

## **DECLARATION**

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

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November 2015

## ABSTRACT

The recovery of cobalt from low grade copper-cobalt heterogenite oxide ores has been the focus of a great deal of research in the recent years. The recovery of cobalt from copper-cobalt oxide ore leach liquor using solvent extraction was investigated in this work. The copper cobalt oxide ore was first leached with sulphuric acid in the presence of a reducing agent namely sodium metabisulphate. The copper and iron were subsequently removed from the solution using hydroxide precipitation. Solvent extraction of cobalt from the resultant copper and iron treated solution was undertaken using Cyanex 272 in Shellsol 2325. Parameters affecting the extraction of cobalt, such as, pH, O/A ratio, temperature, and Co(II) concentration, were investigated. Results show that the extraction rate of cobalt depends on the O/A ratio and possibly the effect of chelation at certain pH ranges.

An O/A ratio of 3:1 gave the highest extraction of 73.50% at a pH of 6 and a temperature of 35°C. A negative effect of cobalt extraction was found at pH of 4 (55.04%) and pH of 5 (60.55%) respectively. Complete stripping of the metal-loaded organic was achieved at 100g/L sulphuric acid. It is concluded that the extraction of Co(II) with Cyanex 272 increases with higher equilibrium pH and high O/A phase ratio while stripping of cobalt is done at a higher acid concentration.

A 2<sup>4</sup> fractional factorial design was applied and the results were analyzed statistically. The results show that only O/A phase ratio, pH and their interaction (O/A phase, pH) influenced the %E significantly.

It was found that temperature of 25°C was favourable for separation of cobalt from loaded Cyanex while the use of 100g/L sulphuric acid as a stripping agent was found to be essential for the purpose of separation of cobalt from impurities. Furthermore, the kinetic reaction during stripping progresses very quickly, reaching equilibrium within 20 minutes.

## **PUBLICATIONS AND PRESENTATIONS**

### *Journal Publications*

1. Kyembo, D.M. and Ndlovu, S. 2015. Recovery of cobalt from copper-cobalt oxide ore leaches solutions using solvent extraction, *International Journal of Mineral*.

### *Conference Proceedings*

1. Kyembo, D.M. and Ndlovu, S., 2013. The establishment of a processing route for the recovery of cobalt from cu-co ores. SAMMRI/MMI Hydrometallurgy. Tuesday 6th August 2013. Vineyard Hotel Cape Town.

## **DEDICATION**

Dedicated to

My lovely Mother, Vicky Ntumba Kabedi for her everlasting love

## ACKNOWLEDGEMENTS

I am thankful to the Almighty God for giving me patience and courage to successfully complete the research work. I express deep gratitude towards my respected supervisor Prof. Sehliselo Ndlovu who has been a constant source of motivation and inspiration right from the beginning till the successful completion of my research work.

My special thanks to Dr. Josias van der Merwe, Prof. Vusumuzi Sibanda, Dr. John Mulopo, Dr. Simate and Mr. Kabyeza for helping, guiding and sparing me their valuable time and providing many helpful suggestions and technical support when I lagged behind certain aspects. I am also thankful to all the staff members of School of Chemical and Metallurgical Engineering who have directly or indirectly helped me during my research work.

I am indebted to my mother Vicky Kabedi, my little sister Dayana Kyembo and my niece Raissa Kabedi for their love and support during my research work. I am extremely thankful to my Mother Vicky Kabedi for encouragement and sponsoring me during my research work.

To my fiancée, thank you for your love, respect, support and encouragement towards me.

General des carriers et des mines “GCM”, a division of EMT and Kambove, are greatly thankful to acknowledge for the copper-cobalt oxide ores used in this work. I express my deep gratitude to Shell company (RSA) for the Shellsol 2325 used in this research.

Finally, special thanks to the Metals Extraction and Recovery Research Group (MERG) for team work.

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## CHAPTER ONE

### INTRODUCTION

#### 1.1 Introduction

Cobalt is a metal of high economic and strategic importance, largely because of its wide range of high performance applications and dwindling supplies. It is an important strategic metal, which is extensively utilized in modern industries. Cobalt is widely used in many industrial applications such as turbine blades for aircraft engines, hard facing alloys, as well as magnets and super alloys because of some unique properties such as ferromagnetism, varying crystal structure with temperature, as well as wear and corrosion resistance properties (Safarzaded et al., 2009a; Wang, 2006). Cobalt is mainly found in different sources such as oxide, sulfide, e-waste, dusts etc. However cobalt is mainly recovered as a co-product of copper production in Central Africa and as a by-product of hydrometallurgical nickel refining elsewhere (Pradhan and Subbaiah, 1997).

Copper mines in central Africa are currently, by far, the most important source of cobalt. Most of the rest of the world's cobalt is a by-product of nickel mining in the form of both sulfide and laterite, primarily the former at present (Boldt and Queneau, 1967; Queneau, 1971). Congo's (DRC) leading position in cobalt production is the result of ores that are the richest in the world, about 0.3 to 0.5 percent cobalt and ten times as much as copper, in the deposits now being exploited. Most of Congo's cobalt comes from open-pit mines, although there are two important underground mines. The vast majority of cobalt resources are preserved in laterite ores which are becoming the predominant source of cobalt (LIU Da-xing, 2002).

Cobalt in the form of heterogenite is commonly associated with copper bearing oxide ores. Hence it is commonly co-extracted with copper. The main oxidation states of cobalt are  $\text{Co}^{+2}$  and  $\text{Co}^{+3}$ . In solution,  $\text{Co}^{+3}$  usually form octahedral complexes, many of which can be isolated as stable salts. In acid solution,  $\text{Co}^{+2}$  is the stable form and  $\text{Co}^{+3}$  is so unstable that it is reduced rapidly and spontaneously to  $\text{Co}^{+2}$ . In order to extract cobalt with copper, a reducing environment is created for reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  as divalent cobalt is soluble at the pH values at which copper dissolution is conducted (Swartz, et al., 2009). The general trend in the development of these copper/cobalt projects is to produce an intermediate cobalt product at start-up and progress to cobalt metal production once the operation has proven to

be viable for a period. The decision not to go all the way to cobalt metal is generally due to the perceived risk associated with operating a complex cobalt refinery in central Africa.

Currently, acid pressure leaching, solvent extraction and biotechnology are the main technologies to extract cobalt from its most important natural form of cobalt oxide. Although both sulfuric acid leaching and ammonium pressure leaching can be used in industry, there are significant challenges. Sulfuric acid leaching for example consumes a lot of acid, while high-concentration sulfate wastes from the recovery process are harmful to the environment. Ammonium pressure leaching requires specialty equipment to sustain high pressure operations, leading to high capital and operating cost (Apua and Mulaba-Bafubiana, 2011; and Arslan, 2002; Gupta et al., 2003).

Cobalt occurs with copper as sulfide, currolite ( $\text{CuS} \cdot \text{Co}_2\text{S}_3$ ), which is characteristic of the cobalt sulfide mineralization of the copper-cobalt ore bodies found in the Katanga province of Congo DR and Zambia. However, in the latter country, other-bearing minerals may also be present in substantial proportions, namely cobaltiferous pyrites, which at some place may contain up to 22 percent cobalt (Dewaele, et al., 2006).

Recent estimates indicate that the bulk of known cobalt reserves (70-80%) are contained in laterite deposits. Yet, 60% of the world's cobalt production still comes from sulphidic ores. There is therefore a considerable attempt to develop the technology for the extraction of cobalt from oxide ores. In contrast to sulphidic ores, that are traditionally processed by pyrometallurgical means, there is an emerging consensus that processing of laterites is best carried out by hydrometallurgical means partly because laterites cannot be easily concentrated and because it allows the recovery of cobalt, a relatively expensive metal that is commonly associated with nickel in the ores. The use of pressure acid leaching (PAL) to dissolve the nickel and cobalt is relatively well understood and is becoming the technology of choice as the first step in the extraction process as it allows high recoveries of metals (Reid, 1996; Motteram et al., 1997).

However, the cobalt electrolyte is usually contaminated with a number of inorganic impurities either at ppm or even higher levels, leading to some cathode contamination. Since high purity cobalt is required for high technology materials, the cathodes produced from such industries are subjected to refining (Derek, and Weir, 1988) if their level of contamination is too high. The probable impurities which are associated with cobalt electrolyte are  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{Al}^{+3}$ ,  $\text{PO}_4^{-3}$  and  $\text{AsO}_4^{-3}$  etc.

These impurities, in general, have the tendency to affect the cathode quality, the current efficiency and the crystal structure of the electrodeposited cobalt. Among these impurities, zinc behaves differently. Although its redox potential is much lower than that of cobalt, it always associates with cathode cobalt. Thus, cobalt electrolyte is subjected to rigorous purification from zinc, either by precipitation (Louis, et al., 1988) or ion exchange. Removal of impurity ions from leach solution through precipitation processes is popular due to the advantages offered such as operational simplicity, low cost of precipitant, low energy consumption, selectivity, etc. However challenges that usually occur are the undesirable co-precipitation of the valuable metals. Co-precipitation invariably takes place when the ratio of impurity and the valuable metal is high. This usually occurs in leach solution produced in the processing of low grade ores

The separation of cobalt from copper, nickel and manganese is of major interest, and a number of works have been conducted on the solvent extraction in the hydrometallurgical field (Rydberg, et al., 1992). The separation of cobalt from nickel in aqueous solution has always been a problem for hydrometallurgists. Their adjacent positions in the periodic table results in aqueous chemical behavior that is too similar for the development of easy separation routes (Adekola, and Baba, 2010). A number of projects, in various stages of development, are currently underway in the DRC. The primary product for most of these projects is copper; however, cobalt is often a significant and sometimes major contributor to the project revenue. The decision to produce an intermediate cobalt product vs. metal significantly affects the processing routes employed subsequent to copper solvent extraction (SX). If an intermediate product is to be produced, then removal of iron, manganese and copper will occur with little if no emphasis placed on reducing the levels of other impurities (Swartz, et al., 2009). Production of cathode necessitates stringent impurity control in the cobalt electrolyte, which is critical in ensuring that cathode metal specifications are met. Typical impurities, other than those mentioned above, are nickel, zinc, aluminium and magnesium. The methods for removal of these are precipitation, SX and/or ion exchange (IX), and the choice of technology depends on impurity concentration, relative capital costs for removal and associated operational preferences. More recent projects are considering the production of high quality metal by EW of an SX electrolyte. The preferred solvent extraction reagent is Cyanex 272 or its analogues. The cobalt is removed from pregnant leach liquor (PLS) at elevated pH; and stripped in a very dilute acid electrolyte (Miller, G., 2008).



The *dialkyl phosphonic acid Cyanex 272* and its thio analogues extract metal ions by a cation exchange mechanism:



Where  $M^{n+}$  is an  $n$ -valent metal cation, RH is the organic acid and the subscripts 'a' and 'o' represent the organic and aqueous phases, respectively. Cytec's dialkyl phosphonic acid, Cyanex 272 and its analogues Cyanex 301 and 302 therefore extract metal ions by the extraction mechanism given above. Apart from the high Co/Ni selectivity, another key factor which distinguishes Cyanex 272 from its competitors is its ability to extract Co selectively from Ca thus eliminating the possibility of the formation of gypsum cruds on stripping cobalt from the organic phase with sulphuric acid (Douglas, 2005).

## 1.2 Problem Identification

If pure cobalt is to be electrowon, the electrolyte or leach solution needs to contain cobalt at sufficiently high concentration and be sufficiently free of elements such as copper, magnesium, zinc, iron, nickel, manganese, selenium, silver and silica that either co-deposit with cobalt or adversely affect the electrowinning of cobalt. A solvent extraction circuit can be used as a purification method to generate pure cobalt rich solution. Although the solvent extraction of cobalt using cyanex is the most studied and commercially exploitable process nowadays, there are fewer studies on recovery of cobalt in the presence of copper, calcium, nickel, magnesium and zinc.

## 1.3 Objectives

The objective of this research is to look at the feasibility of using a solvent extraction process in the purification of cobalt containing solutions arising from the leaching of low-grade Cu-Co ores from the DRC.

The specific objectives of the research will be:

- To characterise the low-grade Cu-Co ores from the DRC used in the study
- To determine the specific parameters and conditions which are suitable for the favorable solvent extraction of cobalt from the leach solutions
- To determine cobalt extraction over other impurity metals
- To characterise the process extraction kinetics

### *RESEARCH QUESTION*

Questions that need to be answered by the research study include;

- What are the characteristics of the low grade Cu-Co ores from the DRC?
- What level of operational parameters (e.g. pH, phase ratio, temperature, time, concentration of extractant) would give optimum cobalt separation?
- How selective is the extractant used during the process with respect to the impurities in the leach solution stream?

### *Research approach:*

- Characterise the low-grade copper-cobalt ores from the DRC used in the study
- Leach in sulphuric acid in the presence of a reducing agent (sodium metabisulfite) which generates leach liquor containing copper and cobalt
- Precipitate Fe and Cu from the leach stream using hydroxide precipitant “Ca(OH)<sub>2</sub>”
- Recovery and concentration cobalt by solvent extraction process

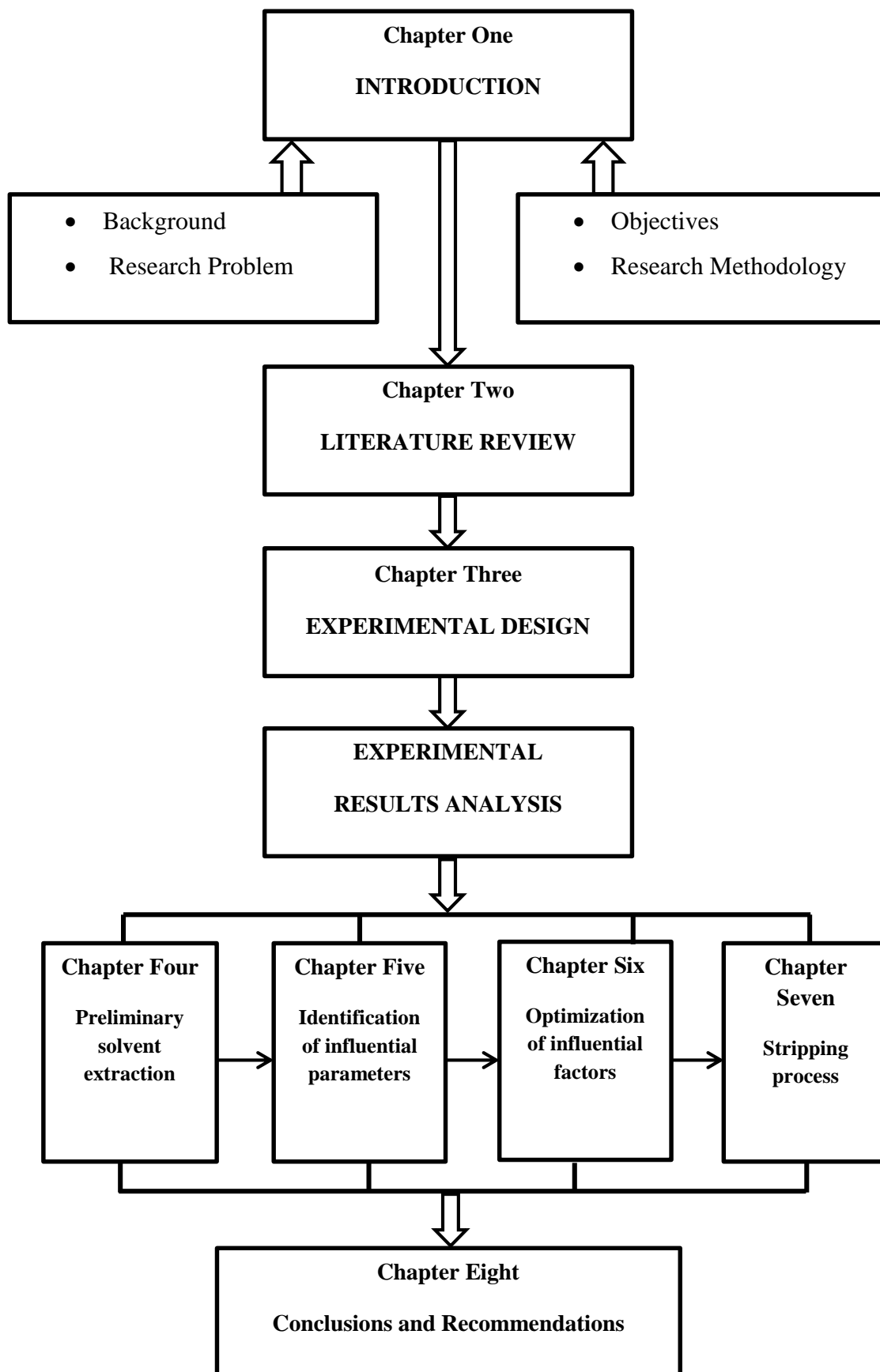
## **1.4 Research methodology**

The methodology of this study involved the following major tasks: literature review, experimental design, laboratory testing, data analysis, conclusions, and recommendations

## **1.5 Dissertation layout**

This thesis consists of eight chapters, including this chapter (Chapter One). This chapter outlines the motivation for this research, the problem statement, and the overall goals of this study. The diagram representation of the layout is summarized in the flowchart in **Figure 1.1**.

The general knowledge of cobalt oxide mineralogy and occurrence is included in the literature review (Chapter two), which include; the current metallurgical processes and the general principles of the leaching of ores. Chapter Three (experimental design) describes the materials and methods used in the study. The laboratories tests, findings and conclusions are presented in the Chapter Four through Eight. The last chapter (Chapter Nine) concludes the dissertation with a summary of the findings and recommendations.



**Figure 1.1** Dissertation layout

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 General introduction

World demand for cobalt is strongly influenced by general economic conditions and by demand from industries that consume large quantities of cobalt, such as super alloys and manufacturers of rechargeable batteries. The rapid rising demand for cobalt and the simultaneous exhaustion of high grade sulphide reserves and the difficulty associated with the processing of low grade copper-cobalt oxide ores, have created significant challenges in the cobalt supply market. Demand is growing, led by China. There are however, large deposits that have yet to be explored using modern technology, so the size of the reserves may be understated. The DRC is by far the largest current producer of cobalt, particularly in the Katanga Province of the Central African Copperbelt.

Heterogenite, which is often considered as a low grade copper-cobalt oxide ore contains several kinds of metal elements including nickel, zinc, iron, silicon, magnesium, manganese and selenium; and thus, constitutes an alternative source of cobalt.

The aim of this chapter is to describe briefly a general knowledge of cobalt oxide ore mineralogy and occurrence and old and new metallurgical processes associated with its recovery from the typical ores in industry. The typical processing route is a pure hydrometallurgical one involving comminution followed by leaching, then separation and purification and lastly electrochemical recovery. Some of the generalizations that can be made in terms of solvent extraction of cobalt as a potential purification process are discussed. In addition to these discussions, the uses of cobalt as the eventual product are also discussed.

##### *2.1.1 Cobalt:*

Cobalt (Co) is a light-grey transition and metallic element with atomic number 27, and atomic mass 58.93. It is diamagnetic like nickel, but has nearly three times the maximum permeability. Like tungsten, it has the property of adding red-hardness to cutting alloys. Its electronic configuration is  $[\text{Ar}] 4s^2 3d^7$ . Cobalt has a specific gravity of 8.756, a melting point at 1493°C, hardness 86 Brinel, and electrical conductivity of about 16% copper.

The metal has two forms, a close-packed hexagonal crystal form, which is stable below 417°C, and a cubic form stable at higher temperatures to the melting point. Cobalt is an

innocuous background material with many applications in the metallurgical industry because of its corrosion resistance (Bard et al, 1985).

Cobalt is not found as a native metal but generally in the form of minerals like cobaltite ( $\text{CoAsS}$ ), erythrite ( $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ), glaukodot,  $((\text{Co}, \text{Fe}) \text{AsS})$ , sphaero-cobalt ( $\text{CoCO}_3$ ), skutterudite  $((\text{Co}, \text{Ni}, \text{Fe}) \text{As}_3)$ , etc. Cobalt is usually not mined alone; as a matter of fact, it tends to be produced as a by-product of nickel and copper mining activities (Shedd, 2008; Shedd, 2006). Two of the largest and most well-known deposits of cobalt are European Kupferschiefer and the Central African Copperbelt. The Central African Copperbelt runs more than 500 kilometres across north-western Zambia and the south-east part of the Democratic Republic of Congo. This belt is estimated to contain six million tonnes of cobalt (Cailteaux et al, 2004). The main market of cobalt are in cutting alloys and tool steels, magnet alloys, high-permeability alloys, as a catalyst and its compounds are used as pigments and for producing many chemicals.

#### *2.1.2 Cobalt mineralogy and occurrence:*

About half of the global production of primary cobalt is extracted as a by-product from copper or nickel oxide and sulfide ores. These types of ores are all economically important. Another deposit in which cobalt occurs is heterogenite, which is a natural oxyhydroxide variety of cobalt with the following ideal chemical composition:  $\text{CoO} \cdot \text{OH}$ . Copper, nickel and manganese represent the main substitutes of cobalt, which commonly disrupt the crystallographic lattice leading to amorphous phase (Deliens, 1972). This mineral is encountered in the upper part of the oxidized horizon of copper-cobalt bearing formations of the neoproterozoic lufilian fold-and-thrust belt in the Katanga Province (Democratic Republic of Congo – DRC). Grades of cobalt in the oxide ores deposits vary widely in the range of 0.1 to 1.5% cobalt.

On the other hand, the mineralised horizons (mainly copper-cobalt sulphides) of the Roan, called “Series des Mines” occur in the southwest-northeast and extend for about 400 km (Porada, and Berhorst, 2000). The Lufilian fold-and-thrust belt is also subdivided on the metallogenic point of view into the Zambian Copperbelt where the deposits are mainly composed of sulphide primary minerals (e.g. currolite, chalcopryrite, bornite, and chalcocite) and the Katanga Copperbelt. The superficial weathering of the primary sulphides resulted in the formation of an extensive set of newly formed minerals including copper and cobalt hydroxides, oxides, silicates and carbonates (Dewaele, et al, 2006).

Cobalt minerals occur in concentrations high enough to support economic extraction in several diverse settings, all of which display very different examples of mineralisation.

The most common groups of minerals are sulphides, sulphosalts arsenides and oxides. In general, common rock-forming minerals do not contain significant amounts of cobalt. However, it can be found in economic concentrations in olivine, spinel and chlorite in lateritic and hydrothermal deposits (Natural Environment Research Council, 2009). Cobalt formation, including type and grade is controlled by geological structure, tectonism, climatic and weathering history as well as regolith landform setting and topography. The conceptual model is based on the geological setting and metallogenesis of sediment-hosted Cu–Co deposits in the Central African Copperbelt. Stratiform copper mineralisation in the Central African Copperbelt occurs in the Roan Group belonging to the Neoproterozoic Katanga Supergroup (François, 1974).

The two main ore bodies are termed the Lower and Upper ore bodies and occur around a barren or minor mineralised member called the Roches Siliceuses Cellulaire (RSC). Both main ore bodies occur in a sequence with dolomitic, sometimes chloritic shales and siltstones and stromatolitic dolomites. The shales and siltstones contain lenticular layers and nodules, pseudomorphs after anhydrite (Cailteux et al., 2005).

## **2.2. Currently Existing Copper-Cobalt Oxide Processing Methods**

On average, 70% of the world's total cobalt production is obtained through hydrometallurgical routes (Pradhan et al., 2001). At the present time economic and environmental requirements have created a need for the development of effective and inexpensive methods for the recovery of the valuable metals from primary or secondary sources (Anand et al., 1983). Cobalt can be extracted from concentrates and occasionally directly from the ore itself by hydrometallurgical and pyrometallurgical processes. Leaching and solvent extraction are the most important processes in the hydrometallurgical production of cobalt from low grade ores (Thakur and Mishra, 1998).

### **2.2.1 Pyrometallurgy**

Cobalt is often a by-product from nickel and copper smelting operations (Matousek, 1982). During the pyrometallurgical processing of cobalt bearing copper sulphide ore, cobalt is mainly accumulated in the converter slag which is subsequently processed for cobalt recovery. Reduction smelting is an efficient process for cobalt recovery from slag, which includes other valuable metal oxides. Molten slag reduction is achieved by adding solid

carbon directly (Hayes, et al., 1995). However, the recovery of cobalt can be as low as 45% and rarely exceeds 60%. The recovery depends on the distribution of cobalt between matte and discards slag in the smelting stage, and an important factor affecting this distribution is the activity coefficient of cobalt oxide in slag (Grimsey, and Liu, 1995).

Fontana, 1989, reported the solubilities of cobalt in iron silicate slags containing lime and equilibrated with Cu-Co alloys by levitation at 1623 K, and at oxygen pressures between  $10^{-7}$  and  $10^{-10}$  atm. Although no activity coefficients were calculated, the solubility of cobalt reported for slags of constant Ca/Si ratio increased with increase in Fe/Si ratio, but the effects of silica and calcia could not be isolated. Katyal and Jeffes (1988) equilibrated iron silicate and ferrite slags with liquid Co-Cu alloys at temperature between 1523 and 1623 K by the levitation technique. The activity coefficient of cobalt in silica unsaturated iron silica slag increased lightly with increase of silica content in slag. The work of Katyal and Jeffes (1988) showed that while the activity coefficient of cobalt oxide increased slightly from calcia-free iron silicate slag to 20 percent calcia in slag, it nearly doubled from 20 percent calcia in slag. Recently, hydrometallurgical processes for cobalt recovery from slag by selective leaching of metal values have been reported (Arslan 2002; Baghalha, et al, 2007).

### 2.2.2 Hydrometallurgy

The use of hydrometallurgical techniques is becoming more attractive, since there are a number of processes that are either in operation or being piloted or evaluated. The most important unit steps of hydrometallurgical process are leaching or dissolution and solvent extraction.

#### 2.2.2.1 Leaching

Several acid leaching methods of metals from oxide ores have been developed for the dissolution of valuable metals. These include, using reagents such as sulphuric acid, chloridric acid, phosphoric acid, nitric acid and many others. Due to the nature of the leaching process, most of the metals within the ore are dissolved during leaching, resulting in high acid consumption (Büyükakinci and Topkaya, 2009).

In industrial heap or vat operations, sulphuric acid is commonly used to leach copper from oxide minerals such as malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ), azurite ( $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ) and chrysocolla ( $\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) (Seo, et al., 2012). Sulphuric acid has also been used to easily leach copper from roasted Cu-Pb matte (Minic, et al., 2004). Such a leaching scheme however needs to be modified to also extract cobalt as this metal exists mainly as Co (III)

(Ferron 2006). Safarzadeh et al., (2011) proposed the well-known shrinking core model to describe the leaching of cobalt (III) from zinc residue and found that cobalt dissolved less than 10% in the sulphuric acid (pH; 1.9) at 33°C within 45 minutes.

Only when >50kg SO<sub>2</sub> /tonne ore is added can the cobalt be fully recovered within (<98%). The leaching of cobalt oxide ores can also be achieved using concentrated HCl at high temperature (Filiz et al., 2006 and Gupta et al. 2003; Shen et al., 2008). However, concentrated HCl is non-selective and results in high reagent consumptions.

The necessity to remove all leached iron results in cobalt losses and the requirement for high cost materials of construction.

Pressure sulfuric acid leaching is currently one of the preferred methods for processing limonitic laterites (Rubisov et al., 2000). Pressure acid leaching can recover >90% both nickel and cobalt at the temperature of 250-280°C, and has a high selectivity due to simultaneous dissolution of ferrous minerals and aluminiferous minerals, as well as simultaneous precipitation as hematite and hydronium alunite. However, pressure acid leaching requires high capital cost and has potential corrosion problems (Rubisov and Papangelakis, 2000; Whittington et al., 2000; Neudorf and Huggins, 2006). Atmospheric leaching, which is conducted at low temperature and under ambient pressure, has attracted attention recently because of less capital and operational cost compared to pressure acid leaching (Büyükkakinci and Topkaya, 2009).

Some of the leaching processes that have been applied include the conventional heap and tank leaching and also bioleaching.

#### 2.2.2.2 Bioleaching

This process involves leaching using the bacterial microorganisms to recover metals from ores or secondary sources. Bacterial oxidation of sulphide ores is mainly based on the action of the aerobic, acidophilic, chemolithotrophic bacteria *Thiobacillus ferrooxidans* (TF<sub>e</sub>) (Chapman and Hall, 1994). Currently the use of biotechnology in extracting valuable metals from different types of ore is an established innovative approach in the mining industry (Dwivedy and Mathur, 1995). However, biohydrometallurgical processing is often confronted with the problem of the low solubility of sulphide ores, especially the low-grade complex ones. Whichever form, the different elements which occur in low-grade complex sulphide ores are usually very difficult to process (Deveci et al., 2004; Rubio and Garcia Frutos, 2002). This



may be due to the close similarities in their mineralogical properties, which make them unsuitable for conventional methods of processing (Olubambi et al., 2006). Kasese Cobalt Company Ltd (KCCL) treats a cobaltiferous pyrite concentrate stockpiled at the Kilembe copper mine in Uganda for the recovery of cobalt, copper and nickel via a bioleaching route (Blanchard, 1995; Morin et al., 1996; Fisher and Pavlides, 1998). The bioleaching of oxide and silicate ores requires heterotrophic microorganisms that are able to produce organic acids such as citric acid, oxalic acid, gluconic acid, tartaric acid, and pyruvic acid. *Aspergillus* and *Penicillium* are the most important filamentous fungi for the extraction of metals from oxide ores (Bosecker, 1986, 1989, 1997; Franz et al., 1991; Coto et al., 2001, 2003, 2005). However, no literatures have been yet publishing on bioleaching of low grade copper-cobalt oxide ore.

#### *2.2.2.3 Heap leaching*

Heap leaching has been widely used for the extraction of the low-grade minerals, including those of copper-cobalt, nickel laterite, gold and many others (include references here). This method has many applications including the processing of non-metallic minerals such as saltpeter (Valencia et al., 2008). A number of experimental studies have been carried out (Wu et al., 2007; Yorio et al., 2006) as well as modelling (Petersen and Dixon, 2007; Leahy et al., 2007) which has allowed for better understanding of the phenomenon and its operation. In heap leaching the process appears to be a simple operation at first glance but quickly becomes complex when one considers some of the factors involved in the sub-processes. Factors, such as chemical reactions that result in dissolution of the metal from the rock, oxidation, precipitation, and other solution phase chemical reactions, need to be considered (McBride, et al., 2012).

The technique of heap leaching of copper-cobalt oxide and sulphide ores is currently being developed at the Disele Mine in Kakanda, South East of the Democratic Republic of the Congo, where it is applied to recover copper from complex malachite-atacamite ores which have mainly siliceous gangue (Lwambiye et al., 2009). The role of silica in acid leaching of the base metal ores has been investigated (Apostolidis and Distin, 1978; Kothukov et al., 1988) and it was reported that dissolution was not impeded by the formation of a silica layer on the surface of the ore particles. However, it was shown that in the case of siliceous minerals such as chrysocolla the crystallinity and permeability of the ore particles becomes an important factors in the acid leaching processes (Horlick et al., 1981). The main controlling economic factor considered in heap leaching of copper-cobalt oxide ore is acid

consumption. The ore particle size and permeability of the lixiviant due to clogging by clay or in-situ precipitation are also important factors in heap leaching as these determine the metal recovery over a given period of time (Rich, 2008). O’Gorman et al. (2004) suggested that ore particles have to be agglomerated before heap leaching in the case of high clay content or when fine crushing of the ore was necessary.

### **2.3 Separation Processes**

Iron is found in most copper-cobalt ores as an impurity which can dissolve during the leaching process. The leaching process for copper- cobalt oxide ores results in the co-dissolution metal ions such as iron, copper, cobalt, manganese, aluminium, zinc and nickel. The leach solution therefore needs to be purified before final cobalt recovery; impurities have to be removed by practicing appropriate metal ion removal techniques. Currently, the most widely used techniques for removing copper from cobalt electrolyte include precipitation, solvent extraction and ion exchange. Precipitation techniques are usually employed Dissolved metal ions in solution can be precipitated as insoluble or sparingly soluble compounds. Removal of impurity ions from leach solution through precipitation processes is popular due to the advantages offered such as operational simplicity, low cost of precipitant, low energy consumption, selectivity, etc. Most of the common heavy metal ions, Fe, Cu, Zn, and Ni etc. in metallurgical effluents can be precipitated as hydroxide, sulfides, carbonates or phosphate. Precipitation as hydroxide using sodium hydroxide or lime (calcium oxide) and sulfide (using a soluble sulfide like sodium sulfide) is most common in effluent treatment mainly for economic reasons (Ramachandra, 2005). However challenges that usually occur are the undesirable co-precipitation of the valuable metals. Co-precipitation invariably takes place when the ratio of impurity and the valuable metal is high. This usually occurs in leach solution produced in the processing of low grade ores. Boliden and Sundkvist (2002) looked at the selective precipitation processes for the recovery of base metals from bioleach solutions, as the existing iron-removal process available was not acceptable, especially with respect to zinc recovery and handling of waste products.

#### *2.3.1 Shituru processes*

The Shituru (Gécamines, DR Congo) hydrometallurgical plant was constructed in 1929 to produce copper and the production of cobalt started in 1947. At that time the plant had undergone many changes and expansions and it currently produces 140,000 tons of copper and 8,000 tons of cobalt annually. The feed to the plant consists of three different types of

concentrates: oxides, dolomitic ores and sulphide. The sulphide roasting is carried out in a fluo-solid furnace with a treatment capacity of 110 tons per day. The procedures for metallurgical extraction remain the same until today (Prasad, 1989). Cobalt oxide minerals, which are present in copper oxide ores in Gécamines concession, are leached in sulphuric acid solution with more than 90% extraction efficiency. If present in the third oxidation state (abundance of superior oxide  $\text{Co}_2\text{O}_3$ ), reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  is necessary in order to dissolve it. The common reducing agents used at the Shituru Hydrometallurgical Plant are ferrous ions which are present in solution as result of ore leaching and also from acid leaching of iron scrap and Sodium metabisulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ ) (Mwema, et al., 2002). A generic flow diagram of the current copper-cobalt recovery at the Shituru plant is presented in **Figure 2.1**.

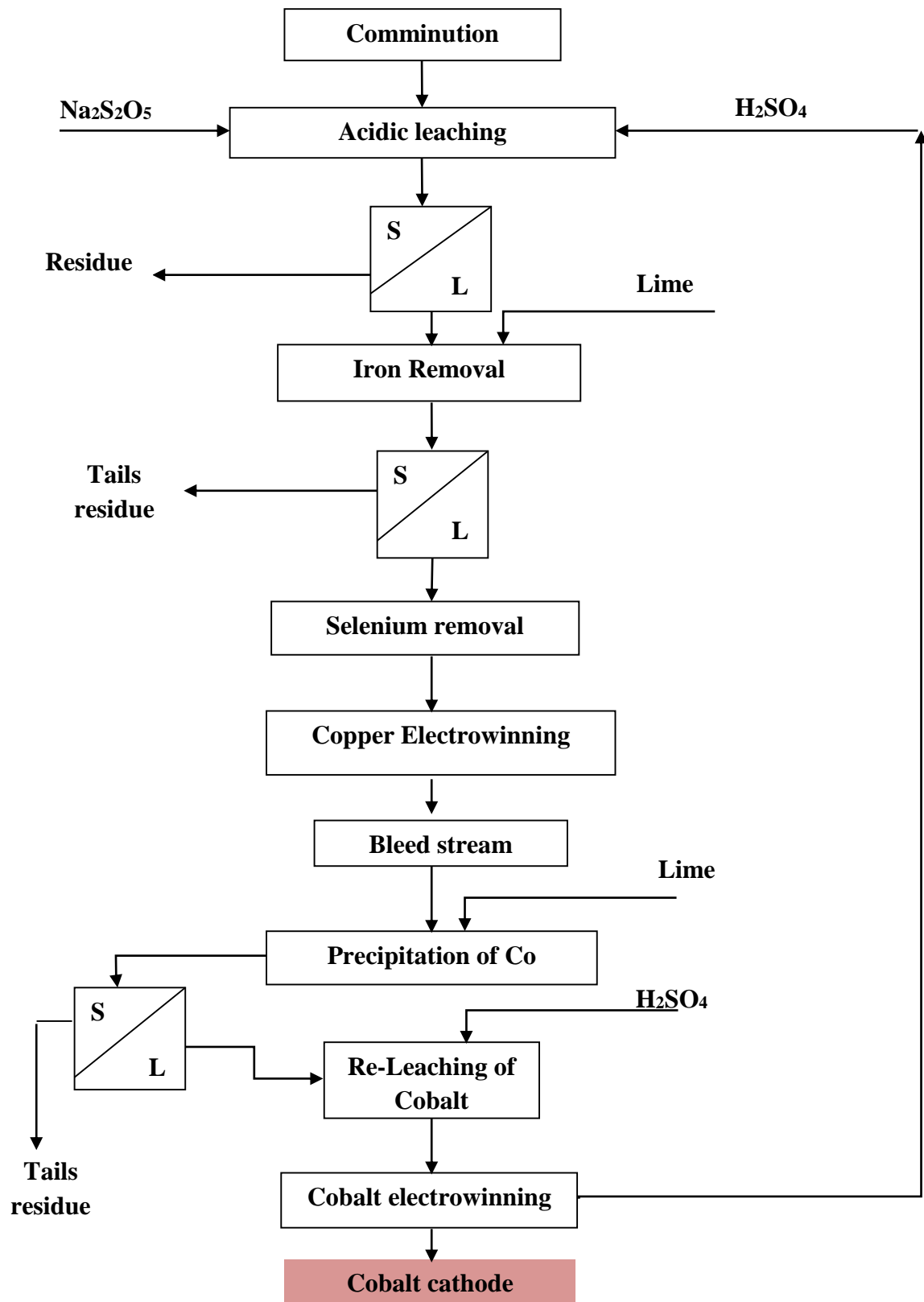


Figure 2.1 Generic Flowsheet of Copper/Cobalt Recovery at the Shituru

Cobalt rich solution is bled from the copper spent electrolyte, and undergoes selective precipitation steps to purify the solution before electrowinning. The cobalt stream is then subjected to final precipitation and re-leaching with sulphuric acid in aim to obtain a suitable cobalt concentration in the advance electrolyte.

The ore minerals occurring within the complex are in decreasing abundance. Minerals present in minor amounts include copper-cobalt oxide ores “*Heterogenite*” which is the main host of cobalt in the Katanga province. The efficiency of heterogenite found in the cited province varies according to the characteristics of the ore. For low grade ores with complex mineralogy, the properties of the gangue minerals and the presence of impurities are major factors that establish challenges at the Shituru Plant during the separation process (impurities removal) of cobalt from other impurities. However challenges that usually occur are the undesirable co-precipitation of cobalt.

The most crucial are the nature and metals content in the pregnant leach solution which depend on the composition of the material, leaching medium, its type and concentration and other leaching parameters. The composition of leach solution is diversified and differs in pH, Co(II) and other valuable metals (Zn, Ni, Mn, Fe etc.) concentration, as well as undesirable contaminants like  $\text{Fe}^{+3}$ .

Nickel, zinc and manganese have become a serious challenge since they are only removed to a minor extent by the traditional lime precipitation process. Many cobalt plants still follow this classic technique of selective precipitation as the purification method. Although this technique ensures an adequate cobalt concentration in the electrowinning circuit, some of the consequences include unwanted losses through the numerous precipitation steps, resulting in lower recoveries. One of the proposed process improvements, which aim at increasing the overall metal recoveries, includes the implementation of a solvent extraction circuit as a purification method for the cobalt rich solution (Roux, 2006).

## **2.4 Solvent extraction**

### *2.4.1 Introduction*

Solvent extraction is now a very well-established process in hydrometallurgy. It is used for the hydrometallurgical processing of copper, nickel, cobalt, zinc, uranium, molybdenum, tungsten, vanadium, rare earths such as zirconium, hafnium, niobium, tantalum, indium, gallium, germanium, the platinum group metals, purification of wet process phosphoric acid,

nitric acid recovery, etc. (Flett, 1999). Solvent extraction of metals such as copper, uranium, cobalt and nickel, besides being of great economic significance has been the spur for the development of the engineering aspects of solvent extraction (Mackenzie, 2011). Various extracting reagents have been developed to be specifically more selective for the separation of these metals.

A lot of work has been performed in the field of solvent extraction to develop extractants selective for either of these two metals. Although some of these reagents have been developed for the selective extraction of nickel (II) over cobalt (II), the more usual route has been to extract cobalt (II) leaving nickel (II) in the aqueous phase (Tsakiridis, 2004). Ritcey et al. (1996) have developed a complete process, for the Bulong project of Resolute, for the separation of cobalt and nickel in the presence of Mn and Mg. Their study proposed the use of Cyanex 272, first, to extract cobalt and manganese at pH= 4.5, leaving nickel and magnesium in the solution. Zhang et al. (1998) suggested a hydrometallurgical process for the separation and recovery of cobalt and lithium from spent lithium ion batteries. This process consists of acid leaching of lithium cobalt oxide, separation of cobalt from the leach liquor by solvent extraction, and precipitation of lithium carbonate. The selective separation of cobalt was achieved in a mixed solution of cobalt and lithium chloride by solvent extraction using PC-88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester).

#### 2.4.2 Extractants Used In Solvent Extraction

An extractant in the solvent extraction processes should be capable of forming an extractable complex of the relevant metal. The overall classes of extractants may be divided into four groups. A review of these extractants commonly used in solvent extraction, is given here in order to provide knowledge in the selection of suitable conditions during the solvent extraction process.

##### *Acidic extractant*

Acidic extractants used in solvent extraction process include the: *Carboxylic acids, Alkyl phosphoric acids, Alkylphosphonic acids, Alkyl phosphinic acids and Alkyl sulphonic acid*. The phosphonic acid groups are relatively strong and hard acids according to the Hard-Soft-Acid-Base theory, with an affinity for lanthanides and actinides and, therefore, they can form relatively stable complexes with rare-earth elements even in highly acidic media (Matulková, and Rohovec, 2005). A literature survey covering the most recent information on solvent extraction of different metals separations reveals that organophosphorus acids are the often

chosen extractants. Extractants such as di-(2-ethylhexyl)-phosphoric acid (D2EHPA) allow an efficient recovery of zinc and copper from sulphuric acid solutions of low pH (2.5-3.5) (Silva, et al., 2005).

Agatzini and Tsakiridis (1997) have studied the use of Cyanex 272 and Ionquest 801 in the simultaneous extraction of cobalt and magnesium from nickel sulphate solutions. Sumitomo Metal Mining Company (Suetsuna et al., 1980) used Versatic 10 for the extraction of cobalt and nickel from sulphate leach liquors arising from oxidizing pressure leaching of mixed sulphides. Recently, some new extractants have been developed. These have the ability to extract cobalt and nickel together at a relatively high pH, leaving behind the impurities such as manganese, magnesium and calcium (Fisher, 2011). These include Cyanex 301 and 302. In particular, Danesi et al., 1985; Preton et al., 1988 and Yuan et al., 1988, have carried out comparative studies of extraction with dialkylphosphoric, alkylphosphonic and dialkylphosphinic acids. Martinez et al., (1992) suggested that Dialkylphosphinic acid such as di (2-ethylhexyl)-phosphinic acid; dibutylphosphinic acid and dioctylphosphinic acid are very important extractants for lanthanides and these have been studied in great detail in this regard.

#### *Chelating extractants*

Metal chelates represent types of coordination compounds in which the metal ion combines with a polyfunctional base, capable of occupying two or more positions of the coordination sphere of the metal ion, to form a cyclic compound (Vladimir, 2012). Of major importance in recent years has been the introduction of acidic chelating extractants, specially designed for hydrometallurgical applications. Certain metal chelates are quite stable in solution with respect to pH, which is obviously advantageous, while others dissociate to various degrees upon dissolution, depending on the acidity or basicity of the medium. However, one can determine the nature and the concentrations of the various dissolution products since there is considerable information available concerning the stability of such complex ions (George, 1964). Recently, metal chelates have been employed in the study of the stability of lyophobic colloids (Kolak., 1968; Catone, David., 1975).

Although chelating extractants have been used in analytical and inorganic chemistry in the past, they have been too expensive for use on industrial scale (Daxayani, 2010). The most common chelating extractants used in solvent extraction are *hydroxyoximes* *Beta diketones* and *Hydroxamic acids*. Recently, the range of chelating extractants has been extended by the

introduction of reagents from Shell, SME-529 (2-hydroxy 5-nonyl acetophenone oxime) and Acorga, who market P-17 (2-hydroxy 5-nonyl benzoylphenone oxime) as well as P-1 (2-hydroxy 5-nonyl benzaldehyde oxime). Nyman and Hummelstedt (1974), have studied the extraction of nickel and cobalt from acidic media using hydroxyoximes and published a flow sheet based upon a mixture of LIX-70, Versatic 911 and Dinonylnaphtalenesulphonic acid.

Flett and West, (1971), investigated the extraction of nickel at low pH by mixture of LIX-63 and carboxylic acids and thereafter reported very slow stripping kinetics, a phenomenon studied further by Flett, et al., (1974). The use of sulfonic acid as a modifier for LIX-63 was first proposed by AMAX researchers and this extraction system was extensively studied later on by Osseo-Assare and his co-workers, (1980 and 1984). However, it was found that the degradation of hydroxyoximes by sulfonic acid makes these extraction systems impractical (Oliver, and Ettel, 1976).

#### *Basic extractants*

Basic extractants are also known as “*amines*”. There are four types of amines with different molecular structures, i.e. primary, secondary, tertiary and quaternary amines the extraction system of amines has a higher extraction yield and better selectivity when extracting iron. Compared with phosphates, amine systems with iron are easier to strip (Chen et al., 1992; Luo et al., 2004; Lupi and Pilone, 2000; Sun and O’keefe, 2002; Zhao et al., 1998). However, when amines are used as extractants, the third phase will usually appear in the extraction process.

In general, metals are favourably extracted by amine solvents from aqueous media in which the metals form anionic complexes with the acid ligands. In chloride medium the anionic complex formed by cobalt enables extraction with tertiary amines and excellent separation from nickel that forms a neutral chloride complex. In sulfate media dialkylphosphorous extractants are used with cobalt-over nickel selectivity improving with increasing basicity of the ligand.

#### *Solvent extraction by solvation*

Solvation occurs when a solute is dissolved in solvent and has come to be seen as a crucial and fundamental feature in determining the behaviour and properties of solutes and of the solution itself (Libo et al., 2007).



The well-known example generally cited in this class is the extraction of Fe (III) in diethyl ether from HCl medium. The extraction of Fe (III) in ethyl ether from strong hydrochloric acid solution was reported by Rothe way back in 1892. Since then, several efforts have been made to identify the extracting Fe (III) species. The coordination chemistry of iron (II) and iron (III) includes a wide variety of possibilities, where the regular octahedral arrangement normally is the preferred configuration (Greenwood, 1997; Huheet, et al., 1993). The octahedral structure is the preferred one as long as six solvent molecules or ligands can be clustered and bound without steric hindrance. This means that the iron (II) and iron (III) ions form the expected six-coordinated octahedral solvate complexes with water, dimethylsulfoxide and other non-space demanding solvents in both solution and solid state (Vladimir, 2012).

#### 2.4.3 Solvent extraction by synergism

The term *synergism* has a well-established usage in the field of solvent extraction of metals. It is defined as the enhancement of the extraction of a metal/ligand complex by the addition of a second donor molecule to the system. The word *synergism* literally means working together. In fact, the two extractants work together to increase the extraction by a huge factor.

In sulphate solutions containing Co(II) and Ni(II), small amounts of Ca(II) and Mg(II) can also be present. During Co(II) and Ni(II) extraction with Cyanex 272, Mg(II) and Ca(II) are co-extracted to organic phase. Cobalt (II) and nickel (II) re-extraction with spent electrolytes causes precipitation of relatively sparingly soluble calcium sulphate and contamination of these electrolytes with calcium and magnesium. To prevent this situation, 2-methyl-2-ethylheptane acid (Versatic 10) with the addition of tributylphosphate (TBP) was suggested for Ni(II) and Co(II) extraction from almost neutral (pH=6.5) sulphatic solutions containing calcium and magnesium (Apostoluk, 2005).

The synergistic extraction of nickel and cobalt with a mixture of D2EHPA and LIX 860 (5-dodecyl salicylaldoxime) was investigated by Zhang et al (2001). The  $\Delta pH_{50}$  differences in the absence and presence of LIX 860 for nickel and cobalt were found to be 1.49 and 0.89, respectively, indicating large synergistic shifts for both metals. The times to obtain stripping equilibria for nickel and cobalt with 0.25 M  $H_2SO_4$  were 10 and 3 min at  $25 \pm 2^\circ C$ , respectively. Separation of cobalt from nickel was found to be possible based on their fast and slow stripping kinetics, respectively.

A synergistic solvent extraction (SSX) system consisting of LIX63, Versatic 10 and TBP has been developed to separate nickel and cobalt from manganese, magnesium and calcium in sulfuric acid leach solutions (Cheng, 2006; Cheng and Urbani, 2005; Cheng et al., 2010a,b ). In the system, LIX63 and Versatic 10 play roles of extractant and synergist, while TBP is added to improve the stripping kinetics of nickel. A mixed extractant system was developed to separate copper, zinc, and iron from nickel and cobalt with CYANEX 272 and LIX 84. Cheng, et al., 2005 and Zhang, et al., 2008 compared with the organic system containing 17% (v/v) CYANEX 272 alone at 55°C with an A:O ratio of 5:1, the addition of 15% v/v LIX 84 resulted in about 3.5  $\text{pH}_{50}$  shift for copper and no observable effect on the  $\text{pH}_{50}$  of iron and zinc.

In the past, much attention has been drawn to the use of combinations of different extractants to improve the extraction of Co (II), Ni (II) and other metal ions. Improved extraction of divalent transition metal ions was found with mixtures of an oxime of aliphatic aldehydes and an organophosphoric acid (Preston, 1983), the enhancements of extraction increasing in the order Fe (II) < Co (II) < Cu (II) < Ni (II). The synergism was greater for nickel extraction and the selectivity of cobalt over nickel shown by an organophosphoric acid alone such as D<sub>2</sub>EHPA (di (2-ethylhexyl) phosphoric acid) was reversed (Groves and Redden, 1990, Redden and Groves, 1993 and Preston, 1983).

Recently the synergistic effect in the solvent extraction has been appreciated as a weighty problem, and many valuable investigations have been performed especially in the system of metal- $\beta$ -diketone-some organophosphorus compounds (Dyrssen, and Kuca, 1960; Newman, and Kotlz, 1963). The mechanism of the synergism was understood as the adduct formation between metal  $\beta$ -diketonate and neutral ligand, and the stability constants of several adduct were also obtained (Sekine, and Dyrssen, 1964; Li et al., 1965).

#### *2.4.4 Third Phase Formation*

A problem faced in solvent extraction is the formation of a third phase. This happens due to solubility issues in the organic phase. The third phase normally occurs during the phase separation stage, a third phase forms between the aqueous and organic interface (which has an intermediate density between the aqueous and organic phase). This phase is primarily an organometallic complex-rich phase. Above this phase forms an organic phase that is rich in the diluent. Regularly an increase in temperature or extractant concentration causes the third phase to disappear and a third phase modifier is not necessary. According to the literature,

different conclusions have been drawn concerning third phase separation problems and third phase formation (Foust et al., 2008):

- Suspended solids often result in phase separation problems.
- Overloading of the ligand/extractant can result in third phase formation.
- Third phase formation is temperature dependent. Increasing the temperature usually causes the third phase to disappear since the organic-aqueous solubility decreases as temperature increases.
- Third phase formation is more common with aliphatic diluents.
- Addition of a third phase modifier can help to overcome the formation of a third phase.

Typical third phase modifiers include isodecanol, 2-ethylhexanol, p-nonyl phenol and TBP (tri-n- butylphosphate). Most researchers use TBP as third phase modifier adding it between 2-5 volume percent to the organic phase (Rodrigues and Mansur, 2009; Reddy et al., 2006; Swain et al., 2006; Tsakiridis and Agatzini-Leonardou, 2004; Sarangi et al., 1999b; Devi et al., 1998).

#### *2.4.5 Diluent Use in Solvent Extraction*

Various diluents exist, both aromatic and aliphatic, and they range from straightforward molecules to complex mixtures. Diluents typically consist of a mixture of naphthenic, paraffinic and aromatic hydrocarbons. The commercial use of the diluents is often restricted due to environmental issues or economic considerations. Most oil companies have developed a range of diluents for commercial application in hydrometallurgy. Some of these companies include Exxon, which produces the Escaid range of diluents (Escaid 100, Escaid 110, and Escaid 350) Shell and Chevron with their range of diluents “ Shellsol D series” (Foust et al., 2008). However, paraffin remains as one of the cheapest and widely used diluent on an industrial scale. Gandhi *et al.* (1993) considered various diluents agents on extraction of cobalt with Cyanex 272 solutions as shown in **Table 2.1**.

**Table 2.1 Effect of various diluents on extraction of cobalt (0.0025g/l) with Cyanex 272 (0.005M) at a pH of 8 (adapted from (Gandhi et al., 1993))**

<b>Diluents</b>	<b>% Extraction</b>
n-hexane	<b>60.8</b>
Carbon tetrachloride	<b>99.9</b>
Cyclohexane	<b>20</b>
Benzene	<b>99.9</b>
Toluene	<b>99.9</b>
Xylene	<b>99.9</b>
Chloroform	<b>99.9</b>
Dichloromethane	<b>98.3</b>
1,2 dichloroethane	<b>77.5</b>
Nitrobenzene	<b>56.5</b>

Gandhi et al. (1993) investigated some of the straightforward molecules most often used on laboratory scale as diluents for Cyanex 272 by extracting cobalt. It has become quite apparent that the diluents are not as inert as they might appear to be. The mechanism of their structure is quite complex. In some instances, a decrease in extraction of metal with the polar nature of diluent has been reported (Vladimir, 2012). Diluents may have a significant influence on the extracting behaviour of the extractant this is investigated by several interactions that may exist between diluents and extractants. Some of these interactions include dipole-dipole interaction, pi-electron interaction, hydrogen bonding and cavity formation. Some diluents also assist in the polymerization of the extractant. This will affect the cation exchange process, making the hydrogen atom on the extractant less free to react (Mohapatra et al., 2007).

The interaction between diluents and extractants is poorly understood; hence a diluent is usually selected based on experimental data (Foust et al., 2008).

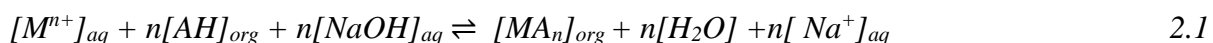
## **2.5 Solvent extraction of cobalt**

Separation of metals such as Fe, Co, Ni, Cu and Zn has been a problem in hydrometallurgy due to their close proximity in transitional metal series from the periodic table. All these metals exist as divalent hexahydrated ions in sulphuric acid. The separation of cobalt and nickel has traditionally presented problems due to their similar chemical and physical properties. However, small differences in chemical behavior do exist between cobalt and nickel, thus complex formation often proceeds much more readily with cobalt than nickel ion (Flett, 2005). Further the development of alkyl phosphoric acid based compounds such as

phosphoric (D2EHPA,  $pK_a = 1.72$ ), phosphinic (PC88A,  $pK_a = 3.42$ ) and phosphonic (Cyanex 272,  $pK_a = 6.37$ ) acids revolutionized the separation of cobalt from nickel from sulphate based solutions (Douglas, 1987). The separation factors for alkyl phosphoric acids are in the tens, for alkyl phosphonics are in the hundreds while alkyl phosphinics are in the thousands. This remarkable variation in separation factor is due to a change in the nature of the cobalt complex organic phase, whereby with increasing temperature and cobalt concentration, the pink hydrated octahedral complex changes into the blue anhydrous tetrahedral polymeric species with a consequent increase in distribution coefficient (Ramchandra, et al., 2009).

The extraction achieved with cyanex 272 is highly dependent on pH, with higher extraction typically being achieved as the pH is increased. This pH dependence on the extraction allows separation of metal ions in the solution, since the pH at which dissolved metals are extracted from the aqueous phase to the organic phase depends on the type of metal under consideration. Metal ions that have a higher tendency to exchange for hydrogen ions can be extracted at lower pH values than metal ions with a lower tendency to replace hydrogen ions in the organic phase (Oliver, et al., 2012). The majority of solvent extraction processes therefore use a base like sodium hydroxide (NaOH) to control the pH, which results in addition of sodium to a purified process solution (Nogueira et al., 2009).

The following are some of the possible reactions that can take place when NaOH is applied



Since cobalt and iron are extracted at different pH values, it is believed that separation of these two species by selective stripping would be possible. A weak acid would be used in the first stripping stage to remove cobalt from the organic phase, followed by a second stripping stage utilising a stronger acid to strip iron. Flett (2005) reported that cobalt can selectively be stripped from co-extracted iron or zinc with 150g/l  $H_2SO_4$  in Cyanex 272.

*Solvent Extraction of cobalt from sulphate media*

Until recently, almost all commercialised leaching processes for sulphides and oxide ores, such as nickel sulphide and laterite ores, containing nickel, cobalt, zinc and copper, have been operated in sulphate systems (Zhu, et al, 2012). Many studies published on the solvent extraction of different metals have involved sulphate media. A survey of literature has indicated the cobalt-nickel separation from sulphate media using phosphoric, phosphinic and phosphonic acids (Sarangi, et al, 1999). The separation ability of cobalt-nickel increases in this order; phosphinic > phosphonic > phosphoric acid due to the increasing stabilization of tetrahedral coordination compound of cobalt with the extractant in organic phase, this is because the tetrahedral compound is more stable than the octahedral one.

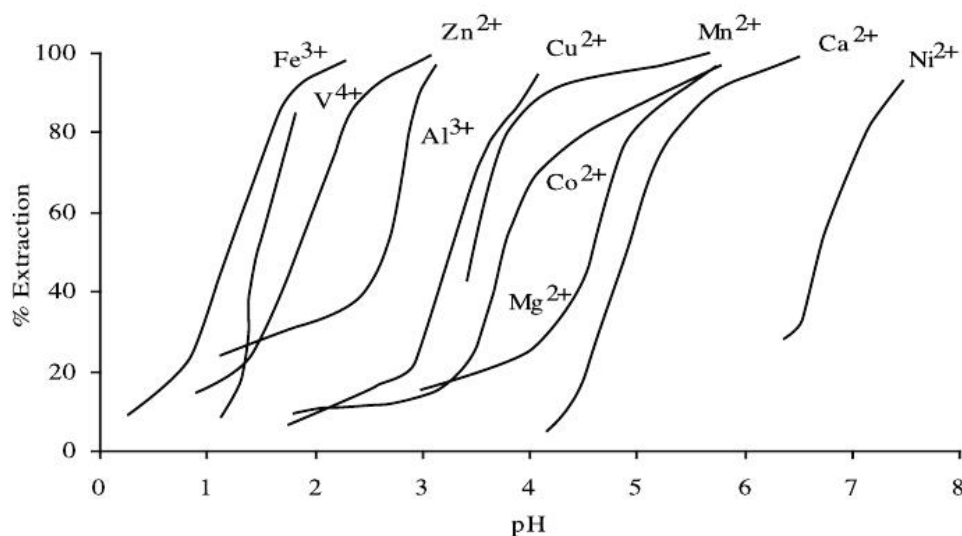
Recently, PC-88A has been reported to be rather effective in separating cobalt from nickel in sulphate media. Devi et al., (1998) studied the cobalt-nickel separation effects of D2EHPA, PC-88A and cyanex 272 from sulfate solution containing 0.01mol/L metal ions each and 0.1 mol/L Na<sub>2</sub>SO<sub>4</sub>. In the case of extractions with 0.05mol/L Na-PC88A, the separation factor can reach over 1000 at equilibrium pH range of 5.75 - 6.2.

**2.6 Factors influencing solvent extraction**

According to literature, the effectiveness of an extractant depends upon a number of variables. On a broader basis, these parameters can be grouped under the category of aqueous and organic phase parameters.

*Solution pH:*

pH is an extremely major parameter for the effective operation of a solvent extraction process. It should be noted that the optimum pH range for the process depends on a variety of metals that can be extracted by the reagent. Ni, Co and Fe are typically extracted from sulphate solutions in the pH ranges 7–8, 5–6 and 2–3, respectively, with Cyanex 272 (Habashi, 1999). This indicates that, of these metals, Fe has the highest tendency to report to the organic phase, while Ni has the highest tendency to remain in the aqueous phase as shown in the **Figure 2.2**.



**Figure 2.2 Extraction of Metals by Cyanex 272 Extractant from Sulfate solution**

The published pH dependence of extraction of different metal species from sulphate solutions with Cyanex 272 (Habashi, 1999) also allows the qualitative prediction of the solvent extraction behaviour of trace amounts of dissolved metals other than Ni, Co, and Fe that might be present in the Ni sulphate leach solution. Zn and Cu, for example, are both extracted at pH values between that of Fe and Co, with copper expected to follow cobalt in the extraction circuit, while Zn will behave similarly to the dissolved Fe. Precise pH control is also necessary to limit the co-extraction of impurities such as Ca and Mg in the case of Co extraction using Cyanex 272.

Recently, different authors have studied the separation of cobalt (II) from sulphate solution by proposing pH ranges according to the extractant used. Devi et al. (2000) examined D2EHPA, PC 88A and Cyanex 272 in order to separate cobalt from manganese in sulfate solutions. His study proposed the use of 0.05 M NaD2EHPA to extract  $\text{Mn}^{2+}$  from  $\text{Co}^{2+}$  at pH = 4.45.

Ritcey and Lucas (1974) have used 0.5 M Kelex 100 with 10% isodecanol in Solvesso 150 in order to determine the preferential extraction of Cu, Fe (III), Ni, Zn, Co, Fe (II), Mn, Ca and Mg from their acidic solution, in the pH range 0.5–6.0. Hoh et al. (1984) studied the extraction of manganese and cobalt in sulfate solutions by di-(-2-ethylhexyl) phosphoric acid (D2EHPA) and determined the optimum pH values at 4.2 and 2.0, respectively.

Dhadke and Ajgaonkar (1996) have quantitatively extracted manganese and cobalt from sulfate solutions using Cyanex 302 in toluene. Co (II) was extracted in the pH range 7.0–7.5 whereas Mn (II) was extracted in the range 8.5–9.5. For most commercially available extractants like phosphonic and phosphinic acids, hydroxyoximes and  $\beta$ -diketones, cobalt is found extracted preferentially over nickel from the aqueous phase at an equilibrium pH of 4 to 6. This relatively high pH range is necessitated by the base properties of these oxygen-donors, and is not effective for recovery of these metals in a highly acidic medium of pH 4. These commercial O-donor extractants also have high affinity for hard ions, such as ferric ions, which necessitates the precipitation of iron(III) ions prior to the extraction of nickel(II) or cobalt(II) ions in these systems (Feather et al., 2002).

#### *Temperature:*

Temperature is the most significant parameter used in accelerated solvent extraction. As the temperature is increased, the viscosity of the solvent is reduced, thereby increasing its ability to wet the matrix and solubilize the target analytes. The added thermal energy also assists in breaking analyte matrix bonds and encourages analyte diffusion to the matrix surface.

In recent years much work has been carried out on the examination of the various factors affecting the solvent extraction of different metals, but only a few studies have been reported concerning the effect of temperature. A change in temperature is accompanied by changes in all the parameters affecting the extraction process, and these changes may be highly variable. It is known that temperature has an influence on the structure of metal complexes formed. For instance cobalt separation from nickel with Cyanex 272 and especially with D2EHPA is affected by temperature due to the different coordination chemistries between the metal ions and organic ligands. Cobalt forms both octahedral and tetrahedral complexes with two dimerised phosphorus acid molecules. The stability of the more hydrophilic octahedral Co complex decreases at temperatures above 40 °C and the complex shifts to the more lipophilic tetrahedral complex. This leads to much better separation from nickel since nickel forms only octahedral complexes with three dimerised phosphoric acid molecules (Preston, 1982; Rickelton et al., 1984).

Darvishi *et al.* (2005) found that the extraction of cobalt (5 g/l) and nickel (5 g/l) from aqueous solutions is endothermic when using mixtures of DEHPA and Cyanex 272 (1:1) as extractant within the temperature range 25-60°C.



It was reported that the separation factor of cobalt and nickel increases from 9.93 to 51.8 when the temperature increases from 25°C to 60°C. Increasing the temperature by 35°C decreased the pH at which cobalt is extracted to a larger extent than that of nickel (roughly 0.4 and 0.8 for nickel and cobalt respectively). This explains the increased separation factor as temperature increases.

The stability issue of the cobalt extracted complex at higher temperatures mentioned by Sarangi *et al.* (1999b) was not reported by Darvishi *et al.* (2005) who extracted cobalt at temperatures up to 60°C. The stability of the cobalt extracted complex at temperatures above 30°C therefore remains unclear even though Sarangi *et al.*, (1999b) and Darvishi *et al.* (2005) extracted metal species with different concentrations of 0.5 and 5 g/l respectively.

#### *Metal ion concentration:*

It has been emphasized that there is effect of metal ion concentration on the distribution ratio of the metal. This will mean that tracer and macro amounts of metals may be expected to be extracted to the same extent under similar equilibrium conditions provided the solubility of the extracting species in the organic phase is not exceeded (Vladimir, 2012). However, different researchers have reported the effect of metal ions concentration during solvent extraction of various metal ions. It has been found that the recovery of metal ions increases with increasing the concentration.

#### *Solvent extraction contactors:*

There is no universal contacting equipment suitable for all solvent extraction operations. Even within a plant, it may be completely wrong to select the same type of contactor for all stages of the extraction process. Each plant, therefore, has to make a choice; the final selection is governed by the type of aqueous feed and composition, the solvent type and composition, and how the respective physical characteristics affect the mixing process, flow patterns and coalescence (Ritcey, 1973).

The classical solvent extraction equipments used are mixer-settlers and different types of counter current extraction columns. On comparing the performance characteristics of these equipments, columns are found highly efficient and exhibit low costs in respect of stage numbers, solvent inventory, settler area, site area and maintenance (Godfrey and Slater, 1994). But their high specific throughputs result in low residence time, which limits the use of columns in case of reactive extraction (Bart, 2005).

For example, in copper production by solvent extraction process, mixer-settlers (Komulainen et al., 2006; Moreno, et al., 2009; Robinson et al., 2003) were preferred to columns (Buchalter et al., 2002). But nowadays, the use of columns is of particular interest, since modern liquid ion exchangers allow fast chemical kinetics, the equilibrium of extraction being attained within 60 seconds.

The mixer-settler combination is usually operated at an O: A ratio of 1:1 by recycling either organic or aqueous phase (as appropriate). This is primarily to achieve good contact between the phases and prevent phase inversion if the advancing flow rates of organic and aqueous are very different. The result is that there is always a significant portion of aqueous in the mixed phase emulsion. The combination of phases close to equilibrium, together with a large volumetric fraction of aqueous, greatly assists in making reliable pH measurement, especially if the mixture is aqueous continuous (Zhuang, 2000). However, there is no literature available on the solvent extraction of cobalt using a column. Most of literature focuses on solvent extraction of cobalt using settlers.

SX mixers may be operated in either the organic continuous or aqueous continuous mode. Most mixers are operated at O/A ratios close to 1.0 with the use of recycle flows if the throughput O/A is not 1.0. The selection of the continuous phase can have significant effects on the physical aspects of the SX plant operation (Mackenzie, 2011).

## 2.7 Stripping

Once the metal ions are extracted by the solvent extraction process, the next step with main difficulty is the recovery of metal ions loaded in the organic, and it depends on the metal ions-extractant complex in the solution (Zagorodni, 2007).

Stripping is the removal of the extracted solute from the organic phase for further analysis. It is the reverse of extraction. The stripping of metals previously extracted into an organic phase is an important step in industrial applications. It enables the recovery of extracted metals on one hand and regeneration or recycling of the extractant for subsequent use on the other hand. This is necessary from the point of view of economics and also to ensure minimal wastes disposal. Thus regeneration of materials consumed during the hydrometallurgical process makes the system more sustainable and cost effective.

In solvent extraction processing there are two basic approaches for metal separation in a multi-elemental system: selective extraction and selective stripping. Sometimes, selective

stripping is more economical and operationally advantageous, because, for example, it requires fewer stages than selective extraction. The selective stripping approach has been used in a series of metal combinations and using various extractants (e.g. zinc from nickel, nickel from cobalt, lead from copper, nickel from copper, LIX 64N, LIX 87QN) Sandhibigraha, et al., (1997).

Cobalt and nickel are often presented together in a number of raw materials, secondary resources and liquid effluents; thus their recovery/separation seems to be attractive from various points of view. Both metals can be extracted by Cyanex 272. The extraction of metals, especially cobalt, by Cyanex 272 can be explained by a cation exchange reaction (2.12). It is therefore desirable to search for an efficient and comparative simple method for the stripping of cobalt-nickel from Cyanex 272 extractant, which at the same time would not lead to degradation of the extractant. Gandhi *et al.* (1993) considered various stripping agents for the removal of cobalt from Cyanex 272 solutions as shown in **Table 2.2**.

**Table 2.2 Effect of various stripping agents for the stripping of cobalt from Cyanex 272 (Gandhi et al., 1993)**

Stripping agents( M)	%Recovery				
	0.01	0.05	0.1	0.5	1-5
HCl	57	71	91.3	99.9	99.9
HNO <sub>3</sub>	47.1	67.3	99.2	99.9	99.9
H <sub>2</sub> SO <sub>4</sub>	71.4	87.6	96.9	99.9	99.9
HClO <sub>4</sub>	73.1	86	98	99.9	99.9
CH <sub>3</sub> COOH	18.4	55.1	66.1	96	99.9

Compared to sulfuric acid, nitric acid is a less efficient stripping agent. Bourget et al., 2005, worked on the binary mixture of Cyanex 301 and Alamine 336 and showed that it was most effective for selective extraction of cobalt and nickel followed by complete stripping of cobalt with H<sub>2</sub>SO<sub>4</sub>; however, complete stripping of nickel was difficult.

Sole and Hiskey (1995) demonstrated this in a comparative study on the stripping of copper from organic phase extracts of CYANEX 301, CYANEX 302 and CYANEX 272: while quantitative stripping of copper from CYANEX 302 extract was obtained with 13.5 M H<sub>2</sub>SO<sub>4</sub>, the use of concentrated (18 M) H<sub>2</sub>SO<sub>4</sub> did not strip any copper from CYANEX 301.

Furthermore, Sole and Hiskey (1995) noted a significant disadvantage in the use of such concentrated acids, as they observed discoloration and increased viscosity of the organic phase. The problem was further compounded as a result of significant deterioration in the phase separation when the organic phase extract was contacted with 18 M H<sub>2</sub>SO<sub>4</sub>.

## 2.8 The kinetics of solvent extraction

Many studies have been performed on the kinetics and mechanism of metal extraction by acidic organophosphorus extractants. In most of these studies, D2EHPA has been used as the extractant (Brisk, and McManamey, 1969; Haung, and Juang, 1986).

All extractants are interfacially active. Adsorption at the interface lowers the interfacial tension and facilitates dispersion of the phases. In a well-dispersed system with appreciable adsorption of the extractant at the interface, the interfacial population will considerably exceed the aqueous concentration of the extractant (Flett, 1976). Thus reactions of kinetics importance could take place at the interface as well as in the bulk aqueous phase. For chemical rate-controlling processes at the interface, the interfacial concentration of the extractant is of prime importance in determining the observed rate of extraction, as is the interfacial area.

When reaction in one of the two phases is very slow relative to physical mass transport, there is a simple homogeneous kinetics in one phase; however, one reactant, at least, is distributed between the two phase (Klein, et al., 1958). It is convenient to express the distribution coefficient and reaction rates by considering an organic (O) and aqueous (A) phase in intimate contact, of volumes  $V_o$  and  $V_a$  respectively in terms of phase reacted. For the first order reaction in phase A:

$$\frac{-dA_a}{dt} = kA_a \quad 2.3$$

Integration of equations 2.3 leads to the rate controlling regimes (equation 2.4) which can be found in the literature (James Carberry, 1976).

$$\ln A_o^0 - \ln A_o = \frac{kt}{(V_o / V_a)K + 1} \quad 2.4$$

An interfacial concentration depends on the interfacial activity of the extractants, its molecular geometry, its bulk phase concentration, and the diluent type. Increasing the bulk

phase concentration increases the interfacial population up to the point of interfacial saturation. With respect to the extraction rate, which is of great importance in industrial extraction operations, it is generally recognized in the extraction of many metal ions by acidic organophosphorus extractants that extraction rate is usually rapid. A number of studies have been carried out on the thermodynamics of solvent extraction to elucidate the parameters involved and to ascertain the properties of various extractants commonly used including di-(2- ethylexyl) phosphoric acid (D2EHPA), which is widely used in solvent extraction of several metals (Darvishi et al., 2005; Owusu, 1998, Sastre and Muhammed, 1984). The extraction rates of metal ions such as  $\text{Cu}^{+2}$ ,  $\text{Co}^{+2}$  and  $\text{Zn}^{+2}$ , and rare earth metal ion were found to be controlled by the diffusional processes in the stagnant layers, and were quantitatively interpreted.

Coleman and Roddy (1971) have reviewed the kinetics of several metals by alkyl phosphoric acids and have emphasized the complicated nature of the extraction mechanisms. However, although much experimental data has been accumulated, the mechanism of extractants has not yet been accumulated; the mechanism of extraction of base metals such as copper, by alkyl- substituted hydroxyoxime extractants has not yet been clearly established.

## 2.9 Mechanism of solvent extraction

The general mechanism proposed for the extraction when the reaction occurs in the aqueous phase is the diffusion of the extractant into the aqueous phase where the molecules react with metal ions in that phase in an  $n$  step process (for the formation of a complex of ligand: metal ion of  $n$ : 1), forming the neutral complex which then moves into the organic phase. A general summary of this mechanism is given by Flett et al. (1975):



And the equilibrium constant as:

$$K_{eq} = \frac{[ML_n]_{org} [H^+]^n}{[M^{n+}] [HL]_{org}^n} \quad 2.6$$

And taking logs.

$$\text{Log}K = \log[R_n M]_{org} + n \log[H^+] - \log[M^{n+}] - n \log[H]_{org} \quad 2.7$$

And rearranging

$$\text{Log}([R_n M]_{org} / [M^{n+}]) = \log D = \log K + n \log [RH]_{org} + n \cdot pH \quad 2.8$$

A number of factors, including the extremely low aqueous solubility and the known interfacial activity of some reagents, lend to support to the hypothesis of an interfacial mechanism in some cases.

Several researchers (Nitsch and Kruis, 1978; Nitsch, 1983; Freiser and Chmupathi, 1989; perera et al., 1992; McCulloch et al., 1993, 1996) have proposed the liquid-liquid interface as the site of the reaction in many systems, whereas previously the mechanism of the reaction was considered to be a bulk aqueous reaction between the ligand (either ionised or neutral) and the metal ion, and the extraction of the neutral complex on completion of the final step in the complexation reaction (Stenes and Perera, 2010). The SX process is usually described by a single net reaction, defined by the extraction constant  $K_{ex}$ . Variations in  $K_{ex}$  is caused by modifications of the solvent system, such as changes in the temperature or aqueous ionic strength, by replacing one solvent by another, or by making substitutions in the extractant molecule, may be explained by careful consideration of the parameters of the system (Vladmir, 2012).

The extraction constant at zero ionic strength,  $K_{ex}^0$ , is the equilibrium constant of the distribution reaction expressed in terms of the reacting species. Thus, for the reaction:



In which the reagent  $HL$  initially dissolved in an organic phase reacts with a metal ion  $M^{n+}$  in aqueous solution to form a product  $ML_n$  which is more soluble in the organic phase than in water, thus:

$$K_{ex}^0 = \frac{a_{ML_{n,org}} \times a_{H_{aq}}^n}{a_{M_{aq}}^{n+} \times a_{HL_{org}}^n} \quad 2.10$$

## 2.10 Summary

The present work aims to investigate the separation of cobalt from copper-cobalt ore leach solutions using solvent extraction with an acidic extractant. Solvent extraction is a process in which extractants are utilised to help in the removal of metals from the aqueous solution. The literature review contained in this chapter has shown the difficulty involved in the processing of cobalt from a complex environment (section 2.4). The leaching process results in the co-dissolution of metal ions beside copper, which include manganese, aluminium, iron, zinc and nickel. Zinc, copper and nickel would co-deposit with cobalt during electrowinning. Manganese does not co-deposit with cobalt, but its presence in the electrolyte at high concentrations can adversely affect the electrowinning of cobalt by reducing the current efficiency. Iron will also reduce the current efficiency of the process. The leach solution needs to be purified before final cobalt recovery can be implemented. In this work, therefore solvent extraction will be applied for the removal of cobalt from copper-cobalt leach solution. The review has identified Cyanex 272 as a possible extractant to separate cobalt from others metals from the aqueous solution via solvent extraction. The next chapter discusses materials and analytical methods used in the study.

## CHAPTER THREE

### MATERIALS AND METHODS

#### 3.1 Introduction

The preparation of materials, as well as the experimental and analytical methods used in the study is discussed in this chapter.

#### 3.2 Material Characterisation and Solution Preparation

##### 3.2.1 Copper Cobalt Oxide Ore

The copper-cobalt oxide ore, used in this study was provided by General of Carriers and Mines (Gecamines), DR Congo. The heterogenite copper-cobalt ore used in this study was obtained from a mine in the Katanga Region (DR Congo). According to the results obtained from the XRD and XRF analysis, the main components of the ore sample were: 0.77% dolomite, 4.68% malachite, 7.27% chlorite, 0.91% muscovite, 4.02% talc and 82.35% quartz.

The ore was crushed in a jaw crusher (Denver) and gyrasphere crusher (Denver cone type) and finely ground in a ball mill. The particle size analysis was done by physically screening the samples using test sieves (MACSALAB MS -300 Motorised Sieve Shaker type) of various screen sizes within the range of -38 $\mu$ m and +150 $\mu$ m. The typical copper-cobalt oxide ore particle size distribution (PSD), phase mineralogy and chemical composition analysis results are presented in **Tables 3.1 and 3.2 and Figure 3.1**.

**Table 3.1 Mineralogy analysis of copper-cobalt oxide ore**

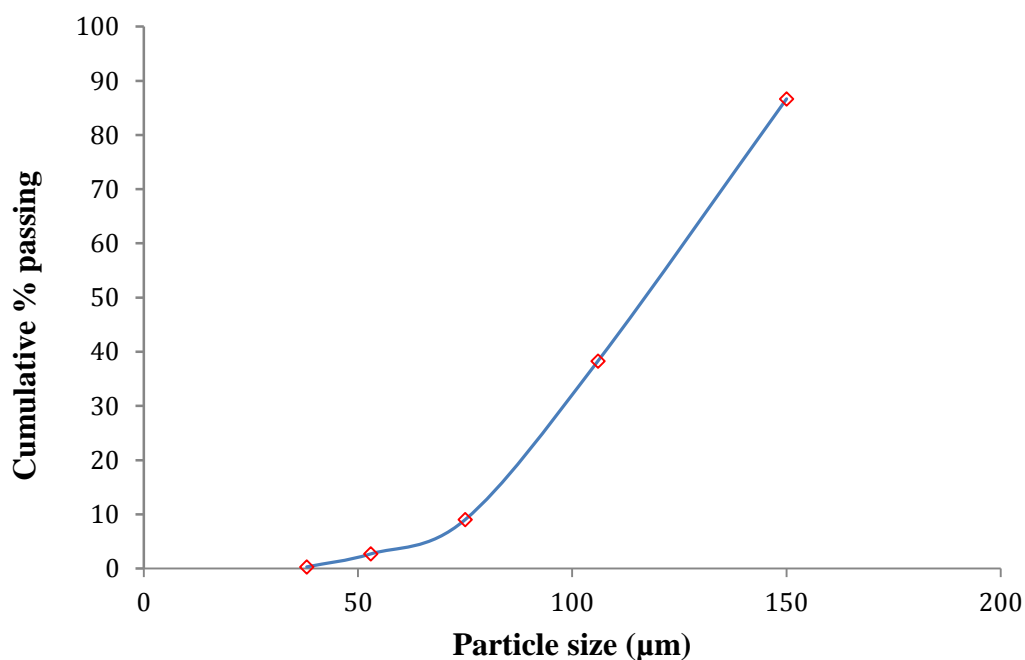
	-75 $\mu$ m		+75 $\mu$ m		mixed
<b>Chlorite</b>	9.64	<b>Chlorite</b>	5.55	<b>Chlorite</b>	7.27
<b>Dolomite</b>	0.56	<b>Dolomite</b>	1.87	<b>Dolomite</b>	0.77
<b>Malachite</b>	6.58	<b>Malachite</b>	4.35	<b>Malachite</b>	4.68
<b>Muscovite</b>	2.23	<b>Muscovite</b>	1.05	<b>Muscovite</b>	0.91
<b>Quartz</b>	76.94	<b>Quartz</b>	83.1	<b>Quartz</b>	82.35
<b>Talc</b>	4.04	<b>Talc</b>	4.07	<b>Talc</b>	4.02



**Table 3.2 Chemical composition of copper-cobalt oxide ore (%)**

Samples ID	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe(tot)	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Zn	Ni	Cu	Co
<b>Mixed</b>	84.5	1.34	1.4	2	0.47	2.48	0.029	0.003	4.53	0.3
<b>+75µm</b>	87.4	1.04	1.2	1.72	0.34	1.92	0.023	0.003	3.96	0.25
<b>-75µm</b>	80.7	1.7	1.75	2.5	0.45	3.28	0.036	0.004	5.24	0.38

It is well known that the particle-size distribution plays an important role in most of metallurgical processes. This is because the mineral composition has been known to vary with particle sizes. The mineralogical variance within an ore affects its reactions and behaviour in different acidic or basic media. This arises due to the differences in the acid/base-mineral interactions of the individual minerals existing within the ore. Knowing the chemical composition of the constituent minerals within the ore and the particle size distribution would therefore be very useful in understanding of the extent of metals dissolution during the leaching process. It was found that in copper-cobalt oxide ore used in this research, fine particles (-75 µm) presented a higher metal grade than the large particles (+75 µm) as seen in the **Table 3.2**. However, in order to closely simulate the typical plant leaching conditions, it was necessary to blend the two size ranges with a view of leaching the maximum size distribution.

**Figure 3.1 Particle size distributions (PSD) of copper-cobalt oxide ore**

### 3.2.2 Reagents

The reagents were all purchased from Merck and Sigma Aldrich. All the reagents used were of analytical grade. There were used as received without further purification. Shellsol 2325 was used as a diluent. The commercial extractant, Cyanex 272 obtained from Cyatex, was used without any further purification.

### 3.2.3 Leaching of Copper-Cobalt Ore

The leaching tests were conducted using 0.2 M  $\text{H}_2\text{SO}_4$ , reaction temperature 40 °C, agitation speed 100 rpm, solid/liquid ratio 6.6:1, reaction time 2 h and Sodium Meta bi-sulfite ( $\text{Na}_2\text{S}_2\text{O}_5$ ) was used as a reducing agent. Leaching experiments were carried out in a glass reactor with 2L capacity in water bath. The leaching experiment was set up in a thermostatically controlled water bath (Mark Scientific), equipped with a digitally controlled thermometer. 150g of the desired particle size blended stream) was added to 1 litre sulfuric acid in a 2 litres glass and the pulp mixed together with sodium meta-bisulphite (250g/L) as a reducing agent. A Büchner funnel mounted on a 2 litre flask was used for the filtration. The residues were dried at 60°C in the oven. Since leaching was not the focus of this research, it was done under constant conditions of acid concentration, solid to liquid ratio, reducing agent volume and concentration, temperature, agitation rate and time as guided by information in literature. The resulting leach solution was analysed for metal ion content specifically, copper, iron and cobalt using ICP/SD analysis (at Set Point).

### 3.2.4 Copper and Iron Removal

Precipitation processes for the removal of copper and iron from the leach solution were conducted with a (IKA C-MAG HS7) brand heater-magnetic stirrer, regular glassware.

Removal of Fe and Cu from the liquor, was performed by adjusting the pH to 6.3 using 2.5 M  $\text{Ca}(\text{OH})_2$  solution at 80°C followed by filtration, The stirring head speed was kept constant at 3.0 m/s and a (827 Metrohm) pH meter was used for measuring the pH values of solutions.

The resulting solid precipitate was first filtered on MUNKTELL filter paper, and then a membrane Supor-200 (0.2micron) was used to remove any gelatinous solids, the residue was washed with distilled water to recover any cobalt ions remaining in the residue. X-Ray Diffraction was used for the analysis of the resulting solid residues whilst the metal ion content in the filtrate solution was analysed for using of ICP-OES analysis which allowed the calculation of the amount of copper and iron precipitated into the solid hydroxide and cobalt loss during precipitation. Since the cobalt ion in the resulting leach solution was quite low the cobalt content in the feed solution to the solvent extraction process was increased by

augmenting the solution with a dissolved specific amount of  $\text{CoSO}_4 \cdot 5\text{H}_2\text{O}$  before commencing the solvent extraction. **Table 3.3** shows the chemical composition of the two feed streams that were used as feed solutions to the solvent extraction plant. A flow diagram of the proposed process for cobalt extraction from copper-cobalt oxide ores solvent extraction process is presented in **Figure 3.1**.

**Table 3.3 Chemical composition of the feed**

Sample	Concentration (g/L)						
	Ca	Co	Cu	Fe	Mg	Ni	Zn
1	0.51	1.30	0.17	0.04	0.15	0.00	0.01
2	0.52	2.12	0.17	0.04	0.15	0.00	0.01

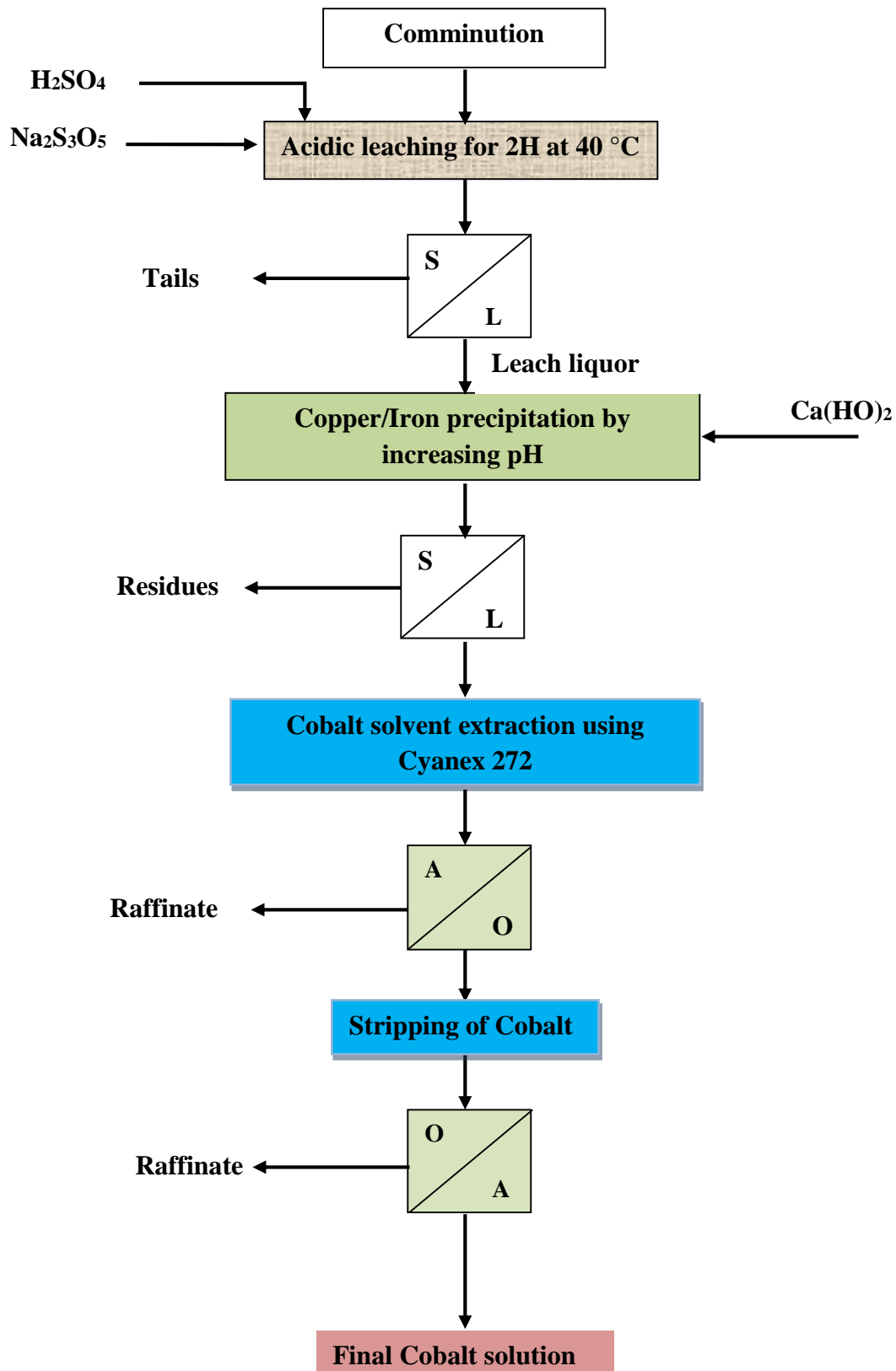


Figure 3.2 proposed route for extracting cobalt from copper-cobalt oxide ores

### 3.2.5 Solvent Extraction

Several different series of extraction experiments were performed during this work. The solvent extraction experimental set-up consisted of a 250ml beaker, thermal magnetic stirrers, a Metrohm pH meter and a separator funnel. The filter funnel was mounted on metallic stand. The solvent extraction process consisted of mixing a measured volume of aqueous and organic phase, typically a ratio of 3:1 to 1:3, then pouring the mixture into a 250ml beaker and stirring at different temperature under the fumehood as shown in **Appendix A**. Since the use of  $\text{NH}_3$  for pH adjustment tends to give a higher impact on nickel removal than that of cobalt (Hu, J. et al., 2012), NaOH was however, used for the pH modification. The pH of the solution, was kept at an appropriate level by manual addition of a certain dosage of 100 g/L NaOH solution. After the extraction, the raffinate and the extract were separated using the separator funnel. The aqueous sample was submitted for Inductively Coupled Plasma (ICP) analyses. Extraction variables studied included cobalt concentration, extraction time, temperature, pH and organic to aqueous phase ratio. The extraction conditions for the tests are given in **Table 3.4**.

**Table 3.4 Solvent extraction parameters**

Parameter	Parameter Level				
	Temperature (°C)	O/A ratio	pH	Cobalt concentration g/L	Contact time (min)
<b>Temperature</b>	25, 35, 50	3:1	6	2.12	20
<b>O/A ratio</b>	25	1:3, 1:2, 1:1, 2:1, 3:1	4,5, 6	2.12	20
<b>pH</b>	25	3:1	4,5,6	2.12	20
<b>Cobalt concentration</b>	25	1:3, 1:2, 1:1, 2:1, 3:1	6	1.30 and 2.12	20
<b>Contact time</b>	35	3:1	6	2.12	20, 30, 40, 50, 60

#### *The Effect of O/A ratio and pH*

The effect of O/A ratio was studied at various pH levels; from 4 to 6. The O/A ratio was varied from 1:3 to 3:1. Other factors were kept constant at temperature of 25°C, cobalt concentration of 2.12g/L and contact time 20 minutes.

*The Effect of Cobalt Concentration*

The effect of cobalt (II) ions concentration on the extraction was studied at a concentration of 1.30, 2.12 and 3.5g/L at a constant temperature of 25°C, contact time of 20 minutes and at pH 6 using various O/A phase ratio.

*The Effect of Temperature*

A change in temperature is accompanied by changes in all the parameters affecting the extraction process, and these changes may be highly variable. Therefore in order to understand the extraction process more, the effect of temperature needs to be determined as this plays a significant contribution in the extraction kinetics. The effect of temperature on cobalt solvent extraction using Cyanex 272 was carried out in beakers using magnetic stirrer (hot plate). Three temperature levels of 25, 35 and 50°C were evaluated. The following factors were kept constant at O/A phase ratio 3:1, pH 6, cobalt concentration 2.12g/L and a contact time of 20 minutes.

*The Effect of Contact time*

The effect of the stirring time on cobalt (II) extraction was studied using aqueous feed solutions containing 2.12g/L of Cobalt (II), temperature of 35°C, O/A phase ratio of 3:1 with a pH of 6 and the shaking time varied from 20 to 60 minutes.

*3.2.6 Stripping Process*

For selective cobalt stripping, loaded organic solution from the extraction tests was mixed with an acidic aqueous solution using beakers at various temperatures (25, 35 and 50°C). The acid levels used in the aqueous solutions (roughly 50, 75 and 100 g/L, respectively) were designed to enable stripping of the cobalt. Stripping variables investigated included acid concentration, temperature and time. The stripping conditions experiments are given in **Table 3.5**.

**Table 3.5 Stripping parameters**

<b>Factor</b>	<b>Factor Level</b>		
	Temperature (°C)	Contact time (min)	Acid concentration (g/L)
<b>Temperature</b>	25, 35, 50	20	50
<b>Contact time</b>	25	20, 30, 40, 50, 60	50
<b>Acid concentration</b>	25	20	50, 75, 100

### 3.3 Experimental Methods

#### 3.3.1 Design of Experiments

The main aim of this study was identification and optimization of factors that have a significant influence on cobalt extraction in the solvent extraction process. A statistical Design of Experiments (DOE) method was employed as a research tool to develop an experimentation plan to execute these two main objectives.

The basic idea of experimental design involves formulating a question and providing a simultaneous study of several process parameters. Factors of interest are changed in a systematic way so as to ensure reliability and independent study of the main factors and their interference. Thus by using DOE, we get more precise and useful information about the studied process.

Detection and screening of factors was done (Chapter 4 and 5) at the beginning so as to explore some coefficients in order to reveal whether they have any influence on the response (cobalt recovery), and to identify their appropriate fluctuations. A statistical analysis of the experimental results was employed to evaluate the significance of the factors using the normal test plot.

Optimisation of factors (Chapter 6) was done to predict the response values for all possible overall factors within the experimental region, and to identify an optimal trial point. A collection of mathematical and statistical techniques for empirical model building was used in

the optimization of significant factors. Most of the criteria for optimal design of experiments are associated with the mathematical model of the process, so the corresponding experiments are designed only for every particular problem. The choice of the design of experiments used in this study had three stages as follows: (1) Designing and conducting of experiments (2) Deriving and developing a mathematical model. To construct an approximation model that can capture interactions between  $N$  design variables, a full factorial approach (Montgomery, 2005) was done to investigate all possible combinations. The lower and upper bounds of each of  $N$  design variables in the optimization problem needs to be defined. The allowable range is then discretized at different levels.

Factorial designs can be used for fitting second-order models to improve the optimization process when a first-order model suffers lack of fit due to interaction between variables and surface curvature. A general second-order model is defined as

$$y = a_o + \sum_{i=1}^n a_i x_i^2 + \sum_{i=1}^n a_{ii} x_i^2 + \sum_{i=1}^n \sum_{j=1}^n a_{ij} x_i x_j \dots \dots \dots i > j \quad 3.1$$

Where  $x_i$  and  $x_j$  are the design variables and  $a$  are the tuning parameters

After the regression coefficients have been obtained, the adequacies of the models were checked using the analysis of variance (ANOVA) technique (Khuri and Cornell, 1987). Fisher's variance ratio test ( $F$ -test), standard errors of model coefficients ( $t$ -test), the coefficient of determination ( $R^2$ ) and, the absolute average deviation (AAD) are the methods that were employed in the ANOVA.

**Table 3.6** shows the overall summary of the experimental process parameters and the values that were evaluated under the study for both solvent extraction and stripping steps.



**Table 3.6 Experimental procedures**

Test	Process test	Test conditions	Replicates
<b>Solvent Extraction</b>	Cobalt solvent extraction	<ul style="list-style-type: none"> <li>• Temperature</li> <li>• O/A ratio</li> <li>• pH</li> <li>• Cobalt ion concentration</li> <li>• Contact time</li> </ul>	2
	Identification of influential parameters	<ul style="list-style-type: none"> <li>• Temperature</li> <li>• O/A ratio</li> <li>• pH</li> <li>• Cobalt ion concentration</li> <li>• Contact time</li> </ul>	2
	Optimization of influential factors	<ul style="list-style-type: none"> <li>• O/A ratio</li> <li>• pH</li> </ul>	2
<b>Stripping</b>	<b>Cobalt stripping process</b>	<ul style="list-style-type: none"> <li>• Temperature</li> <li>• Acid concentration</li> <li>• Contact time</li> </ul>	2

### *3.3.2 Identification of Influential Parameter: Solvent Extraction*

The effects of various process parameters on extraction, and stripping were investigated. Based on full factorial experimental designs, the parameters with great effects on the process performance were determined. These variables were evaluated in further experiments to determine conditions that would allow the production of a high purity cobalt sulphate solution and selective stripping of cobalt from the organic phase.

### *3.3.3 Optimization of Influential Factors*

An optimization technique was applied to this research in order to achieve optimum parameters and select the most appropriate factors between the available choices for a given application. RSM (Response Surface Methodology) is the technique used to find the optimal

conditions by using a quadratic polynomial model and is applied as a consequence of a screening or diagnostic experiment.

### **3.4 Analytical Techniques**

Elemental analyses of the metal in the leach solutions were done with plasma emission spectrometry (Set Point SD/ICP-AES). In order to evaluate their accuracy in the organic phase, some duplicate samples were analyzed. The Agilent Technologies 200 Series AA atomic absorption spectrophotometer (AAS) with an air/acetylene flame was used to determine the stripped cobalt ion and other present metal ion concentration.

### **3.5 Data Analysis**

The data was gathered as described in the previous sections of this chapter. The data collected was used to develop relationships between cobalt recovery and the tested parameters (e.g., pH, temperature, cobalt and acid concentration, etc). These relationships and the observed results are discussed in the subsequent chapters of this dissertation.

## CHAPTER FOUR

### COBALT SOLVENT EXTRACTION

#### 4.1 Introduction

The increase in demand for metals has prompted more studies to focus on resource recovery and valuable metals from primary as well as secondary resources. Recently, the scientific community has paid much regard to research that studies the recovery of cobalt from copper-cobalt oxide or nickel laterite ore using hydrometallurgical routes.

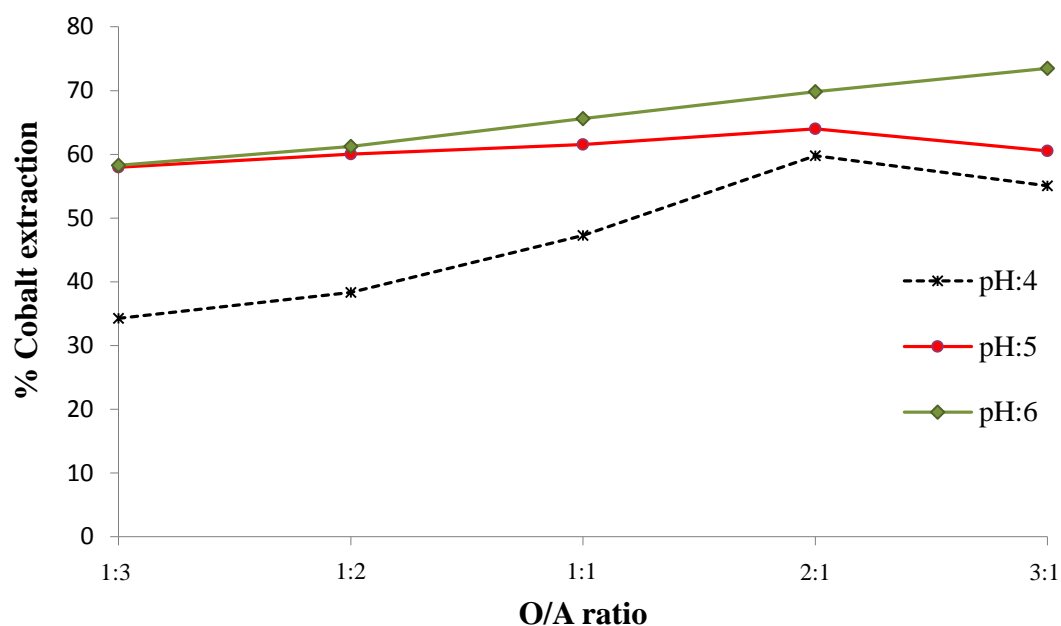
The possibility to employ solvent extraction to treat cobalt from different impurities has been described in Chapter 2 (Section 2.4). The solvent extraction of cobalt is mostly done using cyanex 272 extractant in order to achieve optimum cobalt extraction from low grade ores.

In order to examine the possible influence of factors on the (Cobalt extraction) response and to identify their appropriate upper and lower limits, solvent extraction tests were initially conducted according to the procedure described in Chapter 3 section 3.2.5. In this study several tests were performed looking at different parameters influencing the cobalt solvent extraction from copper-cobalt ore leach solution using Cyanex 272. These parameters were: contact time, organic to aqueous phase ratio, pH and temperature. The concentration of Cyanex was kept constant for all the experiments (30% v/v). This chapter looks at cobalt extraction kinetics and the role of impurities in the extraction behaviour of cobalt by investigating the effect of parameters such as extractant concentration, temperature, contact time and aqueous to organic (A/O) ratio. This understanding will be used as a basis for the subsequent screening, optimization studies that follow from Chapter 5 to Chapter 7.

#### 4.2 Results and Discussion

##### *4.2.1 Effect of O/A ratio and pH*

The results in **Figure 4.1** show the cobalt extraction at different O/A ratio and at different solution pHs. Extractions were performed at O/A ratios of 1:3, 1:2, 1:1, 2:1, and 3:1.

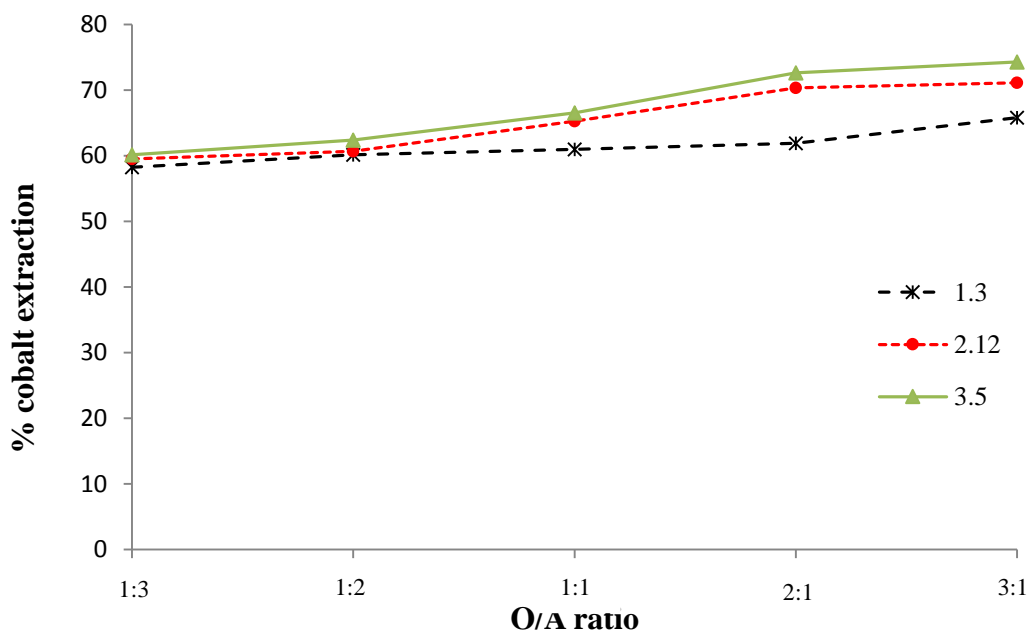


**Figure 4.1 Effect of different O/A ratio on cobalt extraction at different solution pHs (Contact time 20 minutes, Temperature 25°C)**

**Figure 4.1** shows that the extraction process is influenced by the phase ratio (O/A) and the pH of the solution. The maximum extraction of 58.27% was observed at pH 6 and an O/A ratio of 3:1. Extraction of cobalt at pH of 5 and 6 showed more than 50% extraction at all O/A ratios. However, extraction at pH 4 was seen to increase from around 35% at O/A ratio of 1.3 and peaking at 50% at an O/A ratio of 2:1. The results showed that an increase in pH favoured the extraction of the cobalt into the organic phase. The extractability of metal complexes is greatly influenced by the acidity of the aqueous phase, so it is necessary to ensure the optimum concentration of  $H^+$  ions for maximum extraction. The *dialkyl phosphonic acid Cyanex 272* extracts metal ions by a cation exchange mechanism resulting in the release of protons into the solution. If the reagent concentration is maintained constant, the distribution of the metal in a given system will be a function of pH. Therefore, the greater the amount of metal extracted, the more hydrogen ions are produced. This will result in a decrease in the pH of the system and consequently a decrease in the metal extraction process. This therefore, means that for more efficient extraction of cobalt ions into the organic phase, the solution pH should be closely monitored and kept at the level required for the high extraction of cobalt.

#### 4.2.2 Effect of Cobalt Concentration

This study was carried out using two levels of cobalt concentrations (1.30, 2.12 and 3.5 g/L) with the organic phase of 30 % v/v Cyanex 272 in Shellsol 2325. The extraction was conducted at various initial O/A ratios of (1:3, 1:2, 1:1, 2:1, and 3:1).



**Figure 4.2 Effect of initial cobalt concentration on cobalt extraction at different O/A ratio (contact time 20minutes, Temperature of 25°C, solution pH 6)**

The effect of the initial cobalt ion concentration was studied under various organic aqueous ratios. The results are shown in **Figure 4.2**. **Figure 4.2** shows that there were no significant differences in the percent extraction for all cobalt metal ion concentrations levels at a lower O/A ratio. At an initial feed solution of 1.3g/L cobalt, the cobalt extraction into the organic phase increased from 58.28 to 64.84% as the O/A ratio increased from 1:3 to 3:1. At an initial feed concentration of 2.12g/L cobalt, the extraction into the organic phase increased from 59.52 to 71.16% as the O/A ratio increased from 1:3 to 3:1. At an initial feed concentration of 3.5g/L cobalt, the extraction into the organic phase increased from 60.15 to 74.32% as the O/A ratio increased from 1:3 to 3:1.

The more commonly used term for expressing the extraction efficiency is related to the distribution ratio  $D$  and is shown in **equation (4.1)**.

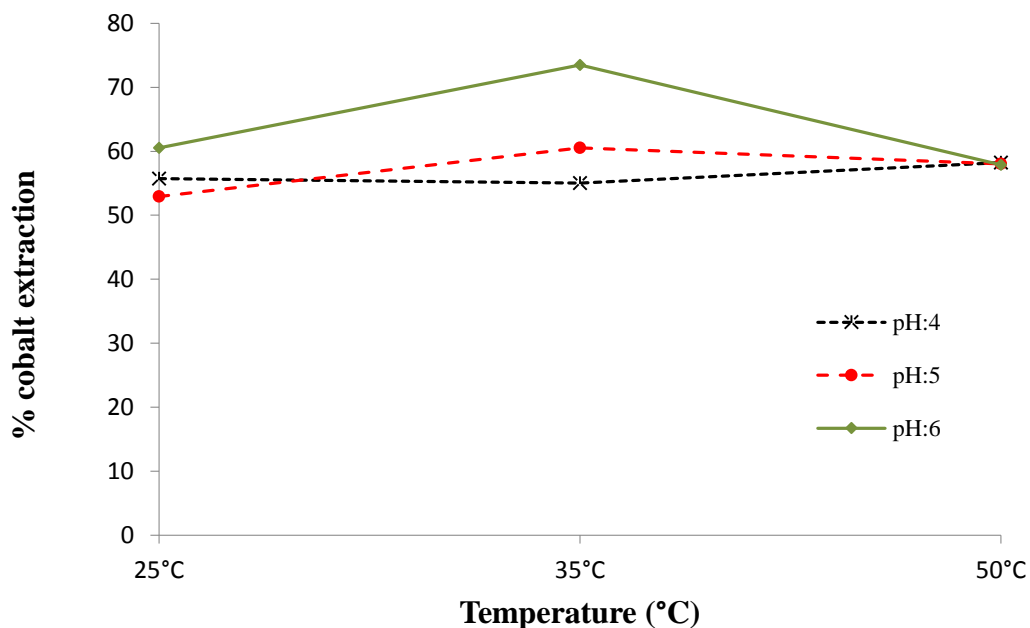
$$\% E = \frac{100D}{D + \frac{V_{aq}}{V_{or}}} \quad 4.1$$

As can be seen from the figure, variation of cobalt concentration at the initial O/A ratio (1:3) does not considerably change the extraction curve and all experimental points correspond on one curve. This was likewise observed when the O/A ratio was increased up to 1:2. In contrast to O/A ratio of 1:1, there are some dissimilarities between 1.3g/L and the other concentrations (2.12 and 3.5 g/L). At 1.3g/L, the curve marginally dropped when the O/A ratio was changed to 1:1. However, with further increasing cobalt concentration in the aqueous phase, the increase of cobalt concentration in the organic phase is limited and becomes almost constant because the cobalt-Cyanex 272 organometallic complexes is saturated in the organic phase. However, **Figure 4.2** shows that variation range of O/A ratio using 1.3g/L of cobalt concentration is not as evident as 2.12 and 3.5g/L, in spite of carrying out this experiment at pH=6. Generally the metal ion concentration should be independent of the initial metal concentration but more dependent on the O/A ratio and the distribution ratio. Thus, both tracer and macro amounts of metal may be expected to extract to the same extent under similar equilibrium conditions. Therefore, it can be concluded that at low cobalt concentration we have to examine carefully the O/A ratio of the loading capacity since it does not give perpendicular trend to other concentrations. Since the concentration did not have a significant effect on the percent extraction, subsequent tests were conducted using a feed solution of 2.12g/L cobalt.

#### *4.2.3 Effect of Temperature*

Detailed and exact information about extraction kinetics is necessary for the design of commercial solvent extraction processes. A change in temperature is accompanied by changes in all the parameters affecting the extraction process, and these changes may be highly variable. Therefore in order to understand the extraction process more, the effect of temperature needs to be determined as this plays a significant contribution in the extraction kinetics. Generally, the extraction kinetics in a high temperature region is different from that in a low temperature region. Taking into account the common temperature range of the solvent extraction of cobalt, the temperature in this work was varied in a moderate range of 25 to 50 °C. **Figure 4.3** shows the cobalt recovery at three different temperatures and at three different solutions pHs used during the solvent extraction tests. **Figure 4.3** shows that for pH 5 and 6 the percentage extraction increased up to 35°C then decreased sharply at temperatures beyond 35°C.

At a pH of 5 the extraction of cobalt increased from and 52.91% to 60.55% whilst at pH 6 it increased from 60.50% to 73.50% with a change in temperature from 25 to 35°C.

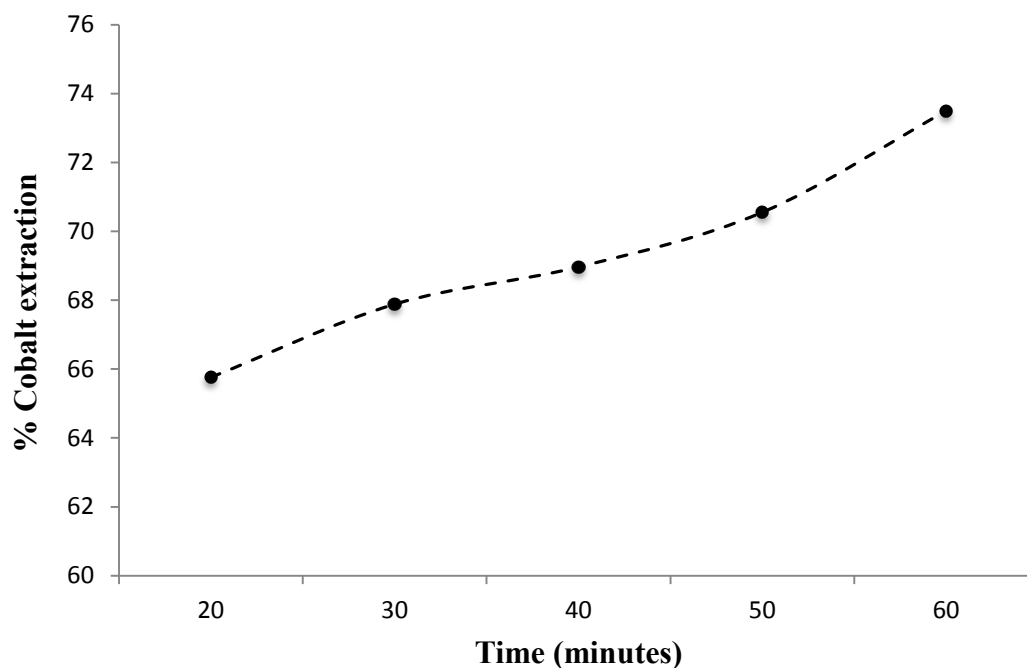


**Figure 4.3 Effect of temperature on cobalt extraction measured at different pH levels (contact time 20 minutes, 2.12g/L cobalt ion concentration, O/A ratio: 3:1)**

Furthermore, depending on the pH of extraction, coordinated bonds between the cobalt cation and water molecules can exist likewise in the metal-ligand complex. Some organometallic complexes can become unstable at elevated temperatures. The results also seem to indicate that the extraction reaction for  $\text{Co}^{+2}$  ions is an exothermic reaction that is, the coordination association between ligand and  $\text{Co}^{+2}$  ions decrease with an increase in temperature.

#### 4.2.4 Effect of Contact Time

The effect of time on cobalt extraction from sulphate solution by Cyanex 272 is presented in **Figure 4.4**. The figure explains that recovery increased with increase in extraction time from 20 to 60 minutes. A cobalt extraction of 65.75% was obtained after 20 minutes of reaction, 67.88% after 30 minutes, 68.97% after 40 minutes, 70.50% after 50 minutes and 73.50% after 60 minutes.



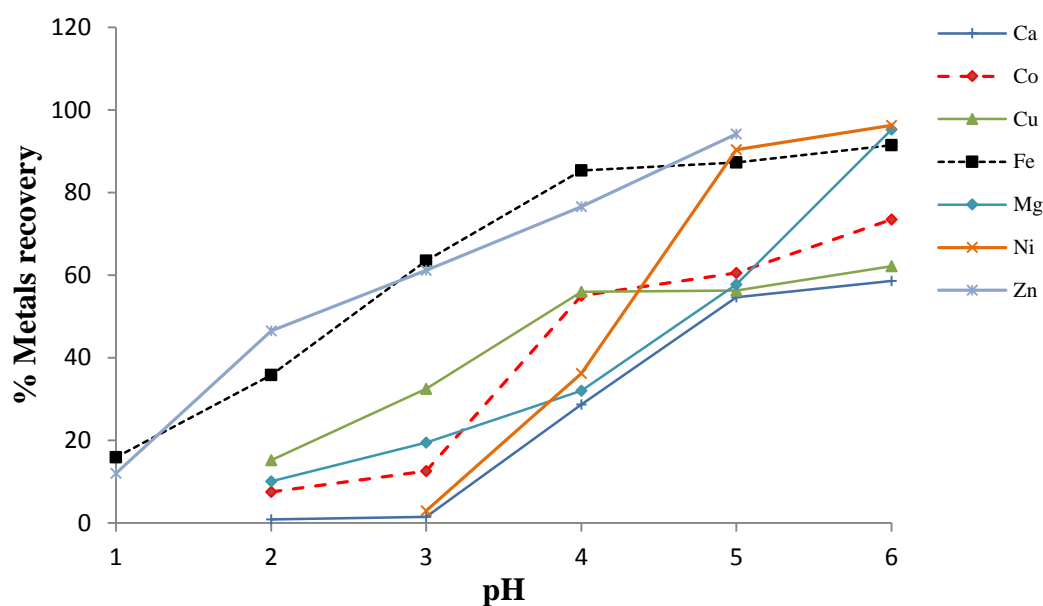
**Figure 4.4 Effect of time on cobalt extraction at pH of 6 (O/A ratio: 3:1, Temperatures: 35°C and Co concentration 2.12g/L)**

Maximum selectivity is usually obtained at very short inert-phase contact time relative to the mass transfer (which requires accurately defined residence times) but implies low recovery (Gilberto et al., 2004). In addition solvent extraction processes, a series of mixer settlers are used and it has been observed that equilibrium within each mixer settler is achieved at relatively short periods. Thus, it was decided that most of the remaining experiments will be run at a contact time of 20 minutes.

#### *4.2.5 Effect of pH on Selectivity of Extraction*

The attainment of selectivity in metal complex extractions is greatly dependent upon proper pH control. This is because the distribution of a metal complex in a given system is a function of pH alone, provided the concentration of the extractant is maintained constant. The selectivity of metals is an important issue in the extraction of the metal ions from multi metal ion sulphate solutions. The behaviour of cobalt ions with Cyanex 272 in the presence of other metal ion species is shown in **Figure 4.5**.





**Figure 4.5 Metal extraction at different pHs (contact time: 20minutes, Temperatures: 35°C, cobalt ion conc.:2.12, O/A ratio: 3:1)**

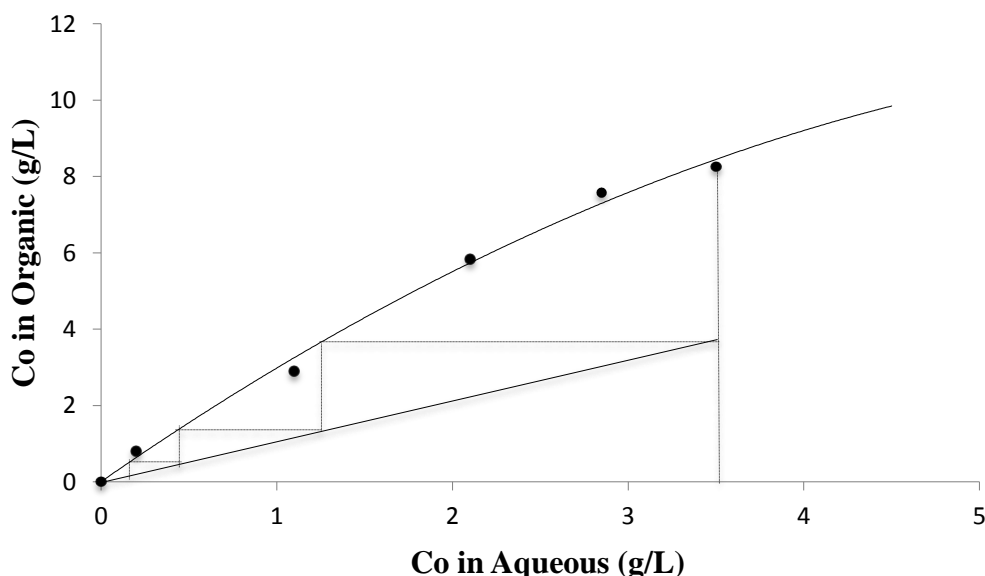
The effect of equilibrium pH on the extraction percentage for simultaneous extraction of Cobalt, in presence of impurities from sulphate medium using Cyanex 272 is shown in the figure. The fact that every metal has its own optimum pH of extraction indicates that moderately, the separations between two or more metals are achievable by regulating the pH of operation. The results prove that the extraction percentage of metal ions depends on the pH. At a pH of 6 91% iron extraction and 94% zinc extraction is attained. The extraction of copper is started at pH 2 and reaches 62.1% at a pH of 6. It was observed that the extraction of cobalt started at the same initial pH of copper and reached about 73.49% at a pH 6. The pH at which 50% of metal ions are extracted into the organic phase is known as  $pH_{0.5}$ . The  $pH_{0.5}$  gives the pH above which the process is predominantly extraction and below which the process favours stripping. The larger the  $\Delta pH_{0.5}$  values between two metals, the greater the selectivity of the extraction and the better the separation efficiency. At least 50% iron extraction occurs at pH of 2.5 whilst 50% zinc occurs at pH around 2.8. The  $pH_{0.5}$  for copper and cobalt is about 3.6 and 3.8 respectively.

Since different  $pH_{0.5}$  were observed for different metal ions in the solution it means that it will then be possible to control the pH such that only the metal ions that get extracted are those for cobalt and the impurity metals that have a lower  $pH_{0.5}$  than that of cobalt i.e. zinc and iron. The impurity extracted metal ions can then be separated from cobalt by strictly controlling the stripping process by using a pH value that allows only for the stripping of

cobalt without the stripping zinc and iron. The smaller difference in the  $pH_{0.5}$  for copper and cobalt imply that selectivity in the separation of these two metals can be difficult; i.e. co-extraction and co-stripping is likely to occur. It is therefore imperative that the level of concentration of copper metal ions in the solution reporting to the solvent extraction plant be as low as possible. This can be achieved through ensuring higher efficiencies in the hydroxide precipitation stage. Hydroxide precipitation can also be implemented to minimise the levels of iron. Zinc metal ions would however, be a bit difficult to control since they tend to precipitate at much higher pH. Its separation would then be mostly via selective stripping. The metal ions that would however present significant problems would be those of nickel. According to the results presented in **Figure 4.5**, 50 % extraction is recorded at pH of about 4.2 and the extraction isotherm shows higher extraction values than that of cobalt at pH of 6. As previously observed, the presence of iron creates some problems as it tends to be extracted at a lower pH than cobalt therefore it should be controlled to make sure there is only a minimum of Fe(II) present in the solution reporting to solvent extraction. This also applies to zinc and copper.

*McCabe-Thiele Diagram for estimating the number of extraction stages*

The number of stages required to achieve a certain metal ion concentration in the organic and raffinate phases can be estimated using the McCabe Thiele diagram.



**Figure 4.6** Plot of McCabe Thiele diagram at pH6 and 35°C contact time 20 minutes, O/A ratio: (3:1)

**Figure 4.6** shows a McCabe–Thiele diagram constructed for cobalt to determine the theoretical extraction stages for the separation of cobalt from impurities at pH 6 and 35°C. Three theoretical extraction stages would be required to reduce the cobalt concentration in the aqueous solution from 3.5 g/L to less than 3 ppm using an O/A ratio 3:1.

#### 4.2.6 Extraction Kinetics

In the extraction procedure, the time to reach equilibrium is controlled by mass transport processes and/or by the rate of chemical reactions. When chelate formation is involved in the extraction process, and the reaction takes place between species, originally present in the two separate phases, the rate of the extraction can be slow. Similarly the rate of the extraction process is unfavourably influenced, if the competing side reactions are slow, and complex displacement reactions are involved (Klein, et al., 1958).

This follows the kinetic equation given below:

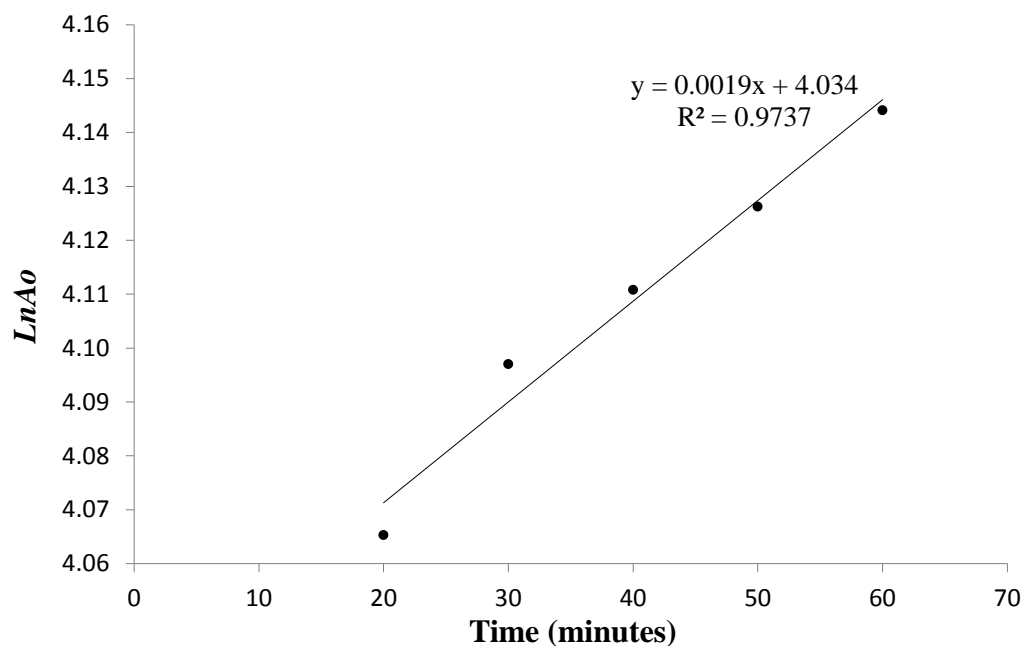
$$\ln A_o^0 - \ln A_o = \frac{kt}{(V_o/V_a)K + 1} \quad 4.2$$

Where  $A_o^0$  is initial concentration of A, that is at  $t = 0$ . A is the concentration. With  $k$ , reaction diffusion and  $K$ , mass transfer coefficient which is a constant in this study.

Plot of  $\ln A_o$  versus  $t$  provides a slope of  $-k [(V_o/V_a)]$ . The variation in  $V_o/V_a$  will provide another slope in agreement with the **Equation. 4.2**. The  $\ln A_o$  plot is approximately independent on the pH of the solution. By plotting the several times according to **Equation 4.2**, one can procure the rate constant. When extraction takes place under mixed control the concentration in the bulk solution at the interface are not equal.

The kinetics of extraction was studied at the optimum temperature (35°C), 3:1 O/A ratio, and 2.12g/L cobalt concentration at pH 6. From the analysis of the kinetics, it was found that the extraction rates at temperatures of 35°C were better expressed by the reaction kinetic model represented by kinetic **Equation 4.2** for diffusion control.

The kinetic equations as functions of time at a pH of 6 is plotted and presented in **Figure 4.7**.



**Figure 4.7 Plot of LnAo versus time at pH 6 and temperature of 35°C**

By plotting the organic-phase concentrations at several times according to **Equation 4.2**, one can procure the rate constant.

When extraction takes place under mixed control the concentration in the bulk solution and the interface are not equal. The results on the kinetics of  $\text{Co}^{+2}$  by Cyanex 272 in Shellsol 2325 show a noticeable modification in the kinetic behavior. The slopes obtained indicate that the metal distribution shows second order dependences on pH (6), on O/A phase ratio (3:1), and on Temperature (35°C).

### 4.3 Summary and Conclusions

The purpose of this work was to determine the ability of Cyanex 272 to extract cobalt from low-grade ore leach solutions. The augmentation of cobalt concentration allowed for the recovery of  $\text{Co}^{2+}$  in the organic phase at a commercial acceptable value as obtained by copper cobalt solvent plants.

Experimental results demonstrated the O/A ratio of 3:1 to be the optimum organic to aqueous ratio for cobalt extraction. Low extractions at lower organic to aqueous ratio were attributed to low mass transfer rates of reactants and products.

An increase in cobalt ions resulted in a parallel increase in cobalt extraction as the O/A ratio was varied.

Experimental results also showed a maximum extraction of 73.50% at a temperature of 35°C and pH of 6. Lower extraction values were observed at temperatures above 35 degrees Celsius. This suggests an exothermic process for the extraction of cobalt using Cyanex 272.

The results also showed that while a high pH and a high O/A ratio can favour the cobalt extraction the separation efficiency or selectivity of extraction over the common impurities such as copper, iron, magnesium, nickel, zinc etc. is quite low over the pH range studied.

Various experiments need to be conducted to know the precise simultaneous effect of all these parameters on solvent extraction, which can prove to be costly and time consuming. The upcoming chapter focuses on identifying factors that are influential in the solvent extraction of cobalt (II) using Cyanex 272 in the presence of Shellsol 2325.

## CHAPTER FIVE

### IDENTIFICATION OF INFLUENTIAL FACTORS

#### 5.1 Introduction

Coefficient interaction is a condition where the effect of one factor on the response depends upon the level of another factor. Different effects might be observed if one or more of the factors are held constant at a specific value. One-factor-at-a-time experimental designs where a unique factor is varied while others are kept constant are often expensive and time consuming, and do not frequently consider the interactive nature of various independent factors that would otherwise impact the results (Box et al, 1978; Schoofs, 1987). Application of experimental design is the most effective way to identify and optimize the significant factors, and to achieve a competent result by a few experimental trials. Therefore, the experimental design can be defined as an approach to solve the problem systematically and, it is applied to collect data and to analyse data for obtaining information-rich results (Gooding, 2004). Optimum and valid results with a minimum effort, time and resources are the primary objectives of applying the experimental design in an analytical process (Montgomery, 2005 and Cornell, 2011; Myers and Montgomery, 2002). In an experimental design, investigators deliberately manoeuvre one or several predetermined factors to know their impact on an experimental outcome.

The objective of the study in this chapter was to investigate the factors that influence the extraction of cobalt using a mixed Cyanex 272 and Shellsol 2325. The significance of each factor and their possible interactive effects were further studied using a statistical design of experiments by way of quarter fractional factorial designs ( $2^4$ ) and the extracted cobalt was taken as the measured response. The purpose is to identify the design variables that have large effects for further investigation. This type of experimental design permits allows the identification of factor settings (operating conditions) that maximize the extraction efficiency for all analyses.

The significant factors can be optimised while the insignificant ones can be set at levels where the least cost is incurred. Identification of influential factors is absolutely vital for process optimization and cost control. When the major factors are identified, they can then be optimized while the non-significant factors are kept at cost effective levels.

## 5.2 Materials and methods

### 5.2.1 Preparation of aqueous and organic phase

Stock solutions of cobalt (II) sulfate were prepared by dissolving copper-cobalt ore using sulphuric acid. The amount of cobalt in the pregnant leach solution was increased by dissolving a specific amount of  $\text{CoSO}_4 \cdot 5\text{H}_2\text{O}$ . The organic phase was prepared by loading Shellsol 2325 oil with cyanex 272. The typical chemical composition of various metals in the solution, are given **Table 3.3**.

### 5.2.2 Experimental Plan for Statistical Design of Experiments (DOE)

The DoE methodology has been widely used in the industry for the development of products and to enhance the quality of processes. DoE techniques are also extensively applied in many scientific areas with several research aims. Although previous researchers have worked on the extraction and separation of cobalt from copper, iron, magnesium and nickel sulphate solutions using the organo-phosphinic extractant (Adeleye, et al., 2012.) DoE techniques were not applied. Statistical Design of Experiments (DOE) was used in this work to study the solvent extraction behaviour of cobalt in the presence of different impurities. Statistical design and analysis of experiments were used in order to determine the main effects and interactions of extraction pH, temperature, extractant concentration, organic to aqueous phase ratio and metal ions concentration. The main purpose was to identify the key factors that affect the response (desired target) and the interactions among themselves (less or more than four factor interactions). The major objective was to come up with the optimum and not necessarily the maximum cobalt extraction using cyanex 272 as an extractant. The factors investigated were four quantitative factors (pH, temperature, cobalt concentration and O/A ratio) and one qualitative factor (time). All factors were evaluated at two levels, low and high level. The controlled factors were the factors that were actually selected for study (Table 5.1). The held constant factor (time) may have some effect on the response, but was not of interest in the current study; so it was held constant at a specific level (20 minutes).

At this diagnostic stage, the use of two levels for each factor allows for facilitation of the analysis and accommodates substantial reduction in the number of runs required (Montgomery, 2005). To evaluate the influence of independent variables on the dependent variable, a factorial design experimental plan with high level and low level (−1 and +1), the levels of controlled variables in coded units (Box et al., 1978) was used.

The low and high levels of factor A (Temperature) were set to be 25 and 50°C, respectively, which is the typical working temperature range for a cobalt extraction process. For factor B (pH), the minimum level of 4 is not the favored pH used in industry but it is known that cobalt is found extracted preferentially over nickel from the aqueous phase at an equilibrium pH of 4 to 6. This pH range is necessitated by the base properties of the oxygen-donors (Feather et al., 2002). For factor C (O/A ratio), lower and higher levels were respectively 1:3 to 3:1, chosen as the extreme ratios to see the separation that could be achieved in an infinite number of stages.

**Table 5.1 Experimental factors and levels for controlled factors**

Factors	Parameter	Low Level	Central point	High Level	Unit
A	Temperature	25	35	50	Celsius
B	pH	4	5	6	pH unit
C	O/A ratio	1:3	1:1	3:1	-
D	Co concentration	4	6	8	g/l

Generally, *coded values* were obtained as follows:

*Quantitative variables; coded value = [physical value – ½(highest value + lowest value)]/½(highest value-lowest value). Qualitative variables; coded variables were assigned at random.*

### 5.2.3 Methodology for Data Analysis

#### *Normal probability plot of standardized effects*

The process of screening involves the ordering of estimates of the effects according to their magnitudes and calculating their cumulative probabilities. These effects are then plotted on a normal probability. The method by Daniel, (1959), where effects are plotted on a normal probability plot often provides an effective way of helping with the selection.

All effects that are insignificant are normally dispensed with mean zero and variance  $\sigma^2$ , and tend to fall along a straight line on the plot. In contrast, significant effects have non-zero means and are located far away from the straight line. The more significant the effect, the further away it is from the straight line. The discordance between the averages at the two levels of each factor is a clue of the significance of that factor in influencing the response that



is measured. In the probability plots, most effects have to be classified from low to high and considered in this order. Hereafter, the numbered effects (i) get a value of percentage based on the following equation:

$$Value: \frac{i-1/2}{n} \times 100\% \quad 5.1$$

With  $i$  = total number of value

#### *Pareto chart*

A Pareto chart, named after Vilfredo Pareto, is a type of chart that contains both bars and a line graph, where individual values are represented in descending order by bars, and the cumulative total is represented by the line.

Variances are shown in their descending order to identify the largest opportunities for improvement, and to separate 'critical few' from the 'trivial many'. Also called a Pareto diagram, (Wilkinson 2006), the vertical line in the Pareto chart indicates the minimum statistically significant effect magnitude for 5% significance level, while the horizontal column lengths are proportional to the degree of significance for each effect. Any effect or interaction that exceeds the vertical line is considered significant.

### **5.3 Results and Discussion**

#### *5.3.1 Significant Parameters*

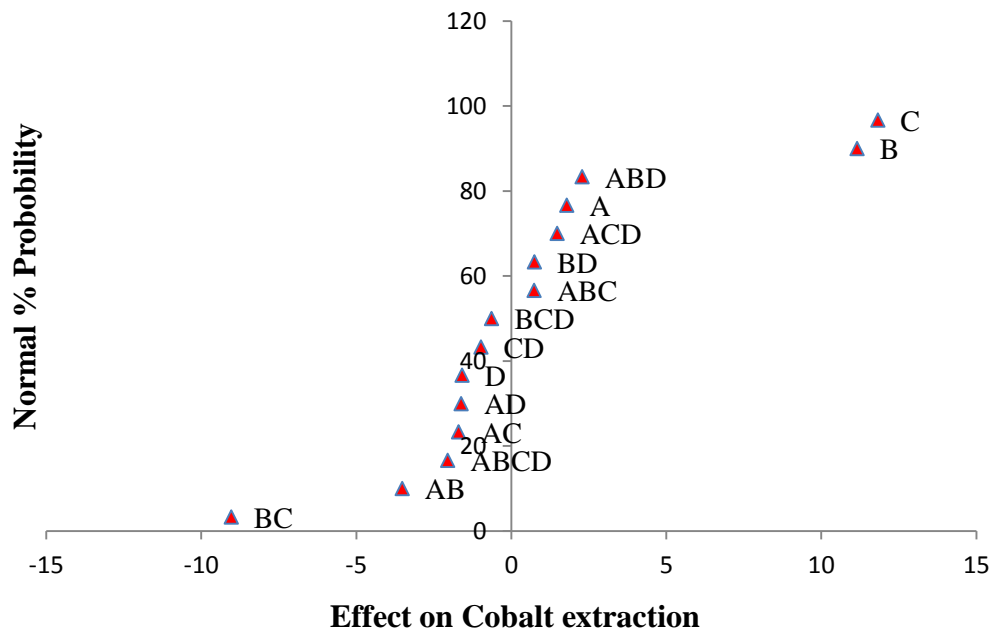
Cobalt extraction performances from experimental runs for the  $2^4$  full factorial designs with codified and actual values are given in **Table 5.2**.

**Table 5.2** shows the experimental layout and standard runs for the  $2^4$  basic designs. In general, the  $n^{th}$  column consists of  $2^{n-1}$  minus signs followed by  $2^{n-1}$  plus signs (Box et al, 1978). The experimental data given in **Table 5.2** was used to estimate the main and interaction effects presented in **Figure 5.1**. All experiments (16 runs) were carried out under a homogeneous state in one block of measurements and the experimental spread (Std Order) was randomized in order to reduce the effects of the uncontrolled factors. Extraction (%E) was estimated by a normal probability plot of standardized effects.

**Table 5.2 Cobalt extraction results for the 2<sup>4</sup> full factorial design**

Random Run Order	Standard Run Order	Control Factors				% Co Extraction (average)
		A	B	C	D	
1	1	-1	-1	-1	-1	<b>30.87</b>
9	2	-1	-1	-1	+1	<b>36.30</b>
14	3	+1	-1	+1	+1	<b>58.23</b>
16	4	+1	+1	+1	+1	<b>57.89</b>
12	5	+1	+1	-1	+1	<b>58.26</b>
4	6	+1	+1	-1	-1	<b>56.26</b>
2	7	+1	-1	-1	-1	<b>46.04</b>
5	8	-1	-1	+1	-1	<b>58.04</b>
6	9	+1	-1	+1	-1	<b>61.27</b>
11	10	-1	+1	-1	+1	<b>57.80</b>
15	11	-1	+1	+1	+1	<b>60.50</b>
3	12	-1	+1	-1	-1	<b>58.28</b>
8	13	+1	+1	+1	-1	<b>60.28</b>
13	14	-1	-1	+1	+1	<b>55.74</b>
7	15	-1	+1	+1	-1	<b>63.03</b>
10	16	+1	-1	-1	+1	<b>36.63</b>

Figure The actual factor levels coded as values of (-1) and (+1) in the table are as follows: A (Temperature): 25°C (-1) and 50°C (+1); B (pH): 4 (-1) and 6 (+1); C (O/A ratio): 1:3 (-1) and 3:1 (+1); D (Co Concentration): 2g/L(-1) and 4g/L(+1).



**Figure 5.1** The actual factor levels coded as values of (-1) and (+1) in the table are as follows: A Temperature, B: pH, C: O/A ratio, D: Co Concentration, AC, BC, AD, BD, CD, ABC, ABD, ACD, BCD and ABCD are factor interactions.

The estimates of main effects of factors, at the same time with their interaction terms, are shown on a normal probability plot of effects (Figure 5.1). All effects which are insignificant are normally distributed with mean zero and variance  $\sigma^2$ , and tend to fall along a straight line on the plot. In contrast significant effects have non-zero means and are located far away from the straight line. The greater the significant effect, the most away it is from the straight line. From this analysis, significant effects that appear are the main effects of C (A/O ratio) and B (pH), and the BC (A/O ratio-pH) interaction. The interaction BC indicates a negative effect on %E. The effect lines attained for the rest of the parameters and their interaction, on the other hand, reveal their insignificant effect on % extraction.

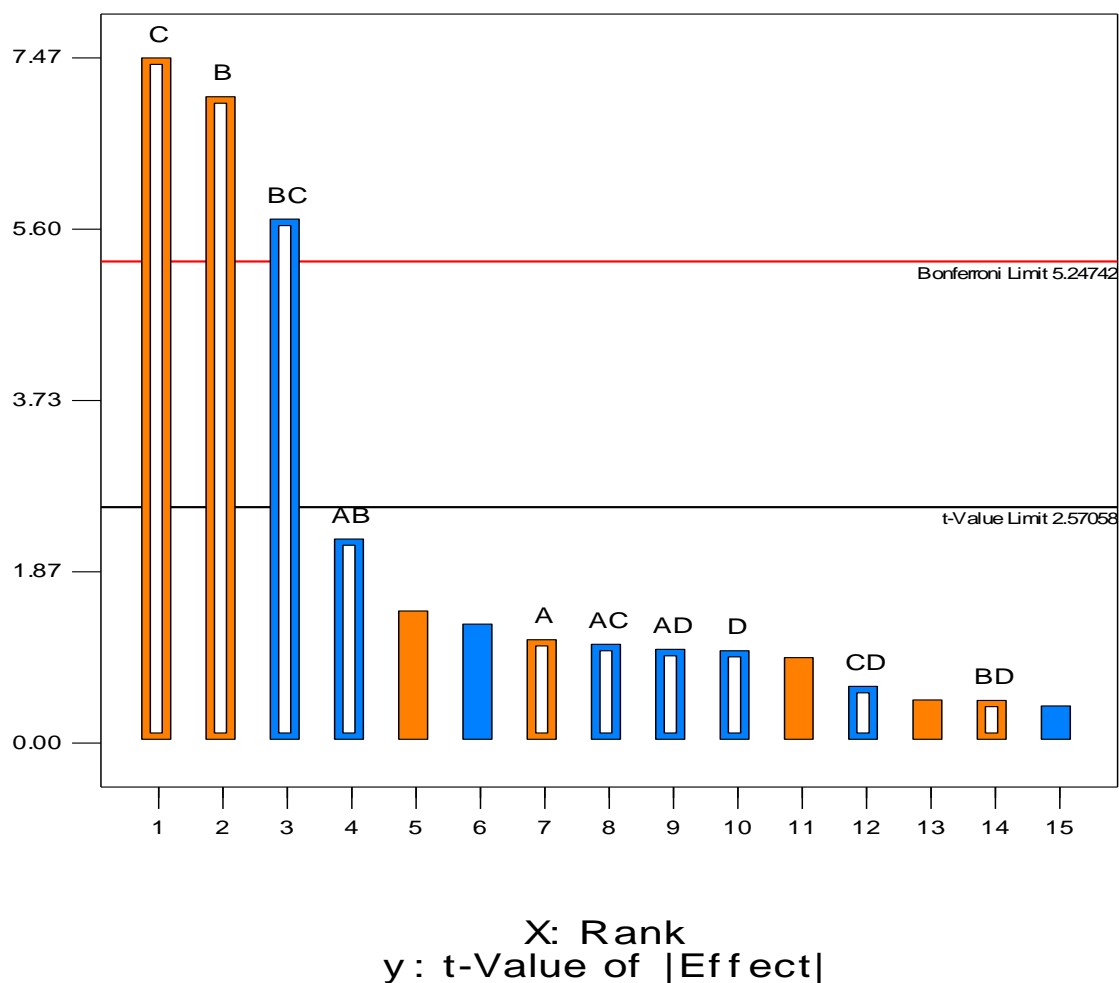
A normal first order polynomial model (fitted model) between significant factors and the response was developed to illustrate the dependence of the response on the significant factors. The model is expressed below as:

$$R = 53.47 + \frac{5.91}{2} Cc + \frac{5.575}{2} Bb - \frac{9.04}{2} BbCc \quad 5.2$$

Where R is the recovery, Cc, Bb, and Bb Cc are the contrast constants (+1 and -1) for the factors B and C respectively.

In **Equation 5.2**, the positive sign of coefficients for main effects C and B indicate their synergistic effects on %E while the negative sign of coefficient for BC interaction denotes an antagonistic effect. In addition, the size of regression coefficients in **Equation 5.2** denotes the degree of significance of each independent variable which, in the order of decreasing significance with respect to the influence on %E, is  $C > B > BC$ . In **Equation 5.2**, the negative signs in the variables of the prediction model equation indicate that in order to maximize cobalt extraction, these factors must be kept at low levels. The positive signs mean that the factors must be kept at high levels.

The results obtained from the normal probability plot of effects (**Figure 5.1**) are confirmed with a Pareto chart as shown in **Figure 5.2**. The purpose of the Pareto chart is to highlight the most important among a set of factors. The horizontal line in the Pareto chart indicates the minimum statistically significant effect magnitude for 5% significance level, while the vertical column lengths are proportional to the degree of significance for each effect. Any effect or interaction that exceeds the horizontal line (Bonferroni limit) is considered significant. The sequence of the significant main and interaction effects with respect to decreasing influence on %E was in agreement with that obtained from the normal probability plot of standardized effects, that is  $C > B > BC$ . Analysis of the individual factors on the Pareto chart showed that pH and A/O ratio were statistically significant since they overshoot the critical value line.



**Figure 5.2** Pareto chart showing significance of main and interactive effects of: A: Temperature, B: pH, C: O/A ratio, D: Co Concentration, AC, BC, AD, BD, CD, AB.

There is a confounding pattern of effects when using fractional factorial designs. This really means that (assuming that three-factor and higher interactions are insignificant) the estimated effect of a factor is a combination of the actual values of the effects of that factor and its two factor interactions (Barrentine, 1999). **Figure 5.3** is a normal plot of residuals. As can be seen, all residuals lie on a straight line with a linear correlation coefficient of 96.27%, which shows that the residuals were distributed normally. All residuals were distributed between -2 and +2 without any systematic structure. Since, the residuals were distributed normally with constant variance, mean zero and independently (**Figures 5.3** and **5.4**), it can be concluded that **Figure 5.1** was good fit to the experimental data.

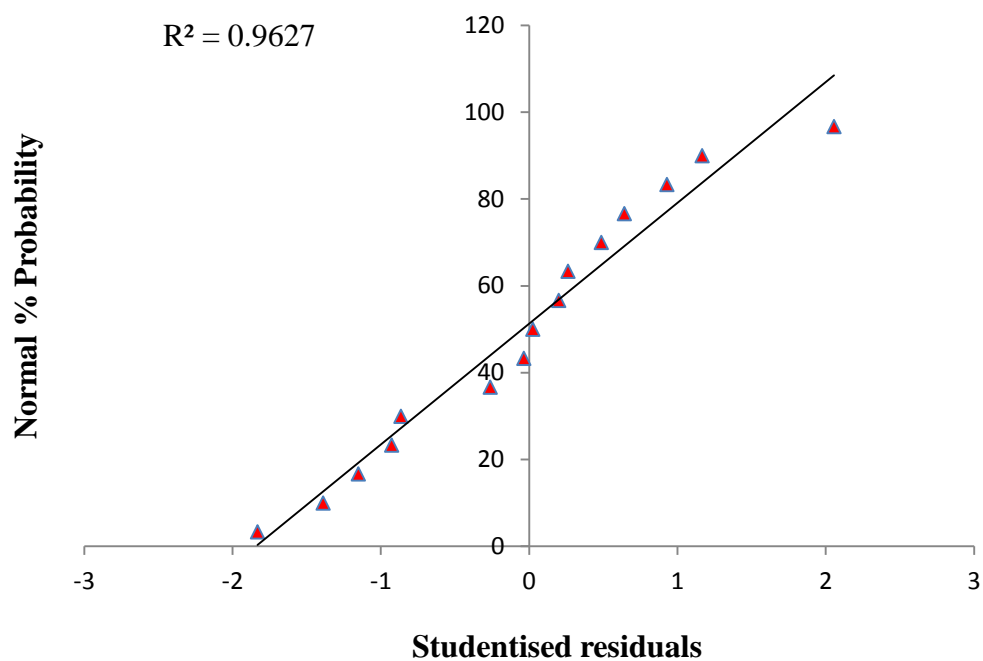


Figure 5.3 Normal plot of residuals

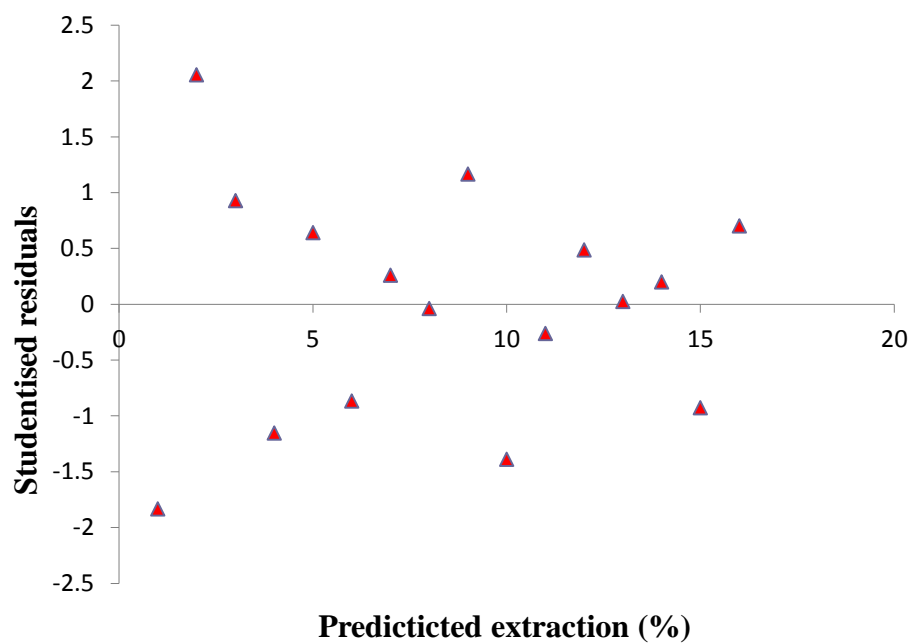
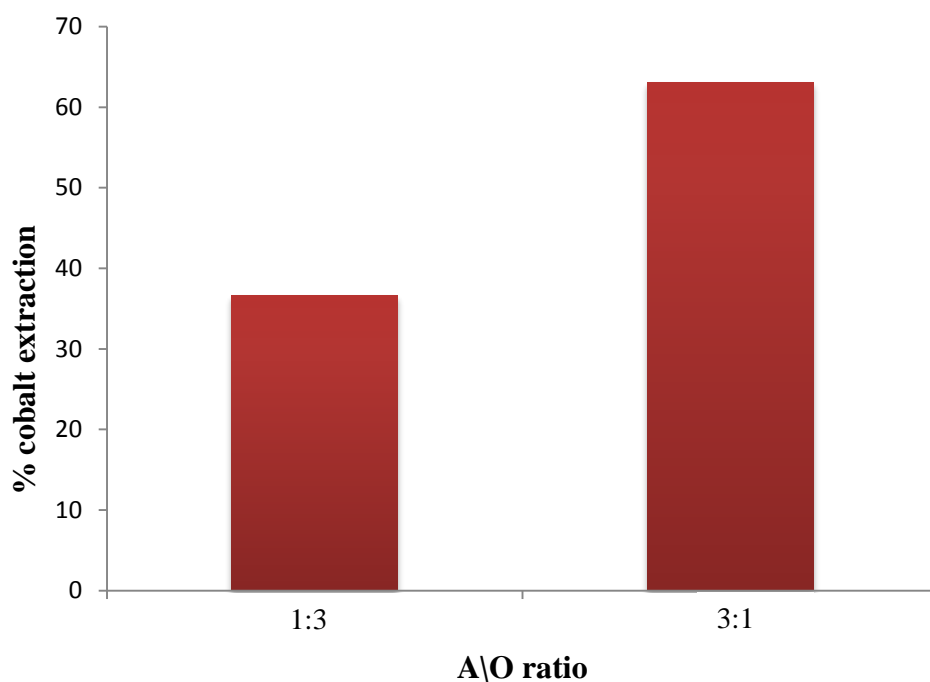


Figure 5.4 Plot of residuals versus predicted extractions

### 5.3.2 Influence of Significant Factors on Extraction

#### *Effect of O/A ratio*

The effect of organic to aqueous ratio on cobalt extraction is presented in **Figure 5.5**. The figure shows cobalt extraction from sulphate solution at organic to aqueous ratios of 1:3 and 3:1 which are high and low levels respectively. Higher cobalt extraction was attained at the higher organic ratio of 3:1 than at the lower organic to aqueous ratio of 1:3. As previously mentioned in **Chapter 4**, this might be attributed to the increase in the quantity of metal ions transferred which is related with the quantity of extractant that will furnish the necessary molecules to form the complex to reach the equilibrium state. As the quantity or volume of the organic phase increases, the amount of metal transferred will increase leading to a decrease in the concentration of metal in the aqueous phase, hence causing an increasing in the extraction coefficient (Ritcey and Ashbook, 1979).



**Figure 5.5 Effect of O/A ratios on cobalt extraction**

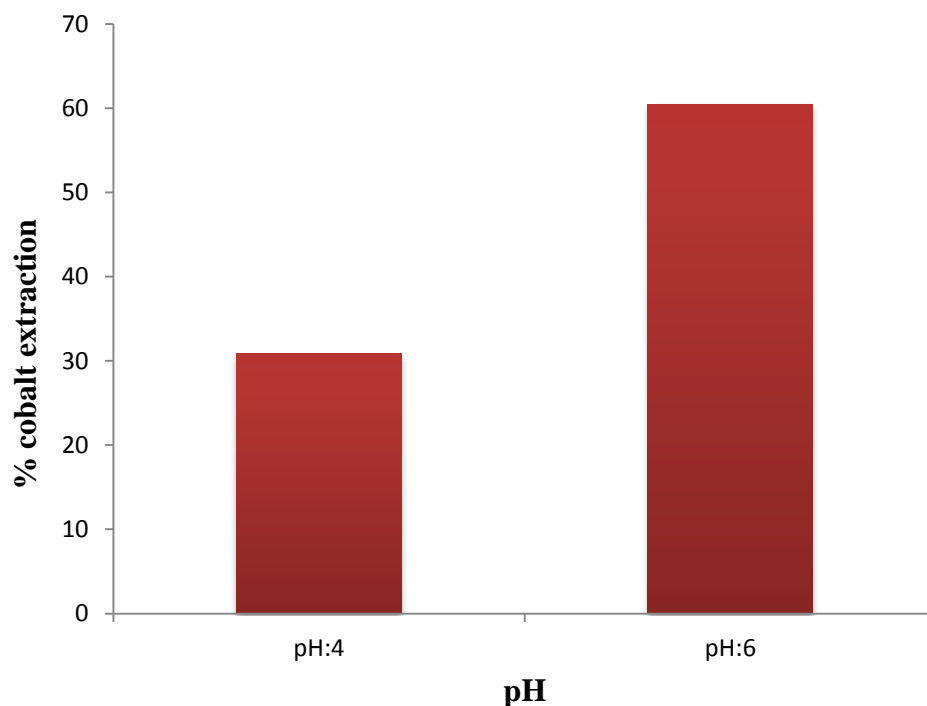
#### *Effect of pH*

The effect of pH is shown in **Figure 5.6**. The figure shows that a higher extraction of cobalt is obtained at higher initial pH of the feed solution under the conditions tested. The higher the pH of the system, the lower will be the extractant concentration needed to achieve a given percent metal extraction, and vice versa (Habashi, 1999).



With  $M = \text{Co}$  and  $LH = \text{extracting agent}$

The equation shows that the greater the amount of metal extracted the more hydrogen ions are generated as seen in the **Equation (5.3)**. This therefore means that to maintain a high metal extraction, the pH of the solution should be closely monitored.



**Figure 5.6 Effect of pH on cobalt extraction**

#### *Effect of factor interaction*

Beside organic to aqueous ratio and pH, the interaction between O/A ratio and pH was also observed. It may be noted from equation (2.11) that the extractability of a metal with a given reagent and organic solvent depends equally upon the organic phase concentration of the reagent and upon the hydrogen ion concentration in the aqueous phase. A tenfold increase in the reagent concentration will increase  $D$  as much as would a rise of one unit in pH. This interaction effect would not be detected in univariate *quantitative analysis* statistic techniques (Montgomery et al., 2002). The interactions between the rests of the main effects were comparatively insignificant.



## 5.4 Summary and Conclusions

The identification of influential factors in this chapter was addressed by: screening the main influential factors using a diagnostic two-level quarter fractional design to obtain data that would serve as an initial approach to the final optimization that is presented in the upcoming chapter (**Chapter 6**).

At this stage, factors were investigated at their upper and lower levels. The experimental results were analyzed statistically for the significance of the factors using the probability plots and a Pareto chart.

The results obtained indicated the following:

- The statistical method and experimental design approach selected has been able to satisfactorily help in determining statistically significant and insignificant factors.
- Organic to aqueous phase ratio and the pH were statistically significant while the other factors were statistically insignificant, meaning that organic to aqueous phase ratio and the pH influence cobalt extraction.
- Under the ranges studied, the interaction between B and C showed a significant influence on the extraction while the interactions between the rests of the main effects were statistically insignificant.
- The Pareto chart confirmed the significant effect of O/A ratio and pH on the cobalt extraction.
- The high  $R^2$  values signify that the model obtained is able to give a reasonably good estimate of response for the system in the range studied.

## CHAPTER SIX

### OPTIMIZATION OF INFLUENTIAL FACTORS

#### 6.1 Introduction

Optimization is the act of obtaining the best result under given circumstances. In design, construction, and maintenance of any engineering system, engineers have to take many technological and managerial decisions at several stages. The ultimate goal of all such decisions is either to minimize the effort required or to maximize the desired benefit. Since the effort required or the benefit desired in any practical situation can be expressed as a function of certain decision variables, *optimization* can be defined as the process of finding the conditions that give the maximum or minimum value of a function (Rao, 2009). Unconstrained optimization is a useful tool for many engineering applications, particularly in the estimation of parameters and states from data, to assess trade-offs for economic analysis and to analyse a variety of engineering systems. Moreover, an understanding of unconstrained optimization concepts is essential for optimization of constrained problems (Biegler, 2010).

Unfortunately several popular optimisation methods usually do not work very well (Öberg and Deming, 2000). They either rely on the classical one parameter at a time approach that ignores the combined interactions between physicochemical parameters or are theoretical in nature.

It is evident that optimizing the solvent extraction process of low grade ore solutions is complex since various parameters/attributes such as metal concentration, temperature, extraction time; agitation rate, aqueous/organic ratio, pH etc. affect the efficiency of the extraction process simultaneously. It is not possible with the tools currently available, to develop methods that are able to solve the general problem. It is thus necessary to divide the general problem into subproblems until a specific solution can be found (Cisternas, 1998).

In this present work, an attempt was made to optimise process parameters identified as significant in the previous chapter. These include the pH, and the aqueous/organic ratio for solvent extraction of cobalt using a statistically-based optimisation strategy called response surface methodology (RSM).

RSM is the most popular technique used to establish the optimal conditions by using quadratic polynomial model and is applied as a consequence of a screening or diagnostic experiment (Myers and Montgomery, 2002). This methodology is based on experimental design with the final goal of evaluating optimal conditions, using a polynomial model. Here, the inputs are called factors or variables and the outputs represent the response that generates the system under the causal action of the factors.

An efficient alternative to factorial design is central composite rotatable design (CCRD), originally developed by Box and Wilson (1951). Therefore, in this study, it was decided to use CCRD to design the experiments. This consists of  $2^k$  factorial or a fractional factorial points (coded  $\pm 1$ ), augmented by  $2k$  axial or star points  $[(\pm\beta, 0, 0, \dots, 0), (0, \pm\beta, 0, \dots, 0), \dots, (0, 0, \dots, \pm\beta)]$  and  $n_c$  replicate points at the centre  $[(0, 0, 0 \dots 0)]$  (Oraon et al., 2006); where  $k$  is the number of factors studied,  $\beta$  is distance of an axial point from the centre. The number of tests required for CCRD includes the standard  $2k$  factorial with its origin at the centre,  $2k$  points fixed axially at a distance. Where  $n_c$  is calculated by:

$$n_c \cong 0.8385 \left( 2^{k/2} + 2 \right)^2 - 2^k - 2k \quad 6.1$$

## 6.2 Experimental Design for the Response Surface Methodology and CCRD

Previously in this dissertation it was identified (Chapter 5) that parameters such as pH and O/A ratio were statistically significant operating parameters in the cobalt extraction process. Response surface methodology and central composite rotatable design have been used in this study in an attempt to determine the optimal conditions of pH and O/A ratio for the cobalt solvent extraction process. The laboratory test consisted of a number of measuring beakers used as mixer settler units. The volume of each beaker was  $250 \text{ cm}^3$ . Feed solutions were mixed by the use of magnetic bar rotating in the same direction within a specific time. The pH was controlled using laboratory Metrohm 809 pH meter. This was done under fumehood. To make simpler the calculations and for uniform assimilation, factors were carefully designed with their codified values. The relationships presented in **Table 6.1** were used to calculate each factor shown in factual and coded values shown in **Table 6.2**.

**Table 6.1 Relationship between coded and actual values of a variable (Box and Wilson, 1951)**

Code	Actual value of variable
$-\beta$	$\chi_{min}$
$-1$	$[(\chi_{max} + \chi_{min})/2] - [(\chi_{max} - \chi_{min})/2\beta]$
$0$	$(\chi_{max} + \chi_{min})/2$
$+1$	$[(\chi_{max} + \chi_{min})/2] + [(\chi_{max} - \chi_{min})/2\beta]$
$+\beta$	$\chi_{max}$

$\chi_{max}$  and  $\chi_{min}$  = maximum and minimum values of  $x$  respectively;  $k$  = number of variables (in this study  $k=2$ ).  $\pm\beta = (2k-q)^{1/4}$  for CCRD,  $-q$  = fraction of the number of factors.

Applying the relationships in **Table 6.1**, the values of the codes were calculated as shown in **Table 6.2**. These were then used to determine the actual levels of the variables for each of the experiments (see **Table 6.3**).

**Table 6.2 Relationship between coded and actual values of a variable (Box and Wilson, 1951)**

Variable	Symbol	Coded variable level				
		<u>Lowest</u>	<u>Low</u>	<u>Centre</u>	<u>High</u>	<u>Highest</u>
		$-\beta$	$-1$	$0$	$1$	$+\beta$
pH	$X_1$	3	4	5	6	7
O/A ratio	$X_2$	0	1	2	3	4

The important objective of the response surface methodology was to amplify the optimum conditions so as to maximize the extraction of cobalt from leach solution using an organic solution (*Cyanex 272 and Shellsol 2325*). Thus, the extraction (conversion) of cobalt was taken as the response. When the response data is obtained from the test work, a regression analysis is carried out to determine the coefficients of the response model ( $b_1, b_2 \dots b_n$ ), their standard errors and significance.

Two important models are commonly used in RSM (first and second order) (Khuri, 1996). In this study, the model used is second order. This is usually the most popular of all designs. This design consists of the following three portions:

- A complete (or a fraction of)  $2^k$  factorial design whose factors' levels are coded as  $-1$ ,  $+1$ , this is called the factorial portion.
- An axial portion consisting of  $2k$  points arranged so that two points are chosen on the axis of each control variable at a distance of  $\alpha$  from the design center (chosen as the point at the origin of the coordinates system).
- $n_0$  center points.

Thus, the total number of design points in a CCD is  $n = 2^k + 2k + n_0$ . For example, a CCD for  $k=2$ ,  $\alpha = \sqrt{2}$ ,  $n_0 = 2$  has a form given in Appendix A.

According to the equation 6.1  $n_c$  is the number of centre point replications and  $k$  is the number of factors studied.  $n_c = 5$  in this study as  $k=2$ .

**Table 6.3 Experimental layout and runs for the central composite rotatable design**

Standard Runs	Coded values of variables		Actual levels of variables	
	<u>pH</u>	<u>O/A ratio</u>	<u>pH</u>	<u>O/A ratio</u>
<b>Factorial portion</b>				
1	-1	-1	4.3	1.29
2	1	-1	5.7	1.29
3	-1	1	4.3	2.70
4	1	1	5.7	2.70
<b>Axial portion</b>				
5	-1.414	0	3	2
6	1.414	0	7	2
7	0	-1.414	5	0
8	0	1.414	5	4
<b>Centre points</b>				
9	0	0	5	2
10	0	0	5	2
11	0	0	5	2
12	0	0	5	2
13	0	0	5	2

Thus for the two variables under consideration, the response model is:

$$y = (\beta_0 + \varepsilon) + \sum_{i=1}^2 \beta_i x_i + \sum_{i=1}^2 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^2 \beta_{ij} x_i x_j \quad 6.2$$

Where  $y$  is the predicted response,  $\beta_0$  is the coefficient for the intercept,  $\beta_i$  is the coefficient of linear effect,  $\beta_{ii}$  is the coefficient of quadratic effect,  $\beta_{ij}$  is the coefficient of interaction effect,  $\varepsilon$  is the term that represents other sources of variability not accounted for by the response function, and  $X_i$  and  $X_j$  are coded independent variables. In general **Equation 6.2** can be written in matrix form:

$$Y = bX + \varepsilon \quad 6.3$$

Where  $Y$  is defined to be a matrix of measured values and  $X$  to be a matrix of independent variables. The matrices  $b$  and  $\varepsilon$  consist of coefficients and errors, respectively (Kwak, 2005).

## 6.3 Results and Discussion

### 6.3.1 Derivation of the model

**Table 6.4 Observed values for the cobalt extraction**

Factor Levels				Cobalt Extraction (Observed)	Standard Run
Coded		Actual			
C-A/O ratio	B-(pH)	C-A/O ratio	B-pH		
Factorial portion					
-1	-1	1.29	4.3	60.50	1
+1	-1	1.29	5.7	54.26	2
-1	+1	2.70	4.3	54.74	3
+1	+1	2.70	5.7	57.89	4
Axial portion					
-1.414	0	2	4.3	33.63	5
+1.414	0	2	5.7	20.87	6
0	-1.414	0	5	60.54	7
0	+1.414	4	5	60.28	8
Centre points					
0	0	2	5	55.8	9
0	0	2	5	34.13	10
0	0	2	5	58.23	11
0	0	2	5	58.04	12
0	0	2	5	58.28	13

The fitted second order model was obtained as:

$$\hat{y} = 53.47 + 0.89x_1 + 5.58x_2 + 5.92x_1x_2 - 0.8x_2^2 \quad 6.4$$

Where,  $x_1$  = O/A ratio and  $x_2$  = pH, within predictor variable limits:  $-\lambda \leq x_i \leq \lambda; i =$

Where  $x_i$  are coded predictor variables and  $-\lambda = 2(k-q)^{1/4} = 1.414$  (for  $k = 2, -q = 0$ ) is the distance of the axial points from the centre of the CCRD that *gives the limits of the valid region* under experimentation.

### 6.3.2 Checking the Adequacy of the Developed Model

The adequacy of the fitted model was carried out using the analysis of variance (ANOVA) given in **Table 6.5**

**Table 6.5 ANOVA for the fitted model**

Source	Sum of Squares	Degree of freedom	Mean Square	F Value	p-value Prob > F	
<b>Model</b>	<b>0.7</b>	<b>10</b>	<b>0.07</b>	<b>9.94</b>	<b>0.0102</b>	<b>significant</b>
	9.51E-03	1	9.51E-03	1.36	0.2964	
	0.23	1	0.23	32.5	0.0023	
	0.25	1	0.25	35.59	0.0019	
	2.84E-03	1	2.84E-03	0.41	0.5522	
	0.024	1	0.024	3.47	0.1217	
	8.68E-03	1	8.68E-03	1.24	0.316	
	7.96E-03	1	7.96E-03	1.14	0.335	
	0.16	1	0.16	23.5	0.0047	
	6.59E-04	1	6.59E-04	0.094	0.7713	
	1.11E-03	1	1.11E-03	0.16	0.7069	
<b>Residual</b>	<b>0.035</b>	<b>5</b>	<b>7.00E-03</b>			
<b>Total</b>	<b>0.73</b>	<b>15</b>				

The Model F-value of 9.94 implies the model is significant. There is only a 1.02% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B, C and BC are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

The "Pred R-Squared" of 0.9663 is not as close to the "Adj R-Squared" of 0.9019 (**Table 6.7**). "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 10.954 is an adequate signal. This model can be used to navigate the design space.

The ANOVA for the re-fitted model is given in **Table 6.6** with the effects and significance of the individual terms in the refitted response surface model. The re-fitted model is:

$$\hat{y} = 53.47 + 0.89x_1 + 5.58x_1 + 5.92x_1x_2 - 0.8x_2^2 \quad 6.5$$

To obtain a simple and yet realistic model, it was refitted using only the variable terms that are significant at greater or equal to 95% confidence level. Results of the refits are given in **Table 6.6**.

**Table 6.6 ANOVA for the re-fitted model**

Source	Sum of Squares	Degree of freedom	Mean Square	F Value	p-value Prob > F	
<b>Model</b>	<b>1079.26</b>	<b>4</b>	<b>269.81</b>	<b>6.53</b>	<b>0.0061</b>	<b>significant</b>
	12.73	1	12.73	0.31	0.59	
	497.4	1	497.4	12.04	0.0052	
	558.97	1	558.97	13.53	0.0036	
	10.16	1	10.16	0.25	0.6298	
<b>Residual</b>	454.55	11	41.32			
<b>Cor Total</b>	1533.81	15				

The significance of the re-fitted regression model was examined using the probability (Prob>F) value for regression model significance.

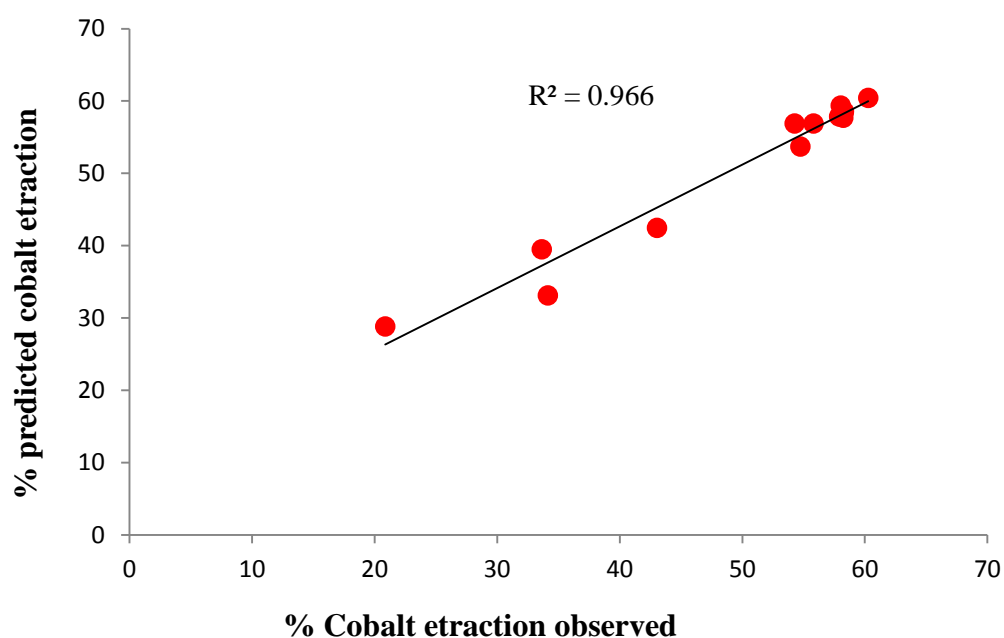


The model F-value of 6.53 implies the model is significant. There is only a 0.61% chance that a “Model F-Value” this large could occur due to noise.

**Table 6.7 Mean Summary Statistics**

<b>Std. Dev.</b>	3.17	<b>R-Squared</b>	0.9663
<b>Mean</b>	53.47	<b>Adj R-Squared</b>	0.9019
<b>C.V. %</b>	5.92	<b>Pred R-Squared</b>	0.6653
<b>PRESS</b>	513.37	<b>Adeq Precision</b>	10.954

From the mean summary statistics presented in **Table 6.7**, the low standard deviation value of 3.17 and high R-squared value of 96% show that the model is statistically likely to define the true performance of the experimental system. Experimental results and predicted values obtained using the refitted models are given in **Table 6.8**. As can be seen from **Figure 6.1**, the predicted values are plausibly comparable to the experimental values, with the linear correlation coefficient ( $R^2$ ) of 0.96. Statistically, this means that 96% of the sample variation can be explained by the independent variables.



**Figure 6.1 Relationships between experimental and predicted values for cobalt extraction**

**Table 6.8 Observed and predicted values for the cobalt extraction**

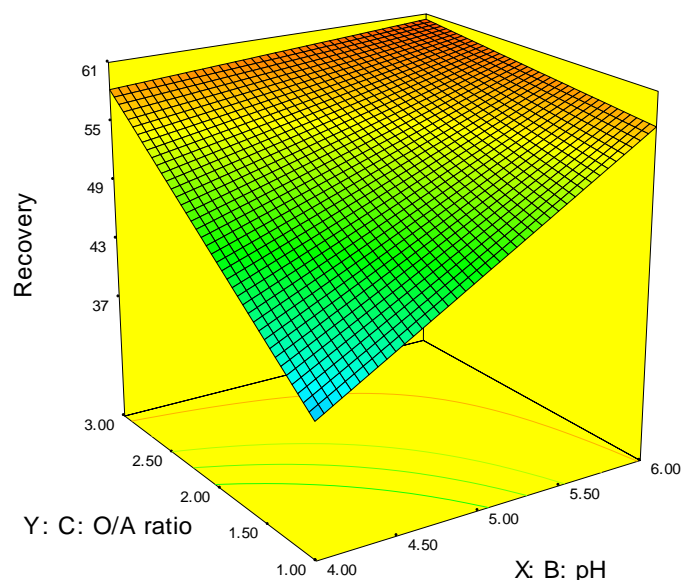
Factor Levels				Cobalt Extraction (%)		Standard Run
Coded		Actual				
C-A/O ratio	B(pH)	C-A/O ratio	B pH	Observed	Predicted	
Factorial portion						
-1	-1	1.29	4.3	60.50	62.04	1
+1	-1	1.29	5.7	54.26	56.88	2
-1	+1	2.70	4.3	54.74	53.67	3
+1	+1	2.70	5.7	57.89	57.87	4
Axial portion						
-1.414	0	2	4.3	33.63	39.48	5
+1.414	0	2	5.7	20.87	28.82	6
0	-1.414	0	5	60.54	62.26	7
0	+1.414	4	5	60.28	60.44	8
Centre points						
0	0	2	5	55.83	56.88	9
0	0	2	5	34.13	33.09	10
0	0	2	5	58.23	57.66	11
0	0	2	5	58.04	59.36	12
0	0	2	5	58.28	58.54	13

### 6.3.3 Response Surfaces

Once the experimental domain was confined, the proportion of organic solvent in the mixture (factor C) and the pH (factor B) were fine-tuned using the Response Surface Methodology (RSM). The model results are plotted as 3D response surface graphs and 2D contour plots (**Figure 6.2 and Figure 6.3**).

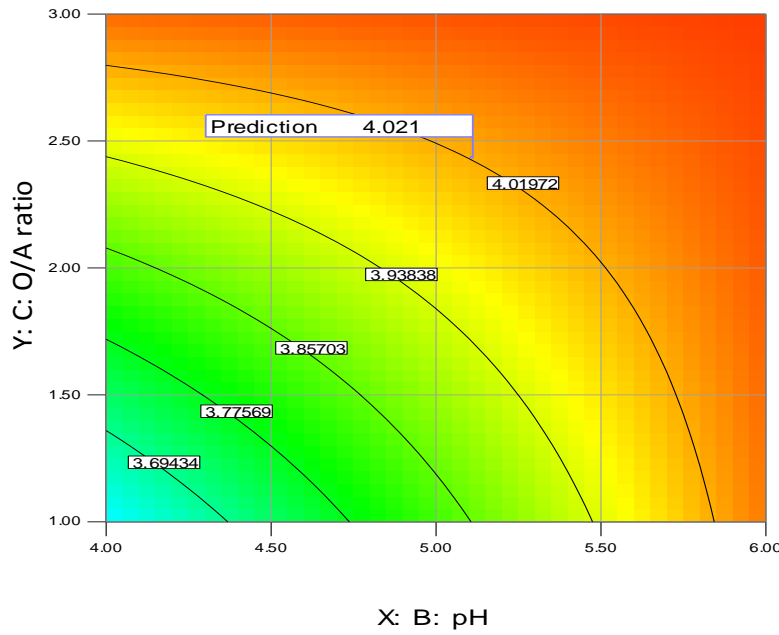
**Figure 6.2** shows the effect of O/A ratio and pH on cobalt extraction at constant temperature. The figure shows that with an increase in pH, the cobalt extraction increases with an increase in O/A phase ratio.

The effect of O/A ratio can be explained by the fact that an increase in organic phase increases the interface area of the two phases that helps in increasing the solvent extraction process. Diagnostics case statistics of this study is presented in the **Appendix D**.



**Figure 6.2 Response surface graph showing the effects of interaction of pH and O/A ratio on cobalt extraction (3D).**

**Figure 6.3** shows a contour plot where cobalt extraction was represented by varying simultaneously the extraction pH from 4 to 6. From this response surface plot, it is also clear that to obtain a higher cobalt extraction; the solvent extraction should be directed at a higher pH and O/A ratio. The lines of contour plots predict the values of cobalt extraction for different pH and O/A ratio at extraction time of 20 minutes. The optimum condition is found as the shaded area which converge the values from 2.50 to 3.00 for O/A and from 5.50 to 6.00 pH of extraction.



**Figure 6.3 Response surface graph showing the effects of interaction of pH and O/A ratio on cobalt extraction (2D).**

#### 6.3.4 Determination of the Optimum Conditions

As previously stated, the major objective of the work described in this chapter is to determine the conditions that maximize cobalt extraction from low concentration leach solutions. Thus, after the model was checked for adequacy of fit in the region defined by the coordinates of the design and was found to be adequate, the model was then used to locate the point of maximum response. The concept of rotatable design is not uniquely related to second order models or central composite designs. Myers (1989); Box (1951) and Hunter (1966) give a detailed description relating to rotatability. Therefore, in order to determine the condition at rotatability, the equation 6.6 was employed in this study.

$$\hat{y} = x^{1 \times p} \hat{\beta}^{p \times 1} \quad 6.6$$

Where

$$\hat{\beta} = \sigma^2 (X' X)^{-1} \quad 6.7$$

Thus Var

$$(\hat{y}) = \sigma^2 x^{1 \times p} (X' X)^{-1} x' \quad 6.8$$

Where  $x^{1 \times p}$  is a particular row of the design matrix as shown in the **Appendix (D)**

$$(X'X) \begin{vmatrix} 13 & 0 & 0 & 7.998 & 7.998 & 0 & 4 \\ & 7.999 & 0 & 0 & 0 & 0 & 0 \\ & & 7.999 & 0 & 0 & 0 & 0 \\ & & & 11.992 & 4.999 & 0 & 0 \\ & & & & 11.992 & 0 & 0 \\ & & & & & 4 & 0 \\ 0 & & & & & & 4 \end{vmatrix}$$

$$(X'X)^{-1} \begin{vmatrix} 0.077 & 0 & 0 & 0.125 & 0.125 & 0 & 0.25 \\ & 0.125 & 0 & 0 & 0 & 0 & 0 \\ & & 0.125 & 0 & 0 & 0 & 0 \\ & & & 0.0834 & 0.2 & 0 & 0 \\ & & & & 0.0834 & 0 & 0 \\ & & & & & 0.25 & 0 \\ 0 & & & & & & 0.25 \end{vmatrix}$$

This gives for the first row of the design matrix

$$\text{Var}(\hat{y}) = \sigma^2 x^{1 \times p} (X'X)^{-1} x'$$

$$\begin{aligned} &= S^2 \begin{vmatrix} 0.077 & 0 & 0 & 0.125 & 0.125 & 0 & 0.25 \end{vmatrix} x' \\ &= S^2 \begin{vmatrix} 0.077 & 0.015625 & 0.069555 & 0.625 \end{vmatrix} \\ &= 0.136 S^2 \end{aligned}$$

### 6.3.5 Confirmatory Experiments

The results discussed are an average of the runs conducted under similar experimental conditions. In order to test the validity of the optimised conditions given by the model, an experiment was carried out with parameters suggested by the model. The conditions used in the confirmatory experiment were as follows: O/A ratio: 3:1 and pH (6).

Predicted cobalt extraction,  $\hat{y} = 73.04\%$ . The re-fitted model with actual values is expressed as: Predicted cobalt extraction,

$$\hat{y} = 53.47 + 5.58 (\text{pH} - 4.3) + 5.9 (\text{ratio} - 1.29) \quad 6.9$$

Using actual values, of O/A ratio = 3:1 for optimum O/A ratio and pH = 6 for optimum pH, in **Equation 6.9**, Predicted cobalt extraction,  $s = 73.04\%$ .

The cobalt extraction at a pH of 6 was found to be 73.50% (Table 6.9), which is coherent with the model. The model can, therefore, be expected to fit the experimental data very well under these experimental conditions.

**Table 6.9 Cobalt extraction at optimum conditions**

Parameter	A/O ratio	pH	%Cobalt Extraction
Model	3:1	6	73.04
Confirmatory tests	3:1	6	73.50

#### 6.4 Summary and Conclusions

Demand for the cobalt metal has led to a need for devising new and effective techniques for cobalt extraction from low concentration leach solutions. In this chapter, the optimization of O/A phase ratio and pH for cobalt extraction from copper-cobalt low concentration leach solution ore was studied using response surface methodology and central composite rotatable design. The data confirms that a “high pH and high O/A ratio is best suited for the extraction of cobalt from the solutions examined in this study.

A second order model representing the cobalt extraction expressed as a function of these variables was developed by computer simulation programming applying least squares method using Design Expert 7. A statistical analysis of variance (ANOVA) was used to study the effects of these individual variables on cobalt extraction. The insignificant terms were then dropped from the second order model to obtain a re-fitted model. The final model validation was accomplished by using the standard deviation value and the coefficient of determination ( $R^2$ ).

Under the experimental conditions considered, the pH of 6 and the O/A ratio of 3:1 gave an optimum extraction of 73.04%. To verify this, a confirmatory run was carried out under these optimum conditions. The cobalt extraction found experimentally was 73.50%, clearly showing that the model fits the experimental data reasonably well, within an error margin of less than 1%.

Moreover, the work undertaken in this chapter is the culmination of the first stage of cobalt extraction process) as well as a prognostic to the stripping process (recovery) in the next chapter. This shows that, the amount of cobalt extracted from the optimized solvent extraction process described in this chapter will become the feed value to the stripping process discussed in the next chapter (Chapter 7).

## CHAPTER SEVEN

### THE COBALT STRIPPING PROCESS

#### 7.1 Introduction

In solvent extraction processing there are two stages involved; extraction and stripping. The stripping reaction is the opposite of the extraction reaction (Eq 7.1), with the forward reaction involving the extraction of the metal into the organic solvent and the backward reaction depicting the extraction from the organic solvent to aqueous solution. Hydrogen ion concentration in the aqueous phase is the only variable, which can be amended to reverse the reaction, once the metal is extracted into the organic phase. Thus, stripping in the example given through equation 7.1 indicates the need for the application of an acidic solution of a concentration sufficiently high enough to shift the equilibrium to the left and thus drive the metal into the aqueous phase.



Before cobalt can be recovered as metal in the electrowinning process, the loaded organic must be stripped. This would give a pure cobalt-containing aqueous solution from which metal would be obtained, via electrowinning. In the cation exchange system of present interest, the conventional stripping process involves contacting the organic solution with a sulphuric acid solution of sufficient concentration to reverse the loading reaction. Since cobalt and other impurities are extracted at different acid concentration, it is believed that separation of these species by selective stripping should be possible.

The possibility of using acidic stripping method to process cobalt from organic phase has been described in Chapter 2 (section 2.2.4). The use of sulphuric acid generates the transfer of cobalt ions from organic to aqueous phase. In order to have an idea on the use of sulphuric acid in this process, it is important to evaluate the role and effects of sulphuric acid. The stripping process depends on a number of coefficients, which have to be evaluated in order to get the best process route. The factors under consideration during most stripping process are: acid concentrations, the contact time and the effect of temperature. To avoid undesired side products the temperature and time will be kept relatively similar to the ones used during solvent extraction.



## 7.2 Materials and Methods

### 7.2.1 Samples and Preparation

Stock organic solutions of 3 liters in volume were prepared for the experiments. The loaded solution was prepared using the factors identified as significant during the solvent extraction process. The chemical composition of organic solution was determined prior to the stripping experiments. The typical chemical composition of the organic phase used for the stripping tests is given in **Table 7.1**.

**Table 7.1 Organic solution with different metals concentration**

Element	Ca	Co	Cu	Fe	Mg	Ni	Zn
Units	g/l	g/l	g/l	g/l	g/l	g/l	g/l
<b>B35-145</b>	0.84	5.02	0.96	0.11	0.76	0.01	0.04

### 7.2.2 The Effect of Acid Concentration

Stripping tests were carried out using analytical grade sulphuric acid ( $\text{H}_2\text{SO}_4$ ). In each experiment, 50 mL of organic solution was added to 50mL of sulphuric having a specified concentration and a temperature of 25°C. In the experiment, the concentration of sulphuric was varied between 50-100 g/L. Time was varied between 20-60 minutes. For the reason of recycling the the organic from a settler to mixer within a stage, it is a common procedure to lead the aqueous to organic phase ratio in the reactor at 1:1 or 2:1 (Gilberto, et al. 2004). Thus some variables were kept constant as follows: contact O/A ratio of 1:1 and stirring speed 800rpm. The stripping efficiency of cobalt from organic phase was calculated as a percentage of cobalt in the aqueous phase to that of the intial cobalt in the organic phase (see example in **Appendix A**).

### 7.2.3 The Effect of Temperature

In each experiment, 50 mL of organic was added to 50 mL of sulphuric acid having a concentration of 75 g/L and temperatures were kept at 25°C, 35°C, and 50°C, respectively.

### 7.2.4. The Effect of Contact Time

In each experiment, 50 mL of organic phase was added to 50 mL of sulphuric acid having a concentration of 75g/L. In the experiment, time was varied between 20 to 60 minutes.

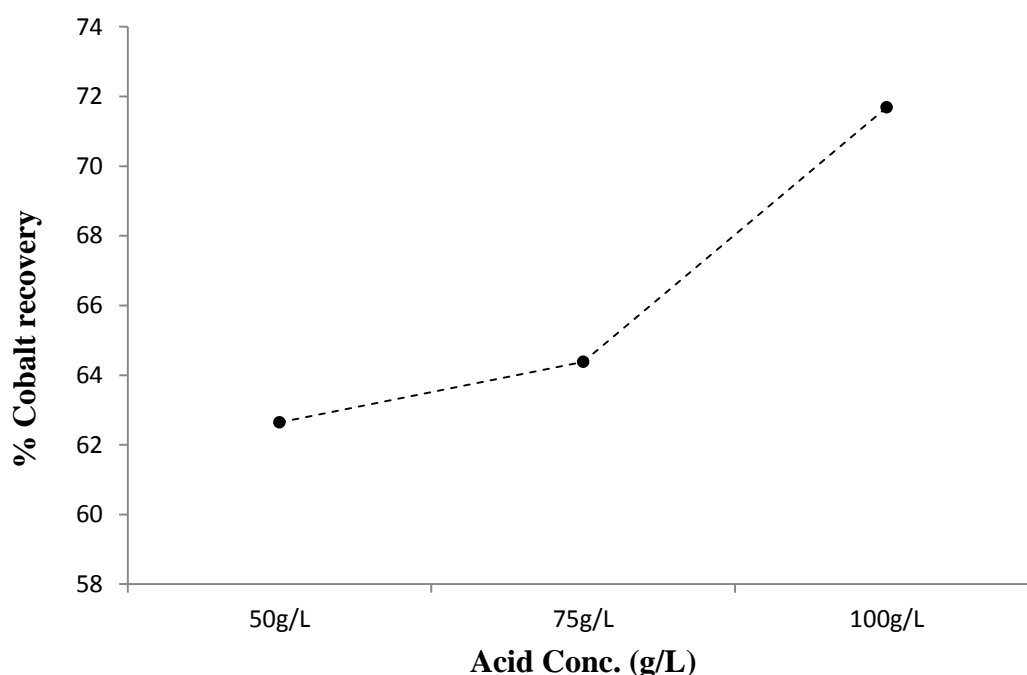
The parameters studied and their levels for cobalt stripping are summarised in **Table 7.2**. Parameters, which were kept constant during experimentation, were:

- Stirring speed = 800 rpm.
- O/A ratio = 1:1

### 7.3 Results and Discussion

#### 7.3.1 Effect of Acid Concentration on Cobalt Stripping

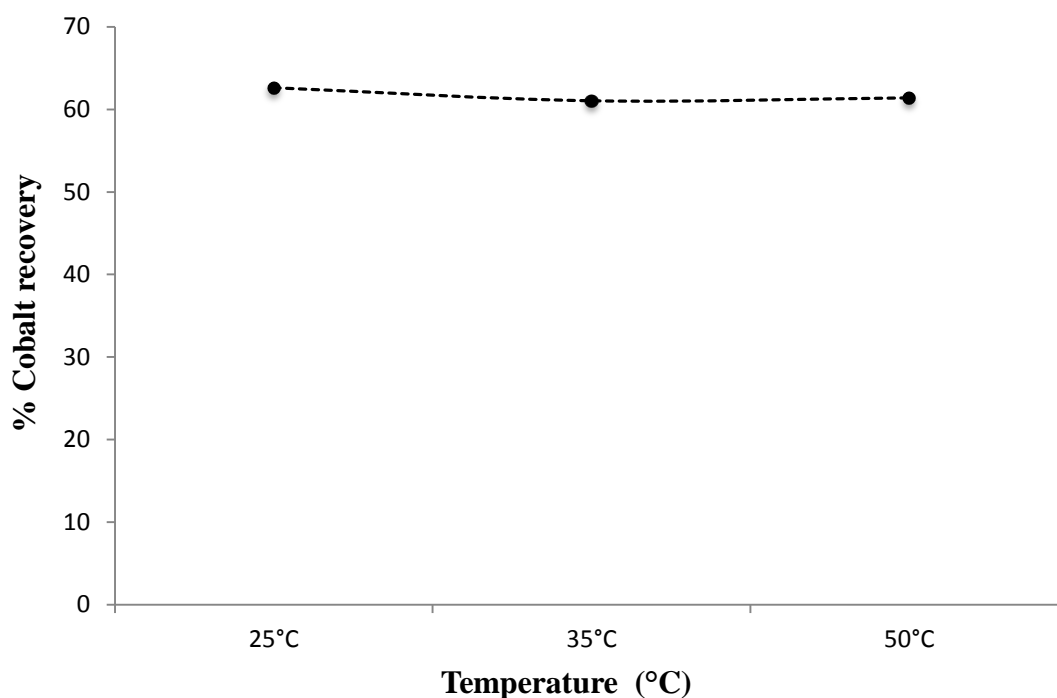
The effect of sulfuric acid concentration on the percentage extraction of metal ions is shown in **Figure 7.1**. The figure shows an overall increase in cobalt extraction as the acid concentration increases from 50g/L to 100g/L.



**Figure 7.1 Effect of acid concentration on cobalt stripping at 25°C (contact time 20 minutes, O/A ratio: 1:1)**

The cobalt loaded Cyanex 272 was studied with different concentrations (50 to 100g/L) of  $\text{H}_2\text{SO}_4$  at 1:1 phase ratio for 20 minutes. The plot (**Figure 7.1**) of (%) percentage recovery versus acid concentration indicated a linear increase in stripping from 50g/L to 100g/L. The figure shows 62.64% cobalt extraction at 50g/L, 64.38% at 75g/L and 71.69% at 100g/L. It is evident that the increase in acid concentration extremely enhances the extraction of cobalt.

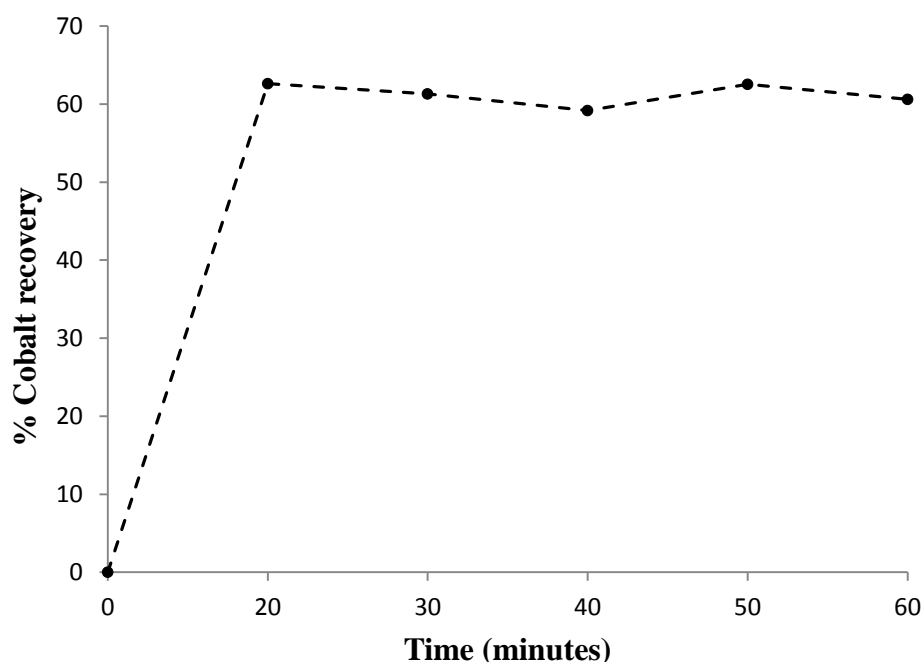
### 7.3.2. Effect of Temperature on Cobalt Stripping



**Figure 7.2 Effect of temperature on cobalt stripping at 50g/L (contact time 20 minutes, O/A ratio: 1:1)**

The effect of temperature on cobalt stripping from Cyanex 272 by sulphuric acid leaching is presented in **Figure 7.2**. From the obtained results, it was found that room temperature can be considered as a good temperature for cobalt stripping. It was perceived that for cobalt, percentage extraction decreases with increase in temperature. In the case of cobalt recovery, percentage extraction of 62.64% was recorded at a temperature of 25°C and this decreased sharply as the temperature increased.

### 7.3.3. Effect of Contact Time on Cobalt Stripping



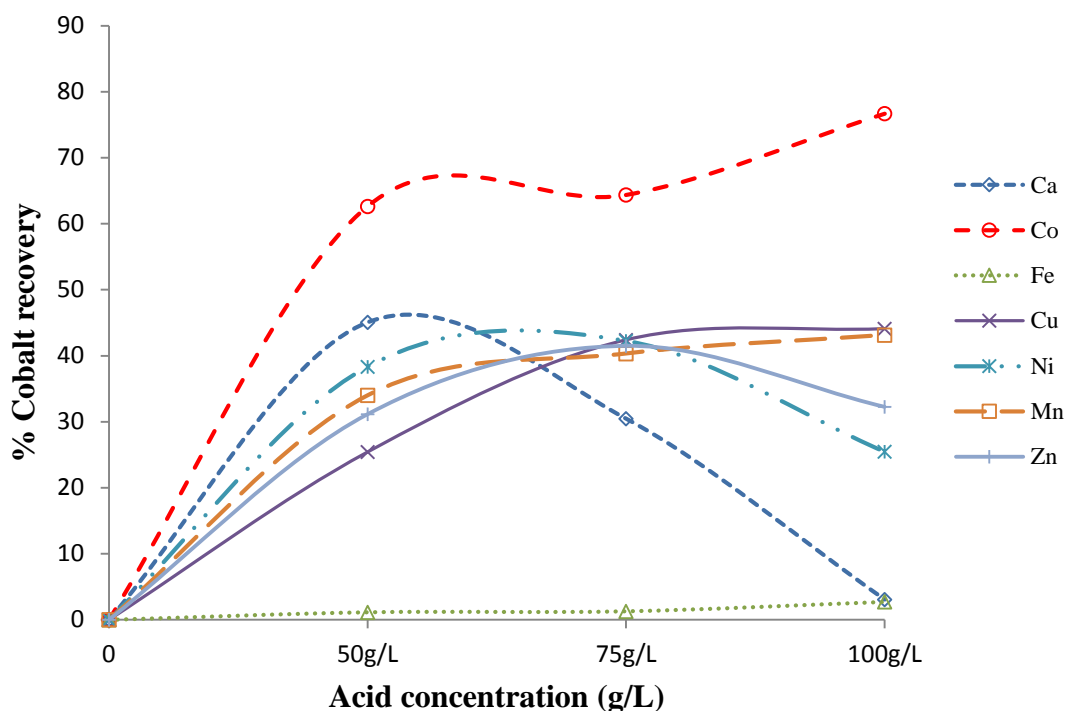
**Figure 7.3** Effect of time on cobalt stripping at 50g/L (contact time 20 minutes, O/A ratio: 1:1)

The effect of contact time on the stripping of cobalt from organic phase was studied at intervals between 20-60 minutes. The results obtained are given in **Figure 7.3**. It is evident that a contact time of 20 minutes is quite sufficient for efficient cobalt extraction. At the beginning of stripping, extraction of cobalt was very fast. At 20 minutes, 62.64% cobalt recovery was achieved. Beyond 20 minutes the cobalt recovery was constant at around 58% and no further increase in extraction occurred. It is important to note that, since equilibrium is reached within 20 minutes, using a contact time longer than this was not necessary for the further stripping process tests.

### 7.3.4. Effect of Acid Concentration on Selectivity

**Figure 7.4** showed the effect of acid concentration on selectivity over a given temperature (25°C), contact time (20 minutes) and cobalt concentration (5.02g/L). The selectivity of cobalt extraction over impurities was investigated. It was found that increasing the acid concentration resulted in a general increase in the cobalt recovery in the aqueous phase. The figure shows 62.64% cobalt recovery at 50g/L, 64.37% at 75g/L and 76.68% at 100g/L. There was however a decrease in the recovery of some of the impurities as the acid

concentration increased. This might mean that the impurity ions had a much higher affinity for the organic solvent compared to the cobalt ions.

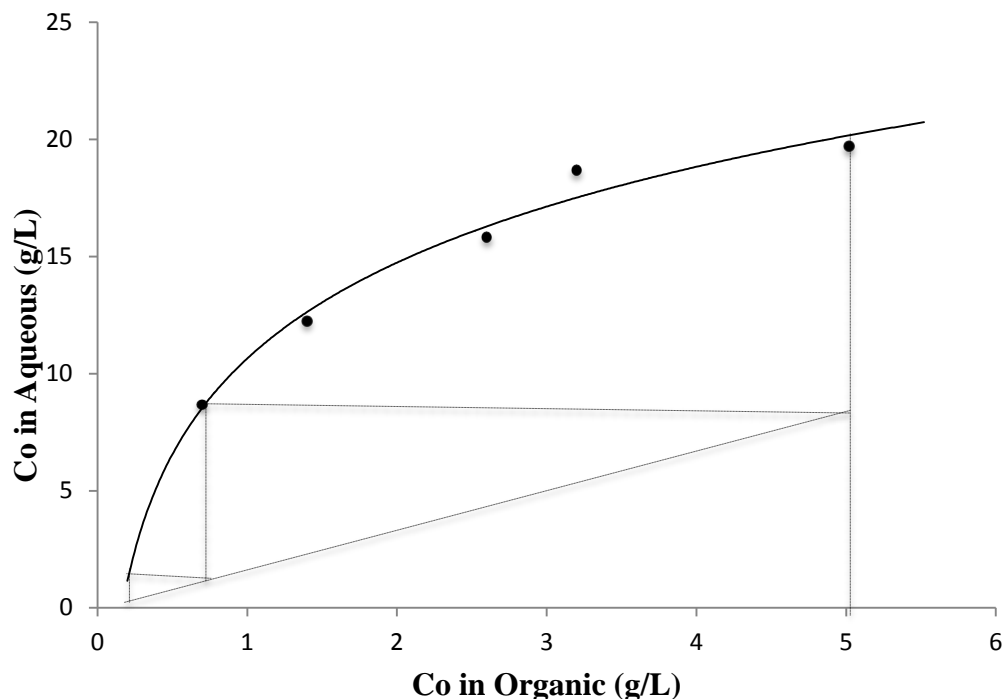


**Figure 7.4** Effect of acid selectivity on cobalt stripping at 25°C (contact time 20 minutes, O/A ratio: 1:1)

Results show that the stripping of the metal ions increases with increasing acid concentration. The stripping of cobalt reached about 62.63% at acid concentration of 50g/L while copper and iron were about 25.42% and 1.13%, respectively. However, at the same acid concentration (50g/L), zinc and nickel were stripped up to 31.14% and 38.34% respectively. Cobalt stripping reached around 64.37% at acid concentration of 75g/L, whereas the extraction of nickel at this acid concentration was only 41.5%. On the other hand, with increasing the acid concentration values to about 100g/L, iron stripping increased to reach 1.2% at 75g/L and increased slowly to reach 2.7% at 100g/L. However, calcium was inadequate at acid concentration 100g/L, probably due to the precipitation.

*McCabe-Thiele Diagram for estimating the number of extraction stages*

**Figure 7.5** shows a McCabe–Thiele diagram constructed for cobalt stripping to determine the theoretical extraction stages for the extraction of cobalt back into the aqueous phase at acid concentration of 100g/L and 25°C.



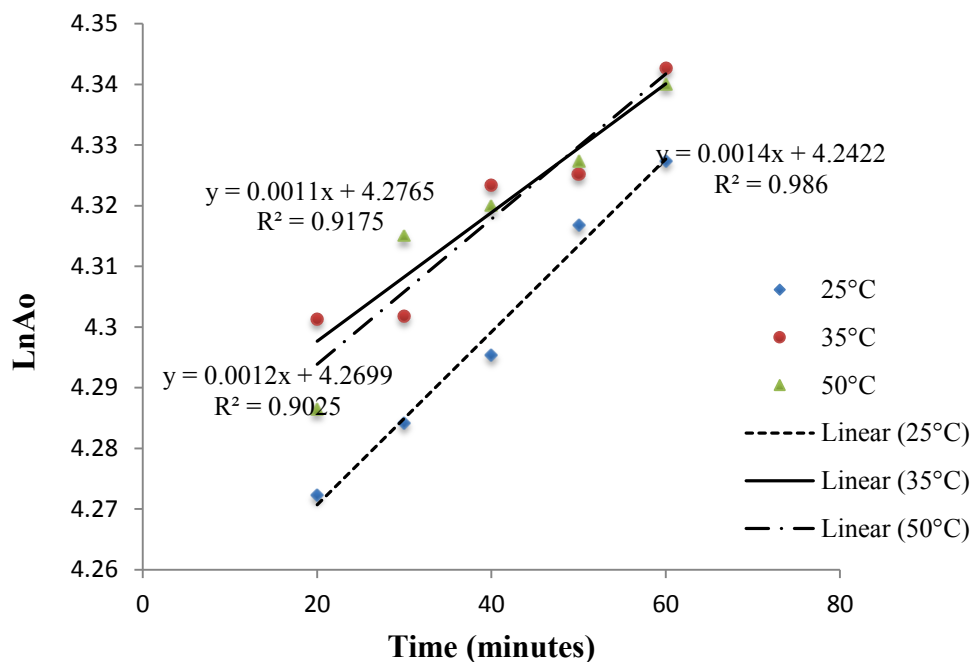
**Figure 7.5** Plot of McCabe Thiele diagram at 100g/L and 25°C contact time 20 minutes, O/A ratio: (1:1)

**Figure 7.5** shows the metal concentration in organic solution after each stage of stripping at acid concentration 100g/L. The concentration of cobalt, decreased with an increase in the number of stages. The stripping of cobalt from solutions containing different impurities by sulphuric acid was affected by acid concentration at room temperature; enough cobalt was stripped from the organic phase.

#### 7.4 Kinetics of Stripping

Stripping kinetics surveys were conducted on the acid concentration used under the earlier determined optimum conditions. The loaded organic solution was initially scrubbed with a solution containing 5 g/l Co at an A/O ratio 1:1. Depending on the availability of the sulphuric acid solution, stripping kinetic tests were conducted under 25.

The kinetic plots as functions of time at 100g/L with different temperatures were plotted and are presented in **Figures 7.6**.



**Figure 7.6 Plot of  $\ln A_o$  at 100g/L versus time at different temperatures**

Analysis of the kinetic equation plots of  $\ln A_o$  at 100 g/L did give perfectly fitting straight lines as can be seen in **Figure 7.6**. However, from the three temperatures used the plot with a linear correlation coefficient of 98.85% at 25°C. This shows that from the kinetic analysis given in **equation 4.2**.

### 7.5 Summary and Conclusions

In order to stipulate useful understandings into the process of stripping cobalt from organic phase with sulphuric acid, the effect of acid concentration, temperature and contact time were investigated. The study also looked at the stripping kinetics.

Experimental results showed an increase in cobalt extraction from the organic phase with an increase in acid concentration. A maximum extraction of 76.71% was obtained at an acid concentration of 100g/L. Therefore, 100g/L was taken as the significant acid concentration during this stripping process. Experimental results showed a high cobalt extraction with a temperature of 25°C. A high cobalt extraction was recorded at 20 minutes contact time and there was no significant variation in the amount extracted beyond 20 minutes. The amount transferred to the aqueous phase remained more or less constant.

While cobalt can be extracted at high pH-O/A ratio from sulphate solution using Cyanex 272, it can also be stripped selectively over the common impurities such as copper, iron, magnesium, nickel, zinc etc. at high acid concentration.



## CHAPTER HEIGHT

### CONCLUSIONS AND RECOMMENDATIONS

#### 8.1 Conclusions

##### 8.1.1 Introduction

The capacity of organophosphorous compounds (Cyanex 272) to extract metals ions from aqueous sulphate media is based on the following three mechanisms: (1) A homogeneous reaction in the aqueous phase, (2) an interfacial reaction with cation, and (3) sequential interfacial reaction which involve the saturation of interface and desorption of the interfacial.

There are several techniques available to treat cobalt containing impurities but most of them are non-selective and turn out to be uneconomical at low concentration levels at which the co-extraction of other metals is kept. Solvent extraction is an innovative procedure that has substantial potential to treat cobalt with high selectivity and recover them even at low concentration levels at a reasonable cost.

The main objective of this work was to extend these principles in order to investigate the possibility of using cyanex 272 in the solvent extraction of cobalt from a low concentration leach solution. A review of the literature suggested that the metal value can be recovered by stripping from the loaded organic phase using high concentration sulphuric acid solutions, which quantitatively back-extracted to the aqueous phase over the entire sulphuric acid concentration range.

This study investigates the extraction and removal of cobalt form aqueous solution as well as its stripping from the loaded Cyanex 272 using sulphuric acid. The significant findings are stated and conclusions are listed.

In order to investigate this possibility, the approach used in this study was:

- Leaching of the copper cobalt ore in sulphuric acid in the presence of a reducing agent (sodium metabisulfite) which generates leach liquor containing copper, cobalt and other impurity ions.
- Precipitation of Fe and Cu from the leach stream.
- Identification of the significant parameters in the recovery and concentration of cobalt by solvent extraction.

- Optimisation of the significant factors in order to maximise the solvent extraction process in terms of the output (cobalt extraction).

The first two steps were based on literature and plant data and did not form the core part of the research studies.

#### *8.1.2 Solvent Extraction of Cobalt with Cyanex 272*

The solvent extraction of cobalt from low concentrate leach solution was undertaken with Cyanex 272 mixed with Shellsol 2325. The results presented in this study have shown that cobalt extraction in sulphate media is influenced by a variety of parameters.

The extraction of cobalt into the organic phase can be increased by changing the organic to aqueous ratio during the extraction stages. An organic to aqueous phase ratio of 2:1 and 3:1 were more efficient than other ratio used in this study (1:3; 1:2 and 1:1). The highest cobalt recovery was found to be 73.50% and the lowest was 34.27% respectively. This showed that the amount of organic phase has a significant influence in the solvent extraction process.

The tests also showed that a higher pH was necessary for a higher cobalt extraction into the organic phase. A decrease in the pH of the system consequently led to a decrease in the amount of metal extracted. It was also found that the higher the equilibrium pH of the system, the lower the amount of extractant concentration needed to achieve a given percent metal extraction.

Although a cobalt concentration of 2.12g/L showed an overall high extraction into the organic phase there was no significant difference when compared to the lower cobalt concentration of 1.30g/L.

While cobalt can be extracted at much higher pH it can however, not be extracted selectively over the common impurities such iron, copper and nickel.

Cobalt extraction showed an increase with increase in temperature up to 35°C with slight variations in extractions between 25°C and 50°C. Higher cobalt extraction at higher temperatures was attributed to the formation of stable octahedral cobalt complexes with the ligand molecules at higher temperatures which decrease at temperature above 40°C.

The McCabe–Thiele diagram for the system showed that at pH 6 and O/A ratio 3:1, three theoretical extraction stages were needed to extract 70% of the cobalt from the leach solution to organic solution and to reduce the cobalt concentration from 3.5 g/L to 3 ppm.

Simultaneous extraction of cobalt, copper, iron, calcium, nickel and zinc with varying pH shows the improbable separation of cobalt in the presence of diver's impurities. Hence, stripping was suggested to improve the selectivity of cobalt in the presence of other co-extracted impurities.

Studies on the identification of influential factors were accomplished using the DOE method. The identification of influential factors was addressed by: screening the main influential factors using a diagnostic two-level quarter fractional design to obtain data that would serve as an initial approach to the final optimization. The experimental results were also analyzed statistically for the significance of the factors using the probability plots and a Pareto chart. The results showed that the organic to aqueous phase ratio and the solution pH were significant factors in the process whilst cobalt ion concentration and temperature were not statistically significant factors.

#### *8.1.3 Optimisation Tests*

It is evident that optimizing the solvent extraction process of cobalt from low concentrate leach solution is complicated since various factors such as extractant agent selection, solvent concentration, organic to aqueous phase ratio, temperature of extraction, time of extraction and pH of extraction etc. affect the efficiency of the solvent extraction process simultaneously. Various experiments need to be conducted to know the precise simultaneous effect of all these parameters on the solvent extraction of cobalt, which can prove to be costly and time consuming. A statistically-based optimization strategy called response surface methodology was used for parametric optimization (pH, O/A ratio, and temperature and cobalt concentration) with 30% v/v Cyanex 272 as the extractant.

In order to obtain optimum parameters and select the most suitable candidate between the choices for a given application, a statistical experimental design called central composite rotatable design was employed to reduce the number of experiments, but being sufficient to describe the responses. Experimental results were analyzed and an appropriate predictive empirical linear model was developed. The linear model representing cobalt extraction was expressed as a function of two variables, pH and O/A phase ratio. The model validation was accomplished using standard deviation and coefficient of determination ( $R^2$ ) tests. The effects of the individual variables and their quadratic terms were found to be statistically significant. The results, however, showed that interactions among the investigated variables were statistically insignificant.

Within the range studied, the optimum conditions established from the statistically based optimization model at the predicted maximum cobalt extraction of 73.04% were found to be an O/A phase ratio of 3:1 and pH of 6. To inspect the optimized results, repeated confirmatory runs were carried out under optimized conditions. The cobalt recovery found experimentally was 73.50%. This indicates that there is a good relationship between the predicted and experimental results. This study has, therefore, showed that by increasing the volume of organic phase and the pH of the solution, cobalt can be extracted by Cyanex 272.

#### *8.1.4 Stripping of Cobalt from Organic Phase*

Stripping was done at different acid concentration (sulphuric acid). The results showed a maximum cobalt extraction at 100g/L acid concentration. Lower extractions below 100g/L acid concentration were attributed to low mass transfer of reactants and products.

This was selectively extracted by cyanex 272 as well as some other impurities such as copper, nickel, iron, manganese and zinc. The higher cobalt recovery during stripping process was found to be 76.68 % and the lower was 62.64% respectively. Therefore, 100g/L was considered as the relevant acid concentration.

Increase in acid concentration resulted in decreased of impurities in the aqueous solution during stripping process. Over a longer period of stripping, the extraction rate remains relatively horizontal meaning time does not play a significant role in the extraction of cobalt. For example, at a 100g/L, temperature 25°C and duration of (20-60) minutes gave recoveries of 73.95% and 75.91% respectively. This means that the extraction kinetic is quite fast.

The McCabe–Thiele diagram for the system showed that at acid concentration 100g/L and 25C, two theoretical extraction stages were needed to extract 76% of the cobalt from the solution and to reduce the cobalt concentration from 5.0 g/L to 2 ppm.

#### *8.1.5 Kinetic Studies*

Cobalt is extracted by a cation exchange reaction, in which extraction increases with increasing pH. The kinetics were analysed by means of a kinetic model involving first order reactions. Values of kinetic explain that the highest cobalt recovery is obtained using Cyanex 272 (higher than 97% correlation coefficient), whereas the lowest cobalt recovery is obtained using Cyanex 272 (lower than 84% correlation coefficient) and pH value of 6 would be desirable for more than 70 % cobalt extraction.

## 8.2 Recommendations

The following recommendations for further studies are proposed.

### *Solvent extraction and stripping of cobalt*

The potential for selective extraction over other common impurities (e.g. Fe, Cu, Mg, Ni and Zn etc.) is a major subject for future work.

This work had shown that during solvent extraction with Cyanex 272, cobalt extraction increase with increase in pH and temperature due to the formation of stable octahedral cobalt complexes with the ligand molecules at temperature of 35°C and pH 6. Impurities co-extraction also increased with increase in pH and temperature. Thus, further investigations need to be carried out to look at the level of parameters that would lead to the minimal co-extraction of impurities from the sulphate solution.

More detailed study on the acid concentration, stirring speed need to be undertaken and the aspect of loading capacity need to be investigated to identify the factors that can contribute to high cobalt stripping.

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**APPENDIX A**  
**SAMPLE CALCULATIONS**

## Leaching test

The % of metal ions extraction during the leaching of copper-cobalt oxide ore was calculated as a percentage of each metal ion in the liquid phase to that in the oxide ore.

*Basis of calculation:*

Cu-Co ore weight (actual) before leaching = 150g

Volume of sulphuric acid used (mls) = 1000

*After Leaching:*

Co in leach liquor (ICP analysis) = 263 ppm ( $263 \times 10^{-3}$  gpl)

**Table A.10 Leaching test at 40°C and different time**

Test 2 at 40°C								
SAMPLES	Cu g/l	Co g/l	Fe g/l	Mg g/l	Mn g/l	Ni g/l	Si g/l	Zn g/l
15040	3.79	0.245	0.174	0.0651	0.011	0.00091	0.0441	0.0128
25040	3.87	0.248	0.178	0.0711	0.0112	0.00091	0.0493	0.0128
35040	3.91	0.25	0.184	0.0773	0.0113	0.00094	0.0533	0.0131
45040	3.06	0.257	0.194	0.0847	0.0118	0.00103	0.058	0.0139
55040	3.03	0.263	0.205	0.0894	0.0123	0.00103	0.0621	0.014

## Precipitation

*Cobalt concentration after precipitation*

The amount of Cobalt after precipitation was calculated as a ratio of cobalt concentration before precipitation to that in liquid after precipitation.



**Table A.11 ions concentration after precipitation**

Co	Cu	Fe	Mg	Ni	Se	Zn
mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
240	3994	350	81	1.2	0.03	24
156	2441	120	75	0.45	0.03	3.9
185	2394	50	79	0.36	0.04	1.2
144	113	1.5	98	0.94	0.13	8.3

**Solvent Extraction****% Cobalt Extraction**

The % cobalt extraction during solvent extraction was calculated as a percentage of the cobalt in the organic phase to the initial concentration in the aqueous phase.

**Example**

*Basis of calculation:*

Cobalt concentration in aqueous phase before solvent extraction = 4g/L.

*Calculations:*

Cobalt concentration in aqueous phase after solvent extraction

Volume of organic phase in = 50mls

Volume after solvent extraction = 50mls

Concentration of cobalt in aqueous phase (ICP analysis) per volume:

$$D = [M]_{org} / [M]_{aq}$$

$$\% E = 100 \times \frac{[M]_{org}}{[M]_{org} \times [M]_{aq}}$$

$$\text{Thus \%E of Co is: } 100 \times \frac{(1.30 * 0.05)}{(5.4 * 0.05 + 1.30 * 0.15)} = 60.16\%$$

The extraction during the solvent extraction and stripping of cobalt was calculated as a percentage of cobalt in the aqueous and organic phase to the initial cobalt feed.

**Table A.12 Different cobalt concentration use for solvent extraction**

Element		Ca	Co	Cu	Fe	Mg	Ni	Zn
Units		g/l	g/l	g/l	g/l	g/l	g/l	g/l
AS4-144		0.51	1.30	0.17	0.04	0.15	0.00	0.01
AS8-184		0.52	2.12	0.17	0.04	0.15	0.00	0.01

## Design of Experiments

### Main Effect

An effect is the difference in response averages that are applicable to the levels of the factor. The effect of factor **A** on the response can be obtained by taking the difference between the average response when **A** is high and the average response when **A** is low.

Effect of factor A = Average response at **A** high – Average response at **A** low

### Example

Average response at A high, is given by averaging the results obtained by running experiments 2, 4, 6, 8, 10, 12, 14 and 16, and average response at A low by averaging the results obtained from running experiments 1, 3, 5, 7, 9, 11, 13 and 15.

Average extractions at A high =  $(10.3+14.0+16.2+20.3+12.0+11.7+13.0+18.10)/8 = 14.45$

Average extractions at A low =  $(11.7+13.5+16.4+18.0+11.13+17.8+17.3)/8 = 14.94$

Thus the Effect of factor A = -0.49

### Interaction Effect

An interaction is a cross product of two or more factors. The net sign of the interaction is also a cross product of the individual signs of the factors. The identity of an interaction comes

from the identity of the individual factors involved in the cross product. Across product of factor C and factor B yields a two factor interaction BC.

An interactive effect is the difference in response averages that are applicable to the levels of the interaction. The interactive effect of interaction **BC** on the response can be obtained by taking the difference between the average response when **BC** is high and the average response when **BC** is low.

**Table A3 Main and interactive effects**

**Table A3 Main and interactive effects**

Term	Effect
A-Temperature	1.78
B-pH	11.15
C-O/A ratio	11.82
D-Cobalt Conc.	-1.59
AB	-3.52
AC	-1.70
AD	-1.62
BC	-9.04
BD	0.74
CD	-0.98
ABC	0.74
ABD	2.28
ACD	1.47
BCD	-0.64
ABCD	-2.05
Lenth's ME	6.19
Lenth's SME	12.56

### Normal probability plots

The scales for making normal probability plot of effects is such that, on the y-axis,  $P_i = 100(i-1/2)/m$  for  $i = 1, 2, 3, 4 \dots m$ , where  $m$  = the number of effects under consideration (main and or interactions), excluding the average. The plot requires that the effects are arranged in order of magnitude, before applying the y-axis scale formula, starting with the smallest and ending with the largest.

**Table A.13 Effects for normal probability plots**

<b>Term</b>	<b>Effect</b>	<b>Probability</b>
<b>BC</b>	-9.04	<b>3.33</b>
<b>AB</b>	-3.52	<b>10.00</b>
<b>ABCD</b>	-2.05	<b>16.67</b>
<b>AC</b>	-1.70	<b>23.33</b>
<b>AD</b>	-1.62	<b>30.00</b>
<b>D</b>	-1.59	<b>36.67</b>
<b>CD</b>	-0.98	<b>43.33</b>
<b>BCD</b>	-0.64	<b>50.00</b>
<b>ABC</b>	0.74	<b>56.67</b>
<b>BD</b>	0.74	<b>63.33</b>
<b>ACD</b>	1.47	<b>70.00</b>
<b>A</b>	1.78	<b>76.67</b>
<b>ABD</b>	2.28	<b>83.33</b>
<b>B</b>	11.15	<b>90.00</b>
<b>C</b>	11.82	<b>96.67</b>

**Modeling the significant effects for extraction prediction**

The model or prediction equation is useful for predicting the outcome for the future validation experiments. A model is an equation that uses only the significant effects. This is due to the hierarchy rule for defining a model (Barrentine, 1999). From the normal probability plot, it is found that the significant factors are B, C and BC. Therefore,

$$\text{Recovery, } R = R = 53.47 + \frac{E(C)}{2} Cc + \frac{E(B)}{2} Bb - \frac{E(BC)}{2} BbCc$$

represents the average of all the data for the runs (i.e average of all the recoveries) and B, are the contrast constants (i.e +1 or -1), E(A), E(B), and E(BC) are effects as indicated.

$$R = 53.47 + \frac{5.91}{2} Cc + \frac{5.575}{2} Bb - \frac{9.04}{2} BbCc$$

Therefore,

$$\text{Predicted recovery, } R = 53.47 + 2.955Cc + 2.7875Bb - 4.52BbCc$$

**Example**

The predictor variables are  $X_B = -1$ ,  $X_C = -1$

$$\text{Predicted extraction} = 53.47 - 2.955 - 2.7875 = 47.7275\%$$

Note that the negative signs in some of the variables of the prediction model equation indicate that in order to maximize solvent extraction of cobalt from leach solution, these factors must be kept in low levels. The positive signs mean the factors must be kept in high levels.

### **Residual**

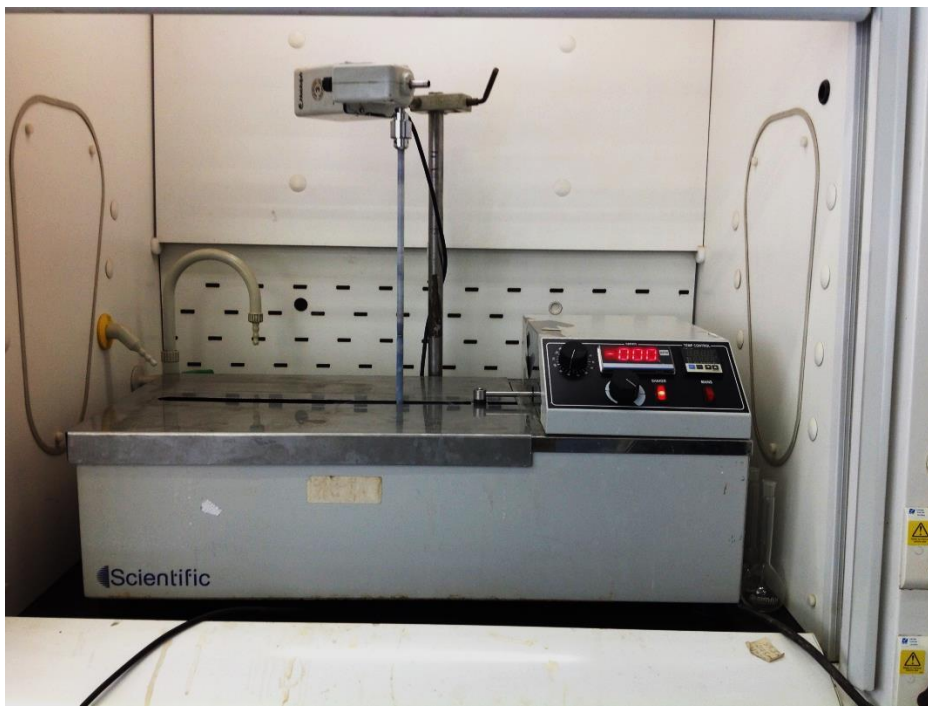
This is the difference between the actual extraction and the predicted extraction for each run.

### **Example**

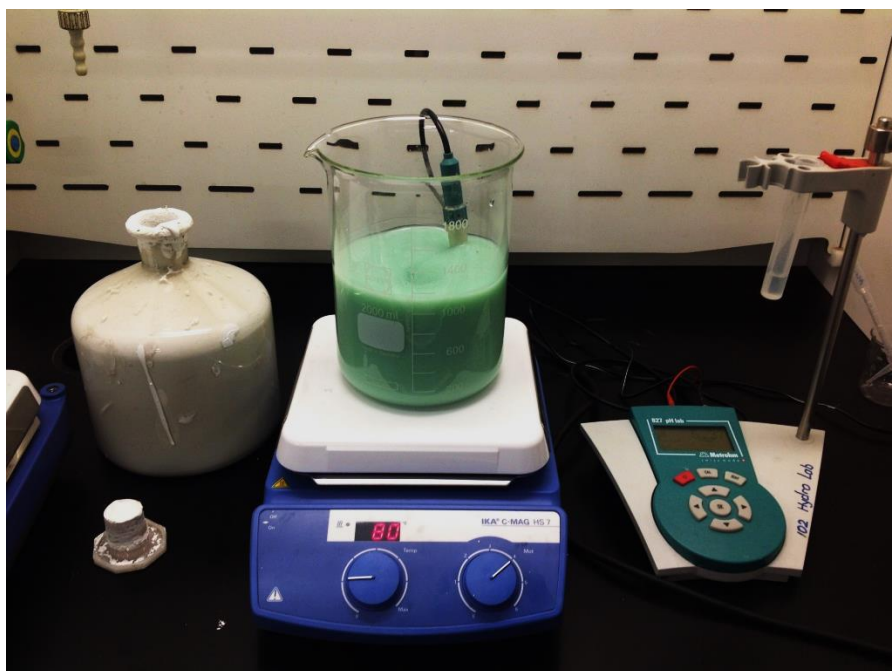
Actual extraction = 53.47, predicted extraction = 47.72

$$\text{Residual} = 53.47 - 47.72 = 5.73\%$$

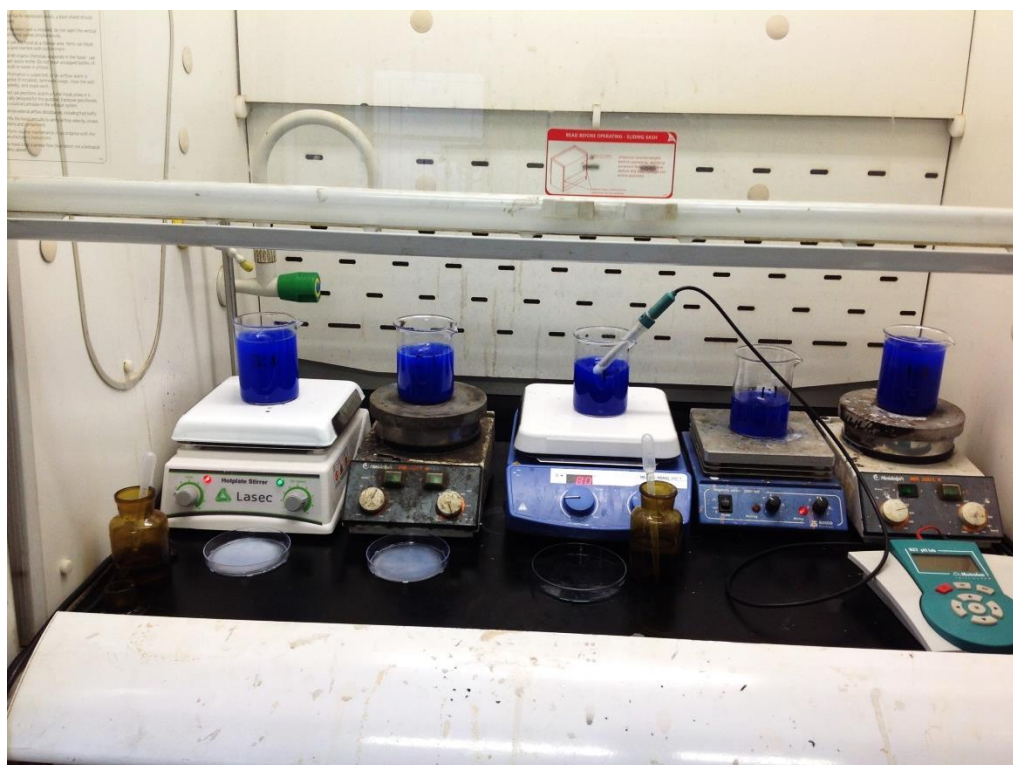
### **Apparatus and Experimentation Set up**



**Figure A.1 Agitation leaching test equipment (set up with a mechanical agitator)**



**Figure A.2 copper and iron removal test equipment (set up with a magnetic hot plate)**



**Figure A.3 Cobalt solvent extraction test (set up with a magnetic hot plate)**



**Figure A.4 The Agilent Technologies 200 Series AA (AAS)**

**APPENDIX B**  
**COBALT SOLVENT EXTRACTION**



**Table B Cobalt concentration (gpl)****Conditions for solvent extraction of cobalt at 25°C Temperature and different pH:****Table B.2 Extraction temperature 25°C, pH of 4**

<b>Ca g/l SD/ICP*</b>	<b>Co g/l SD/ICP*</b>	<b>Cu g/l SD/ICP*</b>	<b>Fe g/l SD/ICP*</b>	<b>Mg g/l SD/ICP*</b>	<b>Ni g/l SD/ICP*</b>	<b>Zn g/l SD/ICP*</b>
0.06	1.74	0.50	0.13	0.03	0.02	0.05
0.17	2.14	0.42	0.13	0.04	0.02	0.04
0.17	1.31	0.24	0.19	0.04	0.03	0.03
0.07	0.89	0.12	0.12	0.06	0.02	0.02
0.06	0.60	0.08	0.11	0.05	0.02	0.02

**Table B.3 Extraction temperature 25°C, pH of 5**

<b>Ca g/l</b>	<b>Co g/l</b>	<b>Cu g/l</b>	<b>Fe g/l</b>	<b>Mg g/l</b>	<b>Ni g/l</b>	<b>Zn g/l</b>
0.38	4.58	0.67	0.10	0.10	0.01	0.05
0.61	3.42	0.46	0.10	0.13	0.01	0.04
0.43	1.82	0.24	0.09	0.11	0.01	0.03
0.38	0.97	0.13	0.08	0.13	0.02	0.02
0.20	0.66	0.08	0.08	0.05	0.02	0.02

**Table B.4 Extraction temperature 25°C, pH of 6**

<b>Ca g/l</b>	<b>Co g/l</b>	<b>Cu g/l</b>	<b>Fe g/l</b>	<b>Mg g/l</b>	<b>Ni g/l</b>	<b>Zn g/l</b>
1.88	5.43	0.67	0.14	0.55	0.01	0.05
1.52	3.91	0.49	0.16	0.44	0.02	0.04
0.75	2.03	0.24	0.14	0.22	0.02	0.03
0.38	1.05	0.13	0.14	0.13	0.02	0.02
0.26	0.74	0.08	0.17	0.09	0.02	0.02

**Conditions for solvent extraction of cobalt at 35°C Temperature and different pH:****Table B.14 Extraction temperature 35°C, pH of 4**

<b>Ca g/l</b>	<b>Co g/l</b>	<b>Cu g/l</b>	<b>Fe g/l</b>	<b>Mg g/l</b>	<b>Ni g/l</b>	<b>Zn g/l</b>
0.09	3.27	0.60	0.06	0.03	0.00	0.04
0.05	1.61	0.40	0.01	0.02	0.01	0.03
0.09	1.39	0.20	0.09	0.02	0.01	0.02
0.14	0.77	0.11	0.07	0.04	0.01	0.01
0.16	0.56	0.07	0.10	0.04	0.02	0.01

**Table B.15 Extraction temperature 35°C, pH of 5**

<b>Ca g/l</b>	<b>Co g/l</b>	<b>Cu g/l</b>	<b>Fe g/l</b>	<b>Mg g/l</b>	<b>Ni g/l</b>	<b>Zn g/l</b>
0.64	5.02	0.66	0.11	0.30	0.01	0.04
1.04	3.66	0.46	0.08	0.33	0.01	0.04
0.50	1.95	0.23	0.08	0.01	0.01	0.02
0.32	0.89	0.11	0.09	0.11	0.01	0.01
0.24	0.65	0.08	0.07	0.08	0.01	0.01

**Table B.16 Extraction temperature 35°C, pH of 6**

<b>Ca g/l</b>	<b>Co g/l</b>	<b>Cu g/l</b>	<b>Fe g/l</b>	<b>Mg g/l</b>	<b>Ni g/l</b>	<b>Zn g/l</b>
1.86	4.96	0.62	0.10	0.54	0.01	0.05
1.27	3.43	0.43	0.07	0.36	0.00	0.03
0.63	1.87	0.21	0.06	0.18	0.01	0.02
0.30	0.77	0.10	0.06	0.09	0.01	0.02
0.25	0.61	0.08	0.09	0.08	0.01	0.02

**Conditions for solvent extraction of cobalt at 50°C Temperature and different pH:****Table B.17 Extraction temperature 50°C, pH of 4**

<b>Ca g/l</b>	<b>Co g/l</b>	<b>Cu g/l</b>	<b>Fe g/l</b>	<b>Mg g/l</b>	<b>Ni g/l</b>	<b>Zn g/l</b>
0.05	3.32	0.62	0.12	0.04	0.01	0.05
0.11	3.02	0.45	0.10	0.06	0.01	0.04
0.07	1.95	0.25	0.07	0.03	0.01	0.02
0.29	0.97	0.13	0.07	0.09	0.01	0.02
0.12	0.68	0.08	0.10	0.04	0.02	0.01

**Table B.18 Extraction temperature 50°C, pH of 5**

<b>Ca g/l</b>	<b>Co g/l</b>	<b>Cu g/l</b>	<b>Fe g/l</b>	<b>Mg g/l</b>	<b>Ni g/l</b>	<b>Zn g/l</b>
0.95	5.45	0.67	0.12	0.48	0.00	0.04
0.95	3.94	0.47	0.07	0.39	0.01	0.03
0.78	2.04	0.26	0.08	0.23	0.01	0.02
0.19	0.94	0.11	0.08	0.07	0.01	0.01
0.16	0.61	0.08	0.08	0.05	0.01	0.01

**Table B.19 Extraction temperature 50°C, pH of 6**

<b>Ca g/l</b>	<b>Co g/l</b>	<b>Cu g/l</b>	<b>Fe g/l</b>	<b>Mg g/l</b>	<b>Ni g/l</b>	<b>Zn g/l</b>
1.81	5.00	0.69	0.11	0.06	0.01	0.05
1.48	3.91	0.51	0.08	0.45	0.01	0.03
0.75	1.96	0.25	0.07	0.22	0.01	0.02
0.33	0.81	0.11	0.07	0.10	0.01	0.02
0.23	0.66	0.08	0.06	0.07	0.01	0.01

NB. All the experiment shown above had different O/A ratio of 3:1 to 1:3 ranged from up to down. (e.g: 0.66 has a ratio of O/A 3:1).

**APPENDIX C**  
**IDENTIFICATION OF INFLUENTIAL FACTORS**

**Table C1** Cobalt extraction (%) for 2<sup>4</sup> full factorial design

Figure The actual factor levels coded as values of (-1) and (+1) in the table are as follows: A (Temperature): 25°C (-1) and 50°C (+1); B (pH): 4 (-1) and 6 (+1); C (O/A ratio): 1:3 (-1) and 3:1 (+1); D (Co Concentration): 2g/L(-1) and 4g/L(+1).

Random Run Order	Standard Run Order	Control Factors				% Co Extraction (average)
		A	B	C	D	
1	1	-1	-1	-1	-1	<b>30.87</b>
9	2	-1	-1	-1	1	<b>36.3</b>
14	3	1	-1	1	1	<b>58.23</b>
16	4	1	1	1	1	<b>57.89</b>
12	5	1	1	-1	1	<b>58.26</b>
4	6	1	1	-1	-1	<b>56.26</b>
2	7	1	-1	-1	-1	<b>46.04</b>
5	8	-1	-1	1	-1	<b>58.04</b>
6	9	1	-1	1	-1	<b>61.27</b>
11	10	-1	1	-1	1	<b>57.8</b>
15	11	-1	1	1	1	<b>60.5</b>
3	12	-1	1	-1	-1	<b>58.28</b>
8	13	1	1	1	-1	<b>60.28</b>
13	14	-1	-1	1	1	<b>55.74</b>
7	15	-1	1	1	-1	<b>63.03</b>
10	16	1	-1	-1	1	<b>36.63</b>

**APPENDIX D**  
**OPTIMIZATION OF INFLUENTIAL FACTORS**

**Table D1. Observed values for the cobalt extraction**

Factor Levels				Cobalt Extraction (Observed)	Standard Run
Coded		Actual			
A-A/O ratio	B-(pH)	A-A/O ratio	B-pH		
Factorial portion					
-1	-1	1.29	4.3	60.50	1
+1	-1	1.29	5.7	54.26	2
-1	+1	2.70	4.3	54.74	3
+1	+1	2.70	5.7	57.89	4
Axial portion					
-λ	0	2	4.3	33.63	5
+λ	0	2	5.7	20.87	6
0	-λ	0	5	60.54	7
0	+λ	4	5	60.28	8
Centre points					
0	0	2	5	55.8	9
0	0	2	5	34.13	10
0	0	2	5	58.23	11
0	0	2	5	58.04	12
0	0	2	5	58.28	13

**Table D.2 Diagnostics Case Statistics**

Standard	Actual	Predicted			Internally	Externally	Influence on	Cook's	Run
					Studentized	Studentized	Fitted Value		
Order	Value	Value	Residual	Leverage	Residual	Residual	DFFITS	Distance	Order
1	0.86	1.36	-0.49	0.313	-1.955	-2.308	-1.556	0.347	11
2	1.51	1.42	0.084	0.313	0.333	0.319	0.215	0.01	9
3	2.02	1.78	0.25	0.313	0.979	0.977	0.658	0.087	2
4	1.96	1.84	0.12	0.313	0.475	0.458	0.309	0.021	15
5	-0.16	-0.42	0.26	0.313	1.024	1.027	0.692	0.095	4
6	-0.17	-0.36	0.18	0.313	0.722	0.706	0.476	0.047	7
7	-0.12	-2.50E-03	-0.11	0.313	-0.451	-0.434	-0.293	0.018	8
8	-0.22	0.062	-0.29	0.313	-1.128	-1.143	-0.771	0.116	13
9	1.49	1.74	-0.26	0.313	-1.012	-1.013	-0.683	0.093	14
10	1.59	1.81	-0.21	0.313	-0.843	-0.831	-0.561	0.065	12
11	2.49	2.16	0.33	0.313	1.293	1.339	0.902	0.152	5
12	2.41	2.23	0.18	0.313	0.73	0.714	0.481	0.048	3



## Cobalt solvent extraction

## Dominique Kyembo

13	0.11	-0.037	0.15	0.313	0.595	0.576	0.389	0.032	6
14	0.31	0.028	0.29	0.313	1.136	1.152	0.777	0.117	16
15	0.26	0.38	-0.12	0.313	-0.473	-0.456	-0.307	0.02	1
16	0.086	0.45	-0.36	0.313	-1.425	-1.505	-1.015	0.185	10

**Table STATISTICAL AND MATHEMATICAL METHODS****Evaluation of the inverse matrix, X**

1	1	1	1	1	1	1	1	1	1	1	1
-1	1	-1	1	-1.414	1.414	0	0	0	0	0	0
-1	-1	1	1	0	0	-1.41	1.414	0	0	0	0
1	1	1	1	1.999	1.999	0	0	0	0	0	0
1	1	1	1	0	0	1.999	1.999	0	0	0	0
1	1	1	1	1	1	1	1	1	1	1	1
1	1	1	1	1	1	1	1	1	1	1	1

**Evaluation of the inverse matrix,  $X^{-1}$** 

1	-1	-1	1	1	1	1
1	1	-1	1	1	1	1
1	-1	1	1	1	1	1
1	1	1	1	1	1	1
1	-1.41	0	1.999	0	0	0
1	1.414	0	1.999	0	0	0
1	0	1.414	0	1.999	0	0
1	0	1.414	0	1.999	0	0
1	0	0	0	0	0	0
1	0	0	0	0	0	0
1	0	0	0	0	0	0
1	0	0	0	0	0	0

**Evaluation of the inverse matrix,  $A^{-1}$** 

Essentially in finding the inverse of a matrix, the evaluation  $\mathbf{A}\mathbf{A}^{-1} = \mathbf{I}$  must be solved where  $\mathbf{I}$  is the unit matrix. In order to examine the procedure two other forms of matrix must be looked at.

**Adjoint matrix,  $A^a$** 

The adjoint matrix is the transpose of the cofactor matrix.

The inverse of a matrix is equal to its adjoint matrix divided by its determinant (Smith, 1971),

$$A^{-1} = \frac{A^a}{|A|}$$

Where  $|A|$  is the determinant of matrix  $A$ .

The concept of rotatable is not uniquely related to second order models or central composite designs. Myers (1989); Box (1951) and Hunter (1966) give a detailed description relating to rotatability. Therefore, in order to determine the condition at rotatability, the equation 6.6 was employed in this study.

$$\hat{y} = x^{1 \times p} \hat{\beta}^{p \times 1}$$

Where  $\hat{\beta} = \sigma^2 (X'X)^{-1}$

Thus  $\text{Var}(\hat{y}) = \sigma^2 x^{1 \times p} (X'X)^{-1} x'$

Where  $x^{1 \times p}$  is a particular row of the design matrix.

$$(X'X) \begin{vmatrix} 13 & 0 & 0 & 7.998 & 7.998 & 0 & 4 \\ & 7.999 & 0 & 0 & 0 & 0 & 0 \\ & & 7.999 & 0 & 0 & 0 & 0 \\ & & & 11.992 & 4.999 & 0 & 0 \\ & & & & 11.992 & 0 & 0 \\ & & & & & 4 & 0 \\ 0 & & & & & & 4 \end{vmatrix}$$

$$(X'X)^{-1} \begin{vmatrix} 0.077 & 0 & 0 & 0.125 & 0.125 & 0 & 0.25 \\ & 0.125 & 0 & 0 & 0 & 0 & 0 \\ & & 0.125 & 0 & 0 & 0 & 0 \\ & & & 0.0834 & 0.2 & 0 & 0 \\ & & & & 0.0834 & 0 & 0 \\ & & & & & 0.25 & 0 \\ 0 & & & & & & 0.25 \end{vmatrix}$$

This gives for the first row of the design matrix

$\text{Var}(\hat{y}) = \sigma^2 x^{1 \times p} (X'X)^{-1} x'$

$$\begin{aligned}
 &= S^2 \{0.077 - 0.125 - 0.125 - 0.0834 - 0.0834 - 0.25 \cdot 0.25\} x' \\
 &= S^2 \{0.077 + 0.015625 + 0.069555 + 0.625\} \\
 &= 0.136 S^2
 \end{aligned}$$

They will be equal for all points in the design except for the center point. (Recall that all of the points are equidistant from the center.) For some of the rotatable CCD (when fractions are used) the points do not all lie on a hypersphere. The designs are still rotatable as the points that are equidistant from the center will have equal variance.

**APPENDIX E**  
**STRIPPING PROCESS**

**Table E Cobalt concentration (gpl)****Conditions for stripping of cobalt at acid concentration 50g/L and different Time****Table E.120 Extraction temperature 25°C, and time 20-60 minutes (From up to down)**

<b>Ca</b>	<b>Co</b>	<b>Fe</b>	<b>Cu</b>	<b>Ni</b>	<b>Mn</b>	<b>Zn</b>
0.6869	8.4188	0.0013	0.3286	0.0051	0.3904	0.019
0.5108	7.9614	0.0008	0.5710	0.0064	0.4306	0.024
0.5829	7.2824	0.0008	0.5270	0.0071	0.4677	0.0268
0.5692	8.3864	0.0005	0.5936	0.0068	0.5382	0.0215
0.4922	7.7198	0.0007	0.5824	0.0059	0.4605	0.024

**Table E.2 Extraction temperature 35°C, and time 20-60 minutes (From up to down)**

<b>Ca</b>	<b>Co</b>	<b>Fe</b>	<b>Cu</b>	<b>Ni</b>	<b>Mn</b>	<b>Zn</b>
0.5848	7.8714	0.000637	0.5914	0.0036	0.5288	0.021
0.5191	7.7628	0.001564	0.5996	0.0061	0.5011	0.016
0.4873	8.6896	0.001058	0.6584	0.007	0.5804	0.028
0.506	8.306	0.001056	0.6026	0.005	0.4953	0.018
0.4284	8.5776	0.00136	0.6126	0.0025	0.4998	0.0213

**Table 21.3 Extraction temperature 50°C, and time 20-60 minutes (From up to down)**

<b>Ca</b>	<b>Co</b>	<b>Fe</b>	<b>Cu</b>	<b>Ni</b>	<b>Mn</b>	<b>Zn</b>
0.4047	7.9894	0.001237	0.5984	0.0046	0.5048	0.0189
0.3958	8.5944	0.000938	0.646	0.0036	0.5429	0.0201
0.4443	10.726	0.001133	0.817	0.0061	0.494	0.028
0.4039	8.7676	0.001124	0.618	0.0054	0.5675	0.026
0.300	9.8482	0.00111	0.6672	0.0061	0.4881	0.021

**Conditions for stripping of cobalt at acid concentration 75/L and different Time****Table 22 Extraction temperature 25°C, and time 20-60 minutes (From up to down)**

Ca	Co	Fe	Cu	Ni	Mn	Zn
0.367	9.074	0.001434	0.7102	0.006	0.5798	0.0298
0.1454	9.5656	0.000977	0.7594	0.005	0.599	0.016
0.1039	8.3916	0.00086	0.6686	0.0025	0.4606	0.021
0.2223	9.4282	0.001151	0.7412	0.0031	0.5931	0.018
0.113	9.3756	0.001058	0.7394	0.0026	0.5711	0.0497

**Table 23 Extraction temperature 35°C, and time 20-60 minutes (From up to down)**

Ca	Co	Fe	Cu	Ni	Mn	Zn
0.1057	9.3088	0.001104	0.4194	0.0014	0.4603	0.019
0.1563	14.8276	0.001769	0.40656	0.0028	0.5041	0.017
0.0498	8.133	0.00153	0.4418	0.0037	0.4858	0.021
0.092	7.7276	0.001617	0.3308	0.004	0.5633	0.038
0.1474	8.873	0.002064	0.5252	0.0032	0.5697	0.016

**Table E.624 Extraction temperature 50°C, and time 20-60 minutes (From up to down)**

Ca	Co	Fe	Cu	Ni	Mn	Zn
0.0685	8.9924	0.001967	0.6494	0.0019	0.5685	0.043
0.1526	7.8018	0.002428	0.647	0.0031	0.6144	0.035
0.00473	7.657	0.002528	0.6796	0.0037	0.4356	0.025
0.0086	8.182	0.002069	0.6586	0.0019	0.4714	0.0081
0.0147	7.7828	0.002039	0.8556	0.0023	0.4866	0.019

**Conditions for stripping of cobalt at acid concentration 100/L and different Time****Table E.7 Extraction temperature 25°C, and time 20-60 minutes (From up to down)**

Ca	Co	Fe	Cu	Ni	Mn	Zn
0.0266	12.7128	0.003055	0.761	0.0028	0.5752	0.02
0.0309	13.2682	0.002733	0.7912	0.0032	0.4007	0.015
0.0261	13.8256	0.001688	0.657	0.0031	0.4626	0.024
0.004	14.2498	0.002403	0.6468	0.0025	0.468	0.014
0.0051	15.678	0.00187	0.6208	0.0026	0.4395	0.015

**Table ED.8 Extraction temperature 35°C, and time 20-60 minutes (From up to down)**

Ca	Co	Fe	Cu	Ni	Mn	Zn
0.0255	15.0612	0.002359	0.7974	0.0023	0.5184	0.0291
0.0147	15.7542	0.002894	0.7344	0.005	0.6007	0.018
0.0189	17.241	0.003059	0.7238	0.0024	0.5236	0.021
0.0154	16.417	0.003166	0.6788	0.003	0.5232	0.02
0.0042	15.823	0.003226	0.7016	0.0023	0.4848	0.026

**Table E.9 Extraction temperature 35°C, and time 20-60 minutes (From up to down)**

Ca	Co	Fe	Cu	Ni	Mn	Zn
0.0137	14.0738	0.003534	0.655	0.0019	0.4671	0.015
0.096	15.7436	0.003533	0.6868	0.0015	0.5	0.0197
0.0425	16.0692	0.003106	0.6798	0.0031	0.4769	0.019
0.0016	19.7686	0.003733	0.719	0.002	0.5183	0.0154
0.00234	16.5406	0.003927	0.7358	0.0018	0.5367	0.017