TREATMENT OF A DOUBLE REFRACTORY ORE FROM BARBERTON USING PRESSURE OXIDATION

Bongiwe Beatrice Pewa

0606090M

A research report submitted to the Faculty of Engineering and Built Environment, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of MSc (Eng) Metallurgy

Supervisors:

Prof S Ndlovu,

Dr G F Ndlovu,

12 October 2021

DECLARATION

I, Bongiwe Beatrice Pewa, declare that this research report is my own unaided work. It is being submitted for the degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any other degree or examination in any other University.

October, 2021

ABSTRACT

The depletion of free milling gold resources, has shifted focus to the treatment of more difficult gold resources. One such example is double refractory gold ores. Double refractory gold ores are known as ores from which gold extraction is poor due to the presence of sulphide minerals and carbonaceous matter (CM) in the ore which preg-rob dissolved gold. In this study, a double refractory flotation concentrate from a mine in Barberton was used to evaluate the effectiveness of pressure oxidation (POX) pre-treatment in enhancing gold extraction. The plant currently conditions the sample in a blinding agent followed by a resin in leach (RIL) process resulting in about 65% gold extraction. Blinding agents are surfactants, usually of hydrocarbon nature which passivate the surface of CM, preventing the adsorption of dissolved gold onto CM.

The flotation concentrate was characterized and subjected to POX and subsequent cyanidation tests were conducted to quantify the improvement and establish best leaching conditions. Base line tests were conducted on the ‘as received sample’ for comparative purposes. Raman spectroscopic analysis indicated that the carbon in the sample was graphitic and a preg-robbing test of the CM in the sample indicated that it was highly preg-robbing. Although the preg-robbing capacity of CM increased after POX, the research study indicated that conditioning the sample in a blinding agent prior to RIL, resulted in the highest gold extraction of 82% obtained at 20 kg/t NaCN and 50mL/L Minix resin. Even though this study confirmed that POX can be used to enhance gold extraction from this double refractory material, there is still room for further optimization in order to increase the gold recovery

ACKNOWLEDGEMENTS

Foremost, I would like to thank the Almighty God for blessing me with wisdom, strength and health which enabled me to finish this work.

I would like to acknowledge MINTEK for the financial support, MINTEK staff and colleagues, who have each assisted and contributed in some way during the course of my study.

I will forever be grateful to Bonginkosi Nkabane for inspiring me to further my studies and our kids Ndumiso and Ngcebo for bringing a smile on my face after a long day of laboratory work.

Lastly, a special thanks goes to my supervisors:

- Dr Gebhu Ndlovu – for the motivation and guidance in all areas of my life
- Prof Sehliselo Ndlovu – for being patient with me even when I felt like giving up and for the guidance provided through the course of the research.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND ACRONYMS

CM	Carbonaceous matter in the ore
CIL	Carbon in Leach
RIL	Resin in Leach
POX	Pressure oxidation
US	United States of America
OPEX	Operational expenditure
PEC	Preg robbing effect of CM
CAPEX	Capital expenditure
BMA	Bulk Modal Analysis
FA	Fire assay
ICP-OES	Inductively-coupled plasma optical emission spectroscopy
XRF	X-ray fluorescence
AAS	Atomic absorption spectroscopy
QEMSCAN^{TM}	Quantitative Evaluation of Minerals by Scanning Electron Microscopy
AutoSEM	Automated Scanning Electron Microscopy (AutoSEM)
MLA	Mineral Liberation Analyser
ECD	Equivalent circle diameter
PSD	Particle size distribution
PSA	Particle size analysis
I_D	Raman intensity for the D band
I_G	Raman intensity for the G band
AMD	Acid-mine drainage

CHAPTER 1 : INTRODUCTION

1.1. Background

South Africa is currently the 9th largest gold producer in the world (Frik, 2019) and has two main gold resources, the Witwatersrand basin and the Archean Barberton Greenstone belt. Most of the gold produced is from the Witwatersrand basin (~95%) and the remaining is from the Barberton greenstone. The cause for lower production could to a certain extent be attributed to the difficult mineralogy of the current existing deposits. Gold particles found in the Barberton Greenstone deposit are usually associated with arsenopyrite, pyrite and other secondary sulphides (Devilliers, 1957; Craig, et al., 1998). Further contributing to the poor extractions, is the presence of carbonaceous material, which act as an absorber of the dissolved gold-cyanide complex from solution. The type of gold ore from which gold extraction is low because of the presence of sulphide minerals which lock up gold particles, as well as carbonaceous material, is known as a double refractory ore.

According to a report by Applied Geology Services cc, the gold grades in the Barberton Greenstone deposit can be as high as 15 g/t (Applied Geology Services cc, 2004). However, the challenge has always been a poor metallurgical performance when using conventional cyanidation.

A highly preg-robbing sulphidic gold sample was procured from one of the mines in the Barberton areas which has been experiencing poor metallurgical performance since they started mining this type of ore. The inconsistent mineralogy of the deposit has resulted in numerous temporary closures of the plant. According to a number of tests conducted by Mintek on samples from deposit, the average gold recovery by direct cyanidation has always been less than 45%.

Previously, double refractory ores from the Greenstone belt were treated in a roaster prior to cyanidation but stringent environmental regulations and increasing operational costs resulted in the operation becoming uneconomical. This led to a growth in initiatives aimed at finding alternative, environmentally friendly pre-treatment options. Currently, bacterial oxidation is used in Fairview mine, to treat mildly preg-robbing sulphidic ores. Although the mineral assemblage of ores from the Barberton Greenstone deposit is the same, the content and the distribution of gold within these minerals is not uniform throughout the deposit. The ore that

is being treated at Fairview mine contains less detrimental carbonaceous matter, in terms of both activity and content compared to the sample used for this investigation. According to work conducted previously, 68% gold was extracted on the sample when it was subjected to bacterial oxidation prior to CIL.

The main disadvantage of bacterial oxidation is the long residence time required for the oxidation of sulphides. Furthermore, strict control of the operating conditions is required for effective oxidation of the sulphide minerals. For ores with high concentrations of arsenopyrite, during oxidation, some arsenic is solubilized as As(III) without having any negative effect on the microorganism used. However, due to the toxicity of As(III), further treatment to stabilize the tailings is often required (Langhans, et al., 1995).

Pressure oxidation (POX) utilizes oxygen and high temperature (170-225°C) under high pressure (350-700 kPa) in order to control the decomposition of sulphide minerals to soluble sulphate minerals. High pressure oxidation is conducted in autoclaves. Pressure oxidation for the treatment of sulfidic gold ores was first commercialised in 1985 at Homestake McLaughlin (US*)* (Argall, 1989). The success of the plant led to commissioning in other areas of the world. High gold recoveries (greater than 90%) can be achieved when using POX. In addition, POX has been used for pre-treating mildly preg-robbing gold ores (different from the highly preg-robbing sample being tested) prior to CIL. POX has also been commissioned successfully for base metals production (Deng, 1993). Processes for recovery of PGMs such as the Kell and PLATSOL^{TM} consist of a pressure oxidation unit which has been proven to be efficient for the operation (Liddell & Adams, 2012).

This research focuses on evaluating the feasibility of using pressure oxidation to pre-treat a specific double refractory gold ore sample from a mine in Barberton. The inclusion of the POX unit in the flowsheet for treating double refractory ores from this deposit could reduce variations in gold extraction as POX is more accommodative to changes in ore mineralogy.

1.2.Motivation for the project

The use of POX or making it adaptable for treating double refractory ores for enhanced gold extraction will have the following benefits:

- Increase revenue due to enhanced gold extraction

- Other commodities such as base metals, sulphuric acid and PGMs can be recovered as by-products as they solubilize/ form during pressure oxidation.
- Stable residues are produced as there are no acid mine drainage forming components after POX and arsenic is stabilized as As(V).

1.3. Problem statement

The flowsheet (Figure 1.1) currently used in the plant (ultra-fine milling → blinding agent → RIL) yields a maximum of 65% gold extraction, resulting in high gold content in the residues. Furthermore, the extraction fluctuates due to the variations in the mineralogy of the deposit. According to the best practice guidelines for water resource protection in the South African mining industry, the acid mine drainage (AMD) potential should be minimized on both the effluent and solid waste streams (Wimberley, et al., 2008). The presence of sulphides in the tailings from the current process poses a threat to the environment as sulphides have an acid generation potential which can contaminate underground water and rivers.

The presence of unstable heavy metals such as arsenic (III) in the effluents which have the potential to contaminate underground and surface water through seepage. The use of POX eliminate both problems as the sulphide content is reduced and arsenic stabilized to As(IV).

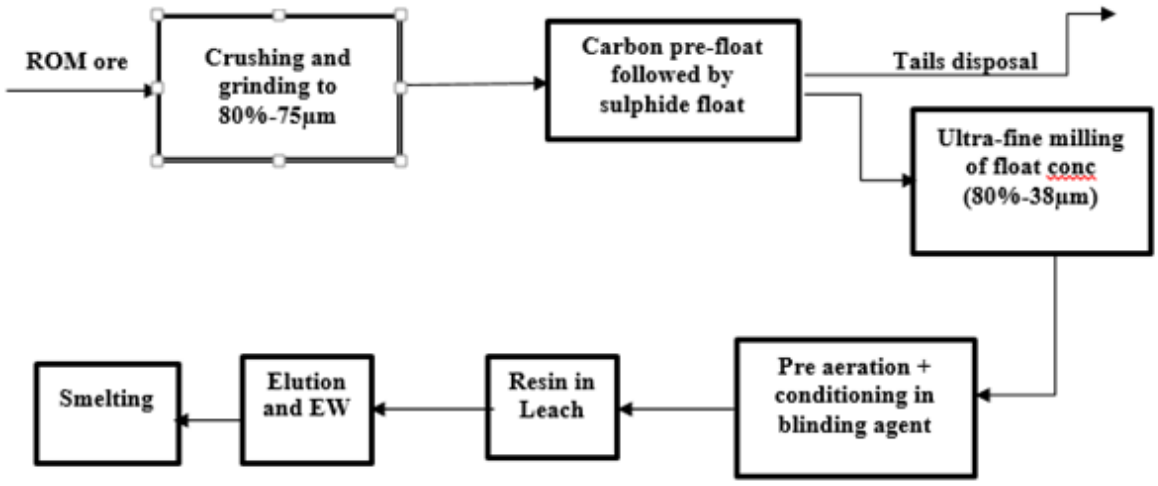

Figure 1.1. Current flowsheet used in the plant

1.4. Research aim

The aim of the research is to establish if pressure oxidation can be used to enhance gold recovery from this specific double refractory gold sample and to further develop a better understanding of the behavior of this type of ore when subjected to pressure oxidation. The suitable cyanide leaching conditions of the POX residue will also be determined in order to maximize gold extraction.

The specific objectives of the research are as follows:

- To undertake a detailed chemical and mineralogical investigation on the sample in order to predict behaviour under various conditions
- To quantify the amount of gold that can be recovered by using a standard cyanidation test. This test will be a base line for all other tests conducted under different conditions
- To pre-treat the gold ore by POX. Conditions that have been found to be favourable based on previous experience will be used.
- To determine the effect of POX on gold recovery by conducting a cyanidation test on the POX residue
- To conduct scouting tests in order to establish best leaching conditions of the POX residue.

1.5. Research questions

- Sample characterization
    - What is the gold grade of the sample?
    - What are the characteristics of gold bearing mineral in the sample (type of gold mineral, grain sizes, free gold, minerals associated with the gold mineral, liberation, etc.)
    - What is the concentration of other base metals, sulphide and carbon species?
    - What is the type of carbon material present in the sample, as well as the preg-robbing capacity of the sample?
- Base line cyanidation tests
    - How much gold can be recovered by cyanidation, CIL and RIL using basic conditions?
- POX

    - How does POX pre-treatment affect the gold mineralisation and chemical composition of the sample?
    - How does POX affect the preg-robbing capacity of the sample?
    - How much gold can be extracted after POX by cyanidation, CIL and RIL using basic conditions?
- Optimization of leaching conditions after POX
    - What is the effect of varying reagents dosage on gold recovery?
    - What is the effect of ultra-fine milling prior to leaching but after POX?
    - What is the effect of using a blinding agent?
- What is the effect of a conducting cyanidation test on POX residue at elevated temperature?

1.6. Scope of research

This study will be conducted using a flotation concentrate from a mine in Barberton. The flotation concentrate was generated in the plant during the time they were experiencing lower gold extraction due to changes in mineralogy. A flotation concentrate was chosen because a flowsheet for processing sulphidic gold ores will almost always include a flotation circuit to reject gangue, thereby reducing the amount of material for downstream processing and improving the grade of the feed.

The study will include a literature review of some of technologies available for treatment of double refractory ores and their respective industrial applications. The study will focus on sample characterization, the behavior of the ore during POX and leaching conditions of POX residue.

<u>Delimitations</u>

This study will not include optimization of the POX conditions for sulphidic gold ores as various studies have been conducted previously at Mintek on sulphidic gold ores from different deposits including those from Barberton and vast knowledge on this subject was generated (including suitable operational parameters). This study will also not include optimization of the flotation circuit as well as an economic feasibility study and downstream processes for gold recovery and purification which is beyond the current scope of work.

1.7. Dissertation layout

The dissertation will contain 5 chapters and each chapter will contain the following information:

Chapter 1 gives a brief background of the type of deposit (double refractory), the research work is based on: the metallurgical challenges associated with this type of ore, current flowsheet used to process this type of ore, previous technologies used, and an introduction to pressure oxidation as a solution to the problem and the objectives of this research.

Chapter 2 gives a brief history of gold mining in South Africa, its impact on the economy, the history of gold extraction and the future, the chemistry of gold extraction using cyanide and the technologies used for processing double refractory gold ores.

Chapter 3 describes the research approach and methodology used in this study.

Chapter 4 details the findings of the study.

Chapter 5 summarises the findings of the study, conclusions and recommendations.

CHAPTER 2 : LITERATURE REVIEW

2.1 History of gold mining in South Africa

Gold was first discovered in the northern parts of South Africa between the mid and the late 19th century. The first recorded alluvial gold discovery was made by Alex Peterson in 1873 in Sabie near Pilgrim's rest (Pilgrims-rest, 2013). The gold discoveries prompted individuals to excavate the area in search of gold and the source of the alluvial gold. A year later, Tom McLachlan 1874 (Marias, 2020) discovered gold near what is now known as Barberton. It was not until the Barber brothers, Harry and Fred discovered a reef in 1884 that mining in the Barberton greenstone belt gold deposit commenced (Resources, 2018).

Around the same time (1884), Gerrit Bantjies discovered a minor gold reef on a farm in Vogelstruisfontein, Witwatersrand. Several other discoveries were made but it was only after George Harris discovered a main gold reef that the first mining company was formed in around the Witwatersrand area (SA-History, 2011).

The discovery of gold in the two regions resulted in gold rush which, in turn led to rapid industrialization and urbanization around the areas where gold was discovered. The economy of South Africa changed from being agricultural based to being industrial based (mining and manufacturing) as can be seen in Figure 2.1 (Stats, 1990).

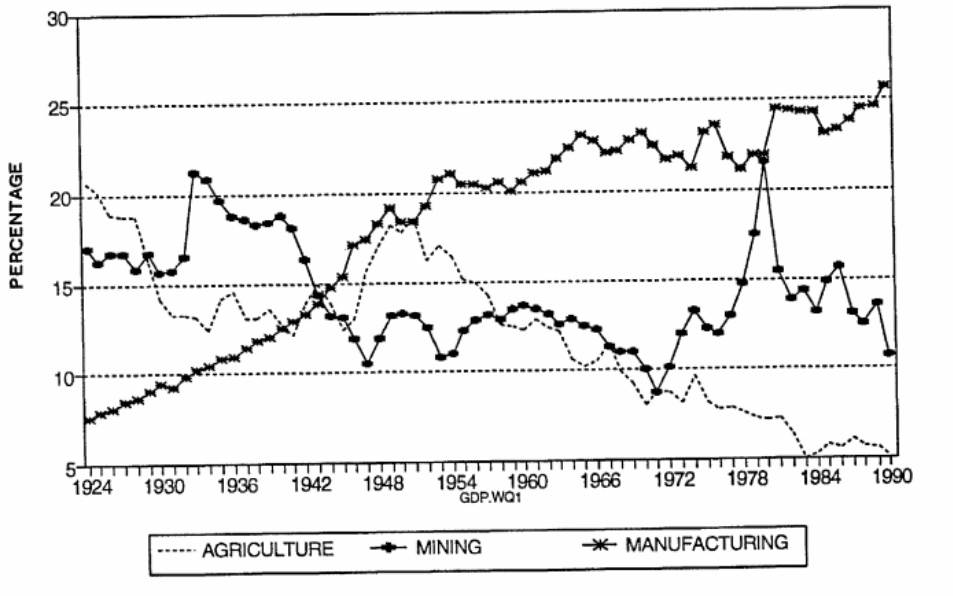

Figure 2.1 GDP contribution, Source: Union Statistics for Fifty Years (1960), South African Statistics (1990), IDC (1992).

2.2 History of gold extraction in South Africa

Prior to the discovery of major gold deposits, placer mining was the main form of mining used, where gravity concentration techniques were used to recover gold from other sand minerals found in river beds. With this form of mining, suitable for native gold, gold was recovered as gold nuggets.

The recovery of profitable gold reefs attracted larger capital from investors and mining companies were able to acquire mining equipment for mining from deeper levels. Mined ore was then milled using stamp milling and gold was recovered using amalgamation. Amalgamation involves using mercury to form an amalgam (Schnabel, 1921). Amalgamation yielded poor extraction as the mineralogy of the mined ore was more complex than the alluvial gold.

Gravity and amalgamation were found to be unsuitable for fine gold and gold associated with sulphide minerals. It wasn't until 1890 that a first cyanidation plant was commissioned in South Africa, following the intensive collaborative work of John Stewart MacArthur, Robert Forrest and William Forrest on gold and silver extraction using cyanidation. The work was a remarkable breakthrough in the gold industry as the cyanidation technique was more economical, highly selective to gold and silver, forms stable aurocyanide complexes and the chemistry is relatively simpler (Stanley, 1987). To date, cyanide is still the mostly used lixiviant

for dissolving gold from gold bearing ores despite its toxicity. A typical flowsheet (Figure 2.2) for gold recovery includes a leaching circuit, carbon adsorption circuit, carbon elution and electro winning. Flowsheets will vary based on gold occurrence in the ore that is being treated.

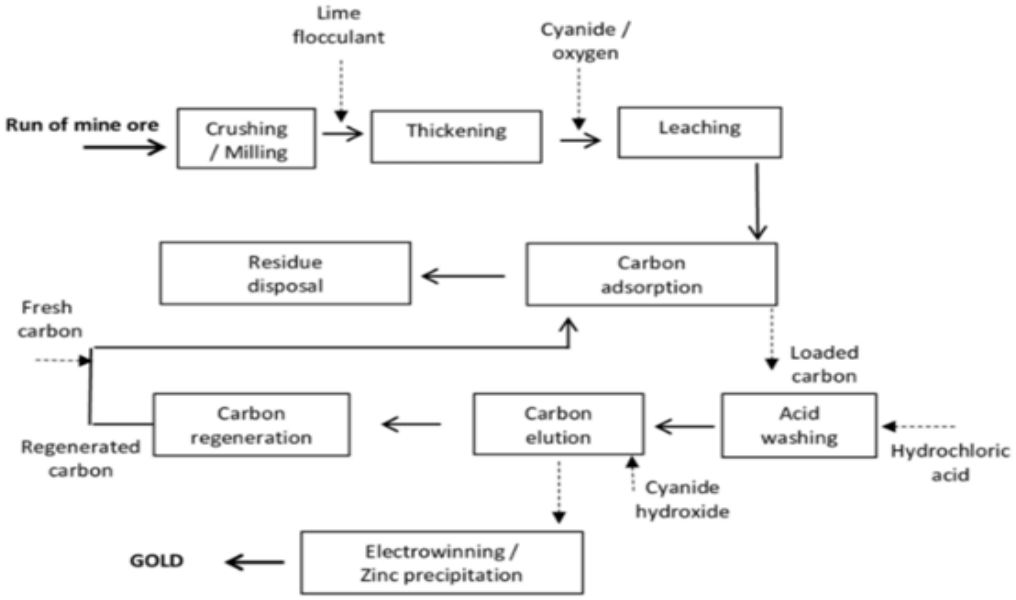

Figure 2.2. A typical flowsheet for gold recovery (Source: Researchgate https://www.researchgate.net/figure/Block-diagram-for-gold-extraction-from-ore_fig1_336742273)

2.3 Chemistry of gold dissolution in cyanide medium

Gold is known for its resistance to lose electrons under very oxidative conditions. Gold commonly exist as native gold or electrum gold, a naturally occurring alloy of gold and silver. Other alloys of gold such as maldonite (Au_2Bi), aurostibite ($AuSb_2$) and tellurides ($AuTe_2$) are known to have extremely poor leaching properties (Ellis, 2005).

According to literature, the most likely Au ions to form are Au^{3+} and Au^{+} with the following half reactions:

$$Au^{3+} + 3e^{-} = Au^{0}; E = 1.52 + 0.0197 \log[Au^{3+}] \quad \text{……Eqxn 2.1}$$

$$Au^{+} + e^{-} = Au^{0}; E = 1.83 + 0.0591 \log[Au^{+}] \quad \text{…….Eqxn 2.2}$$

For Au^0 to be oxidized to either of the two ions, a very strong oxidant is required (Marsden & House, 2006). Eqxn 2.2 requires an even stronger oxidant as it has a higher E^0 than Eqxn 2.1 and therefore Au^+ is least likely to form in solution. A Pourbaix diagram showing the stability of various gold ions/compounds under various redox potentials and a range of different pHs is

shown in Figure 2.3. As shown, metallic gold (Au^0) is stable even above the water region, indicating that it cannot be oxidized by dissolved oxygen.

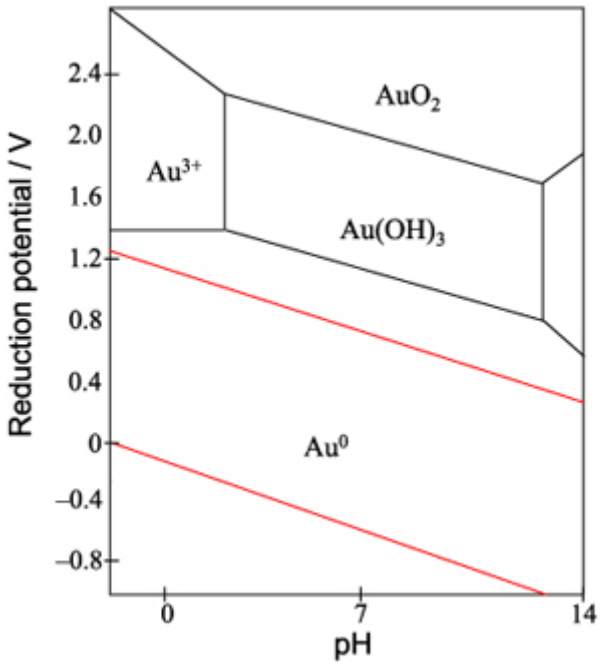

Figure 2.3. Pourbaix diagram for the Au-H_2O system, Source (https://www.scielo.br/scielo.php?script=sci_arttext&pid=S0103-50532014000900026)

The redox potential of the water reaction (Eqxn 2.3) is 1.23V

$$O_2 + 4H^+ + 4e^- = 2H_2O \ldots\ldots \text{Eqxn 2.3}$$

Because, the Eh of the water reaction is less than that of oxidation of metallic gold reaction, oxidized Au^{3+} ions are unstable in water and are reduced (water being the reducing agent) to metallic gold in the absence of a complexing agent (Nicol, et al., 1987). Therefore, for gold to dissolve in water, an oxidizing agent and a complexing agent (ligand) are necessary. Some of the gold complexes with their respective stability constants are shown in Table 2.1. The higher the stability, the more stable the gold complex is. Cyanide complexes with both ions of gold to form a complex with a highest stability constant, with Au^{3+} being more stable than Au^+.

Table 2.1. Stability constants for selected Au(I) and Au(III) complexes (Source: (Adamson, 1973)

Ligand	Au(I),β_2	Au(III),β_3
CN^-	2×10^{38}	10^{56}
SCN^-	1.3×10^{17}	10^{42}
$S_2O_3^{2-}$	5×10^{28}	-
$H_2NCH_2COO)^-$	10^{18}	-
Cl^-	10^9	10^{26}
Br^-	10^{12}	10^{32}
I^-	4×10^{19}	5×10^{47}
$CS(NH_2)_2^+$	2×10^{23}	-

The addition of cyanide to the Au-H_2O system shifts down the stability region of Au^0 to be within the water region. The half reaction of gold cyanidation is given in below:

$$Au(CN)_2^-(aq) + 3e = Au^0 + CN^- ; E < 0\ V\ at\ pH > 8 \ldots . Eqxn\ 2.4$$

Since the redox potential of the water reaction (Eqxn 2.3) is greater than that of Eqxn 2.4, Au^0 can be readily oxidized by oxygen (Figure 2.4) (Osseo-Assare, et al., 1984). In essence, cyanide plays a dual role, modifies the stability region of Au^0 and is a complexing agent and this makes it superior to most of commercially available alternative lixiviants.

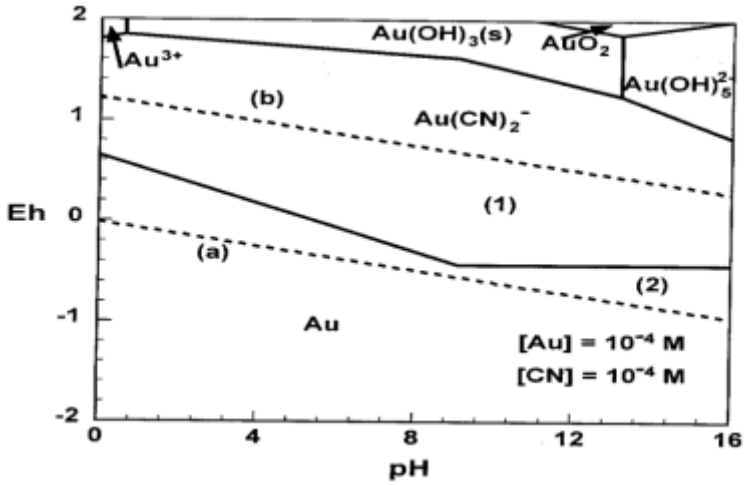

Figure 2.4.Pourbaix diagram of the Au-CN-H_2O system at 25ºC (Osseo-Assare, et al., 1984)

Because HCN is a weak acid, increasing H^+ (decreasing the pH) favors the formation of HCN according to Eqxn 2.5:

$$HCN\ (aq) = H^{+}(aq) + CN^{-}(aq)\text{.....Eqxn 2.5}$$

For this reason, even though the $Au(CN)_2^-$ is stable over a wide pH region, cyanidation is carried out at pH>9.5 to avoid volatilization of a highly toxic HCN. According to the cyanide stability diagram (Figure 2.5), at a pH of 9.3-9.5, the HCN (g) and CN^-(aq) are at equilibrium. Increasing the pH increases the stability of CN^- in solution.

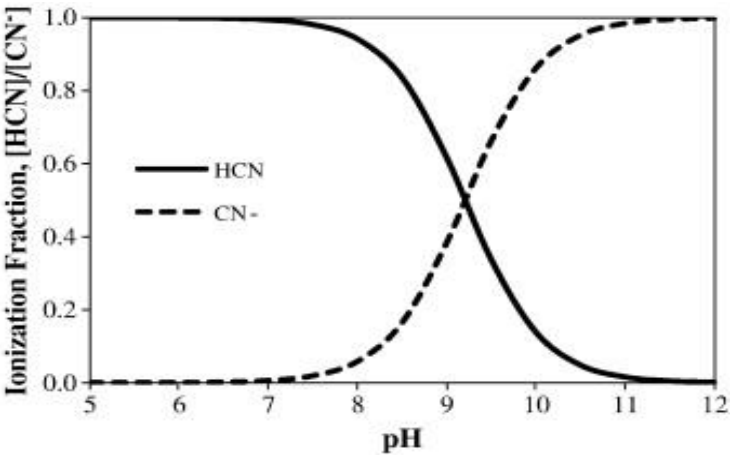

Figure 2.5. Cyanide stability diagram (https://ars.els-cdn.com/content/image/1-s2.0-S0304386X11002726-gr2.jpg)

2.3.1 Mechanism and factors affecting gold dissolution

Gold dissolution is governed by Elsner's equation (Elsner, 1846).

$$Au + 8\,CN^{-} + O_2 + H_2O = 4[Au(CN)_2]^{-} + 4\,OH^{-}\text{....}\ \text{Eqxn 2.6}$$

Based on Eqxn 2.6, there should be adequate free cyanide and dissolved oxygen in solution for gold particles to dissolve.

For any heterogeneous system involving solid-liquid-gas phases, the rate of reaction is controlled by the following factors (Evans, 1979):

- Step 1: Dissolution of gas in the solution phase
- Step 2: Mass transportation of reactants to the surface of reaction
- Step 3: Chemical reaction at the solid phase
- Step 4: Mass transportation of reacted species from surface to solution.

According to Kudryk, the gold cyanide reaction is based on the diffusion (Step 1, 2 and 4) and surface adsorption model (Kudryk & Kellogg, 1954) , Step 3. A type of reaction where the rate is dependent on all 4 steps as highlighted above is said to proceed under mixed control. In Au-CN-H_2O, Step 2 and Step 4 (partially) are controlled by ensuring adequate agitation of the slurry and enough dissolved oxygen for Step 1, which can be achieved by bubbling air through the slurry.

Kirk & Foulkes, 1984 proposed that the reaction progresses (at the solid-solution interface), Step 3 in two main stages:
Au is oxidized from Au^0 to Au (I), forming an intermediate product AuCN(s) which coats the gold particles according to Eqxn 2.7.

$$Au\ (s) + CN^-(aq) = AuCN^-(ads) \quad \text{.....Eqxn 2.7}$$

$$AuCN^-(ads) = AuCN(s) + e^- \quad \text{.....Eqxn 2.8}$$

The intermediate product, AuCN further dissolves according to Eqxn 2.9

$$AuCN(s) + CN^-(aq) = Au(CN)_2^-(aq) \quad \text{.....Eqxn 2.9}$$

According to Kirk and Folkes, Eqxn 2.9 is the rate limiting step (Kirk & Foulkes, 1984). In the presence adequate free cyanide in solution formation AuCN(s) is negligibly low, the formation of $Au(CN)_2^-$ is favoured and gold dissolution is rapid (Nicol, et al., 1987). Additionally, the gold surface needs to be exposed to the cyanide solution, liberated and available for gold leaching. This is achieved by milling a gold ore to conventional grind size of 80% - 75 µm.
In summary, factors that affect gold dissolution can be summarized as follows:

- Dissolved oxygen
- Efficient mixing of slurry to allow efficient mass transfer between the liquid and solid phase
- Free cyanide
- Surface exposure to solution.

There has been ongoing research focused on finding a suitable replacement for cyanide due to the health and environmental concerns associated with its use. Prospective lixiviants include thiosulphate, thiourea and glycine. Thiosulphate is explained in detail in Section 2.5.2.2.

2.3.2 Thiourea

Gold reacts with thiourea ($CS(NH_2)_2$) to form a stable complex with a pK value of 21.75 (Marsden & House, 2006). The reaction proceeds as follows;

$$2CS(NH_2)_2 + Au = Au(CS(NH_2)_2)_2^+ + e^- \text{.....Eqxn 2.10}$$

The reaction requires a strong oxidant to proceed. Ferric (Fe^{3+}) is normally used for this purpose, being reduced to Fe^{2+} in the process. According to the Fe-H_2O Pourbaix diagram, Fe^{3+} is stable at pH < 2. Leaching is therefore carried out at a pH range of 1.4-1.8. The gold-thiourea complex is recovered from solution using activated carbon.

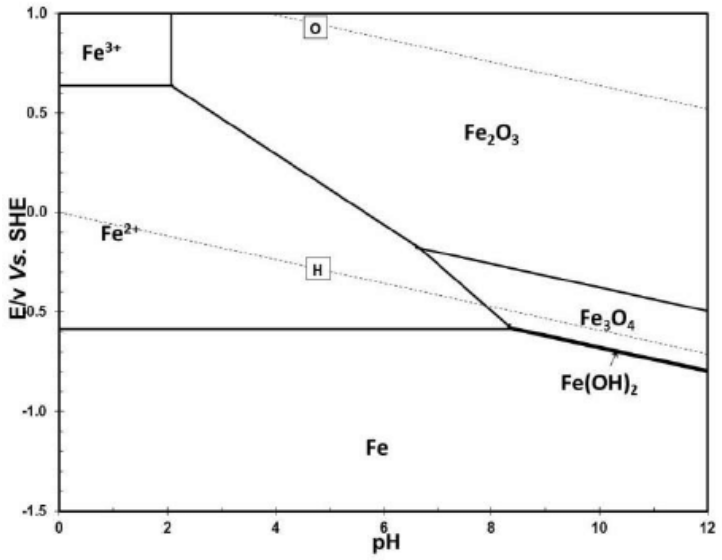

Figure 2.6.Pourbaix diagram for Fe-H_2O system at 25 °C, (https://www.researchgate.net/figure/Pourbaix-diagram-for-H-2-O-Fe-system-T-25 °C-Fe-2-10-ppm-Fe-3-10-6_fig1_276500273)

Thiourea is also oxidized in stages, increasing the consumption during leaching. The first oxidation product, formamidine disulphide ($NH_2(NH)CSSC(NH)NH_2$) is useful during gold leaching as it also acts as a strong oxidant, accelerating gold dissolution kinetics. The first oxidation product is also further oxidized to cyanamide, hydrogen sulfide and elemental sulphur, undesirable products as the latter also passivates gold particles. Sulphur dioxide is normally added to inhibit second stage oxidation thus reducing thiourea consumption.

A study was carried out by Orgul & Atalay, (2002) to determine the amount of gold that can be recovered from a Turkish gold ore using thiourea. Under optimum conditions, ~86% gold

was extracted in 6 hrs. Several other studies have proved the efficiency of thiourea with an added advantage of faster leaching kinetics compared to cyanide. Despite the positive prospect, the main disadvantage of the Au-thiourea system is that it becomes costly due to high thiourea consumption and the requirement of other reagents such as SO_2 and H_2SO_4 (Hiskey & Atluri, 1988). New England Antimony Mine is the first plant to commercialize gold leaching in acidic thiourea in 1982 (Hisshion & Waller, 1984). There has not been any more commercial plants recorded but studies on improving the process are ongoing.

2.3.3 Glycine

Gold leaching in glycine medium is one of the latest developments in gold leaching technologies and there is an increasing interest in this area of research because glycine is relatively cheaper than other alternative lixiviants, recyclable and environmentally friendly (Oraby, et al., 2020).

Gold dissolves in alkaline glycine medium to form a stable gold glycinate complex with a pK value of 18 according to the following reaction:

$$4Au + 8NH_2CHOOH + 4NaOH + O_2 = 4Na[Au(NH_2CH_2COO)_2] \text{.....Eqxn 2.11}$$

Gold leaching is normally carried out at pH >9. Gold dissolution in an alkaline glycine medium is generally very slow but using a stronger oxidant such as peroxide improves kinetics and efficiency. A study conducted by Oraby & J.J, (2015) indicated that, using a high concentration of hydrogen peroxide,increasing the pH from 10 to 11 and increasing the temperature to 60 °C resulted in improved efficiency and gold dissolution kinetics. Base metals such as copper and zinc readily dissolve in alkaline glycine medium. However, the outcomes of a study by Oraby, et al., (2020) showed that the addition of a small amount of cyanide (far less than the concentration required during cyanidation) to the glycine leach resulted in precious metals recovery >85%.

2.4 Refractory gold ores

Free milling gold ore are those from which at least 95% of gold can be extracted by cyanidation when the ore is milled to 80% - 75 µm, without incurring high reagent consumption (Marsden & House, 2009). Typical gold deposits from the Witwatersrand region fall under this category.

Refractory gold ores are those which are insusceptible to conventional cyanidation (Swash, 1988). The degree of refractoriness (resistance to recovery by cyanidation) can be classified based on the proportion of gold recovered (Table 2.2).

Table 2.2. Classification of Refractory Gold Ores Based on Degree of Refractoriness. (Asamoah, et al., 2014)

Classification	Gold recovery (%)
Free milling	> 95
Mildly refractory	80 - 90
Moderately refractory	50 - 80
Highly refractory	< 50%

The insusceptibility of a gold ore to cyanidation can be due to the following reasons:

- Gold particles locked within host minerals such as silicate, oxide or sulphide minerals. Different types of gold-sulphide minerals associations are shown in Figure 2.7. Non–reactive sulphide minerals may be present in the ore but have no effect on the gold recovery or reagents consumption (type 1 association), as is the case with most Witwatersrand ores (Marsden & House, 2009).

- Chemical encapsulation is the formation of complex intergrowths of native gold with tellurides resulting in poor gold recovery by cyanidation (Marsden & House, 2009). Ores containing gold-telluride minerals generally have poorly optimized, processing requirements. The dissolution of gold tellurides is extremely slow under normal cyanidation conditions.

- Reactive gangue minerals such as copper bearing minerals, pyrrhotite which compete with gold for free cyanide and oxygen, thereby increasing the cyanide and oxygen consumption and reducing the gold recovery by cyanidation.

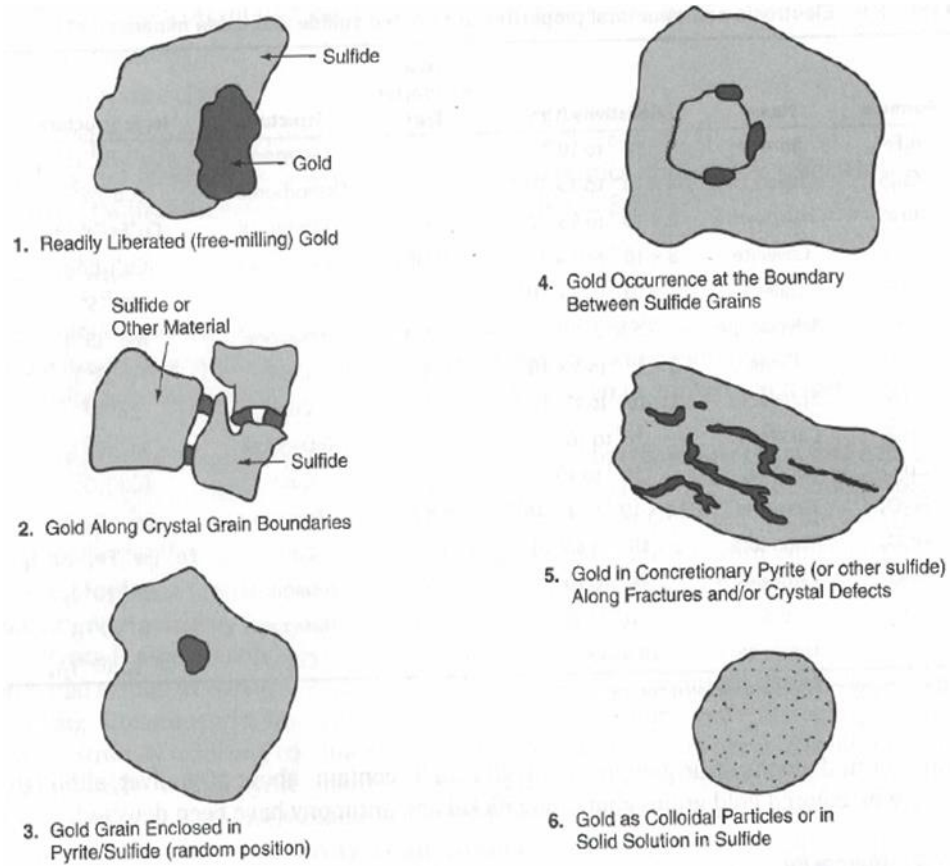

Figure 2.7: Schematic representation of types of gold association with sulphide minerals (Marsden & House, 2009)

Preg robbing is the adsorption of the dissolved auro-cyanide complex ($Au(CN)_2^-$) in solution by carbonaceous matter (CM) or other minerals such as clay, pyrophyllite etc. in the ore. The process can be either reversible (preg-borrowing) or irreversible depending on the amount and activity of the preg-robbing material present in the ore. Mustapha, et al., (2014) conducted research work to determine the preg-robbing effect of carbon (PEC) on different gold ores from Ghana and they classified the ores according to Table 2.3 (Mustapha, et al., 2014).

$$PEC = vol\ of\ sol(L) \times \frac{(Au(initial,solution - Au(final,solution))\left(\frac{mg}{L}\right)}{mass\ of\ solid\ sample\ (kg)} \text{.....Eqxn 2.12}$$

For the purpose of this report, a similar classification will be used.

Table 2.3. Preg robbing classification (Mustapha et al., 2014)

Classification	Preg-robbed, %	PEC, g/t
Mildly preg-robbing	Less than 50	1-19
Moderately preg-robbing	50-80	20-32
Highly pre-robbing	Greater than 80	>32

2.4.1 Double refractory gold ores

The gold recovery can be affected by both the physical encapsulation of gold particles within sulphide minerals and the presence of carbonaceous matter in the ore. Gold ores which exhibit this phenomenon are known as double refractory ores (Baron, et al., 2016). For efficient gold extraction from double refractory ores, the effect of the presence of sulphide and carbonaceous components on gold extraction must be minimized. The challenge with treating double refractory ores is that the degree to which each component affects gold recovery differs from one deposit to the other. Various studies have been conducted on the behavior of various sulphide minerals during gold leaching and the pre-treatments methods thereof. One of such studies was conducted by Aghamirian, 1997. It was found that pyrrhotite, pyrite and chalcopyrite had a negative effect on the gold anodic dissolution, moreover pyrrhotite had a negative effect also on the gold cathodic reaction. The sulphide oxidation method is selected based on the type of sulphide mineral present, gold deportment and the concentration of sulphide minerals. Some of the oxidation processes used include pre-earation, pressure oxidation, roasting, bacterial oxidation, nitric acid oxidation and chlorine oxidation (Marsden & House, 2006)

The presence of carbonaceous matter makes it less possible to adopt a flowsheet used to treat another refractory ore successfully, because the extent to which overall gold recovery reduces is not only dependent on the concentration of carbon, but also on the type of carbon materials, as well as the degree of maturation of the carbon material (Helm, 2009). According to Adams, (2005), the carbon materials that have been reported in gold ores include charcoal, anthracite, graphite, coal, shale, decaying wood, wood ashes and other vegetable matter. The different carbon materials can be classified according to maturity and the preg-robbing capacity generally increases with increasing carbon maturity. Graphitic carbon and anthracite are categorized as high maturity carbon material (Pyke, et al., 1999).

2.5 Methods used to treat double refractory ores

In order to recover gold from double refractory ores, the following combination is required:

- The gold particles encapsulated by sulphide minerals must be liberated or exposed to the cyanide solution
- Deactivation of the carbonaceous matter in the ore.

Gold ores containing sulphides and organic carbon can be divided into the following categories (Asamoah, et al., 2014) (Mustapha, et al., 2014):

1. Mildly refractory, midly preg-robbing (Not considered double-refractory)
2. Moderately refractory, mildly preg-robbing (Not considered double-refractory)
3. Highly refractory, mildly preg-robbing (Not considered double-refractory)
4. Mildly refractory, moderately preg-robbing (Not considered double-refractory)
5. Moderately refractory, moderately preg-robbing (double refractory)
6. Highly refractory, moderately preg-robbing (double refractory)
7. Mildly refractory, highly preg-robbing (double refractory)
8. Moderately refractory, highly preg-robbing (double refractory)
9. Highly refractory, highly preg-robbing (double refractory)

2.5.1 Mildly to moderately preg-robbing ores

2.5.1.1 CIL and RIL

Gold from these type of ores can be recovered by the carbon in leach (CIL) or the resin in leach (RIL) method. The ability of carbon to adsorb auro-cyanide complex was first discovered in the early 19th century. Activated carbon is added during cyanide leaching to recover gold dissolved in cyanide solutions. For mildly preg-robbing gold ores, dissolved gold will have a high affinity for the added activated carbon than the CM in the ore. The advantage of the process is that activated carbon is highly selectivity to the auro-cyanide complex, however the carbon is vulnerable to breakage resulting in gold losses to the residue. Carbon is also susceptible to fouling by flotation reagents, significantly reducing the gold loading capacity of carbon. The selectivity of carbon for gold is also subject to other factors such as free cyanide, pH and the presence of other metals.

A study was conducted on a midly preg-robbing gold ore from Navachab in Namibia which currently use the carbon in pulp (CIP) set up in the plant, to quantify gold extraction if CIL is

used (Amwele & Groot, 2018). It was found that gold extraction increased by 10% when CIL was used.

Ion exchange resin works on the same principle as activated carbon. Mintek in partnership with Dow Chemicals developed a strong base ion exchange resin called Dowex-Minix for gold recovery from pulp. The mechanical properties of the resin are superior to that of carbon, in turn minimising gold losses due to attrition. Resin addition of 10-25 mL/L of slurry is commonly used. Better gold recoveries are obtained from ores containing high levels of clay or organic compounds because resin is less susceptible to blinding. Furthermore, the CAPEX and OPEX of a plant using resin is approximately 30% less than that of a plant using carbon as an adsorbent (Deventer, et al., 2000).

Both CIL and RIL can be used alone if the ore is mildly refractory but can be used in conjunction with a sulphide pre-treatment method if the sulphide content in the ore is high.

2.5.2 Moderately to highly pre-robbing ores

2.5.2.1 Blinding agent

Hydrocarbons such as diesel, kerosene, and sacrosote have been used in various mines to deactivate the carbonaceous matter in the ore prior to cyanidation (Pyke, et al., 1999). Although the actual mechanism for the deactivation is poorly understood, the method has been used in plant operations such as Penjom mine in Malaysia (Siearra and Ramli, 2015).

The blinding agent is added at a concentration of 1% (m/m) to the feed slurry to blind the carbonaceous matter in the ore. The conditioning is carried out for at least 1 hour after which, the normal RIL procedure is followed. The blinding agents also foul the activated carbon added during CIL. Therefore, ion exchange resin is normally used in conjunction with blinding agent treatment, since it is less susceptible to blinding.
A study to investigate the effectiveness of using a blinding agent followed by RIL to recover gold from preg-robbing ore containing 2% carbon was conducted by Mubarok & Irianto, (2016). They compared gold extraction from the sample by direct cyanidation vs pre-treatment in a blinding agent followed by direct cyanidation and lastly blinding agent followed by RIL. It was found that using a blinding agent followed by cyanidation improved gold extraction by 25.4% and using blinding agent followed by RIL improved gold extraction by 34%.

Blinding agent only deals with the carbonaceous component of the double refractory ore and thus, an additional process is required to overcome the sulphide component of the material.

2.5.2.2 Thiosulphate leaching

Thiosulphate has been used since the early 90s in regions of the world where the use of cyanide is prohibited. The $Au(S_2O_3)^{3-}{}_2$ complex does not adsorb onto carbon and is less toxic than cyanide, making it a good alternative lixiviant for leaching carbonaceous gold ores (Aylmore, 2016). Thiosulphate forms a stable complex with gold according to Eqxn 2.13; however, the reaction is slow. Copper in the presence of ammonia is added to catalyse the chemical reaction. Thiosulphate leaching is stable over a wide range of pHs, but it is normally carried out at pH levels between 9 and 10.5 (Hackl, et al., 2010). The gold-ammonia-thiosulphate chemistry is complex and is still subject to further investigation.

$$4\,Au + 8S_2O_3^{2-} + \ O_2 + 2H_2O = 4Au(S_2O_3)_2^{3-} + 4OH^- \quad \text{……..Eqxn 2.13}$$

The advantages of thiosulphate leaching are as follows:

- Silver and copper can also be leached and selectively recovered from thiosulphate solution using resins
- The gold-thiosulphate complex formed does not adsorb onto carbon and therefore preg-robbing is completely eliminated
- The reagent is less toxic than cyanide.

The disadvantages are as follows:

- The chemistry is not fully understood and therefore optimisation can be difficult
- High reagents consumption as thiosulphate easily oxidises and ammonia can also be lost by volatilization, rendering the technology very expensive.

2.5.2.3 Roasting

Roasting is a pyrometallurgical process which is normally applied to sulphide ores or concentrates to partially or completely oxidise sulphides, arsenic and other volatile components of the ore according to Eqxn 2.14.

$$MS\ (s) + O_2(g) = M(s) + SO_2(g)\text{……..Eqxn 2.14}$$

The technology has been around for decades, but a resurgence of interest has occurred due to the depletion of free milling reserves and an increase in the gold price. Roasting can be conducted in rotary kilns, fluidised beds or in a multiple hearth furnace. The process entails the use of high temperature in the presence of oxygen enriched air to form sulphur dioxide gas as per Eqxn 2.13. During the oxidative roast process, partial oxidation (60-75%) of carbon is also feasible depending on the type of carbon present and roasting temperature applied (Fernandez, 1996).

Roasting has been effectively used for treatment of high grade >3 g/t carbonaceous sulfidic (double refractory) gold ores and sulphide concentrates as it deals with both the sulphide components and carbon components of the ore (Fernandez, 1996). Roasting can increase the gold recovery in double refractory ores to more than 95%.

The treatment of double refractory ores is carried out in two stages, the first stage operates at 540-650ºC for oxidising most of the sulphides and carbonaceous material while the second stage is operated at 600-650ºC to oxidise the remaining sulphides and oxides. Pure oxygen is fed counter-currently (Birak, 1987). A residence time of less than 3 hours is sufficient for oxidation of sulphides.

A roaster was commissioned at what was then the Eastern Consolidated Mines (Fairview, Barberton and Sheba mines) in Barberton in 1988 and yielded gold extractions greater than 89%. Although roasting resulted in satisfactory recoveries, there were challenges associated with the operation, such as the high operational cost (OPEX) due to the presence of arsenic which required “fixing”, the 2-3% gold losses due to volatilization of gold as well the environmental concerns with respect to gas emissions (Ferreira, et al., 1989). The company then adopted bacterial oxidation as a processing option of choice.

2.5.2.4 Chloride oxidation

Chlorine modifies the organic carbon surface by the formation of chloro-hydrocarbon layer which passivates the active sites. The technology was developed in the late 1960s and it employs the strong oxidising ability (E^0 = 1.358 V) of chlorine to deactivate CM in the ore. It was first commercialised in Carlin mine in Nevada, USA. Although the chemistry involved in the deactivation of carbon by chlorine is not well understood, the technology yielded high gold

recoveries (>90%). (Guay, 1989). The oxidation of sulphides using chlorine can be summarised using Eqxn 2.15. The chlorine can be supplied as a gas, aqueous or as an inorganic hypochlorite salt.

$$2FeS_2 + \ 15HOCl + 7H_2O = 2Fe(OH)_2 + 23\ H^+ + 4SO_4^{2-} + 15Cl^- \ldots\ldots \text{Eqxn 2.15}$$

The flowsheet included milling, thickening and heating the pulp to 27ºC and 38ºC before transferring the pulp to an agitated tank sparged with chlorine. The off gases were scrubbed using soda ash to form sodium hypochlorite which was recycled back into the agitated tanks, reducing the chlorine requirement.

Conventionally, oxidation is carried out at pH between 3 and 5 because the hypochlorous (HOCl) species which has a redox potential of 1.64 V is stable at this range. For feed material with high sulphide content, pre-treatment in sodium carbonate (25 kg/t addition) is carried out at 60-80ºC to reduce the chlorine consumption in the chlorination circuit.
For organic carbon deactivation, the slurry is conditioned in HOCl (1.0 g/L addition) for at least 1 hr. The residual slurry is then subjected to flash chlorination by spurging chlorine for 15 minutes and allowing the hypochlorous species to decay for 10-20 hrs. The presence of hypochlorous in the feed to cyanidation results in high cyanide consumption (Helm, et al., 2009).The technology is CAPEX (high grade materials of construction required when working with chlorine) and OPEX intensive (chlorine gas, energy costly).

2.5.2.5 Bacterial oxidation

The bacterial oxidation technology was developed for the pre-treatment of gold bearing sulphide ores before cyanidation. It was first commercialised in 1984 at Fairview gold mine in a process known as the BIOX®, in South Africa, following extensive research dating back to the early 1960s. The process makes use of a culture of acidophilic bacteria to oxidise the sulphides and iron phases in the ore (Adan, et al., 1989).

The bacterial culture used in sulphide mineral oxidation is normally made-up of three types of bacteria i.e. *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans*. Various sulphide minerals such as pyrite, arsenopyrite, pyrrhotite, chalcopyrite, galena, etc. can be oxidised using the technology. The bacterial culture requires oxygen and

carbon dioxide for maintenance and growth. The mechanism of bacterial oxidation is shown in Figure 2.8. Bacteria are believed to play an indirect (catalytic) role in the oxidation of sulphides.

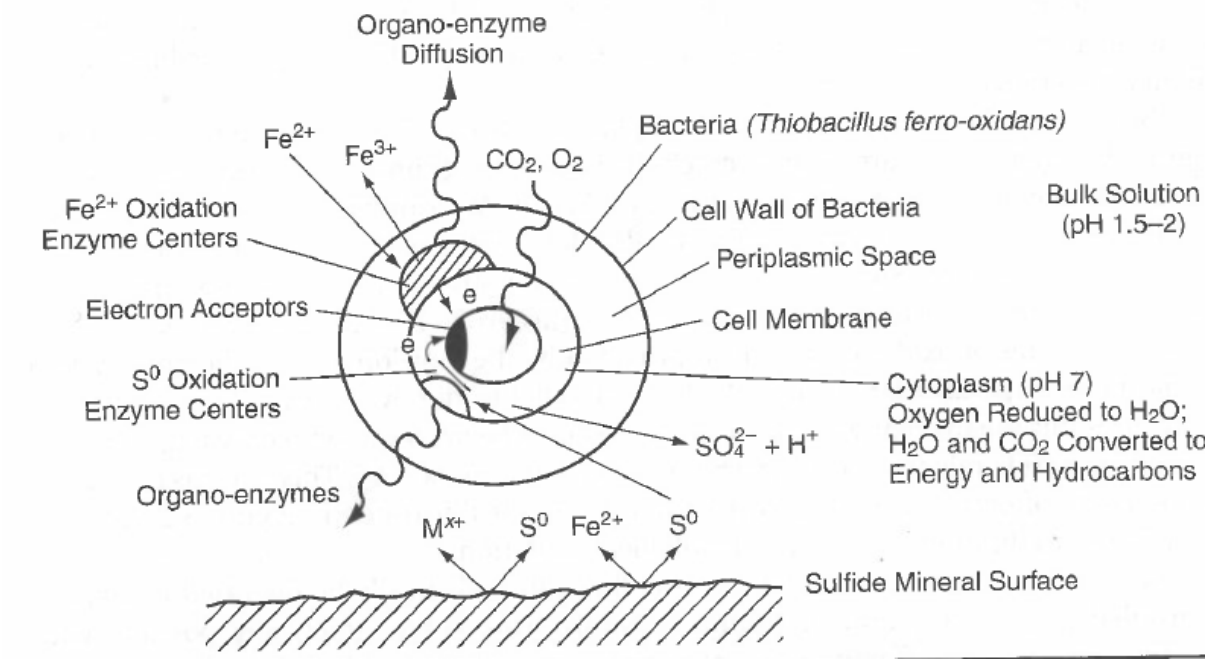

Figure 2.8. Simplified mechanism of bacterial oxidation. (Marsden and House, 2009)

Bacterial oxidation of pyrite and arsenopyrite can be illustrated by the equations:

$$4FeS_2 + 15\,O_2 + 2H_2O = 2\,Fe_2(SO_4)_3 + 2H_2SO_4 \ldots\ldots \text{Eqxn 2.16}$$

$$FeAsS\ + 7O_2 + H_2SO_4 + 2H_2O = \ Fe_2(SO_4)_3 + 2H_3AsO_4 \ldots.. \text{Eqxn 2.17}$$

Bacterial oxidation has over the years resulted in gold extraction >95% at Fairview mine and the process was deemed to be less cost intensive. Although the mineral assemblage of ores from the Barberton Greenstone deposit is the same, the content and the distribution of gold within these minerals is not uniform throughout the deposit. The ore that is being treated at Fairview mine contain less detrimental carbonaceous matter, in terms of both activity and content. Previous work conducted at Mintek on this ore indicated that gold extraction of 68% could be achieved by bacterial oxidation followed by CIL.

There has been ongoing research into the bacterial deactivation of carbonaceous component. A two stage bacterial treatment of double refractory ore was investigated (Amankwaha, et al.,

2005). The normal sulphide oxidation was carried out in the first stage, followed by the treatment using bacterium Streptomyces setonii. The two stage treatment resulted in improvement of 13% in gold recovery. The research has not resulted in any industrial application.

Recently, (Sasaki and Konadu, 2020) conducted a study to investigate the microbial alternative for CM degradation. They used lignin degradation enzymes (lignin peroxidase, manganese peroxidase, laccase) to decompose CM in a preg-robbing ore. It was found that gold recovery improved from 24%-92%. The promising outcomes of the studies on decomposition of CM using microbial culture indicates that this could potentially be a solution. The main disadvantage is the long residence time required for the oxidation of sulphides. Strict control of the operating conditions is required for effective oxidation of sulphide minerals. Due to the exothermic nature of the reaction, cooling is usually required. Bio-oxidation products have a potential of fouling the carbon during cyanidation.

2.5.2.6 High Temperature Caustic Conditioning Process

The high temperature caustic conditioning (HITeCC) process resulted from a collaboration between BIOX® and BIOMIN® and it is said to improve gold recoveries by more than 10% (Hankock, 2013). It involves conditioning the residual slurry from CIL using heat, carbon and high caustic reagents to desorb gold from CM in the ore. The gold stripped from organic carbon in the ore is loaded on fresh activated carbon through a two-stage temperature process. The process can be easily incorporated into conventional leach circuits. There is still ongoing research to improve the process.

The first commercial BIOMIN technology was constructed in 2009 at Crocodile Gold Corp's Fosterville BIOX®, Australia. It has been running successfully and the plant has been realising economically attractive recoveries (Nordgold, 2017). Approximately 40% of gold previously lost to CIL tails is recovered by the process, which amounts to an overall increase in gold extraction of 10%. The second commercial application was in 2016 at Suzdal Mine in Kazakhstan where extractions between 40% and 70% (on current tailings) were recorded

2.5.2.7 Pressure oxidation

Pressure oxidation in the aqueous medium utilizes oxygen and heat (170-225ºC) under pressure (350-700 kPa) in order to control the decomposition of sulphide minerals. High pressure oxidation is conducted in autoclaves. Pressure oxidation for treatment of gold ores was first commercialised in 1985 at Homestake McLaughlin (US) (Argall, 1989). The success of the plant led to commissioning in other areas of the world.

High gold recoveries can be achieved when using POX however, the operation is associated with high costs due to high energy and oxygen requirements. The technology is normally used for pre-treating samples with a sulphide content, >4%. For these type of samples, the process becomes economical as the heat of reaction produced during sulphide oxidation is sufficient to maintain the required operating temperature, thus lowering process costs (Marsden and House, 2006).

Two autoclave pressure oxidation processes have been developed, namely:

- Acidic, used for the materials with high sulphur and low carbonate content
- Non acidic, used for the materials with low sulphur and high carbonate content.

Acidic POX is the most widely used of the two developments. The chemistry of the pressure oxidation process is complex and also different for each sulphide mineral and conditions applied. Pressure oxidation of sulphide mineral results in the formation of sulphuric acid.
Elemental sulphur could be formed as an intermediate product (Marsden and House, 2006):

$$FeS_2 + 2O_2 = FeSO_4 + S$$ ……Eqxn 2.18

and oxidized further at high temperature:

$$4S + 3O_2 + 2H_2O = H_2SO_4$$ ……Eqxn 2.19

Acidic oxidation of pyrite at 170-225°C occurs according to the following reactions:

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$ …….Eqxn 2.20

$$4FeSO_4 + O_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + H_2O$$ ……Eqxn 2.21

Ferric then hydrolyses to form different compounds such as hematite, basic ferric sulphate and jarosite:

$$Fe_2(SO_4)_3 + 3H_2O = Fe_2O_3 + 3H_2SO_4$$ …… Eqxn 2.22

$$Fe_2(SO_4)_3 + 2H_2O = Fe(OH)SO_4 + H_2SO_4$$ …… Eqxn 2.23

$$3Fe_2(SO_4)_3 + 14H_2O = 2H_3OFe_3(SO_4)_2(OH)_6 + 5H_2SO_4$$ Eqxn 2.24

In the case of arsenopyrite, oxidation, final products of oxidation are insoluble ferric arsenate sulphate containing compounds:

$$4FeAsS + 11\,O_2 + 2H_2O = 4HAsO_2 + 4FeSO_4$$ ……Eqxn 2.25

$$HAsO_2 + 2FeSO_4 + H_2SO_4 + O_2 = Fe_2(SO_4)_3 + H_3AsO_4$$ ……Eqxn 2.26

$$Fe(SO_4)_{1.5} + xH_3AsO_4 + \left(w + \frac{z}{2}\right)H_2O = Fe(AsO_4)_x(SO_4)_Y(OH)_{Z.W}H_2O + (1.5 - y)H_2SO_4$$ Eqxn 2.27

There are a number of As-containing mineral phases identified in POX residue including sulphate containing scorodite, ferric arsenate sub-hydrate (FAsH), basic ferric arsenate sulphate (BFAS) and arsenate-containing basic ferric sulphate (As-BFS).

Alkaline POX has been proposed for the arsenical ores. Oxidation of the arsenopyrite and pyrite in the presence of limestone (or NaOH) at elevated temperature (180ºC) occurs according to the following reactions:

$$2FeAsS + 5CaCO_3 + 7O_2 = Ca_3(AsO_4)_2 + Fe_2O_3 + 2CaSO_4 + 5CO_2$$ ……..Eqxn 2.28

$$2FeS_2 + 4CaCO_3 + \frac{15}{2}O_2 = Fe_2O_3 + 4CaSO_4 + 4CO_2$$ …….Eqxn 2. 28

Typical operating conditions for the acidic POX are shown in Table 2.4. Prior to POX, the slurry is treated with sulphuric acid to neutralize the carbonates and other acid consumers in the ore. Acid is added in the case of acidic oxidation and sodium hydroxide is added in the case of alkaline POX.

Table 2.4.Operation conditions for POX

Temperature	170-225˚C
Solids percentage	15%
Operating pressure	700 kPa over steam pressure (~2100 kPa operating pressure
Retention time	30 -180 minutes

The formation of elemental sulphur, basic iron sulphates (BIS) and jarosite is undesirable, since it increases the consumption of cyanide during cyanidation. Sulphur oxidation process is

temperature dependent as shown in Figure 2.9 and formation of elemental sulphur could be avoided at high temperature.

Excess free acid will promote the formation of BIS and jarosite (Figure 2.10). Strict control of pH and temperature is required in order to achieve desired products.

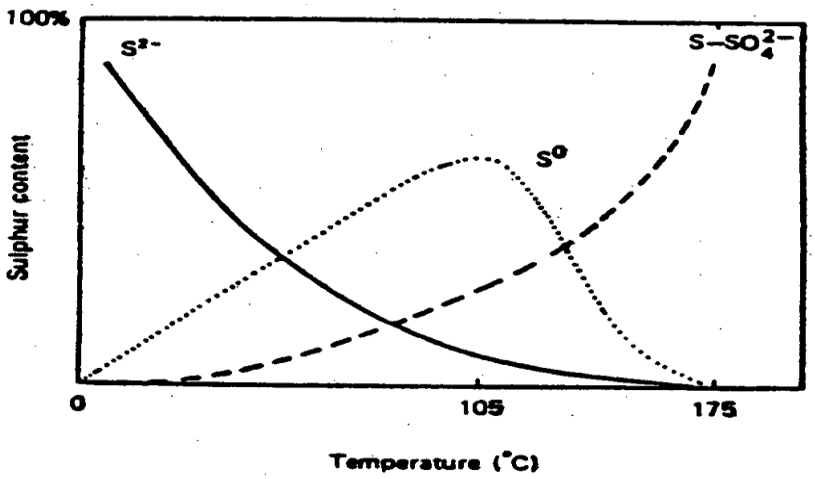

Figure 2.9. Sulphide oxidation at pH<3 (Long, 2000)

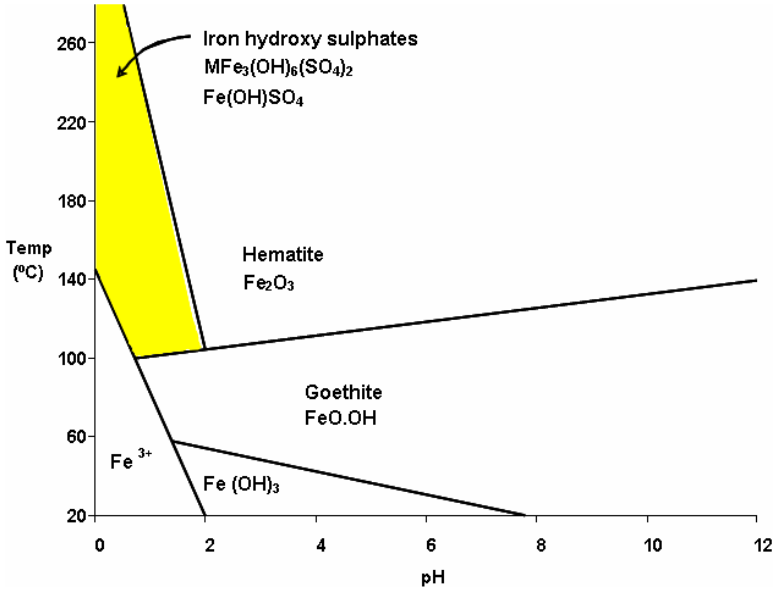

Figure 2.10. Areas of stability of different compounds in the system Fe-O-S (Fleming, 2010)

Oxidation of pyrite results in acid formation. Therefore, a neutralization step before cyanidation is required. Often POX oxidizes sulphide minerals but not carbonaceous material. It was reported that pressure oxidation can deactivate the indigenous carbon, but it is not sufficient for highly preg-robbing ores (Fomenko, et al., 2013).

Nevertheless, the POX technology is used in a number of plants that treat double refractory ores. The gold from the resulting POX residue can then be recovered using thiosulphate leach or conditioning with blinding agents followed by RIL/CIL.

Fomenko, et al., (2013) conducted a study on the use of pressure oxidation to recover gold from preg-robbing ores with carbon content ranging from 0.3 to 2.1% organic carbon. It was found that after POX, gold extraction decreased with increasing organic carbon content and that the presence of chloride ions during POX resulted in lower gold extraction during cyanidation. The latter is believed to be due to the solubilization of gold as AuCl and adsorption onto CM during POX, which is difficult to extract during cyanidation. Although, the solubilization of gold during pressure oxidation is a major issue for double refractory ores, there are various ways of reducing the likelihood of this happening, such as using scavenger ion exchange resin to remove chloride ions prior to pressure oxidation. This method will only work if the chlorides are present due to contamination or from process water. If halides are found in the ore, pressure oxidation conditions are adjusted to reduce the oxidizing conditions in the slurry (Simmons, et al., 1998).

Advantages of POX

The advantages of POX are as follows:

- Complete oxidation of sulphide achieved in a short period
- Other bases metals, PGM and uranium can solubilize and are recoverable from solution
- Arsenic is oxidized to stable As/Fe/SO_4 compounds which are more stable and can be disposed.

Moreover, alkaline POX has the following advantages:

- Relatively low process temperature
- Less corrosive environment and therefore a cheaper material of construction can be used reducing CAPEX
- No subsequent neutralization required.

Disadvantages of alkaline POX

The disadvantages for POX are as follows:

- The technology is energy intensive resulting in high OPEX
- Oxygen generation plant is required further adding to OPEX and CAPEX

- Acid neutralization is required before cyanidation in case of acidic POX
- Loss of silver during POX
- Iron oxide can coat the gold and sulphide reducing the recovery (basic POX)
- Applicable for ores with high amount of basic constituents (basic POX)
- High arsenic solubility (in the case of NaOH leach).

All previous pressure oxidation work conducted on double refractory ore has been on samples containing less than 5% organic carbon, with varying outcomes. The research work is focused on determining if the process can be used on ores with higher carbon content.

2.6 Summary of literature review.

The plant from which the sample was obtained currently consists of the following operation units: Comminution circuit → Flotation → Ultra-fine milling → Blinding + RIL → Electrowinning → Smelting. The focus area for the study is maximizing gold extraction from the flotation concentrate and while producing benign residues. During the desktop study it was found that the important factors affecting gold extraction were the availability of reactants (in adequate concentration) required for the chemical reaction to proceed, i.e. oxygen and cyanide (leaching conditions) as well the exposure of gold particles to the cyanide solution (gold occurrence and mineralogy of the sample). The challenge with the sample is that gold concentrate is associated with sulphide minerals and contains preg-robbing minerals in the sample which 'steal' dissolved gold from solution. Preg-robbing minerals include carbonaceous matter (CM), clay etc.

Some of the technologies available for liberating gold particles from a sulphide matrix are bacterial oxidation, roasting and pressure oxidation. The presence of CM in the ore complicates the process of gold extraction as normally another treatment method is required to deactivate/oxidize the preg-robbing component in the ore. The method used to overcome the negative effect of CM depends on preg-robbing capacity of the CM. For mildly preg-robbing samples, CIL/RIL can be added to compete with the CM in the ore for the aurocyanide complex. RIL is generally more effective in overcoming the negative effect of CM compared to CIL. For moderately to highly preg-robbing samples treatments options include preconditioning with a blinding agent (deactivate) before RIL, roasting (oxidation), chlorination (deactivate), thiosulphate leaching, HiTeCC®. There are current studies being done on deactivation of CM using bacterial oxidation. Pressure oxidation has been used to treat

mildly to moderately preg-robbing refractory gold ores. The sample used for the investigation is highly preg-robbing (PEC> 30 according to **Error! Reference source not found.** classification) and the objective of the study is to evaluate if pressure oxidation can improve gold extraction for this type of sample. The main challenge associated with pre-treatment of double refractory ores in an autoclave is that in the presence of chloride ions, gold can dissolve and be absorbed by CM, which is difficult to recover during subsequent CIL. To eliminate this problem, scavenger ion exchange resin can be used to remove chloride ions from the slurry or adjust the pressure oxidation conditions such that it is less oxidative.

CHAPTER 3 : MATERIALS AND METHODOLOGY

3.1 Materials

Feed sample

A flowsheet for processing sulphidic gold ores will almost always include a flotation circuit to reject gangue, thereby reducing the amount of material for downstream processing and improving the gold grade. It is for this reason that the investigation was conducted on a concentrate from the flotation circuit of the plant.

Activated carbon

Granular activated Haycarb carbon (GAC) was used for all CIL tests. Before use, the GAC was prepared to remove fine materials which can potentially report to the residue if not removed. A sub-sample weighing 200 g was placed in a bottle with 2 L of water and rolled for 8 hrs to remove carbon fines. After 8 hrs, the sample was screened through an 850 µm screen, the carbon on the screen was air dried and packaged for test work.

Minix Resin

Minix ion exchange resins (200 mL) were washed with distilled water to remove fine particles. Washed resins were transferred to a column and 6 bed volumes (BV) of 2M Na_2SO_4 was passed at a flow rate of 2BV/hr. This was done to convert the active groups in the resins from chloride to sulphate form to prevent the release of chloride ions into the cyanide leach solutions. After converting resins to sulphate form, resins were washed thoroughly to remove excess Na_2SO_4. Converted resins were stored with entrained water.

3.2 Equipment

3.2.1 pH meters and balances

A set including a Metrohm 827 pH Lab meter and a calibrated pH probe was used to measure and control the pH during cyanidation and pressure oxidation tests. The probe was calibrated daily using Hamilton pH 7 and pH 4 buffer solutions.

Control of pH is important in order to achieve conditions suitable for the dissolution of targeted ions. Furthermore, during cyanidation, the pH needs to be maintained above 10 to prevent volatilization of toxic HCN gas.

Balances are calibrated annually, however, the accuracy of the balance used during the test work was verified by weighing mass pieces with known weights.

Experimental setup

3.2.2 Bottle roll tests

A bottle roll test is a standard method for determining gold dissolution. The tests were conducted in a 2L Schott bottle and mixing was achieved by placing the bottle on a motorized roller rotating at 32 rpms (Figure 3.1).

Figure 3.1. Bottle roll set-up

3.2.3 Pressure vessel

Pressure oxidation tests were conducted in a 2 Gallon Parr pressure reactor (Figure 3.2) made of stainless steel. The reactor is fitted with an impeller to ensure adequate mixing and a temperature control system which includes thermocouples, heating and cooling coils. The inside of the reactor is coated with titanium to prevent oxidation of steel under harsh operating conditions. A system consisting of a pressure gauge and a pressure release valve is used to monitor and control pressure inside the reactor.

Figure 3.2. 1 Gallon Parr pressure reactor

3.3 METHODOLOGY

The method of approach is shown in Figure 3.3.

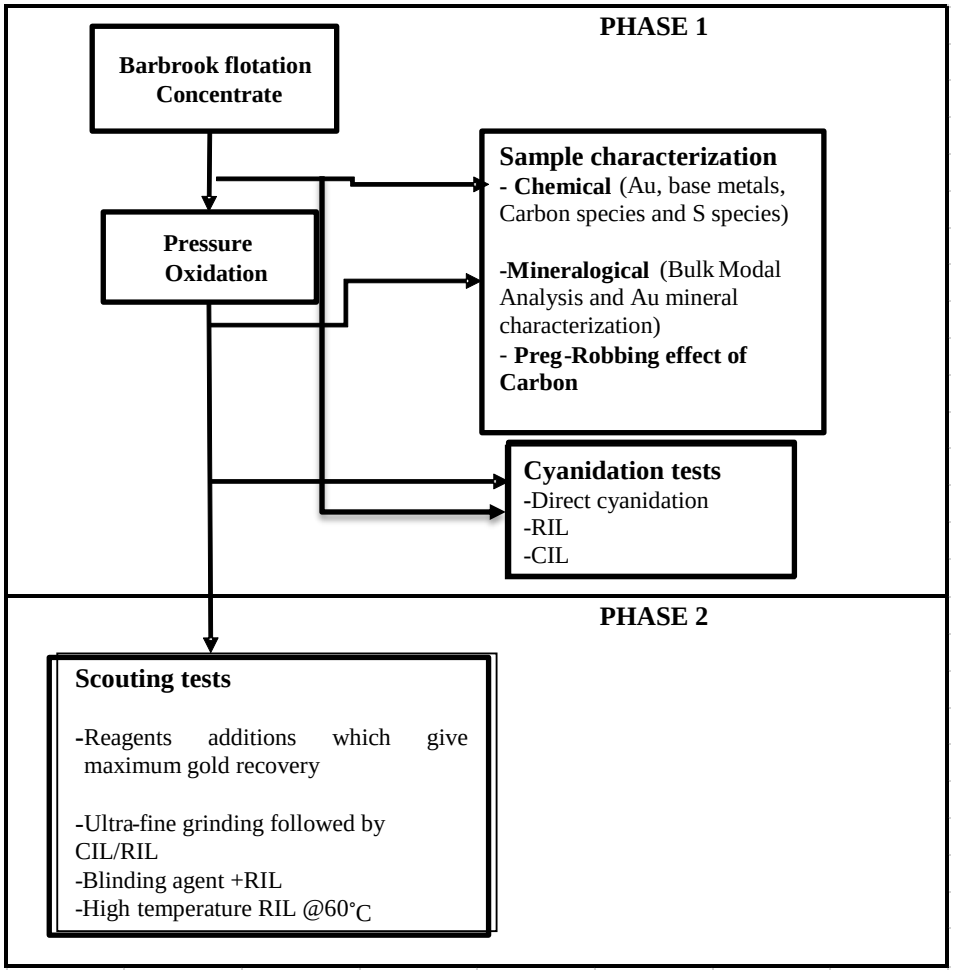

Figure 3.3. The test work programme.

PHASE 1

3.3.1 Sample characterization

Sample characterization was conducted in order to understand the chemical and mineralogical composition of the sample as well as the behaviour of carbonaceous matter in the sample. Sample characterization included the following:

- Full chemical analysis (base metals, Au, Ag, As, carbon species, sulphide species)
- Mineralogical analysis (bulk modal analysis (BMA), Au mineral characterization)
- Raman spectroscopy for analysing the type of carbon present in the sample
- Preg-robbing effect of carbonaceous matter (CM) in the ore

3.3.1.1 Head chemical analysis

A full chemical analysis was conducted on the flotation concentrate using the analytical methods for solids shown in Table 3.1.

Analytical Methods

The analytical methods with their respective detection limits that were used for solids and solution analysis during the course of the test work are shown in Table 3.1.

Table 3.1. Analytical methods and detection limits.

Method	Elements	Detection limit
Solids		
Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)	Mg, Al, Si, Ca, Cr, Mn, Fe, Ni, Cu, Co, Zn and Pb	Lower limit 0.05%
Fire assay (FA) - Gravimetric finish (triplicate)	Au	Lower limit 0.08 g/t
XRF (X-Ray Fluorescence) analysis: All elements at detectable concentrations	Matrix dependent	Lower limit 1 g/t
Atomic Absorption Spectroscopy (AAS)	Ag, As	Lower limit 5 g/t
Total Sulphur	Combustion ("LECO")	0.01%
S^{2-} S	Combustion LECO	0.01%
Sulphate S	Combustion LECO	0.01%
Organic Carbon	Combustion, after extraction	0.01%
Total C	Combustion, after extraction	0.01%
Solution samples		
ICP-OES	Mg, Al, Si, Ca, Cr, Mn, Fe, Ni, Cu, Co, Zn and S	2 mg/L for all elements,
Atomic Absorption Spectroscopy (AAS)	Au,	0.08mg/L

3.3.1.2 Mineralogical analysis

The flotation concentrate was subjected to the following mineralogical analyses:

- Bulk Modal analysis (BMA) - to identify the minerals present in the ore and quantify the abundance of each mineral. Knowing minerals present is an important tool to predict leaching efficiencies and identifying potential causes for poor gold extraction.
- Au mineral characterisation – this analysis is often used during flowsheet development as it gives important information about the characteristics of the gold minerals in the

sample. Such information includes concentration of gold, the type of gold minerals present, the size of the gold grains, the minerals associated with gold grains and the liberation of the gold minerals.

3.3.1.2.1 Bulk modal analysis (BMA)

The bulk modal analysis measurement involved analysing mineral grains in the sample at pre-set equidistant points and identifying the minerals at each analysis point by Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN^{TM}). The sample was screened into different size fractions in order to achieve more accurate results, as each fraction could be analysed at an optimal magnification. Results from the size fractions were re-combined into a total sample result during data processing.

3.3.1.2.2 Au mineral characterisation

The Au samples was sub-sampled representatively to produce polished sections for analysis by Automated Scanning Electron Microscopy (AutoSEM). A bright phase search was conducted using a Mineral Liberation Analyser (MLA), which identifies Au minerals high backscatter intensity that it has compared to gangue minerals. A maximum of 28 polished sections per sample were searched. The results from the search give information about the species present, the relative abundance, grain size distributions, liberation characteristics of the species and mineral associations (i.e. what other minerals are associated with the identified Au grains in particles).

3.3.1.2.3 Raman spectroscopy

Raman spectroscopy is a quantitative and semi-qualitative spectral analytical tool used to study chemical composition or structure of samples, i.e., identify unknown compounds. The technique uses monochromatic light which interacts with the compound molecules and results in two light scatterings: elastic scattering and inelastic or Raman scattering which is responsible for the technique. This test was conducted to determine the structure and nature of carbon material (CM) in the sample.

3.3.1.3 Preg-robbing effect of carbon in the sample

The preg-robbing effect of carbon (PEC) test was conducted to get an indication of the degree of preg-robbing effect of carbonaceous matter in the sample. The test was conducted by contacting a 10 g sample of flotation concentrate with 25 mL solution of 16 mg/L gold concentration. The slurry was agitated at 200 rpm for 24 hrs in a stirred reactor after which it was filtered and the solution was analysed for gold using AAS (See Table 3.1).

3.3.2 Baseline cyanidation tests

The flotation concentrate was subjected to cyanidation, CIL and RIL in order to quantify the amount of gold that can be recovered. These results were used as a base case for other tests.

3.3.2.1 Direct Cyanidation

A sub-sample weighing 200 g was placed in a 1 L Schott bottle. Rand water board (RWB) water was added to achieve a pulp density of 33 (m/m)%. The bottle was placed on a roller for an hour, after which the pH of the slurry was adjusted to 11 using hydrated lime ($Ca(OH)_2$). After the target pH was reached, the bottle was placed on a roller for a further 1 hour, and sodium cyanide (NaCN) at a dosage of 10 kg/t was added. The pH was monitored throughout the test.

After a 24-hour residence time, the bottle was weighed and filtered using a vacuum filtering system. The filter cake was washed twice with RWB water via re-pulping. A wash water mass ratio of 1:1 (liquid: solids) was used during the re-pulping steps. The filtrate was analysed for Au and other base metals (refer to Table 3.1 analytical methods for solution). The washed wet filter cake was dried in an oven at 60°C for 8 hours. The dry filter cake was assayed for the elements listed in Table 3.1.

3.3.2.2 Carbon in Leach (CIL)

A CIL test was conducted similarly to direct cyanidation except that washed activated carbon was added (25 g/L) prior to NaCN addition. After 24 hrs, the carbon was screened out and the slurry was filtered as described in Section 3.3.2.1. Carbon and dried filter cake were assayed for gold using the fire assay method.

3.3.2.3 Resin in Leach (RIL)

RIL test was carried out similarly to CIL, except that Minix resin was added (25 mL/L) prior to cyanide addition.

3.3.3 Pressure oxidation

From past research done at Mintek, pressure oxidation has proved to be the most effective process for oxidation of all sulphide minerals. The flotation concentrate was subjected to pressure oxidation in an attempt to improve the gold recovery.

POX was conducted on the flotation concentrate to generate a residue which is amenable to direct cyanidation. The POX test conditions were chosen to ensure that hematite is produced as the main iron precipitate. A subsequent curing step was also included to ensure any other iron precipitates (i.e., jarosite and basic ferric sulphate) which could have also precipitated, dissolved. Jarosites and basic ferric sulphates consume excessive amounts of lime during cyanidation thus resulting in difficulties with the control of pH.
In order to produce sufficient residue for downstream test work, 14 tests were conducted and the residues combined.

Pre-acidification

A combined flotation concentrate (6000 g) was received and a bulk pre-acidification on this concentrate was carried out. This was done to ensure decomposition of carbonates and also yielded a homogenous feed introduced into the autoclave.

The pre-acidification conditions are included in Table 3.2.

Table 3.2. Pre-acidification conditions

Slurry density	wt % solids	50
Target pH (Ag/AgCl)	-	1.0
Residence time	min	60
Temperature	°C	65

The concentrate was pulped to 50 (m/m) % with deionised (DI) water. The slurry was agitated and heated to 65°C. The temperature was subsequently controlled at 65°C for the duration of

the test (i.e. 60 minutes). The pH was monitored and controlled to a value of 1.0 at 65°C by the stagewise addition of 800 g/L H_2SO_4. On completion of the test, the slurry was vacuum filtered and the residue washed twice with pH 2 H_2SO_4 adjusted water and once with DI water in a displacement wash. A wet mass to water ratio of 1:5 (wt/wt) was employed during each washing stage. The washed residue was air-dried and a representative sample was submitted for chemical analysis.

The filtrate was collected and analysed for free acid and Fe^{2+} content via potentiometric titrations as well as base metals in solution via ICP-OES.

Pressure oxidation (POX) followed by hot curing

The pre-acidified residue formed the feed to the POX test. The residue was pulped to a slurry density of 10% (m/m) solids with DI water which was then introduced into the 1 gallon Parr titanium autoclave, sealed and purged with nitrogen to check for leaks. The impeller speed was adjusted to 500 rpm. According to the Fe(II), Fe(III) and free acid concentrations analysed in the pre-acidification filtrate, a concentrated synthetic solution was prepared. Once the autoclave had reached the set-point temperature (210°C), the concentrated synthetic solution was injected into the reactor with 50 kPa overpressure of oxygen. This brought the initial concentrations of the important species (Fe(II), Fe(III) and free acid) to their desired concentration levels and ensured the correct total slurry volume in the autoclave had been attained. A pre-determined amount of water was also injected into the reactor to purge the feed bomb (which contained the synthetic solution). This was done with the remaining oxygen partial pressure and brought the autoclave to the total set point oxygen overpressure of 700 kPa. "Injection at temperature" of the iron salts and acid was done to eliminate the effect of the heating period on the POX results.

The slurry was maintained at temperature and the total operating pressure (25 bar(g)) for the selected residence time (90 minutes). A summary of the conditions employed is provided in Table 3.3.

Table 3.3. POX conditions

Slurry density	wt % solids	10
Residence time	min	90
Temperature	°C	210
Oxygen partial pressure	kPa	700
Total operating pressure	kPag	2523
Steam pressure*	kPag	1823
Initial acid concentration (after injection)	g/L	4.25
Initial Fe^{2+} concentration (after injection)	g/L	1.87
Initial Fe^{3+} concentration (after injection)	g/L	2.26

**based on an atmospheric pressure of 83 kPa in Randburg, SA*

At completion of the pressure leaching test, the slurry was cooled to 90°C and the reactor head space vented which signified the start of the curing test. The slurry was maintained at 90°C for 3 hours. The curing conditions are provided in Table 3.4. Hot curing is the process of breaking down and converting basic iron sulphate (BFS) minerals to iron oxides using the heat and acid that has been generated in the acid. The presence of BFS is undesirable as it results in high lime consumption during cyanidation.

Table 3.4. Curing conditions

Residence time	min	180
Temperature	°C	90

After the curing test was completed, the slurry was cooled to 40°C and vacuum filtered. The wet cake was washed twice with pH 2 H_2SO_4 adjusted water by re-pulping at a wash ratio of 1:5 m/m (wet solids to wash water) followed by a displacement wash with DI water also in a 1:5 m/m ratio. The resulting POX residue was air-dried.

The cooled POX filtrate was submitted for chemical analysis (i.e., base metals via ICP-OES). A representative sub-sample of the dried POX residue was taken, pulverised and submitted for sulphide sulphur analysis.

The POX residues from the 14 tests were blended together and split into 200 g sub-samples. One sub-sample was used to determine the chemical composition (Table 3.1) and mineralogical composition (Section 3.3.1.2).

3.3.3.1 Cyanidation tests after POX

Cyanidation tests were conducted on the POX residue to determine the effect of pressure oxidation on gold recovery. Direct cyanidation, CIL test and RIL test were conducted similarly to the baseline cyanidation tests in section 3.3.2.1, 3.3.2.2 and 3.3.2.3.

PHASE 2

3.3.3.2 Scouting tests

Scouting tests were conducted by varying leaching conditions to determine the conditions that yield best gold extraction after POX.

3.3.3.3 Reagents scouting

CIL/RIL tests were conducted as outlined in Section 3.3.2.2, but 2 more cyanide additions (20 kg/t and 40 kg/t) were evaluated while keeping the carbon/resin addition constant. The resin or carbon addition were evaluated by testing 2 different additions (50 (mg/mL)/L and 100 (mg/mL)/L) on the optimum cyanide addition.

3.3.3.4 Ultra-fine milling

In the plant, the flotation concentrate is subjected to ultra-fine milling before conditioning with a blinding agent. The objective of the test was to determine if this unit is still required if the sample is treated in an autoclave. The added benefit is that any iron hydroxide layer formed on gold particles could be broken down to allow the cyanide solution to come into contact with gold particles. The POX residue was milled to 100%-38 µm in a ball mill and was leached using best conditions as established in Section 3.3.3.3.

3.3.3.5 Addition of a blinding agent

A sub sample of the POX residue weighing 200 g was slurried to 33% using RWB water in a bottle while diesel was added at a dosage of 16 mL/L and the bottle was rolled for 2 hrs prior to RIL (resin addition to be determined in 3.3.3.3). The blinding agent is believed to be effective in de-activating the carbonaceous constituent of the double refractory ores.

3.3.3.6 High temperature leaching

High temperature is known to improve dissolution kinetics but the limit is 60ºC because of the poor dissolution of oxygen at higher temperatures. The reason for conducting this test was to subject the POX residue to extreme conditions in order to give all soluble gold particles a chance to dissolve in the cyanide solution. The normal CIL/RIL was conducted using best conditions established but at 60ºC.

CHAPTER 4 : RESULTS AND DISCUSSION

4.1 Sample characterization

4.1.1 Chemical head analysis

The chemical composition of the concentrate is given in Table 4.1. Six gold assays were conducted to determine the grade of the sample. The gold grade varied between 56.3 and 59 g/t, and the average grade of concentrate was 57.6 g/t. The sample also contained 59.1 g of silver/ ton of ore. The presence of silver could indicate the presence of silver minerals in the sample such as Argentite (Ag_2S) or that the gold in the sample existed as an Au-Ag alloy (electrum). In the Barberton area it is very common to find electrum gold (Anhaeusser, 1966) (Argapadmi, et al., 2018).The presence of silver in the alloy will only have a significant impact on gold processing if the Ag-Au ratio >10:1 (Marsden & House, 2006). In the case of the sample, the Ag-Au ratio is ~1:1.

Fe, S and C were the predominant elements in the sample and the total C and total S content were found to be 14.9% and 17.3%, respectively. Arsenic was also detected in the sample, with a concentration of 1.46%. From these results, it can be concluded that the sample contained a high concentration of iron sulphide minerals and further has a high preg-robbing potential. The presence of sulphide minerals can be detrimental to gold extraction because of likely encapsulation of gold particles within the sulphide matrix, competition with gold for free cyanide and formation of a passivating sulphide layer on gold particles.

Table 4.1. Head chemical analysis

Analyte	Flotation concentrate
Au_1, g/t	56.3
Au_2, g/t	56.0
Au_3, g/t	58.0
Au_4, g/t	59.0
Au_5, g/t	57.3
Au_6, g/t	59.0
Average Au, g/t	**57.6**
Ag, g/t	59.1
S^{2-}, %	15.1
S combustion,%	17.3
C combustion, %	14.9
Organic C,%	13.1
Fe,%	20.6
Si,%	10.8
Zn,%	2.04
As,%	1.46

Mineralogical analysis

4.1.1.1 Bulk Mineral analysis (BMA)

The relative proportions of all minerals present in the concentrate as determined by the QEMSCAN bulk mineral analysis (BMA) measurement method are presented in Table 4.4. The major minerals present were found to be pyrite and silicate minerals. Pyrrhotite was present in minor concentrations. Pyrrhotite, arsenopyrite, galena, sphalerite and chalcopyrite were present in concentrations less than 5.4%. Pyrrhotite readily dissolves in aerated alkaline cyanide solutions resulting in the formation thiocyanates, ferrocyanides, polythionates and sulphates which may negatively affect gold extraction (Nicol, et al., 1987).

The mineralogy results correlate with head chemical analysis of the concentrate which identified Fe, S and Si as the major elements.

Table 4.2. BMA – flotation concentrate

Mineral	Ideal formula	Flotation concentrate (Mass %)
Pyrite	FeS_2	23.96
Pyrrhotite	Fe_7S_8	6.62
Arsenopyrite	FeAsS	2.20
Chalcopyrite	$CuFeS_2$	3.53
Galena	PbS	1.77
Sphalerite	ZnS	4.06
Other Sulphides		0.17
Quartz	SiO_2	18.86
Feldspar	$(Ca,Na)Al_2Si_2O_8$	5.24
Garnet		1.83
Chlorite	$Mg,Fe,Al)_6\ (Si,Al)_4O_{10}(OH)_8$	14.57
Muscovite	$KAl_2(Si,Al)_4O_{10}(OH)_2$	1.81
Pyrophyllite	Al2(Si4O10)(OH)2	3.20
Amphibole	$(Ca,Mg,Fe^{2+})(SiO_2)OH$	1.05
Pyroxene	$MgSiO_3$	0.77
Talc		0.12
Kaolinite		0.47
Fe Oxide	Fe_2O_3, Fe_3O_4	5.11
Fe Sulphate		<0.01
Calcite		1.22
Dolomite/Ankerite	$CaMg(CO_3)_2$	3.10
Other		0.36
Total		**100.00**

4.1.1.2 Au mineral characterisation

The Au modal distribution results are reported in Figure 4.1. The majority of the Au in the concentrate was found to be electrum (93.2 mass %). These results correlated with the chemical head analysis results where the sample was found to contain silver at a mass ratio (Au-Ag) of ~1:1. Electrum gold is an alloy of gold with the silver content ranging between 25% and 55% (Cohn & Stern, 1979). Generally, electrum gold behaves similar to native gold except that sodium cyanide consumption might be slightly higher due to competing Ag species and a higher carbon inventory may be required. Electrum gold dissolution kinetics may be slightly slower than for native gold.

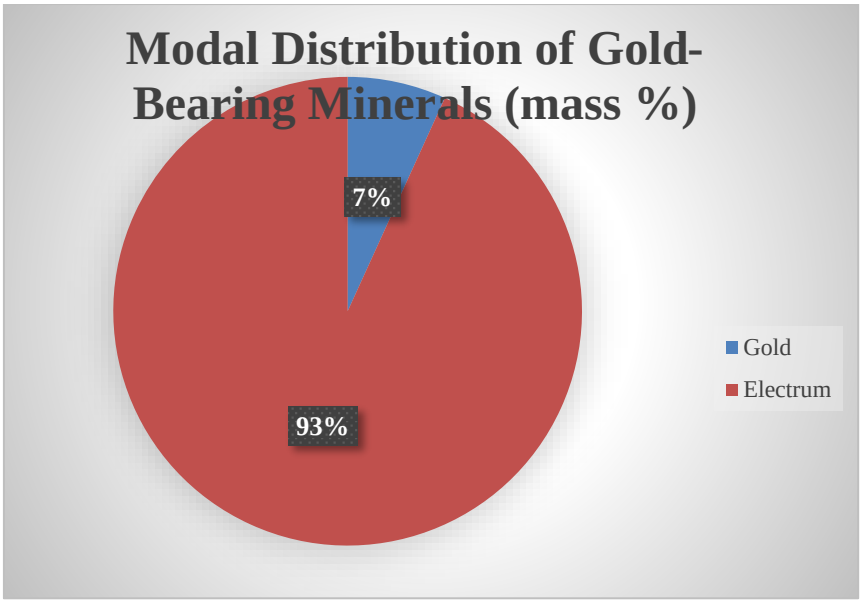

Figure 4.1: Au modal distribution, head sample

All the gold grains detected were smaller than 24 µm ECD (Table 4.5). No native gold grains larger than 8 µm ECD were detected. Electrum was coarser than gold, with grains up to 24 µm ECD detected. For small gold grains, dissolution kinetics are faster.

Table 4.3. Au bearing mineral grain size distribution-head sample

Au-bearing Mineral Grain Size Distribution (vol %)			
Size Class (µm ECD)	**Gold**	**Electrum**	**All Au Minerals**
0 - 4	31.1	6.3	7.7
4 - 8	68.9	26.4	28.7
8 - 12	-	9.5	9.0
12 - 16	-	26.4	24.9
16 - 20	-	19.8	18.7
20 - 24	-	11.7	11.0
Total	**100.0**	**100.0**	**100.0**

The mineral association results for the concentrate are shown in Table 4.4. Association is determined by calculating the percentage of gold bearing minerals (by area) either attached to or locked in a particular gangue mineral. Only approximately 25% of the gold in the sample was not attached or associated with any mineral while ~ 24% was associated with silicate minerals. More than 50% of the gold bearing grains were associated with sulphide minerals.

Table 4.4. Au mineral association-head sample

Au-bearing Mineral Association (%)		
Mineral	**Gold**	**Electrum**
Pyrite	17.3	47.5
Pyrrhotite	39.2	3.5
Arsenopyrite	1.4	0.6
Chalcopyrite	1.6	0.0
Quartz	0.0	4.7
Chlorite	0.0	4.8
Ankerite	13.7	14.0
Liberated	26.9	24.8
Total	**100.0**	**100.0**

The gold bearing mineral mode of occurrence results are shown Table 4.5. The results indicated that 50.5% of the total gold bearing grains (electrum and native grains) were locked in other minerals and cannot be recovered by cyanidation without partial or complete breakdown of the matrix of the host minerals.

Table 4.5. Gold bearing mineral mode of occurrence-head sample

Au-bearing Mineral Mode of Occurrence (%)		
Occurrence	**Gold**	**Electrum**
Liberated	26.9	24.8
Attached	5.9	25.7
Locked	67.2	49.5
Total	**100.0**	**100.0**

4.1.2 Raman spectroscopy analysis

Figure 4.2 shows a Raman spectrum of the flotation concentrate. The spectra showed pronounced D(1320 cm^{-1}) and G(1612 cm^{-1}) bands. The D and G-bands are characteristic for graphitic materials. The D-band emanates from the defects/disorder of the Sp^2 graphitic carbon while the G-band results from Sp^2 hybridized graphitic carbon. A well-ordered graphitic material will have a high G band intensity and low D band intensity. The activated carbon has a similar structure to graphite but is less well-ordered (Marsden & House, 2006) and will have a G-band with a lower Raman intensity (Helm, et al., 2009) and a higher intensity D band. The carbonaceous matter (CM) in the sample therefore, had a similar pattern to that of granulated activated carbon used during leaching indicating that it had a fairly high absorption capacity for the aurocyanide complex.

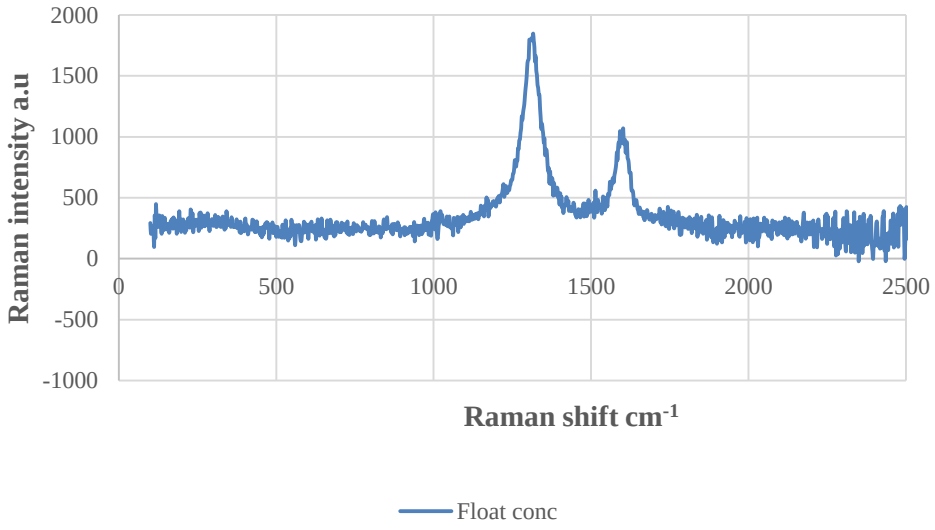

Figure 4.2 Raman spectrum of the Babrook Mine samples

4.1.3 Preg-robbing effect of carbonaceous matter in the sample

The PEC indicates the preg-robbing capacity of the CM in the ore. This is determined by contacting the sample that is being analysed (10 g) with a 25 mL cyanide gold solution of 15 mg/L Au strength for 24 hrs. The solution is then analysed to determine the final gold concentration. The PEC results shown in Table 4.6 indicated that the flotation concentrate was highly preg-robbing according to classification prescribed in Table 4.6**.** The amount of gold preg-robbed was calculated by using the formula below:

$$\%\, preg\ robbed = \{\frac{[Au\ (initial,solution) - Au(final\ solution)]}{Au(initial,solution)}\} \times 100 \ldots\ldots\ldots\ldots \text{Eqxn 4.1}$$

86.4% of gold was preg-robbed by CM in the sample from solution, indicating a high preg-robbing capacity**.** This correlates with the findings of the Raman spectroscopy which indicated that the CM in the sample has similar spectra to that of activated carbon.

Table 4.6. Preg-robbing effect of carbon

Sample ID	Solution volume (mL)	Mass of ore (g)	Initial Au (mg/L)	Final Au (mg/L)	Gold Preg-robbed,%	PEC (g of gold/tonne of ore)
Flotation concentrate	25	10	15	2.04	86.4	32.4

4.2 Base line cyanidation tests

Direct cyanidation with a 10 kg/t NaCN addition resulted in low gold extraction of 13%. As expected, the addition of an adsorbent (activated carbon (25 g/L) and gold selective resin (25mL/L) during cyanidation improved gold extraction, but was still low with 46.4% and 21.1% gold extraction obtained for the CIL and RIL options, respectively. Gold concentration on activated carbon and resin was 975 mg/kg and 1525 mg/kg, respectively. The poor performance of the RIL option could be due to the formation of thiocyanates and polythionates from dissolution of sulphide minerals in the sample during cyanidation. When present in high concentrations, these species can compete with gold cyanide for adsorption sites on the resin (Yahorava & Bazhko, 2018), depressing the resin loading capacity. The chemical composition of filtrates from the tests are given in *Table 4.7*. The concentration of sulphur species in the RIL filtrate was significantly lower than that of direct CN and CIL. This proves that sulphur species adsorbed onto the ion exchange resin. Further investigation will have to be conducted to determine the nature of the sulphur species that adsorbed onto the resin. The concentration of other base metals such as Zn, Ni and Cu were also lower when an adsorbent was added during leaching which implies base metals loaded onto carbon/resin although Au selectivity for both was greater than base metals selectivity. The baseline tests results correlated with the mineralogy results (Table 4.5) which indicated that more than 50% gold was locked in other minerals.

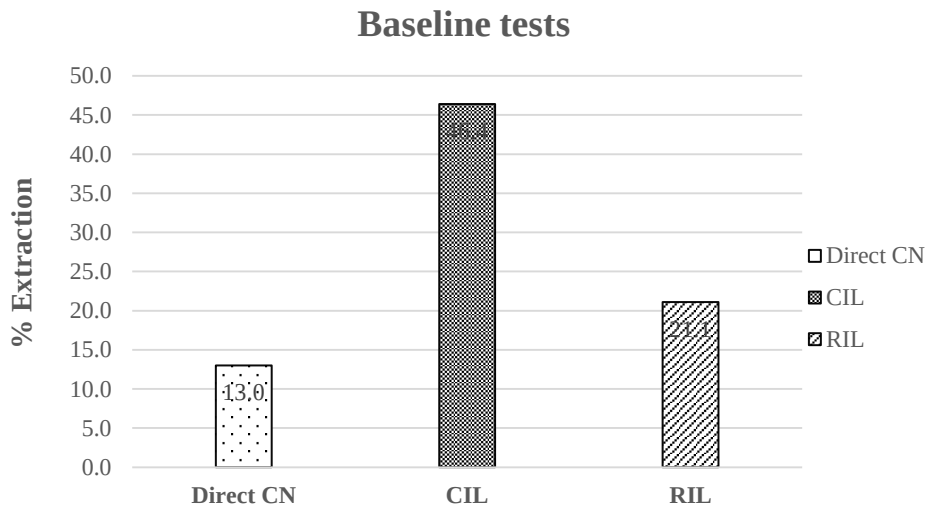

Figure 4.3. Gold extraction, baseline tests, 25 mL/L resin, 10 kg/t NaCN and 33% solids

Table 4.7. Chemical composition of the filtrates of baseline tests

Analyte (mg/L)	Direct CN	CIL	RIL
Ca	1210	980	1110
Cu	1290	1010	950
Ni	21	21	18
S	1070	1090	650
Zn	1040	1040	970

4.3 Pressure oxidation

4.3.1 Sample characterization

4.3.1.1 Chemical analysis of the POX residue

On average, a sulphide oxidation extent of 97% was obtained during POX (Table 4.8). The cured residue generated had a sulphate content of 3.5% and an iron content of 25.3%, which clearly indicated that the bulk of the iron in the oxidised cured residue was not associated with sulphates i.e., iron oxides were produced.

Table 4.8. POX and curing

Feed Composition		
Au	g/t	57.9
Ag	g/t	59.1
Total S	%	16.83
Fe	%	20.68
Organic C	%	13.1
Main Results POX and curing		
Slurry pH after POX-cure	-	0.48
Slurry Eh after POX-cure (Ag/AgCl reference electrode)	mV	505.62
Sulphide oxidation	%	96.84
Mass loss	%	21.88
Acid concentration in filtrate	g/L	33.88
Acid production	kg/t	273.37
Chemical Composition of Residue		
Ag	g/t	70.0
Au	g/t	66.8
Fe	%	25.3
Sulphide S	%	0.73
Elemental S	%	<0.01
Sulphate S	%	3.50
Organic C	%	17.8
Accountability		
Ag	%	96
Si	%	90
Fe	%	96
Total S	%	94
Organic C	%	94
Overall Au accountability (pre-acidification, POX and curing)	**%**	**90**

4.3.1.2 Mineralogical analysis of the POX residue

The BMA of the POX residue shown in Table 4.9, indicated complete oxidation of all sulphide minerals except pyrrhotite with 60% oxidation. The incomplete oxidation of pyrrhotite is unexpected as pyrrhotite oxidizes more readily than pyrite. One of the reasons for incomplete oxidation of pyrrhotite that has been reported before is due to the formation of an impervious layer of elemental sulphur on the unreacted surface of pyrrhotite (shrinking core model) as per reaction below:

$$Fe_{(1-x)}S + (2 - 2x)Fe^{3+} = (3- 3x)Fe^{2+} + S^{0} \quad \text{……Eqxn 4.2}$$

Pyrrhotite oxidizes according to the reaction above at temperatures below the melting point of sulphur, 180ºC (Marsden & House, 2006). The temperatures under which the pressure reactor was operated was 210ºC and it is expected that all elemental sulphur formed during the heating

up of the slurry to the operating temperature would have been dissolved. Furthermore, based on the chemical composition of the POX residue, there is no evidence to support the presence of elemental sulphur. The presence of pyrrhotite in the POX residue will have to be confirmed by repeating the analysis and further investigation on the mechanism of pyrrhotite oxidation will have to be conducted under a different study. The presence of pyrrhotite is undesirable during cyanidation.

The majority of iron sulphide minerals were converted to Fe oxide minerals and only a small portion was converted to Fe-sulphate minerals. This confirms that the hot curing conducted after pressure oxidation was effective. Fe oxide minerals, specifically hematite, is the desired POX product for downstream processing. Majority of silicate minerals dissolved during POX except quartz. All the silicate minerals which dissolved are known to susceptible to chemical weathering which is exacerbated by high temperatures. Quartz is the most stable silicate mineral.

Table 4.9. BMA- POX residues

Mineral	**Flotation concentrate**	**POX Residue**
	(Mass %)	**(Mass %)**
Pyrite	23.96	0.02
Pyrrhotite	6.62	2.65
Arsenopyrite	2.20	0.05
Chalcopyrite	3.53	0.12
Galena	1.77	0.19
Sphalerite	4.06	<0.01
Other Sulphides	0.17	0.05
Quartz	18.86	26.97
Feldspar	5.24	2.22
Garnet	1.83	1.07
Chlorite	14.57	1.95
Muscovite	1.81	1.24
Pyrophyllite	3.20	1.04
Amphibole	1.05	0.01
Pyroxene	0.77	1.01
Talc	0.12	0.06
Kaolinite	0.47	0.32
Fe Oxide	5.11	57.23
Fe Sulphate	<0.01	3.05
Calcite	1.22	0.01
Dolomite/Ankerite	3.10	0.30
Other	0.36	0.43
Total	100.00	100.00

The minerals association analysis (Table 4.10) indicated an increase in the quantity of liberated gold bearing grains (from 24.8% to 46.3% for electrum grains) coupled with the decrease in the quantity of gold bearing grains associated with sulphide minerals. This indicates that gold that had been locked in sulphide minerals was liberated and available for recovery via cyanidation.

Table 4.10. Au bearing mineral association-POX residues

Au-bearing Mineral Association (%)		
Mineral	**Gold**	**Electrum**
Pyrrhotite	6.8	7.8
Quartz	0.0	3.6
Fe-Oxide	25.1	42.3
Chlorite	43.8	0.0
Liberated	24.2	46.3
Total	100.0	100.0

Mineral liberation is defined as the percentage of its surface (seen as the perimeter in 2D) that is exposed, i.e. the surface is not shared with that of another mineral. Particles are categorised into different classes, as illustrated in the diagram below (Figure 4.4). Au mineral association data (*Table 4.4*Table 4.10) is related to liberation data (Table 4.11) as the former gives information about minerals in which gold particles are locked or are attached to.

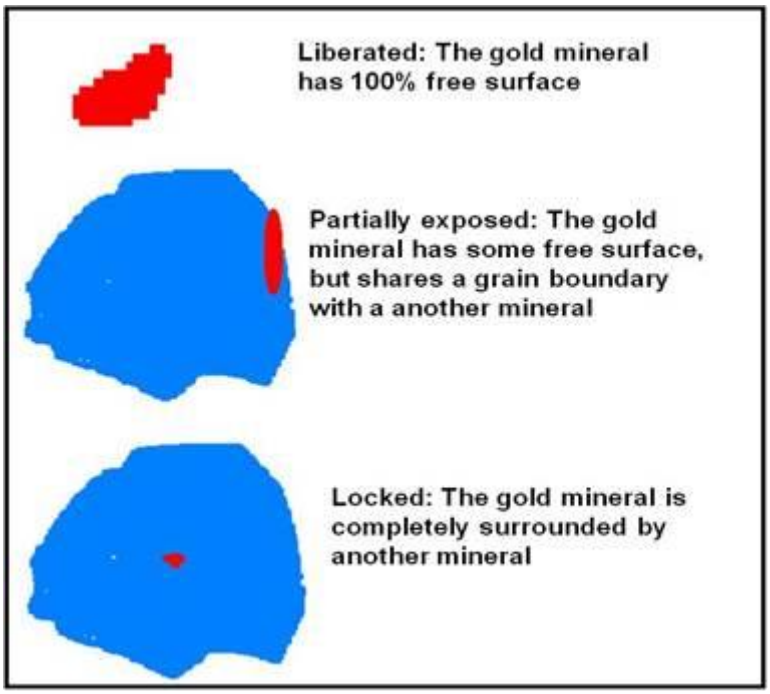

Figure 4.4. Liberation illustration

Only 6.6% of the electrum gold bearing grains was locked within other minerals (Table 4.11). Based on the results in Table 4.11 , 93% of total gold (both electrum and native) in the sample could potentially be extracted from the sample provided that favourable leaching conditions are used.

Table 4.11. Au-bearing mineral mode of occurrence-POX

Occurrence	Gold	Electrum
Liberated	24.2	46.3
Attached	61.3	47.1
Locked	14.5	6.6
Total	**100.0**	**100.0**

4.3.1.3 Raman spectroscopy

A Raman spectra of the POX is shown in *Figure 4.5*. Similarly, to the flotation concentrate, the CM in the POX residue exhibited characteristics of a highly disordered graphitic carbon. The spectra below do not show any changes in the characteristics of the CM in the POX sample in relation to the flotation concentrate. A study conducted by Dimov & Hart, (2017) concluded that there is a good correlation between the increasing preg-robbing capacity and decreasing order in the carbon structure. In order to compare the defects on the flotation concentrate and on the POX residue, a Raman intensity ratio (I_D/I_G) was calculated from each spectra. The higher the ratio, the higher the defects/disorder. The Raman intensity ratio (calculated from the peaks) for the flotation concentrate and the POX residue were 1.73 and 1.80 respectively. There was a small increase in the structural disorder of the CM in the POX residue, which could imply worsening of the preg-robbing effect.

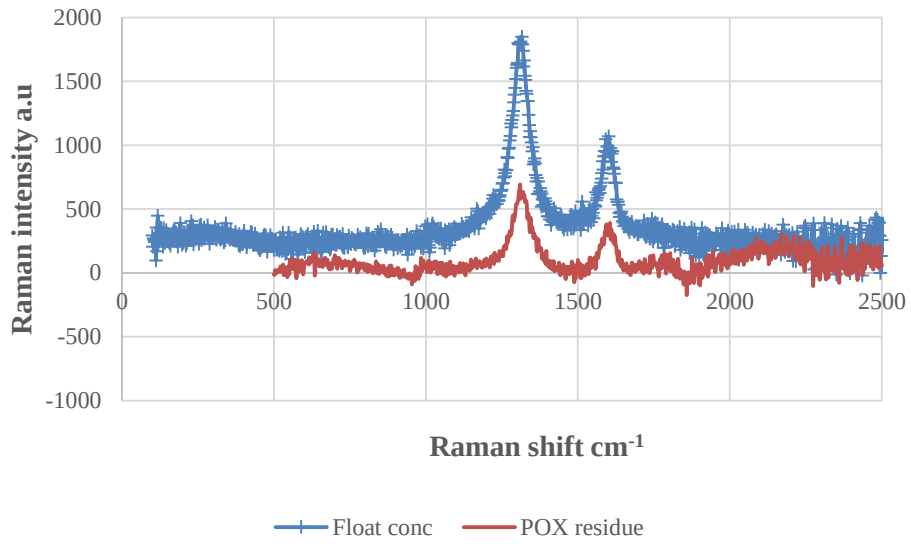

Figure 4.5. Raman spectra of the float concentrate and the POX residue

4.3.1.4 PEC of POX residue

The PEC results shown in Table 4.12 indicated that the POX residue was highly preg-robbing and had a higher PEC than the concentrate. This indicates that the graphitic carbon in the sample was further activated in the autoclave. This also confirms the Raman spectroscopy findings which showed a slight increase in disorder after POX.

Table 4.12. Preg-robbing effect of carbon in POX residue

Sample ID	Solution volume (mL)	Mass of ore (g)	Initial Au (mg/L)	Final Au (mg/L)	Gold Preg-robbed,%	PEC (g of gold/tonne of ore)
Flotation concentrate	25	10	15	<0.08	>99.5	37.3

4.3.2 Cyanidation of POX residues

Gold extraction via direct CN, CIL and RIL on the POX residue is shown in Figure 4.6. The results indicated that gold extraction from POX residue via direct CN and CIL was low compared to baseline tests. Due to the increased preg-robbing capacity of the CM in the POX residue, the efficiency of carbon as an adsorbent was relatively poor. Higher gold extraction was achieved by RIL of the POX residue compared to the baseline RIL (49.2% vs 21.1%). Ion exchange resin is generally a stronger adsorbent than activated carbon and the oxidation of sulphides improved the efficiency of resin as the concentration of thiocyanates and polythionates species competing with gold for adsorption sites was low. The gold extraction

by RIL correlates to the mineralogy results which indicated that 46% of gold in the POX residue is liberated and 42% associated with Fe-Oxides. The difference in gold extraction by RIL-POX (which yielded the highest extraction) and CIL (on the flotation concentrate) was only 2.8% but scouting tests were conducted on POX residue+ RIL because of the following reasons:

- According to mineralogical analysis of the flotation concentrate (Table 4.5), ~50% gold was locked in sulphide and silicate minerals and all the liberated gold was recovered by CIL (Figure 4.3). To increase gold extraction, a process for breaking down the sulphide matrix will still be required to liberate locked gold. The conventional approach has always been of apply chemical processes (roasting, bacterial or pressure) but lately there has been an insurgence in the use of physical processes (ultra-fine milling) to break down the sulphide matrix. According to the mineralogical analysis only 6% gold was locked after POX (Table 4.11)
- The plant currently uses RIL so changing the adsorbent will have cost implications

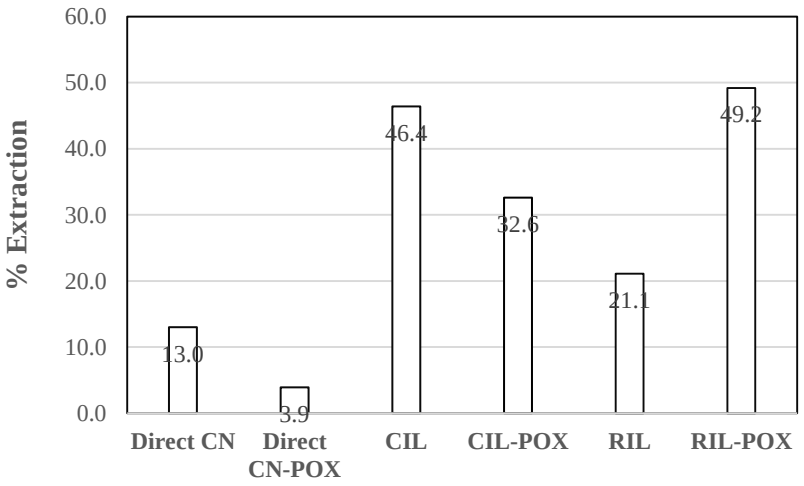

Figure 4.6.Gold extraction from POX residue vs baseline

4.4 Scouting tests

4.4.1 The effect of NaCN addition

Increasing sodium cyanide addition from 10 kg/t to 20 kg/t increased gold extraction from 49.2% to 65% (Figure 4.7). Increasing sodium cyanide addition further (40 kg/t) only increased gold extraction by as further 3%. From these results, it can be concluded that a sodium cyanide addition of 10 kg/t was not sufficient for gold recovery but increasing the addition from 20 kg/t

to 40 kg/t did not have a significant impact. The latter could be due to at least one of the following reasons:

- The maximum amount of gold that can be extracted using RIL had been reached
- The maximum loading capacity of resin under these conditions had been reached, resulting in slow adsorption kinetics (low competitiveness with CM in the ore) with some of the gold in solution preg-robbed by CM. To evaluate this, different resin to solution ratios were tested (see Section 4.4.2).

It was therefore decided that a sodium addition of 20 kg/t will be used for further scouting tests.

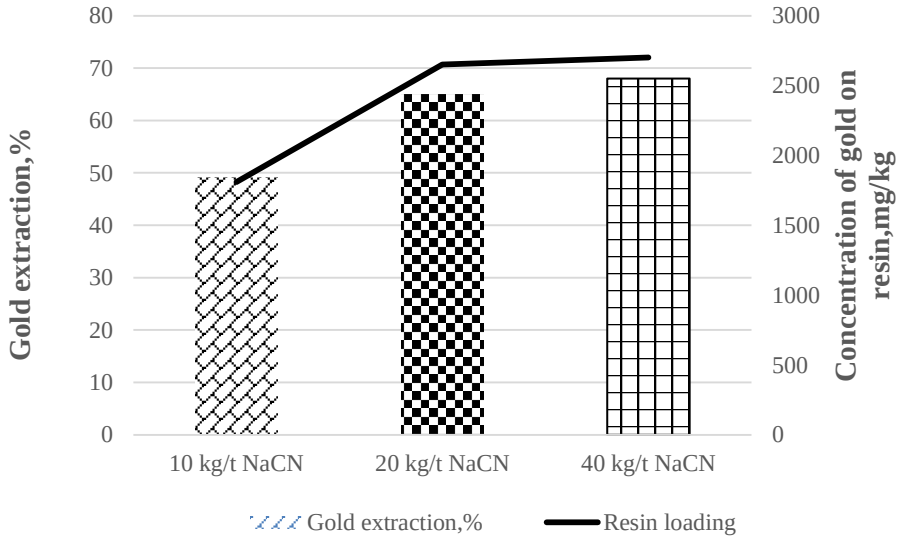

Figure 4.7. The effect of NaCN on gold extraction. RIL tests conducted at different NaCN additions, 25 mg/L Minx resin addition, 33(w/w)% solids

4.4.2 The effect of resin concentration

The results for the tests where the effect of resin concentration on gold extraction was evaluated are given in *Figure 4.8*. It is clear that increasing resin concentration had a positive impact on gold extraction. Gold extraction increased by 5% (from 65% to 70%) when the resin concentration was increased to 50 mL/L. This shows that 25 mL of resin /L of slurry was not sufficient to overcome PEC in the POX residue. Although, a resin concentration of 100 mL/L resulted in the highest extraction (72%), the low gold concentration on resin indicate that the

resin concentration was in excess. Subsequent tests were conducted on resin concentration of 50 mL/L.

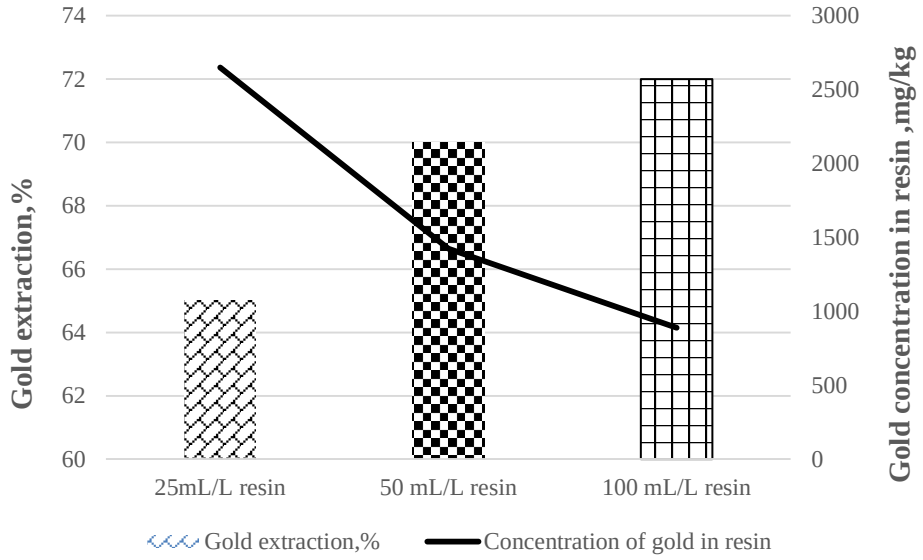

Figure 4.8. The effect of resin concentration. RIL tests conducted at 20 kg/t NaCN addition and different resin concentration

4.4.3 Ultra-fine milling

The effect of ultra-fine milling was evaluated because ultra-fine milling is known to break down host minerals resulting in liberation of gold particles. The particle size distribution of the sample before ultra-fine milling is shown in Figure 4.9. The concentrate was fairly fine with ~80% of the particles in the sample passing a 75 µm screen and gold was evenly distributed within the different size classes.

Milling the sample did not improve gold extraction (Table 4.13). This implies that the locked gold was not liberated suggesting that the gold that was not recovered could have been sub microscopic.

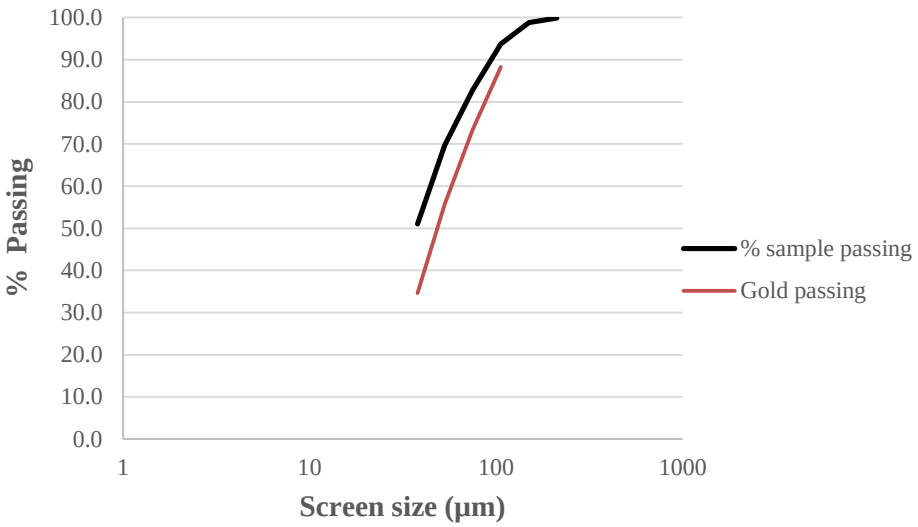

Figure 4.9. PSD and PSA of the concentrate before ultra-fine milling

Table 4.13. The effect of ultra-fine milling on gold extraction (tests conducted using similar leaching conditions but different grind sizes)

Test ID	Head grade, g/t	Residue, g/t	Loaded resin. g/t	% Extraction	% Au accountability
50 mL/L resin, 20 kg/t NaCN	66.8	20.0	1423	70.0	93.9
Ultra-fine milled	66.8	21.2	1350	68.3	95.6

4.4.4 The effect of blinding agent and temperature

The effect of temperature and blinding agent on gold extraction was evaluated and the results are shown in Table 4.14. The results indicated that increasing temperature during leaching did not affect gold extraction but conditioning the POX residue with a blinding agent yielded the highest gold extraction (82% gold extraction). This implies that increasing resin concentration (Section 4.4.2) did not completely negate the preg-robbing effect of CM in the POX residue. The grade of the residue of the test with the highest gold extraction was still high (12 g/t). Further optimization can be conducted to further reduce the residual grade. It can be concluded that the POX can be used to treat double refractory ore but only in conjunction with conditioning in a blinding agent for higher extraction efficiencies

Table 4.14. The effect of temperature and blinding agent

Test ID	Head grade, g/t	Residue, g/t	Loaded resin. g/t	% Extraction	% Au accountability
50 mL/L resin, 20 kg/t NaCN	66.8	20.0	1423	70.0	93.9
High temperature, 60ºC	66.8	19.5	1400	68.3	92.1
Blinding agent, 16 mL/L	66.8	12.0	1625	82.0	90.9

CHAPTER 5 : CONCLUSIONS AND RECOMMENDATIONS

The key to determine if pressure oxidation could be used to improve gold recovery from the double refractory ore tested was to first characterize the raw sample and to further assess the characteristics of the sample after being subjected to pressure oxidation.

The flotation concentrate contained 57.6 g/t Au, 59.1 g/t Ag, 13.1% organic C, 15.1% sulphide S and 20% Fe. From the chemical analysis of the sample, it could be deduced that the sample was refractory and preg-robbing. The presence of silver indicated that gold bearing grains in the sample were electrum which was confirmed by the mineralogical investigation. All gold bearing grains were <24 µm, favoring faster dissolution kinetics when exposed to a suitable lixiviant. At least 50% of gold in the sample was associated with sulphide minerals and only approximately 25% was liberated while the other 25% was attached to other minerals. Raman and PEC results confirmed that the carbonaceous material in the sample was of highly disordered graphitic nature.

Treating the sample in a pressure reactor resulted in 97% sulphide S oxidation, liberating 50% of gold in the sample, with only 6% locked in other minerals and 44% attached to other minerals. However, the PEC and Raman spectroscopy results showed an increase in the preg-robbing effect of the CM in the sample. As a result of increased PEC in the CM in the sample, gold extraction was lower for both direct cyanidation (3.9% vs 13%) and CIL (32.6% vs 46.4%) compared to the baseline tests. There was an improvement (49.2% vs 21.1%) in gold extraction from the RIL test conducted on the POX residue compared to baseline. Poor efficiencies by RIL of the flotation concentrate although resins are a stronger adsorbent than carbon, were believed to be due to preferential loading of the sulphur species resulting from the dissolution of highly reactive sulphides. This caused some of the dissolved gold to load on to the CM in the sample. Oxidation of sulphides in a pressure reactor improved RIL efficiency as there were no sulphur species competing with gold for active sites on resins.

Gold extraction was still low after POX. Leach parameters were then adjusted in an attempt to find conditions suitable for improved gold extraction. Increasing NaCN from 10 to 20 kg/t addition in RIL increased gold extraction by 15%. There was no evidence to support that increasing the NaCN higher than 20 kg/t could improve gold extraction. The additional gold extracted could have been the gold that was attached to the pyrrhotite component or Fe-O minerals.

Increasing resins addition from 25 mg/L to 50 mg/L improved gold extraction at 20 kg/t NaCN addition by an additional 5% (70% vs 65%). Increasing addition to 100 mg/L only resulted in 2% increase in gold extraction. The improvement in gold extraction when resins addition is increased indicated that the PEC of the CM in the sample was not completely negated.

Blinding the CM in the sample by conditioning in l6 mL of diesel/L of slurry prior to RIL at 20 kg/t NaCN and 50 mL/L resins resulted in the highest gold extraction (82%). However, milling the sample finer did not have any positive effect on gold extraction. These results indicates the great extent to which the CM in the sample affected gold extraction.

It can be concluded that POX can be used to treat this double refractory ore but in conjunction with treating the sample with a blinding agent prior to RIL using intensive conditions (high NaCN and 50 mL/L resin). The grade of the residue for the test which gave best gold extraction was still high (12 g/t). Although there is no specific maximum cut-off (economic) grade in residues for disposal, a typical grade of calcine dumps from Barberton, with a similar composition to the POX residue ranges from 2 g/t to 10 g/t. The high residue of 12 g/t indicates that there is still a room for optimization of the process for higher gold extraction.

Recommendations and future work

It is recommended that a further study be conducted to determine the gold deportment in the residue of the test which resulted in the 82% extraction. This can assist in devising ways of further improving gold extraction. The mechanism for pyrrhotite oxidation needs to be investigated in order to find the cause for its lower oxidation compared to other sulphide minerals. An economic evaluation will have to be conducted to determine if the use of POX is economically feasible.

CHAPTER 6 REFERENCES

Adams, M. D., 2005. *Gold ore processing: Project Development and Operations, pg 97.* Singapore: Elsevier.

Adamson, R., 1973. *Gold metallurgy in South Africa.* Johannesburg: Chamber of Mines.

Adan, K., Stefananas, M. & Kontopoulos, A., 1989. Biotechnology in Mineral&Metallurgical processing. *SME,* pp. 131-138.

Afidenyo, J. K., 2008. *Microbial pre-treatment of double refractory gold ores,* Ontario: Queen's University.

Aghamirian, M., 1997. *Reactivity of Sulfide minerals and its Effect on Gold dissolution and its electrochemical behaviour in cyanide solution,* Ontario: Queen's University.

Amankwaha, R., Yena, W. & Ramsay, R., 2005. A two stage bacterial treatment process for double refractory ores. *Minerals Engineering Volume 16, Issue 1,* pp. 103-108.

Amwele, M. & Groot, D., 2018. Test work to examine the potential for improving gold leaching performance at Navachab Gold Mine, Namibia. *SAIMM,* 118(5).

Anhaeusser, C., 1966. *Supergene gold enrichment in the Barberton mountain land with particular reference to LiLY Mine,* Johannesburg: University of the Witwatersrand.

Applied Geology Services cc, 2004. *Independent qualified person's report barbrook mines limited, Mpumalanga province, South Africa,* Barberton: Caledonia Mining.

Argall, G., 1989. Perseverance and winning ways at McLaughlin Gold. *Engineering and Mining 10,* pp. 26-32.

Argapadmi, W. et al., 2018. Silver Isotopes as a Source and Transport Tracer for Gold: A Reconnaissance Study at the Sheba and New Consort Gold Mines in the Barberton Greenstone Belt, Kaapvaal Craton, South Africa. *Economic geology,* 113(7), pp. 1553-1570.

Asamoah, R., Amankwah, R. & Addai-Mensah, J., 2014. *Cyanidation of Refractory Gold Ores: A Review.* Tarkwa, Ghana, s.n., pp. 204-212.

Aylmore, M., 2016. Alternative Lixiviants to Cyanide for Leaching Gold Ores. In: M. Adams, ed. *Gold ore processing.* Singapore: Elsevier, pp. 447-484.

Baron, J., Choi, Y. & Jeffrey, M., 2016. Double refractory carbonaceous sulfidic gold ores. In: M. Adams, ed. *Gold ore processing.* s.l.:Elsevier, pp. 909-918.

Birak, D. & Deter, K., 1987. Changes in the Jerrit Canyon metallurgical process as a result of geological characteristics of the ore. *Proceedings of International Symposium on Gold metallurgy,* pp. 135-140.

Caledonia mining corporation, 2007. *Caledonia mining.* [Online]
Available at: https://www.caledoniamining.com
[Accessed 02 November 2019].

Cohn, J. & Stern, E., 1979. Gold and Gold compounds. In: Othmer-Kirk, ed. *Encyclopedia of Chemical Technology.* New York: Academic press.

Coleman, R., 1990. Roasting of refractory ores and concentrates. *Society for mining metallurgy and exploration,* pp. 381-388.

Craig, J., Volkes, F. & Solberg, T., 1998. Pyrite: Physical and chemical textures. *Mineralium deposita,* Volume 34, pp. 82-101.

Deng, T., 1993. Aqueous Pressure Oxidation of Minerals - A Salient Development in Hydrometallurgy. *Mineral processing and extractive metallurgy review,* 12(2-4), pp. 185-222.

Deventer, J., Wyethe, J., Kotze, M. & Shannon, J., 2000. Comparison of resin in solution and carbon in solution for the recovery of gold from clarified solutions. *SAIMM,* pp. 221-228.

Devilliers, J., 1957. The mineralogy of the Barberton gold deposits. 24(60 pp).

Dimov, S. & Hart, B., 2017. *Applications of microbeam analytical techniques in gold deportment studies and characterizaion of losses during the gold recovery process,* s.l.: Wiley online library.

Ellis, S., 2005. Treatment of gold-telluride ores. In: M. Adams & B. Wills, eds. *Developments in mineral processing.* s.l.:s.n., pp. 975-984.

Elsner, L., 1846. *Observations on behavious of reguline metals in an aqueous solution of potassium cyanide,* s.l.: s.n.

Evans, J., 1979. Mass transport with chemical reaction. *Minerals Science and Engineering,* 11(4), pp. 207-222.

Fernandez, R., 1996. *Refractory ore treatment plant at Newmont Gold Company.* Lima, Peru, s.n.

Ferreira, P., Knott-Craig, K. & Boydell, D., 1989. Roasting of the refractory gold concentrates at New Consort. *Mining Journal,* pp. 26-29.

Fleming, C., 2010. Basic iron sulphate-A potential killer in the processing of refractory gold concentrates by pressure oxidation.. *Minerals and Metallurgical processing,* Volume 27, pp. 81-88.

Fomenko, I. et al., 2013. *Pressure oxidation of double refractory gold concentrates.* Perth, ALTA.

Frik, E., 2019. *Mining.com.* [Online]
Available at: https://www.mining.com
[Accessed 08 September 2020].

Guay, W., 1989. How Carlin treats Gold ores by double oxidation. *World mining,* pp. 17-49.

Hackl, R., Ji, J. & West-Sells, P., 2010. *Method for Thiosulphate leaching of precious metals containing materials.* United states, Patent No. 7,722,840 B2.

Hankock, T., 2013. *MINING WEEKLY.* [Online]
Available at: https://www.miningweekly.com/article/technology-to-enhance-gold-recovery-for-double-refractory-ore-processing-2013-11-14
[Accessed 27 JULY 2020].

Helm, J., Vaughan, J., Staunton, W. & Avraamides, J., 2009. *An investigation of the carbonaceous component of preg-robbing gold ores.* Western Australia, SAIMM.

Helm, M. V. J. S. W. a. A. J., 2009. An investigation of carbonaceous component of preg-robbing gold ore. *SAIMM,* pp. 139-144.

Hiskey, J. & Atluri, V., 1988. Dissolution chemistry of gold and silver in different lixiviants. *Mineral Processing and Extractive Metallurgy Review,* Volume 4, pp. 95-134.

Hisshion, R. & Waller, C., 1984. Recovering gold with thiourea. *Mining Mag,* 3(151), pp. 237-243.

International, P., 2020. *www.polymetalinternational.com.* [Online]
Available at: https://www.polymetalinternational.com/en/assets/where-we-operate/amursk-pox-hub/
[Accessed 05 December 2020].

Kirk, D. & Foulkes, F., 1984. potentiodynamic study of metal affecting precious metal recovery from alkaline solutions. *Journal of metals,* pp. 760-769.

Kudryk, V. & Kellogg, H., 1954. Mechanism and rate controlling factors in the dissolution of gold in cyanide solutions. *Journal of metals,* pp. 541-548.

Langhans, D. et al., 1995. Bio-oxidation of asrsenic bearing refractory gold ores. *Mining engineering,* 8(1-2), pp. 147-158.

Liddell, K. & Adams, M., 2012. Kell hydrometallurgical process for extraction of platinum group metals and base metals from flotation concentrates. *SAIMM,* 112(1).

Liedtke, S., 2020. *Mining weekly.* [Online]
Available at: https://www.miningweekly.com/article/new-business-rescue-plan-proposed-as-lily-barbrook-mines-dispute-continues-2020-06-23/rep_id:3650
[Accessed 05 December 2020].

Long, H., 2000. *A fundamental study of the acidic pressure oxidation of orpiment and pyrite and high temperature,* Columbia: University of Columbia.

Marias, J., 2020. *South Africa online Pty(Ltd).* [Online]
Available at: http://southafrica.co.za/barberton-gold-rush.html
[Accessed 30 November 2020].

Marsden, J. & House, C., 2006. *The chemistry of gold extraction.* 2nd ed. Colorado: Society of mining,metallurgy and exploration Inc.

Marsden, J. & House, C., 2009. *The Chemistry of gold extraction, pg 30.* s.l.:Society for Mining, Metallurgy, and Exploration, Inc.

Mubarok, Z. & Irianto, P., 2016. Improving godl recovery from artificial preg-robbing ore by pre-treatment using blinding agent and RIL. *J.ENG.TECH.SCI,* 48(3), pp. 276-287.

Mustapha, A., Asamoah, R., Ofori-Sapong, G. & Amankwah, R., 2014. *Preg-robbing characteristics of gold ores in Ghana.* Ghana, s.n.

Nicol, M., Fleming, C. & Paul, R., 1987. The chemistry of the extraction of gold. In: G. Stanley, ed. *The extractive metallurgy of gold in south africa.* Johannesburg: SAIMM, pp. 831-905.

Nordgold, 2017. *Nordgold.* [Online]
Available at: ,http://www.nordgold.com/investors-and-media/news/nordgold-launches-hot-leach-process-at-suzdal-mine/

Oraby, E. & J.J, E., 2015. The leaching of gold,silver and their alloys in alkaline glycine-peroxide solutions and their adsorption on carbon. *Hydrometallurgy,* Volume 152, pp. 199-203.

Oraby, E., Li, H. & Eksteen, J., 2020. An Alkaline Glycine-Based Leach Process of Base and Precious Metals from Powdered Waste Printed Circuit Boards. *Waste Biomass Valor,* Volume 11, p. 3897–3909.

Orgul, S. & Atalay, S., 2002. Reaction chemistry of gold leaching in thiourea solution for a Turkish gold ore. *Elsevier Hydrometallurgy,* Issue 67, pp. 71-77.

Osseo-Assare, K., Xue, T. & Ciminelli, V., 1984. Solution chemistry of cyanide leaching systems in precious metals:Mining extraction and processing. *The metallurgical society,* pp. 173-197.

Pilgrims-rest, 2013. *Pilgrims-rest.* [Online]
Available at: https://pilgrims-rest.co.za/blog/?p=122
[Accessed 07 December 2020].

Pyke, B., Johnston, R. & & Brooks, P., 1999. Chracteristics and behaviour of carbonaceous material in refractoy gold bearing ores. *Minerals Eng,* 12(8), pp. 851-862.

Resources, P.-A., 2018. *Pan African Resources.* [Online]
Available at: https://www.panafricanresources.com/2020/04/09/gold-mining-in-barberton/
[Accessed 07 December 2020].

SA-History, 2011. *SA History.* [Online]
Available at: https://www.sahistory.org.za/article/discovery-gold-1884#:~:text=The%20first%20recorded%20discovery%20of,%2C%20near%20present%2Dday%20Roodepoort.
[Accessed 07 December 2020].

Sasaki, K. & Konadu, K., 2020. *Biotechnological Approaches to Facilitate Gold Recovery from Double Refractory Gold Ores*, s.l.: Intechopen.

Schnabel, C., 1921. *Hndbook of metallurgy.* 3rd ed. London: Macmillan.

Siearra, C. & Ramli, M., 2015. Meeting the challenge of Penjom Gold Mine's geology in the recovery of fine gold in carbonaceous ores. *Geological society of Malaysia,* Volume 61, pp. 1-9.

Simmons, G., Baughman, D., Gathje, J. & Oberg, K., 1998. Pressure oxidation problems and solutions: Treating carbonaceous gold ores containing trace amounts of chlorine (halogens). *Mining engineering,* 50(1), pp. 69-73.

Stange, W., 1999. The process design of gold leaching and carbon in pulp circuits. *The Journal of SAIMM,* pp. 13-26.

Stanley, G., 1987. *The extractive metallurgy of gold in South Africa*. Johannesburg: SAIMM.

Stats, S., 1990. *South african statistics,* s.l.: s.n.

Swash, P. M., 1988. A mineralogical investigation of refractory gold ores and their beneficiation. *SAIMM J. S. Atr. Inst. Min. Metal/., vol. 88, no. 5.*, pp. 173-188.

Wimberley, F., Jodaarn, J. & Pulles, W., 2008. *Best Practice Guideline - A2: Water Management for Mine Residue Deposits -*, Johannesburg: Department of water affairs and forestry.

Yahorava, V. & Bazhko, V., 2018. Polythionate formation during uranium recovery from sulphide flotation concentrate. *Journal of the Southern African Institute of Mining and Metallurgy*, 118(2).