show a total extraction less than 0.02% for both the 1 and 3 hours of treatment respectively. However what is interesting is the instant dissolution of 13% and 2% of Cu and Ni respectively within the first $\frac{1}{4}$ of an hour of the treatment. Looking at the total extraction, this indicates that there was little if any further dissolution of Cu and Ni. Two batch stirred tank reactors were run for 1 hour in order to show reproducibility of the tests and this is shown in Figure 38.

4.1.5 Discussion of base metal extraction

Both the column and the batch stirred tank treatments showed the extraction of base metals, Cu, Ni and Fe. However, each of these base metals has varying extraction trends.

Copper (Cu) extraction

The ammonia column results show relatively high Cu extraction (>50% for 2 and 10 day treatments, compared to <2% for both Ni and Fe extractions). However, these copper extractions are inconsistent. The three columns which were run under the same operating conditions (ammonia concentrations, ammonium carbonate concentration, and temperature) were run for different lengths of time. Similar extraction trends and rates (with varying total extractions) would be expected for the three columns. However, the copper extraction after 1.5 days of leaching for column 1, column 2 and column 3 was 46%, 14% and 12% respectively. The Ni and Fe extractions had similar rates and trends.

It is suspected that these inconsistencies are related to grade variability in the sample, given the very low grade of copper in this ore (0.02%). It is therefore important to determine the mass of sample that provides a fair representation of the total population. This is a function of the type of mineral ore, the particle size distribution of the sample, and the grade of the ore. Several sampling calculation methods exist in order to determine the mass of sample. For the purpose of this work, formulae such as the Gy and the Gaudin methods were investigated. The Gaudin method is used when calculating samples with precious metals, as it takes into account that precious metals make up a minute fraction of the mass of the ore, like is the case in this project. However due to the wide usage of the Gy method and simplifications that can be made to accommodate precious metal ores, it was used in the present context (Francis, 1993; Taggart, 1945).

The basic Gy equation is:

$$\frac{WM}{W - M} = \frac{Cd_{max}^3}{s^2}$$

Equation 23

Where

M= Minimum sample weight needed, grams

W= Weight of the entire lot being sampled, grams

C= Sampling constant for the material being sampled, g/cm³

d_{max}= Dimensions of the largest pieces in the sample, cm

s= value of the standard deviation that will be needed to give the desired level of assurance (assay units, such as % wt.).

For the purpose of this work,

Equation 23 can be simplified to Equation 24 when W>>>M, as is the case with precious metal ores.

$$M = \frac{C d_{max}^3}{s^2}$$

Equation 24

(Francis, 1993)

In order to make preliminary calculations, the same assumptions as in the work by Holmes (2004) were made, as a similar ore was used. This calculation using the following parameters (shown in appendix section 8.3) resulted in a minimum sample mass of 27 kg in order to have a fair representation of the ore. A summary of the parameters used in this calculation is presented in Table 21

Table 21: Summary of parameters used in calculation of minimal sample size

Variables	Units	Coarse ore	Milled ore
Cu assay	%	0.024	0.024
s	%	0.022	0.022
C	g/cm ³	162	610
d_{max}	cm	0.43	0.03
Mass	kg	26.64	0.04

This calculation was done on the basis of the Cu concentration and the top size of the ore used. Due to limitations of the columns in the laboratory, only 3kg of ore was used, therefore this explains the inconsistent nature of the Cu extraction curves for the 2, 5 and 10 day column treatment curves (see Figure 35). Further, for a much smaller top size such as the ore used for the batch stirred tank treatment, the minimal sample requirement was 35g. Given that 200g were used for each batch test, the Cu extraction curves were more consistent in this case (see Figure 38).

Iron (Fe) extraction

In terms of the Fe extraction, the total extraction of Fe in both the column and the batch stirred tank treatments was below 0.02% and therefore it can be assumed to be zero/no extraction. This shows that Fe was hardly dissolved in the ammonia solution. This is in line with work by Beckstead and Miller and Muzawazi (Muzawazi, 2013; Beckstead & Miller, 1977) that alluded to the oxidation of iron to ferric and subsequently the precipitation of ferric to iron oxides which are insoluble in ammonia under the given conditions. In the case of this project (see Table 6), Fe is hence considered insoluble as it is in the form of Fe oxides/hydroxides.

Nickel (Ni) extraction

In terms of the nickel extraction, in an attempt to dissolve the oxidation layer, the results of both the column treatment and the batch stirred tank treatments, show that the longer the treatments, the higher the Ni extractions, this was expected. However, a low total Ni extraction was observed for both the column and the batch stirred tank reactors (a minimum of 1.1% and 2.5% respectively).

Finally, due to the inconsistencies with the Cu extraction rates and the insignificant Fe extractions, Ni extraction will be used as a proxy to investigate the leaching of base metals from here onwards. Further, due to the instant dissolution of the base metals, especially in the stirred batch tank tests (see Figure 38), the long term tests were used to investigate what happens to Ni extraction over a longer period of time.

The column and batch stirred tank treated ore was floated in order to determine the effect of the treatment on the flotation of this ore. The subsequent flotation results will be presented in Chapter 5 (flotation results). The long term ammonia leaching of the ore was also investigated and the results of the column and batch stirred tank ammonia leaching tests is presented below.

4.2 Extraction of Valuable Metals

This section presents the results of the long term ammonia column and batch stirred tank reactor leach. The head sample analysis (elemental base and precious group metals) and the extraction results of Cu, Fe and Ni (base metals) has been presented and discussed.

4.2.1 Long-term column leach

Table 22 shows the base metal and PGM head sample analysis of column 1 and column 2 which were run under identical conditions (ammonia concentration, temperature, leaching time and aeration) for reproducibility.

Table 22: Base and PGM elemental analysis for ammonia leaching columns

Columns	Cu (%)	Fe (%)	Ni (%)	Pt (ppm)	Pd (ppm)	Au(ppm)
1	0.026	9.7	0.19	0.58	0.28	0.05
2	0.024	9.9	0.19	0.85	0.32	0.08

The graphs in this section show the extraction of Ni from the ore with the use of ammonia solution in columns over a period of 28 days. This section also presents the corresponding pH and ORP values.

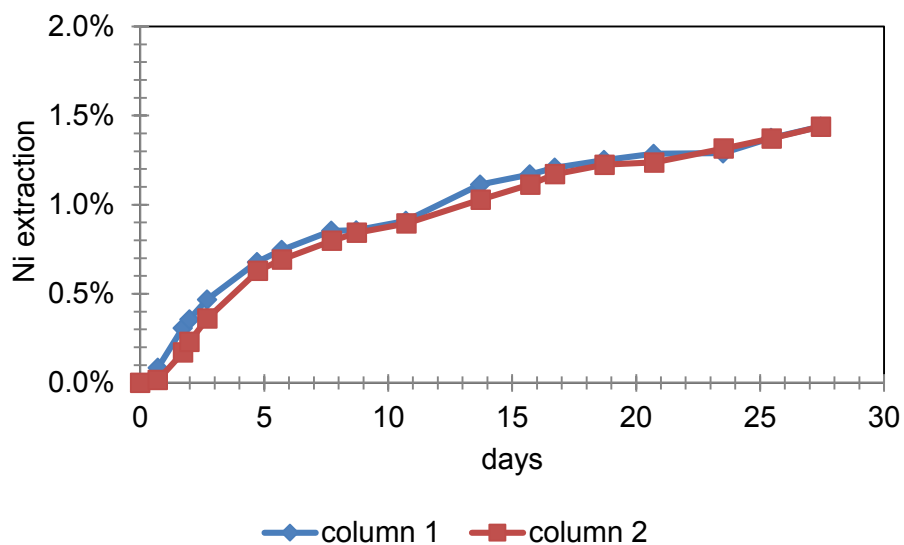


Figure 39: Graphs showing Nickel extraction in columns for 28 days, with 5M ammonia, aerated at 80ml/min and ambient temperatures

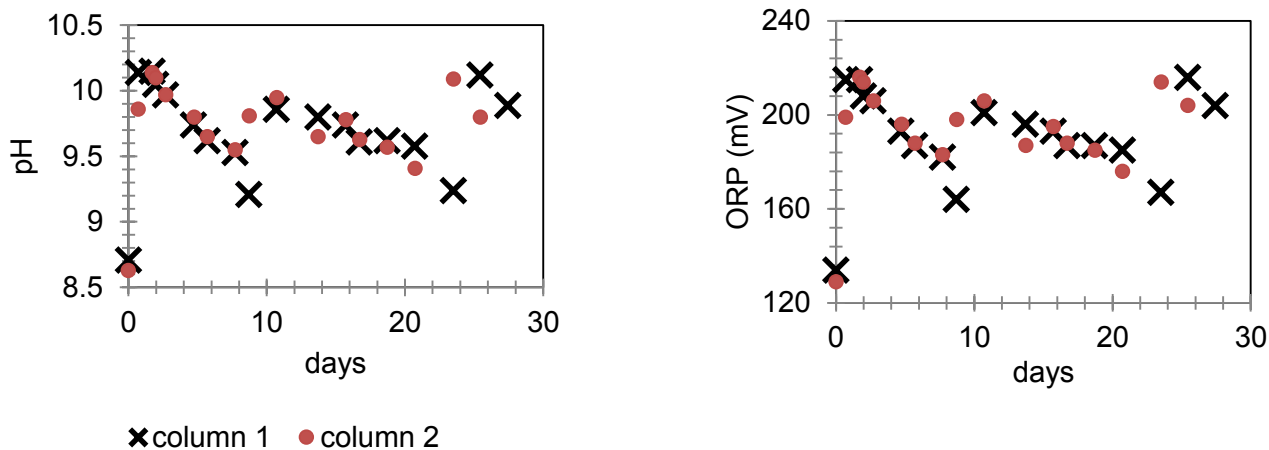


Figure 40: pH and ORP values for 28 day column treatment with 5M ammonia, aerated at 80ml/min and ambient temperatures

The results of the long term ammonia columns show a total of 1.5% for Ni extraction over 28 days (see Figure 39). This indicates a low extraction rate of Ni from oxidized/weathered ores. In terms of the pH and ORP values, these were all within the range of 8.6-10 and 130-220 mV respectively. These values lie within the range that allows for the formation of metal-amine complexes. However, day 10 and 23 show a dip in the ORP values (see readings which resulted in a lag in the extraction of Ni (see Figure 39)). This is consistent in the following batch stirred tank reactors. ORP values below 180mV resulted in a lag in the extraction of Ni.

A calculation of the rates using linear regression has been summarised in Table 23. The rates indicate a steady decrease in the rate of extraction and a levelling off towards the end of the extraction.

Table 23: Calculation of Ni extraction rates (mg/day) at different times of leaching process

Rates (mg/day)	Column 1	Column 2
Initial rates (0-4 days)	5.9	4.7
Middle rates (10-16 days)	4.3	4.0
Final rates (20-27 days)	3.1	3.0

The rates and the similarities in Table 32 show that column 1 and column 2 had similar rates and trends and hence this experiment had good reproducibility.

4.2.2 Long-term batch stirred tank leach

Table 24 shows the base metal and PGM head sample analysis of batch reactors 1 and 2. Batch reactors are run under identical conditions for reproducibility.

Table 24: Base and PGM elemental analysis for ammonia leaching columns

Columns	Cu (%)	Fe (%)	Ni (%)	Pt (ppm)	Pd (ppm)	Au(ppm)
1	0.026	9.7	0.19	0.58	0.28	0.05
2	0.024	9.9	0.19	0.85	0.32	0.08

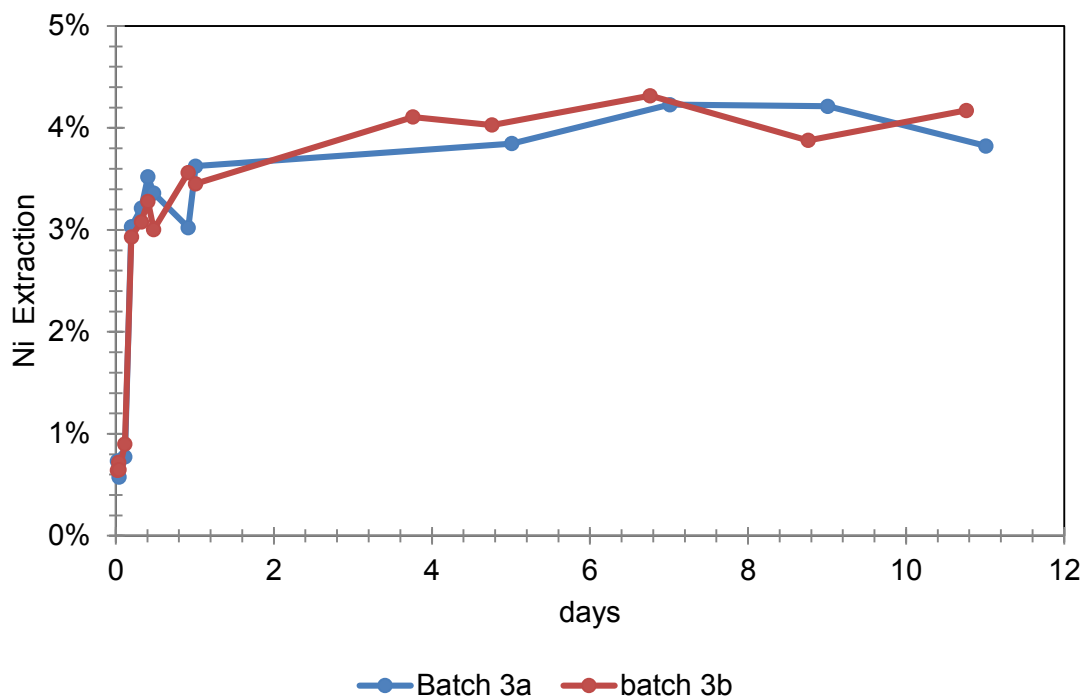


Figure 41: Graph showing the Nickel extraction in batch stirred tank reactors over 10 days, with 5M total ammonia, aerated at 80ml/min and ambient temperatures

It is clear from batch stirred tank reactors that the Ni extraction levels off after 3 days of leaching. This occurs after only 4% of the Ni has been extracted. Initially there is an instant dissolution of Ni and then the extraction rate increases steadily. This is also confirmed by the pH and ORP diagrams (Figure 42) which also level off at pH 9.3 and ORP reading of 172 mV.

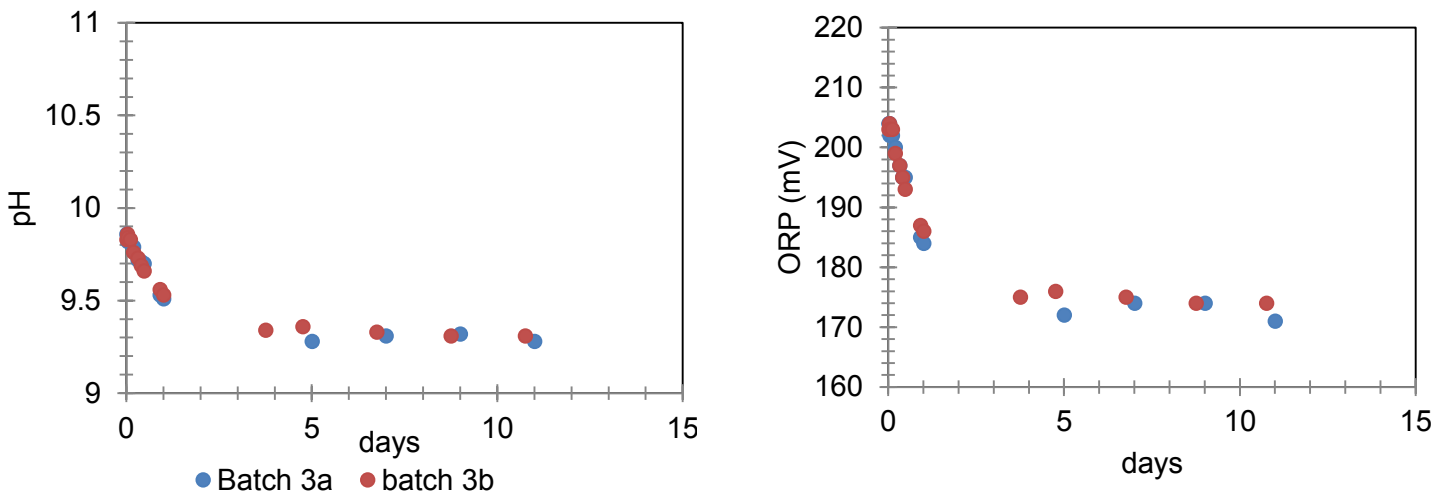


Figure 42: Graph showing the pH and ORP of Ni extraction in batch stirred tank, with 5M total ammonia, aerated at 80ml/min and ambient temperatures

4.2.3 Discussion of results: Batch stirred tank and column treatment

The results show a levelling off (in the batch stirred tank reactors) and low total extraction (in the column reactors) of Ni after 4 days of leaching. This shows that there is a maximum amount of nickel available for leaching and the rest of the nickel may be in forms that are not leachable. Further, the oxidation layer which acts as passivation layer prevents the access of ammonia to the base metal oxides.

This is a very different outcome to that of the work done by Muzawazi (2013). In that case results showed 95% Ni extraction over a 3 day period for similar ammonia batch stirred reactor tests (ambient temperature, 4M total ammonia concentration, 2% pulp density). However, the ammonia column tests run at similar conditions (ambient temperature, 4M total ammonia) show a 15% extraction of Ni. This indicates that even though a low Ni extraction was expected in the columns, 1.5% was too low at these conditions.

The major difference between these tests and the tests run by Muzawazi is the mineralogy of the ore used. The ore used by Muzawazi was a low grade concentrate and had an abundance of base metal sulphides. As shown by Table 5 and Table 6, there are very little if any sulphides especially base metal sulphides. Further, differences in mineralogical content require differences in processing operations.

4.3 Batch stirred tank tests: Varying conditions

The results in this section focus on the extraction of Ni from the ores with the use of ammonia solution with varying conditions. Batch stirred tanks were run and conditions such as Initial

copper concentration, pulp density, ammonia concentration and an acid pre-leach were all tested over a 2-day (3000 minutes) batch leach. Table 25 shows the experimental matrix.

Table 25: Table shows the experiments run with the different variables and their respective parameters

Variable	Low	High
Initial copper concentration	0ppm	500ppm
Ammonia concentration	4M	8M
Pulp density	5%	15%
Acid pre-leach	0 hour leach	2 hour leach

4.3.1 Effect of Initial Copper Concentration

The initial copper concentration was varied between 0ppm and 500ppm. The extraction rates shown in Figure 43 indicate a higher initial concentration of Ni due to the instant dissolution of Ni in the 0ppm batch stirred tank reactor. However after 170 minutes of leaching there is a steep increase in the extraction of Ni in the 500ppm stirred batch tank reactor, Overall, a higher extraction was achieved with a higher initial Cu concentration.

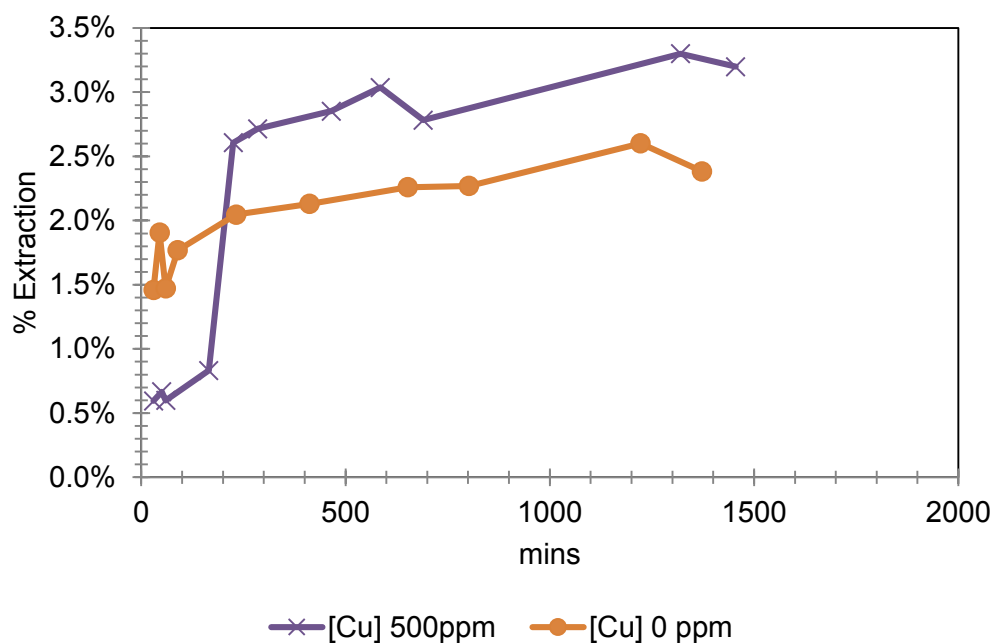


Figure 43: Graphs showing comparable nickel extraction rates between 0 ppm and 500 ppm of initial copper concentration

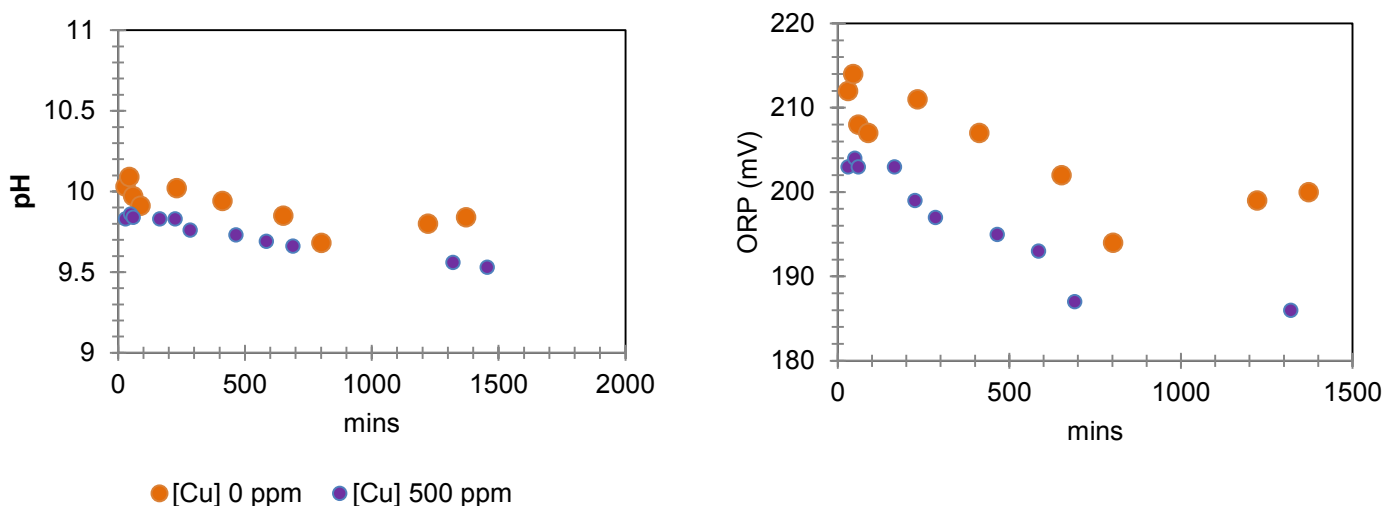


Figure 44: Graphs showing comparable a) pH and b) ORP values between 0 ppm and 500 ppm of initial copper concentration

Beckstead and Miller (1977) observed that an initial cupric concentration increases the rate of extraction of other base metals. Work by Ghosh, Das & Biswas (2003) also indicated a strong influence of Cu (II) ion on leaching of ZnS ore. In this case Cu (II) is formed as a soluble amine complex which acts as an oxygen carrier through the Cu (II)/Cu (I) redox couple reaction. In the presence of ammonia this is made feasible through the cupric ammine $\text{Cu}(\text{NH}_3)_4^{2+}$ which is reduced to the cuprous ammine $\text{Cu}(\text{NH}_3)_2^+$.

Figure 44 indicates a pH range of 9.5-10.2 and an ORP range of 190-215 mV which is within the range of both the cuprous and the nickel ammine complex (refer to Figure 17).

4.3.2 Effect of pulp density

Figure 45 shows the effect of pulp density on the extraction of Ni. As shown in the graph, the extraction of Ni for the 15% (pulp density) mixture was slightly lower than the extraction of Ni for the 5% (pulp density) solution. This is a result of the fact that at a 5% solution, the ore is exposed to more lixiviant and therefore one would expect a higher extraction (especially if the reagent is limiting). This is probably the reason that there is an initial spike in the extraction of Ni after 120 minutes of leaching of the 5% solution. However, the total extraction of both tests is approximately 3%; this shows that the effect of pulp density is negligible under these conditions. Further, the shapes of both extraction curves are similar.

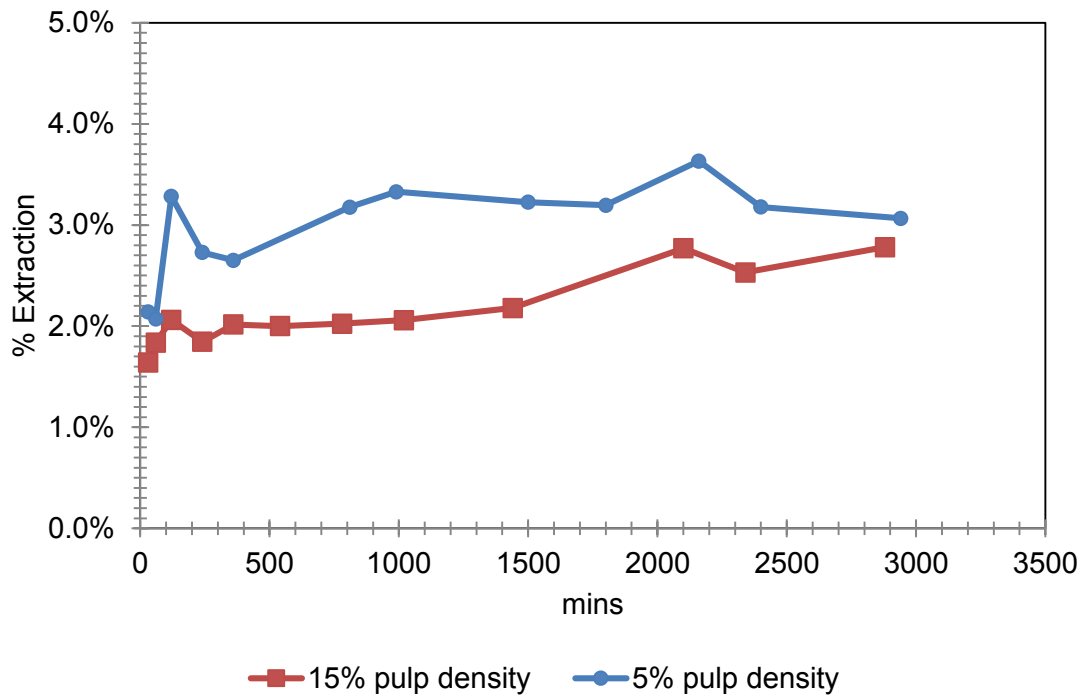


Figure 45: Graphs showing comparable Ni extraction rates between 5% and 15% pulp densities (w/v)

In terms of the pH and ORP, for both tests, pH ranges between 9.2-10 and the ORP values in the range of 170-215 mV. The graphs indicate that there is no significant difference between the 5% and the 15% pulp density tests in terms of the nickel amine complexes present. This corresponds to Muzawazi's (2013) results, where it was proved that the effect of pulp density was largely negligible.

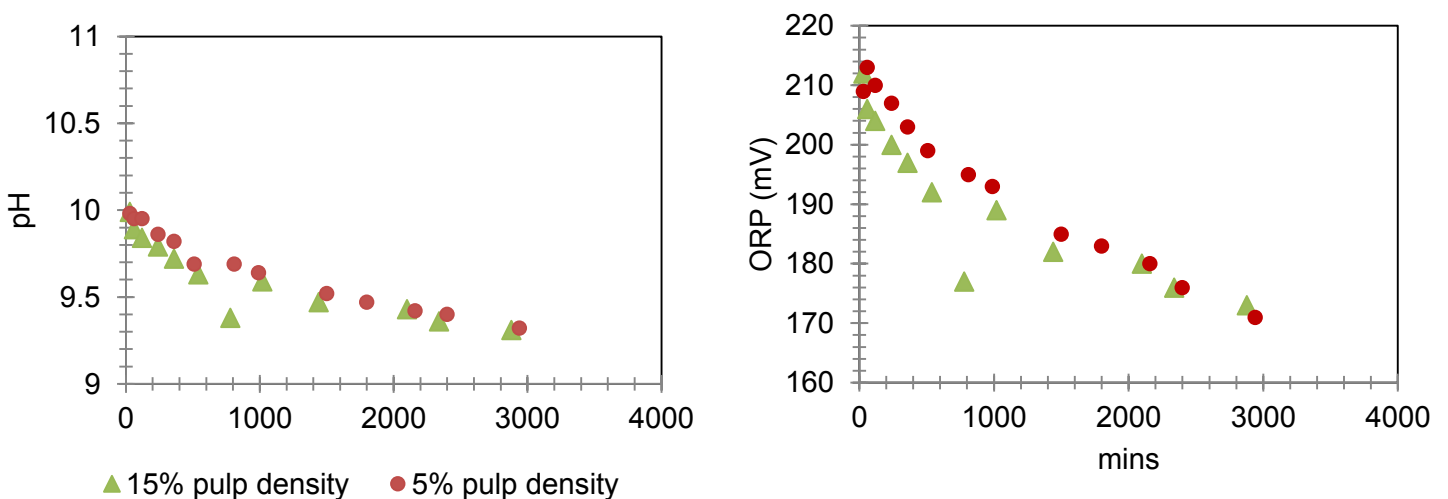


Figure 46: Graphs showing comparable a) pH and b) ORP values between 5% and 15% pulp densities (w/v)

4.3.3 Effect of Ammonia concentration

Figure 47 shows a comparison between leaching tests conducted at a 4M concentration and an 8M concentration. The graph shows that by doubling the ammonia concentration the total extraction of Ni remained the same (3.4% to 3.2% respectively). This indicates that these batch tests are not dependent on the concentration of ammonia. An investigation by Park *et al.* (2007), where the oxidative leach of a Cu-Ni-Co-Fe matte by ammonia/ammonium sulphate was investigated, proved that an increase in ammonia concentration from 0.5M – 2M resulted in an increase in total extraction from 42% -85% respectively. However, any increments above 2M showed no improvement in the total Ni extracted. Further, work by Muzawazi (2013) showed that an increase in Ni extraction corresponded to an increase in ammonia concentration up until 3M. Similarly to Park *et al.* (2007), concentrations above 6M had little/no effect on the extraction of Ni. This means that beyond a certain concentration, the concentration of ammonia ceases to affect the extraction of Ni. This was also shown in work done by (Liu & Tang, 2010)

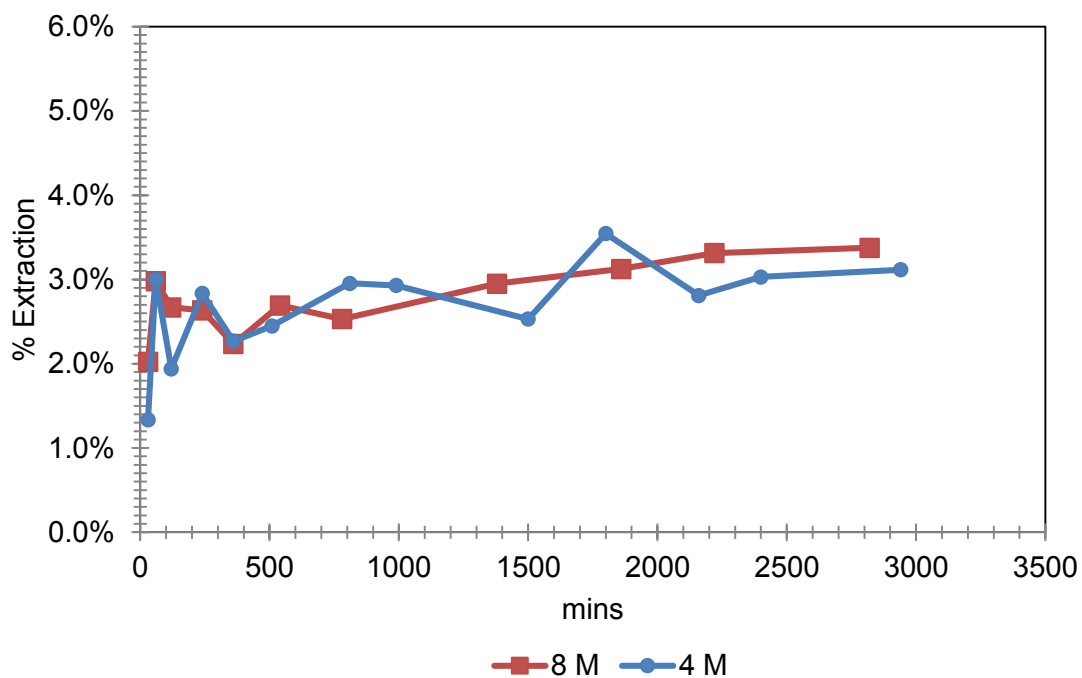


Figure 47: Graphs showing comparable Ni extraction rates between 4M and 8M ammonia tests

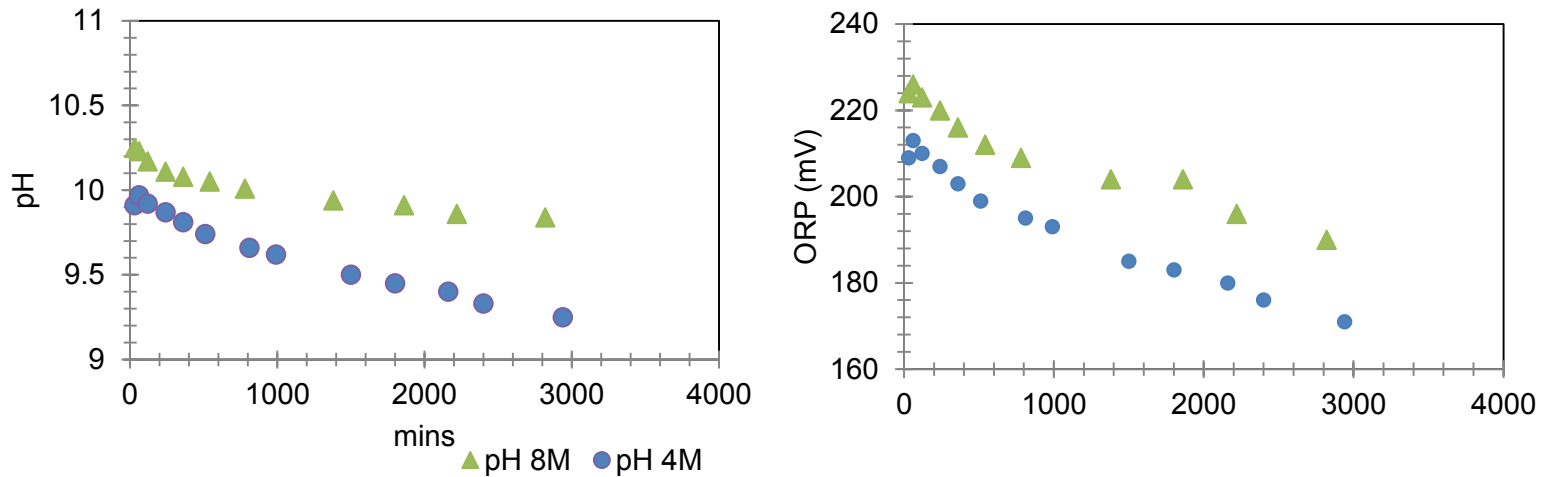


Figure 48: Graphs showing comparable pH and ORP values for 4M and 8M ammonia tests

Figure 48 shows the pH and ORP values obtained in the 4M and 8M tests. In terms of the pH and ORP pH ranges between 9.3-10.3 and the ORP values are in the range of 170-225 mV for both tests. The 8M tests have a higher ammonium carbonate concentration and hence a greater buffering effect than the 4M tests. Therefore, the pH and ORP values for the 4M test are slightly lower.

4.3.4 Effect of acid pre-leach

Figure 49 shows the result of pre-treating the ore with a 0.54M sulphuric acid leach prior to an ammonia leach. The ammonia leach extracted 5% and 3% Ni from the acid treated ore and the untreated ore respectively. This shows the treatment improved the extraction of Ni. However, a total of 5% dissolution of nickel is still considered a low extraction.

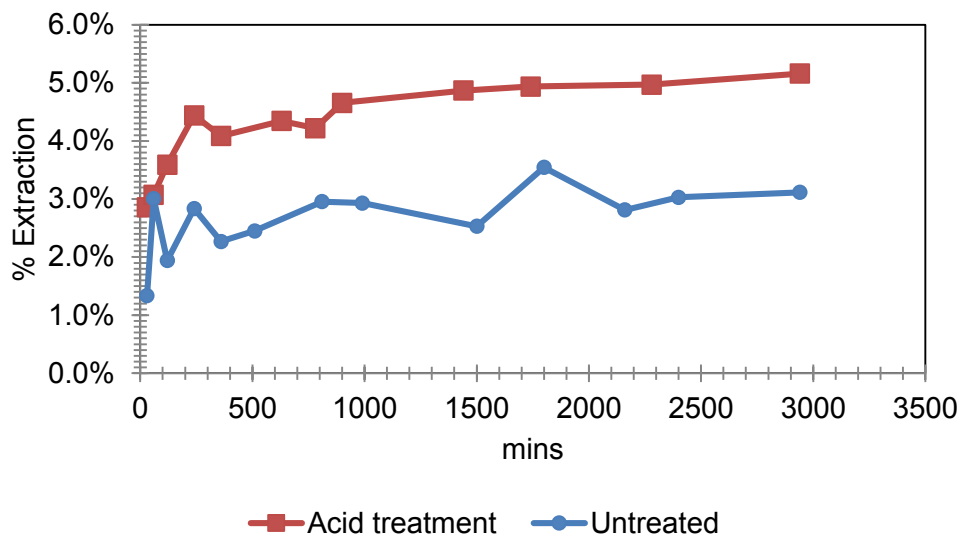
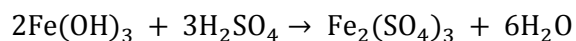
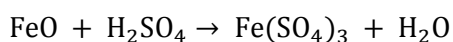


Figure 49: Graphs showing comparable Ni extraction rates between ore pre-treated with acid and untreated ore

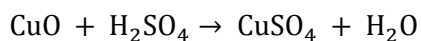
The acid treatment is a wash to dissolve the oxidation layer to allow the ammonia leach to extract the base metals more easily. Further, Ramonotsi (2011) and Luszczkiewicz and Chmielewski (2008) used a sulphuric acid pre-leach to enhance the recovery of valuable metals via the flotation process. The equations below show the chemical reactions involved in the dissolution of the oxidation layer using sulphuric acid.



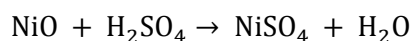
Equation 25



Equation 26



Equation 27



Equation 28

However, the downside of this process is the unselective nature of sulphuric acid. This may lead to the depletion of Ni and Cu (see Equation 27 and Equation 28) and also high consumptions rates. The ore was analysed for Fe, Cu and Ni to determine how much of the base metals were dissolved in the pre-treatment. Table 26 shows these results.

Table 26: Showing the dissolution of base metals in acid pre-treatment

Base metal	Fe	Cu	Ni
(%) dissolved	1.5	25.3	6.7

Figure 50 shows the pH and ORP values of the acid pre-treated and the untreated tests. It shows the pH and ORP values of the acid treated tests were slightly higher than that of the untreated tests. Further, a water wash is required after the acid leach to ensure appropriate pH levels for the ammonia leach.

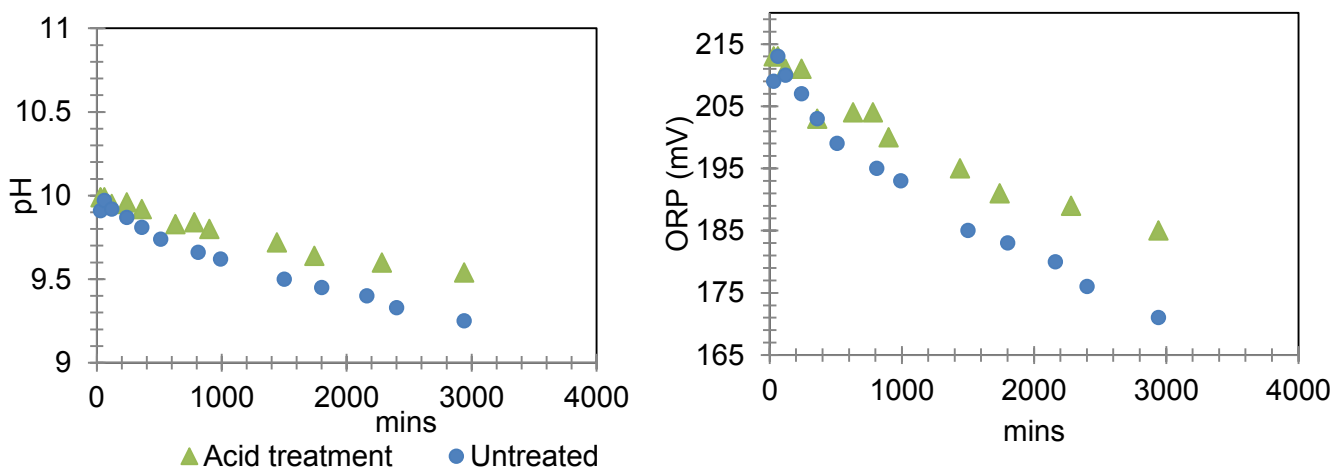


Figure 50: Graphs showing comparable pH and ORP values rates between ore pre-treated with acid and untreated ore

4.4 Cyanide Column leach

This section shows the results of a sodium cyanide leach in order to extract base metals (Ni) and PGMs (Pd and Pt) over a 40 day period. Further, the impact of an ammonia leach (to extract base metals) prior to a cyanide leach was investigated and the results and discussions are presented in this section.

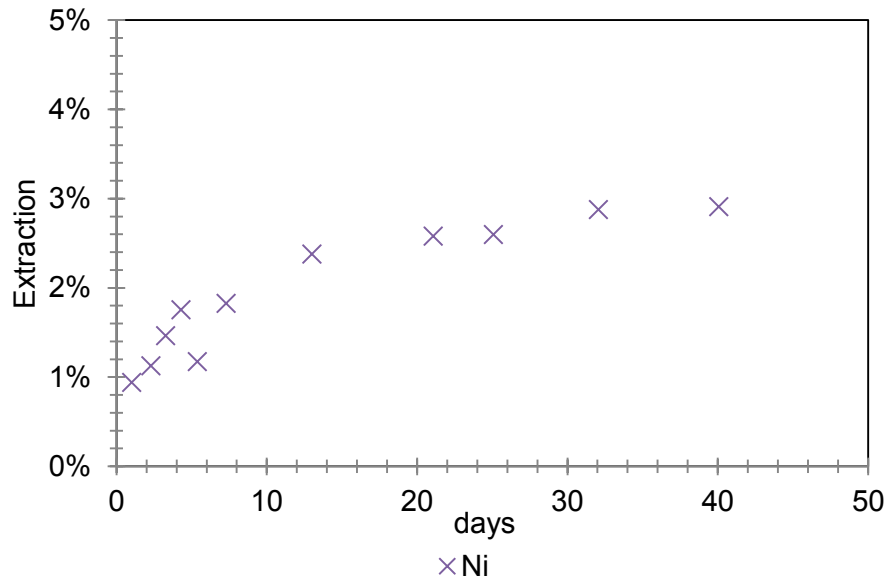


Figure 51: Extraction curves for base metals (Ni) with direct sodium cyanide leach, with 0.5M cyanide, aerated at 80ml/min at 40°C

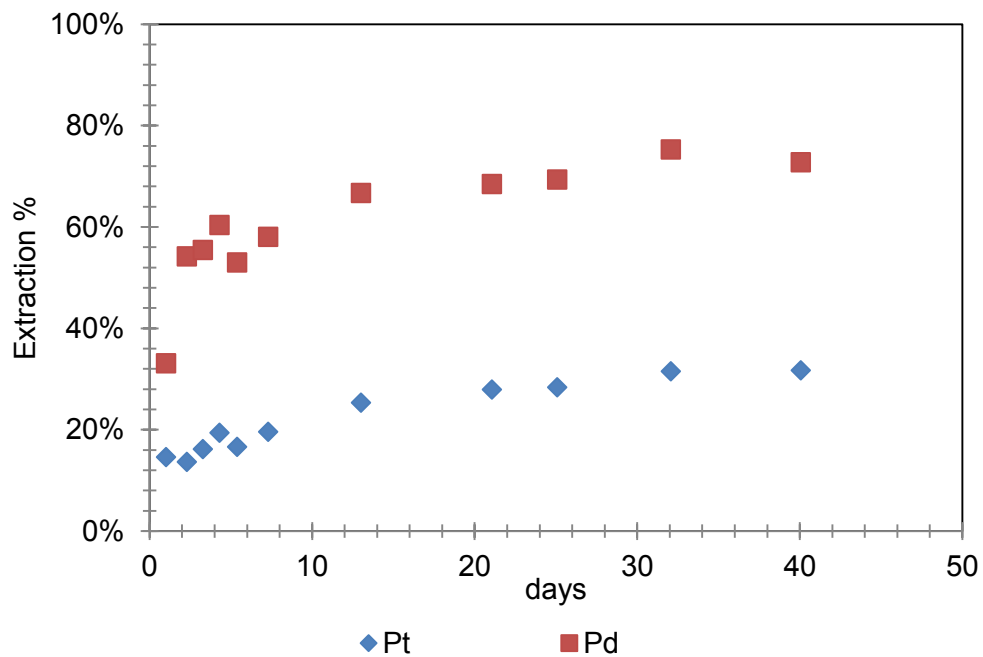


Figure 52: Extraction curves for PGMs (Pt and Pd) with direct sodium cyanide leach, with 0.5M cyanide, aerated at 80ml/min at 40°C

Figure 51 and Figure 52 shows the total extraction of valuable metals from a direct sodium cyanide leach of untreated whole ore. In terms of the base metals, the total extraction of Ni is 3%. The graphs also show a total extraction of 32% and 73% for Pt and Pd respectively.

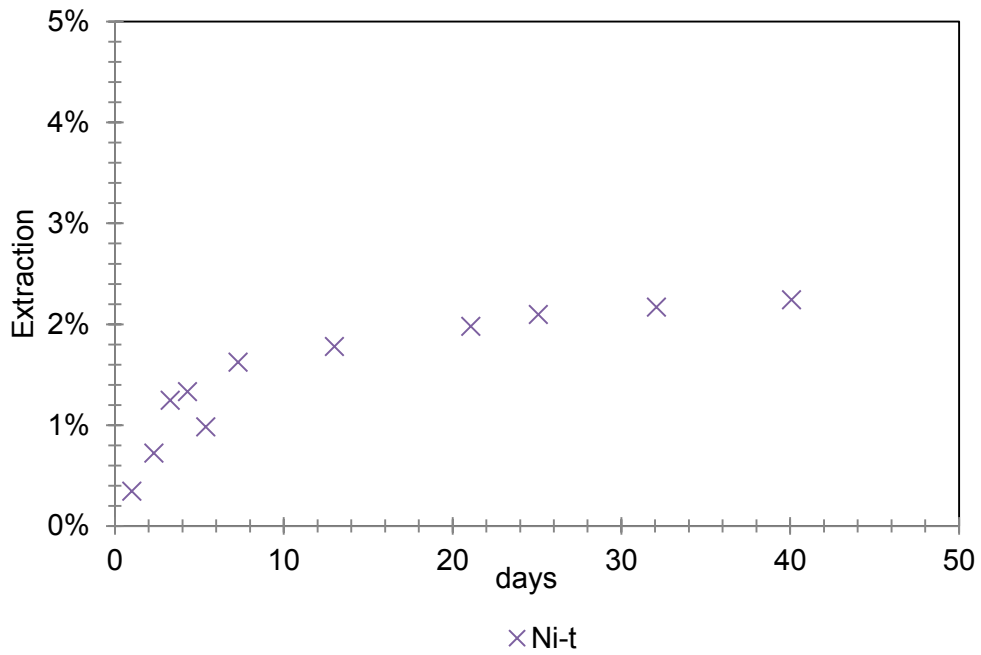


Figure 53: Extraction curves for base (Ni and Fe) with an ammonia leach followed by a direct sodium cyanide leach, with 0.5M cyanide, aerated at 80ml/min at 40°C

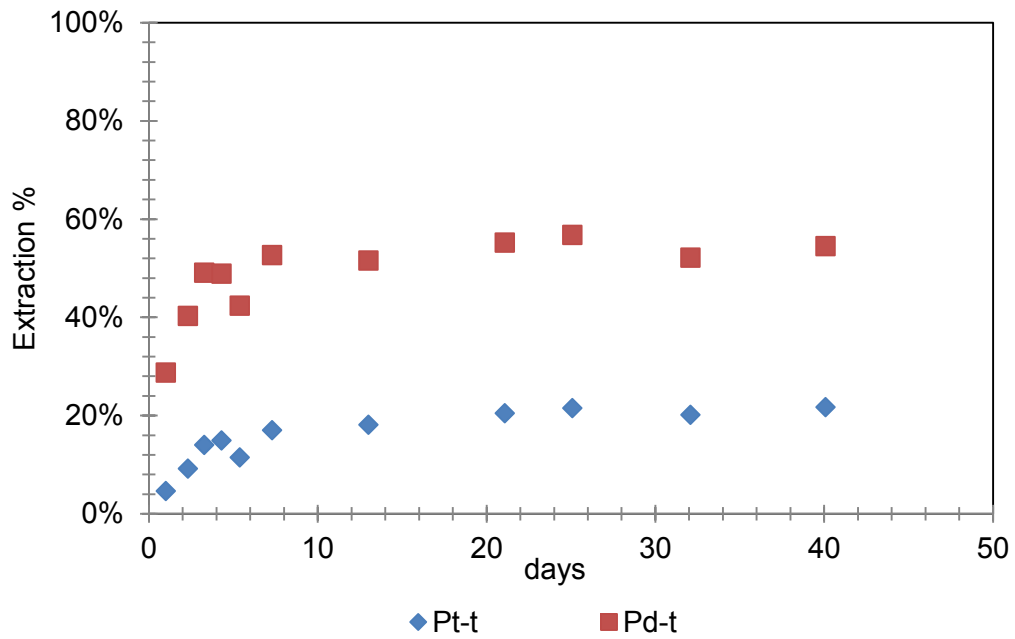


Figure 54: Extraction curves for PGMs (Pt and Pd) with an ammonia leach followed by a direct sodium cyanide leach, with 0.5M cyanide, aerated at 80ml/min at 40°C

Figure 53 and Figure 54 shows the total extraction of valuable metals from an ammonia leach followed by a sodium cyanide leach of PGMs. In terms of the base metals, the total extraction of Ni is 2% and total extraction of 22% and 55% for Pt and Pd respectively.

A comparison between the column 1 and column 2 (untreated and ammonia treated) shows a higher extraction was achieved in the untreated column for Pt, Pd and Ni. Therefore the ammonia treatment decreases the total extraction of both the base metals and PGMs. A water wash could be introduced to ensure that any ammonia residues do not interfere with the cyanide leach.

5 FLOTATION RESULTS AND DISCUSSION

This section will present the milling curve data and the flotation test results for both the column and the batch stirred tank reactor tests. Figure 55 shows the experimental procedure and highlights the results presented in this section.

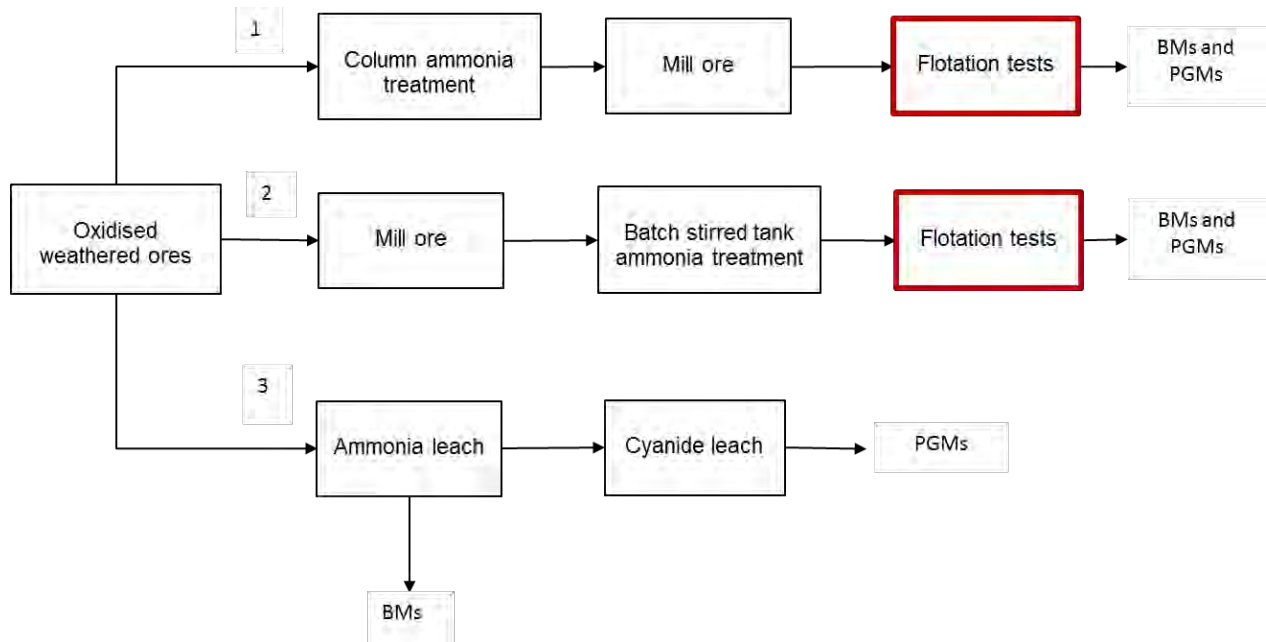


Figure 55: Schematic of the experimental procedure with the flotation test results highlighted

This section includes cumulative solid against cumulative water recovery curves, and due to the association of PGMs with base metals, total base metal recovery and total PGM recoveries will be presented. In order to quantify the ability of the pre-treatments to improve the grade of the ore (in terms of the valuable metals), an upgrade factor and the total base metal and PGM recoveries were evaluated. The upgrade factor is a comparison between the grade of the concentrate and the grade of the feed. It is calculated by Equation 29

$$\text{Upgrade factor} = \frac{\text{metal grade of concentrate \%}}{\text{metal grade of feed \%}}$$

Equation 29

According to Equation 29, an increase in the upgrade factor with an increase in the treatment time indicates that the treatment increases the total recovery of the metal. Due to inconsistencies in the Cu extractions in the leaching tests (see section 4.1.2) and the unreactive iron oxide/hydroxide species, only the Ni recovery and upgrade will be discussed in detail in the flotation of base metals.

5.1 Column treatment: Flotation results

This section gives flotation results and discussion on the column treated ore in terms of the cumulative solids and water recoveries, base metal recoveries and PGM recoveries.

5.1.1 Cumulative solids and water recovery

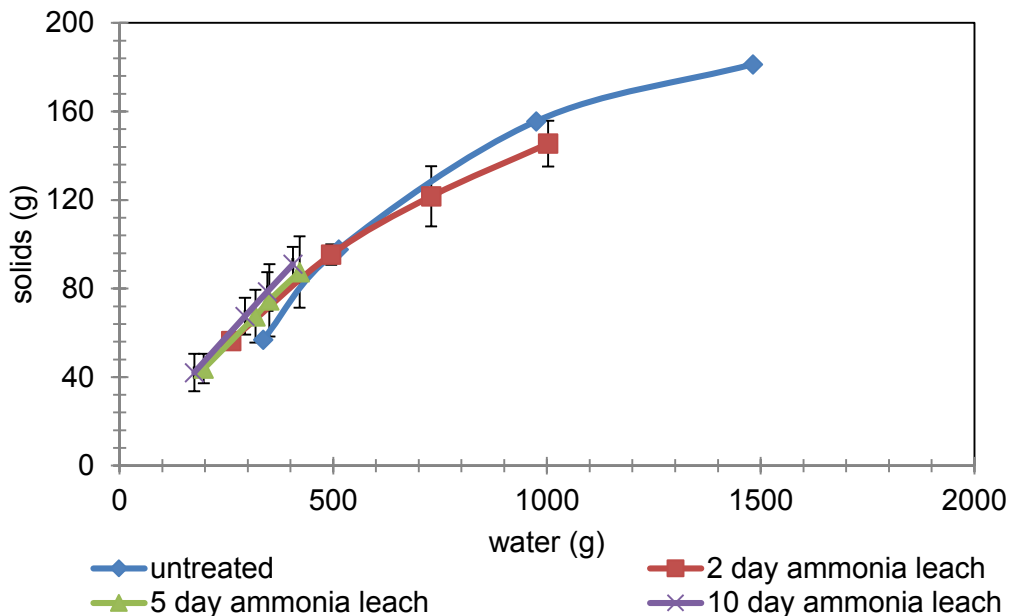


Figure 56: Total solids and water recovery for column treated ore with 30% pulp density, impeller speed of 1200rpm and aeration of 7l/min

Figure 56 shows the effect of the column (coarse ore) ammonia treatment on the flotation of the ore. This shows that treatment decreased the total cumulative water recovered, the results show the untreated ore, 2 day, 5 day and 10 day treated ore recovered 1482g, 1003g, 513g and 405g of water respectively. In terms of cumulative solids recovered, the untreated ore, 2 day, 5 day and 10 day treated ore recovered 181 g, 146 g, 91 g and 91 g of solids respectively. This shows that the treatment decreased the total solids recovered. However, in order to determine the effect on the valuable (base metal and PGM) recovery, the total solids recovered were analysed for their base metal and PGM content.

5.1.2 Cumulative solid recovery over time: Column reactors

In order to determine the effect of the treatment on the rate of recovery, total solids vs time graphs (Figure 57) were plotted for the column test material.

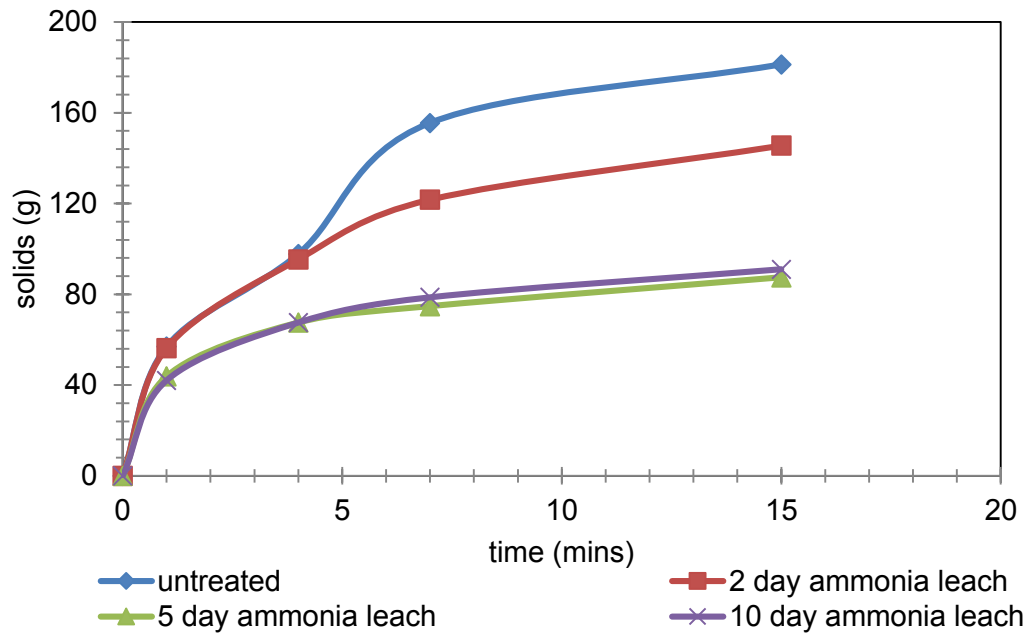


Figure 57: Graph of solids vs time for column flotation tests with 30% pulp density, impeller speed of 1200rpm and aeration of 7l/min

The plot of solids recovered against time shows that the ammonia treatment reduced the initial rate of solid recovery marginally, but over the longer term, solids flotation was significantly depressed after longer treatment.

5.1.3 Base metals recovery

Table 27 shows the upgrade factor and the total recoveries for Cu, Ni and Fe for the column treatment. Total recoveries for all the base metals were all $\leq 50\%$, which is a poor recovery. Looking at the upgrade factor for all three base metals, Cu and Fe, there is no direct correlation between the upgrade factor and the treatments. Ni on the hand shows an increasing upgrade factor with increased length of pre-treatment although there are perhaps too few data points to confirm this.

Table 27: Summary of upgrade factor and total base metal recoveries of column treatment flotation

	Copper (Cu)		Nickel (Ni)		Iron (Fe)	
	Upgrade factor	Recovery %	Upgrade factor	Recovery %	Upgrade factor	Recovery %
Untreated	1.83	45	1.52	37	1.35	33
2 day leach	1.33	30	1.65	37	1.07	24
5 day leach	2.55	52	1.38	28	0.53	11
10 day leach	1.89	28	2.81	42	2.60	39

5.1.4 PGM recovery: 4E analysis

Table 28 shows the upgrade factor and the total 4E (Pt, Pd, Rh, Ag) recovery for the column treatment. Total recoveries for PGMs were all between 50-60%. An upgrade factor of 2.73, 2.48, 2.83 and 4.03 was achieved for the untreated, 2 day; 5 day and 10 day leach respectively. This shows PGM upgrade of the ore was improved with length of the ammonia column pre-treatment.

Table 28: Summary of upgrade factor and total PGM recoveries of column treatment flotation

4E (Pt, Pd, Rh, Ag)		
	Upgrade factor	Recovery %
Untreated	2.73	67
2 day leach	2.48	56
5 day leach	2.83	57
10 day leach	4.03	60

5.2 Batch stirred tank treatment

5.2.1 Cumulative solids and water recovery

Figure 58 represents the cumulative solids vs water recovery curves for the batch stirred tank treated ore (milled ore).

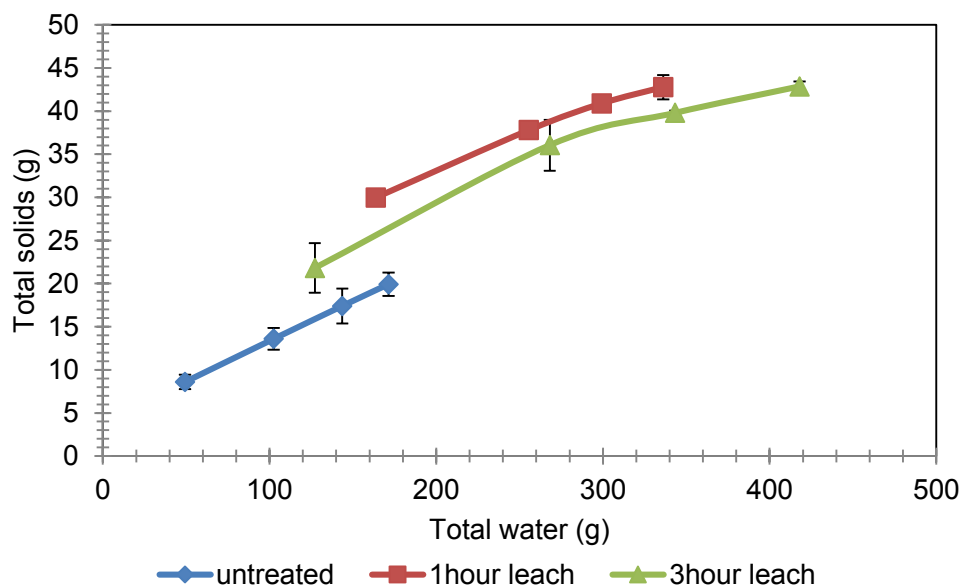


Figure 58: Total solids and water recovery for batch stirred tank treated ore with 30% pulp density, impeller speed of 250rpm and aeration of 3ml/min

Figure 58 shows the effect of the batch stirred tank (milled ore) ammonia treatment on the flotation of the ore. In terms of cumulative water recovered, the results show the untreated ore, 1 hour and 2 hour treated ore recovered 171 g, 336 g and 418 g of water respectively. This shows that treatment increased the total water recovered. In terms of cumulative solids recovered, the untreated ore, 1 hour and 2 hour treated ore recovered 20 g, 40 g and 42 g of solids respectively. This shows that pre-treatment increased the total solids recovered – the opposite of what was observed in the column pre-treated material. Once again, in order to determine the effect on the valuable (base metal and PGM) recovery, the total solids recovered were analysed.

5.2.2 Cumulative solid recovery over time: Batch stirred tank reactors

In order to determine the effect of the treatment on the rate of recovery, total solids vs time graphs were plotted for the batch stirred tank treatment material. This relationship is shown in Figure 59

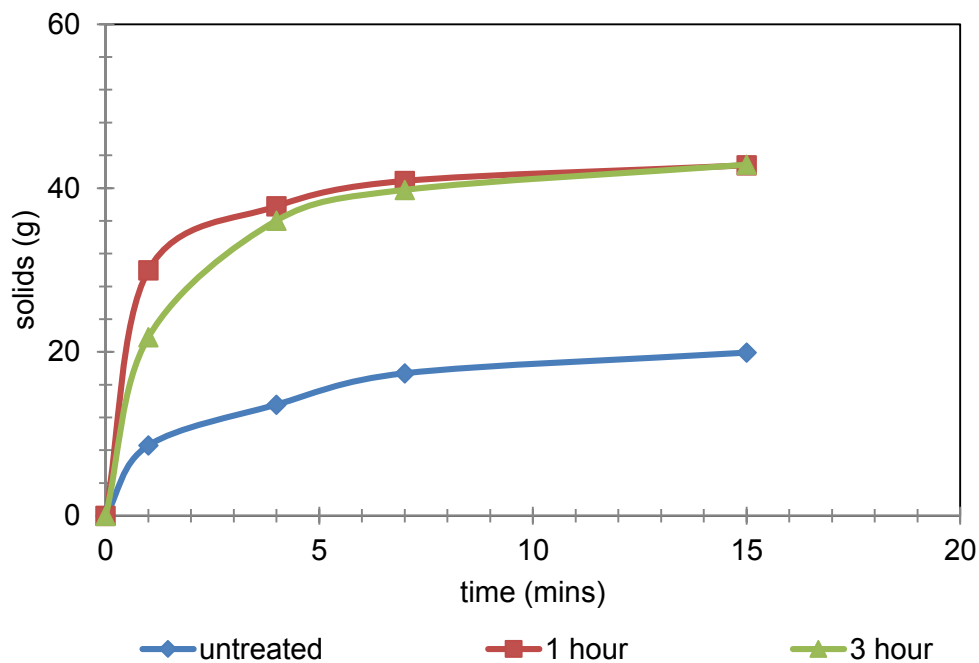


Figure 59: Graph of solids vs time for column flotation tests with 30% pulp density, impeller speed of 250rpm and aeration of 3ml/min

The plot of solids recovered against time shows that the ammonia treatment increased the initial rate of solid recovery as well as the extent of flotation. Over the 1st minute of flotation, the total solids recovered were 9g, 22g and 30g for the untreated, 1 hour and 3 hour pre-treatments respectively.

5.2.3 Base metal recovery

Table 29 shows the upgrade factor and the total recoveries for Cu, Ni and Fe for the batch stirred tank treatment. Even though total recoveries for all the base metals were all $\leq 40\%$, there is an increase in the total base metal recovery for Cu, Ni and Fe. In terms of the upgrade factor for the base metals, there is a general decrease in the upgrade factors for Ni, an increase in the Fe upgrade factor and no impact on the Cu upgrade factor.

Table 29: Summary of upgrade factor and total base metal recoveries of batch stirred tank treatment flotation

	Copper (Cu)		Nickel (Ni)		Iron (Fe)	
	Upgrade factor	Recovery %	Upgrade factor	Recovery %	Upgrade factor	Recovery %
Untreated	1.00	14	1.00	14	0.76	10
1 hour leach	1.00	24	0.81	20	1.28	31
3 hour leach	1.00	26	0.82	21	1.31	34

5.2.4 PGM recovery: 4E analysis

Table 30 shows the upgrade factor and the total 4E (Pt, Pd, Rh, Ag) recovery for the batch stirred tank treatment. Total recoveries for PGMs were all between 50-60%. An upgrade factor of 2.73, 2.53 and 2.26 was achieved for the untreated, 1 hour and 2 hour leach respectively. These values show a decrease in the upgrade factor, which indicates that the treatment has a negative impact on the PGM grade of the ore. There is an overall increase in the total recoveries of both base metals and PGMs (some PGMs are associated with base metals). Despite the increase in total recoveries, there is no concentration of either base metals or PGMs, this alludes to the possibility of an increase to total gangue recovered.

Table 30: Summary of upgrade factor and total PGM recoveries of batch stirred tank treatment flotation

	4E (Pt, Pd, Rh, Ag)	
	Upgrade factor	Recovery %
Untreated	2.73	50
1 hour leach	2.53	61
3 hour leach	2.26	59

5.3 Discussion of Column and Batch stirred tank treatment flotation

Total solid recovery

An increase/decrease in total solids recovered could either be a result of an increase/decrease in the recovery of valuable metals or an increase in gangue recovery. However the increase in the mineral content does not fully account for the mass increments. This could have been confirmed only if solids recovered after the first minute could have been analysed separately, but this data was not available – all float concentrates were analysed together. Therefore it is merely postulated that the higher amounts of solids floated in the less treated or untreated column material is as a result of an increase in gangue recovery, especially in the later stages of the float.

Column treatments

In the column flotation tests, the treatment decreased the total solids recovered. The ammonia treatment reduced the solid recovery rates, but more significantly, it decreased the total recovery. Looking at the Ni recovery and upgrade factor, the treatment shows no impact on the total recovery of Ni but shows an improvement the Ni grade of the ore (increase in upgrade factor). This is in line with an increase in total gangue recovery as an increase in total gangue would not affect the total Ni recovery but would affect the Ni grade (more gangue would dilute Ni and lower the grade). Therefore, it is postulated that the ammonia column treatment has a *suppressing* effect on the gangue recovery, rather than that it enhances Ni recovery. The column treatments show a significant increase in the PGM grade but did not affect the total PGM recovery. Like the Ni recovery, this is related to the fact that the column treatments suppressed gangue recovery and hence improved grade but not the total recovery.

Batch stirred tank treatments

In the batch stirred tank reactor treatments an increase in the total solids recovered corresponds to an increase in the total Ni and PGE (valuable metals) recovered. Due to the nature of the batch treatments (solids suspended in agitated tank, refer to section 3.2.2), the direct transfer of treated material to the flotation cell may have caused the presence of appreciable amounts of ammonia in the flotation pulp. This could have raised the pH of the pulp and hence improved the overall recovery of the PGMs. The results show (see Table 30) a slight increase in the total recovery and a general decrease in the grade of PGMs. This is in agreement with work by Muzendu *et al.* (2011) who determined that at a pH between 9 and 10, as PGM recovery improved and the grade dropped.

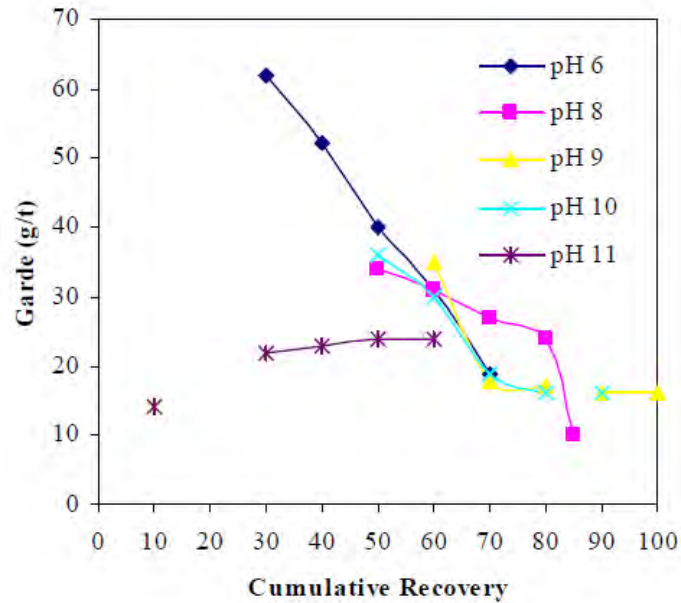


Figure 60: PGM grade vs recovery (cumulative) curves at different pH levels (Muzendu, et al., 2011)

In terms of the rate of solid recovery in batch stirred tank reactors the ammonia treatment increases the solids recovery. Again, due to the nature of the batch stirred tank tests, the decantation process always leaves behind a certain amount of the liquid in the solid residue; therefore this liquid ammonia residue had an impact on the flotation pulp. Like the column treatments, the increase in total Ni recovered could not account for the increase in total solids recovered. Therefore the total solid recovered is due to an increment in gangue recovery, which is detrimental for both the Ni and PGM grade. Despite an increase in the total Ni recovered, the total recoveries were still below 50% which makes this increment insignificant.

The ammonia treatment in the columns and batch stirred tank reactors show opposing effects in terms of gangue recovery. This is probably due to the residual ammonia in the flotation cell from the batch stirred tank ammonia treatment, which could have led to an increase in gangue recovery. The milling step subsequent to the column treatment allowed for ammonia vaporisation and hence reduced the chances of any residual ammonia in the flotation cell.

PGM recovery

The PGM recoveries in both the column and batch stirred tank treatments were inconsistent with the Ni grades and recoveries. This suggests that the PGMs in this case were not highly associated with the base metals. As Figure 3 suggests, most of the PGMs are liberated and very few if any are associated with base metal sulphides. Further, what is interesting to note is that PGMs are also found locked in the gangue material. Therefore an increase in the total gangue recovered (increase in total solids recovered) in the batch stirred tank reactors would

have led to the increase in the PGMs recovered as shown in the results above. For both the tests (column and batch stirred tank reactors), the untreated yielded a different PGM recovery (67% and 50% respectively), this was probably due to a difference in the size of the cell used, even though this should not have had an impact on the recoveries and grades.

Naturally floated gangue

According to work done by Becker *et al.* (2009), the concentration of PGMs and base metals is diluted by Naturally Floated Gangue (NFG) in the flotation of Merensky ore. The four main silicate minerals that contribute to the dilution of valuable metals are orthopyroxene, clinopyroxene, plagioclase and talc. Of these four, talc is known to be hydrophobic and naturally floatable (Becker *et al.*, 2009; Shortridge, 2002). The high content of these silicate minerals in this ore, orthopyroxene (24.6%), clinopyroxene (10.3%), plagioclase (4.4%) and talc (18%) in this ore (see Table 6), would explain why an increase in total base metal and PGMs recovered did not correspond to an upgrade of the ore, specifically for the column treatment tests. Even though the recovery of NFGs is minimised by the use of depressants, this is sometimes achieved at the expense of valuable minerals (Wiese, Harris & Bradshaw, 2007).

Examination of the iron (Fe) species could also explain the low valuable metal recoveries. In terms of base metal recoveries work done by Peng *et al.* (2002), on the flotation of base metals from chalcopyrite, indicated that the hydrophilic iron oxidation species on the surface of minerals play a role in depressing the mineral and hence led to poor flotation. Work by Yelloji and Natarajan (1988) also emphasized the negative impact an iron hydroxide or oxide layer had on the floatability of chalcopyrite. Similarly, in this case, the high iron oxides/hydroxides concentration (see Table 6) has resulted in the poor flotation. Further even though both the column and the batch stirred tank treatments showed some leaching of Cu and Ni, there was no significant leaching of Fe. Therefore, on the assumption that the oxidation layer contained iron oxides/hydroxides, the treatments aimed at dissolving the oxidation layer proved unsuccessful, especially in the dissolution of iron.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The main aim of this thesis was to investigate the use of an ammonia treatment in order to improve the conventional processing of oxidized/weathered ores. These improvements included a chemical pre-treatment for the flotation of the ores and an extraction of valuable metals from the ore. Hence the following key questions were addressed:

- Can ammonia be used as a lixiviant to treat PGM oxidized/weathered ores?

As a pre-treatment for the flotation process, the ammonia treatment was used to dissolve the oxidation layer (base metal oxides) formed on the oxidized/weathered ores, however, due to the low extraction of base metals, this was unsuccessful.

As a lixiviant to extract valuable metals from the ore, low extractions were observed in both columns and batch stirred tank reactors. Various factors such as pulp density, ammonia concentration, initial copper concentration and an acid pre-treatment were investigated in batch stirred tank reactors and the acid pre-treatment showed the most significant effect on the extraction of nickel. However, the use of sodium cyanide solutions as a lixiviant showed some promising Pt and Pd extractions.

Fe oxides/hydroxides which form 10% wt. of the ore inhibit effective leaching in both the pre-treatment and extraction tests.

- Can an ammonia solution be used for treatment of PGM oxidized/weathered ores make the PGM ores more amenable to flotation?

As shown by the flotation results, the treatment increased total solids recovery in the batch stirred tank and decreased total solids recovery in the column tests. However, an increase in total solids recovered did not correspond to the metals recovered in terms of masses. This alludes to the fact that the treatments could have more of an impact on the gangue recovery and not valuable metal flotation.

In the column tests, the ammonia treatment suppressed gangue recovery (decreased the total solids recovered) and hence improved the efficiency of the flotation by improving the Ni and PGM grade recovery. However, the Ni and PGM total recovery were independent of the ammonia treatment.

In the batch stirred tank tests, the ammonia treatment showed a marginal improvement in total Ni recoveries and a decrease in the Ni grade. The ammonia batch stirred tank treatment showed a marginal decrease in the PGM grade and slight improvement in total PGM recovery.

Further, in both the batch stirred tank and the column reactors, the total base metal recoveries are all below 50%. Therefore any improvement is still limited by the presence of iron oxides/hydroxides which decrease the hydrophobicity and collection adsorption of the minerals hence in poor recoveries.

- What are the optimal reactor configurations (columns or batch stirred tank reactors)?

In terms of the impact on flotation, both treatments had relatively low base metal recoveries (<50%) and hence they had no success in the dissolution of the oxidation layer. The column flotation tests showed an upgrade in the Ni and PGM grades but inconsistent total Ni recovery. On the other hand, batch stirred tank reactors showed a downgrade in the Ni grade and poor total Ni recoveries. Therefore, based on the upgrading factors, only the column treatment has the ability to concentrate the ore in terms of base metals and PGMs and is therefore the preferred treatment.

6.2 Recommendations

In order to fully determine the effect of the treatment, a mineralogical analysis (MLA) would have to be done on the treated ore. These results would be compared to the feed mineralogical results shown in Table 6. A look into what impact the various ammonia treatments have on the mineralogy of the ore would be useful.

Further, analyses on the individual concentrates (in terms of base metals and PGMs) would give more detailed on the flotation trends and not merely the total recovery. This would help understand the effect of the treatment. This would also lead to gangue recovery data that would help investigate what happens to the gangue material during the flotation process after the treatments.

In order to better determine the effect of the ammonia treatment on the oxidised PGM ores, higher base metal and PGM concentrations would better show the impact of the ammonia pre-treatment on oxidised PGM ores.

To further understand the impact of ammonia on the pulp alkalinity, further studies that involve the monitoring of the pulp pH should be conducted.

7 BIBLIOGRAPHY

Adams, M., Liddell, K. & Holohan, T. 2011. Hydrometallurgy processing of platreef flotation concentrate. *Mineral Engineering*, 1(24), pp. 545-550.

Africa, C. o. M. S., 2008. *Platinum group metals in Africa*. [Online] Available at: <http://www.bullion.org.za/content/?pid=86&pagename=Platinum> [Accessed 19 April 2013].

ALS Geochemistry, 2013. *Schedule of sevices and fees*, Johannesburg: ALS Geochemistry.

Alymore, M., 2001. Treatment of a refractory gold-copper sulfide concentrate by copper ammoniacal thiosulfate leaching. *Mineral engineering*, 14(6), pp. 615-637.

Arbriter, N. & Milligan, D., 1976. Reduction of copper ammine solutions to metal with sulfur dioxide. *Extractive Metallurgy of Copper*, 2, pp. 974-993.

Aspola, L., Matuszewicz, K., Haavaniammi, S. & Hughes, S., 2012. *Outotec smelting solutions for the PGM industry*, s.l.: s.n.

Atkins, P. & Paula, J., 2010. *Atkins' Physical chemistry*. 9th ed. United Kingdom: Oxford university press.

Bartlett, R., 1992. *Solution Mining: Leaching and fluid recovery of materials*. 1st ed. Amsterdam: Gordon and Breach science publishers S.A.

Bartlett, R., 1998. *Solution Mining: Leaching and Fluid Recovery of Materials*. 2nd ed. Perth: Gordon and Breach Science Publishers.

Bau, M., Koschinsky, A. & Mohwinkel, D., n.d. Experiments on carboxylic acids and siderphore-promoted disolutionof supergene, oxidised PGE ores from the Great Dyke.

Becker, M., Harris, P., Wiese, J. & Bradshaw, D., 2009. Mineralogical characterisation of naturally floatable gangue in Merensky Reef ore flotation. *International Journal of Mineral Processing*, 93(3-4), pp. 246-255.

Becker, M., Ramonotsi, M. & Petersen, J., 2011. *Effect of alteration on the mineralogy and flotation performance of PPM platinum ore*. Trondheim, ICAM.

Becker, M., Wiese, J. & Ramonotsi, M., 2014. Investigation into the mineralogy and flotation performance of oxidised PGM ore. *Minerals Engineering*, 65, pp. 24-32.

Beckstead, L. & Miller, J., 1977. Ammonia, oxidation leaching of chalcopyrite-reaction kinetics. *Metallurgical and materials transactions*, 8(1), pp. 19-29.

Bell, S., Welch, G. & Bennett, P., 1995. Development of ammoniacal lixiviants for the in-situ leaching of chalcopyrite. *Hydrometallurgy*, 39(1-3), pp. 11-23.

Bingol, D., Canbazoglu, M. & Aydogan, S., 2005. Dissolution kinetics of malachite in ammonia/ammonium carbonate leaching. *Hydrometallurgy*, 76(1-2), pp. 55-62.

Black, W., 2000. *The Platinum Group Metals Industry*. 1st ed. Cambridge: Woodhead Publishing Limited.

Boulton, A., 2002. *Improving sulphide mineral flotation selectivity against iron sulphide gangue*. 1st ed. Adelaide: Ian Wark Research Institute.

Castro, S., Soto, H. & Goldfarb, J. L. J., 1974. Sulphidizing reactions in the flotation of oxidised copper minerals, II. Role of the adsorption and oxidation of sodium sulphide in the flotation of chrysocolla and malachite. *Minerals Processing*, 1(2), pp. 151-161.

Cawthorn, G., 2010. The platinum group element deposits of the Bushveld complex in South africa. *Platinum metals*, 4(54), pp. 205-215.

Cawthorn, R., 1999. The platinum and palladium resources of the Bushveld complex. *South African Journal of Science*, 95, pp. 481-489.

Cawthorn, R. G., 2010. *Geological interpretations from the PGE distribution in the Bushveld Merensky and UG2 chromitite reefs*. Sun City, The Southern African Institute of Minings and Metallurgy.

Cawthorn, R., Lee, C., Shouwstra, R. & Mellowship, P., 2002. Relationship between pge and pgm in the bushveld complex. *The Canadian Mineralogist*, 40, pp. 311-328.

Chamberlain, P. & Pojar, M., 1984. *Gold and Silver leaching practices in the Unites States*, Washington: Bureau of Mines Information Circular.

Chang, C. & Liu, J., 1998. Feasibility of copper leaching from an industrial sludge using ammonia solutions. *Journal of hazardous materials*, 58(1-3), pp. 121-132.

Chen, J. & Huang, K., 2006. A new technique for extraction of platinum group metals. *Hydrometallurgy*, 82(3-4), pp. 164-171.

City of Cape town, 2008. *Integrated Development plan (IDP) 2007/8 - 2011/12*, Cape Town: City of Cape Town.

Clarke, P., Fornasiero, D., Ralston, J. & Smart, R. S. C., 1995. A study of the removal of oxidation products from sulfide mineral surfaces. *Minerals engineering*, 8(11), pp. 1347-1357.

Cottrell, A., 1967. *An introduction to metallurgy*. 1st ed. London: Edward Arnold Publishers.

Cramer, L. A., 2008. *What is your PGM concentrate worth? Third International Platinum conference*. Sun City, The Southern African Institute of Mining and Metallurgy.

Crozier, R., 1992. *Flotation - Theory, reagents and ore testing*. 1st ed. Chille: Pergmon Press.

Crundwell, F; Moats, M; Ramachandran, V; Robinson, T; Davenport, W. 1995. *Extractive metallurgy of Nickel, Cobalt and Platinum Group Metals*. London: Elsevier.

Deng, T. & Chen, J., 1991. Treatment of oxidized copper ores with emphasis on refractory ores. *Mineral Processing and Extractive Metallurgy Review*, 7(3-4), pp. 175-207.

Dixon, P. & Madigan, D., 1975. *Hydrometallurgical recovery of copper nickel or zinc from sulphide ores by oxidation in ammoniacal chloride or nitrate solutions*. United States, Patent No. US 3927170 A.

Dunne, C., 2011. *The Ugly duckling (UG 2)*. s.l., MMA President's technical Seminar.

Dutrillac, J. E., 1981. Ammonia Percolation Leaching of Copper Ores. *Canadian metallurgy quarterly*, 20(3), pp. 307-315.

Environmental Radiation Survey and Site Execution, 2009. *Environmental Radiation Survey and Site Execution*. [Online] Available at: <http://www.eurssem.eu/> [Accessed 23 January 2015].

Eurus Mineral Consultants, 2012. *Laboratory flotation rate test procedure for PGM, base metal sulphide and oxide ores*, Johannesburg: Eurus mineral consultants.

Fraiser Institute, 2012. *Miningfacts.org*. [Online] Available at: <http://www.miningfacts.org/environment/what-is-the-role-of-cyanide-in-mining/> [Accessed 19 May 2014].

Francis, P., 1993. *Pierre Gy's sampling theory and sampling practice*. 2nd ed. Florida: CRC press.

Fuerstenau, D. W., 1999. *The Froth Flotation Century*. Denver, Society for Mining, Metallurgy, and Exploration, pp. 3-21.

Fuerstenau, M., Jameson, G. & Yoon, R., 2007. *Froth flotation: A century of Innovation*. 1st ed. Colorado: Society for Mining, Metallurgy and Exploration.

Gaudin, A., 1939. *Principles of Mineral dressing*. 1st ed. New York: McGraw-Hill Book Company.

Ghorbani, Y., Becker, M., Mainza, A., Franzidis, J., Petersen, J., 2011. Large particle effects in chemical/biochemical heap leach processes – A review. *Minerals Engineering*, 24(11), pp. 1172-1184.

Ghosh, M., Das, R. & Biswas, A., 2003. Oxidative ammonia leaching of sphalerite: Part II: Cu(II)-catalyzed kinetics. *International Journal of Mineral Processing*, 70(1-4), pp. 221-234.

Gos, S. & Rubo, A., 2001. *The relevance of alternative lixivants with regard to work safety and environmental safety*, Hanau: CyPlus.

Grosse, A., Dicoski, W., Shaw, M. & Haddad, P., 2003. Leaching and recovery of ammoniacal thiosulfate leach liquors (a review). *Hydrometallurgy*, 69(1-3), pp. 1-21.

Gupta, C. K., 2003. *Chemical Metallurgy: Principles and practice*. Mumbai: Wiley-VCH Verlag GmbH & Co.

Gupta, C. & Mukherjee, T., 1990. *Hydrometallurgy in Extraction processes*. Florida: CRC press.

Habashi, F., 1993. *A textbook of hydrometallurgy*. Quebec: Metallurge Extractive Quebec, Enr.

Habashi, F., 1999. *Hydrometallurgy*. 2nd ed. Quebec: s.n.

Habashi, F., 2005. A short history of hydrometallurgy. *Hydrometallurgy*, 79(1-2), pp. 15-22.

Halpern, J., 1953. Kinetics of the dissolution of copper in aqueous ammonia. *Journal of Electrochemical society*, 100(10), pp. 421-428.

Hawley, C., 2008. *Alaska Mining hall of fame*. [Online] Available at: <http://alaskamininghalloffame.org/inductees/stannard.php> [Accessed 01 December 2014].

Holmes, R., 2004. Correct sampling and measurement - the foundation of accurate metallurgical accounting. *Chemometrics and intelligent laboratory systems*, 74(1), pp. 71-83.

Illinois State Water Survey, n.d. *Nitrogen Cycles project*. [Online] Available at: <http://www.isws.illinois.edu/nitro/terms.asp?lpg=glossary&lsec=hinfl&term=NSpecies> [Accessed 06 February 2015].

Jones, R. T., 1999. *Platinum Smelting in South Africa*, Randburg: s.n.

Kappes, D., 1998. *Heap leach or mill? Economic considerations in a period of stable gold prices*, Reno: Kappes, Cassidy and Associates.

Kawatra, S., 2001. *Flotation Fundamentals*, Michigan: University of Michigan.

Kawatra, S. K., 1989. *Froth Flotation - Fundamental principles*, Houghton: Michigan technological University.

King, R. P., 1982. Flotation of fine particles. In: R. P. King, ed. *Principles of flotation*. Johannesburg: South African Institute of Mining and Metallurgy, pp. 215-225.

Kinnaird, J., 2005. *The Bushveld Large Igneous Province*, Johannesburg: School of Geosciences.

Knell, M. & Kroll, H., 1954. *Polyhydroxyethyl polyamine compound*. United States of America, Patent No. 2906762.

Koski, R., Munk, L., Foster, A., Shanks, W., Stillings, L., 2008. Sulfide oxidation and distribution of metals near abandoned copper mines in coastal environments, Prince William Sound, Alaska, USA. *Applied Geochemistry*, 23(2), pp. 227-254.

Kuhn, H., Forsterling, H. & Waldeck, D., 2009. *Principles of Physical Chemistry*. 2nd ed. New Jersey: John Wiley & sons.

Lee, A., n.d. *Uriahsweety*. [Online] Available at: <http://uriahsweety.wordpress.com/the-process-of-froth-flotation/> [Accessed 27 November 2014].

Lee, J., Nagaraj, D. & E, C., 1998. Practical aspects of oxide copper recover with alkyl hydroxamates. *Minerals Engineering*, 11(10), pp. 929-939.

Lee, K., Archibald, D. & McLean, J. R. M., 2009. Flotation of mixed copper oxide and sulphide minerals with xanthate and hydroxamate collectors. *Minerals Engineering*, 22(1), pp. 395-401.

Legrand, D., Bancroft, G. & Nesbitt, H., 2005. Oxidation/alteration of pentlandite and pyrohotite surfaces at pH 9.3. *American Mineralogist*, 90, pp. 1042-1054.

- Liddell, K. & Adams, M., 2012. Kell hydrometallurgical process for extraction of platinum group metals and base metals from flotation concentrates. *The Southern African institute of mining and metallurgy*, 112, pp. 31-35.
- Liu, W. & Tang, M., 2010. Dissolution kinetics of low grade complex copper ore in ammonia-ammonium chloride solution. *Transaction of nonferrous metals society of china*, 20(5), pp. 910-917.
- Luszczkiewicz, A. & Chmielewski, T., 2008. Acid treatment of copper sulfide middlings and rougher concentrates in the flotation circuit of carbonate ores. *International Journal for Mineral Processing*, 88(1-2), pp. 45-52.
- McInnes, C., Sparrow, J. & Wookcock, J., 1994. Extraction of Platinum, palladium and gold by cyanidation of Coronation Hill ore. *Hydrometallurgy*, 35(2), pp. 141-159.
- Meng, X. & Han, K., 1996. The principles and applications of ammonia leaching of Metals-A review. *Mineral processing and Extractive Metallurgy Review*, 16(2), pp. 23-61.
- Milbourne, J., Tomlinson, M. & Gormely, L., 2003. *Use of hydrometallurgy in direct processing of base metal/PGM concentrates*. Vancouver, The Minerals, Metals and Materials society, pp. 617-630.
- Musonda, K. & Mwase, J., 2009. *Cyanide Protocol for laboratory use*, Cape Town: Univeristy of Cape Town.
- Muzawazi, C., 2013. *Base metal heap and tank leaching of a platreef flotation concentrate using ammonical solutions*, Cape Town: s.n.
- Muzawazi, C., 2013. *Base metal heap and tank leaching of a platreef flotation concentrate using ammonical solutions*, Cape Town: Univeristy of Cape Town.
- Muzawazi, C., 2013. *Base metal heap and tank leaching of a platreef flotation concentrate using ammonical solutions*, Cape Town: University of Cape Town.
- Muzendu, E., Afolabi, A., Abdulkareem, A. & Ntuli, F., 2011. *Effect of pH on the recovery and Grade of Base metal sulphides by flotaiton*. San francisco, World Congress on Engineering and Computer science.
- Mwase, J., 2009. *Hydrometallurgy extraction of platinum group metals from low grade concentrate*, Cape town: s.n.

Mwase, J., 2009. *Hydrometallurgy extraction of platinum group metals from low grade concentrate*, Cape town: University of Cape town.

Mwase, J., Petersen, J. & Eksteen, J., 2011. A conceptual flowsheet for heap leaching of platinum group metal (PGMs) from a low-grade ore concentrate. *Hydrometallurgy*, 111, pp. 129-135.

Mwase, J., Petersen, J. & Eksteen, J., 2012. Assessing a two-stage heap leaching process for Platreef flotation concentrate. *Hydrometallurgy*, 129-130 pp. 74-81.

Newell, A. & Bradshaw, D., 2007. The development of a sulfidisation technique to restore the flotation of oxidised pentlandite. *Minerals Engineering*, 20(10), pp. 1039-1046.

Newell, A., Bradshaw, D. & Harris, P., 2006. The effect of heavy oxidation upon flotation and potential remedies for Merensky type sulfides. *Mineral Engineering*, 19(6-8), pp. 675-686.

Obethur, T., Melcher, F., Buchholz, P. & Locmelis, M., 2013. The oxidised ores of the main sulphide Zone, Great dyke, Zimbabwe: Turning resources into minable reserves. *Journal of Southern African Institute of Mining and Metallurgy*, 113(3), pp. 191-201.

Obethur, T., Melcher, F., Buchholz, P. & Locmelis, M., 2013. The oxidised ores of the main sulphide Zone, Great dyke, Zimbabwe: Turning resources into minable reserves- mineralogy is key. *Journal of Southern African Institute of Mining and Metallurgy*, 113(3), pp. 191-201.

Osseo-Asare, K., J, L., Kim, S. & Pickering, W., 1983. Cobalt extraction in ammoniacal solution: Electrochemical effect of metallic iron. *Metallurgical and Materials Transactions*, 14(4), pp. 571-578.

Park, K., Mohapatra, D., Reddy, B. & Nam, C., 2006. A study on the oxidative ammonia/ammonium sulphate leaching of a complex matte. *Hydrometallurgy*, 86(3-4), pp. 164-171.

Peng, Y., Grano, S., Fornasiero, D. & Ralston, J., 2002. Control of grinding conditions in the flotation of chalcopyrite and separation from pyrite. *International Journal of Mineral Processing*, 69(1-4), pp. 87-100.

Polinares, 2012. *Fact Sheet: Platinum Group Metals*, s.l.: Polinares Consortium.

Prestidge, C. & Ralston, J., 1995. Contact angle studies of Galena particles. *Journal of Colloid and interface Science*, 184(2), pp. 512-518.

Pryor, E. J., 1965. *Mineral Processing*. 3rd ed. London: Elsevier Publishing Co Ltd.

Ramonotsi, M., 2011. *characterisation of the effect of alteration on the PPM Platinum ore and evaluation of selected strategies to improve metallurgical performance*, Cape Town: Univeristy of Cape Town.

Ramonotsi, M., 2011. *Characterisation of the effect of alteration on the PPM platinum ore and evaluation of selected strategies to improve metallurgical performance*, Cape town: University of Cape Town.

Ramonotsi, M., 2011. *Effect of alteration on the mineralogy and flotation performance of ppm platinum ore*, Cape Town: University of Cape town.

Rao, S., 2006. Aqueous processing of minerals and metals; Past , present and future. *Everyman's Science*, XLI(2), pp. 120-126.

Rhamadhani, M., Chen, J., Hidayat, T., Jak, E., Hayes, P., 2009. *Advances in research on nickel production through the Caron process*. s.l., European Metallurgical conferecen.

Ross, V., 1997. Particle-bubble attachment in flotation froths. *Minerals engineering*, 10(7), pp. 695-706.

Royal Bafokeng Platinum, 2014. *Mining and processing of PGMs*. [Online] Available at: <http://www.bafokengplatinum.co.za/b/process.php> [Accessed 08 January 2015].

Schouwstra, R., Kinloch, E. & Lee, C., 2000. A short geological review of the Bushveld Complex. *Platinum Metals Review*, 44(1), pp. 33-39.

Shamaila, S. & O'Connor, C., 2008. The role of synthetic minerals in determining the relative flotation behaviour of Platreef PGE tellurides and arsenides. *Minerals Engineering*, 21(12-14), pp. 899-904.

Shortridge, P., 2002. *The influence of polymeric charge and structure, molecular weight and ionic conditions on depressant ability to reduce the natural floatability of talc*, Cape Town: University of Cape Town.

Smart, R., 1991. Surface layers in base metal sulphide flotation. *Minerals Engineering*, 4(7), pp. 891-909.

Smart, R., Amarantidis, J., Skinner, W., Prestidge, C., LaVanier, L., Grano, S., 1996. Surface analytical studies of oxidation and collector adsorption in sulfide mineral flotation. *Scanning Microscopy*, 12(4), pp. 553-583.

Sohn, H. & Wadsworth, E., 1979. *Rate of extractive metallurgy*. 1st ed. New York: Plenum Press.

Solomon, N., 2010. *Effect of HPGR on platinum bearing ores and the flotation response as compared to the conventional ball mill*, Cape Town: University of Cape town.

South African government, 2014. *Minerals -South African Government*. [Online] Available at: <http://www.gov.za/about-sa/minerals> [Accessed 15 November 2014].

Stewart, M. & Kappes, D., 2012. SART for copper control in cyanide heap leaching. *The Southern African Institute of Mining and Metallurgy*, 118, pp. 1037-1043.

Taggart, A., 1945. Handbook of Mineral Dressing; Ores and Industrial Minerals. In: *Wiley Engineering Handbook Series*. s.l.:Wiley & Sons Inc, p. Section 19.

Takeno, N., 2005. *Atlas of Eh-pH diagrams - Intercomparison of thermodynamic databases*, Japan: National Institute of Advanced Industrial Science and Technology.

The Royal Society of Chemistry, 2010. *Atomic absorption spectrometry*, London: The Royal society of Chemistry.

Tozowa, K., Umetutsu, Y. & K, S., 1976. Chemistry of ammonia leaching of copper concentrates. *The extractive metallurgy of copper*, 20, pp. 13-20.

U.S. Environmental Protection Agency, 1994. *Treatment of cyanide heap leaches and tailings*, Washington: U.S. Environmental Protection Agency.

University of Cape Town, 2008. *Hydrometallurgy: Theory and Practice, Study guide*, Cape Town: University of Cape Town.

Valix, M. & Cheung, W., 2002. Effect of sulfur on the mineral phases of laterite ores at high temperature reduction. *Minerals Engineering*, 15(7), pp. 523-530.

van Wyk, A., 2014. *Flowsheet development and comparison for the recover of precious metals from cyanide leach solutions*, Stellenbosch: Stellenbosch University.

Vermaak, F., 1995. *The platinum group metals - a global perspective*. Randburg: Minktek.

Vermaak, F., 1995. *The platinum-group metals – a global perspective*. Randburg: Mintek.

Vermaak, M. K., 2005. Pretoria: University of Pretoria.

Vignes, A., 2011. *Extractive metallurgy 3: Processing operations and routes*. 1st ed. United States: Wiley-ISTE.

Voordouw & Buekes, 2000. South African Journal of Geology. *GeoScienceWorld*, Issue 112.

Welham, N., Johnston, G. & Sutecliffe, M., 2010. *Method for ammoniacal leaching*. United States, Patent No. US 2010/0180728 A1.

Wiese, J., Harris, P. & Bradshaw, D., 2005. The influence of the reagent suite on the flotation of ores from the Merensky reef. *Minerals engineering*, 18(2), pp. 189-198.

Wiese, J., Harris, P. & Bradshaw, D., 2007. The response of sulphide and gangue minerals in selected Merensky ores to increased depressant dosage. *Minerals Engineering*, Volume 20, pp. 986-995.

Wilhelm, N., Johnson, G. & Mathew, L., 2010. *Method for ammonia leaching*. Australia, Patent No. US 2010/0180728A1.

Wills, B., 1997. *Mineral Processing Technology*. 6th ed. London: Butterworth Heinemann.

Wolf, R., 2005. *What is ICP-MS? and more importantly, what can it do?*, Virginia: USGS.

Yelloji, M. & Natarajan, K., 1988. Influence of Galvanic interaction between chalcopyrite and some metallic materials on flotation. *Minerals Engineering*, 1(4), pp. 281-294.

Zhou, R. & Chander, S., 1993. Kinetics of sulfidization of malachite in hydrosulfide and tetrasulfide solutions. *International Journal of Mineral Processing*, 37(3-4), pp. 257-272.

8 APPENDICES

8.1 Calculation of extraction curves

- In order to calculate the extraction curves of the various metals, the following procedure was followed.
- Times, pH and ORP values were obtained at the time of sampling
- Ppm/ppb values (concentration values) were obtained from the analysis of the effluent solution from the column and batch stirred tank reactors.
- The amount of metal dissolved in the effluent is calculated by:

$$Cu \text{ dissolved (mg)} = ppm \left(\frac{mg}{L} \right) \times \text{effluent (L)}$$

- The cumulative metal dissolved is calculated and the % dissolved over a period of time is calculated by:

$$\% \text{ Metal dissolved} = \frac{\text{Metal dissolved}}{\text{Total metal in head sample}} \times 100$$

Table 31 shows an example of the calculations in the extraction of Cu in the column treatment.

Table 31: Calculation sample of the extraction of metal

Column	Time	pH	Eh	Effluent (L)	AAS Reading	Cu diss. (mg)	% Diss.
1	07:00	9.8	205	0.61	86.5	52.79	9%
1	17:00	9.94	208	0.5	178.8	89.40	25%
1	17:00	9.81	207	0.8	141.5	113.16	46%
1	08:00	9.86	210	0.36	143.3	51.57	55%

8.2 Calculation of flotation data

In terms of the flotation tests performed, the concentrates were collected and the data was tabulated as shown in the tables below:

8.2.1 Column flotation data

Table 32: Untreated column flotation raw data

Mass	Conc 1	Conc 2	Conc 3	Conc 4	Feed	Tails 1
------	--------	--------	--------	--------	------	---------

C + paper	61.97	45.98	62.74	30.81	63.78	786.9
Paper	5.04	5.18	4.96	5.04	5.09	11.43
C	56.93	40.8	57.78	25.77	58.69	775.47
B + H2O	478.13	350.55	414.31	400.98		
Bottle	341.3	158.06	237.22	245.19		
H2O	136.83	192.49	177.09	155.79		
D+C+H2O	574.08	601.5	886.3	762.1		
Dish	127.62	170.19	215.45	217.69		

Table 33: 2 day treated column flotation raw data

Mass	Conc 1	Conc 2	Conc 3	Conc 4	Feed	Tails
C + paper	57.53	56.38	49.09	22.08	59.91	790.1
Paper	4.56	4.66	4.82	4.8	5.03	11.1
C	52.97	51.72	44.27	17.28	54.88	779
B + H2O	566.6	556.38	567.61	568.05		
Bottle	495.71	324.2	437.2	382		
H2O	70.89	232.18	130.41	186.05		
D+C+H2O	494.23	805.1	757	576.69		
Dish	127.62	217.69	215.45	170.19		

Table 34: 5 day treated column flotation raw data

Mass	Conc 1	Conc 2	Conc 3	Conc 4	Feed	Tails 1
C + paper	62.25	39.64	21.38	17.69	57.14	811.2
Paper	5.14	5.36	5.32	5.51	5.54	10.19
C	57.11	34.28	16.06	12.18	51.6	801.01
B + H2O	538.04	373.18	349.78	314.49		
Bottle	507.57	140.72	151.24	130.13		
H2O	30.47	232.46	198.54	184.36		
D+C+H2O	470.79	643.6	547.68	497.72		
Dish	127.62	170.19	215.45	217.69		

Table 35: 10 day treated column flotation raw data

Mass	Conc 1	Conc 2	Conc 3	Conc 4	Feed	Tails 1
C + paper	47.13	30.63	16.42	17.52	61.8	873.3
Paper	5.06	5.18	5.31	5.15	4.08	12.57
C	42.07	25.45	11.11	12.37	57.72	860.73
B + H2O	481.43	566.11	364.92	494.65		
Bottle	453.87	246.58	131.92	267.52		
H2O	27.56	319.53	233	227.13		
D+C+H2O	372.06	633.9	511.84	516.75		
Dish	127.62	170.19	215.45	217.69		

8.2.2 Batch stirred tank reactor flotation tests

Table 36: Untreated batch stirred tank reactor raw data

Mass	Conc 1	Conc 2	Conc 3	Conc 4	Feed	Tails 1
C + paper	12.23	9.34	7.33	8.82	0	186.97
Paper	5.31	5.21	5.06	4.94	0	10.09
C	6.92	4.13	2.27	3.88	0	176.88
	1	3	3	8		
B + H2O	563.42	493.3	433.71	475.35		
Bottle	552.04	406.26	291	378.1		
H2O	11.38	87.04	142.71	97.25		
D+C+H2O	237.87	296.73	333.78	341.1		
Dish	176.83	174.1	154.23	214.26		

Table 37: 1 hour treated batch stirred tank reactor raw data

Mass	Conc 1	Conc 2	Conc 3	Conc 4	Feed	Tails
C + paper	35.25	12.47	8.12	7.13	0	155.89
Paper	5.28	4.65	5.03	5.23	0	10.31
C	29.97	7.82	3.09	1.9	0	145.58
B + H2O	551.84	559.76	544.18	561.63		
Bottle	532.75	450.15	375.43	473.96		
H2O	19.09	109.61	168.75	87.67		
D+C+H2O	389.62	383.37	369.79	340.69		

Dish	176.83	174.1	154.23	214.26
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Table 38: 3 hour treated batch stirred tank reactor raw data

Mass	Conc 1	Conc 2	Conc 3	Conc 4	Feed	Tails
C + paper	20.99	13.66	8.2	7.25	0	159.37
Paper	4.92	5.32	4.99	5.32	0	9.88
C	16.07	8.34	3.21	1.93	0	149.49
B + H2O	516.85	369.03	524.01	391.16		
Bottle	500.83	256.15	365.47	291.81		
H2O	16.02	112.88	158.54	99.35		
D+C+H2O	306.84	378.74	350.51	347.45		
Dish	176.83	174.1	154.23	214.26		

8.3 Calculation of minimum mass required (Gy method)

Table 39: Gy formula raw data

Variables			Unit	Values				
Cu assay			%	0.0236				
s			%	0.0216				
C	<i>f</i>	0.5		162.2				
	<i>g</i>	0.5						
	<i>l</i>	0.21693						
	<i>m</i>	2990.806						0.002
	<i>a</i>	0.002						
	<i>r</i>	6						
dmax			cm	0.425	0.04			
M			g	26641	26.6411			
m calculation								
1st		499						
2nd		5.988						
3rd		0.0056						
4th		5.9936						
m		2990.806						

Variables			Unit	Values				
Cu assay			%	0.0236				
s			%	0.0216				
C	<i>f</i>	0.5		610.5				
	<i>g</i>	0.5						
	<i>l</i>	0.816497						
	<i>m</i>	2990.806						0.002
	<i>a</i>	0.002						
	<i>r</i>	6						
dmax			cm	0.03	0.04			
M			g	35.268	0.03527			
m calculation								
1st		499						
2nd		5.988						
3rd		0.0056						
4th		5.9936						
m		2990.806						

8.4 Material Safety Data: Sodium cyanide



Health	3
Fire	1
Reactivity	0
Personal Protection	J

Material Safety Data Sheet Sodium Cyanide MSDS

Section 1: Chemical Product and Company Identification		
Product Name: Sodium Cyanide	Contact Information:	
Catalog Codes: SLS2314, SLS3736	Sciencelab.com, Inc.	
CAS#: 143-33-9	14025 Smith Rd.	
RTECS: VZ7525000	Houston, Texas 77396	
TSCA: TSCA 8(b) inventory: Sodium Cyanide	US Sales: 1-800-901-7247	
CI#: Not available.	International Sales: 1-281-441-4400	
Synonym:	Order Online: ScienceLab.com	
Chemical Name: Sodium Cyanide	CHEMTREC (24HR Emergency Telephone), call:	
Chemical Formula: NaCN	1-800-424-9300	
	International CHEMTREC, call: 1-703-527-3887	
	For non-emergency assistance, call: 1-281-441-4400	
Section 2: Composition and Information on Ingredients		
Composition:		
Name	CAS #	% by Weight
Sodium Cyanide	143-33-9	100
Toxicological Data on Ingredients: Sodium Cyanide: ORAL (LD50): Acute: 6.44 mg/kg [Rat]. DERMAL (LD50): Acute: 10.4 mg/kg [Rabbit].		
Section 3: Hazards Identification		
Potential Acute Health Effects:		
Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (permeator). Corrosive to eyes and skin. The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.		
Potential Chronic Health Effects:		
CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to skin, eyes, central nervous system (CNS). Repeated or prolonged exposure to the substance can produce target organs damage. Repeated exposure of the eyes to a low level of dust can produce eye irritation. Repeated skin exposure can produce local skin destruction, or dermatitis. Repeated inhalation of dust can produce varying degree of respiratory irritation or lung damage. Repeated exposure to a highly toxic material may produce general deterioration of health by an accumulation in one or many human organs.		

Section 4: First Aid Measures

Eye Contact:

Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention immediately.

Skin Contact:

In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

Serious Skin Contact:

Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation:

If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Serious Inhalation:

Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. **WARNING:** It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

Ingestion:

If swallowed, do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature: Not available.

Flash Points: Not available.

Flammable Limits: Not available.

Products of Combustion: Some metallic oxides.

Fire Hazards in Presence of Various Substances: Slightly flammable to flammable in presence of acids, of moisture.

Explosion Hazards in Presence of Various Substances:

Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions:

SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards:

Dangerous on contact with acids, acid fumes, water or steam. It will produce toxic and flammable vapors of CN-H and sodium oxide. Contact with acids and acid salts causes immediate formation of toxic and flammable hydrogen cyanide gas. When heated to decomposition it emits toxic fumes hydrogen cyanide and oxides of nitrogen

Special Remarks on Explosion Hazards: Fusion mixtures of metal cyanides with metal chlorates, perchlorated or nitrates causes a violent explosion

Section 6: Accidental Release Measures

gastrointestinal tract irritation with nausea, vomiting. May affect behavior and nervous systems (seizures, convulsions, change in motor activity, headache, dizziness, confusion, weakness stupor, anxiety, agitation, tremors), cardiovascular system, respiration (hyperventilation, pulmonary edema, breathing difficulty, respiratory failure), cardiovascular system (palpitations, rapid heart beat, hypertension, hypotension). Massive doses by produce sudden loss of consciousness and prompt death from respiratory arrest. Smaller but still lethal doses on the breath or vomitus. Chronic Potential Health Effects: Central Nervous system effects (headaches, vertigo, insomnia, memory loss, tremors, fatigue), fatigue, metabolic effects (poor appetite), cardiovascular effects (chest discomfort, palpitations), nerve damage to the eyes, or dermatitis, respiratory tract irritation, eye irritation, or death can occur. may prolong the illness for 1 or more hours. A bitter almond odor may be noted

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:

Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The products of degradation are less toxic than the product itself.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:

Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: CLASS 6.1: Poisonous material.

Identification: : Sodium cyanide UNNA: 1689 PG: I

Special Provisions for Transport: Marine Pollutant

Section 15: Other Regulatory Information

Federal and State Regulations:

Connecticut carcinogen reporting list.: Sodium Cyanide Illinois chemical safety act: Sodium Cyanide New York release reporting list: Sodium Cyanide Rhode Island RTK hazardous substances: Sodium Cyanide Pennsylvania RTK: Sodium Cyanide Minnesota: Sodium Cyanide Massachusetts RTK: Sodium Cyanide Massachusetts spill list: Sodium Cyanide New Jersey: Sodium Cyanide New Jersey spill list: Sodium Cyanide Louisiana RTK reporting list: Sodium Cyanide Louisiana spill reporting: Sodium Cyanide California Director's List of Hazardous Substances: Sodium Cyanide TSCA 8(b) inventory: Sodium Cyanide TSCA 4(a) final test rules: Sodium Cyanide TSCA 8(a) PAIR: Sodium Cyanide TSCA 8(d) H and S data reporting: Sodium Cyanide TSCA 12(b) one time export: Sodium Cyanide SARA 302/304/311/312 extremely hazardous substances: Sodium Cyanide CERCLA: Hazardous substances.: Sodium Cyanide: 10 lbs. (4.536 kg)

Other Regulations:

OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200). EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada):

CLASS B-6: Reactive and very flammable material. CLASS D-1A: Material causing immediate and serious toxic effects (VERY TOXIC). CLASS E: Corrosive solid.

Specific Gravity: 1.595 (Water = 1)

Vapor Pressure: Not applicable.

Vapor Density: Vapor Density of Hydrogen Cyanide gas: 0.941

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.

Dispersion Properties: See solubility in water.

Solubility:

Soluble in cold water. Slightly soluble in Ethanol

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Excess heat, moisture, incompatibles.

Incompatibility with various substances: Reactive with oxidizing agents, acids, moisture.

Corrosivity:

Corrosive in presence of aluminum. Non-corrosive in presence of glass.

Special Remarks on Reactivity:

Violent reaction with fluorine gas, magnesium, nitrates, nitric acid. Dangerous on contact with acids, acid fumes, water or steam. It will produce toxic and flammable vapors of CN-H and sodium oxide. Cyanide may react with CO₂ in ordinary air to form toxic hydrogen cyanide gas. Strong oxidizers such as acids, acid salts, chlorates, and nitrates. Contact with acids and acid salts causes immediate formation of toxic and flammable hydrogen cyanide gas.

Special Remarks on Corrosivity: Corrosive to aluminum

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Absorbed through skin. Dermal contact. Eye contact. Inhalation. Ingestion.

Toxicity to Animals:

Acute oral toxicity (LD₅₀): 6.44 mg/kg [Rat]. Acute dermal toxicity (LD₅₀): 10.4 mg/kg [Rabbit].

Chronic Effects on Humans: May cause damage to the following organs: skin, eyes, central nervous system (CNS).

Other Toxic Effects on Humans:

Very hazardous in case of skin contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (permeator).

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans: May cause adverse reproductive effects (maternal and paternal fertility) based on animal data.

Special Remarks on other Toxic Effects on Humans:

Acute Potential Health effects: Skin: May cause itching and irritation. May be fatal if absorbed through injured skin with symptoms similar to those noted for inhalation and ingestion. Eyes: May cause eye irritation and eye damage. Inhalation: May cause respiratory tract irritation. May be fatal if inhaled. The substance inhibits cellular respiration causing metabolic asphyxiation. May cause headache, weakness, dizziness, labored breathing, nausea, vomiting. May be followed by cardiovascular effects, unconsciousness, convulsions, coma, and death Ingestion: May be fatal if swallowed. May cause

Small Spill: Use appropriate tools to put the spilled solid in a convenient waste disposal container.

Large Spill:

Corrosive solid. Poisonous solid. Stop leak if without risk. Do not get water inside container. Do not touch spilled material. Use water spray to reduce vapors. Prevent entry into sewers, basements or confined areas; dike if needed. Eliminate all ignition sources. Call for assistance on disposal. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precautions:

Keep locked up.. Keep container dry. Keep away from heat. Keep away from sources of ignition. Empty containers pose a fire risk, evaporate the residue under a fume hood. Ground all equipment containing material. Do not ingest. Do not breathe dust. Never add water to this product. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away from incompatibles such as oxidizing agents, acids, moisture.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area. Do not store above 24°C (75.2°F).

Section 8: Exposure Controls/Personal Protection

Engineering Controls:

Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection:

Splash goggles. Synthetic apron. Vapor and dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:

Splash goggles. Full suit. Vapor and dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits:

STEL: 5 (mg/m3) from ACGIH (TLV) [United States] SKIN CEIL: 4.7 from NIOSH CEIL: 5 (mg/m3) from NIOSH Consult local authorities for acceptable exposure limits.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid. (Granular solid. Flakes solid.)

Odor:

Faint almond-like odor. Odorless when perfectly dry. Emits odor of hydrogen cyanide when damp.

Taste: Not available.

Molecular Weight: 49.01 g/mole

Color: White.

pH (1% soln/water): Not available.

Boiling Point: 1496°C (2724.8°F)

Melting Point: 563°C (1045.4°F)

Critical Temperature: Not available.

DSCL (EEC):

R27/28- Very toxic in contact with skin and if swallowed. R41- Risk of serious damage to eyes. S1/2- Keep locked up and out of the reach of children. S26- In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. S28- After contact with skin, wash immediately with plenty of water S36/37- Wear suitable protective clothing and gloves. S39- Wear eye/face protection. S45- In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible). S46- If swallowed, seek medical advice immediately and show this container or label.

HMIS (U.S.A.):

Health Hazard: 3

Fire Hazard: 1

Reactivity: 0

Personal Protection: j

National Fire Protection Association (U.S.A.):

Health: 3

Flammability: 0

Reactivity: 0

Specific hazard:

Protective Equipment:

Gloves. Synthetic apron. Vapor and dust respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Splash goggles.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

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8.5 Material Safety Data: Ammonium hydroxide



Health	3
Fire	0
Reactivity	0
Personal Protection	

Material Safety Data Sheet Ammonium hydroxide MSDS

Section 1: Chemical Product and Company Identification

Product Name: Ammonium hydroxide Catalog Codes: SLA3667, SLA3490, SLA1144 CAS#: 1336-21-6 RTECS: BQ9625000 TSCA: TSCA 8(b) inventory: Ammonium hydroxide CI#: Not applicable. Synonym: Aqueous Ammonia; Strong Ammonia Solution; Stronger Ammonia Water Chemical Name: Not applicable. Chemical Formula: Not applicable.	Contact Information: Sciencelab.com, Inc. 14025 Smith Rd. Houston, Texas 77396 US Sales: 1-800-901-7247 International Sales: 1-281-441-4400 Order Online: ScienceLab.com CHEMTREC (24HR Emergency Telephone), call: 1-800-424-9300 International CHEMTREC, call: 1-703-527-3887 For non-emergency assistance, call: 1-281-441-4400
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Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Ammonia, anhydrous	7664-41-7	27-31
Water	7732-18-5	69-73

Toxicological Data on Ingredients: Ammonia, anhydrous: GAS (LC50): Acute: 2000 ppm 4 hours [Rat]. 4230 ppm 1 hours [Mouse].

Section 3: Hazards Identification

Potential Acute Health Effects:

Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant), of ingestion, . Non-corrosive to the eyes. Non-corrosive for lungs. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

Potential Chronic Health Effects:

CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Mutagenic for bacteria and/or yeast. [Ammonia, anhydrous]. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance is toxic

to upper respiratory tract, skin, eyes. Repeated or prolonged exposure to the substance can produce target organs damage. Repeated or prolonged contact with spray mist may produce chronic eye irritation and severe skin irritation. Repeated or prolonged exposure to spray mist may produce respiratory tract irritation leading to frequent attacks of bronchial infection. Repeated exposure to a highly toxic material may produce general deterioration of health by an accumulation in one or many human organs.

Section 4: First Aid Measures

Eye Contact:

Check for and remove any contact lenses. Immediately flush eyes with running water for at least 15 minutes, keeping eyelids open. Cold water may be used. Get medical attention immediately. Finish by rinsing thoroughly with running water to avoid a possible infection.

Skin Contact:

In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

Serious Skin Contact:

Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation:

If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

Serious Inhalation:

Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. **WARNING:** It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek medical attention.

Ingestion:

If swallowed, do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: Non-flammable.

Auto-Ignition Temperature: Not applicable.

Flash Points: Not applicable.

Flammable Limits: Not applicable.

Products of Combustion: Hazardous decomposition include Nitric oxide, and ammonia fumes

Fire Hazards in Presence of Various Substances: Not applicable.

Explosion Hazards in Presence of Various Substances: Non-explosive in presence of open flames and sparks, of shocks.

Fire Fighting Media and Instructions: Not applicable.

Special Remarks on Fire Hazards: Not available.

Special Remarks on Explosion Hazards:

Forms explosive compounds with many heavy metals such as silver, lead, zinc and their halide salts. It can form shock sensitive compounds with halogens, mercury oxide, and silver oxide.

Section 6: Accidental Release Measures

Small Spill:

Dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container. If necessary: Neutralize the residue with a dilute solution of acetic acid.

Large Spill:

Corrosive liquid. Poisonous liquid. Stop leak if without risk. Absorb with DRY earth, sand or other non-combustible material. Do not get water inside container. Do not touch spilled material. Use water spray curtain to divert vapor drift. Use water spray to reduce vapors. Prevent entry into sewers, basements or confined areas; dike if needed. Call for assistance on disposal. Neutralize the residue with a dilute solution of acetic acid. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precautions:

Keep locked up. Keep container dry. Do not ingest. Do not breathe gas/fumes/ vapor/spray. Never add water to this product. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away from incompatibles such as metals, acids.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area. Do not store above 25°C (77°F).

Section 8: Exposure Controls/Personal Protection

Engineering Controls:

Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapors below their respective threshold limit value. Ensure that eyewash stations and safety showers are proximal to the work-station location.

Personal Protection:

Face shield. Full suit. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Gloves. Boots.

Personal Protection in Case of a Large Spill:

Splash goggles. Full suit. Vapor respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits:

TWA: 25 (ppm) from ACGIH (TLV) [United States] TWA: 50 STEL: 35 (ppm) from OSHA (PEL) [United States] TWA: 25 STEL: 35 from NIOSH Consult local authorities for acceptable exposure limits.

Section 9: Physical and Chemical Properties

Physical state and appearance: Liquid.

Odor: Ammonia-like (Strong.)

Taste: Acrid.

Molecular Weight: 35.05

Color: Colorless.

pH (1% soln/water): 11.6 [Basic.] This is the actual pH in a 1 N solution.

Boiling Point: Not available

Melting Point: -69.2°C (-92.6°F)

Critical Temperature: Not available.

Specific Gravity: 0.898 (Water = 1)
Vapor Pressure: 287.9 kPa (@ 20°C)
Vapor Density: Not available
Volatility: Not available.
Odor Threshold: 5 - 50 ppm as ammonia
Water/Oil Dist. Coeff.: Not available.
Ionicity (in Water): Not available.
Dispersion Properties: See solubility in water
Solubility: Easily soluble in cold water.

Section 10: Stability and Reactivity Data

Stability: The product is stable.
Instability Temperature: Not available.
Conditions of Instability: Incompatible materials, high temperatures
Incompatibility with various substances:
Highly reactive with metals. Reactive with acids. Slightly reactive to reactive with oxidizing agents.
Corrosivity:
Extremely corrosive in presence of zinc, of copper. Corrosive in presence of aluminum. Non-corrosive in presence of glass, of stainless steel(304), of stainless steel(316).
Special Remarks on Reactivity:
Incompatible with the following: Organic acids, amides, organic anhydrides, isocyanates, vinyl acetate, epichlorhydrin, aldehydes, Acrolein, Acrylic acid, chlorosulfonic acid, dimethyl sulfate, fluorine, gold + aqua regia, hydrochloric acid, hydrofluoric acid, hydrogen peroxide, iodine, nitric acid, oleum, propiolactone, propylene oxide, silver nitrate, silver oxide, silver oxide + ethyl alcohol, nitromethane, silver permanganate, sulfuric acid, halogens. Forms explosive compounds with many heavy metals (silver, lead, zinc) and halide salts.
Special Remarks on Corrosivity:
Dissolves copper and zinc. Corrosive to aluminum and its alloys. Corrosive to galvanized surfaces. Severe corrosive effect on brass and bronze
Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Absorbed through skin. Dermal contact. Eye contact. Inhalation. Ingestion.
Toxicity to Animals: Acute oral toxicity (LD50): 350 mg/kg [Rat].
Chronic Effects on Humans:
MUTAGENIC EFFECTS: Mutagenic for bacteria and/or yeast. [Ammonium hydroxide]. May cause damage to the following organs: mucous membranes, skin, eyes.
Other Toxic Effects on Humans:
Very hazardous in case of skin contact (corrosive, irritant, permeator), of ingestion, . Hazardous in case of eye contact (corrosive), of inhalation (lung corrosive).
Special Remarks on Toxicity to Animals: Highly toxic to aquatic organisms
Special Remarks on Chronic Effects on Humans:
May affect genetic material based on tests with microorganisms and animals. May cause cancer (tumorigenic) based on animal data. No human data found at this time. (Ammonia, anhydrous)

Special Remarks on other Toxic Effects on Humans:

Acute Potential Health Effects: Skin: Causes severe irritation. Causes skin burns. May cause deep, penetrating ulcers of the skin. Contact with skin may cause staining, inflammation, and thickening of the skin. Eye: Contact with liquid or vapor causes severe burns and possible irreversible eye damage including corneal injury and cataracts. Inhalation: Causes severe irritation of the upper respiratory tract with coughing, burns, breathing difficulty. May cause acute pulmonary edema, pneumoconiosis, fibrosis, and even coma. It is a respiratory stimulant when inhaled at lower concentrations. It may also affect behavior/ central nervous system (convulsions, seizures, ataxia, tremor), cardiovascular system (increase in blood pressure and pulse rate). Ingestion: Harmful if swallowed. Affects the Gastrointestinal tract (burns, swelling of the lips, mouth, and larynx, throat constriction, nausea, vomiting, convulsions, shock, and may cause severe and permanent damage), liver, and urinary system (kidneys) May affect behavior (convulsions, seizures, ataxia, excitement). Chronic Potential Health Effects: Ingestion: May cause effects similar to those of acute ingestion. Inhalation: Repeated exposure to low concentrations may cause bronchitis with cough, phlegm, and/or shortness of breath. May also cause liver and kidney damage, and affect the brain, and blood. Eye: May cause corneal damage and the development of cataracts and glaucoma. Skin: Repeated skin contact to low concentrations may cause dryness, itching, and redness (dermatitis)

Section 12: Ecological Information

Ecotoxicity:

Ecotoxicity in water (LC50): 0.1 ppm 24 hours [Rainbow trout]. 8.2mg/l 96 hours [Fathead minnow]. 0.1 ppm 48 hours [Bluegill].

BOD5 and COD: Not available.

Products of Biodegradation:

Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The products of degradation are less toxic than the product itself.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:

Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: Class 8: Corrosive material

Identification : Ammonia Solution UNNA: 2672 PG: III

Special Provisions for Transport: Not available.

Section 15: Other Regulatory Information

Federal and State Regulations:

Connecticut hazardous material survey.: Ammonium hydroxide Illinois toxic substances disclosure to employee act: Ammonium hydroxide Illinois chemical safety act: Ammonium hydroxide New York release reporting list: Ammonium hydroxide Pennsylvania RTK: Ammonium hydroxide Massachusetts RTK: Ammonium hydroxide Massachusetts spill list: Ammonium hydroxide New Jersey: Ammonium hydroxide New Jersey spill list: Ammonium hydroxide New Jersey toxic catastrophe prevention act: Ammonium hydroxide Louisiana spill reporting: Ammonium hydroxide California Director's List of Hazardous Substances (8 CCR 339): Ammonium hydroxide TSCA 8(b) inventory: Ammonium hydroxide CERCLA: Hazardous substances.: Ammonium hydroxide: 1000 lbs. (453.6 kg)

Other Regulations:

OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200). EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada):

CLASS D-1B: Material causing immediate and serious toxic effects (TOXIC). CLASS E: Corrosive liquid.

DSCL (EEC):

HMIS (U.S.A.):

Health Hazard: 3

Fire Hazard: 0

Reactivity: 0

Personal Protection:

National Fire Protection Association (U.S.A.):

Health: 2

Flammability: 0

Reactivity: 0

Specific hazard:

Protective Equipment:

Gloves. Full suit. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Face shield.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

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