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The recovery of gold from tailings material by means of an organic ligand in a gas phase

MSc Dissertation

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Submitted to

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September, 2020

DECLARATION

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

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ABSTRACT

Current research is now starting to focus on the gas phase extraction of metals using organic volatile ligands because it reduces many problems associated with the extraction of metals using conventional mineral processing methods. The tailings from the Ergo plant were used as the source of gold for the gas phase extraction process. Acetylacetone, trifluoroacetylacetone and hexafluoroacetylacetone were identified from literature as potential ligands for the gas phase extraction. However, fluorinated acetylacetone derivatives were not used in the process due to safety considerations and only acetylacetone was used for the investigations. The gas phase extraction was shown to be dependent on the reaction temperature, bed mass and flow rate of the volatile organic ligand. The extraction was shown to increase from 190^{0}C to 250^{0}C i.e. extraction percentage increased from 27.7% at 190^{0}C to 64.8% at 250^{0}C with constant ligand flow rate of 1 mL/min and 50g bed mass within a time period of 240 minutes. The extraction increased with an increase in ligand flow rate from 1 mL/min to 6 mL/min i.e. 64.8% was extracted at 1 mL/min and 78% extracted at 6mL/min at 250^{0}C and 50g bed mass within a time period of 240 minutes. The extraction percentage decreased with increasing bed mass from 30g to 70g i.e. 48.8 % was extracted for a 30g bed mass and only 24.5% of gold was extracted for a 70g bed mass at constant temperature of 210^{0}C and a constant ligand flow rate of 1 mL/min. Shrinking core reaction models were used to model the data and their fit evaluated on the experimental data. The reaction process was shown to be chemical reaction controlled. There is a need to further investigate the effect of particle size on the extraction and to find the effect of other metals within the tailings sample on the gas phase extraction process.

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TABLE OF CONTENTS

DECLARATION i
ABSTRACT ii
ACKNOWLEDGEMNTS iii
LIST OF FIGURES vi
LIST OF TABLES viii
NOMENCLATURE x
1. INTRODUCTION 1
1.1. Background 1
1.2. Problem statement 3
1.3. Research objective(s) 4
1.4. Hypothesis 5
1.5. Dissertation lay-out 5
2. Literature review 6
2.1. Extractive metallurgy and sources of low grade ores 6
2.2. Treatment of low grade ores 7
2.2.1. Hydrometallurgy 8
2.2.2. Pyrometallurgy 9
2.2.3. Electrometallurgy 10
2.3. Gold 11
2.3.1. Industrial production of gold 11
2.3.2. Problems associated with cyanide leaching 15
2.4. Emerging technologies for the extraction of metals 16
2.4.1. Uses of ligands (extractants) for metal extraction and description of the ligands to be used 16
2.4.2. Supercritical fluid extracting ligands 18
2.4.3. Gas phase extraction 18
2.5. Fluidization 22
2.5.1. Principles of fluidization 22
2.5.2. Minimum fluidizing velocity 24
2.5.3. Influence of particle size and density on fluidization 26
2.5.5. Industrial applications of fluidized bed reactors 29
2.6. Summary 31
3. EXPERIMENTAL METHODS and PROCEDURES 32
3.1. Materials 32

3.1.1. Gold ore from the dumps of the Ergo mine plant 32
3.1.2. Reagents used for the investigation 32
3.2. Experimental Set-up 33
3.3. Experimental Procedure 34
3.4. Experimental conditions 35
3.5. Analytical measurements for product 36
3.6. Liquid phase extraction of gold 37
3.6.1. Experimental method 37
4. RESULTS AND DISCUSSIONS 38
4.1. The effect of reaction temperature 38
4.2. The effect of ligand flow rate on extraction 41
4.3. The effect of bed mass 43
4.4. Kinetic model 44
4.4.1. Shrinking core model development 44
4.4.2. Modelling the extraction of gold 47
5. CONCLUSIONS and RECOMMENDATIONS 57
5.1. Conclusions 57
5.2. Recommendations 57
6. REFERENCES 59
7. APPENDICES 63
7.1. Appendix A: Properties of the tailings sample and determining the percentage of the gold extracted 63
7.1.1. Properties of the tailings sample 63
7.1.2. Extraction percentage of gold 66
7.2. Appendix B: Detailed experimental results 67
7.2.1. Effect of temperature on gas phase extraction of gold 67
7.2.2. Liquid phase extraction of gold 69
7.2.3. Effect of acetylacetone flow rate 69
7.2.4. Effect of bed mass 71
7.2.5. Reaction process model for gas phase extraction 72
7.3. Appendix C: Experimental 75
7.3.1. Start-up and operating procedure 75
7.3.2. Shut-down procedure 75

LIST OF FIGURES

Figure 2-1: Industrial process for the production of gold (Eugene & Majumdar, 2009)..... 11

Figure 2-2: β-diketone structures, (a) acetylacetone (b) trifluoroacetylacetone (c) hexafluoroacetylacetone (Urbaniak et al., 2011). 17

Figure 2-3: Flowsheet for the gas phase extraction of metals (Potgieter et al., 2006; Alimann-Lecourt et al., 2002). 20

Figure 2-4: The behaviour of the bed at various stages of fluidization (Kunii & Levenspiel, 1991). 23

Figure 2-5: Behaviour of a packed before and at minimum fluidization velocity (Kunii & Levenspiel, 1991). 24

The following derivation has been adapted from Kunii & Levenspiel (1991). 25

Figure 2-6: Pressure drop versus fluid velocity for packed and fluidized beds (Rhodes, 2008). 26

Figure 2-7: Geldart's fluidization classification of powders (Geldart, 1986). 27

Figure 3-1: Particle size distribution of the ore sample (gold tailings) 32

Figure 3-2: Experimental set-up (Olehile, 2017). 34

Figure 4-1: The effect of temperature on the extraction of gold with acetylacetone as a ligand at a flow rate of 1mL/min and a bed mass of 50 g. 40

Figure 4-2: The effect of acetylacetone flow rate on the extraction of gold at flowrates of 1, 3 and 6 ml/min in a fluidized bed reactor with a bed weight of 50g at 250 ^{0}C. 41

Figure 4-3: Effect of bed mass on the extraction of gold at a flow rate of 1 mL/min at a temperature of 210 ^{0}C and bed masses of 30, 50 and 70 g. 43

Figure 4-4: Chemical reaction control for shrinking-core model linear graphs for determining the k value. 48

Figure 4-5: Comparison of conversion predicted by chemical reaction control model with actual data obtained at 190°C. 48

Figure 4-6: Comparison of conversion predicted by chemical reaction control model with actual data obtained at 210°C. 49

Figure 4-7: Comparison of conversion predicted by chemical reaction control model with actual data obtained at 230°C 49

Figure 4-8: Comparison of conversion predicted by chemical reaction control model with actual data obtained at 250°C. 50

Figure 4-9: Arrhenius plot for chemical reaction control model of gold extraction by acetylacetone at a bed weight of 50 g and flowrate of 1 mL/min. 51

Figure 4-10: Gas diffusion control for shrinking-core model linear graphs for determining the k value. 52

Figure 4-11: Comparison of conversion predicted by gas film diffusion control model with actual data obtained at 190°C. 53

Figure 4-12: Comparison of conversion predicted by gas film diffusion control model with actual data obtained at 210°C. 53

Figure 4-13: Comparison of conversion predicted by gas film diffusion control model with actual data obtained at 230°C. 54

Figure 4-14: Comparison of conversion predicted by gas film diffusion control model with actual data obtained at 250°C 54

Figure 4-15: Arrhenius plot for gas film diffusion control model of gold extraction with acetylacetone in a fluidized bed with bed weight of 50g at a flow rate of 1ml/min. 55

LIST OF TABLES

Table 3-1: Properties of acetylacetone.....33

Table 3-2: summary of the experimental conditions used.....35

Table 4-1: Liquid-phase extraction of gold from tailings sample from Ergo mine plant at different temperatures for a period of 24 hours.....39

Table 4-2: Mass extracted for different bed weight at constant temperature of 210 ^{0}C and the ligand flow rate of 1 ml/min.....44

Table 4-3: Reaction rate constants at different temperatures under chemical reaction control for the shrinking-core model.....47

Table 4-3 shows the values of k obtained at different temperatures.....52

Table 4-4: Reaction rate constants at different temperatures under gas film diffusion control for the shrinking core model.....52

Table A-1: Chemical composition of the Ergo feed sinks and concentrate (conc)......64

Table A-2: Percentage extraction of gold at a temperature of 190°C, flow rate of 1mL/min and a bed mass of 50g.....67

Table A-3: Percentage extraction of gold at a temperature of 210°C, flow rate of 1mL/min and a bed mass of 50g.....67

Table A-4: Percentage extraction of gold at a temperature of 230°C, flow rate of 1mL/min and bed mass of 50g.....68

Table A-5: Percentage extraction of gold at a temperature of 250°C, flow rate of 1mL/min and a bed mass of 50g.....68

Table A-6: Percentage extraction for a liquid phase acetylacetone ligand at different temperatures.....69

Table A-7: Percentage extraction of gold at a temperature of 250°C, flow rate of 1mL/min and a bed mass of 50g.....69

Table A-8: Percentage extraction of gold at a temperature of 250°C, flow rate of 3mL/min and a bed mass of 50g. 70

Table A-9: Percentage extraction of gold at a temperature of 250°C, flow rate of 6mL/min and a bed mass of 50g. 70

Table A-10: Percentage extraction of gold at a temperature of 210°C, flow rate of 1mL/min and a bed mass of 30g. 71

Table A- 11: Percentage extraction of gold at a temperature of 210°C, flow rate of 1mL/min and a bed mass of 50g. 71

Table A-12: Percentage extraction of gold at a temperature of 210°C, flow rate of 1mL/min and a bed mass of 70g. 72

Table A-13: Data used to plot the graph for determining the reaction constant k for shrinking model-chemical reaction controlling. 72

Table A-14: Data used to plot the graph for determining the reaction constant k for shrinking model-gas film diffusion controlling. 73

Table A-15: Data for Arrhenius plot for shrinking model-chemical reaction controlling..... 73

Table A-16: Data for Arrhenius plot for shrinking model-gas film diffusion controlling..... 74

NOMENCLATURE

A_t – Cross-sectional area, m^2.

d_p – Diameter of a particle, μm.

E_a – Activation energy, J/mol.

g – Gravitational acceleration, m/s^2.

g_c – Conversion factor, $\frac{1\ kg.m}{N.s^2} = \frac{32\ lb.ft}{lbf.s^2} = \frac{kg.m}{kg-wt.s^2}$.

k – Reaction rate, min^{-1}.

k_0 – Pre-exponential factor in Arrhenius equation.

L_{mf} – Height of the bed at minimum fluidization, m.

ΔP_b – Pressure drop across the bed, Pa.

r – Rate of reaction.

R – Gas constant, J/mol. K.

Re – Reynold's number.

T – Reaction temperature, K.

t – Time, s.

u_0 – Superficial velocity, m/s.

u_{mf} – Velocity at minimum fluidization, m/s.

u_t- Terminal velocity, m/s.

W – Weight of the particles, g.

Greek letters

α – Fractional conversion of the reaction.

ε_{mf} – Bed voidage at minimum fluidization, %.

μ – Dynamic viscosity, Pa.s.

ρ_g – Density of the gas/fluid, kg/m^3.

ρ_s – Density of the solids, kg/m^3.

ϕ_s – Sphericity of a particle, dimensionless.

1. INTRODUCTION

1.1. Background

Durban Roodepoort Deep Limited (DRD Ltd) currently retreats old surface mine dumps around Johannesburg to recover gold. Surface gold retreatment is largely a highly mechanized operation that is significantly different from that of conventional mining (DRD Gold, 2016). Tailings material at the reclamation (dumps) site is recovered by using high-pressure water jets or front-end loaders and is fed as a slurry to the metallurgical plant for gold recovery. The mine dumps have a concentration of around 0.3 g/t of gold (Dworzanowski, 2018). The gold from the old mine dumps is recovered in the Ergo plant. Ergo plant tailings still contain some gold with a concentration of between 0.10-0.15 g/t (Dworzanowski, 2018). There is a need for a new process which can further treat the tailings since after some time the old mine dumps will be depleted and there will be new dumps from the Ergo plant tailings which still contains some gold.

Traditionally the recovering processes of metals can be classified into the following categories: pyrometallurgy, hydrometallurgy, solvent extraction and ion exchange. Several extraction processes such as solvent extraction, supercritical carbon dioxide and gas phase extraction can be considered which use ligands in their extraction. These processes can be considered because they have been used previously to extract other base and precious metals. In solvent extraction, ligands have been used for the removal of metals from solutions (Kondo et al., 1978; Moffett & Zika, 1978). Ligands were also used in supercritical fluid with CO_2 as the fluid to extract metals in solid phase (Kersch et al., 2000; Ozel et al., 2000; Takeshita et al., 2000) and the liquid phase (Galand & Wipff, 2005).Current research is now starting to focus on gas phase extraction because of the potential high yield of metal recovery that is possible, with the advantage that the extractants can continuously be regenerated and recycled. Gas phase extraction is a new technology used for the extraction of heavy metals from matrices such as low grade ore, soil sediment and industrial waste (Allimann et al., 2002). A reaction that occurs in a gas phase between a gas ligand and a metal oxide or metal sulphide can be represented by the following reaction:

$$\mathrm{Ext_{gas}} + \mathrm{M(matrix)_{solid}} \rightarrow \mathrm{M(Ext)_{gas}} + \mathrm{Matrix_{solid}} \qquad (1\text{-}1)$$

where,

$\mathrm{Ext_{gas}}$ – Extraction gas

$\mathrm{M(matrix)_{solid}}$ – Solid matrix containing the metal to be extracted

$M(Ext)_{gas}$ – Metal complex

$Matrix_{solid}$ –Unreacted solid.

Gas phase extraction of metals has been used to recover a variety of metals from different sources such aluminium from fly ash (Allimann et al., 2002), vanadium, lead, and chromium from their oxide ores (Potgieter et al., 2006), and iron from its oxide ore (Van Dyk et al., 2010). The gas phase extraction process typically uses acetylacetone, bis-(pentane-2, 4, dionato), propan-1, 2-diamine and tetra-iso-propyldithiophosphorimine (Allimann et al., 2004). They were able to extract a considerable amount of metals, i.e. 18.7%, 18.6% and 13.6% of iron, vanadium and chromium were extracted respectively at a range of temperatures within a given time. This just goes to show the process does actually work and with some improvements in the technology and some changes in the chemistry involved it can give an improved yield of metal. Potgieter et al. (2006) used a different set of temperatures and managed to extract around 60% of aluminium, iron, vanadium and chromium from their oxides. Since the process showed potential, Van Dyk et al. (2010) studied the effect of different factors that affect the process such as temperature and flowrate. Mariba (2010) successfully extracted above 80% iron from its low concentration metal oxide after 4 hours using acetylacetone. Mpana (2012) used the gas phase process to extract aluminium from fly ash from Eskom's Kendal power station using acetylacetone. The author further investigated the effect of temperature, reaction time, and the flow rate of the ligand on the gas phase process. The author found the process depends on temperature, reaction time and the flow rate of the ligand.

This project focusses on gas-phase extraction of gold in a fluidized bed. Gas-phase extraction can be considered as an alternative process which can be used to recover gold from the dumps which have a fairly low concentration compared to the ores which are directly from the mines. The extraction of gold using a gas phase extractant can be less expensive compared to the traditional hydrometallurgical processes for the extraction of gold.

This research can potentially help the industry by providing a solution to the treatment of gold from low grade dumps from the Ergo plant. The kinetics, energy, recycling and the extraction ability could be used to design a process that can be used to recover gold from a very low grade material from the plant.

1.2. Problem statement

The use of the concept of fluidization is becoming more and more popular in different kinds of industrial processes. It has been applied in mineral processing and metallurgy before (Allimann et al., 2002; Potgieter et al., 2006; Van Dyk et al., 2010). The process achieves extraction through the use of a volatile organic reagent, which reacts with the desired metal in a fluidized bed. There has been research on the extraction of various metals and the process has proved to be successful. The process also proved to be successful on low grade ores with heavy metal contaminants (Barr et al., 1985).

Can gas phase extraction be used to extract gold from Ergo plant material? DRD Gold limited currently retreats gold from old mine dumps in their plant. The retreated dumps also creates new dumps, which still have a small amount of gold in them, and these dumps can be regarded as very low grade ore. This study focusses on the extraction of gold from the ore in a gas phase process. The study will explore a volatile organic reagent acetylacetone to extract the gold and design and build a suitable lab scale extraction rig. The lab scale rig will then be used to do the gas-phase extraction experiment to understand the chemical reaction and the process in general. In addition, the study will seek to investigate the kinetics of the gas phase process.

1.3. Research objective(s)

Aim of the research is to determine if the gas phase extraction process can be used to extract sufficient amounts of gold successfully from typical gold tailings material at the Ergo plant.

The **objectives** of this study are as follows:

- Design and build a suitable gas-phase lab scale extraction rig.
- Perform the gas-phase extraction experiment to:
  - Understand the chemical reaction and the process.
  - Investigate the effect of the extraction temperature on the extraction of gold.
  - Investigate the effect of the bed weight on the extraction of gold.
  - Investigate the effect of the flow rate of the reagent on the extraction of gold.
  - Study the kinetics of the reaction.

1.4. Hypothesis

Gas phase extraction with the use of acetylacetone as a ligand can be used to extract gold in the tailings from Ergo plant. Various variables such as temperature, ligand flow rate and tailings bed weight in the fluidized bed have an effect on the extraction of gold in a gas phase extraction process. From the known effect of the different variables investigated it will be possible to develop the kinetic model of the process which can be used to predict the extraction of the metal by the ligand acetylacetone in a fluidized bed reactor.

1.5. Dissertation lay-out

This dissertation contains six chapters and they are as follows:

Chapter 1 gives the background and the motivation for the study, it also gives the problem statement and the objectives of the study. Chapter 2 is the literature review, which looks at the current practices in the extraction of gold and other metals in general together with their advantages and disadvantages, the recent work on gas phase extraction of metals. Chapter 3 presents the material and chemicals used, experimental set-up and the experimental procedures utilized to achieve the objectives of the study. Chapter 4 presents the experimental results and discussion, and the kinetic model of the gas phase extraction will be developed. Chapter 5 summarises the conclusions of the study and the recommendations for future work to be done. At the end of the dissertation a list of references and appendices are presented.

2. Literature review

This chapter starts by giving the role of extractive metallurgy and identifies the various sources of low grade ores that can be used for gas phase extraction. Then the conventional methods used to treat these low-grade ores and the problems associated with the methods are discussed. The industrial production is outlined and the problems associated with the leaching (cyanidation), which is one of the most important steps in the treatment process of gold is reviewed. In the next section previous work that used ligand extraction in processing various materials are given. Finally, the characteristics, properties, advantages and disadvantages of fluidized bed reactors are outlined.

2.1. Extractive metallurgy and sources of low grade ores

Extractive metallurgy involves the removal of valuable metals from an ore and refining the metals to get them into a purer form. In order to convert a metal oxide or sulphide to a purer metal, the ore must be reduced physically, chemically or electrolytically (Extractive Metallurgy, 2016). Grinding is the first step in the mineral processing which is used for the liberation of mineral (metal) from the ore body. Grinding creates particles which are either mostly valuable or mostly waste. Before the ore enters the processing step, pre-concentration is normally achieved through flotation techniques (Extractive Metallurgy, 2016). There can be more than one valuable metal in an ore. Tailings of the previous process may be used as a feed into another process to extract a secondary product from the original ore. The concentrate may contain more than one valuable metal, which means that the concentrate would be processed to separate the valuable metals into individual constituents.

Low grade ores as a primary source in the metallurgical refining comes from underground ore bodies which are accessed by mining them and then they undergo physical liberation processes before being refined. Recently ore bodies are increasingly being exhausted, and the new sources of low grade ores which are being discovered are becoming more important. Some of these resources are non-renewable so there is a need to recycle the available resources (Groot & Pistorius, 2008). Some of the main alternative sources of metals that have been identified include slag, scrap metals, fly ash from smelters (Allimann et al., 2002). Mine dumps have become a new source of low grade ores, and DRD Gold is extracting gold from them. Metal concentration in residues (e.g. tailings, slag and fly ash) can exceed the concentration of pure metals in natural ores, which presents an opportunity for the recovery of metals from them

(Berry et al, 2001). As of 1997, South Africa produced an estimated 468 million tons of mineral waste per annum (DWAF, 2001). Gold mining waste was estimated to account for 221 million tons or 47% of all mineral waste produced in South Africa, making it the largest single source of waste and pollution (DWAF, 2001). The USA generate between 23.3 million and 24 million metric tons per year process residues from the non-ferrous industry (copper, lead, and zinc) (Berry et al., 2002). The iron and steel industry also produce large amounts of process residues in the form of slag (Mariba, 2010).

Some of the residues have been found to contain selected metals in them included in the dust, fine particles and tailings which are produced during the beneficiation of the ore in the processes of grinding, flotation, etc. Slag waste and gas cleaning sludge also form part of the residues which contain metals in them. Fly ash is a residue which is from the coal waste produced as a result of coal combustion in a coal fired power plants and it is considered as a potential source of aluminium because it contains 48.8-31 wt% Aluminium(III) oxide in amorphous and mullite phases depending on the type of coal (Mpana, 2012). Gas cleaning sludge is a form of fine dust particles which can potentially contain metals. They are found during gas cleaning operations for example passing gas through venturi scrubbers and a hydrocylone as sludge, which can be used as a source of metals for recovery (Berry et al., 2002). It can be beneficial to use the process residues as raw materials for metal recovery because they can have a higher percentage of metals in them than in the natural ores. This can also solve the problem of disposal associated with the process residues, because after processing, lower volumes of residues are left to dispose (Mariba, 2010).

2.2. Treatment of low grade ores

Metals are technically distributed into groups of metals with significantly different physical and technological properties. Technically they can be distributed into two groups namely, iron and its alloys and non-ferrous metals (e.g. copper, lead, zinc and etc.). These metals have significant importance in the metal processing industry. Before the metals can be recovered from their ores, there are pre-concentration stages. From the mining of the ore, large pieces of ore are broken down through crushing and/or grinding. The material found can either be mostly waste or mostly valuable. More than one valuable metal is usually found in the ore bodies. Tailings of the previous process may be used as a feed in another process to extract a secondary product from the original ore. Traditional ways of processing the low-grade sources of these

metals (sulphide, oxide, and slags) follow either hydrometallurgical, pyrometallurgical, or electrometallurgical routes selectively or collectively (Cox et al., 1985).

2.2.1. Hydrometallurgy

Hydrometallurgy uses aqueous solutions to extract valuable metals from low grade ores, which results in the valuable metal being dissolved in the aqueous solution. This treatment method uses the differences in the solubility and/or electrochemical properties of the different elements in the ore while in aqueous solution. In this process the metal is first dissolved into solution through the process called leaching. Leaching is the dissolution of a valuable metal into an aqueous solution. The lixiviant solution differs in terms of pH, oxidation-reduction potential, the availability of the chelating agents and temperature to optimize the rate, extent and the selectivity of dissolution of the desired metal component into the aqueous phase. The process is then followed by the removal of the metal, which is achieved through electrowinning or electrorefining. The problem that this procedure entails is that it seldom involves just a single process. It normally requires subsequent steps to produce a pure metal. The process also requires long residence times for the reaction in order to obtain economic yields (Van Dyk, 2010). The leaching process can be defined by the following simple equation:

$$\text{Material(leachee)} + \text{leachant} \rightarrow \text{Leachate} \tag{2-1}$$

The material is assumed to be known, although its physical chemical/mineralogical properties will affect the final results. What you want to find as a result of the leachate will determine what leachant to use.

Leaching can be executed on a sulphate-based processes. This process is widely used as it reduces the corrosion on the leaching equipment compared to the other hydrometallurgical processes. In sulphate processes, the sulphate ion (SO_4^{2-}) forms a complex with the metal ion from the ore. Due to not being a strong complexing ion, the sulphate ion can selectively complex with some metal ions whilst leaving others in solution, which results in the separation of different metals from the ore. The following reaction happens when leaching is done using a sulphate lixiviant:

$$MO_{(s)} + H_2SO_{4(aq)} \longrightarrow MSO_{4(s)} + H_2O_{(aq)} \tag{2-2}$$

where,

M is the metal to be leached.

This reaction causes the metal to dissociate into solution.

The leaching process can also be done with chloride-based processes, where hydrochloric acid, ferric chloride or brine is used as a lixiviant depending on the best pH, redox potential or chloride concentration that is required for the process (Wesley, 1985). The reaction forms soluble chlorides, which can be further processed to produce a pure metal. The problem that comes with chloride solutions is that they are very corrosive and they tend to damage the reactor walls. Other leaching processes include nitric acid or organic based systems, and in these systems, the metal is removed from the solution by passing an electric current through the solution in the process of electro-winning. The electro-winning reactions are as follows:

At the anode: $M^{2+}_{(aq)} + 2e^- \rightarrow M_{(s)}$ (2-3)

At the cathode: $H_2O \rightarrow {}^1/_2\, O_{2_{(g)}} + 2H^+_{(aq)} + 2e^-$ (2-4)

Unfortunately, the leaching process is rarely selective. The metal required is therefore extracted with other unwanted metals in the ore/matrix. In order to separate these metals to get the required metal in a high percentage, other subsequent processes such as liquid-liquid extraction using an organic reagent in an organic phase, or ion exchange are required. It is possible to produce pure concentrated aqueous solution of the desired metal from the two processes, which can then be recovered by other techniques such as electrolytic deposition to have a product of pure metal.

2.2.2. Pyrometallurgy

Pyrometallurgical extraction of metals involves subjecting the ore concentrate to high temperatures, either in a blast furnace or a sinter plant (Wesley, 1985). This process uses the difference between constituents' oxidation potential, melting point, vapour pressure, density and/or miscibility when melted. Techniques in pyrometallurgy involves roasting, drying, calcining, sintering, retorting and smelting (Van Dyk, 2010). Since high temperatures are used in these processes, they require a large amount of energy and this makes them expensive. These processes have waste streams that can be harmful to the environment, for example large amounts of SO_2 produced in smelters (Berry et al., 2002). They also produce large amounts of

slags which can be a potential hazard to the environment because of the small amount of metals in them that can be leached into the ground (Van Dyk, 2010).

2.2.3. Electrometallurgy

Electrometallurgy is a metallurgical process where the extraction happens in some form of electrolytic cell. Common forms of electrometallurgical processes are electro-winning and electro-refining. Electro-winning is an electrolysis process used to recover metals in aqueous solution, usually as result of an ore having undergone one or more hydrometallurgical processes (Eugene & Majumdar, 2009). Electro-refining is used to dissolve an impure metallic anode (typically from a smelting process) and produce a high purity cathode (Eugene & Majumdar, 2009). Electrometallurgy has a significant overlap with areas of hydrometallurgy and pyrometallurgy.

2.3. Gold

Gold is one of the least reactive chemical elements and is solid under standard conditions. Gold is one of the metals that contributes significantly in South Africa's economy. South Africa's economy was built on gold and diamond mining, and this sector is an important foreign exchange earner, with gold accounting for more than one third of exports (Brand South Africa, 2012).

2.3.1. Industrial production of gold

The industrial process for gold production is illustrated by Figure 2-1. It depicts all the steps from mining of the ore to the production of gold metal.

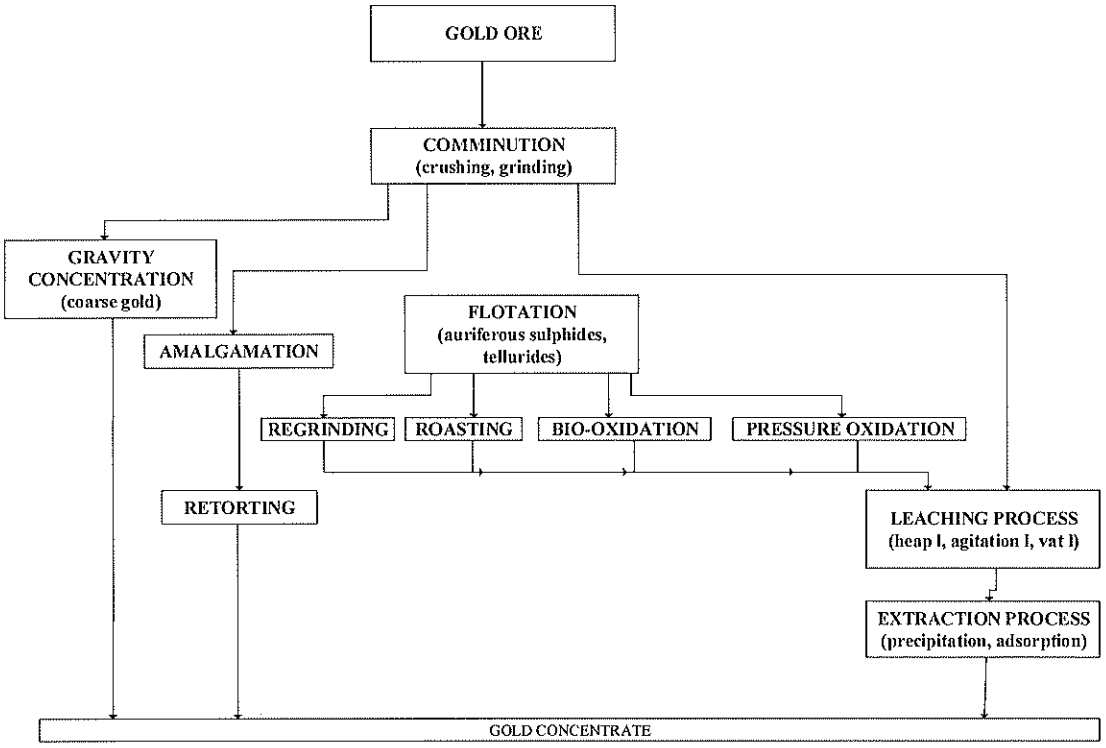


Figure 2-1: Industrial process for the production of gold (Eugene & Majumdar, 2009).

Generally, gold ores can be classified as free milling or refractory depending on their response to cyanide leaching (La Brooy et al., 1994). While high gold recoveries (>90%) from free ore can be readily achieved, refractory gold ores are often characterized by low gold recoveries (50-60 %) in conventional leaching (Rubisov et al., 1994). Most of the gold metal is industrially

produced through leaching with cyanide from ore concentrates (Eugene & Majumdar, 2009). Despite the difficulties and hazards of working with cyanide, no other process has yet been proven to be an economically viable alternative. The first steps in gold processing involves the concentration of gold in the ore by discarding the unwanted material and then then the ore is sent to the leaching process where gold can be recovered chemically. The final gold metal is produced by smelting.

Crushing and comminution

This stage is one of the most important steps in the processing of gold since it has a majority contribution in the plant's operating cost (65-70% of the total cost) (Michaud, 2016). Conventional crushing and grinding circuits have been used traditionally for processing of gold. In each case gold is formed either as a coarse native particle or is part of a coarse grained sulphide. It is recovered by gravimetric concentration in the comminution circuit in addition to recovery of finer values by leaching. Jigs are the most common types of gravimetric equipment placed to intercept the ball mill discharge prior to classification. Lime and sodium cyanide are used in the dissolution of gold and there is a considerable advantage in including them in the grinding circuit due to high dissolution rates that usually results from agitation and oxygenation of slurry during the grinding operation (Michaud, 2016).

Concentration

Various minerals may be found present alone or combined with the host rock, therefore it is required that the unwanted material be discharged in order to increase the concentration of the gold to economic levels. The valuable minerals are separated from the gangue through concentration. The final concentrate is obtained by repeated processing and is smelted or leached in order to get a dore bar. In general, the concentration of gold includes three stages: roughing, cleaning and scavenging. The reason for concentration is to separate the raw material into two parts; concentrate and tails. Ideally, in free gold recovery all the gold will report in the concentrate and the other part will be in tailings (Michaud, 2016). Separations are not perfect and in practice some waste material will report into the concentrate and some gold will report in the tails. Intermediate products are called middlings and can be identified as that belonging in either the concentrate or tails. Sometimes this product creates a serious problem in separation.

Roughing upgrades the ore to produce either a low grade, preliminary concentrate or to reject tails that contain gangue at an early stage. The equipment used can produce a large volume of concentrate and allow for the recovery of a very high percentage of gold, produce clean tails or a combination of both (Michaud, 2016). The rougher concentrate is sent to the ***cleaning*** stage in order to remove the impurities; the process can be as simple as washing black sands by using a vanish dish. Mineral concentrate can pass through several stages of cleaning before the final concentrate is attained. The last stage is called the ***scavenger*** and it deals with the process tails from the rougher and cleaning stages before discarding. The material is treated through equipment that concentrates the last particles of gold. This stage is included in accordance with the design adopted in the operation and can be simple or complex, depending on the ore type. In operations where there is amalgamation, this stage is employed to recover quicksilver that otherwise will report to the environment.

Flotation

Flotation is one of the most important gold recovery processes and its main limitation is to recover coarse gold particles ranging from 400 to 250 μm (Michaud, 2016). This process recovers fine particles of free gold, gold associated in any form of sulphides, and native gold present in polymetallic deposits with a certain degree of oxidation. For many years a combination of amalgamation, cyanidation and flotation made it possible to get high gold recoveries. With time the technology and design consideration changed and flotation and/or cyanidation processes are the favourite combination. When gold is recovered by flotation, a high-grade concentrate contains gold and can give an extra value to copper and lead concentrates. The concentrate can be ground, roasted, treated by cyanidation and the final product is gold bullion.

Leaching

The cyanidation process is one of the most employed hydrometallurgical treatments in the gold mining industry. The cyanidation process was invented in 1887 by the Scottish chemists John S. MacArthur, Robert W. Forrest and William Forrest when gold recovery started to have some problems due to lack of good technology (Fivaz, 1988). Basically, gold is soluble in dilute solution and the pregnant solution can be processed successfully by using zinc powder or activated carbon and electro-winning which makes cyanidation a viable process for extraction

of gold. In the other words, the process involves several steps from crushing until obtaining a Dore bar.

The basic principle of the cyanide process is that alkaline cyanide solutions have a preferential dissolving action on precious metals contained in the ore. The reaction of gold extraction is as follows:

$$4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4Na[Au(CN)_2] + 4NaOH \quad (2\text{-}5)$$

The reaction of silver sulphide, commonly associated with gold ores is not quite so straight forward and it is as follows:

$$Ag_2S + 4NaCN \rightarrow 2NaAg(CN)_2 + Na_2S \quad (2\text{-}6)$$

The rate of gold dissolution is dependent on the concentration of NaCN and on the alkalinity of the solution. The optimum pH is around 10.5. For efficient leaching, the gold should occur as free, fine size, clean particles in an ore. An adequate amount of dissolved oxygen should be supplied in the cyanidation system to oxidise the gold. Cyanidation by agitation and heap leaching are the most used processes for the treatment of gold ores. Normally the process of leaching is employed when the gold content is ranging between 5 and 15 g/t. The grinding circuit is the first cyanidation circuit and the ball and milling operate as leaching drums. Once the liberation is complete, the next step is to agitate the slurry for complete dissolution of gold. The solution and the non-valuable ore must be separated directly if the gold content is high, otherwise it must be enriched by activated carbon (Michaud, 2016). The activated carbon is eluted and feeds the electrolytic cell where gold will be recovered in the form of cathodes. If the solution is rich enough it can be treated by zinc powder and the precipitate obtained will be sent to retorting and smelting. For gold extraction the strength of cyanide solution ranges from 0.01 to 0.05 %. Lime is added continuously to the process in order to have the pH near to 10-11.

Smelting and electro-winning

Gold can be concentrated and recovered by applying different gold refining process methods and the final product has a variable quality. At this stage the gold bearing solution from the leaching process is ready for electro-winning, which recovers gold from the leaching solution. In electro-winning, operators pour gold bearing solution into a special container called a cell.

Positive and negative terminals in the cell deliver a strong electric current to the solution. This causes gold to collect on the negative terminal. Smelting then results in nearly pure gold. It involves melting the negative terminal in a furnace at 1149 ^{0}C (Harris, 2009). When the operators add a chemical mixture know as flux to the molten material, the gold separates from the metal used to make the terminals. Operators pour off the flux and then the gold into solid bars called dore bars. These low-purity bars are then sent to refineries all over the world for further processing.

2.3.2. Problems associated with cyanide leaching

- One of the most frequent sources of trouble in cyanidation is the presence of copper minerals in the ore. The copper content may be less than 0.10 % but its effect on both dissolution and precipitation of gold can be very noticeable (Michaud, 2015). Not only do copper minerals dissolve in cyanide solution and causes excessive consumption of this chemical, but also, the copper cyanogen complexes thus formed indirectly affect the dissolution of gold. The copper dissolved in solution also affect the precipitation of gold by zinc. The resulting gold contains copper which in turn frequently presents a problem in the subsequent melting operation.

- Zinc also forms cyanogen complexes but their effect on the dissolution of gold is low compared to those of copper. Zinc complexes are more likely to create problems in the cyanidation of silver ores since such ores contain much more silver than gold ores contain gold. This means more zinc will be required to precipitate the dissolved silver, resulting in cyanide solutions carrying a relatively high percentage of zinc cyanogen complexes and in some cases zincate.

- The effect of nickel on precipitation of gold can be controlled by monitoring its level in the pregnant solution below a certain danger percentage (Michaud, 2016). This is done by discarding the barren solution at regular intervals. Although this procedure avoids the problem, provided that the amount of nickel dissolved in one cyanidation cycle is not in excess of the critical amount, it does not solve the problem.

- Metallic gold is frequently associated very intimately with minerals such as pyrite and arsenopyrite. In order to ensure contact between the gold and the cyanide solution, the ore must be ground very finely.

2.4. Emerging technologies for the extraction of metals

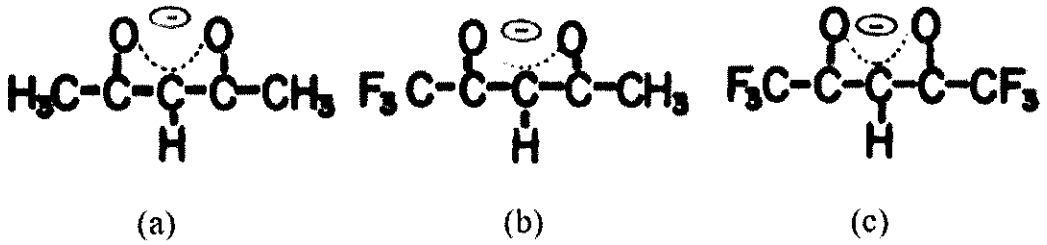
2.4.1. Uses of ligands (extractants) for metal extraction and description of the ligands to be used

A ligand is an ion, atom or molecule that donates one or more of its electrons through a coordinate covalent bond to one or more central atoms or ions to form larger complexes. The complexes formed are known as coordination compounds, and they arise when a metal compound is bonded to one or more anions through coordinate covalent bonds (Siedle, 1987). The use of ligands has been extensive in industry, for example the use of EDTA (ethylene diamine tetra acetic acid ligand) for the binding of metals in water purification and the textile industry (Chaundhary et al., 2000). The catalyst building blocks is found to be the ligands, e.g. diphosphine ligand (BINAP) is used in the catalytic hydrogenation of rhodium or ruthenium, and also for catalytic isomerization of olefins and all alkylation reactions (Pretorius, 2004). Organic bonded metals in soils have been extracted selectively with the use of ligands (Hamblin & Posner, 1979). Moffett & Zika (1987) used the acetylacetone ligand for the extraction of Cu(II) to form its complex with acetylacetone selectively in matrix with other natural chelators. These metals can also be coupled with the use of appropriate liquid surfactant membranes in solvent extraction (Kondo et al., 1978).

Beta-diketones

The ligands that have been chosen for the extraction of gold in the gas phase reaction are the β-diketones and their fluoride derivatives. β-diketones are chelating ligands, which means that they have more than one lone pair of electrons which they can use to bind with the metals. β-diketones exist in a keto-enol tautomeric equilibrium. The position of the equilibrium is dependent on a number of factors such as temperature, the solvent, the concentration, and the structure of the compound (Benson & Schweitzer, 1968). They contain two ketone groups that are separated by a carbon. The equilibrium of the β-diketones turns out to be strongly shifted towards the enol form due to the formation of distant resonance structure of a six membered

ring (Urbaniak et al., 2011). The ability to form complexes with most metals is a direct consequence of the occurrence of such compounds in the enol form. The outer part of the complex formed when the metal and the ligand bind, is made up of organic groups, making most metal diketonates hydrophobic, insoluble in water and volatile (Sievers & Sadlowski, 1978). The metal is shielded by the β-diketone ligands from the intermolecular forces that render it nonvolatile by surrounding it with hydrocarbon or fluorocarbon shell. The following figure show the structure of the beta-diketones that will be tested in the investigation.



(a) (b) (c)

Figure 2-2: β-diketone structures, (a) acetylacetone (b) trifluoroacetylacetone (c) hexafluoroacetylacetone (Urbaniak et al., 2011).

Inclusion of strongly electronegative fluorine atom to the organic compound changes the β-diketone's physical and chemical properties substantially. However, this does not lead to a significant change in size and spatial structure of the molecule (Urbaniak et al., 2011). Replacing hydrogen atoms with fluorine atoms in the ligand shell significantly increases the volatility of the β-diketonate complexes (Sievers & Sadlowski, 1978). In this case the electronegative fluorine atoms dominate the outer periphery of the complex. The fluorocarbon shell may reduce the van der Waals forces and intermolecular hydrogen bonding between fluorine substituted β-diketonates (Sievers et al., 1963). There is a direct proportionality between the volatility and the number of fluorine atoms substituted into the hydrocarbon (Sievers & Sadlowski, 1978). The presence of additional electron-withdrawing substituents changes the electron distribution in the diketone molecule and increases the content of the enol form (Benson & Schweitzer, 1968). Thus, fluoro-substituted β-diketones are mostly enolized, the proportion of enol tautomer increasing with an increase in degree of fluorination. The ability of a β-diketone to form complexes with the majority of metals on the periodic table is the most valuable characteristic from practical point of view (Benson & Schweitzer, 1968).

Owing to their properties, β-diketones and their complexes have been used both in science and industry. The compounds are mostly used in polymer technology for example as substitutes for the manufacture of homogeneous and heterogeneous catalysts, as polymerization catalysts (metal complexes), and as substrates that modify the properties of resulting polymers. β-diketones complexes (especially with transition metals) are often used as catalysts of reactions such as olefin oxidation and epoxidation or olygomerisation (Urbaniak et al., 2011). Complexes formed with β-diketones have been shown to be highly volatile, and forming gaseous complexes at relatively low temperatures compared to other compounds.

2.4.2. Supercritical fluid extracting ligands

Ligands mixed with supercritical fluid (usually CO_2) has been used largely in supercritical fluid extraction for most applications. The mixture of the supercritical fluid and the organic ligand easily diffuse through the sample to be extracted, and the formed metal complex is carried away in the supercritical fluid. This technology has been successfully used to extract cobalt from a model matrix using SFE-CO_2 with acetylacetone and hexafluoride acetylacetone (Burford et al., 1999). Galland and Wipff (2005) have studied the effect of β-diketone ligand fluorination on the SFE-CO_2extraction of uranyl and they have also shown that SFE-CO_2 can be used for the complixation of Fe^{3+}. Copper can be extracted using SFE-CO_2 from contaminated material (Takeshita et al., 2000).

2.4.3. Gas phase extraction

This is the extraction method which will be investigated in this project. The 1970s saw the development of volatile compounds being used for extraction and recovery of various metals. This process has been used to extract heavy metal contaminants from matrices such as low-grade ore, soil, sediment, used catalysts, industrial waste, and fly ash (Allimann et al., 1999). In this process a volatile, organic, chelating acid is passed through the heated feed material in a stream of a carrier gas. The chosen extractant must be able to react with the selected metal to produce a metal-extractant complex that is volatile and which can then be removed from the residual solids by a carrier gas. The metal can then be reduced in the vapour phase with the use of one of several proposed potential ways of separating the metal from the ligand for recycling, e.g. recovery by hydrogen reduction (Demopoulos and Distin, 1985), recovery by reacting with mineral acid (Kersch et al, 2005), or recovery by electrochemical separation (Chaundhary et al., 2000) to produce the desired metal product. Following separation of the

liquid phase both the metal and the organic extractant can be recovered by appropriate techniques (Allimann-Lecourt et al., 2002). The speciation of the metals is an important factor for the success of using the gas phase extraction. This is due to the nature of the chelating reagents which are been used which are only weak acids. Therefore the metals to be extracted must be present as oxides, hydroxides, or sulfides.

Even though it is possible to separate a metal complexes and form a pure metal and a ligand, metal β-diketonates are useful too. They are highly efficient as catalysts in different organic compounds, e.g. oligomerization, polymerization, hydrogenation, isomerization, coupling etc. They are also used in the rubber industry for vulcanization, and for extraction and separation of metals (Willis et al, 2007). This production occurs by chemical vapour deposition (CVD) where complexes acts as precursors, and has been shown for acetylacetone complexes of Fe^{3+}, Al^{3+}, Cr^{3+}, Mn^{3} and Ni^{2+} (Pal & Sharon, 2000; Siddiqi et al., 2007). The produced oxides from CVD have been found to be of high purity, which makes the process of gas phase extraction an advantageous way for the production of pure metal oxides, since it has been shown to work with matrices of low purity.

Equation 2-7 represents the general equation for the extraction of the metal from solid matrices (Allimann-Lecourt et al., 2002).

$$\mathrm{Ext_{gas}} + \mathrm{M(Matrix)_{solid}} \xrightarrow{\mathrm{T}} \mathrm{M(Ext)_{gas}} + \mathrm{Matrix_{solid}} \qquad (2\text{-}7)$$

where,

Ext represent an extractant.

M is the metal

Matrix represents the source of the metal

Potgieter et al. (2006) and Alimann-Lecourt et al. (2002) proposed the following flowsheet for the gas phase extraction of metals.

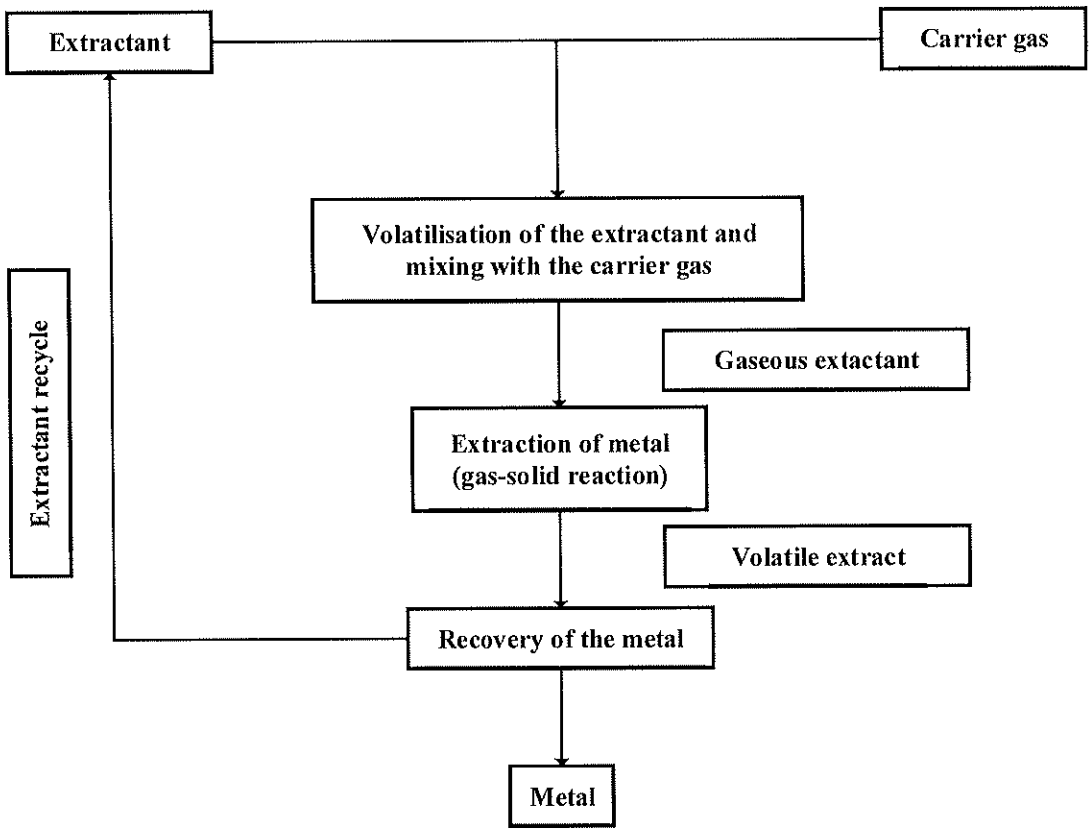


Figure 2-3: Flowsheet for the gas phase extraction of metals (Potgieter et al., 2006; Alimann-Lecourt et al., 2002).

The organic compounds that are used as extractants for gas phase extraction of metals are those that form compounds that generally exhibit high volatility. β-diketones and their derivatives (fluorinated derivatives) are typical examples of such compounds. Extractants such as β-diketones, β-diketoneimine and tetra-iso-propyldiphosphoramides were successfully used to extract metals from the oxide phase of metals in fly ash and different sediments (Alimann-Lecourt et al., 2002, 1999). The use of various extractants shows that one can selectively extract some metals from an ore whilst others remain in the solid matrix. Cox et al. (1985) showed that, through the selectivity of the extractants, it is possible to extract copper, not iron, using different derivatives of β-diketoneamine.

Barr (1989) directed the research towards adapting the SERVO process for selectively extracting nickel over iron from low grade nickel laterite ore. The study was done by optimizing the operational conditions for the extraction and the recovery of nickel from New Caledonian laterite ore. It appeared that the better the physical contact between the ore and the volatile

reagent, the higher the extraction (Barr, 1989). So the optimum flow rate and temperature would correspond to the conditions where the concentration of the reagent is the highest.

Allimann-Lecourt et al. (2002) used a gas phase extraction process to extract iron, vanadium, lead, nickel, copper and zinc from fly ashes using acetylacetone, bis-(pentane-2,4-dionato) propan-1,2-diamine and tetra-iso-propyldithiophosphorimine. They extracted 18.7% iron, 18.6% vanadium and 13.6% chromium at 130 ^{0}C to 235 ^{0}C after 120 minutes. They also demonstrated that by changing the ligand used, you can be able to selectively extract some metals while others remain in the solid matrix.

Potgieter et al. (2006) investigated the effect of temperature on the extraction of aluminium, iron, vanadium and chromium from their oxides mixed with silica using gas phase extraction and acetylacetone as an extractant. They successfully extracted more than 60 % of each metal.

Van Dyk et al. (2010) studied factors such as temperature, ligand flowrate, mass percentage of iron (III) oxide that affects gas phase extraction of iron on mixtures of iron (III) and silica in a fluidized bed reactor. They showed that temperature, ligand flowrate and iron oxide mass percentage influence the extraction of iron.

Mariba (2010) successfully used the gas phase extraction to extract iron using acetylacetone from Fe_2O_3 in a fluidized bed reactor, with above 80% extraction being achieved after four hours for some experimental conditions. The author also showed that the extraction depends on temperature, ligand flowrate and surface area available for reaction, with extraction increasing as each variable was increased (Mariba, 2010). It was also shown that iron could be removed from a mixture of iron and chrome oxide since chrome could not be extracted by acetylacetone.

Mpana (2012) extracted aluminium from fly ash from Eskom's Kendal power station using acetylacetone. The work also shows that the extraction depends on extraction temperature, reaction time, acetylacetone flowrate, fly ash particle size distribution and bed weight. Many different research groups have shown the possibility of extracting metals in the gas phase from various solid matrices.

2.5. Fluidization

Fluidization is a process where an upward flow of a gas (or liquid) converts a bed of particles to a fluid state. When a fixed bed of particles is exposed to an upward flow of gas the individual particles gradually tend to move apart and an expansion of the bed becomes noticeable (expanded bed). The fluidization engineering uses the unusual characteristics of the contacting method to their advantage.

2.5.1. Principles of fluidization

If a bed of fine particles is exposed to an upward flow of a fluid, the fluid percolates through the void spaces. The pressure drop increase with an increase in gas flow. When there is an increase in the gas flow rates, a point is reached where the pressure drop is equals to the weight of the bed and it is referred to as a bed at minimum fluidization (Kunii & Levenspiel, 1991).

Any additional increase in the flow rate tend to make particles touch each other most of the time, but the inter-particle friction is so small in non-cohesive particles that the fluid/solid assembly behaves like a liquid having a density equal to the bulk density of the powder (Geldart, 1986).

In gas-solid systems a further increase in velocity above the point of minimum fluidization tends to create an unstable form of rising bubbles and channeling of the gas. Figure 2-4 shows the behaviour of the bed at various stages of fluidization.

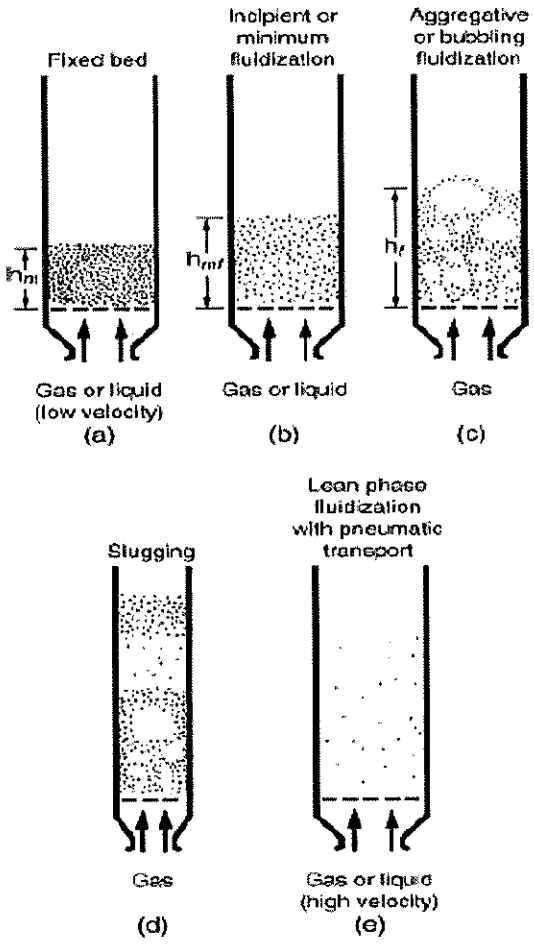


Figure 2-4: The behaviour of the bed at various stages of fluidization (Kunii & Levenspiel, 1991).

The behaviour of the fluidized bed will depend on the velocity of the fluidizing gas and the following is description of possible observed behaviours (Kunii & Levenspiel, 1991).

- Aggregate fluidized bed – It is characterised by violent movement of the solids within the bed. The bed does not expand much beyond its volume at minimum fluidization.

- Slugging fluidized bed – It is usually found in long narrow fluidized beds. As the gas bubbles rise up through the bed they coalesce and grow; and may become large enough to spread across the whole bed. As the gas rises, the solid particles, in a case of fine particles, will flow smoothly down the walls of the fluidized bed around the void of rising gas.

- Turbulent fluidized bed – This occurs when the terminal velocity of the solids is exceeded. The upper surface of the bed disappears, with some of the solid particles being entrained. Instead of bubbles in the bed, there are solid clusters and voids of gas of differing size and shape.

- Lean phase fluidization – High velocities are experienced which causes the solids to be carried out with the gas. This is a range of operation which is used if pneumatic transportation of solids is required

2.5.2. Minimum fluidizing velocity, u_{mf}

This is a point in which the upward drag force exerted by the fluid of the particles in the bed is equal to the apparent weight of particles in the bed. At this point the particles are lifted by the fluid, the separation of the particles increases, and the bed becomes fluidized. This behaviour is shown in Figure 2-5.

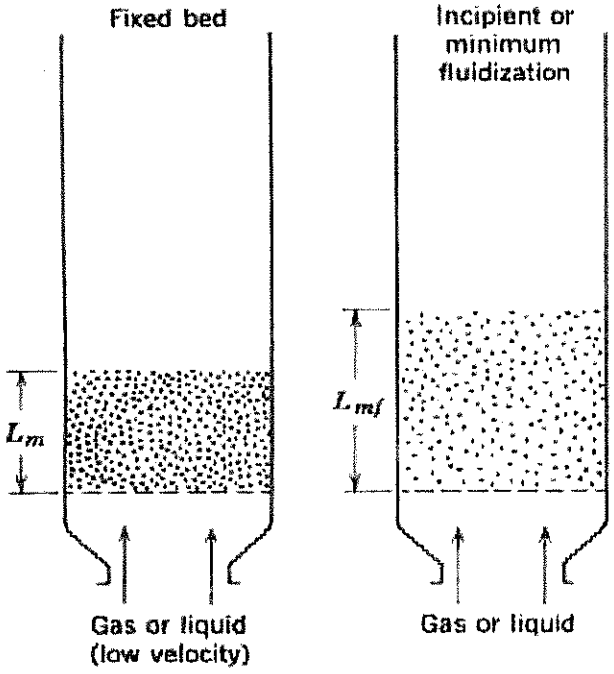


Figure 2-5: Behaviour of a packed before and at minimum fluidization velocity (Kunii & Levenspiel, 1991).

The following derivation has been adapted from Kunii & Levenspiel (1991).

Minimum fluidization occurs when

$$\begin{pmatrix}\text{drag force by}\\ \text{upwards moving gas}\end{pmatrix} = \begin{pmatrix}\text{weight of}\\ \text{particles}\end{pmatrix} \tag{2-8}$$

Or

$$\begin{pmatrix}\text{pressure drop}\\ \text{across bed}\end{pmatrix}\begin{pmatrix}\text{cross}-\text{sectional}\\ \text{area of the tube}\end{pmatrix} = \begin{pmatrix}\text{volume}\\ \text{of bed}\end{pmatrix}\begin{pmatrix}\text{fraction}\\ \text{consisting}\\ \text{of solids}\end{pmatrix}\begin{pmatrix}\text{specific}\\ \text{weight}\\ \text{of solids}\end{pmatrix} \tag{2-9}$$

In terms of symbols,

$$\Delta p_b A_t = W = A_t L_{mf}(1-\varepsilon_{mf})\left[(\rho_s-\rho_g)\frac{g}{g_c}\right] \tag{2-10}$$

$$\frac{\Delta p_b}{L_{mf}} = (1-\varepsilon_{mf})(\rho_s-\rho_g)\frac{g}{g_c} \tag{2-11}$$

$$\frac{\Delta p_{fr}}{L_{mf}}g_c = 150\frac{(1-\varepsilon_{mf})^2}{\varepsilon_{mf}^3}\frac{\mu u_0}{(\phi_s d_p)^2} + 1.75\frac{1-\varepsilon_{mf}}{\varepsilon_{mf}^3}\frac{\rho_g u_0^2}{d_p} \tag{2-12}$$

By combining equation 2-11 and 2-12, it yields a general equation for the superficial velocity at minimum fluidization conditions (u_{mf}).

$$\frac{1.75}{\varepsilon_{mf}^3\phi_s}\left(\frac{d_p u_{mf}\rho_g}{\mu}\right)^2 + \frac{150(1-\varepsilon_{mf})}{\varepsilon_{mf}^3\phi_s^2}\left(\frac{d_p u_{mf}\rho_g}{\mu}\right) = \frac{d_p^3\rho_g(\rho_s-\rho_g)g}{\mu^2} \tag{2-13}$$

In a case where $Re_{p,mf} < 20$, i.e. for very small particles, equation 2-13 reduces to

$$u_{mf} = \frac{d_p^2(\rho_s-\rho_g)g}{150\mu}\frac{\varepsilon_{mf}^3\phi_s^2}{1-\varepsilon_{mf}} \tag{2-14}$$

In order to obtain u_{mf} the voidage of the bed at minimum fluidization should be known. If it is not known Wen and Yu (1966) suggested the following equation for correlation:

$$Re_{p,mf} = [33.7^2 + 0.0408Ar]^{1/2} - 33.7 \tag{2-15}$$

where,

$$Re_{p,mf} = \frac{d_p u_{mf}\rho_g}{\mu} \text{ and } Ar = \frac{d_p^3\rho_g(\rho_p-\rho_g)g}{\mu^2} \tag{2-16}$$

Pressure drop versus velocity

Figure 2-6 gives a rough indication of the quality of the fluidization in a case where visual observations are not possible.

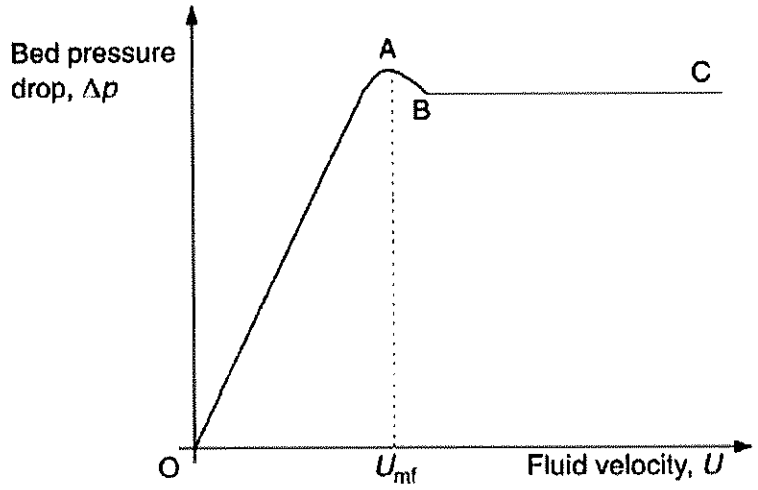


Figure 2-6: Pressure drop versus fluid velocity for packed and fluidized beds (Rhodes, 2008).

At relatively low flow rates the pressure drop across the bed is directly proportional to the gas velocity as shown in Figure 2-6 by the straight-line region OA. In this region there is no movement of particles in relation to one another and their separation is constant. Point A is a point of fluidization u_{mf}. An increase in gas velocities above the point u_{mf}, cause the bed to expand and gas bubbles to appear (Kunii & Levenspiel, 1991). Even though there is an increase in the gas flow, the pressure drop remains constant.

2.5.3. Terminal velocity

A particle's terminal velocity is the lowest gas velocity that causes particles to start moving with the gas. Following is the equation used to determine the terminal velocity of particles.

$$u_t = \left[\frac{4d_p(\rho_s-\rho_g)g}{3\rho_g C_D}\right]^{1/2} \quad (2\text{-}17)$$

Where C_D is an experimentally determined drag coefficient.

2.5.4. Influence of particle size and density on fluidization

Fluidization is not only controlled/influenced by gas velocity and shape of the particle. Particle size and density of the solids to be fluidized have an impact on how fluidization will proceed. This is due the impact that the combination of particle size and the superficial gas velocity have on determining major hydrodynamic characteristics of fluidized beds. Geldart (1986) observed the fluidization of different types of particles and their different sizes to come up with four recognisable types of particle behaviour (Kunii & Levenspiel, 1991). These particles were grouped from the smallest in diameter to the largest diameters. Figure 2-7 shows this grouping and the types of behaviour (Geldart, 1986).

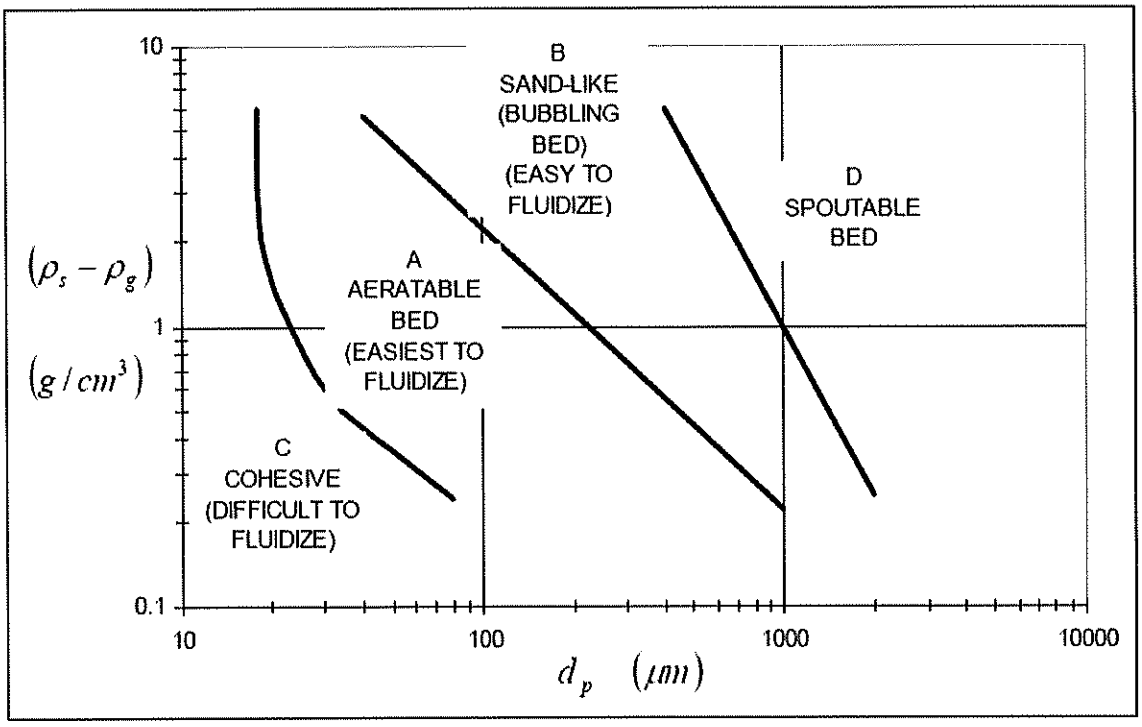


Figure 2-7: Geldart's fluidization classification of powders (Geldart, 1986).

The observed characteristics of the particles are as follows:

- Group C – These powders are very fine and are incapable/ very difficult to fluidize under normal conditions. The cohesiveness is caused by the inter-particle forces (van der Waals) which are larger than those arising from the action of the gas, making the

particles to be attracted to one another and form clumps. They tend to rise as plugs of solids. Group C particles generally exhibit particle diameters less than 30μm.

- Group A – These powders have particles with low density and/or small mean particle size (typically 30μm-100μm) which are capable of being aerated. When compared to the particles in Group C, their inter-particle forces are not large and they are capable of fluidization. At minimum fluidization these particles are in a region of non-bubbling fluidization, and above this velocity bubbling occurs.

- Group B – The particles from this type of powders are in a range $100\mu m<d_p<1000\mu m$ and density $1.4<\rho_s<4.5 g/cm^3$. These solids start bubbling at minimum fluidization and those bubbles grow large.

- Group D – These particles are coarse and/or dense. It is difficult to fluidize these particles if they are in deep beds, because it produces large exploding bubbles, or severe channelling. The solids spout easily if the gas is very unevenly distributed.

2.5.5. Advantages and disadvantages of fluidized bed reactors

2.5.5.1. Advantages of fluidized beds

- The smooth, liquid like flow of the particles allow continuous automatically controlled operations with ease of handling.
- The rapid mixing of solids leads to nearly isothermal conditions throughout the reactor, hence the operation can be controlled simply and reliably.
- They are suited for large-scale operations.
- The circulation of solids between two fluidized beds make it possible to transport the vast quantities of heat produced or needed in large reactors
- The rate of heat transfer between a fluidized bed and an immersed object is high, hence heat exchange within fluidized beds require relatively small surface area.
- Heat and mass transfer rates between gas and particles are high when compared to other forms of contacting systems.
- There is a large margin for safety in avoiding temperature runaways for highly exothermic reactions since the vessels resists rapid temperature changes and it responds slowly to instantaneous temperature changes.

2.5.5.2. Disadvantages of fluidized beds

- The difficult-to-describe flow of gas with its large deviation from plug flow and the bypassing of solids by bubbles.
- Friable solids are pulverised and entrained by the gas.
- Erosion of the pipes and vessels from abrasion by particles.
- For non-catalytic operations at high temperature the agglomeration and sintering of fine particles can necessitate a lowering in temperature of operation, reducing the reaction rate.

2.5.6. Industrial applications of fluidized bed reactors

2.5.6.1. Early uses of fluidized bed reactors

Fluidized bed reactors are used widely in the chemical processing industries for separations, rapid mass and heat transfer operations, and catalytic reactions. Winkler coal gasifiers is one of the first processes which used the fluidized bed reactor for coal gasification in 1926 (Kunii & Levenspiel, 1991). In the petroleum industry a fluidized bed reactor was also used in a fluid catalytic cracking unit to separate oil fractions in the 1940s. The Fischer-Tropsch reaction which converts natural gas to high grade gasoline in the 1940s was also done with the use of a fluidized bed reactor but it was stopped in 1957 because of the increase in the cost of natural gas and the low conversion rates in the reactor. Fluidization technology was also used in the metallurgical processing for the roasting of sulphide ores in the fluid-solid system in the late 1940s.

2.5.6.2. Application of fluidized bed reactors in physical processes

Due to the excellent mixing capabilities of the fluidized bed reactors, they have been used in a variety of physical processes, such as drying where a wet solid is contacted with and fluidization by hot gas is used to get solids dried, mixing of the solids, and granulation. Other applications include the coating of metals with plastic, which is achieved by having a metal at a temperature above the boiling point of the plastic contacting fine particles fluidized in air, and adsorption of dilute components using a carrier gas. As stated in the advantages of fluidized bed reactors, good solids mixing gives rise to good heat transfer, temperature uniformity and ease of process control and therefore fluidized bed reactors can also be used for cooling.

2.5.6.3. Commercial application of fluidized bed reactors.

- Solid-catalysed gas phase reactions
  - Fluidized-bed catalytic cracking (FCC) is the most important and widely used in the refinery process for converting low value heavy oils into more valuable gasoline and other lighter petroleum products (Kunii & Levenspiel, 1991). The catalytic hydrocracking is an endothermic process. The required temperature is achieved by the heat from the catalyst feed. The mixture of catalyst and hydrocarbon vapour travels up the riser into the reactor. The catalyst used is made of very fine particles, therefore the mixture of catalyst and vapour behaves like a fluid (Kunii & Levenspiel, 1991).
  - Fischer-Tropsch synthesis uses fluidized bed reactors for the production of liquid hydrocarbons or wax. Catalytic reactions require strict temperature control and for this reason fluidized bed reactors are preferred over fixed bed reactors. If there is no strict temperature control the catalyst might end up deteriorating because they are very sensitive to fluctuations in temperature or develop hot spots during the process.
  - Other solid-catalysed gas phase reactions include the production of phthalic and maleic anhydride, chlorination and bromination of hydrocarbons, acrylonitrile and aniline, polyethylene and polypropylene and oxidation of SO_2 to SO_3.
- Gas-solid reactions
  - Fluidized bed combustion (FBC) was first researched in the 1960s in an effort to find a combustion process suitable for low grade coal and shale fines. In the FBC, air is used to fluidize silica sand, and then small coal particles are injected into the bed.
  - Other gas-solid reactions include roasting of ores (ZnS, Cu_2S, NiS), gasification, coking and pyrolysis, carbonisation, calcination (limestone, phosphates, aluminium hydroxide), reduction of iron ore and catalyst regeneration.
- Gas-liquid-solid
  - Hydrotreating, hydro-processing and biochemical processes uses fluidzed beds in a gas-liquid-solid system.

Fluidized bed reactor ensures low temperature gradients within the reactor and good enough particle mixing to yield good contact between the ligand and the particles. This together with the advantages given in the discussion has led to the selection of a fluidized bed reactor as the reactor to be used for the gas phase extraction of gold in the tailings from the Ergo mine.

2.6. Summary

DRD currently retreats old surface mine dumps around Johannesburg to recover the gold which is still available in them. This dumps still contain gold concentration of around 0.3 g/t (Dworzanowski, 2018). After treatment at the Ergo plant, the tailings from there still contain between 0.10-0.15 g/t (Dworzanowski, 2018). The conventional methods of metal extraction such as hydrometallurgy and pyrometallurgy bring about a lot of problems as indicated in this Chapter, which means that there is a need for a process which will be able to further treat the tailings since they still contain enough gold which can be extracted. A new promising emerging process called gas phase extraction process for the extraction of metals from low grade ore, soil sediment and industrial waste is proposed for the extraction of gold using acetylacetone as the ligand. Most of the work done on this subject shows that the process is feasible for the extraction of different metals such as iron, chromium, aluminium, vanadium etc. To date no work has been published on the extraction of gold in a gas phase process. This work looks at whether this process can be used to extract gold from a low grade ore of the tailings from Ergo Mine plant or not.

3. EXPERIMENTAL METHODS and PROCEDURES

Gas phase extraction experiments were carried out to determine the extraction of gold from the tailings from the Ergo plant. The experimental methods and procedures which were used, are described in this chapter.

3.1. Materials

3.1.1. Gold ore (tailings) from the dumps of the Ergo mine plant

The sample material was obtained from Ergo plant and it was analysed using AAS to find the initial amount of the metal in the sample, which is 1.6ppm (mass).

Figure 3-1 shows the particle size distribution of the sample tested and used for the experiments. The data used to construct the graph is shown on Table A-1 in Appendix A. It is assumed that the density of the particles does not change, therefore mass percentage is equals volume percentage.

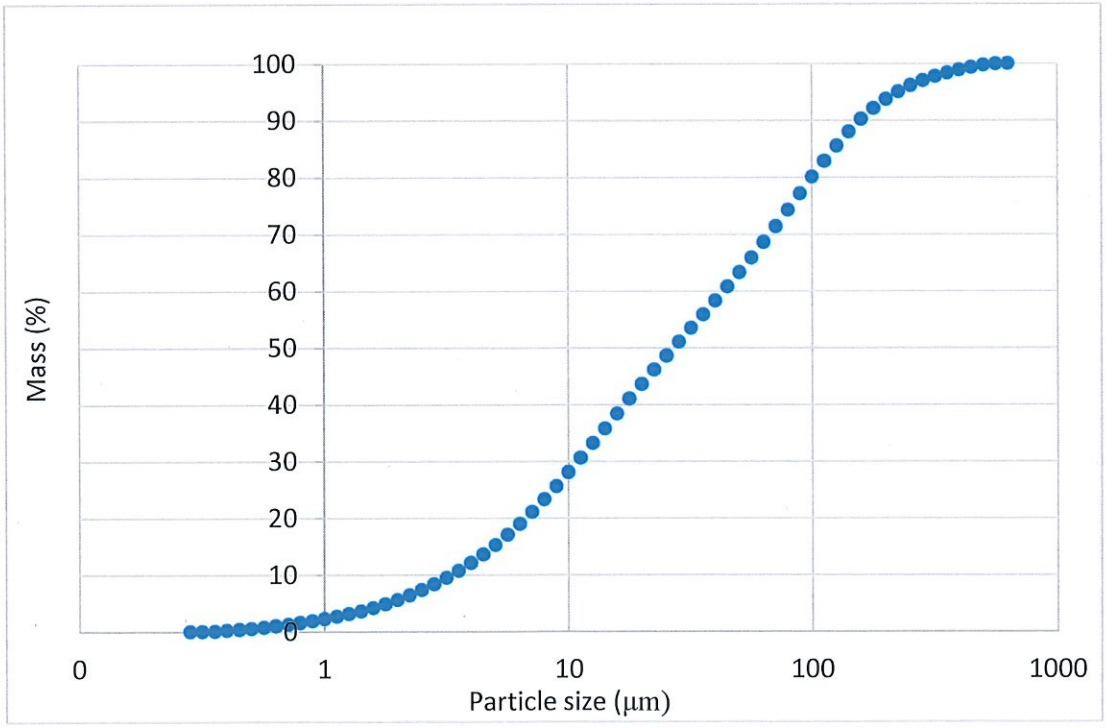


Figure 3-1: Particle size distribution of the ore sample (gold tailings).

The sample has the specific surface are of **0.772 m^2/g** and an average diameter (d [3,2]) of **8 µm** (obtained from Malvern Instruments Ltd (Master sizer 2000) and the density of **2810 kg/m^3** found by the use of Helium pyconometry. Figure 2-7 was used to determine if the material to

be tested can be fluidized. Particle diameter (d_p=8 μm) and (ρ_p- ρ_g)≈2810 kg/m^3 because the density of the gas is insignificant compared to the density of the particles. The material was found to be impossible to fluidize because the particle size of the material is too low and the graph doesn't even accommodate it. The ALS laboratory report (2011) states that in particles smaller than 10 μm the gold was almost entirely exposed, while the amount exposed decreased with increasing particle size. The average diameter of the sample tested is smaller than 10 μm, which means that the sample had the gold almost entirely exposed.

3.1.2. Reagents used for the investigation

The reagents used in this study were purchased from Sigma-Aldrich and it was used without further purification. Table 3-1 shows the properties of the reagent employed.

Table 3-1: Properties of acetylacetone.

	Reagent	**Form**	**Boiling point**	**Purity**	**Function**
1	Acetylacetone ($C_5H_8O_2$)	Colourless liquid	140.4 ^{0}C	≥99 %	Extractant

3.2. Experimental Set-up

A cylindrical borosilicate glass fluidized bed reactor (30cm long and dimeter of 11.5 cm at the bottom and 14 cm at the top), fitted with a perforated frit that served as a gas distributor was the major apparatus required for the conduction of the investigation. It was heated with a heating wire (5m long and 5mm thick) wrapped along the length of the column and insulated with a ceramic wool covered with aluminium foil. The temperature increase provided by the heating wire was controlled with a temperature controller. A 1.5 mm thick stainless steel type K thermocouple with a probe of 5.5 cm was also connected to the PID controller and inserted midway along the length of the column to measure the temperature inside the column. The bottom part of the column was connected to an evaporation flask that was heated by a ceramic heating mantle connected to a temperature controller. The flask is 3 neck borosilicate glass round bottom flask of 500 mL capacity with female joints of 24/29 and two of 19/26 angled. The portion of the flask surface not immersed in the mantle was insulated with 4 cm thick ceramic wool to ensure that there is minimal heat loss. The gaseous products going out of the column was condensed in a 40 cm long borosilicate glass condenser composed of an internal

spiral glass tube for cooling water to run through. The ligand was fed to the system by first passing it through a pre-heater to heat up the extractant, which helps with the evaporation process before the ligand is fed into the evaporation flask. In a case where a carrier gas is used, the reactor will have its own preheating section. In this study air was not used. The full experimental set-up is shown in Figure 3-1 adapted from the set-up used by Olehile (2017).

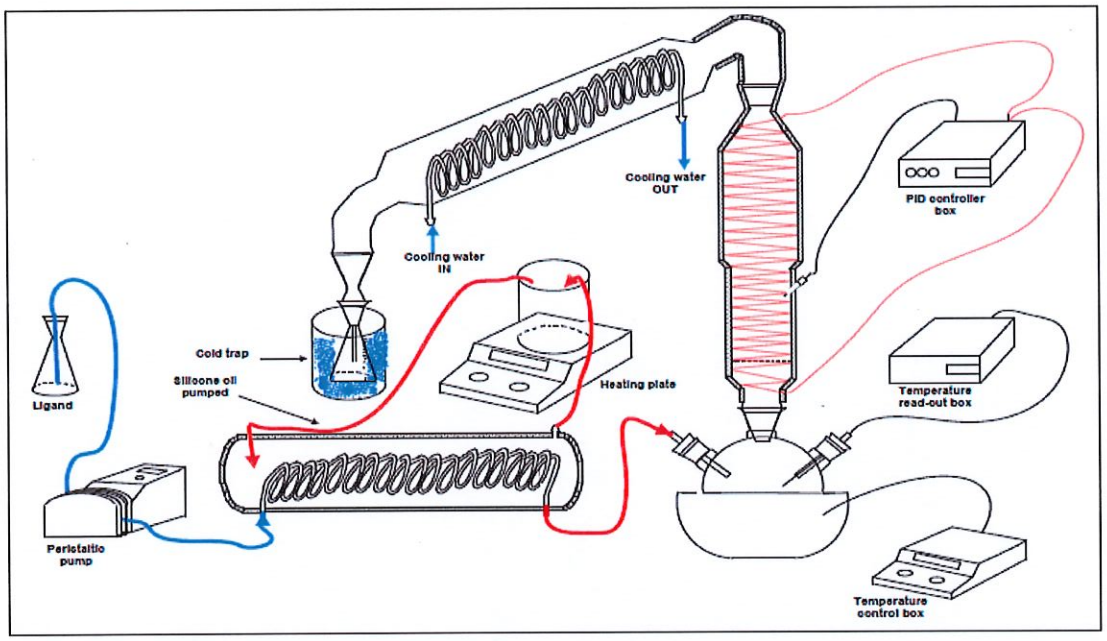


Figure 3-2: Experimental set-up (Olehile, 2017).

3.3. Experimental Procedure

- The extraction runs were performed using the sample of tailings from Ergo mine. The tailings were used as they were from the mine. A splitter was used to make sure a representative sample was obtained.
- A charge of prepared sample was loaded into the reactor. The amount of the sample was varied for different experiments.
- Then all the equipment were connected as shown in Figure 3-1 and the desired temperature for the reaction was registered as the set-point temperature (T2) in the PID controller before the reactor was preheated. The evaporation flask was heated to temperature T1=141 ^{0}C, which was regulated by the volatilisation temperature of the ligand acetylacetone.

- 250 ml of the ligand was then added into the conical flask and the ligand flow rate was adjusted and varied using a peristaltic pump.
- Silicone oil (heating fluid) was heated and magnetically stirred for 20 minutes, and then circulated in the preheater using a peristaltic pump operating at 220 rpm. At the same time the cooling water was also circulated counter currently to the flow of the product gas through the condenser to cool the product gas and collected it as a liquid.
- The peristaltic pump feeding the ligand was switched on once the temperature inside the heating flask and the reaction temperature inside the fluidized bed were stable for the process to start running.
- The reaction was allowed to run for a period of t_1 (30 minutes for the first hour and then 1 hour for the next three hours) and the system was allowed to continue running for a period of 5 minutes so that the product remaining in the reaction zone can be collected by allowing it to evaporate into the collection flask.
- The sample was then collected before fresh solvent was put into the collection flask and reconnected back to the system. The pump was then started for the next interval.
- This procedure is repeated for a certain set period of time.
- The liquid sample was analysed using AAS.

3.4. Experimental conditions

The major variables investigated included the effects of the acetylacetone (ligand) flow rate, bed size (ore mass), the reaction temperature and the effect of time on the process of gas phase extraction. The following table shows the summary of the conditions utilised for the test of the variables.

Table 3-2: summary of the experimental conditions used.

Bed mass (g)	**Temperature (^{0}C)**	**Ligand flow rate (ml/min)**	**Time (hours)**
30, 50, 70	190, 210, 230, 250	1, 3, 6	4

The minimum fluidization of the process has been calculated in Appendix A and it was assumed that when the ligand boils it expands so much that its flow rate into the fluidized bed column is higher than the minimum fluidization calculated.

The following table shows the static bed height at different bed mass:

Table 3-3: Static bed height at different bed mass.

Bed mass (g)	Bed height (mm)
30	30 mm
50	48 mm
70	69 mm

3.5. Analytical measurements for product

Atomic absorption spectrometry (AAS)

AAS is an analytical technique that measures the concentration of elements. Atomic absorption is so sensitive that it can measure down to parts per billion of a gram ($\mu g/dm^3$) in a sample (Levison, 2001). Wavelengths of light specifically absorbed by an element is used in this analytical technique. The wavelengths correspond to the energies needed to promote electrons from one energy level to another higher energy level. In industry the concentration of toxic or target materials in the raw material is checked using AAS (Skoog et al, 1963). Atoms of various elements absorb characteristic wavelengths of light. Analysing a sample to see if it contains a particular element means using light from that element. In AAS, the sample is atomised i.e. converted into ground state free atoms in the vapour state and a beam of electromagnetic radiation emitted from the excited silver atoms passed through the vaporised sample. Some of the radiation is absorbed by the silver atoms in the sample. The greater the number of atoms there is in the sample the more radiation is absorbed (Levison, 2001). The amount that the standards absorb is compared with the calibration curve and this allows the calculation of the concentration in the unknown sample.

3.6. Liquid phase extraction of gold

A batch reactor was used for the liquid phase extraction of gold. The required volume of acetylacetone was determined for a given mass using the stoichiometric reaction between the reactants.

3.6.1. Experimental method

20g of the sample was added into a 250 ml flask containing 100 ml of acetylacetone for the liquid phase extraction of gold. The flask was placed on a magnetic heating stirrer where it was run at various temperatures (room temperature (20.8 ^{0}C)), 45 ^{0}C, 60 ^{0}C, 70 ^{0}C, 90 ^{0}C) for different experimental runs and the agitation speed of 1083 rpm and allowed to run for 48 hours. The sample was filtered and then analysed.

The liquid product was analysed using the same procedure used when analysing the product from the gas phase system.

4. RESULTS AND DISCUSSIONS

Gold in the tailings from Ergo Mine plant was extracted using a volatile organic substance acetylacetone as a ligand. Recent publications on the gas-phase extraction show that acetylacetone has the ability to extract metals from low-grade ores (Allimann et al., 2002; Potgieter et al., 2006; Van Dyk et al., 2010). The gold tailings were chosen because the amount of gold extracted using the current cyanidation system at the Ergo plant is low. Only 36.7% of the initial amount fed into their system is recovered. The gold reserves in this country are becoming depleted, and gold is one of South Africa's economy powerhouse commodities (DRD Gold, 2016). There are large volumes of waste dump being created that still contain gold that can be extracted (DRD Gold, 2016). This section presents the results of the experimental studies done and their discussion together with the kinetic modelling of the results. The following reaction represents the reaction that takes place between the gold oxides contained in the tailings with acetylacetone in the fluidized-bed reactor:

$$4Au + 3O_2 + 12H(C_5H_7O_2)_{(g)} \rightarrow 4Au(C_5H_7O_2)_{3_{(g)}} + 6H_2O_{(g)} \quad (4\text{-}1)$$

The experimental studies where used to investigate and determine the effects of various parameters on the production of the gold complex using acetylacetone. The effect of reaction temperature, flow rate of the ligand acetylacetone, and the bed weight were investigated and determined.

4.1. The effect of reaction temperature

Initial experiments tested the influence of temperature in a liquid phase acetylacetone as a ligand for the extraction of gold from the tailings sample. The results of the experimental tests are shown in Table 4-1.

Table 4-1: Liquid-phase extraction of gold from tailings sample from Ergo mine plant at different temperatures for a period of 24 hours.

Temperature (^{0}C)	% Gold extraction
RM (20.8)	0.78
45	1.81
60	2.50
75	3.13
95	5.94

The extraction of gold from the tailings sample is indeed dependent on the temperature of the reaction. Increasing temperature resulted in an increase in the extraction of Gold. 5.94% of the initial available gold was extracted in a period of 24 hours at 95 ^{0}C, while only 0.78% was extracted at room temperature (20.8 ^{0}C) for the same reaction time. Table 4-1 shows that an increase in temperature increases the amount of gold extracted from the sample in the same experimental conditions.

The lower extraction may be because most particles in this range of temperatures do not have enough energy to react, or alternatively that the ligand could not reach locked up particles to interact with them. The collision theory states that an increase in the number of particles with enough energy (equal or above the activation energy) results in an increase in the rate of the reaction. This means that to influence the extraction efficiency positively, more reaction time may be required, or the locked-in particles have to become more accessible.

To study the effect of temperature on extraction, the experimental studies of the gas phase extraction of gold from the tailings sample were conducted at four temperatures with a constant feed rate of the ligand of 1 mL/min and a bed mass of 50 g of sample. The reaction was allowed to run for a maximum of 4 hours and it was stopped at intervals to allow for the collection of the product sample. The results of the experiments are depicted in Figure 4-1.

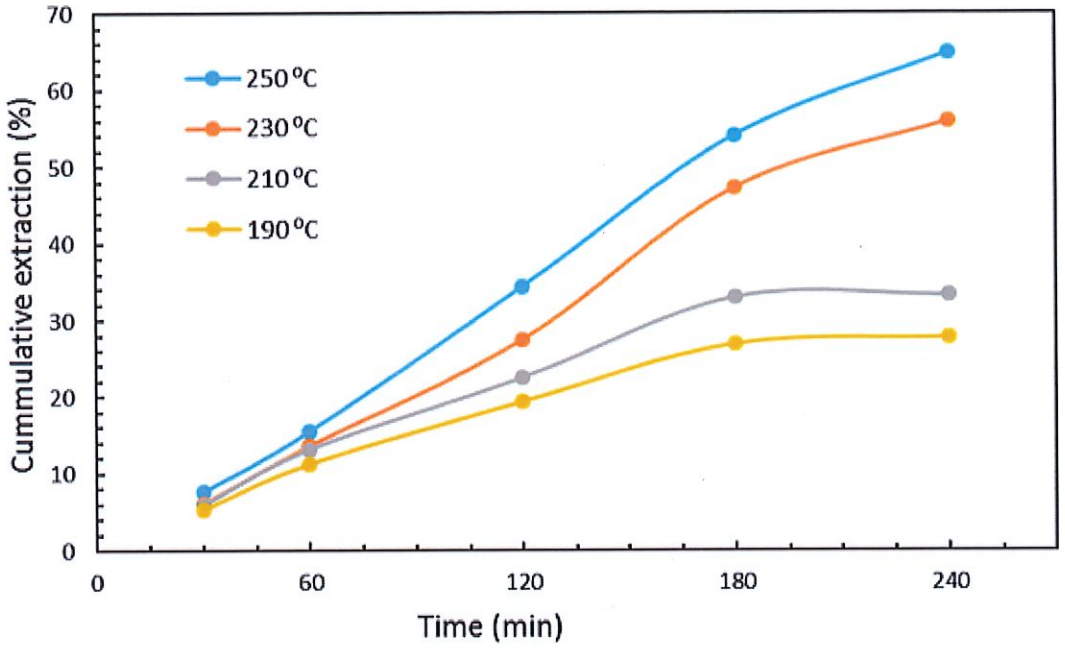


Figure 4-1: The effect of temperature on the extraction of gold with acetylacetone as a ligand at a flow rate of 1mL/min and a bed mass of 50 g.

The extraction of gold from the gold tailings sample is dependent on the reaction temperature. Higher temperature yields a high extraction; increasing the temperature from 190 °C to 250 °C resulted in more gold being extracted. The reaction starts of rapidly and as indicated by the steep slope on the graph in Figure 4-1 and then slows down, as shown by the graph as it starts to reach a plateau which implies that the progress of the reaction decreases with time. Under these conditions, the highest extraction of 64.8% was achieved in a period of 240 minutes. For the period of time in which the reaction was allowed to run, there was a 37% increase in extraction for a change in reaction temperature from 190 °C to 250 °C. Figure 4-1 shows that there is a small change in extraction between 190 °C and 210 °C; 27.7% of Gold was extracted after 240 minutes at the reaction temperature of 190 °C and 33.3% was extracted at 210 °C. There is a significant difference in extraction between the reaction temperatures 210 °C and 230 °C: only 33.3 % is extracted at 210 °C and 56.0 % is extracted at 230 °C (see figure 4-1). The difference in extraction at 230 °C and 250 °C is also small as shown in Figure 4-1.

The results follow trends obtained in previous work, those of Potgieter and co-workers (2006), Allimann and co-workers (2002), and Van Dyk and co-workers (2010, 2012), all of which showed that temperature increases the extraction in organometallic reactions. The results also

shows that more extraction is achieved using acetylacetone in a gas-phase reaction than in a liquid-phase reaction. The difference in extraction between 95 ^{0}C and 190 ^{0}C is significant even though at 95 ^{0}C the reaction ran for longer; only 5.9 % (Table 4-1) of gold was extracted in 24 hours at 95 ^{0}C and 27.7 % was extracted at 190 ^{0}C (Figure 4-1) in 4 hours.. This increase also suggest that between the two temperatures there is also potential energy barrier required for a reaction to take place.

4.2. The effect of ligand flow rate on extraction

Van Dyk and co-workers (2010) noticed that the ligand flow rate can limit higher concentrations of the metal being extracted in the feed. They showed that that the ligand flow rate has an effect on the extraction of metals. Gas-phase extraction of gold from the tailings was carried out at a constant temperature of 250 ^{0}C and bed mass of 50 g for a variety of ligand flow rates (1, 3, and 6 mL/min). Figure 4-2 depicts the results obtained.

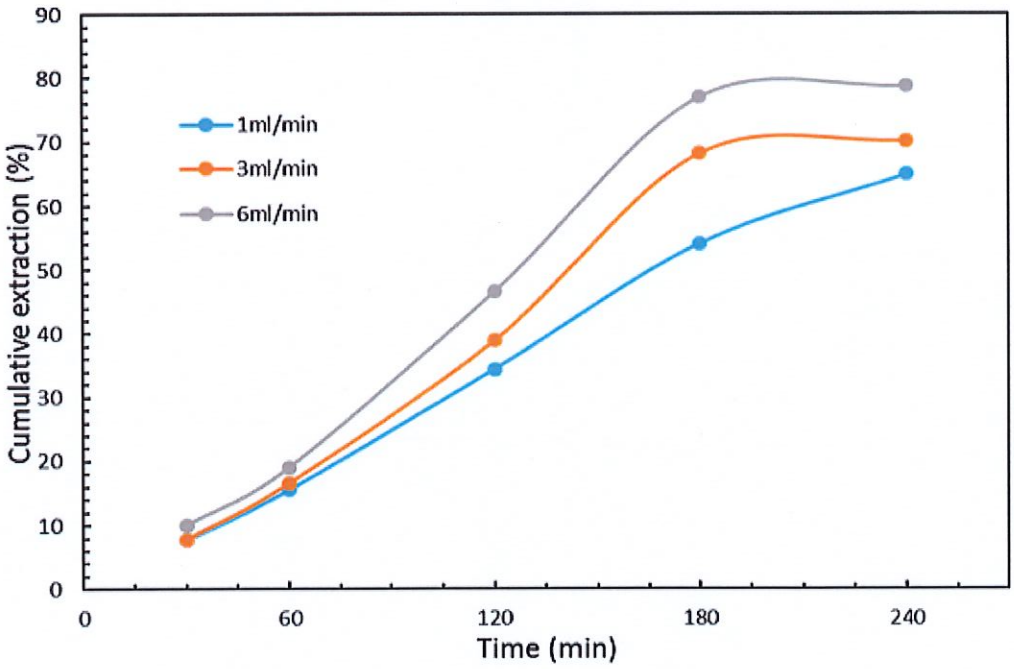


Figure 4-2: The effect of acetylacetone flow rate on the extraction of gold at flowrates of 1, 3 and 6 ml/min in a fluidized bed reactor with a bed weight of 50g at 250 ^{0}C.

Figure 4-2 shows clearly that the flow rate has an influence on the extraction of gold. An increase in flow rate from 1 mL/min to 6 mL/min resulted in an increase in extraction of gold.

It can be seen from Figure 4-2 that there is an increase from 64.8% to 70% with a change of flow rate from 1 mL/min to 3 mL/min with the reaction time of 240 minutes. Increasing the flow rate from 3 mL/min to 6 mL/min increases the cumulative recovery from 70% to 78%. This increase in extraction and rate of reaction (shown in figure 4-2 by the steeper gradient) may be due to that an increase in ligand flow rate means that there is more ligand present to come in contact with the tailings particles. It then improves the residence time of the reaction in the fluidized bed. At the lower ligand flow rate, even though the ligand is present in excess, it probably quickly passes through the fluidized reactor without having enough time to react with the ore (tailings) i.e. the residence time is no enough for the reaction to occur.

The effect of that the ligand flowrate has on the extraction of the gold agrees with the trend established in the previous work on the extraction of the metal from the ore (tailings) (Mpana, 2012; Mariba, 2010). With an increase in ligand flow rate from 2 mL/min to 6 mL/min Mpana (2012) improved the extraction of aluminium from 25.7 % to 46.7 % after 360 minutes at 250 ^{0}C. This work shows a low improvement in the extraction because the concentration of the gold is low, which means that there is less limitation in the reaction due to the ligand flow rate as compared to the previous work of Van Dyk and co-workers (2010) where they had high concentrations of the metal to be extracted in the feed and there was a significant improvement in the metal extraction.

4.3. The effect of bed mass

The influence of bed mass was tested. The experimental studies were done at a constant temperature of 210 °C and a constant ligand flow of 1 mL/min. The results are presented in Figure 4-3.

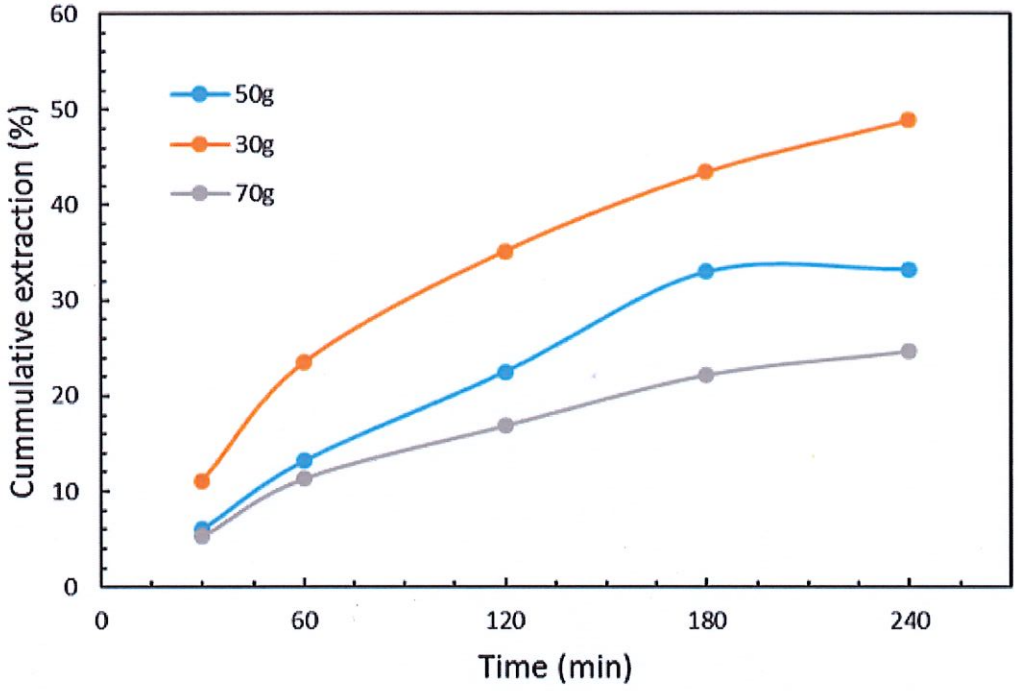


Figure 4-3: Effect of bed mass on the extraction of gold at a flow rate of 1 mL/min at a temperature of 210 °C and bed masses of 30, 50 and 70 g.

Figure 4-3 shows that bed mass has an effect on the extraction of gold in a fluidized bed. The greater the bed mass, the lower the extraction percentage of gold. At a bed mass of 70 g, only 24.5% of gold was extracted in 240 minutes. An increase in bed mass from 50 g to 70 g shows a small decrease in extraction: 33.3 % was extracted from 50 g and 24.6% was extracted from 70 g. At 30 g we see a significant increase in gold extracted over that extracted at 50 g; 48.8% of gold extracted from the tailings of 30 g in mass compared to only 33.3% extracted from 50 g. The following table show the actual mass extracted at different bed weights investigated. Despite the decrease in % extraction with the increasing size of the bed weight, the actual mass extracted increases (shown in Table 4-2).

Table 4-2: Mass extracted for different bed weight at constant temperature of 210 ^{0}C and the ligand flow rate of 1 ml/min.

Bed weight	Mass of Au extracted (mg)
30 g	0.023
50g	0.027
70g	0.028

The results follow a pattern noted by Mpana (2012) in the extraction of aluminium from fly ash. The highest extraction obtained by him was 17.1% for a bed of 30 g; only 7.9% was extracted from 70 g, both tests were ran at 220^{0}C in a stream of acetylacetone flowing at 2 mL/min.

4.4. Kinetic model

A number of reaction models have been proposed for gas-solid reactions. This work will focus on the shrinking-core model. The shrinking-core model will tested in this study with the equations from literature developed by Levenspiel (1979).

4.4.1. Shrinking core model

The rate of reaction is the change in the concentrations of reactants or products with time:

$$\text{rate} = \frac{-\text{d[reactant]}}{\text{dt}} = \frac{\text{d[product]}}{\text{dt}} \tag{4-2}$$

$$\frac{dX}{dt} = k(T)f(X) \tag{4-3}$$

where,

k (T)is the apparent rate constant which takes into account the effect of temperature.

f(X) describes the change in physical or chemical properties of the sample as the reaction proceeds.

The dependence of the rate constant, and in turn the chemical reaction, on temperature is given by the Arrhenius expression:

$$k = k_0 e^{E_a/RT} \quad (4\text{-}4)$$

Where

k_0 is a pre-exponential factor

E_a is the activation energy

R is the universal gas constant

T is the absolute temperature

A gas-solid reaction is a heterogeneous reaction that can be represented by any of the following reactions:

$$aA_{fluid} + bB_{solid} \rightarrow \text{fluid product}$$

$$\rightarrow \text{solid product}$$

$$\rightarrow \text{fluid} + \text{solid product}$$

The model development for a gas-solid reaction should be able to interpret experimental kinetics, provide indication of the rate-controlling mechanisms and predict the rate of conversion under different operating conditions (Patisson Ablitzer, 2000).

The shrinking-core model is one that is frequently applied to non-catalytic fluid-solid reactions. It is applicable to an initially non-porous particle that reacts with a reagent leaving a reacted layer around an unreacted core. Levenspiel (1979) proposed that the model mostly focused on the gas-solid reactions. The common form of the model considers three resistances that could control the rate of reaction. They are (1) diffusion of the reactant through a gas film surrounding the particle, (2) diffusion of the 'reactant' or 'product' through the product layer (or annulus), and (3) the reaction at the core-annulus interface. In this model the reaction is considered to be taking place at the surface of the solid particle which results in both fluid and solid products which may form on the surface of the particle. As the reaction is going on, the unreacted core of the particle gets smaller in size.

The general reaction equation can be represented by the following equation:

$$aA_{(g)} + bB_{(s)} \rightarrow cC_{(g)} + dD_{(s)} \quad (4\text{-}5)$$

The reaction mechanism for gas-solid reactions is as follows:

- Diffusion (through a boundary layer) of gas from the bulk gas stream to the surface of the particle
- Adsorption of the gas on the surface of the solid particles. Reaction between the gas and the solid particles takes place
- Formation of the products.
- Desorption of the products from the surface of the particles

One or more of these steps can be rate controlling. Hence can be used to develop a model that will predict how that particular chemical process will proceed with time.

The only products produced from the gas phase extraction of gold are gas (see equation 4-1). Reaction equation 4-5 will therefore be in the form

$$aA_{(g)} + bB_{(s)} \rightarrow cC_{(g)} + dD_{(g)} \tag{4-6}$$

When a chemical reaction is the controlling step the process can be modelled as

$$kt = 1 - (1 - \alpha)^{1/3} \tag{4-7}$$

When diffusion of a gas through a boundary film on the particle controls, for small particles in the Stokes regime, the process can be modelled as

$$kt = \alpha \tag{4-8}$$

And when diffusion through the solid annulus controls the rate, the process can be modelled as

$$kt = 1 - 3(1 - \alpha)^{\frac{2}{3}} + 2(1 - \alpha) \tag{4-9}$$

Where:

α is the fractional conversion of the solid.

When both chemical reaction and diffusion through the gas film controls, the overall resistance can be found by summing the two resistances as the resistances occur in series (Szekely *et al.*, 1976).

4.4.2. Modelling the extraction of gold

The gas phase extraction of gold was modelled using the shrinking core model, assuming either chemical reaction controlled or gas film diffusion controlled the rate of reaction.

4.4.2.1. Shrinking core model- chemical reaction controlling

The data from the experimental studies for the charge of 50 g and 1 mL/min at different reaction temperatures (see Figure 4-1) were used to determine the reaction constant k for a rate of reaction controlled by a chemical reaction (Equation 4-7). The plot of $1-(1-\alpha)^{1/3}$(y-axis) *vs* t (x-axis) was plotted to find the value of k (gradient of the plot). Table 4.3 shows the values of k obtained at different temperatures.

Table 4-3: Reaction rate constants at different temperatures under chemical reaction control for the shrinking-core model.

Temperature (°C)	**190**	**210**	**230**	**250**
k (min^{-1})	0.000419	0.000527	0.00108	0.00132
Correlation coefficient, R^2	0.939	0.934	0.989	0.995

The following figure shows the graph used to find the reaction rate constants (k) at different temperature (190 to 250 ^{0}C) for shrinking core model when the chemical reaction is controlling:

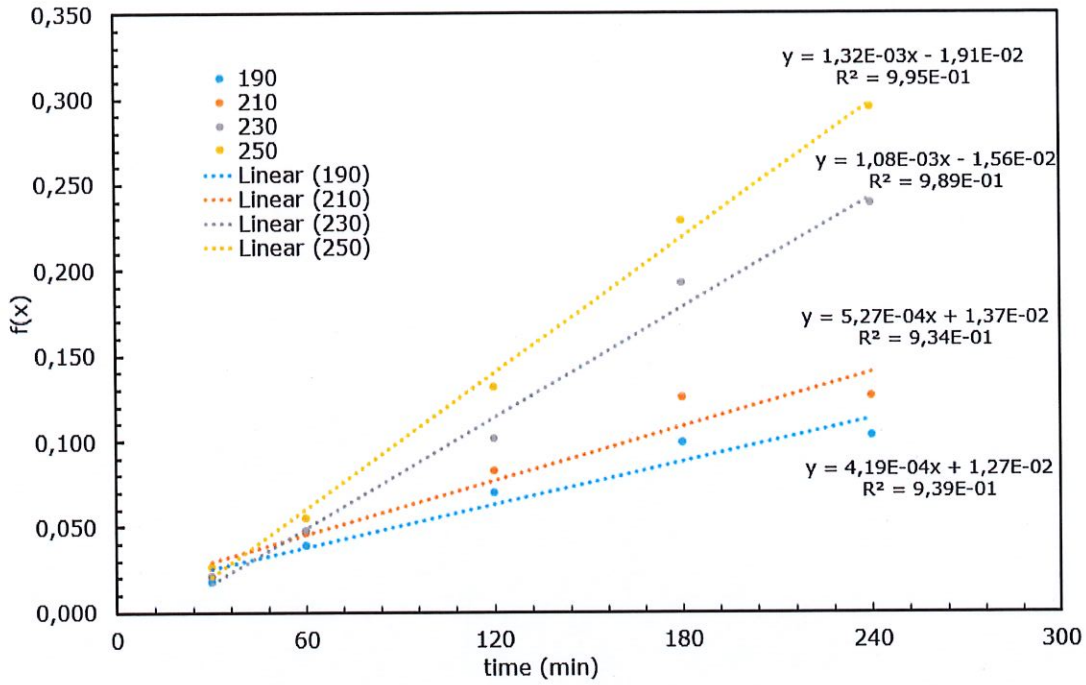


Figure 4-4: Chemical reaction control for shrinking-core model linear graphs for determining the k value.

Figure 4-5 to Figure 4-8 shows the comparison of the fitted model to the experimental data points.

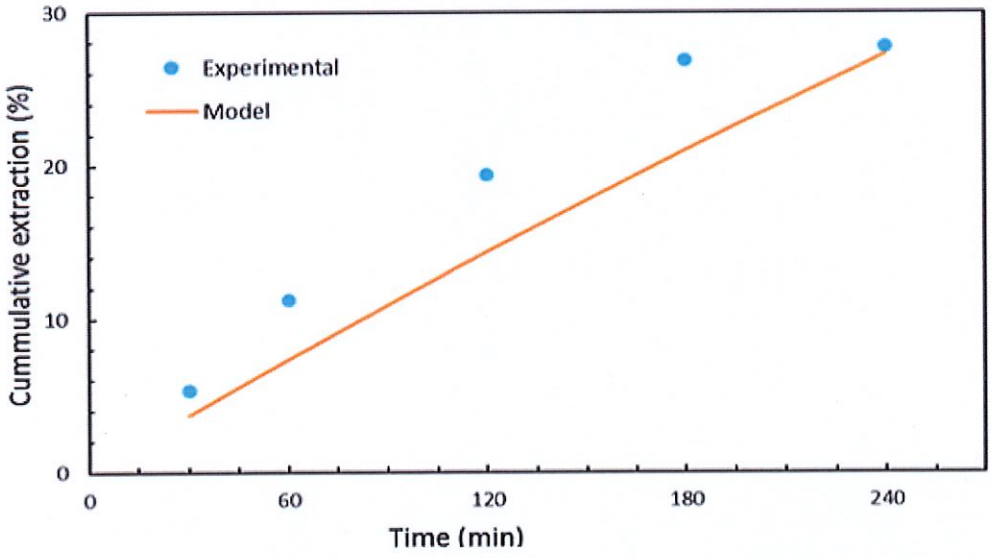


Figure 4-5: Comparison of conversion predicted by chemical reaction control model with actual data obtained at 190°C.

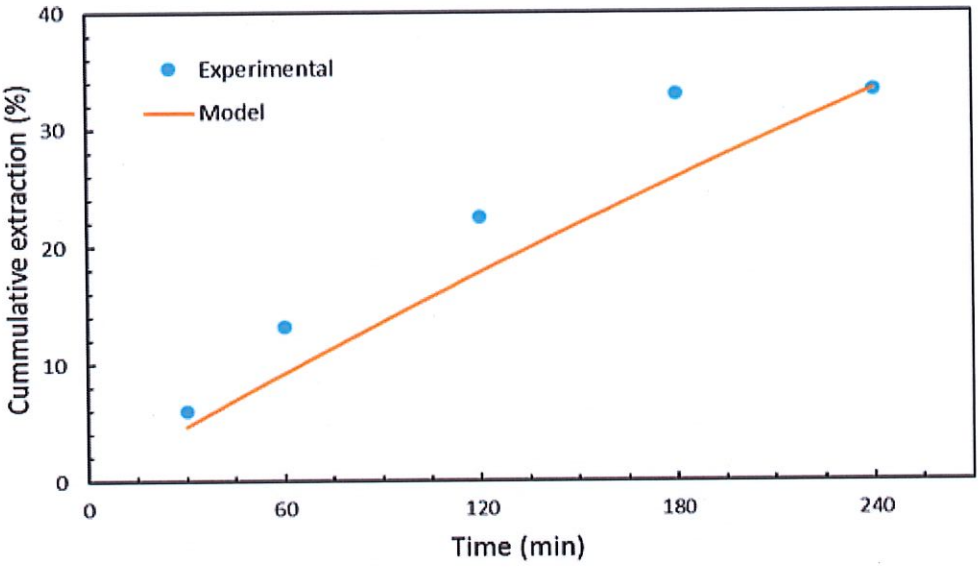


Figure 4-6: Comparison of conversion predicted by chemical reaction control model with actual data obtained at 210°C.

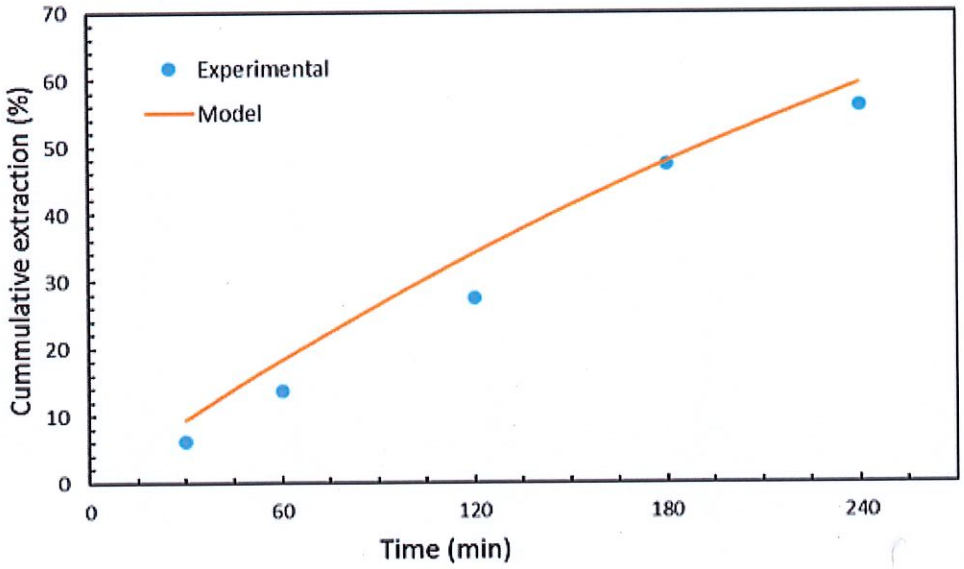


Figure 4-7: Comparison of conversion predicted by chemical reaction control model with actual data obtained at 230°C

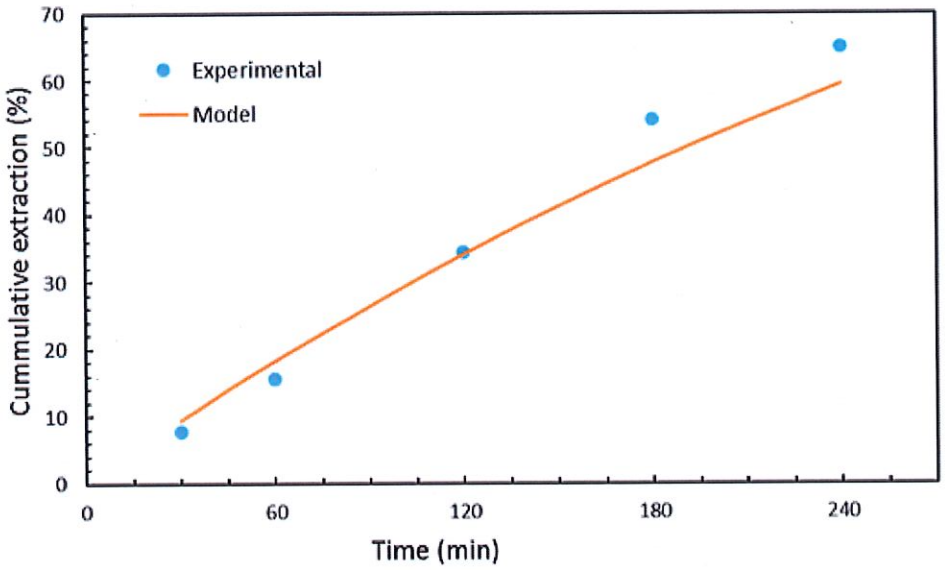


Figure 4-8: Comparison of conversion predicted by chemical reaction control model with actual data obtained at 250°C.

From Figure 4-5 and Figure 4-6 it can be seen that the extraction predicted by the shrinking core model when the chemical reaction is controlling differs from the data obtained experimentally. It is evident from the figures that the values predicted from the model are much lower than those observed experimentally at lower temperature i.e. 190°C and 210°C. For higher temperatures (230 °C and 250 °C) the chemical reaction control models appears to have a better fit compared to the lower temperatures (190 °C and 210 °C) as it can be seen in Figure 4-7 and figure 4-8.

The values of k found from the gradient of the fitted model of shrinking model with the chemical reaction controlling were used to determine the activation energy of the reaction using Equation 4-4. Figure 4-8 show the plot of $\ln k$ vs $1/T$ and it was used to calculate the activation energy.

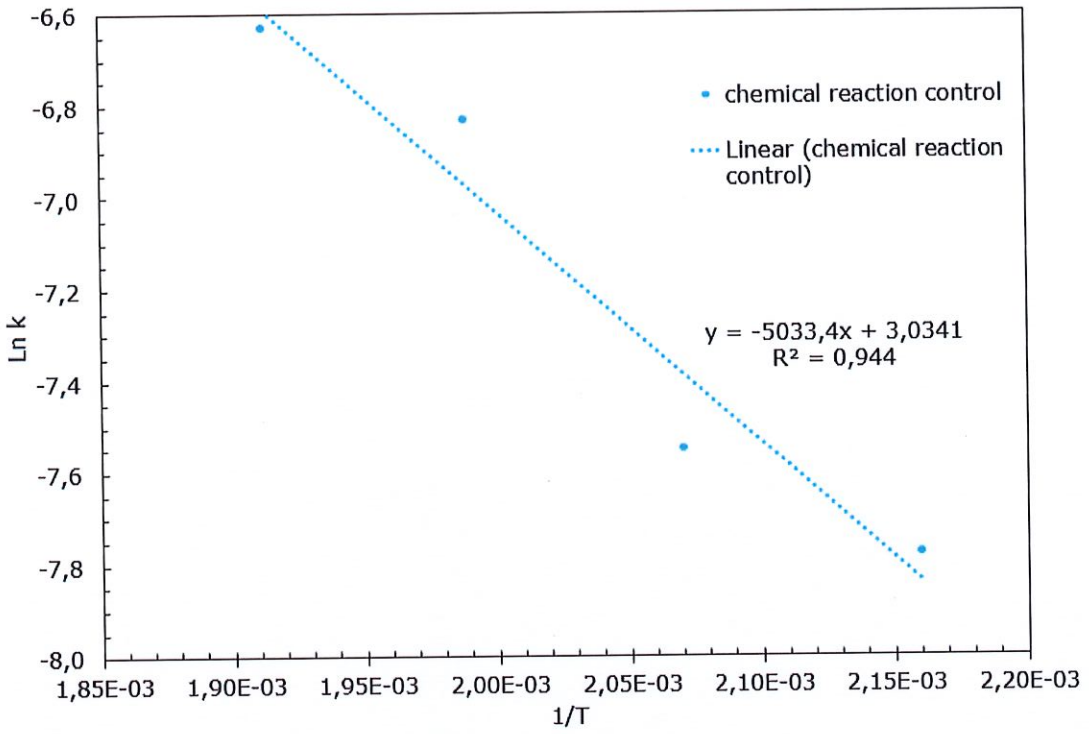


Figure 4-9: Arrhenius plot for chemical reaction control model of gold extraction by acetylacetone at a bed weight of 50 g and flowrate of 1 mL/min.

The activation energy calculated from the Arrhenius plot Figure 4-9 was found to be 41.99 kJ/mol. The activation energy of a diffusion controlled process is usually 4-12 kJ/mol, while for a chemical reaction controlled process is usually >41.84 kJ/mol, and for an intermediate process it is between 20 kJ/mol and 34 kJ/mol (Habashi, 1969). From the value found from the calculation the process is within the range of chemical reaction controlled process (Habashi, 1969; Rosenqvist 1974; Wen, 1968). The gas phase extraction of gold is dependent on temperature as depicted in Figure 4-1.

4.4.2.2. Shrinking core model- gas film diffusion controlling

The data from the experimental studies for the charge of 50 g and 1 mL/min at different reaction temperatures were used to determine the reaction constant k for a reaction rate controlled by diffusion of a gaseous species through a boundary layer on the particles (Equation 4-8). The plot of α (y-axis) vs t (x-axis) was plotted to find the values of k (gradient of the plot). Table 4-3 shows the values of k obtained at different temperatures.

Table 4-4: Reaction rate constants at different temperatures under gas film diffusion control for the shrinking core model.

Temperature (°C)	**190**	**210**	**230**	**250**
k (min^{-1})	0.00282	0.00246	0.00134	0.00110
Correlation coefficient R^2	0.932	0.928	0.988	0.991

The following figure shows the graph used to find the reaction rate constants (k) at different temperature (190 to 250 ^{0}C) for shrinking core model when gas film diffusion is controlling:

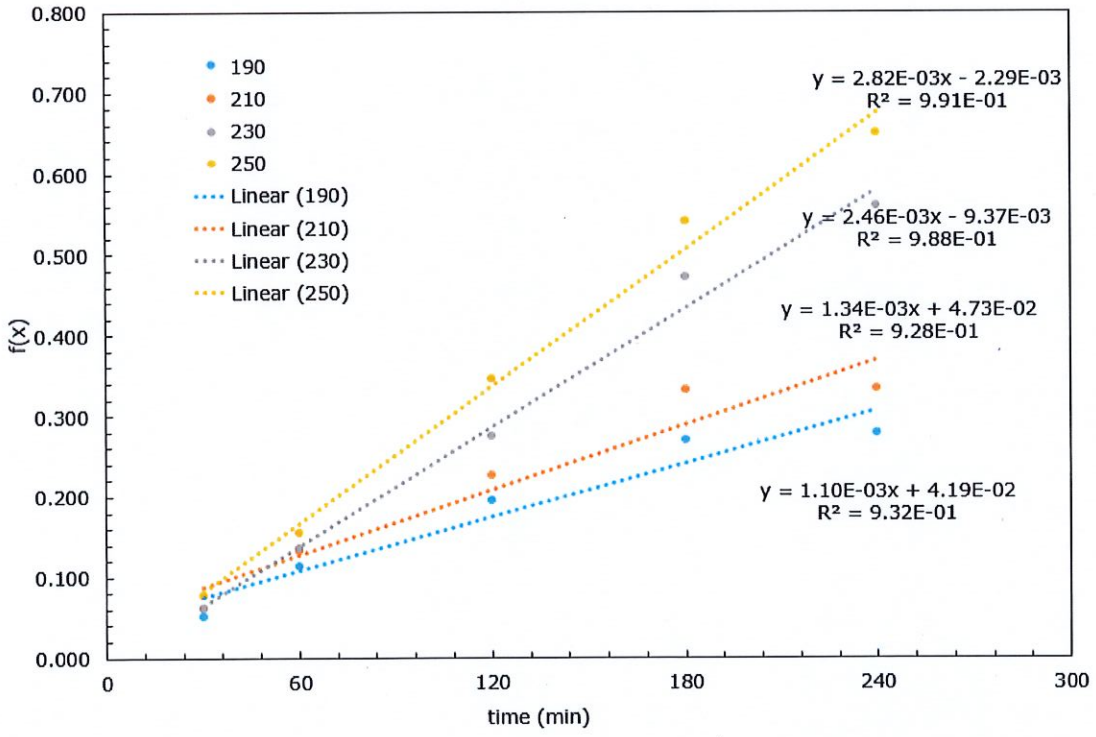


Figure 4-10: Gas diffusion control for shrinking-core model linear graphs for determining the k value.

Comparison of experimentally obtained data with the model was also done and Figure 4-11 to Figure 4-14 show the results obtained.

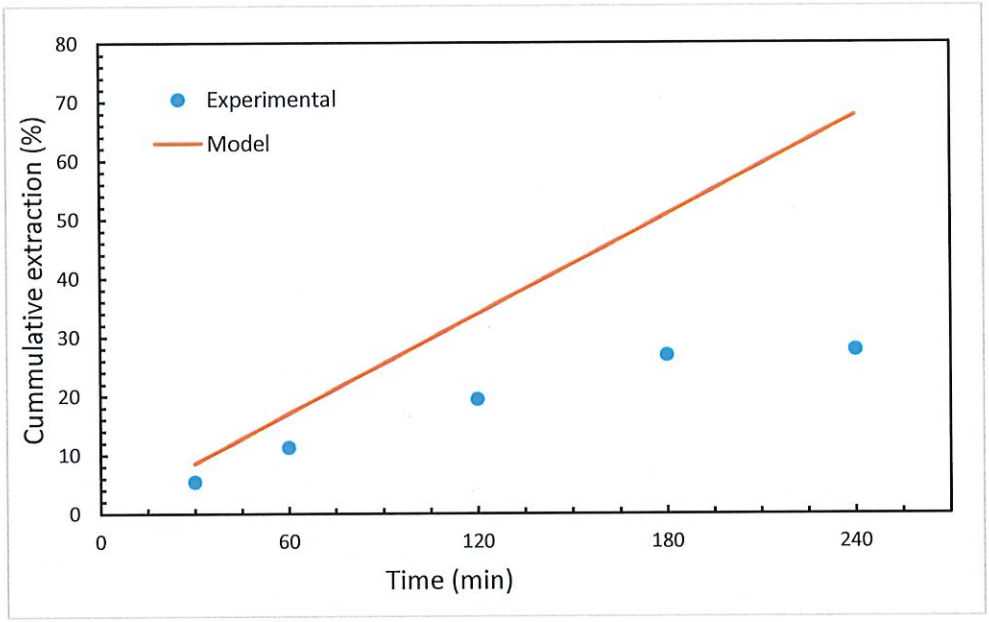


Figure 4-11: Comparison of conversion predicted by gas film diffusion control model with actual data obtained at 190°C.

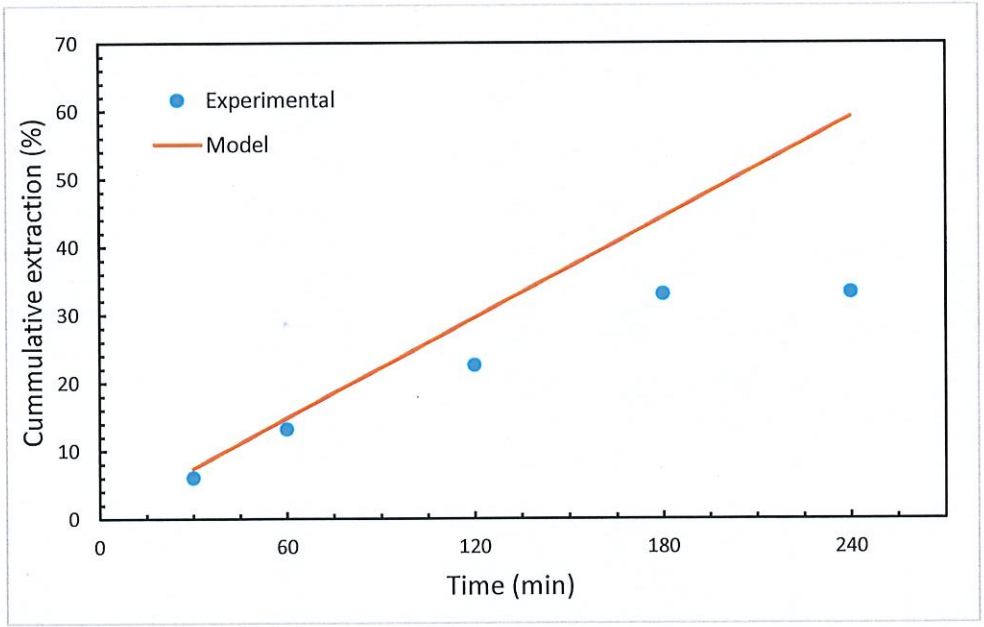


Figure 4-12: Comparison of conversion predicted by gas film diffusion control model with actual data obtained at 210°C.

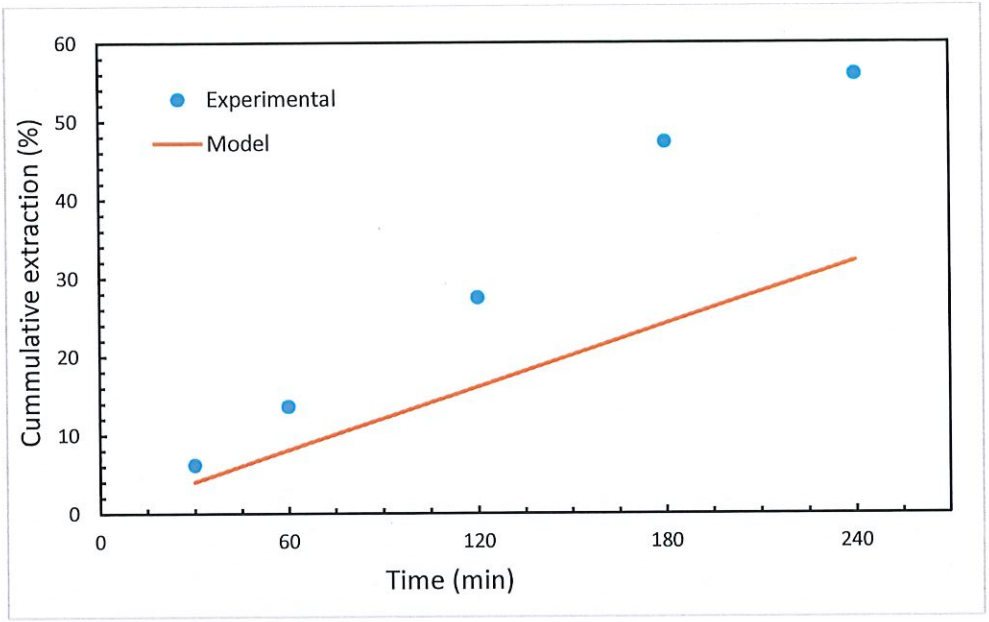


Figure 4-13: Comparison of conversion predicted by gas film diffusion control model with actual data obtained at 230°C.

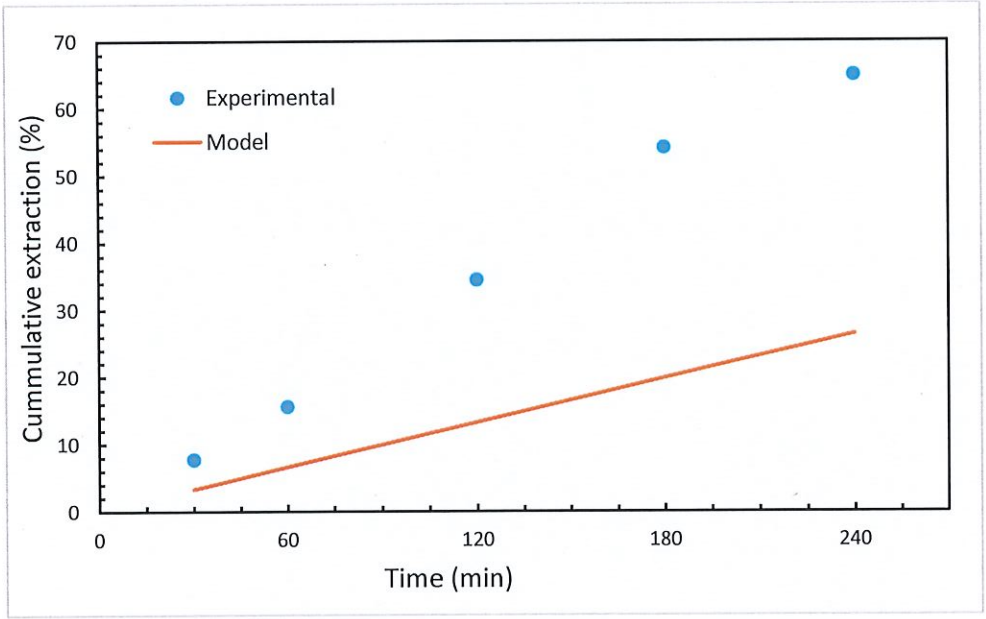


Figure 4-14: Comparison of conversion predicted by gas film diffusion control model with actual data obtained at 250°C

It can be seen from the figures even in this model, the experimental data obtained also differ significantly from the model at lower temperatures (Figure 4-11 and Figure 4-12). The gas film controlling model does not fit the data as it can be seen in Figure 4-11 to Figure 4-14. When

comparing Figure 4-13 and Figure 4-14 with Figure 4-7 and Figure 4-8, the deviation between the experimental data and the model values for the gas film diffusion controlling model is bigger as compared to the deviation when the chemical reaction is controlling. This means that at higher temperatures the chemical reaction controlling model gives a better prediction of the extraction.

Figure 4-15 depicts the Arrhenius plot for the gas film diffusion controlling model:

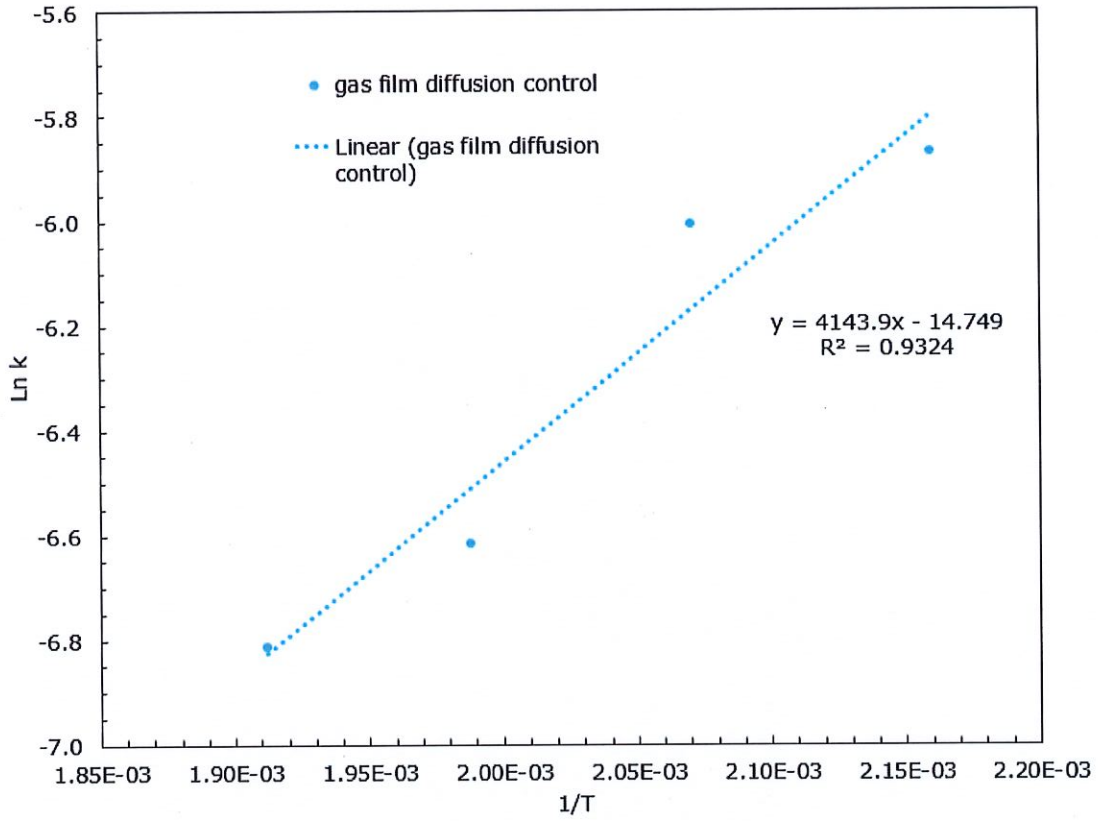


Figure 4-15: Arrhenius plot for gas film diffusion control model of gold extraction with acetylacetone in a fluidized bed with bed weight of 50g at a flow rate of 1ml/min.

The model predicts the activation energy of 34.5 kJ/mol using Figure 4-15. This activation energy is high as compared to the gas film diffusion controlled reaction proposed by Habashi (1969).

In the conditions used for modelling of the reaction, it can be said that the chemical reaction controlled process controls the process based of the activation energies obtained from the

calculation done. The kinetic modelling of the data shows that the shrinking core model under chemical reaction control can predict the extraction that fits the data, particularly at high temperatures. Therefore there is a need for a model that will take into account all the factors that may affect the reaction process.

5. CONCLUSIONS and RECOMMENDATIONS

5.1. Conclusions

The aim of this investigation was to find out if gas phase extraction process can be used to extract gold from its ore the tailings from Ergo plant. The focus of the research was to investigate the effect of time, reaction temperature, bed mass and the flow rate on the extraction of gold. The time required to obtain reasonable extraction of the metal has reduced compared to the previously reported when extracting other metals using the gas phase process. Allimann and co-workers (1999) ran their experiments for 25 hours and Hamblin & Posher (1979) carried their experiments for 8 days as compared to this work where within 4 hours of the experiments reasonable extractions of gold were attained. Gas phase extraction process was shown to be dependent on the reaction temperature where the extraction percentage increased with an increase in reaction temperature. The process also depends on the flowrate of the ligand acetylacetone, extraction increased as the flow rate of the acetylacetone increased. The results obtained also showed that the extraction process of gold also depends on the bed mass of the ore (tailings), an increase in bed mass resulted in a decrease in the extraction percentage, though the amount of the gold increased with an increase in bed mass. The data obtained was also used to model the gas phase extraction process. The process was modelled using shrinking core model where the chemical reaction controlling the process is controlling. It was found that chemical reaction control has an effect on the gas phase extraction process. Gas phase extraction is showing promise on the extraction of metals from low grade ores.

5.2. Recommendations

To have a good understanding of the gas phase extraction of gold the following recommendations are made for future studies:

- The variables tested have an effect on the extraction of gold but there is a need to do a further study on what effect the different variables have when combined to find the optimum conditions for the process.
- The effect of particle size on the rate of the reaction needs to be explored as a way forward of this process.
- The tailings sample contains a variety of metals which might also be extracted by the ligand thus consuming it. The extraction of other metals in the sample needs to be tested.

- Different ligands were identified, such as trifluoracetylacetone and hexa-fluoroacetylacetone as the potential ligands for the extraction but could not be used due to safety regulations and their availability on the market. Therefore it is suggested that a better experimental set-up which will take into account the safety regulations be implemented and find a way in which the potential ligands can be synthesised I high amounts since the process requires large amounts.
- Do the test with a fluidized bed reactor with constant feed.

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7. APPENDICES

7.1. Appendix A: Properties of the tailings sample and determining the percentage of the gold extracted

7.1.1. Properties of the tailings sample

7.1.1.1. Particle size distribution

The following table shows the data obtained from the analysis of the sample by laser diffraction from Malvern PSD analysis.

Table A-1: Data used to draw the particle size distribution (PSD) graph.

size (μm)	Volume under %	size (μm)	Volume under %	size (μm)	Volume under %	size (μm)	Volume under %	size (μm)	Volume under %
0.142	0.00	1.002	2.24	7.096	21.04	50.238	63.24	355.656	98.34
0.159	0.00	1.125	2.64	7.962	23.26	56.368	65.85	399.052	98.88
0.178	0.00	1.262	3.09	8.934	25.60	63.246	68.55	447.744	99.35
0.200	0.00	1.416	3.60	10.024	28.04	70.963	71.35	502.377	99.73
0.224	0.00	1.589	4.17	11.247	30.56	79.621	74.22	563.677	99.96
0.252	0.00	1.783	4.82	12.619	33.14	89.337	77.13	632.456	100.00
0.283	0.00	2.000	5.55	14.159	35.76	100.237	80.03	709.627	100.00
0.317	0.01	2.244	6.37	15.887	38.37	112.468	82.85	796.214	100.00
0.356	0.09	2.518	7.28	17.825	40.98	126.191	85.52	893.367	100.00
0.399	0.21	2.825	8.30	20.000	43.55	141.589	87.98	1002.374	100.00
0.448	0.36	3.170	9.43	22.440	46.09	158.866	90.19	1124.683	100.00
0.502	0.54	3.557	10.68	25.179	48.58	178.250	92.10	1261.915	100.00
0.564	0.75	3.991	12.06	28.251	51.02	200.000	93.72	1415.892	100.00
0.632	0.99	4.447	13.57	31.698	53.44	224.404	95.05	1588.656	100.00
0.710	1.26	5.024	15.22	35.566	55.44	251.785	96.13	1782.502	100.00
0.796	1.55	5.637	17.02	39.905	58.26	282.508	97.00	2000.000	100.00
0.893	1.88	6.325	18.96	44.774	60.72	316.979	97.73		

7.1.1.2. Chemical composition of the tailings sample

Table A-1 shows the chemical composition of the feed sinks and the concentrate sinks from Ergo Mine plant from which the composition of the tailings can be found.

Table A-2: Chemical composition of the Ergo feed sinks and concentrate (conc) (Dworzanowski, 2018).

Mineral	Ergo Feed Sinks	Ergo Conc Sinks
	Gold	
Free Surface	6,52	25,37
Arsenopyrite	3,62	5,19
Mixed Cu-Fe-S phase *	17,39	8,33
Pyrite	28,99	24,07
Pyrrhotite	3,26	5,19
Other Sulphides*	1,45	1,48
Microcline	0,36	2,04
Plagioclase	0,00	0,37
Quartz	6,52	5,37
Fe Silicate	0,72	2,96
Other Silicates*	11,23	12,78
Other Oxides	0,36	0,19
Rutile	8,70	0,00
U-bearing phases (Uraninite and Coffinite)	7,97	6,67
Monazite	2,90	0,00
Total	100,00	100,00

The chemical composition of the gold in the tailings can be inferred from the feed sinks (Dworzanowski, 2018).

Minimum fluidization velocity at the reactor operating conditions, where the gas fluidizing is acetylacetone.

The minimum fluidization for the process was calculated using Equation 2-15 and Equation 2-16 with the following parameters:

d_p= 7.78 μm, ρ_p=2810 kg/m^3, ρ_g=4.2372 kg/m^3, μ=0.01781 kg/ms, g=9.81 m/s^2

$$Ar = \frac{d_p^3 \rho_g (\rho_p - \rho_g) g}{\mu^2}$$

$$= \frac{(7.78*10^{-6})^3 * 4.2372(2810-4.2372)*9.81}{(17.81*10^{-6})^2}$$

$$= 0.173$$

$$Re_{p,mf} = [33.7^2 + 0.0408Ar]^{1/2} - 33.7$$

$$Re_{p,mf} = 1.0472 \times 10^{-4}$$

$$Re_{p,mf} = \frac{d_p u_{mf} \rho_g}{\mu} = 1.0472 \times 10^{-4}$$

$$u_{mf} = \frac{1.0472 \times 10^{-4} * 17.81 * 10^{-6}}{7.78 * 10^{-6} * 4.2372}$$

$$u_{mf} = 0.0000566\ m/s$$

$$u_{mf} = 0.00566\ m/s$$

The minimum flow rate to achieve u_{mf} is

$$Q = u_{mf} * A$$

$$Q = 0.00566 * \pi * \left(11.5/2\right)^2$$

$$Q = 0.588\ cm^3/s$$

$$Q = 35.27\ cm^3/min$$

It was assumed that when the ligand boils it expands so much that its flow rate into the fluidized bed column is higher than the minimum fluidization calculated above.

7.1.2. Extraction percentage of gold

The concentration of gold in the sample was determined using AAS and the initial amount of gold in the feed was found to be 1.6 ppm (mass) with the use of AAS. The concentration at time (t) was measure in mg/l and it can be represented by the following equation:

$$C_{Au}(t) = \frac{m_{Au}}{V_{collected}(t)} \quad \text{A-1}$$

Where:

m_{Au} : Mass of gold,

$V_{collected}(t)$: Volume of the extraction liquor at time t,

$C_{Au}(t)$: Concentration of gold at time t.

Equation A-1 can also be written as,

$$C_{Au}(t)V_{collected}(t) = m_{Au} \quad \text{A-2}$$

The cumulative mass of gold was calculated as follows:

$$Cum\ (m_{Au}(t_i)) = m_{Au}(t_i) + m_{Au}(t_{i-1}) \quad \text{A-3}$$

Cum : cumulative.

Cumulative gold extraction percentage was calculated using the following equation:

$$Cum\ (Au\ Ext\ \%) = \frac{Cum\ (m_{Au}(t_i))}{m_{Au\ in\ the\ feed}} * 100\% \quad \text{A-4}$$

7.2. Appendix B: Detailed experimental results

The samples were collected after 30 minutes in the first hour, thereafter hourly intervals. The following tables show the experimental results which corresponds with graphs in the results and discussions section.

7.2.1. Effect of temperature on gas phase extraction of gold

Table A-2: Percentage extraction of gold at a temperature of 190°C, flow rate of 1mL/min and a bed mass of 50g.

Time (min)	Concentration (mg/L)	Volume collected (L)	Mass of Au Extracted (mg)	Cumulative mass (mg)	Extraction %
30	0.21	0.021	0.004	0.004	5.36
60	0.21	0.023	0.005	0.009	11.25
120	0.25	0.026	0.007	0.015	19.37
180	0.24	0.025	0.006	0.021	26.87
240	0.03	0.023	0.001	0.022	27.74

Table A-3: Percentage extraction of gold at a temperature of 210°C, flow rate of 1mL/min and a bed mass of 50g.

Time (min)	Concentration (mg/L)	Volume collected (L)	Mass of Au Extracted (mg)	Cumulative mass (mg)	Extraction %
30	0.23	0.021	0.005	0.005	6.04
60	0.22	0.026	0.006	0.011	13.19
120	0.34	0.022	0.007	0.018	22.54
180	0.38	0.022	0.008	0.026	32.99
240	0.01	0.021	0.000	0.027	33.25

Table A-4: Percentage extraction of gold at a temperature of 230°C, flow rate of 1mL/min and bed mass of 50g.

Time (min)	Concentration (mg/L)	Volume collected (L)	Mass of Au Extracted (mg)	Cumulative mass (mg)	Extraction %
30	0.24	0.021	0.005	0.005	6.15
60	0.26	0.023	0.006	0.011	13.63
120	0.41	0.027	0.011	0.022	27.46
180	0.72	0.022	0.016	0.038	47.26
240	0.33	0.021	0.007	0.045	55.93

Table A-5: Percentage extraction of gold at a temperature of 250°C, flow rate of 1mL/min and a bed mass of 50g

Time (min)	Concentration (mg/L)	Volume collected (L)	Mass Au Extracted (mg)	Cumulative mass (mg)	Extraction %
30	0.28	0.022	0.006	0.006	7.70
60	0.30	0.021	0.006	0.012	15.58
120	0.52	0.029	0.015	0.028	34.43
180	0.50	0.032	0.016	0.043	54.11
240	0.42	0.021	0.009	0.052	64.88

7.2.2. Liquid phase extraction of gold

Table A-6: Percentage extraction for a liquid phase acetylacetone ligand at different temperatures.

Temperature (^{0}C)	Concentration (mg/L)	Mass of Au (mg)	Extraction %
RM (20.8)	0.003	0.0003	0.78
45	0.006	0.0006	1.81
60	0.008	0.0008	2.50
75	0.010	0.0010	3.13
95	0.019	0.0019	5.93

7.2.3. Effect of acetylacetone flow rate

Table A-7: Percentage extraction of gold at a temperature of 250°C, flow rate of 1mL/min and a bed mass of 50g.

Time (min)	Concentration (mg/L)	Volume collected (L)	Mass of Au Extracted (mg)	Cumulative mass (mg)	Extraction %
30	0.28	0.022	0.006	0.006	7.70
60	0.30	0.021	0.006	0.012	15.58
120	0.52	0.029	0.015	0.028	34.43
180	0.50	0.032	0.016	0.043	54.11
240	0.42	0.021	0.009	0.052	64.88

Table A-8: Percentage extraction of gold at a temperature of 250°C, flow rate of 3mL/min and a bed mass of 50g.

Time (min)	Concentration (mg/L)	Volume collected (L)	Mass of Au Extracted (mg)	Cumulative mass (mg)	Extraction %
30	0.25	0.025	0.006	0.006	7.81
60	0.27	0.026	0.007	0.013	16.59
120	0.54	0.033	0.018	0.031	38.86
180	0.67	0.035	0.023	0.055	68.18
240	0.05	0.032	0.002	0.056	70.18

Table A-9: Percentage extraction of gold at a temperature of 250°C, flow rate of 6mL/min and a bed mass of 50g.

Time (min)	Concentration (mg/L)	Volume collected (L)	Mass of Au Extracted (mg)	Cumulative mass (mg)	Extraction %
30	0.23	0.035	0.008	0.008	10.06
60	0.20	0.036	0.007	0.015	19.06
120	0.44	0.050	0.022	0.037	46.56
180	0.58	0.042	0.024	0.062	77.01
240	0.03	0.046	0.001	0.063	78.74

7.2.4. Effect of bed mass

Table A-10: Percentage extraction of gold at a temperature of 210°C, flow rate of 1mL/min and a bed mass of 30g.

Time (min)	Concentration (mg/L)	Volume collected (L)	Mass Au Extracted (mg)	Cumulative mass (mg)	Extraction %
30	0.26	0.021	0.005	0.005	11.10
60	0.22	0.027	0.006	0.011	23.48
120	0.20	0.028	0.006	0.017	35.15
180	0.18	0.022	0.004	0.021	43.40
240	0.10	0.026	0.003	0.023	48.81

Table A- 11: Percentage extraction of gold at a temperature of 210°C, flow rate of 1mL/min and a bed mass of 50g.

Time (min)	Concentration (mg/L)	Volume collected (L)	Mass of Au Extracted (mg)	Cumulative mass (mg)	Extraction %
30	0.23	0.021	0.005	0.005	6.04
60	0.22	0.026	0.006	0.011	13.19
120	0.34	0.022	0.007	0.018	22.54
180	0.38	0.022	0.008	0.026	32.99
240	0.01	0.021	0.000	0.027	33.25

Table A-12: Percentage extraction of gold at a temperature of 210°C, flow rate of 1mL/min and a bed mass of 70g.

Time (min)	Concentration (mg/L)	Volume collected (L)	Mass Au Extracted (mg)	Cumulative mass (mg)	Extraction %
30	0.28	0.021	0.006	0.006	5.25
60	0.26	0.026	0.007	0.013	11.29
120	0.25	0.025	0.006	0.019	16.87
180	0.22	0.027	0.006	0.025	22.17
240	0.11	0.025	0.003	0.028	24.63

7.2.5. Reaction process model for gas phase extraction

The Table A-13 and Table A-14 has the kt values calculated from equation of chemical reaction controlling and gas diffusion controlling.

Table A-13: Data used to plot the graph for determining the reaction constant k for shrinking model-chemical reaction controlling.

chemical-reaction control			
190 °C	210 °C	230 °C	250 °C
0.017	0.021	0.021	0.027
0.039	0.046	0.048	0.055
0.070	0.082	0.101	0.131
0.099	0.125	0.192	0.229
0.103	0.126	0.239	0.294

Table A-14: Data used to plot the graph for determining the reaction constant k for shrinking model-gas film diffusion controlling.

diffusion through a boundary layer			
190 °C	210 °C	230 °C	250 °C
0.051	0.062	0.062	0.078
0.113	0.133	0.136	0.156
0.194	0.226	0.274	0.345
0.269	0.331	0.472	0.541
0.278	0.332	0.559	0.649

Table A-15: Data for Arrhenius plot for shrinking model-chemical reaction controlling

	1/T	**k(1/min)**	**ln(k)**
190 °C	2.16E-03	4.19E-04	-7.78
210 °C	2.07E-03	5.27E-04	-7.55
230 °C	1.99E-03	1.08E-03	-6.83
250 °C	1.91E-03	1.32E-03	-6.63

Table A-16: Data for Arrhenius plot for shrinking model-gas film diffusion controlling

	1/T	**K (1/min)**	**ln(k)**
190 °C	2.16E-03	2.82E-03	-5.87
210 °C	2.07E-03	2.46E-03	-6.01
230 °C	1.99E-03	1.34E-03	-6.62
250 °C	1.91E-03	1.10E-03	-6.81

7.3. Appendix C: Experimental

7.3.1. Start-up and operating procedure

The following experimental procedure describes how the sample is measured at a given time interval.

- Switch on the pump pumping cooling water into the condenser.
- Switch on the heating mantle.
- Set the required reaction temperature on the temperature controller and wait for the temperatures to stabilise.
- Switch on the peristaltic pump (at required acetylacetone flow rate).
- At the end of each interval, switch off the ligand (acetylacetone) peristaltic pump.
- Collect the sample and measure the volume collected.

7.3.2. Shut-down procedure

At the end of the reaction period t_1, the peristaltic pump feeding acetylacetone into the system was switched off and all other units were allowed to run for an additional 5 minutes. This was done to ensure that the entire gaseous product was collected in the conical flask. Subsequently, the reactor heating wire and the heating mantle were switched off 3 minutes later. Following the later step, the cooling water pump was stopped, and the liquid product sample was collected. At the end of the process, the condenser was disconnected, followed by the reactor column and the evaporation flask, to allow for the collection of the residue. The liquid sample was analysed using AAS.