



**AQUEOUS BEHAVIOUR OF COBALT IN THE PRESENCE OF COPPER, IRON  
AND SULPHUR DIOXIDE WITH AND WITHOUT MICROWAVE PROCESSING**

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**by**

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## DECLARATION

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I hereby declare that this dissertation, which I herewith submit for the research qualification

### **MASTER OF TECHNOLOGY DEGREE IN CHEMISTRY**

to the University of Johannesburg, Department of Chemical Technology, is, apart from the recognised assistance of my supervisors, my own work and has not previously been submitted by me to another institution to obtain a research diploma or degree.

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*(Co-supervisor)*

## DEDICATION

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I dedicate this work to my parents (Nelson and Hildah Ndalamo), my wife and son (Thivhavhudzi and Michael Ndalamo) and my brother (Jeffrey Ndalamo). May the Lord of mercy continue to bestow his blessings upon your lives.

*Phillipians 4:13*

*"I can do everything through him who gives me strength"*



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## ABSTRACT

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Recent studies have explored the capabilities of sulphur dioxide (SO<sub>2</sub>), a reducing agent that shows great potential to enhance the leaching efficiency of cobalt from mixed Co-Cu oxidized ores. The research study reported in this dissertation was conducted to further explore the efficacy of SO<sub>2</sub> as a suitable reagent to improve the cobalt yield in solution from mixed Co-Cu oxidised ores. Four mixed Co-Cu oxidised ores were used in this study; namely, high cobalt ore (34% Co), low cobalt ore with mica (4% Co), low cobalt ore without mica (3% Co) and high copper ore (0.5% Co). The mechanistic leaching pathways of cobalt from these ores with and without SO<sub>2</sub> were investigated and monitored using Ultra-Violet/Visible spectroscopy. Mineralogical studies of these ores was carried out by X - ray diffraction (XRD), X - ray fluorescence (XRF) and flame atomic absorption spectroscopy (AAS). Microwave processing of these ores prior to leaching experiments was also investigated. The experimental work was carried out on a laboratory scale and highlights of results obtained are summarized as follows:

- Although not much information pertaining to Co<sup>2+</sup> bearing minerals in mixed Co-Cu oxidised ores was derived from XRD results, two forms of heterogenite minerals (CoOOH-2H and CoOOH-3R), which bear cobalt as Co<sup>3+</sup> were noted in the low cobalt ores.
- High percentage cobalt dissolutions (85% to 95%) were achieved when leaching mixed Co-Cu oxidised ores in the presence of SO<sub>2</sub>.
- UV/Visible spectroscopy confirmed concentrations of Co<sup>3+</sup> and Co<sup>2+</sup> before and after SO<sub>2</sub> treatment of mixed Co-Cu oxidised ores.
- Percentage cobalt dissolutions improved by 10% to 20% in microwave irradiated mixed Co-Cu oxidised ores
- The presence of iron and copper in leach solutions can limit the dissolution of cobalt from mixed Co-Cu oxidised ores to a certain extent.

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## LIST OF ABBREVIATIONS

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AAS	Atomic Absorption Spectroscopy
CDI	Cobalt Development Institute
DEHPA	Di-(2-Ethyl Hexyl) Phosphonic Acid
DRC	Democratic Republic of Congo
GHz	Giga Hertz
KOV	Kamoto-Oliveira-Virgule
MHz	Mega Hertz
LAS	Liquid Added to Solids
PGM's	Platinum Group Metals
PDF	Powder Diffraction File
SAL	Solids Added to Liquids
SAIMM	Southern Africa Institute of Mining and Metallurgy
UK	United Kingdoms
UMHK	Union Miniere du Haut Katanga
USA	United States of America
UV/Vis	Ultra Violet Visible
WBMS	World Bureau of Metal Statistics
XRD	X Ray Diffraction
XRF	X Ray Fluorescence

# CHAPTER 1

## INTRODUCTION

---

### 1.1 Historical Background and Problem statement

Cobalt is one of the most important metals used extensively in commercial and military aircraft engines. Cobalt is mainly recovered from its ores by metallurgical processes and is commonly produced as a by-product of copper and nickel extraction, either by chemical or electrochemical reduction of cobalt sulphate.<sup>1 - 4</sup> The latter route is more important since most of the cobalt presently produced is obtained by electrowinning from a solution of salts. The commonly encountered cobalt extraction route involves leaching of cobalt ores in sulphuric acid and attempts have been made to recover cobalt from tailings and plant residues.<sup>5 - 6</sup>

Cobalt metal is commonly produced as a by-product of copper extraction in the Katanga Province of the Democratic Republic of Congo (DRC), and as minor traces of the base-metal sulphides in platinum group metals (PGMs) in South Africa.<sup>5 - 6</sup> Initially the mineral heterogenite ( $\text{CoOOH}$ ) was discovered and it was found that it originated from the weathering of the smaltite ( $\text{CoAs}_2$ ).<sup>7</sup> Some years later this mineral was discovered in Katanga Province (DRC). It did not originate from smaltite but from the cobalt nickel sulphide, Linnaete ( $\text{Co}_3\text{S}_4$ ).

It has been reported that many challenges are encountered when one tries to leach (i.e. dissolve) cobalt from mixed Co-Cu oxidized ores.<sup>1</sup> One of the main challenges is the poor cobalt yield when leaching these ores in dilute sulphuric acid. This is especially observed if the minerals in mixed Co-Cu oxidized ores bear cobalt in the third oxidation state ( $\text{Co}^{3+}$ ). However, it has been found that direct reductive acid leaching of these cobalt ( $\text{Co}^{3+}$ ) bearing minerals, particularly with

the use of sulphur dioxide gas ( $\text{SO}_{2(g)}$ ), results in improved solution-based cobalt recovery.<sup>1</sup>

In view of the above, an understanding of the aqueous chemistry of cobalt and its leaching pathways from mixed Co-Cu oxidized ores in the presence of  $\text{SO}_2$  should result in significant improvement in the cobalt leaching efficiency. In other words, cobalt-containing ores not previously considered leachable will readily become treatable. Four mixed Co-Cu oxidized ores containing cobalt at different concentrations were received from the DRC, namely, the high cobalt ore, low cobalt ore with mica, low cobalt ore without mica and high copper ore. These mixed Co-Cu oxidized ores were characterized by XRD, XRF and AAS and were subjected to hydrometallurgical leaching processes, an important step in the extraction of cobalt.

The leaching process was conducted in leach media which were dilute sulphuric acid ( $\text{H}_2\text{SO}_4$ ), sulphurous acid ( $\text{H}_2\text{SO}_3$ ) and admixtures of sulphur dioxide ( $\text{SO}_2$ ). This investigation, therefore, not only required the application of a variety of leaching media to underpin the role of  $\text{SO}_2$ , but also the development of monitoring methods in order to gain insight on the increase of the total cobalt content in the solution, hence the use of UV/Visible spectroscopy. Besides flushing of  $\text{SO}_{2(g)}$  in an acidified leach-solutions, microwave processing of mixed Co-Cu oxidized ores prior to leaching experiments was also investigated to improve the cobalt yield and also reduce processing time. This was and still is industrially important in view of the increased demands for more environmentally friendly processing techniques.

The need to produce high purity cobalt has accelerated the development of numerous separation and purification methods of cobalt from copper and iron solutions. Since most leaching processes are not metal specific and need to be followed by one or more downstream processes to remove co-extracted elements, precipitation of copper and iron was carried out on the final leached cobalt.

## 1.2 Justification of the research project

Research has been directed towards finding the best route of leaching cobalt from mixed Co-Cu oxidized ores. In contrast to copper minerals which readily dissolve in sulphuric acid solutions, cobalt minerals are not easily soluble in  $\text{H}_2\text{SO}_4$ , especially if these minerals bear cobalt in the third oxidation state.<sup>1-3</sup> However, it has been found that using a suitable reducing agent cobalt from these minerals becomes soluble when reduced from  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$ . One of the process routes developed was the use of  $\text{SO}_{2(g)}$  as a reducing agent in a direct acid-leaching system where a substantial improvement in the cobalt yield was observed in a plant situation.<sup>1</sup> No study has been carried out that explains from a chemistry perspective the role of  $\text{SO}_{2(g)}$  in the leaching of oxidized cobalt-containing ores.

Due to an unstable political situation in the grand lake of Africa, the Gecamines were closed and small scale operators started to “mine” oxidized ores and commercialized their products in South Africa.<sup>2</sup> In light of this, there is a need to develop South African based expertise in the field of processing oxidized cobalt ores. This research should thus pave the way for improved processes that would help promote an excellent leaching efficiency of cobalt from its ores. An important anticipated spin off from this research project is the development of innovative methods for obtaining maximum cobalt extraction from mixed Co-Cu oxidized ores. This also includes the identification of viable downstream process routes within the framework of the minerals processing industry.

## 1.3 The research questions

The metal and material industries, which are the major consumers of hydrometallurgical products, are increasingly demanding materials of higher purity.<sup>6</sup> A typical example is copper metal where 5-nines (with low oxygen) has almost become a standard requirement.<sup>7</sup> Similar trends can be traced in the cobalt market which demands products of specific purity and this continues to provide scientists with considerable challenges in meeting such demands. Extracting cobalt from mixed Co-Cu oxidized ores generally leads to the inclusion of copper



in the produced cobalt at a reduced yield. Can an appropriate metallurgical solution preparation lead to a considerable increase of the cobalt leaching yield? How would the use of  $\text{SO}_2$  as a reducing agent in the leaching system promote the above? Would microwave processing of mixed Co-Cu oxidized ores prior to leaching increase the cobalt yield? Finally, what is the effect of the presence of iron and copper on the leaching efficiency of cobalt from mixed Co-Cu oxidized ores?

#### 1.4 Objectives of the study

This research was conducted with the following specific objectives:

- i. To characterize mineral phases in mixed Co-Cu oxidized ores using XRD and to fully quantify elemental compositions within these ores using XRF and AAS.
- ii. To perform direct acid leaching of the mixed Co-Cu oxidized ores with and without  $\text{SO}_{2(g)}$  and to carry out an assay for cobalt, copper and iron on the resulting leach solution using AAS.
- iii. To investigate the behaviour of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  during cobalt dissolution from mixed Co-Cu oxidized ores in the presence of  $\text{SO}_{2(g)}$  using UV/Visible Spectroscopy.
- iv. To establish the leaching kinetics of cobalt from mixed Co-Cu oxidized ores, and as a corollary, to also use precipitation methods in monitoring the effect of the presence of copper and iron during the leaching of cobalt.
- v. To undertake microwave processing of the mixed Co-Cu oxidized ores prior to leaching experiments and monitor the effect of microwave on the leaching efficiency of cobalt.

- vi. To compare the kinetics of leaching of cobalt, copper and iron in microwave and non microwave-treated mixed Co-Cu oxidized ores.

## 1.5 Outline of the dissertation

The succession and brief description of the chapters in this dissertation are as follows:

**Chapter 2 (Literature review)**, literature reports are discussed in this chapter, although not exhaustive, major references related to this study are cited. Currently used methods for processing cobalt-containing ores are also discussed.

**Chapter 3 (Experimental methodology)** provides detailed description of the analytical techniques and experimental procedures used to achieve the objectives expressed in section 1.4.

**Chapter 4 (Results and discussion)** presents the findings of the entire study, discussions and interpretation of results.

**Chapter 5 (Conclusions and recommendations)** summarizes major findings of the entire research study. Recommendations for future work are also enlisted in this chapter.

The **appendix** section at the end of the dissertation presents selected raw data, AAS calibration plots and calculations. While some of this data will be referred to in chapter 4, provision of processed data for repeated experiments has been provided for clarity purposes.

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## CHAPTER 2

### LITERATURE REVIEW

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#### 2.1 Introduction

This chapter describes the literature reports, current technologies and analytical aspects that relate to this research project. The rationale for providing solutions to the problem statements addressed earlier in **section 1.1** has also been given the appropriate industrial relevance in this chapter. Classical processes previously used for the extraction of cobalt from various ore deposits are also discussed.

#### 2.2 Occurrence and geology of cobalt

Whereas copper has been known for ages, metallic cobalt had not been isolated until the 18th century.<sup>1</sup> The colouring properties of its oxides have nonetheless been known in ancient times, particularly in the Middle East, Egypt and China. Materials such as pottery, earthenware, glass, enamelware and pearls were tinted blue by heating them with cobalt oxides at high temperatures in clay furnaces. Some objects could also be decorated with paints derived from cobalt oxides.<sup>1-3</sup>

##### 2.2.1 Cobalt ore deposits

Cobalt is produced mainly as a by-product in the mining and processing of other ore materials, particularly those of copper, nickel, silver, gold, lead and zinc. The deposits of cobalt are usually classified as follows:<sup>1-4</sup>

- **Hypogene deposits.** These are associated with iron-nickel-copper sulphides containing cobalt at an average cobalt content of 0.07%. Typical examples of these deposits are pyrrhotite, pentlandite, pyrite, marcasite and cobaltite.
- **Contact metamorphic deposits.** These deposits have been associated with the carbonate rock formed by contact metamorphism. Examples of these deposits include magnetite, chalcopyrite, and cobalt containing pyrite.
- **Lateric deposits.** These deposits are generally as a result of weathering of other minerals such as peridotite and serpentine. As a result, laterite that is rich in iron, nickel, cobalt, and chromium is generally produced. Commercially valuable deposits contain 40-50% iron, 1-2% nickel, and 0.01-0.1% cobalt.
- **Massive sulphide deposits.** These deposits originate from metamorphic rocks and such deposits consist mainly of pyrite and pyrrhotite.
- **Hydrothermal deposits.** These are commonly subdivided into two classes; namely, vein deposits (containing cobalt at 1-10% levels) and replacement deposits. Some of these deposits are the only ones that have been mined specifically as a source of cobalt.

- **Strata-bound deposits.** These types of copper-cobalt deposits provides the world's major source of cobalt and are generally found in Zambia. These deposits contain a number of minerals including chalcopyrite, bornite, chalcocite, linnaeite, and carrolite.

### 2.2.2 The Katanga cobalt deposits

Cobalt produced in the Katanga province originates from strata-bound deposits.<sup>2</sup> To date, cobalt has been mined as a by-product of copper production but strategies are underway for cobalt to be extracted as the main ore metal, with copper being the by-product. In the Katanga province, the Union Minière du Haut-Katanga (U.M.H.K.) which had operated mines there from 1906 to 1966 identified over 100 deposits containing cobalt and copper.<sup>2-4</sup> It is generally found that cobalt is always associated with copper, both in the primary ores and in the oxidation zone and the grade of the ore bodies vary over a substantial range.

There are generally two principal strata which tend to be mineralized as the "upper" and "lower" ore-bodies.<sup>5</sup> It has been found that cobalt-rich patches generally overlaps copper-rich patches in distribution, and these patches are typically separated by barren or very low grade zones. Individual patches range from a few hundred metres to several kilometres in maximum dimension.<sup>4-6</sup>

In the huge Kolwezi region (**Figure 2.1**) where there are many mines including the Musonoi, Kamoto, Mutoshi, Mupine, Mashamba and Dikuluwe, cobalt content decreases steadily from south to north and disappearing entirely in the northern half of the region.<sup>7</sup> It has been reported that cobalt extraction in the Katanga began in 1925 at the Panda-Likasi electrical refinery.<sup>6-7</sup> An iron-cobalt mixture called "white alloy" was produced from this pilot plant and regular production continued until the 1940's, at the Shituru-Likasi electrolytic plant, and in the 1960's at the Lulu-Kolwezi plant.<sup>5</sup>



**Figure 2.1:** Map for the Democratic Republic of Congo (DRC).<sup>5</sup>

Actual production of cobalt ore first began in 1907 with the opening of the famous Star of the Congo mine near Lubumbashi, the capital of Katanga province. It should be noted that in the upper portion of the oxidized zones of the deposits there are local enrichments, mainly of cobalt, in which a heterogenite heap is more resistant than the copper oxides to being washed out by meteoric waters.<sup>7</sup> This is the case particularly at an outcropping of the Musonoi deposit, where exploitation of the particularly well developed "cobalt cap" was begun in 1940, while the mine itself did not begin operation until 1945. A similar scenario is true with the upper zone of the Oliveira fragment, in the Kamoto-Oliveira- Virgule (K.O.V) deposit, also in the western sector, where there is a superficial enrichment of cobalt, while the copper has been entirely leached away.<sup>6-9</sup>

From 1939 to 1943, the U.M.H.K. substantially increased its cobalt ore production with the opening of the rich cobalt mines of Kasombo (Southern sector), Mindigi and Kabolela (Central sector), Kingamyambo, and the Gossan zone of the Kamoto mine (Western sector).<sup>5</sup> Cobalt, copper and uranium are important ore metals in a

large number of deposits within and near the Katanga region. Many cobalt containing minerals have come from this famous area, including carrollite, cattierite, siegenite, comblainite, heterogenite, kolwezite, oursinite, sphaerocobaltite, and brilliant pink cobaltoan calcite and dolomite.<sup>2,5</sup>

The cobalt ores used extensively for tinting initially came from Persia and Burma and the preparation involved roasting the ore in red heat, followed by fine grinding with the product being a pigment with a very high colouring capacity simply referred to as "cobalt blue." Since cobalt was not of any economic value at that time, it posed a considerable problem in the metallurgical processing of the so-called "useful" metals. In addition, since the cobalt was associated with sulphur and arsenic, the roasting process released noxious fumes. As a result, this mineral was regarded by the miners as a divine curse<sup>5-9</sup> hence the term "cobalt" which comes from the German Kobold, which means "demon," or, according to an old Germanic legend, the evil-minded gnome-like spirits of the mines.

The name cobalt first made its appearance in the literature on mining (in the Latin forms, cobaltus and cobaltum) in the celebrated treatise on the mining operations in Saxony and Bohemia entitled *De Re Metallica* (1556) by Georgius Agricola. It was not until 1735 that the Swedish chemist Georg Brandt isolated cobalt as a pure element. The research subsequently undertaken on this new element led to industrial applications that were far more important than its simple use as a colouring agent.<sup>10</sup>

### 2.2.3 Cobalt Mining Worldwide

By the early 19th century, cobalt deposits had been found in many locations in the world, particularly in Germany (the Black Forest, Harz, Hesse), Norway, Sweden, Transylvania (now part of Romania), France, Spain, England, Chile, Argentina, Tasmania, etc. The chronology of the most recent discoveries of large cobalt deposits is as follows:<sup>11</sup>

- 1874: New Caledonian deposit.



- 1904: Ontario deposits (Canada).
- 1907: Katanga deposits (Democratic Republic of Congo).
- 1930: Bou Azzer deposit (Morocco).
- 1933: Deposits of the Zambian copper belt which overlaps south eastern Katanga.
- 1939: Outokumpu deposits (Finland).

Other deposits of varying importance have also been discovered in the USA (which is also the leading consumer of cobalt), in Kazakhstan, in Azerbaijan, and in the lateritic soils of Cuba. Cobalt has been mined intermittently in the USA for more than a century at localities in Idaho, Maryland, Missouri, Pennsylvania, Virginia and Wisconsin. Known reserves are abundant but generally too low-grade to be economical. To date, only a few mines in Pennsylvania are producing cobalt as a by-product of iron mining.<sup>3,11</sup>

The old Blackbird mine in Idaho is among those that once produced cobalt despite a very low ore grade (0.015% Co). Reserves in this area are extensive, consisting primarily of copper ore with trace amounts of cobalt. The mine was shut down purely for environmental reasons. At best, domestic USA production of cobalt has rarely exceeded 1,000 tonnes per year. Consequently, the USA remains heavily dependent on foreign producers for the roughly 20,000 tons of cobalt it consumes each year.<sup>11</sup>

Cobalt production worldwide is almost invariably a by-product of mining of other metals, and ore grades are typically very low (a few hundredths to a few tenths of percentage cobalt). The rare exceptions where ores containing over 1% Co are found include Bou Azzer, Morocco, the hydrothermal veins in the Cobalt-Gowganda area, Ontario, and the Katanga copper-cobalt deposits. High-grade

cobalt ores in Katanga occur mainly as enrichment of oxidized ore bodies. Despite the enrichment, cobalt content alone is generally too low to make mining profitable.<sup>11-12</sup>

It should also be noted that the alteration of carrollite (virtually the only primary cobalt ore mineral in the stratiform deposits) proceeds far more readily than the alteration of primary copper sulphides. Consequently, the alteration of copper and cobalt sulphides results in the concentration of cobalt ions in solution dominating during the deposition of Co-Cu secondary minerals until the carrollite has been exhausted. Thereafter only copper secondary minerals will form. This dephasing of the cobalt and copper secondary minerals is particularly obvious at one of the Fungurume outcrops where heterogenite mineral (CoOOH) is found associated with chalcocite.<sup>7</sup> Unaltered carrollite is only found at a depth of about 300 feet below the outcrop.

The relatively small number of secondary cobalt species is a result of the limited compatibility and affinity of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ions for copper and nickel (for primary minerals), and to some extent copper and nickel (for secondary minerals). Physicochemical characteristics of the alteration environment may further restrict the possibilities. Cobalt, however, can replace copper, calcium and perhaps magnesium also to a limited degree in such minerals as cobaltiferous, malachite and cobaltoan calcite and dolomite, respectively.<sup>13</sup>

Katanga's carrollite contains 36% cobalt and virtually no nickel. Carrollite ( $\text{CuCo}_2\text{S}_4$ ) is the principal primary cobalt mineral in the stratiform deposits.<sup>14</sup> The most common crystal of cobalt forms are the cube and the octahedron in some combination; the cube or octahedron alone are exceedingly rare. Unaltered crystals are steel-grey to silvery white with a bright metallic lustre. Altered crystals are dull and frosty, grey to black in colour, and may bear a thin coating of heterogenite. Remarkable crystals of carrollite have been found in some mines, the Kambove West underground mine produced a 10cm cobalt crystal which was unfortunately broken by blasting.<sup>11,14</sup>

#### 2.2.4 Secondary Cobalt Minerals

The alteration of primary sulphide minerals in Katanga has led to secondary associations that differ greatly in quality and in copper/cobalt ratio. One of the principal characteristics of the oxidation zones in the southern Katanga deposits, whether in the stratiform layers or the vein beds, is the lack of diversity in the cobalt mineral assemblages as compared to the very broad range of copper minerals.<sup>15</sup>

It is believed that the leaching of primary sulfides created sulphate solutions that reacted with dolomitic rocks to produce secondary carbonates (malachite, sphaerocobaltite)<sup>13</sup> and with the siliceous rocks to produce silicates, such as chrysocolla, plancheite, shattuckite and diopside. However, cobalt tends to accumulate in the form of hydrous oxides associated with siliceous rocks, but frequently retaining the indices of the primitive carbonate rock. Katanga malachites may contain an appreciable percentage of cobalt (up to 6.5%). In the western mines (Musonoi and Kamoto), a double carbonate of copper and cobalt (kolwezite) has been found which belongs to the rosasite structural group and contains nearly 20% cobalt.<sup>13</sup>

#### 2.2.4.1 Calcite $\text{CaCO}_3$ and Dolomite $\text{CaMg}(\text{CO}_3)_2$

Tiny pink crystals of cobaltoan dolomite on gray dolomite originate from deposits in the Kakanda area, and are well known in the mineral market. The large, pink scalenohedrons of cobaltoan calcite from the Mashamba West mine are reported to be the most beautiful in the world; some crystals also have a partial kolwezite coating. Like Shinkolobwe, the Mashamba West mine has also produced spectacular cobaltoan calcite in pink hexagonal prisms of several centimetres, with three-faced rhombohedron terminations.<sup>7-8</sup>

#### 2.2.4.2 Heterogenite ( $\text{CoOOH}$ )

The compact or powdery black oxyhydroxides of cobalt were given the name "heterogenite" (literally "of a different nature") by Frenzel in 1872 in order to distinguish them from black oxides of manganese obtained from cobalt, nickel and manganese ore at the Maasen mine in Schneeberg (Saxony, Germany). In 1962, Max Hey concluded that all the heterogenites have a single formula,  $\text{CoOOH}$ , analogous to that of manganite ( $\text{MnOOH}$ ) and goethite ( $\text{FeOOH}$ ).<sup>8</sup>

Deliens<sup>1</sup>, who studied the southern Katanga heterogenites, confirmed Hey's views and retained the single name "heterogenite" to describe the hydrated black oxides of cobalt. This latter author also revealed the existence of a hexagonal polytype, which he called "heterogenite 2H". Since then, common heterogenite has been termed heterogenite 3R in mineralogical treatises, in order to distinguish it from the 2H polytype. Heterogenite 3R shown in **Figure 2.2**, which occurs with the widest range of appearances, is the heterogenite most commonly found in southern Katanga.



**Figure 2.2:** Picture of Heterogenite 3R ( $\text{CoOOH}\cdot 3\text{R}$ ).<sup>8</sup>

From a chemistry perspective, three factors characterize the difference between heterogenite polytypes. They are the cobalt valence, the presence of copper, and the water content. The crystalline varieties are almost exclusively made up of trivalent cobalt ( $\text{Co}^{3+}$ ). They contain very little copper (maximum 3.8%), and the  $\text{H}_2\text{O}$  content is approximately 1 %. In addition, they contain a low percentage of nickel (not over 1.5%). The formula representing heterogenite is  $\text{CoOOH}$ .



**Figure 2.3:** Picture of Heterogenite 2H ( $\text{CoOOH}\cdot 2\text{H}$ ).<sup>8</sup>

Experiments in synthesizing hydrated oxides of cobalt under normal temperature and pressure conditions have clearly confirmed the role of copper in limiting the degree of crystallinity in the heterogenites, whereas the presence of a little nickel favours crystallization. The most beautiful heterogenites in the world have been

collected at the Kabolela mine. They are found at that site in botryoidal masses, in stalactites, and in cavern draperies.<sup>13</sup>

Heterogenite 2H is a hexagonal polytype of rhombohedral heterogenite 3R.<sup>8</sup> It is very closely associated with the crystals of heterogenite 3R in the little veins with a metallic lustre found in certain specimens obtained from the oxidation zone of the Mindigi mine. The polytype 2H crystals appear as flattened prisms with regular hexagonal contours. They are black in colour with a bright metallic lustre shown in **Figure 2.3**. The formula is thus identical to that of heterogenite 3R:  $\text{CoOOH}\cdot 3\text{R}$ . The clearest distinction between the two polytypes is the 2H polytype rarity in comparison to the 3R, which is almost always present in the oxidation zones of the Cu-Co deposits in southern Katanga.

### 2.3 Production

The most important producers of cobalt to date are Zambia, Canada, Kazakhstan and Azerbaijan. Congo was the leader until the 1970's, producing up to 16,000 metric tons per year. At present, cobalt production in Congo is negligible but with reserves estimated at 600,000 tonnes of metallic cobalt and with good market conditions forecast, Congo may soon be a major cobalt producer once again.<sup>11</sup>

**Table 2.1** illustrates 2005 availability of refined cobalt as reported by the Cobalt Development Institute (CDI).<sup>11</sup> Cobalt production has grown steadily over the last decade, from a total production of 23,207 tonnes in 1995 to 52,870 tonnes in 2005. This more than two-fold increase corresponds to an annual average production growth rate of 8.7%, with year to year growth rates ranging between 4.3% and 18.4%. According to CDI estimates which are based on assumptions and publicly available sources, the total cobalt production in 2010 could reach 80,030 tonnes, mainly due to the anticipated startup or ramping up of eight major projects with a cumulative estimated contribution of 18,400 tonnes of additional supply.

**Table 2.1:** Refined Cobalt Production/Availability (tonnes).<sup>11</sup>

<b>Europe</b>	<b>Production/Supply</b>	<b>Source of Feed</b>
Belgium	3,300	Various secondary/Australia/DRC
Finland	8,170	New Caledonia/Africa/Australia/Others
France	280	Nickel by-product New Caledonia
Norway	5,000	Canada/Africa/Australia/Russia/Others
<b>Africa</b>		
Morocco	1,600	Domestic
South Africa	220	Domestic
D.R of Congo	600	Domestic
Uganda	630	Domestic
Zambia	5,400	Domestic
<b>Americas</b>		
Brazil	1,150	Domestic
Canada	4,950	Domestic/Australia/Cuba/Secondary
<b>Asia</b>		
China	12,000	Domestic/DRC
India	1,200	Domestic/DRC/Cuba
Japan	470	Australia
<b>Others</b>		
Australia	3,150	New Caledonia/Domestic
Russia (Export)	4,750	Domestic
<b>Total</b>	<b>52,870</b>	

Published data by the World Bureau of Metal Statistics (WBMS), which includes apparent cobalt demand by geological location calculated from import/export data, suggested that worldwide cobalt demand in 2005 was about 55,000 tonnes, an increase of about 48% over that in 2004. Further increases are projected over the next decade in line with increases in the number of new commercial aircrafts being manufactured, chemical applications and most notably rechargeable batteries. Demand estimates at individual market segments<sup>11</sup> are shown in **Table 2.2**.

**Table 2.2:** The Cobalt Market.<sup>11</sup>

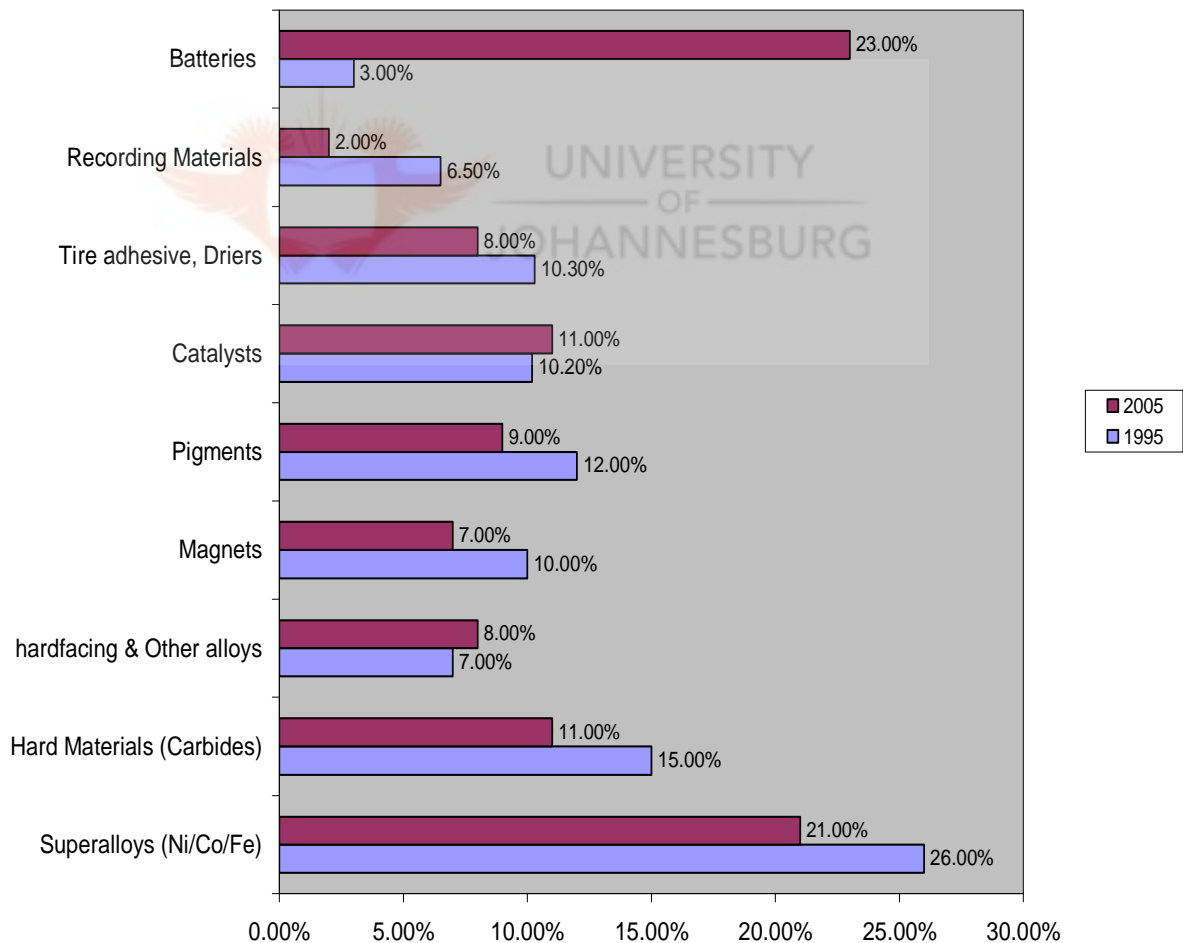
Market	Percentage %	Cobalt materials possibility
Superalloy (Ni/Co/Fe	20.0	Metal, Recycle
Hardfacing & Other Alloys	5.5	Metal & mesh powders, recycle
Magnets All Type	7.0	Metal, Powders Recycle
Hard Materials-carbides, Diamond tolling	10.5	Powders-Fine and very fine
Catalyst	11.0	Salts-Carbonate, Sulphate, Nitrate, Acetate, metal
Colours-glass, Enamels, Plastics, Ceramics, Artists Colours, fabrics	11.0	Oxide, + some sulphate, Hydroxide, Carbonate
Feestuffs, Anodising, Recording, Electrolysis, Cu Electrowinning	4.5	Mainly sulphate, but some carbonate and hydroxide
Batteries	21.0	Hydroxide, Powder, LiCoO <sub>2</sub>
Tyre adhesives, Soaps, Driers (paint/ink)	9.5	Soap & complexes made from metal starting point
	100	

Cobalt metal is stable and has a higher tensile strength than steel. cobalt is bluish white and lustrous in appearance. Like iron it is ferromagnetic, but on heating above 1000 °C it changes to a non-magnetic form. Cobalt is relatively unreactive in H<sub>2</sub>O, H<sub>2</sub> or N<sub>2</sub>, although it reacts with steam forming CoO. It is oxidized when heated in air and burns at white heat to form Co<sub>3</sub>O<sub>4</sub>. Cobalt dissolves slowly in dilute acids, but like iron it is rendered passive by concentrated HNO<sub>3</sub>.

In the metals industry cobalt is employed in the manufacture of alloys, ferrous and non-ferrous. It is an essential constituent of a group of high speed steels. Thus tungsten tool steels consisting of 18% tungsten, 4%chromium, 1% vanadium, 5 to 12% cobalt and 0.5 to 0.8% carbon are capable of heavy cuts and feeds at high speed in the machining of steels. Cobalt is the only alloying element which serves to lower the hardness of steel. The addition of cobalt to molybdenum high-speed steels also improves their quality. Steel containing about 85% cobalt is useful for permanent magnets.



Non-ferrous alloys containing 20% to 65% cobalt are resistant to wear, oxidation and corrosion under extreme corrosive media and elevated temperature conditions. Addition of 2% carbon and 1% silicon to various cobalt-chromium-tungsten alloys produces suitable high strength alloys at elevated temperature for jet engines. Cobalt is also used in electroplating. It is utilized for making blue glass and enamels. Cobalt powder finds application in the production of sintered hard metals, sintered magnets, etc. Cobalt and its compounds are used in a wide array of applications and a number of emerging applications of cobalt are owned by innovative companies. The chart in **Figure 2.4** shows cobalt demand by end use (1995 versus 2005).



**Figure 2.4:** Cobalt demand by end use (1995 versus 2005).<sup>11</sup>

### 2.3.1 Extraction

The first stages of extracting of cobalt from its ores involve the separation of cobalt bearing minerals from the gangue and from minerals containing other undesirable metals.<sup>10</sup> The concentrates obtained by applying physical separation methods such as gravity separation or froth flotation to ores can increase the cobalt content from cobalt rich ores. Two methods have been used on a commercial scale to float oxide ores, the palm oil process and the sulphidization process. The *palm oil process* collects the concentrate in a 3:1 mixture of hydrolyzed palm oil and gas oil emulsified in carbonated hot water. The *sulphidization process* is used for mixed oxide-sulfide ores to float sulfide ores first and to concentrate oxide minerals subsequently in a xanthate flotation.

Cobalt is extracted from concentrates and occasionally directly from the ore itself by hydrometallurgical, pyrometallurgical, and electrometallurgical processes. However, most extraction methods are based on hydrometallurgy. These hydrometallurgical processes involve (1) leaching of concentrates to give a cobalt containing solution, (2) separation of cobalt from other cobalt metal ions in solution, and (3) reduction of cobalt ions to the metal. Electrometallurgical processes are used in the electrowinning of the metal from leach solutions and in refining the cobalt that has been extracted by hydrometallurgical methods.

### 2.3.2 Leaching as a hydrometallurgical process

Leaching is central to hydrometallurgical operations. Leaching aims at recovering the element from its ore mineral at the lowest cost and in a form requiring minimum cost for further processing. Two principal leaching practices are followed, namely; (i) Mine, Dump and Heap Leaching, and (ii) Vat and Pressure Leaching.<sup>10</sup>

### 2.3.2.1 Mine, Dump and Heap Leaching

Low grade underground ore bodies cannot be processed profitably by mining, but the mineral can be recovered economically by leaching the ore *in situ* in the ground. For example, in mine leaching ores containing less than 0.5% Cu can be leached by simply diverting surface water down boreholes to the top of the deposit and pumping the extract up to the surface from the bottom of the bed. For efficient extraction *in situ*, the ore must be permeable or shattered by explosives and resting on impermeable rock. The pillars and walls left as roof supports in old mine workings can also be leached by this method. The only capital costs involved are for the drills to form the boreholes and the pumps for recovery of the liquor, but the concentration of the metal in the extracted solution is very low and it may take up to 20 years to recover most of the valuable metals.<sup>10</sup>

Waste dumps of rock left from mining operations in earlier times when beneficiation treatments were less efficient than present practice, often contain sufficient metal values to justify leaching the dump. A more expensive but still low cost route for low-grade deposits is to mine the ore and, following primary crushing, pile it into a large heap that is exposed to percolation by the leaching reagent. This is particularly useful when a low-grade ore contains large amounts of pyrites, which is difficult to remove during beneficiation. In both dump and heap leaching, the ore must again rest on an impermeable risk of contamination by other surface waters. All of these leaching methods are very slow, but they are accelerated by the presence of a particular bacterium<sup>9</sup>, ***Thiobacillus ferrooxidans***, which occurs naturally in some mine waters. These micro-organisms use oxygen and carbon dioxide for growth and derive their energy from the oxidation of both sulphides to sulphates and ferrous sulphate to ferric sulphate.

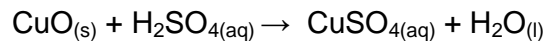
### 2.3.2.2 Vat and Pressure Leaching

In Vat leaching, the ore is first crushed and ground to produce a feed usually in the size range 5 mm to 20 mm to increase the mineral exposure to the leaching reagent and it is then loaded into large open containers. Several vats are

connected in series and are emptied and filled in rotation. A fresh leach solution is introduced into the vat containing the ore nearest to exhaustion and allowed to percolate through the ore and then pumped to the next container. The process is repeated until the liquor is finally recovered from the vat that was the last to be loaded with fresh ore. Each tank may contain up to 10,000 tonnes of ore and is completely extracted in a few days, producing a leach solution containing as much as 40 g/L of the metal ions.

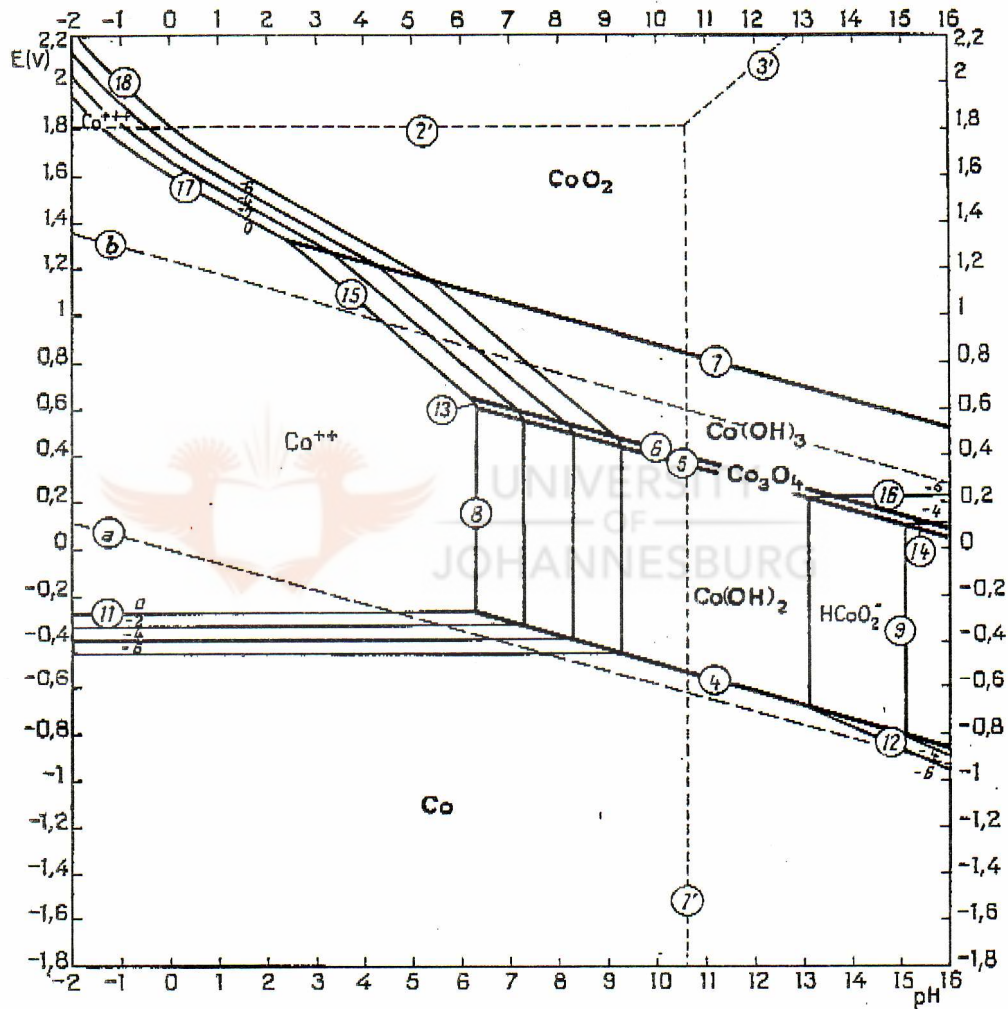
Pressure leaching in an autoclave, first applied to sulphides ores about 40 years ago, avoids the need for roasting treatment and gives even more rapid dissolution. The leaching rate of a metallic mineral is accelerated as the temperature is raised, but the solution boils if the temperature is raised to 100<sup>0</sup>C under atmospheric pressure. Much higher temperatures, up to about 350<sup>0</sup>C, can be used if the pressure above the solution is increased. Furthermore, sulphide minerals can be oxidised directly to sulphates at elevated temperature if the solution is pressurized with oxygen gas. The exothermic oxidation reaction can provide all the thermal energy required and the process is autogenous when more than about 5%S is oxidized.

Abundant supplies of sulphuric acid are produced from the treatment of the exhaust gas produced during roasting and smelting of sulphide ores. This acid satisfies the requirements for the leaching of oxide ores of elements such as Co, Cu, Fe, Ni and Zn at ambient or slightly elevated temperatures as per the reaction below:



Pourbaix diagrams (**Figure 2.5**) are used to identify the conditions required to dissolve a metallic compound in an aqueous solution at a specific temperature and pressure. Water is the predominant species in the solution. The potential-pH diagrams for the relevant metal-water systems can be used to examine the equilibrium conditions. The phase fields shown on the Pourbaix diagram for any chosen metal are dependent on the solid and ionic phases considered as possible

participants. **Figure 2.5** shows the potential-pH diagram at 25 °C for the Co-H<sub>2</sub>O system. This type of diagram shows that an ion can exist over a wider range of potential and pH as the activity of this ion in solution decreases. The horizontal lines separating the metal-ion phases at unit ion activity are located at the standard electrode potentials for the reduction of these ions.



**Figure 2.5:** Eh-pH Pourbaix diagram for Co-H<sub>2</sub>O system.<sup>10</sup>

### 2.3.2.3 Leaching of Cobalt Ores and Concentrates

Cobalt can be leached from its ores and concentrates in both acidic and alkaline media. Processes involving acid sulphate leaching include (1) treatment of oxide ore concentrates with sulphuric acid containing a reducing agent, (2) extraction of

cobalt sulphate from sulphide ores following an oxidizing roast, (3) extraction following a sulphidizing roast, and (4) extraction by pressure leaching with sulphuric acid, often in the presence of oxygen.<sup>10</sup>

#### **2.3.2.4 Leaching of cobalt from copper-cobalt concentrates**

The copper-cobalt ores are treated by a sulphidizing roast in a fluidized bed furnace to convert copper and cobalt sulphides into soluble oxides and iron into insoluble haematite. The calcine is subsequently leached with sulphuric acid from the spent copper recovery electrolyte. Oxide concentrates are introduced at this leaching step to maintain the acid balance in the circuit. Iron and aluminium are removed from the leach solution, and copper is electrowon on copper cathodes. A part of the spent electrolyte enters the cobalt recovery circuit and is purified by the removal of iron, copper, nickel, and zinc prior to precipitation of cobalt as its hydroxide. In the final stages this cobalt hydroxide is re-dissolved and the metal is refined by electrolysis and degassing to remove any traces of hydrogen.

#### **2.3.2.5 Cobalt from Nickel Sulphide Concentrates**

Nickel sulphide concentrates are treated by either roasting or flash smelting to give a matte from which nickel and cobalt can be recovered by leaching. The concentrates may also be treated directly by an ammonia solution pressure leach. In the Sherritt Gordon process<sup>10</sup> used at Fort Saskatchewan in Canada, a feed of matte and sulphide concentrate, containing about 10% nickel, 2% copper, 0.4% cobalt, 33% iron, and 30% sulphur, is pressure leached in autoclaves at 83°C and 7 bar with an ammoniacal medium. This converts most of the sulphide *via* thiosulphate to sulphate and solubilizes nickel, copper, and cobalt as amine complexes.<sup>16</sup>

Most of the copper in the leach solution is precipitated as copper sulphide when the solution is distilled to recycle ammonia. The solution is treated with hydrogen sulphide to remove any residual copper, and any sulphide remaining at this stage is converted to sulphate by a pressure oxidation hydrolysis reaction at 65 bar.

The solution then enters reduction autoclaves, where nickel powder is precipitated by reduction with hydrogen at 36 bar. The remaining solution, which contains 1-1.5g/L of both cobalt and nickel, is treated in an autoclave with hydrogen sulphide to precipitate cobalt and nickel sulphides, which are subsequently leached with sulphuric acid at 140<sup>0</sup>C and 64 bar. Iron is removed from this leach liquid at pH 2.5-3 by the addition of ammonia solution.

The cobalt (II) in ammonia solution is oxidized in air to give a very stable cobalt (III) pentammine complex. Nickel is subsequently precipitated from the solution in two steps as a nickel ammonium sulphate. Cobalt powder is then added along with sulphuric acid to reduce the cobalt (III) pentammine complex to cobalt (II), which is finally reduced to cobalt powder by treatment with hydrogen at 120 <sup>0</sup>C and 46 bar. Cobalt containing mattes and mixed sulphide concentrates have also been treated by pressure leaching with sulphuric acid, for example, at Amax at Port Nickel in the USA, Nippon mining and Sumitomo Metals Mining company in Japan, and Outokumpu Oy in Finland.

#### **2.3.2.6 Cobalt from Arsenide Ores**

Arsenic-containing concentrates are roasted in a fluidized bed at 600<sup>0</sup>C to 700<sup>0</sup>C to remove 60% to 70% of the arsenic present as arsenic (III) oxide. The roasted ores can be treated with hydrochloric acid and chlorine or sulphuric acid to give a leach solution that can be purified by hydrometallurgical methods and from which cobalt can be recovered by electrolysis or by carbonate precipitation.<sup>16</sup>

#### **2.4 Separation of cobalt from other metal ions leach solutions**

A major part of cobalt recovery from leach solutions pertains to its separation from other elements. Because of the similarities in chemical behaviour of cobalt and nickel, the separation of these two elements has been studied extensively.



### 2.4.1 Chemical methods of separation

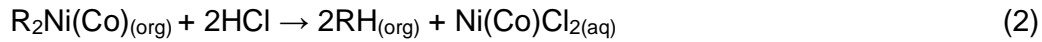
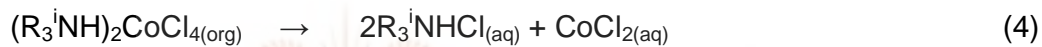
The chemical methods of separating cobalt from other metals use the different solubilities and kinetic or thermodynamic stabilities of their compounds. The most important compounds that have been used in separation are hydroxides, carbonates, amine complexes, double ammonium sulphates, sulphites, chlorides, and carbonyls; the cementation to metal is also utilized. The solubilities of cobalt (III) and nickel (II) hydroxides, and of cobalt (II) and nickel (II) carbonates in solutions containing  $\text{NH}_3$  and  $\text{CO}_2$  have also been used to separate these elements. Fractional crystallization of chloride-containing media can be used to concentrate cobalt in solution and nickel in solid nickel-chloride dihydrate.

### 2.4.2 Physical methods of separation

Many physical methods have been used to separate cobalt from other elements, but the three most important are electrolysis, solvent extraction, and ion exchange. In most solvent extraction processes, cobalt is extracted using a tertiary amine from chloride solutions although cobalt and nickel can be separated from each other with phosphate or carboxylic acid reagents from ammoniacal sulphate solutions. In the sulphuric acid leach process of Nippon Mining at Hitachi, solvent extraction is employed to extract zinc from the leach solution with di-(2-ethylhexyl) phosphonic acid (DEHPA) at pH 2 to pH 3 prior to solvent extraction of cobalt with an alkylphosphonic acid.<sup>10</sup>

The Falconbridge process<sup>10</sup> involves solvent extraction of cobalt from chloride solution with triisooctylamine. The Sumitomo Metals Mining company.<sup>10</sup> uses a solvent extraction process to co-extract cobalt and nickel with acid. The extract is then stripped with hydrochloric acid and cobalt is re-extracted from the chloride solution with tri-*n*-octylamine to give an extract from which cobalt is stripped and electrowon. This solvent extraction process can be expressed in terms of the following chemical reactions:



**Extraction:****Stripping:****Extraction:****Stripping:***Dilute HCl*

Where RH is an acid in kerosene and  $R_3^iN$  is tri-n-octylamine in xylene; (org) and (aq) are organic and aqueous phase, respectively.

**2.5 Electrowinning of cobalt**

Cobalt can be extracted and obtained as high-purity metal by electrolysis of sulphate or chloride solutions. Solutions of pH 1 to pH 4 are necessary for the electrowinning of cobalt, and the pH is often maintained by suspending cobalt hydroxide or cobalt carbonate in the electrolyte to use up the acid produced at the anode. Current densities of  $5 \text{ A/dm}^2$  are used with current consumptions of approximately 6.5 kWh per kilogram of cobalt. Electrolytically refined cobalt has a purity of greater than 99.5%.

During the electrolysis of cobalt sulphate  $\text{CoSO}_4$  solution, the predominant reactions at the electrodes are as follows:

*At the cathode*



*At the anode*



The reduction of  $\text{H}^+$  ions at the cathode results in a rise in pH while the generation of  $\text{H}^+$  ions at the anode results in a decrease of pH. If the anolyte and catholyte are allowed to mix, then, in normal cobalt electro-winning where current efficiency for cobalt deposition is in the range of 90%, the pH of the electrolyte will drop. Similarly, the cobalt strength of the electrolyte will also be depleted. If the above three reactions are the only reactions taking place, then the drop in pH is proportional to the Co ion depletion. Therefore, if  $\text{Co}(\text{OH})_2$  is added to this solution, then, when the pH of the solution is restored, the Co strength of the solution can also be restored. Thus, restoring the pH is an effective method of regenerating the bath with respect to both the pH and the cobalt concentration. Other reactions do take place at the electrodes, the prominent amongst these being:



Most of the  $\text{Co}^{3+}$  ions are deposited at the anode as a black oxide/hydroxide powder. The probability of a small fraction reaching the cathode cannot be ruled out. The presence of multivalent ions in the electrolyte affects the nature of the deposit. However, in the purified solutions, the activity of other ions is usually very low and their discharge at the electrodes is negligible. Similarly, reaction 4 could also be neglected because the cobalt oxide deposited at the anode is only a small fraction of the Co deposited at the cathode.

## 2.6 The chemistry of cobalt

One of the most striking features of the transition elements (d-block) is that the elements usually exist in several different oxidation states. Furthermore, the oxidation states change in units of one, e.g.  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cu}^+$ . There is a trend for the elements in the second half of the d-block not to utilize all their outer electrons for bonding. A report of possible Co (+V) has been disproved, and even Co (+IV) is considered unstable. For cobalt, the  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  states are by far the most stable.  $\text{Co}^{2+}$  ions and the hydrated ion  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  exist in many simple compounds and the hydrated ion is stable in water. In contrast,  $\text{Co}^{3+}$  is very stable and very important in complexes.<sup>17-18</sup>

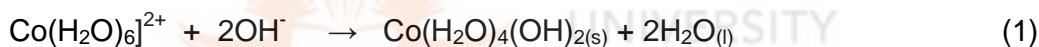
Divalent cobalt forms numerous complexes of various stereochemical types. Octahedral and tetrahedral ones are the most common.  $\text{Co}^{2+}$  forms tetrahedral complexes more readily than any other transition metal ion. This is in accord with the fact that for a  $d^7$  ion, ligand-field stabilization energies somewhat disfavour the tetrahedral configuration compared to the octahedral configuration. Because of the small stability difference between octahedral and tetrahedral  $\text{Co}^{2+}$  complexes, there are several cases in which the two types of complexes with the same ligand are both known and may exist in equilibrium. The existence of some  $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$  in equilibrium with  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  has been noted. Tetrahedral complexes,  $[\text{CoX}_4]^{2-}$  are generally formed with mono-dentate anionic ligands such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$  and  $\text{OH}^-$ .<sup>18-19</sup>

Most known discrete  $\text{Co}^{3+}$  complexes are octahedral, although tetrahedral and square-antiprismatic  $\text{Co}^{3+}$  complexes are known in a few solid-state situations. In solution,  $\text{Co}^{3+}$  shows a particular affinity for nitrogen donors and the majority of its complexes contain ammonia, amines such as ethylene diamine, nitro groups, especially nitrogen bonded  $\text{SCN}$  groups.<sup>20-22</sup>

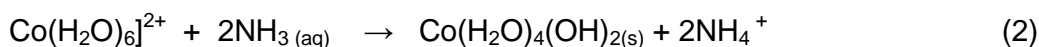
A literature survey<sup>21</sup> shows an extensive array of solution techniques like liquid extraction, gas chromatography, paper and thin layer chromatography, column-liquid chromatography, high-performance liquid chromatography and ion

chromatography which could be used for the separation of cobalt from nickel and other metals. Very little information is however available on the quantitative and qualitative separation of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  species. In one of the few direct methods mentioned in the literature, Hausler *et al* managed to distinguish between the two cobalt species as their acetylacetonate complexes by size exclusion chromatography.<sup>23</sup> The two complexes could however not be properly baseline resolved and a broad, unsymmetrical peak was observed for the cobalt (II) acetylacetonate complex.

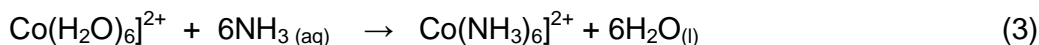
It has been reported that the simplest ions that cobalt forms in aqueous solution is the pink hexaaquacobalt (II) ion  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and hexaaquacobalt (III) ion  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ .<sup>24</sup> Since these ions are acidic in aqueous solutions, base hydrolysis of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ , either by hydroxide ions ( $\text{OH}^-$ ) or ammonia ( $\text{NH}_3$ ), results in a neutral complex which is insoluble in water as shown in reaction 1.



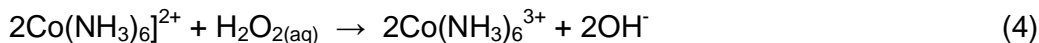
In contrast, base hydrolysis of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  using  $\text{NH}_3$  results in two reactions. In reaction 2, dilute  $\text{NH}_3$  serves as a base by accepting hydrogen ions from the water molecules in  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  to form weakly acidic  $\text{NH}_4^+$  and a neutral complex.



Under high concentrations of  $\text{NH}_3$  as shown in reaction 3, however, a ligand-exchange behaviour between  $\text{H}_2\text{O}$  and  $\text{NH}_3$  molecules is observed.<sup>24</sup> In this case the insoluble  $\text{Co}(\text{H}_2\text{O})_4(\text{OH})_{2(s)}$  dissolves to yield hexamminecobalt(II) ions  $\text{Co}(\text{NH}_3)_6]^{2+}$ .



Upon oxidation by a strong reagent such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), the  $\text{Co}(\text{NH}_3)_6^{2+}$  is converted to the corresponding cobalt (III) complex  $\text{Co}(\text{NH}_3)_6^{3+}$ . This oxidation is shown in reaction 4.<sup>24</sup>



The reaction between  $\text{Co}^{2+}$  hexaaqua ions and carbonates simply results in the formation of a cobalt carbonate precipitate as shown in reaction 5.<sup>24</sup>



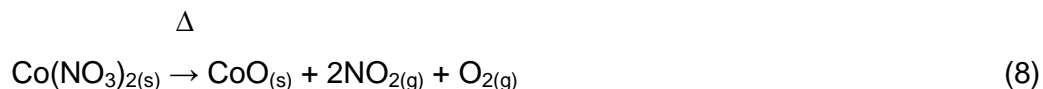
Separation of cobalt from other metals such as nickel, iron and copper in the final leach solution is usually carried out by neutralizing the solution with calcium carbonate or sodium hydroxide. The neutralized solution is then carefully treated with bleaching powder to precipitate cobalt only as a hydroxide,  $\text{Co}(\text{OH})_{3(\text{s})}$ . The other metals remain in solution.<sup>23</sup>

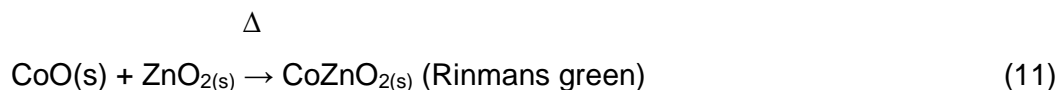
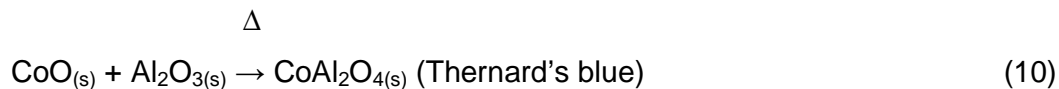


The precipitate is washed, dried and ignited to form cobalto-cobaltic oxide,  $\text{Co}_3\text{O}_4$ . The cobalt metal is obtained by reduction of  $\text{Co}_3\text{O}_4$  by heating with charcoal and limestone in an electric furnace or by hydrogen or aluminium as shown in reaction 7.<sup>22</sup>



Cobalt (II) oxide ( $\text{CoO}$ ) is prepared by thermal decomposition of cobalt hydroxide, carbonate or nitrate in absence of air. It is an olive-green powder which is stable in air at ordinary temperatures but when heated to  $600^\circ\text{C}$  to  $700^\circ\text{C}$  it gives  $\text{Co}_3\text{O}_4$ . This derivative dissolves in acid to form cobaltous salts. With aluminium, zinc and magnesium oxides cobaltites are produced which are the  $\text{CoAl}_2\text{O}_4$  (Thernard's blue), green  $\text{CoZnO}_2$  (Rinman's green and pink  $\text{CoMgO}_2$  respectively).





A solution of cobalt salt, when mixed with ammonium thiocyanate in the presence of acetone, produces a deep blue colour due to the complex cobalt (II) thiocyanate,  $[\text{Co}(\text{SCN})_4]^{2-}$ . It can be extracted with ether. Furthermore, the most recognizable cobaltamine complex,  $\text{Co}(\text{NH}_3)_6^{3+}$  gives a yellowish tinge in solution.<sup>20</sup>

### 2.6.1 Sulphur dioxide as a reducing agent

Sulphur dioxide ( $\text{SO}_2$ ) is produced on a large scale by the oxidation of sulphur,  $\text{S}_8$ . It is also obtained as a by-product of the roasting of sulphide ores (such as  $\text{FeS}_2$ ,  $\text{CuS}$ ,  $\text{ZnS}$  and  $\text{PbS}$ ).



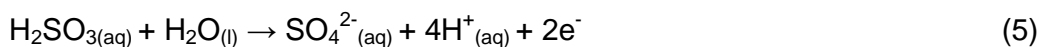
Sulphur dioxide has a characteristic pungent odour. This gas combines with oxygen to give sulphur trioxide ( $\text{SO}_3$ ) but the reaction is ordinarily slow. In the **Contact process**, a mixture of sulphur dioxide and oxygen is passed over a platinum metal or vanadium (V) oxide catalyst (a surface or "contact" catalyst).<sup>25</sup>



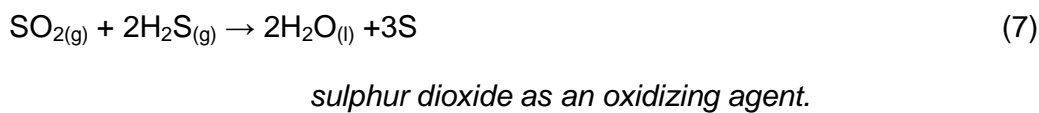
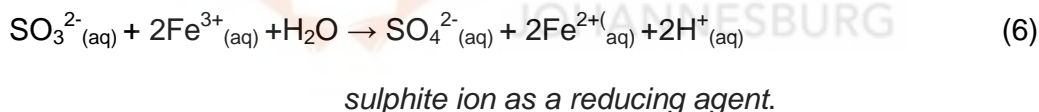
Sulphur trioxide dissolves in water to form sulphuric acid.



The direct dissolution of sulphur trioxide in water forms sulphuric acid mist. In practice the oxide is usually dissolved in concentrated sulphuric acid. The resulting solution, oleum, is then diluted with water to form concentrated sulphuric acid.  $\text{SO}_2$  is the anhydride of sulphurous acid as shown in equation 4.



The corresponding anions are bisulfite,  $\text{HOSO}_2^-$ , and sulfite,  $\text{SO}_3^{2-}$ . Sulphur dioxide can serve either as a reducing agent or as an oxidizing agent, although the former is its more usual role:



The latter equation represents a process that can be used to remove sulphur-containing substances from natural gas by converting them to sulphur.

## 2.7 Microwave technology

It is widely perceived<sup>28</sup> that microwaves can be controlled so that water molecules absorb microwaves into rotational energy levels which causes molecular motion and subsequent heating. While this is a common misconception, it emanates from a failure to realise that it is in fact *gaseous* water that quantizes rotational energy levels in the microwave region. In the liquid state, for all practical purposes, the quantization of rotational levels is not possible.

A simple way to visualise the true mechanism is to picture microwaves as a high frequency oscillating electric and magnetic fields. Anything which exists in this field may be electrically or magnetically polarised at this oscillation frequency. Two principal microwave heating methods operate, dipolar polarization and conduction mechanisms.<sup>26-28</sup> A third mechanism, interfacial polarisation, occurs although this is often of limited importance.

### 2.7.1 Dipolar Polarisation

For a molecule in a polar liquid such as water, methanol, ethanol, etc, there are intermolecular forces which give any motion of the molecule some inertia. Under a very high frequency electric field, a polar molecule would attempt to follow the field, but intermolecular inertia would stop any significant motion before the field has reversed, and as a result no net motion results. If the frequency of field oscillation is very low, then the molecules will be polarised uniformly, and no random motion results. In the intermediate case, the frequency of the field will be such that the molecules would be almost able to keep in phase with the field polarity. In this case, the random motion resulting as molecules jostle to attempt in vain to follow the field results in the heating effect that is observed in the sample.

### 2.7.2 Conduction Mechanisms

Whereas the irradiated sample is an electrical conductor, the charge carriers (electrons, ions, etc) are moved through the material under the influence of the electric field resulting in a polarisation. These induced currents will cause heating in the sample due to any electrical resistance. For a very good conductor, complete polarisation may be achieved in approximately  $10^{-18}$  seconds, indicating that under the influence of a 2.45GHz microwave, the conducting electrons move precisely in phase with the field.

If the sample is *too conducting*, such as a metal, most of the microwave energy does not penetrate the surface of the material, but is reflected. However, the colossal surface voltages which may still be induced are responsible for the arcing that is observed from metals under microwave radiation



### 2.7.3 Interfacial Polarisation

An example illustrating interfacial polarisation would be a dispersion of metal particles in, say, sulphur. Sulphur is microwave transparent and metals reflect microwaves yet, curiously, the combination forms an extremely good microwave absorbing material. Interfacial polarisation is an effect which is very difficult to treat in a simple manner, and is most easily viewed as a combination of conduction and dipolar polarisation effects.

### 2.7.4 Microwave treatment of ores prior to leaching

The principal disadvantage of hydrometallurgical operations is probably the process times required to achieve high metal recovery since these processes are often carried out at low temperatures compared to pyrometallurgical processes. Microwave treatment of ores prior to leaching has been investigated in an attempt to improve the yield of extracted metal and to reduce process time, especially with the increasing demand for more environmental friendly processes.<sup>29</sup> Unique microwave heating characteristics are the main driver for potential implementation in metal extraction. These include: low processing time, direct, selective and volumetric heating, and a more controllable heating process.

Although research into heating of minerals with microwave energy is still at its early stages, microwaves had been applied to several oxides and sulphides and it was discovered that dark coloured ore heated faster than lighter ore.<sup>27</sup> Generally, it was found that many ore minerals are good heat absorbers, whereas, the gangue minerals (silicate type) heated poorly. Furthermore, microwaves have the potential to reduce the energy cost of comminution, enhance mineral surface chemistry and facilitate new forms of metal extraction in a controlled environment.<sup>30-31</sup>

Nickel and cobalt have been recovered from laterite ores by smelting operations to obtain ferronickel-cobalt and these were then selectively dissolved with ammonia-ammonium carbonate. However, it was discovered later that this process was energy intensive. Alternatively, nickel and cobalt could be recovered by applying

microwave radiation to the mixture of laterite, ferric chloride and sodium chloride. When the mixture was microwaved for 4 to 8 min, chlorides were formed which were subsequently leached in water.<sup>32</sup> Microwave heating had also been applied directly to the leaching slurry of nickel, cobalt and manganese sulphuric and hydrochloric acids. In this instance, metal extraction increased considerably compared with conventional leaching at temperatures between 230°C and 250°C.<sup>33</sup>

Kruesi and Kruesi<sup>31</sup> investigated the leaching of laterite ores in ammonia chloride using microwave energy as a heating source. Laterite containing nickel, cobalt, iron and magnesium oxides was mixed with ammonium chloride and irradiated at a power level of 1200W for 4 to 5 minutes under a nitrogen atmosphere. The product was then leached in water at a temperature of 80°C for 30 min. It was found that 66% nickel and 78% Co were extracted. Microwave pulses were examined to avoid any possible thermal runaway effect. After irradiation of a similar mixture with a total pulsing time of 5 min in an air atmosphere, 70% Ni and 85% Co were extracted after only 15 min of water leaching. These results are comparable to conventional treatment at 300°C in a rotary kiln for 2 hours.

The effect of microwaves on the leaching kinetics of sphalerite in a solution of 1.0M FeCl<sub>3</sub> and 0.1M HCl at 95°C has also been investigated.<sup>33-34</sup> It was observed that the total zinc extracted after one hour of microwave treatment reached 90%, whereas under conventional leaching conditions, the maximum zinc recovery was about 52%. Microwave treatment was carried out in an adapted microwave oven with an energy output of 650 W at 2.45 GHz. In a similar study, it was found that microwave leaching kinetics of sphalerite in ferric sulphate were much faster than those produced by conventional leaching. The results showed that 92% of zinc was leached within 90 min when microwave were applied compared to 41% total zinc recovery under conventional conditions.

It has been found that sphalerite is a poor absorber of microwave energy compared to other sulphide minerals.<sup>35</sup> After 7 min of microwave exposure in a 1kW microwave oven, a 25g sample of sphalerite reached a maximum temperature of only 88°C. This may indicate the existence of a microwave effect, which enhanced the kinetics of the leaching process.

### **2.7.5 Applications of microwave technology**

Until recently, microwave heating has been applied to sinter only oxide ceramics and semi-metals like carbides and nitrides. However, literature search reveals that in powdered form, virtually all metals, alloys, and inter-metallics will couple and heat efficiently and effectively in a microwave field, and their green parts will produce highly sintered bodies with improved mechanical properties. For example, microwave treatment of two common commercial steel compositions, namely Fe-Ni-C (FN208) and Fe-Cu-C (FC208) produced improved mechanical properties such as the modulus of rupture (MOR) and hardness.<sup>35</sup>

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## CHAPTER 3

### EXPERIMENTAL METHODOLOGY

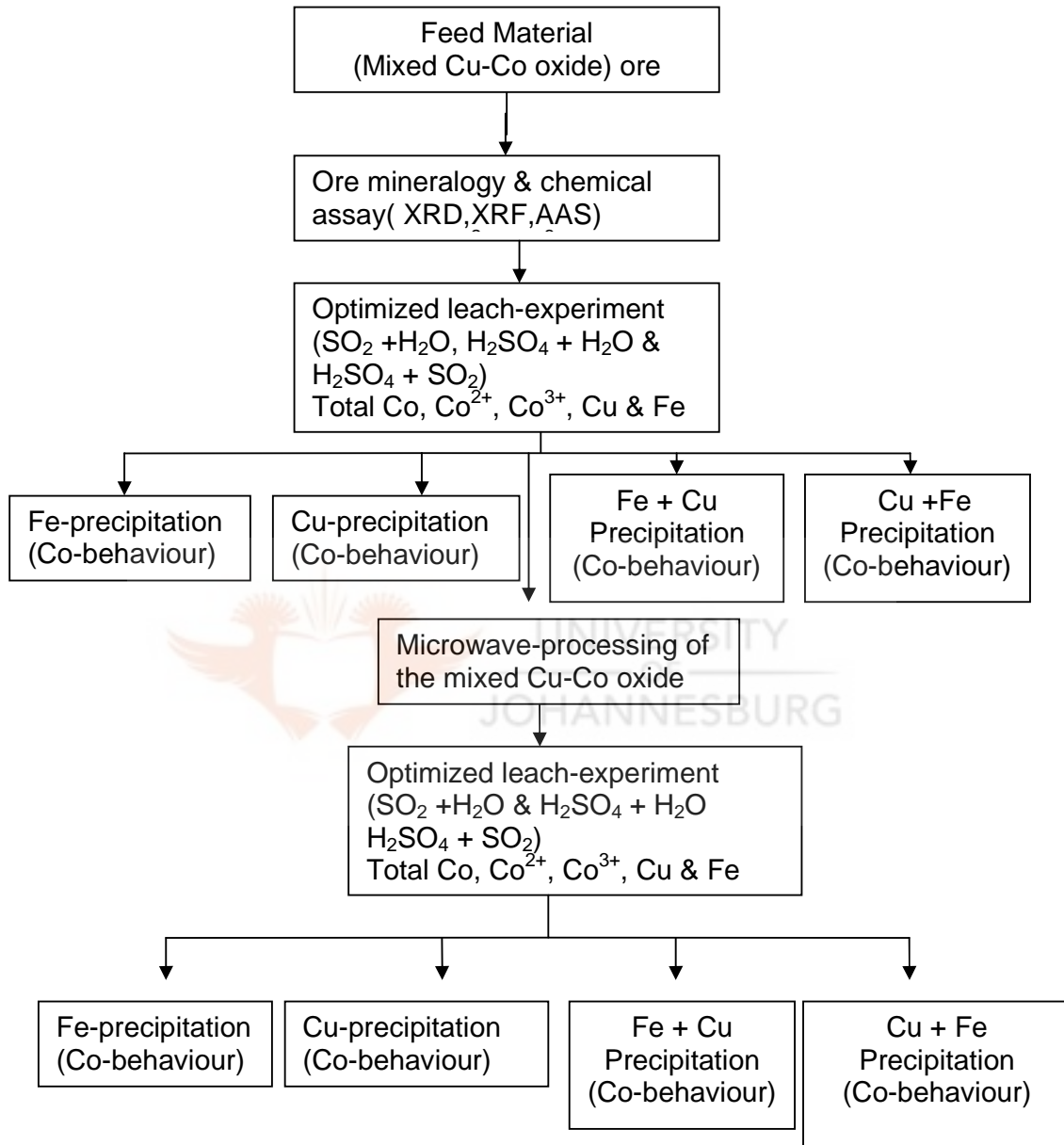
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#### 3.1 Introduction

In this chapter, a detailed exposition of the fundamental concepts and experimental techniques that were used are discussed. Furthermore, this section also expounds on the basic principles and practical applications of instrumental techniques employed. All experiments and instrumental techniques applied in this research project were generic for all four mixed Co-Cu oxidized ores. For example, the methodology for the analysis of low cobalt ore with mica by flame atomic absorption spectroscopy (AAS) was carried out in the same way as the rest of the other ores.



The experimental protocol used to achieve the objectives in **Section 1.4** is outlined in **Scheme 3.1**:



**Scheme 3.1:** The project flow diagram

## **3.2 Chemicals and materials**

All chemicals used in this research project were of reagent grade and were obtained at high purity from suppliers. The four types of mixed Co-Cu oxidized ores used contained cobalt at variable levels and were collected from the earth surface as oxides by small scale entrepreneurs in Katanga Province of the Democratic Republic of Congo (DRC). Unless otherwise stated, all experiments were carried out at room temperature.

## **3.3 General material preparation**

In this section, methods used to mill mixed Co-Cu oxidized ores to particle size of less than 75 $\mu$ m screens are described.

### **3.3.1 Siebtechnik vibratory mill**

This is an equipment mainly used by extraction metallurgists to mill ore materials to their smallest particle size possible at a vibration frequency of 50Hz/cycle. The basic operational principle of this technique is that the characteristics of the ore determine the proper particle size required for extractability of valuable minerals. Owing to the variety of ores used and differences in cobalt grades, the smaller the particle size, the better the extraction efficiency. This technique can be adjusted to mill the ores to any specified particle size required.

#### **3.3.1.1 Milling of ores by the Siebtechnik vibratory mill**

The ore material (200g) was milled using Siebtechnik Vibratory mill for 5 minutes. A size-distribution of the milled material was carried out with screens of size 500, 355, 212, 150, 106 and 75 $\mu$ m. The undersized fractions with the particle size of less than 75 $\mu$ m were collected, split and re-split in ten representative samples each weighing 10g. These were coned and quartered to obtain a reasonable statistical accuracy in a sampling program. The representative material was therefore used in further instrumental analysis and leaching experiments.

### 3.4 General material preparation

Methods that were used for mineralogical studies, chemical assays and leaching of the ores are described in this section.

#### 3.4.1 X-ray Diffraction (XRD) technique

X-ray diffraction (XRD) is one of the most important non-destructive tools to analyse all kinds of matter - ranging from fluids, to powders and crystals. From research to production and engineering, XRD is an indispensable method for material characterization and quality control. Phase identification of minerals in ores by XRD is an established routine method in the mining and mineral processing industry. This technique is only useful whenever the Bragg's law (equation 1) is obeyed:

$$2d \sin \theta = n\lambda \quad (1)$$

Where  $d$  = the interplanar spacing

$\theta$  = the angle between the phases and the x-ray beam

$\lambda$  = x-ray wavelength

$n$  = an integer called the order of reflection

In the XRD technique, X-rays from a copper anode source strike the powder sample. A flat sample is mounted on a turntable around which moves a detector. As the sample rotates, the angle theta ( $\theta$ ) between the incident beam and the sample also changes. Whenever the Bragg condition is fulfilled, X-rays are reflected and diffracted to the detector.<sup>1</sup>To record a diffraction pattern, the detector is positioned at or near zero angle on the graduated  $2\theta$  scale, and driven by a motor at constant speed or step size. The X-rays reaching the detector are registered and displayed on a paper chart recorder as a series of peaks on top of the background due to white radiation. Based on this diffraction pattern, the identification of phases and the phase characterization of multi-component

minerals in ore can be achieved by computer based search-match techniques using recognized software, either in the automatic or the operator-assisted mode.

#### **3.4.1.1 Analysis of the ores by XRD**

The powder sample (10g) was finely ground in an agate mortar prior to analysis by XRD. The fine powder was packed into a steel holder backed by a stainless steel slide and smoothed off by sliding a flat steel slide over the surface. The holder was slightly overfilled and the powder was pressed down using a stainless steel weight. A computer-controlled Phillips Diffractometer, type PW3710, equipped with an automatic divergence slit and a copper anode producing  $\alpha$ -rays of  $\lambda_1 = 1.54060\text{\AA}$  and  $\lambda_2 = 1.54443\text{\AA}$  was then used to analyze the sample. The diffractometer was operating at 40kV and 40mA, and automatic routines allowed absolute scanning for values of  $2\theta$  from  $3^\circ$  to  $80^\circ$ , using a step size of  $0.0170^\circ$  and scan step time of 49.2601s. Identification and attribution of mineral phases in ores was achieved with the aid of Xpert computerized database.

#### **3.4.2 X-ray fluorescence(XRF)**

XRF is an elemental analysis technique with unique capabilities such as highly accurate determinations for major elements and a broad elemental survey of the sample composition without standards. XRF is used in the analysis of rocks and metals with an accuracy of  $\sim 0.1\%$  of the major elements. Detection limits of the XRF technique are generally in the 10 to 100 ppm range for heavy elements, and elements lighter than sodium are difficult or impossible to detect.

There are generally two types of XRF spectrometers - wavelength dispersive and energy dispersive. The wavelength dispersive system uses a diffraction crystal to focus specific wavelengths onto a detector. A wavelength range is scanned by changing the angle in which the X-rays strike the crystal. An energy dispersive spectrometer, on the other hand, focuses all the emitted x-rays onto an energy analyzing detector. While this is faster and less expensive, wavelength dispersive

spectrometers are more sensitive and have a higher resolution. For this reason, a wavelength dispersive system was used in this research project.

In XRF, high energy photons (X-rays) displace inner shell electrons. Outer shell electrons then fall into the vacancy left by the displaced electrons. In doing so, they normally emit light (fluoresce) equivalent to the energy difference between the two states. Since each element has electrons with more or less unique energy levels, the wavelength of light emitted is characteristic of the element. The intensity of light emitted is proportional to the element's concentration.

#### **3.4.2.1 Analysis of the ores by XRF**

The finely ground ore sample (8g) was mixed with an amorphous binder (12g) using a mechanical mixer. The mixture was transferred into an aluminium holder and then pressed into a disc using a hydraulic press. A computer controlled XRF system with a super iq+ database was used to analyze the sample.

#### **3.4.3 Flame- atomic Absorption Spectroscopy(AAS)**

AAS is an analytical technique in which an atomic cloud is produced in the flame and the elements in the cloud are identified by determining the component wavelengths of the absorbed radiation. The concentrations of these elements are therefore determined by measuring their absorbances at the characteristic wavelengths and then comparing them with those of calibration standards of known concentrations. Basically, the operational principle of AAS is such that the required wavelength is selected, and the radiation emitted by the source is detected both in the absence and in the presence of absorbing atoms. The logarithm of the ratio of these intensities (i.e. absorbances) is calculated and related to concentration by means of a standard calibration curve as controlled by Beer-Lambert's law (**Equation 2**).

$$\log [I_0/I_t] = a.l.c = \text{absorbance} \quad (2)$$

a = absorptivity

l = pathlength

c = concentration

$I_0$  = incident intensity

$I_t$  = transmitted intensity

Thus, absorbance is directly proportional to concentration for a given path length at any given wavelength.

#### 3.4.3.1 Chemical assays of ores by AAS

The finely ground ore sample (0.2g) was dissolved in aqua-regia (40ml) and heated on a hot plate for 10 minutes. The resulting solution was cooled and transferred to a 250 ml volumetric flask and diluted to the mark with de-ionized water. Scanning of this solution against calibration standards on the AAS revealed that multiple dilutions were required in order for the unknown concentrations of Co, Cu and Fe to fall within the calibration range, and 10% nitric acid ( $\text{HNO}_3$ ) was used as a diluent for all dilutions. 1% lanthanum nitrate [ $\text{La}(\text{NO}_3)_3$ ] was added in all diluted samples as a releasing agent. The AAS instrument was calibrated with 0, 1, 2, 5, 10 parts per million (ppm) concentrations for Co, Cu, and Fe against which the assays for these metals in the ore were determined.

### 3.4.4 Ultra-Violet Visible spectroscopy(UV/Vis)

UV/Vis spectroscopy is used to determine the absorption or transmission of UV/Vis light (180 to 820 nm) by a sample. It can also be used to measure concentrations of absorbing materials based on developed calibration curves of the material. UV/Vis spectroscopy is widely used as a technique in chemistry, for analysis of chemical structure, most notably conjugated systems. UV radiation is often used in visible spectrophotometry to determine the existence of fluorescence in a given sample.

Solutions of transition metal ions are coloured and therefore absorb visible light. The colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. Samples are charged into a transparent cell, known as a **cuvette**. Cuvettes are usually rectangular in shape, with an internal width of 1 cm. A sample is placed in the UV/Vis beam and a graph of Transmittance or Absorbance versus Wavelength is obtained. Alternatively, samples are prepared in known concentrations and their absorbances are read by the UV/Vis spectrophotometer. Results are then plotted to produce a calibration curve from which the unknown concentration can be determined through its absorbance.

#### 3.4.4.1 Cobalt speciation by UV/Vis spectroscopy

All Ultraviolet (UV/Vis) experiments were performed using a Varian UV/Vis Carry 50 Spectrophotometer at normal room temperature and all samples were measured using a 10mm quartz cuvette cell. The UV/Vis experiments were carried out to monitor the levels of  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  in the ore prior to leaching and in residues after the leaching of mixed Co-Cu oxidized ores. In a typical experiment, a finely ground ore or residue sample (0.2g) with a particle size of less than  $75 \mu\text{m}$  was dissolved in aqua-regia (40ml) and heated on a hot plate for 10 minutes. The resulting solution was cooled and transferred to a 250 ml volumetric flask. A solution of 2M Ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ) was then added as a diluent and a chromogenic (colour forming) reagent in order to convert cobalt species to

complex forms which can readily absorb the visible light. Aliquots of this solution were immediately scanned on a Varian UV/Vis Carry 50 spectrophotometer for qualitative purposes. The absorbances of both  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  were collected between 190 to 900 nm and plotted against absorption wavelengths. For quantitative purposes, standard samples of concentrations 0, 20, 40, 60, 80 and 100 ppm were prepared for both  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  and measurements were made at 425nm for  $\text{Co}^{3+}$  and 625nm for  $\text{Co}^{2+}$  using the UV/Vis Spectrophotometer. The absorbances obtained were then plotted to produce calibration curves for both  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  from which the unknown concentration of cobalt species in ores and residues could be determined by their absorbances.

### 3.4.5 Leaching of mixed Co-Cu oxidized ores

Leaching generally refers to the removal of a substance from a solid *via* a liquid extraction medium. The desired component to be extracted diffuses into the solvent from its natural solid form, for example, the removal of nickel salts or gold from their natural solid beds with sulphuric acid solutions. There are many different types of equipment used for leaching. Most of these pieces of equipment fall into one of two categories mentioned below:

#### (i) Percolation – Liquid Added to Solids (LAS)

The solvent is brought into contact with the solids in a continuous or batch method. This method is popular with in-place ore leaching or large scale heap leaching.

#### (ii) Dispersed solids – Solids Added to Liquid (SAL)

Here the solids are usually crushed into small pieces before being brought into contact with solvents. This is a popular leaching method especially when a high recovery rate can economically justify higher operating costs, for example, in gold extraction.



Whether the leaching is taking place *via* percolation or by dispersed-solids, there are three important factors that aid in leaching. These are temperature, contact time/area, and solvent selection. The temperature is adjusted to optimize solubility and mass transfer. Liquid-to-solid contact is essential for the extraction to take place and maximize contact area per unit volume. Solvent selection plays an important role in solubilities as well as in the separation steps that follow leaching. Nearly all leaching equipments employ some type of agitation to aid in mass transfer while also ensuring proper mixing.

#### 3.4.5.1 Leaching experiments

The main apparatus for the experiment consisted of a glass beaker (500 cm<sup>3</sup>), magnetic stirrer, and a pH/Eh meter. Buffer solutions of pH 4 and pH 7 were used to calibrate the pH probe. The ore sample (20g) with the particle size distribution of less than 75 μm was poured into a glass beaker (500 cm<sup>3</sup>) that was charged with H<sub>2</sub>SO<sub>4</sub> (400 cm<sup>3</sup>, 0.5 M). SO<sub>2</sub> gas was flushed at a rate of 50cm<sup>3</sup>/min and was monitored with the help of calibrated bubble flow meters. The residence time for all experiments was 2 hours. The magnetic stirrer was set at 300rpm. Samples were collected at 30min time intervals and analyzed for cobalt, copper, and iron by flame-AAS. Cobalt speciation by UV/Visible spectroscopy was only carried out on the final leach liquor.

#### 3.4.6 Separation of iron and copper from cobalt leach solution

Iron and copper were precipitated out of the cobalt leach solution as hydroxides by means of pH control with sodium hydroxide (NaOH). Precipitation of iron was carried out in two stages: (i) Oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and (ii) precipitation Fe<sup>3+</sup> as Fe(OH)<sub>3(s)</sub>. H<sub>2</sub>O<sub>2</sub> (5ml) was added to the leach solution (100ml) and stirred slowly with a magnetic stirrer. Drops of NaOH (5M) were added slowly to raise the pH from pH 1 to pH 4 while stirring. For the precipitation of copper as Cu(OH)<sub>2(s)</sub>, the pH was controlled from pH 4.5 to pH 6.

### 3.4.7 Microwave treatment of ores prior to leaching

Microwave heating is a process within the family of electro-heating techniques, such as induction, radio frequency, direct resistance, and infrared heating which utilize specific parts of electromagnetic energy.<sup>3</sup> The most commonly used frequencies for heating purposes are 915 MHz and 2.45 GHz, which correspond to wavelengths of 33.5cm and 12.2cm, respectively. Microwave heating of dielectric materials lies in the ability of the electric field to polarize the charge of the material where polarization cannot follow the rapid change of the electric field.

When applying microwave radiation to the material, the electric and magnetic components change rapidly ( $2.4 \times 10^9$  per second at a frequency of 2.45 GHz) and the molecules cannot respond quickly to the change in direction, giving rise to friction and causing them to warm up.<sup>2</sup> This internal heating together with differential effects mechanically agitate or rupture the surface layers of the dielectric material sample and in doing so expose new surfaces to the acid. Unique microwave heating characteristics are the main drivers for the potential implementation in metal extraction.<sup>3</sup> This include low processing time, direct heating, selective and volumetric heating and a more controllable heating process.

#### 3.4.7.1 Microwave treatment and leaching of cobalt bearing ores

The LG-MS-283MC domestic microwave with 900 watts (W) output power was used for heating the cobalt-bearing ores at 2.45GHz radiation frequency. A portable Infrared Thermometer Minity 100 with an input range of -32 °C to 500°C was used to measure the temperature of the irradiated sample. A 100ml beaker was used to contain 20g of the ore material to be irradiated. The exposure time of the ore to microwaves was 30 minutes and leaching experiments were performed on the irradiated ore. The leaching experimental conditions remained the same as indicated in **Section 3.4.5.1**.

### 3.5 References

1. Whiston C., (1987), X-Ray Methods, UK, John Wiley and Sons, pp 45-66
2. Al-Harahsheh, M., Kingman, S.W., (2004), Microwave Assisted Leaching- A review, Hydrometallurgy, 73 (3-4), pp 189-203.
3. Galema, S.A., (1997), Microwave Chemistry. Chemistry Society Reviews 26, pp 233-238



## CHAPTER 4

### RESULTS AND DISCUSSIONS

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#### 4.1 Introduction

The aim of this chapter is to present the results obtained and to discuss the findings of the entire research study. The results obtained are reported according to the experimental protocol given in Chapter 3 (**Scheme 3.1**). Four mixed Co-Cu oxidized ores, namely: high cobalt ore, high copper ore, low cobalt ore (with mica) and low cobalt ore (without mica) were investigated. The mineralogical composition of each ore was studied first by means of X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and Atomic Absorption Spectroscopy (AAS). The dissolution or leaching process was optimized to achieve the best dissolution conditions for cobalt and copper from mixed Co-Cu oxidised ores.

The results obtained from the dissolution process include the dissolution behaviour of cobalt from each ore and the chemistry involved. Furthermore, Ultra-Violet Visible spectroscopy (UV/Vis) was used to monitor such cobalt behaviour during the dissolution process. The effect of the presence of copper and iron during the dissolution of cobalt was also studied using precipitation methods. The mixed Co-Cu oxidized ores were also subjected to microwave radiation and the dissolution process repeated for the microwave irradiated ores.

#### 4.2 Milling of ores

The ore particle size of less than 75  $\mu\text{m}$  was achieved during milling since all four mixed Co-Cu oxidised ores contained cobalt at variable concentrations. This particle size was necessary for the mineralogical studies of cobalt bearing minerals by XRD<sup>1</sup> and the leaching process.

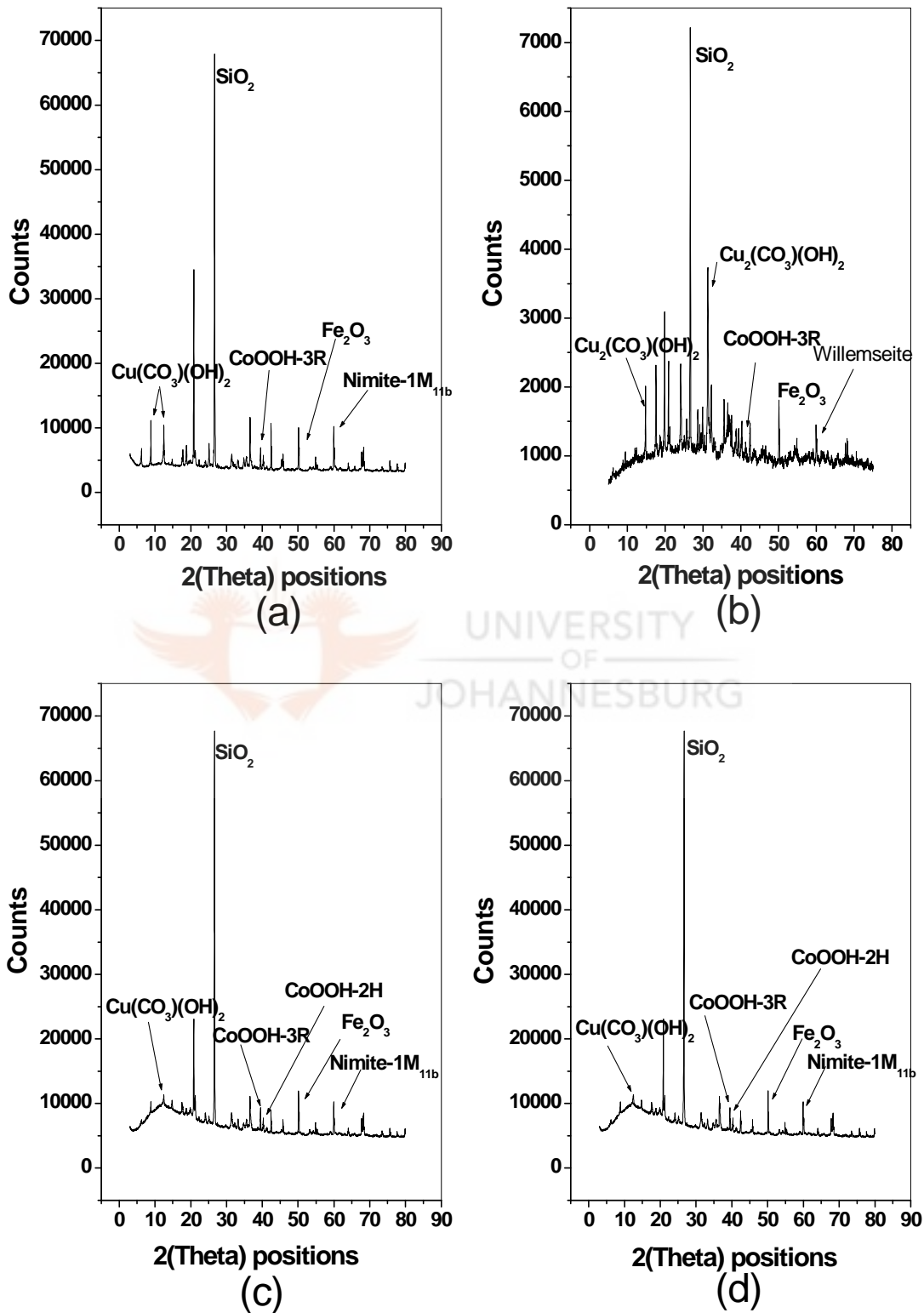
### 4.3 Mineralogical studies

The mineralogical investigations of the mixed Co-Cu oxidised ores used in this project were carried out by XRD, XRF and AAS. While XRD was used for identifying the mineral phases present in mixed Co-Cu oxidised ores, XRF and AAS were used for the quantitative determination of elements present in these ores. The results obtained for the mineralogical studies are discussed in the following sections:

#### 4.3.1 Analysis of mixed Co-Cu oxidised ores by XRD

The XRD diffraction patterns shown in **Figure 4.1** were obtained for the analysis of the high cobalt ore – **Figure 4.1(a)**, high copper ore – **Figure 4.1(b)**, low cobalt ore (with mica) – **Figure 4.1(c)** and low cobalt ore (without mica) – **Figure 4.1(d)**. Since the levels of sulphur content in these ores were not analysed, it was assumed that the mixed Co-Cu ores were completely oxidised. The attribution of mineral phases as shown in **Figure 4.1** was achieved by comparing principal peak intensities with reference to XRD cards. Results of the most intense values are shown in appendix 1 with the specific powder diffraction file (PDF) number for each mineral identified and only the mineral phases which had the highest score were considered (**Table 4.1**).

Heterogenite ( $\text{CoOOH}$ ), Malachite ( $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ ) and Limonite ( $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) were identified as common phases in all four mixed Co-Cu oxidised ores. Nimite-1M<sub>11b</sub> [ $(\text{Ni},\text{Mg},\text{Al})_6(\text{Si},\text{Al})_6\text{O}_{10}(\text{OH})_8$ ] and Willemseite [ $(\text{Ni},\text{Mg})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ] were also identified as prominent minerals which contained nickel. In addition, two forms of heterogenite mineral were identified in the low cobalt ores, that is, heterogenite-2H ( $\text{CoOOH}\cdot 2\text{H}$ ) and heterogenite-3R ( $\text{CoOOH}\cdot 3\text{R}$ ). As a general comment, it was noted that XRD failed to detect any  $\text{Co}^{2+}$  bearing minerals in all four mixed Co-Cu oxidised ores investigated. While reasons for this failure are not fully known, it is suspected that this could be caused by the low detection limit (3%) of the XRD instrument used in this study.



**Figure 4.1:** Diffraction patterns; (a) The high cobalt ore, (b) The high copper ore, (c) The low cobalt ore(with mica) and (d) The low cobalt ore without mica

The results shown in **Table 4.1** summarises mineral phases derived from the mineralogical studies of all four mixed Co-Cu oxidised ores by XRD. The percentage (%) match score or percentage modal in **Table 4.1** refers to the relative match factor with the data given in XRD mineral powder diffraction file. As can be noted in **Table 4.1**, the ratio of silica ( $\text{SiO}_2$ ) to iron (Fe) content is high in all four ores. Willemseite was identified as a nickel containing mineral in the high copper ore instead of nimite which appears to be common in the other three ores. It can also be noted that the minerals identified for the low cobalt ores with and without mica are identical in all proportions. This means that the presence of mica in the low cobalt ore does not affect the crystal structure of minerals in the ore. It was yet to be ascertained whether the presence of mica had any effect on the leaching efficiency of cobalt from the low cobalt bearing ores.

**Table 4.1: Identification of mineral phases in mixed Co-Cu ores using XRD**

HIGH COBALT ORE		HIGH COPPER ORE	
Mineral phase	% match score	Mineral phase	% match score
$\text{SiO}_2$	64	$\text{SiO}_2$	76
$\text{CoOOH-3R}$	22	$\text{CoOOH-3R}$	11
$\text{Cu}_2(\text{CO}_3)\text{OH}_2$	17	$\text{Cu}_2(\text{CO}_3)\text{OH}_2$	41
$\text{Fe}_2\text{O}_3$	13	$\text{Fe}_2\text{O}_3$	23
Nimite-1M <sub>11b</sub>	10	Willemseite	10
LOW COBALT ORE WITH MICA		LOW COBALT ORE WITHOUT MICA	
Mineral phase	% match score	Mineral phase	% match score
$\text{SiO}_2$	56	$\text{SiO}_2$	59
$\text{CoOOH-2H}$	5	$\text{CoOOH-2H}$	4
$\text{CoOOH-3R}$	11	$\text{CoOOH-3R}$	8
$\text{Cu}_2(\text{CO}_3)\text{OH}_2$	19	$\text{Cu}_2(\text{CO}_3)\text{OH}_2$	16
$\text{Fe}_2\text{O}_3$	12	$\text{Fe}_2\text{O}_3$	11
Nimite-1M <sub>11b</sub>	11	Nimite-1M <sub>11b</sub>	10

### 4.3.2 Analysis of mixed Co-Cu oxidised ores by XRF

The XRF results shown in **Table 4.2** reveal a variety of oxide forms following the assumption that the mixed Co-Cu ores were fully oxidised. The amount of cobalt as  $\text{Co}_3\text{O}_4$  is 45.7% in the high cobalt ore – hence the name high cobalt ore. The amount of copper as  $\text{CuO}$  was found to be 41.5% – hence the name high copper ore. The quantities of cobalt as  $\text{Co}_3\text{O}_4$  in the low cobalt ores, with and without mica, were found to be 5.37% and 2.88%, respectively – hence the names low cobalt bearing ores. In all these ores there is substantial amounts of  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  with low percentage quantities of  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MnO}$  and  $\text{NiO}$ . The mineral  $\text{Co}_3\text{O}_4$  contains cobalt in two oxidation states,  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$ . This mineral can also be written as  $\text{CoO} \cdot \text{Co}_2\text{O}_3$  which shows  $\text{CoO}$  as the  $\text{Co}^{2+}$  and  $\text{Co}_2\text{O}_3$  as the  $\text{Co}^{3+}$  bearing parts of the mineral.

**Table 4.2: Quantification analysis of mixed Co-Cu ores using XRF**

HIGH COBALT ORE		HIGH COPPER ORE	
Compound name	% in ore	Compound name	% in ore
$\text{SiO}_2$	25.3	$\text{SiO}_2$	26.3
$\text{Co}_3\text{O}_4$	45.7	$\text{Co}_3\text{O}_4$	0.68
$\text{CuO}$	18.6	$\text{CuO}$	41.5
$\text{Fe}_2\text{O}_3$	7.14	$\text{Fe}_2\text{O}_3$	8.42
$\text{MgO}$	0.03	$\text{MgO}$	0.07
$\text{Al}_2\text{O}_3$	0.04	$\text{Al}_2\text{O}_3$	0.05
$\text{MnO}$	0.06	$\text{MnO}$	0.04
$\text{NiO}$	0.02	$\text{NiO}$	0.01
LOW COBALT ORE WITH MICA		LOW COBALT ORE WITHOUT MICA	
Compound name	% in ore	Compound name	% in ore
$\text{SiO}_2$	49.6	$\text{SiO}_2$	47.8
$\text{Co}_3\text{O}_4$	5.37	$\text{Co}_3\text{O}_4$	2.88
$\text{CuO}$	8.21	$\text{CuO}$	5.19
$\text{Fe}_2\text{O}_3$	14.8	$\text{Fe}_2\text{O}_3$	10.1
$\text{MgO}$	3.62	$\text{MgO}$	2.38
$\text{Al}_2\text{O}_3$	8.00	$\text{Al}_2\text{O}_3$	6.13
$\text{MnO}$	0.18	$\text{MnO}$	0.09
$\text{NiO}$	0.04	$\text{NiO}$	0.05



### 4.3.3 Analysis of mixed Co-Cu oxidised ores by AAS

The results for the elemental composition of mixed Co-Cu oxidised ores as determined by flame AAS are shown in **Table 4.3**. The AAS analysis revealed that the high cobalt ore contained 34.2% Co, 14.1% Cu and 5.13% Fe. The high copper ore contained 0.5% Co, 31.5% Cu and 6% Fe. The Co, Cu and Fe contents in the low cobalt ore with mica were found to be 3.96%, 6.45% and 10.6%, respectively, whereas the low cobalt without mica contained 2.81% Co, 4.14% Cu and 7.24% Fe. In short, the entire study involves the investigation of mixed Co-Cu oxidised ores containing cobalt as traces amounts (i.e. high copper ore), moderate cobalt contents (i.e. low cobalt ores, with and without mica) and substantially higher cobalt content (i.e. high cobalt ore). Therefore the results in **Table 4.3** imply that the entire study covers a wide range of cobalt contents in ores. Furthermore, the leaching behaviour of cobalt observed is not only restricted to ores investigated in this study but could be relevant to any other ore bearing cobalt within the range of 0.5% to 35% cobalt content.

**Table 4.3: Quantification analysis of mixed Co-Cu ores using flame-AAS**

HIGH COBALT ORE		HIGH COPPER ORE	
Element	% in ore	Element	% in ore
Co	34.2	Co	0.50
Cu	14.1	Cu	31.5
Fe	5.13	Fe	6.00
LOW COBALT ORE WITH MICA		LOW COBALT ORE WITHOUT MICA	
Element	% in ore	Element	% in ore
Co	3.96	Co	2.81
Cu	6.45	Cu	4.14
Fe	10.6	Fe	7.24

#### 4.4 The leaching process

A series of leaching experiments was carried out to investigate the behaviour of cobalt dissolution from mixed Co-Cu oxidised ores. Aqueous solutions of sulphuric acid ( $\text{H}_2\text{SO}_4$ ), sulphurous acid ( $\text{H}_2\text{SO}_3$ ), sulphur dioxide ( $\text{SO}_2+\text{H}_2\text{O}$ ) and admixtures of  $\text{SO}_2 + \text{H}_2\text{SO}_4$  were used as leaching reagents. Four mixed Co-Cu oxidised ores containing cobalt at different levels were used, namely: High cobalt ore (34.2%Co), High copper ore (0.499%Co), Low cobalt ore with mica (3.963%Co) and Low cobalt ore without mica (2.806%Co). It was observed that the use of different leaching reagents to dissolve cobalt from these ores resulted in various cobalt yields in the solution. High cobalt yields were obtained when admixtures of  $\text{SO}_2 + \text{H}_2\text{SO}_4$  were used as a leaching solution, whereas low cobalt yields were achieved when aqueous  $\text{H}_2\text{SO}_4$  was used as the only leaching solution. The results for these findings are shown in **Figure 4.2**.

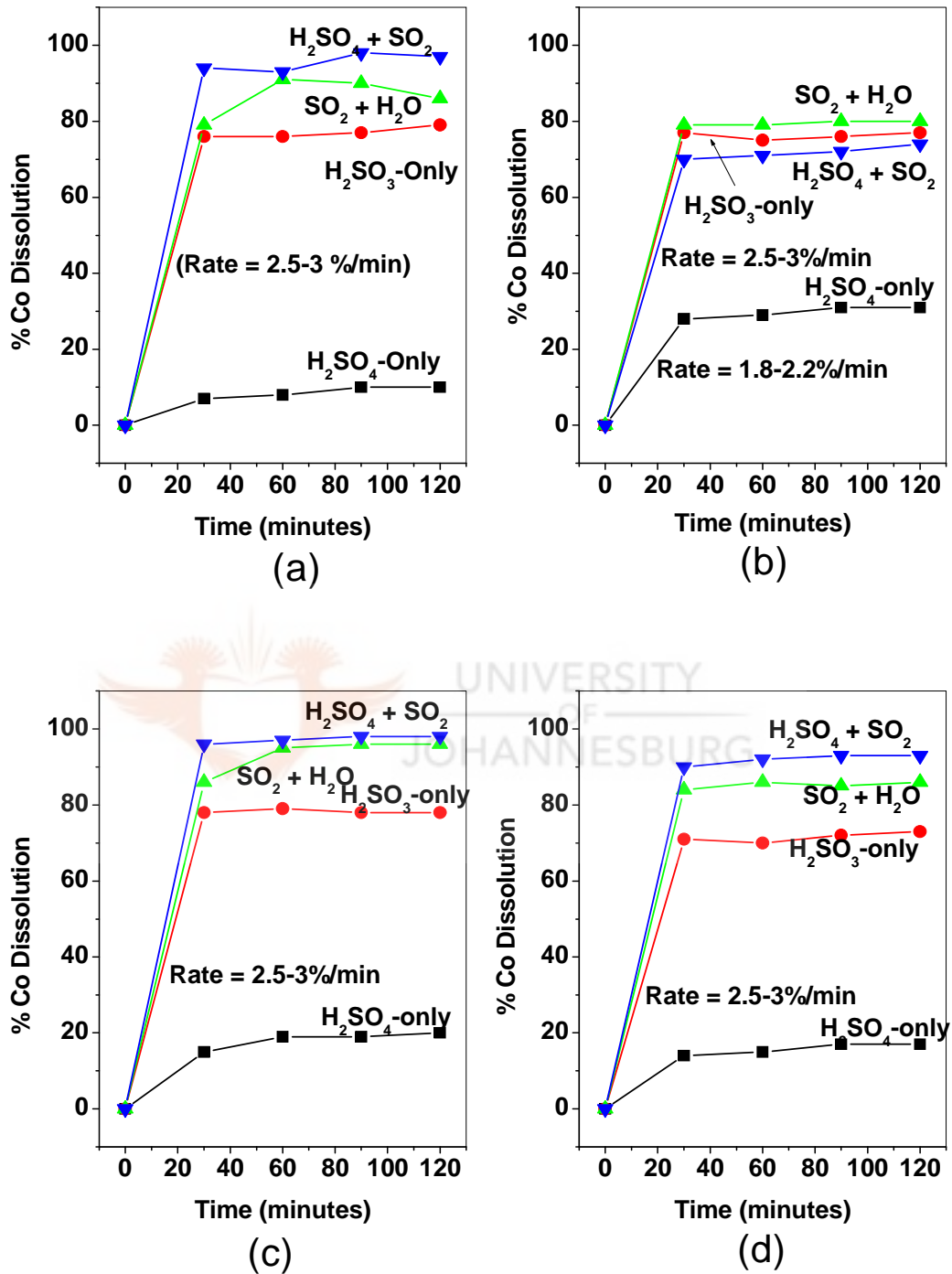
Leaching reactions are generally a combination of chemical reaction control and diffusion control. While the exposed surface of the mineral is attacked quickly and vigorously, time is required to penetrate cracks, crevices or porous minerals to achieve the maximum desired extraction. The percentage cobalt dissolution (%Co dissolution) achieved during the leaching process is plotted against the leaching time (minutes) as shown in **Figure 4.2**. Percentage cobalt dissolutions were calculated with respect to the cobalt content in ores, that is, %Co in leach solution divided by %Co in ore multiplied by hundred. The results obtained for the leaching behaviour of cobalt per ore are all shown in **Figure 4.2**. While **Figure 4.2(a)** represents the leaching behaviour of cobalt from the high cobalt ore and **Figure 4.2(b)** show the leaching behaviour of cobalt from the high copper ore, **Figure 4.2(c)** and **Figure 4.2(d)** represents the leaching behaviour of cobalt from the low cobalt ore with mica and low cobalt ore without mica, respectively.

#### 4.4.1 The leaching behaviour of cobalt from mixed Co-Cu oxidised ores

It can be noted that in **Figure 4.2(a)** that the rate of cobalt dissolution from the high cobalt ore initially accelerated and reached a plateau after 30 minutes of leaching time. Beyond 30 minutes of leaching time, the leaching rate became progressively slower until the reaction reached equilibrium. This trend was observed for leaching reagents  $\text{H}_2\text{SO}_4 + \text{SO}_2$ ,  $\text{H}_2\text{SO}_3$  and  $\text{SO}_2 + \text{H}_2\text{O}$  achieving yields as high as 80% to 98% cobalt dissolutions, while with the use of aqueous  $\text{H}_2\text{SO}_4$  as the leaching reagent, only 10% Co dissolution was achieved. In general, it can also be inferred in **Figure 4.2** that the extent of % Co dissolution is high when admixtures of  $\text{H}_2\text{SO}_4 + \text{SO}_2$  are used as leach media, instead of aqueous  $\text{H}_2\text{SO}_4$  alone. This is in line with the findings made by Mwema *et al.*<sup>2</sup>

The extent of % Co dissolution with respect to the high copper ore as shown in **Figure 4.2(b)** was found to be generally lower than in **Figure 4.2(a)** reaching a maximum of 80% Co dissolutions. Reasons for this trend have been attributed to the difference in ore matrices of both the high cobalt and high copper ores. In comparison, it was observed that the leaching behaviour of cobalt from the high copper ore (0.499%Co) followed similar leaching trends as observed in the high cobalt ore (34.2%Co) but at a slower leaching rate. In other words, more time is required to leach cobalt from a low cobalt bearing ore (i.e. high copper ore) than leaching cobalt from a high cobalt bearing ore (i.e. high cobalt ore).

The kinetic curves shown in **Figure 4.2(c)** and **Figure 4.2(d)** also show an elevated initial rate of cobalt leaching within the first 30 minutes which levels out beyond 30 minutes of leaching time. It was also noted that maximum %Co dissolutions from the low cobalt ore with mica (3.963% Co) and low cobalt ore without mica (2.806% Co) were achieved in admixtures of two acids. The results obtained for leaching cobalt from both the low cobalt bearing ores were similar, indicating that the presence of mica did not affect the leaching efficiency of Co since the dissolution remained as efficient in both cases. In general, high cobalt yields were achieved when admixtures of  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  were used as leaching reagents.



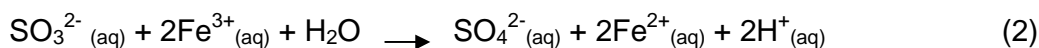
**Figure 4.2:** Leaching behaviour of cobalt; (a) High cobalt ore, (b) High copper ore (c) Low cobalt ore with mica and (d) Low cobalt ore without mica

#### 4.4.2 The chemistry of cobalt during the leaching process

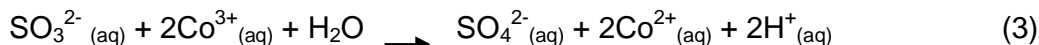
Given the trends in **Figure 4.2**, there was a need to elucidate and understand the role of  $\text{SO}_2$  in leaching cobalt from mixed Co-Cu oxide ores.  $\text{SO}_2$  is the anhydride of sulphurous acid:



The sulphurous acid produced by reaction 1 is unstable with the reverse reaction more favoured. The corresponding anions are bisulphite,  $\text{HSO}_3^-$ , and sulphite,  $\text{SO}_3^{2-}$ . Sulphur dioxide can behave as either a reducing agent or as an oxidizing agent, although the former is its more usual role:

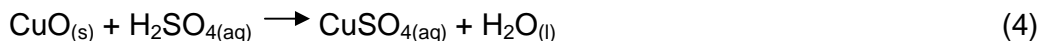


The role of the sulphite ion,  $\text{SO}_3^{2-}{}_{(aq)}$  in reaction 2 is that of a reducing agent. It reduces ferric ion,  $\text{Fe}^{3+}$ , to ferrous ion,  $\text{Fe}^{2+}$ . This reduction potential of  $\text{SO}_2$  was applied during the leaching of mixed Co-Cu oxidised ores which bear cobalt mainly as  $\text{Co}^{3+}$  ( $\text{CoOOH}$ ) as evidenced by the mineralogical studies.  $\text{SO}_3^{2-}$  (formed as shown in reaction 1) reduces  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  as shown in reaction 3:

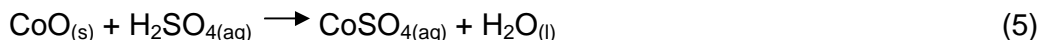


In contrast, sulphuric acid,  $\text{H}_2\text{SO}_{4(aq)}$ , is diprotic; the first dissociation is strong, the second moderately strong ( $K_2 = 1.1 \times 10^{-2}$ ). The sulphate anion,  $\text{SO}_4^{2-}$ , has a tetrahedral geometry. The S–O bond length is  $1.51\text{\AA}$ , which is quite small compared with the value predicted from the sum of the sulphur and oxygen single – bonded radii ( $1.70\text{\AA}$ ). This indicates that the bond in  $\text{SO}_4^{2-}$  has a substantial double bond character. Double bonds can form by the overlapping 2p orbitals on the oxygen atoms with the 3d orbitals on the sulphur atom. Therefore, not only is sulphuric acid a powerful dehydrating agent, but also a very strong oxidising agent.

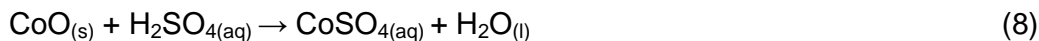
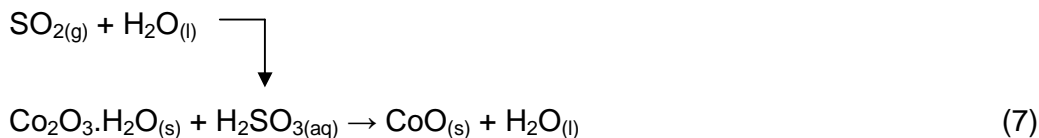
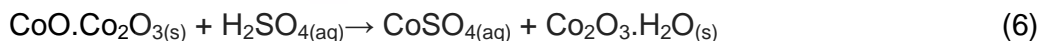
In reaction 4, copper is oxidised from  $\text{Cu}^0$  to  $\text{Cu}^{2+}$  by sulphuric acid,  $\text{H}_2\text{SO}_4$ :



In the same manner, cobalt in  $\text{CoO}_{(s)}$  can be oxidised from  $\text{Co}^0$  to  $\text{Cu}^{2+}$  by  $\text{H}_2\text{SO}_4$  as shown in reaction 5:



In view of the above, the leaching pathways in reactions 6 to 8 show the dissolution behaviour of cobalt from mixed Co-Cu oxidised ores from a chemistry perspective. These mechanistic pathways elucidate the interaction of  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  during the leaching process. As indicated in the mineralogical studies of mixed Co-Cu oxidised ores, the mineral  $\text{Co}_3\text{O}_4$  can also be written as  $\text{CoO} \cdot \text{Co}_2\text{O}_3$  which clearly denotes  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  forms, that is,  $\text{CoO}$  bears  $\text{Co}^{2+}$  and  $\text{Co}_2\text{O}_3$  bears  $\text{Co}^{3+}$ . Since it was generally observed that  $\text{Co}^{3+}$  bearing minerals are not directly soluble in acid, dissolution of cobalt from  $\text{Co}_3\text{O}_4$  mineral is shown in the reaction schemes below:



Reaction 6 illustrates the dissolution of Co from  $\text{CoO} \cdot \text{Co}_2\text{O}_3$  and one of the products is  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$  which is simply a hydrated form of  $\text{Co}_2\text{O}_3$ . It can be noted that  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$  bears Co as  $\text{Co}^{3+}$  in reaction 6 and thus most of the cobalt recovered as  $\text{CoSO}_4$  in reaction 6 comes from  $\text{CoO}$ . Reaction 7 illustrates a situation whereby  $\text{SO}_2$  also forms part of the leaching solution, that is, reaction 7 is a continuation of reaction 6 and here  $\text{SO}_2$  is flushed into the acidified cobalt leaching solution. As can be noted in reaction 7,  $\text{H}_2\text{SO}_3$  reduces  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$

(product from reaction 6) to CoO which is directly soluble in H<sub>2</sub>SO<sub>4</sub>. Reaction 8 illustrates how easily the dissolution of Co from CoO can be and how crucial it is to incorporate a reduction step (SO<sub>2</sub>) during the leaching of mixed Co-Cu oxidised ores.

In view of the above, a substantial improvement in cobalt yields observed during the leaching of mixed Co-Cu oxidised ores in admixtures of SO<sub>2</sub> can be attributed to the reduction of Co<sup>3+</sup> to Co<sup>2+</sup>. This reduction was further confirmed by the UV/Visible spectroscopy technique. Compounds analyzed by this technique must absorb UV-light and have chromophores (covalently bonded but unsaturated groups such as NO<sub>2</sub>, SCN, C=C and C=O) that absorb electromagnetic radiation in the ultraviolet and visible regions of the spectrum. Thiocyno-complexes of Co<sup>3+</sup> and Co<sup>2+</sup> have characteristic yellow and blue colours, respectively, that absorb electromagnetic radiation in the visible range. It was possible therefore to monitor the levels of Co<sup>3+</sup> and Co<sup>2+</sup> both in ores and residues during SO<sub>2</sub> treatment of mixed Co-Cu oxide ores using this technique.

#### 4.4.3 UV/Vis spectra of Co<sup>2+</sup> and Co<sup>3+</sup> during the leaching of cobalt

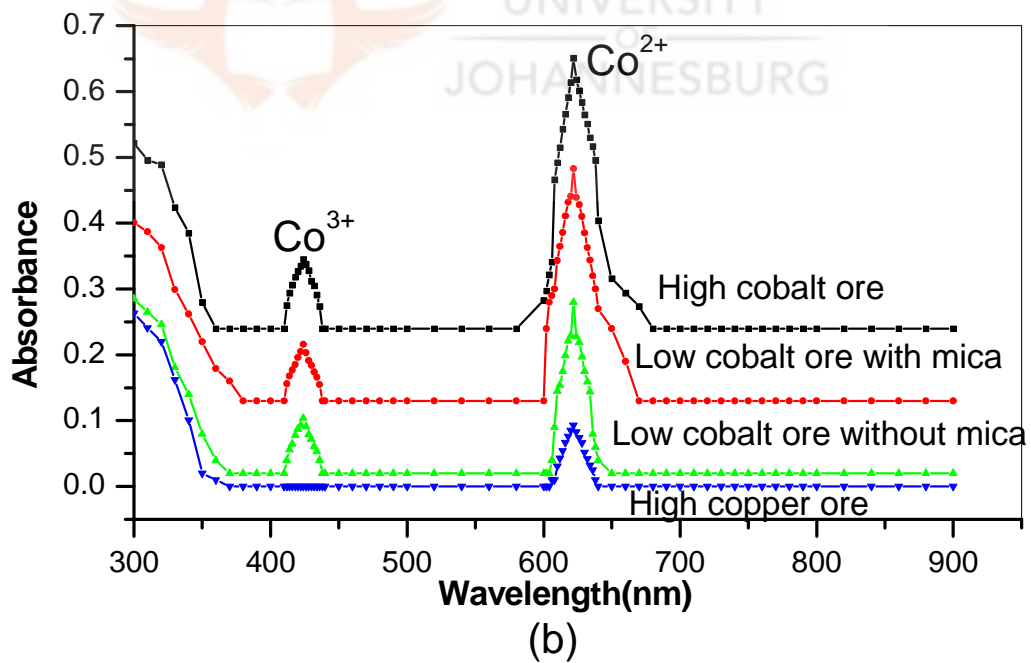
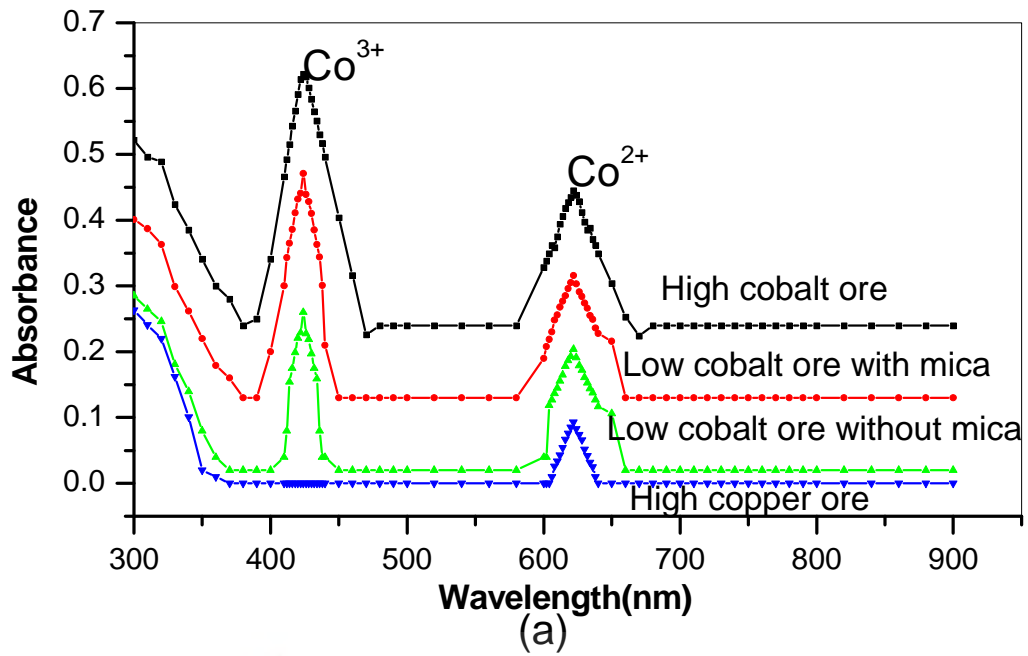
In order to underpin and confirm the reduction of Co<sup>3+</sup> to Co<sup>2+</sup> minerals as SO<sub>2</sub> is flushed into the acidified leaching medium during the leaching process, the concentrations of Co<sup>3+</sup> and Co<sup>2+</sup> in ores before SO<sub>2</sub> treatment were determined by UV/Vis spectroscopy. Absorbance of both Co<sup>3+</sup> and Co<sup>2+</sup> were plotted against wavelengths of Co<sup>3+</sup> and Co<sup>2+</sup>. The results for the levels of Co<sup>3+</sup> and Co<sup>2+</sup> before SO<sub>2</sub> treatment are shown in **Figure 4.3(a)**.

The mixed Co-Cu oxidised ores were therefore leached in aqueous H<sub>2</sub>SO<sub>4</sub> while SO<sub>2</sub> was being flushed into the leaching system. The leaching process was allowed to take place for 30 minutes and then stopped. The mixture was then filtered off and the residue analysed for the concentrations of Co<sup>3+</sup> and Co<sup>2+</sup> by UV/Vis spectroscopy. The absorbances of both Co<sup>3+</sup> and Co<sup>2+</sup> were again plotted against their respective absorption wavelengths and this plot is labelled as "After SO<sub>2</sub> treatment" in **Figure 4.3(b)**.

It can be seen in **Figure 4.3(a)** that before  $\text{SO}_2$  treatment, the concentration of  $\text{Co}^{3+}$  is greater than the concentration of  $\text{Co}^{2+}$  in ores. After  $\text{SO}_2$  treatment, **Figure 4.3(b)**, the concentration of  $\text{Co}^{2+}$  in the residue is greater than the concentration of  $\text{Co}^{3+}$ . in all ores with the exception of the high Cu bearing ore. Given this trend, the role of  $\text{SO}_2$  in reducing  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  minerals with subsequent improvement in the solution-based recovery of Co was clarified. The reasoning behind the stable trend in the  $\text{Co}^{2+}$  observed with the high copper ore is not understood.





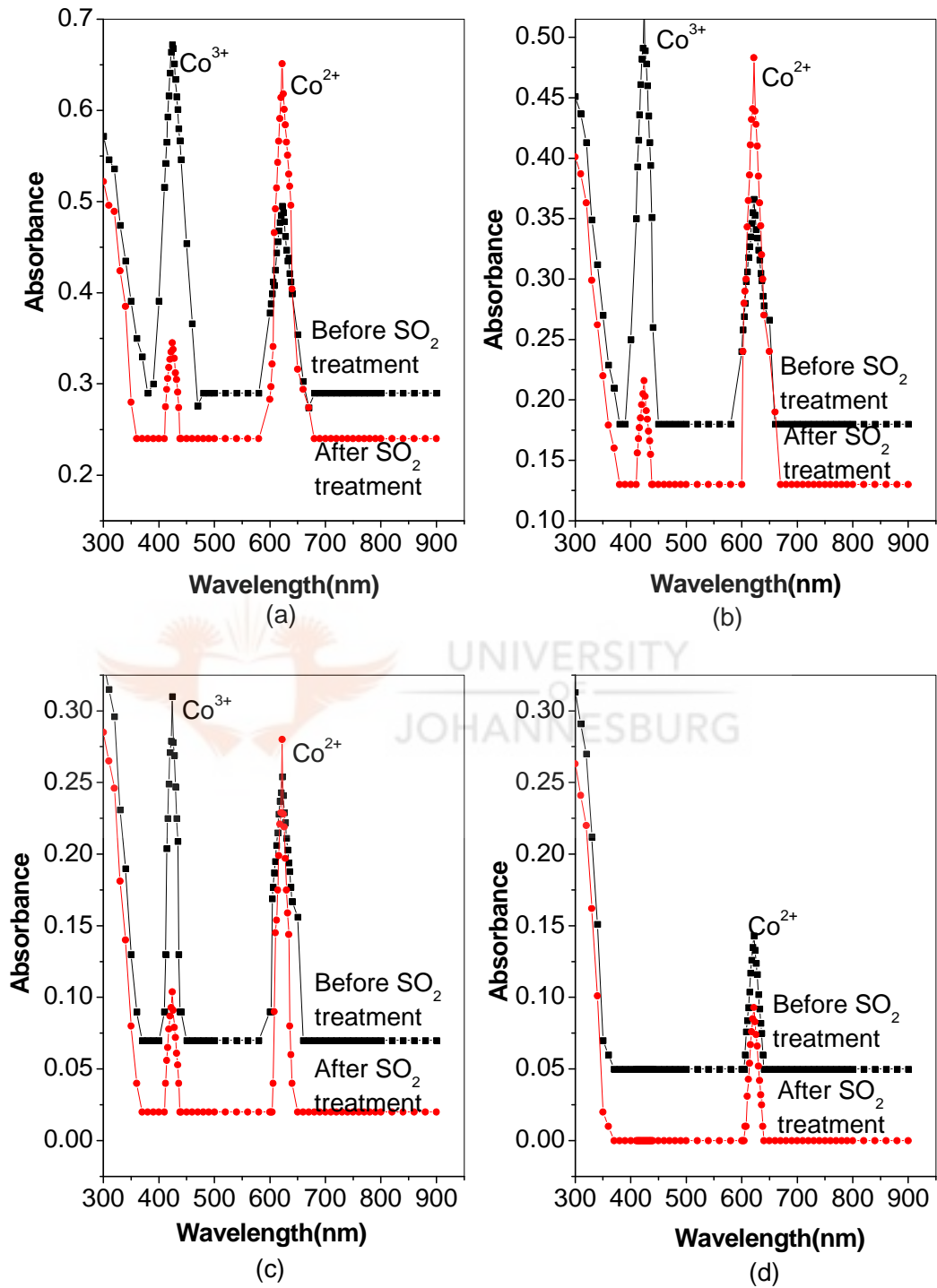


**Figure 4.3:** UV/Vis Spectra for samples; (a) Before  $\text{SO}_2$  treatment, (b) After  $\text{SO}_2$  treatment

While **Figure 4.3** illustrates the trend observed in all the samples, **Figure 4.4** illustrates the individual behaviour of  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  in the individual ores before and after  $\text{SO}_2$  treatment. The red coloured plots indicate the behaviour of  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  after  $\text{SO}_2$  treatment. The black coloured plots shown in **Figure 4.4**, illustrate the behaviour of  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  before  $\text{SO}_2$  treatment.

It can also be noted in **Figure 4.4(a)** that the absorbance of  $\text{Co}^{3+}$  before  $\text{SO}_2$  treatment in the high cobalt ore is high compared with the absorbance of  $\text{Co}^{2+}$  - the black coloured plot. The reverse trend is observed after leaching the high cobalt ore in the presence of  $\text{SO}_2$ . Here the absorbance of  $\text{Co}^{3+}$  is smaller than that of  $\text{Co}^{2+}$ . Similar trends are observed in the case of low cobalt ores, with and without mica, in **Figure 4.4(b)** and **Figure 4.4(c)**, respectively. This trend in the behaviour of  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  shows a reduction effect on the  $\text{Co}^{3+}$  with an increase in the  $\text{Co}^{2+}$  as the mixed Co-Cu ores were leached in the presence of  $\text{SO}_2$ . The reasons for the behaviour observed in **Figure 4.4(d)** could not be explained. Further experiments still need to be conducted..

It was generally observed that high yields of cobalt were achieved when leaching mixed Co-Cu oxidised ores in the presence of  $\text{SO}_2$ . During the 2 hours of leaching time, it was noted that the maximum solution based recovery of cobalt from these ores was achievable even within the first 30 minutes (**Figure 4.2**) of leaching in admixtures of  $\text{SO}_2$ . It was therefore of interest to focus on the reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  within the first 30 minutes of leaching and have insight about the rate at which this was happening.

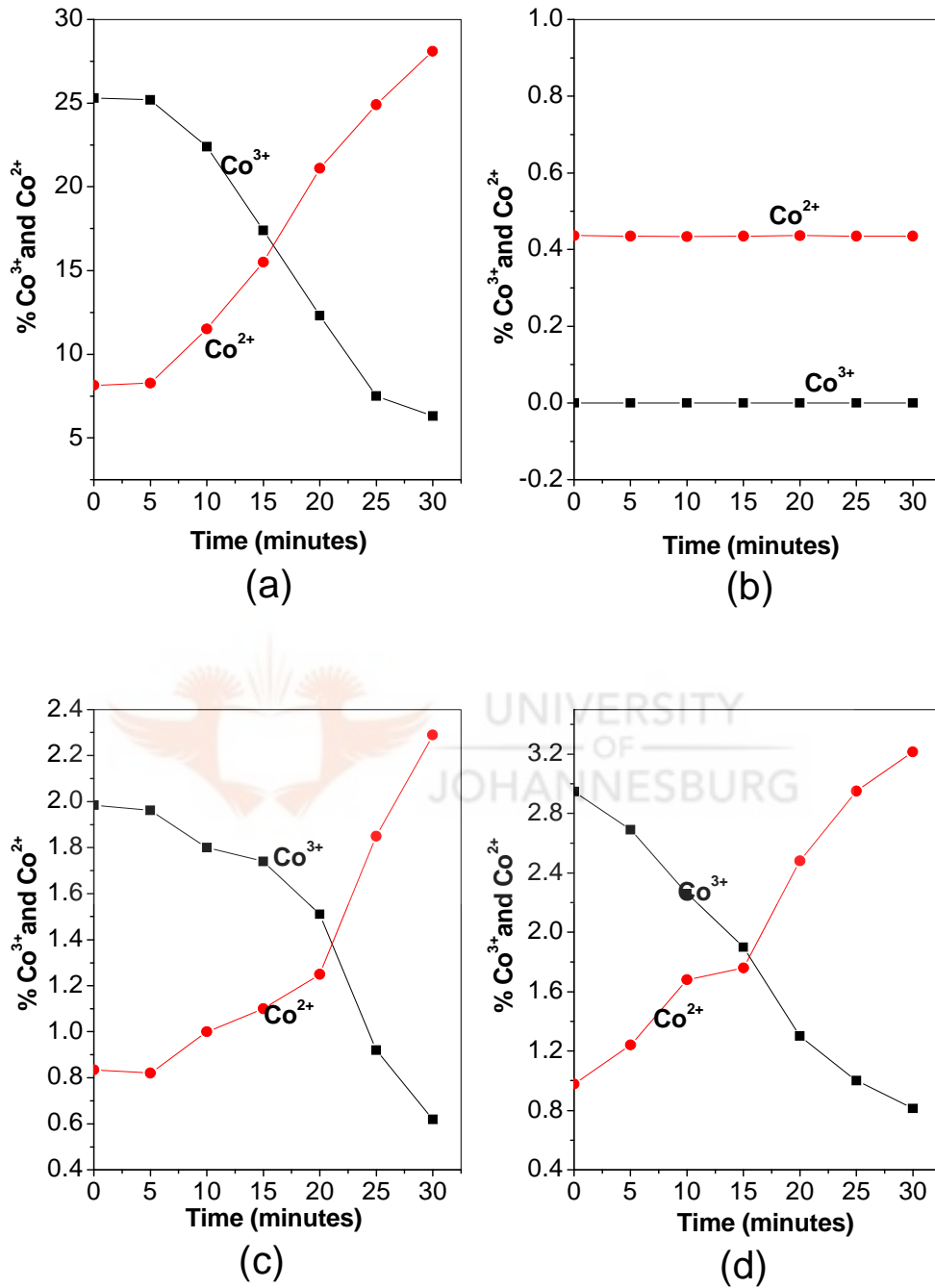


**Figure 4.4:** UV/Visible spectra for; (a) High cobalt ore, (b) Low cobalt with mica, (c) low cobalt ore without mica, (d) High copper ore

#### 4.4.4 The leaching behaviour of $\text{Co}^{2+}$ and $\text{Co}^{3+}$

The UV/Vis spectroscopy analysis was carried out on 6 aliquots sampled at 5 minutes intervals (i.e. 0, 5, 10, 15, 20, 25, 30) during the leaching of mixed Co-Cu oxidised ores in the presence of  $\text{SO}_2$ . The %  $\text{Co}^{3+}$  and %  $\text{Co}^{2+}$  in residues obtained were then directly plotted against the sample time to arrive at the curves shown in **Figure 4.5**. The analysis of the high cobalt ore, in **Figure 4.5(a)**, revealed that after 15 minutes of leaching time, 50% of  $\text{Co}^{3+}$  was already reduced to  $\text{Co}^{2+}$  as shown in **Figure 4.5**. A similar trend was observed in the analysis of low cobalt ores (with and without mica), in **Figure 4.5(d)** and **Figure 4.5(c)**, respectively. However, the reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  in the low cobalt ores seems to be taking place at about 20 minutes of leaching time. The explanation for this observation was that cobalt in the high cobalt ore was probably easily accessible to the leaching medium since it contained less gangue material. In contrast, the low cobalt ores were thought to be heavily masked by gangue materials and this explains why more time was required to reduce 50% of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$ .

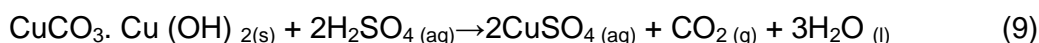
UV/Visible spectroscopy technique could not quantify  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  in the high copper ore due perhaps to the low cobalt content (ca.0.5%) present in ore. Since the high copper ore contains 31.5% Cu, it was thought that such a huge amount of copper could have a suppression effect on the behaviour of  $\text{Co}^{3+}$  during the leaching process, hence the pattern in **Figure 4.5(b)**. Further experiments still need to be conducted in order to understand the unusual behaviour observed during the leaching of high copper ore.



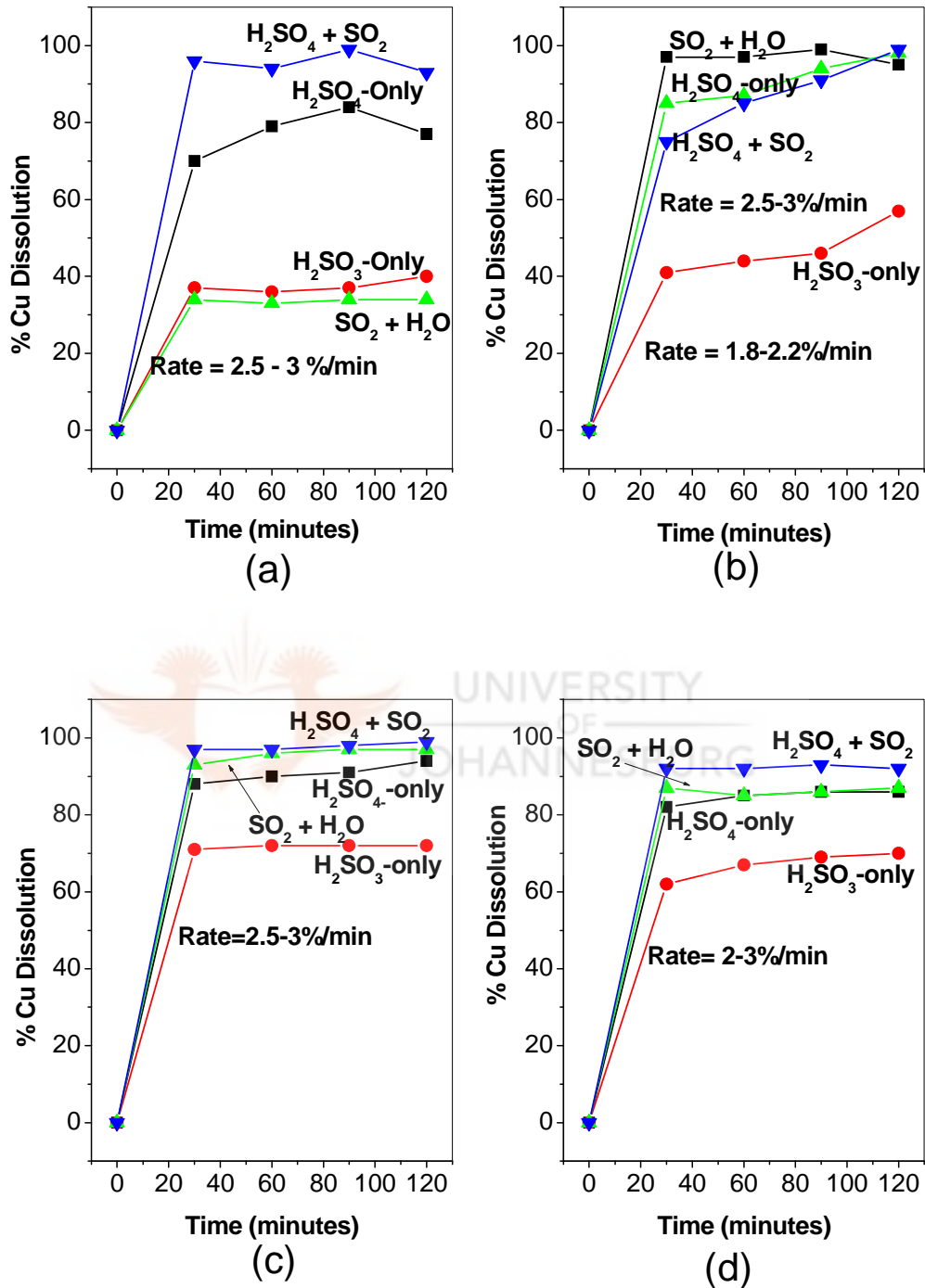
**Figure 4.5:** Behaviour of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  during cobalt dissolution; (a) High cobalt ore, (b) High copper ore, (c) Low cobalt without mica and (d) Low cobalt with mica

#### 4.4.5 The leaching behaviour of copper in mixed Co-Cu oxidised ores

Generally, It can be seen from **Figure 4.6** that high copper yields (85%-98%) were achieved when all four mixed Co-Cu oxidised ores were leached in aqueous sulphuric acid,  $\text{H}_2\text{SO}_4$  (aq). Although in some cases the admixtures of  $\text{SO}_2$  seem to be yielding a high copper yield. Furthermore, it can be noted that the rate of copper dissolution from all ores is initially high within the first 30 minutes of leaching and levels out beyond 30 minutes. In addition, information obtained from XRD experiment reveals that the main copper bearing mineral in mixed Co-Cu oxidised ores is malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (s)). The dissolution of malachite in sulphuric acid is illustrated in reaction 9.



It can be noted from reaction 9 that dissolution of copper from  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2(\text{s})$  does not require  $\text{SO}_2$  to promote its recovery. In fact, the presence of  $\text{SO}_2$  on its own in the leaching of Cu from mixed Co-Cu oxide ores seems to disfavour the maximum % copper dissolution as can be seen in **Figure 4.6**, except in admixtures of  $\text{SO}_2$ . Admixture of  $\text{H}_2\text{SO}_4 + \text{SO}_2$  seems to yield the maximum percentage copper for the dissolution of the high cobalt ore as shown in **Figure 4.6(a)**, and this is due to the oxidative properties of  $\text{H}_2\text{SO}_4$ . In the leaching of the high copper ore, in **Figure 4.6(b)**,  $\text{H}_2\text{SO}_4$  yields the highest percentage copper dissolution, whereas  $\text{H}_2\text{SO}_3$  yields the least percentage copper dissolution. The same trend in copper dissolution was observed with the low cobalt ores in **Figure 4.6(c)** and **Figure 4.6(d)**. This indicates that the dissolution of copper from mixed Co-Cu oxidised ores is favoured more under  $\text{H}_2\text{SO}_4$  conditions as shown in reaction 9.

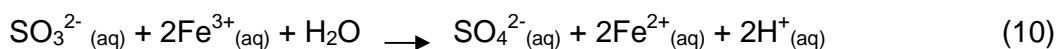


**Figure 4.6:** Leaching behaviour of copper; (a) High cobalt ore, (b) High copper ore (c) Low cobalt ore with mica and (d) Low cobalt ore without mica

#### 4.4.6 Analysis of iron dissolution in mixed Co-Cu oxidised ores

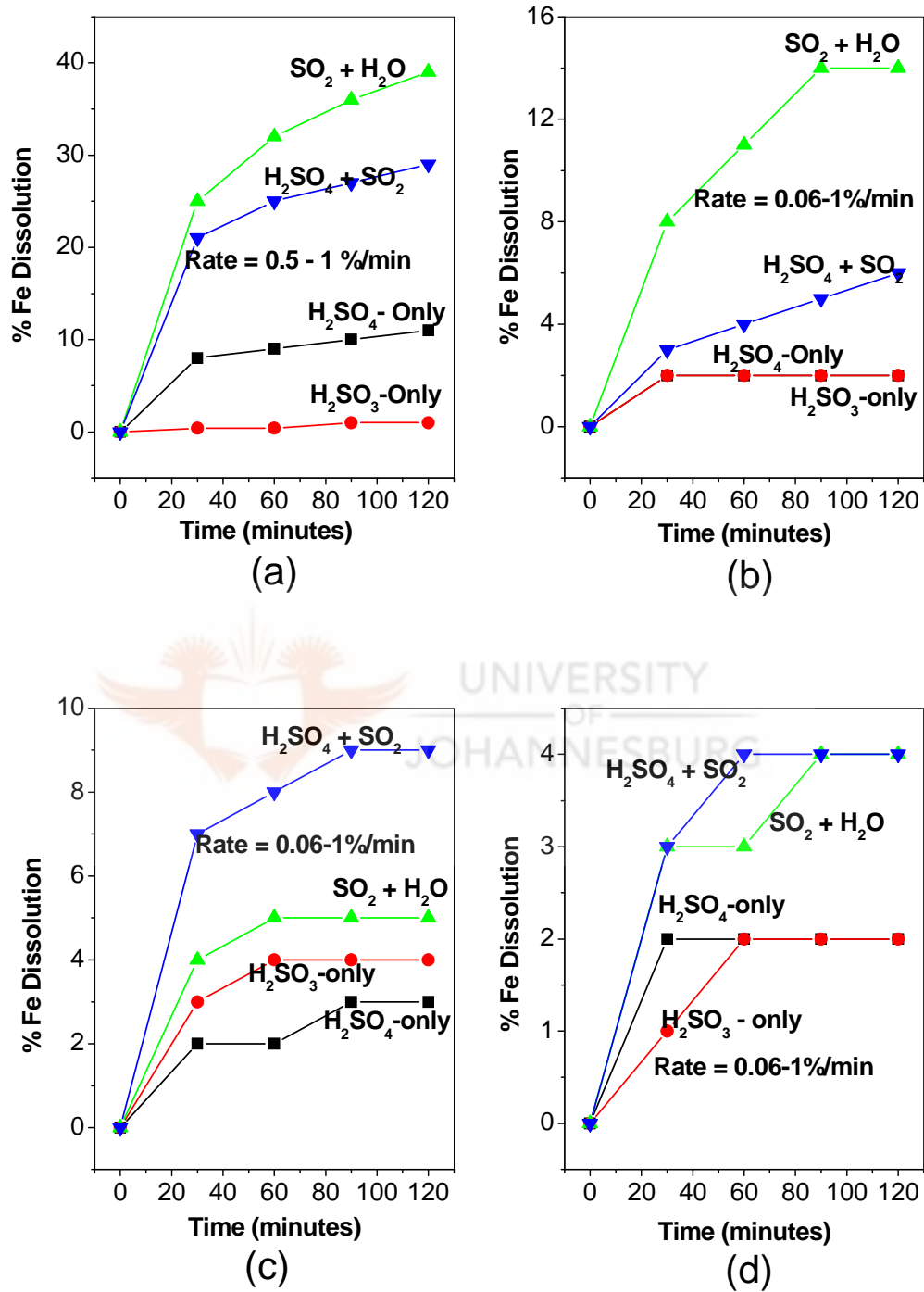
The maximum % iron dissolution that could be achieved in leaching the four mixed Co-Cu oxide ores was at best 40% when using the H<sub>2</sub>SO<sub>4</sub> + SO<sub>2</sub> admixture. Generally, It is assumed that the poor iron dissolution as observed in **Figure 4.7** is due to the poor solubility of iron bearing minerals present in the composition of these ores. The rate of dissolution shown in **Figure 4.7** was simply taken as the slope of the plots to show how fast the leaching process was taking place. Although XRD results do not provide adequate information about all iron bearing minerals present in mixed Co-Cu oxidised ores, Fe<sub>2</sub>O<sub>3</sub> (as identified by XRD) is known to be soluble under extremely acidic solutions, pH<1, hence the poor solubility of iron as can be noted in **Figure 4.7**. A more sensitive instrumental technique is thus required to fully characterise all iron bearing minerals in mixed Co-Cu oxidised ores.

Noteworthy, the similar leaching trend observed during the analysis of cobalt dissolution in mixed Co-Cu oxide ores also holds true for iron dissolution from these ores. As can be inferred in **Figure 4.7(a)**, the maximum percentage iron dissolution (40%) from the high cobalt ore was achieved in the admixture of SO<sub>2</sub> + H<sub>2</sub>O, and the minimum percentage iron dissolution (4%) was achieved when either H<sub>2</sub>SO<sub>4</sub> or H<sub>2</sub>SO<sub>3</sub> was used independently as a leaching medium. Similar leaching trends seem to be followed by the high copper ore in **Figure 4.7(b)**. Higher iron yields for the low cobalt ores in **Figure 4.7(c)** and **Figure 4.7(d)**, respectively, were achieved in an admixture of H<sub>2</sub>SO<sub>4</sub> + SO<sub>2</sub>. It is believed that SO<sub>2</sub> plays a major role in the dissolution of iron from mixed Co-Cu oxidised ores. The explanation for the improved iron dissolutions under SO<sub>2</sub> conditions is provided in the following reaction scheme:



The formation of sulphurous acid, H<sub>2</sub>SO<sub>3</sub>, from SO<sub>2</sub>+H<sub>2</sub>O produces the sulphite ion, SO<sub>3</sub><sup>2-</sup>, which reduces Fe<sub>3</sub>O<sub>2</sub> to Fe<sup>2+</sup> as shown in reaction 10.





**Figure 4.7:** Leaching behaviour of iron; (a) High cobalt ore, (b) High copper ore (c) Low cobalt ore with mica and (d) Low cobalt ore without mica

#### 4.5 Precipitation of iron and copper from cobalt leach solutions

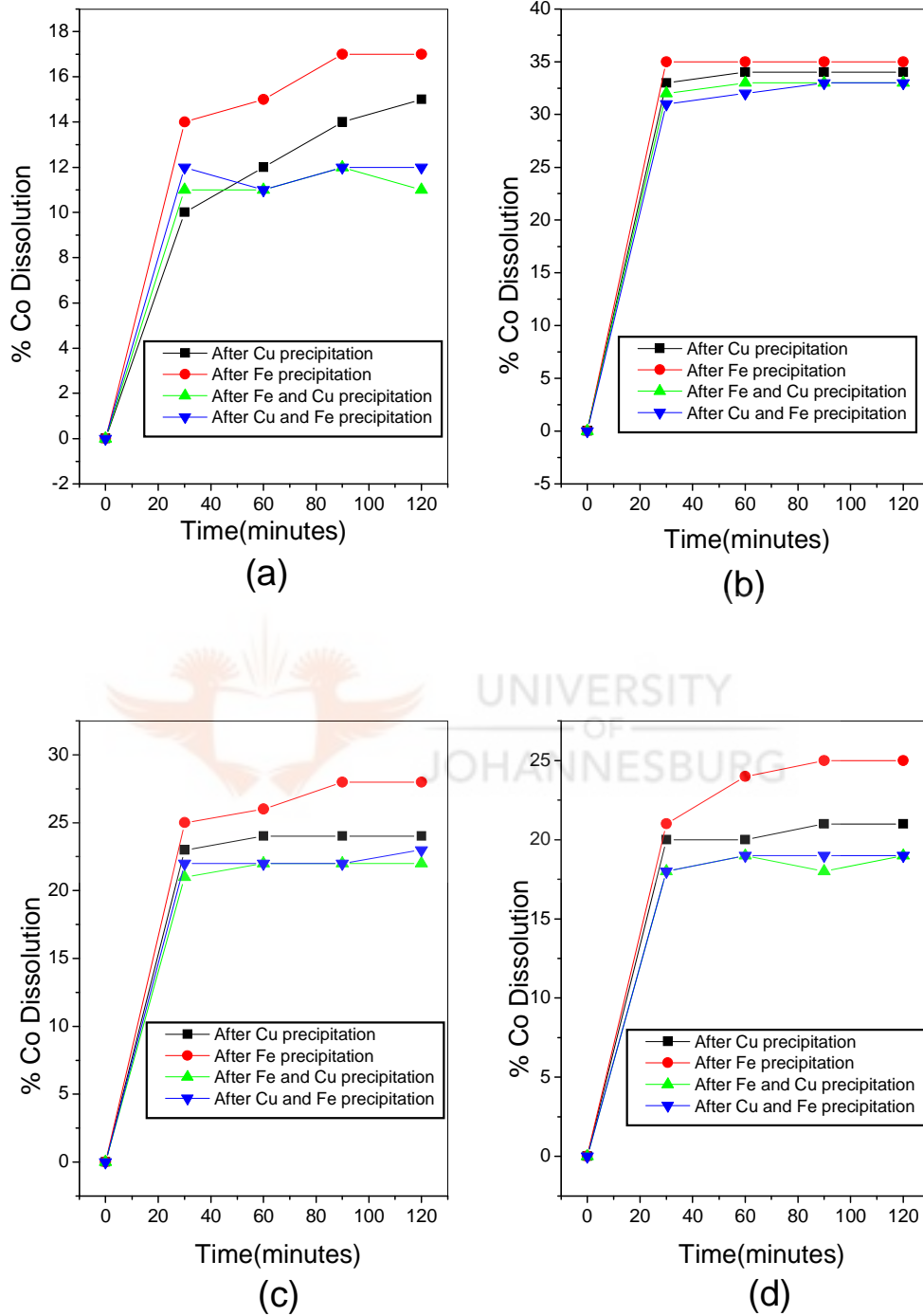
Sodium hydroxide (NaOH) was used as a precipitating reagent for iron and copper from cobalt leach solutions. Since these were pH dependant experiments, the pH range between pH 2 and pH 5 was maintained. The purpose of these experiments was to determine the effect of the presence of both iron and copper on the leaching efficiency of cobalt from mixed Co-Cu oxidised ores. The cobalt leach liquor from each mixed Co-Cu oxidised ore was treated individually and the sequence of precipitation was in two stages:

- In stage 1, iron and copper were precipitated from the leach solutions of the high cobalt ore – **Figure 4.8(a)**, high copper ore – **Figure 4.8(b)**, low cobalt ore with mica – **Figure 4.8(c)** and low cobalt ore without mica – **Figure 4.8(d)**. After iron precipitation, the iron-free leach solution was then used to wash or re-leach each ore's residue for two hours. The same was done with the copper-free solution. The percentage cobalt dissolution achieved after washing or re-leaching of residues was then added to the percentage cobalt dissolutions obtained during the leaching process. The sum of percentage cobalt dissolutions was then plotted against the re-leaching time, with samples taken at 30 minutes intervals. These results are shown in **Figure 4.8**.
- In stage 2, iron and copper were both precipitated from cobalt leach liquors of mixed Co-Cu oxidised ores. The iron-copper – free solutions were thereafter used to re-leach the residues. The purpose of precipitation experiments in stage 2 was to determine whether there was any difference in performing precipitations starting from pH 2 to pH 5 (i.e. precipitating iron first (pH2) and then copper (pH5) or start precipitation from pH 5 down to pH 2 (i.e. precipitating copper first and then iron). In other words, the difference between the two stages is that in stage 1, the purpose of precipitation was to determine the effect of the presence of Fe and Cu in leach solutions on the leaching efficiency of Co from mixed Co-Cu residues. These results are also shown in **Figure 4.8**

In general, percentage cobalt dissolution after iron precipitation increased by 3 to 4%. After copper precipitation, percentage cobalt dissolution increased by 2% in all four mixed Co-Cu oxidised ores. As can be noted in **Figure 4.8(a)**, **Figure 4.8(b)**, **Figure 4.8(c)** and **Figure 4.8(d)**, the maximum percentage cobalt dissolution was achieved after iron precipitation. This means that the presence of iron in cobalt leach solutions can limit the dissolution of cobalt from mixed Co-Cu oxidised ores to a certain extent.

It was generally observed that precipitation while monitoring the pH closely a more efficient method of precipitation was to start precipitation from pH 2 to pH 5 (i.e. iron first and then copper) rather than precipitating from pH 5 to pH 2 (i.e. Cu first and then Fe). Although iron precipitates obtained from cobalt leach solution were of colloidal nature, it was noted that precipitating from pH 5 down to pH 2 always resulted in heavily hydrated iron precipitates that were not easily filtered off by gravity than when precipitating from pH 2 up to pH 5.

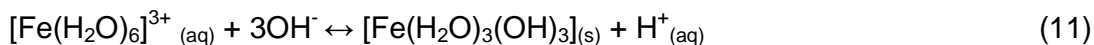




**Figure 4.8:** Cobalt leaching after precipitation; (a) High cobalt ore, (b) High copper ore, (c) Low cobalt ore with mica and (d) Low cobalt ore without mica

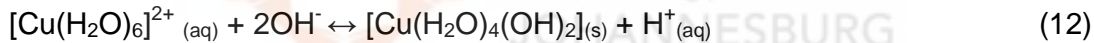
#### 4.5.1 The chemistry of iron and copper precipitation

The underlying reason for the hydrated and colloidal nature of the  $\text{Fe}(\text{OH})_{3(s)}$  precipitate is given in the following reaction:



In the final leach liquor,  $\text{Fe}^{3+}$  exist as the hexaaquairon(III) ion,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  giving acidic solutions with pH 1.5-2.5 as shown in reaction 11. Addition of  $\text{OH}^-$  solution results in the formation of a partially hydrated  $[\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3]_{(s)}$  precipitate. This explains why in general Fe precipitates were of colloidal nature and required at least 30 minutes to filter by gravity.

The explanation with regards to copper precipitation is similar as that for iron precipitation. The only difference is the operating pH (i.e. pH 4.7). The following reaction (reaction 12) takes place during copper precipitation:



#### 4.6 Microwave treatment of mixed Co-Cu oxidised ores

So far results obtained in this study show that  $\text{SO}_2$  can be used as the best and economic reagent to improve the extraction of cobalt from its ores. However, the use of  $\text{SO}_2$  in pilot plants could be detrimental to the environment causing acid rains if not properly monitored. There is, therefore, a need to seek methods that are environmentally friendly and that are capable of enhancing the leaching efficiency of cobalt from mixed Co-Cu oxidized ores. To this end, microwave technology has, to the best of our knowledge, not been applied in the improvement of the leaching efficiency of cobalt from mixed Co-Cu oxidized ores.

Unique microwave heating characteristics were the main drivers for treating mixed Co-Cu oxidised ores with microwaves prior to leaching experiments. Some of the advantages that microwave heating offers include low processing time, direct, selective and volumetric heating, and a more controllable heating process. It is understood that since selective heating by microwaves results in ruptured surface layers of the dielectric components in the ore material, this could subsequently lead to more surface area leaving cobalt bearing minerals exposed to the leach medium (i.e. aqueous  $\text{H}_2\text{SO}_4$ ) resulting in an improvement in the leaching efficiency of Co from mixed Co-Cu oxidised ores.

In a typical microwave heating experiment, a mixed Co-Cu oxide ore sample (20g) was radiated with microwaves for 30 minutes. The microwave-treated sample was then leached for 2 hours in a chosen leach medium. One major alteration in the physical properties of the microwave-treated sample was noted as this sample became highly porous and darker in colour compared to the non-microwave-treated ore samples. Furthermore, it was observed that microwave treatment of the high cobalt ore and high copper ore resulted in a sintered product which required re-milling prior to leaching. The underlying reason for this behaviour was attributed to the electric and magnetic components within the high cobalt ore and the high copper ore which generate more internal heating when exposed to microwave radiation – hence sintering.

#### 4.6.1 Leaching of microwave - treated mixed Co-Cu oxidised ores

In order to underscore the effect of microwave on the leaching efficiency of cobalt from mixed Co-Cu oxidised ores, microwave-treated samples were leached in aqueous  $H_2SO_4$ . The percentage cobalt dissolution from microwave-treated samples was compared with percentage cobalt dissolution from non-microwave irradiated samples. A comparative study of results obtained for this experiment is shown in **Table 4.4**.

As can be noted in **Table 4.4** that simple microwave radiation of mixed Co-Cu ores even with a microwave output power of 900W, resulted in high leaching efficiencies of cobalt. Similar observational results were noticed with copper and iron leaching efficiencies. This improvement in leaching efficiencies can be attributed to the absorption of microwave energy by dielectric components in mixed Co-Cu oxidised ores which generate internal heating. Depending on the nature of components present in ore and their dielectric properties, the heat generated leads to greater proportion of free mineral grain within the ore material and this subsequently leads to the improvement in mineral leaching.

As can be inferred in **Table 4.4**, cobalt dissolution after microwave treatment increased from 10% to 34% in the high cobalt ore, 31% to 42% in the high copper ore, 20% to 55% in the low cobalt with mica and from 20% to 42% in the low cobalt without mica. Similar trends are observed with copper and iron although the effect here is less pronounced than in the case of cobalt after microwave treatment. In a nutshell, there is a significant improvement in the leaching efficiency of cobalt from mixed Co-Cu oxidised ores after microwave treatment of these ores prior to leaching. This improvement can be attributed to unique microwave heating characteristics.

**Table 4.4:** Comparison between microwave and non-microwave treated samples

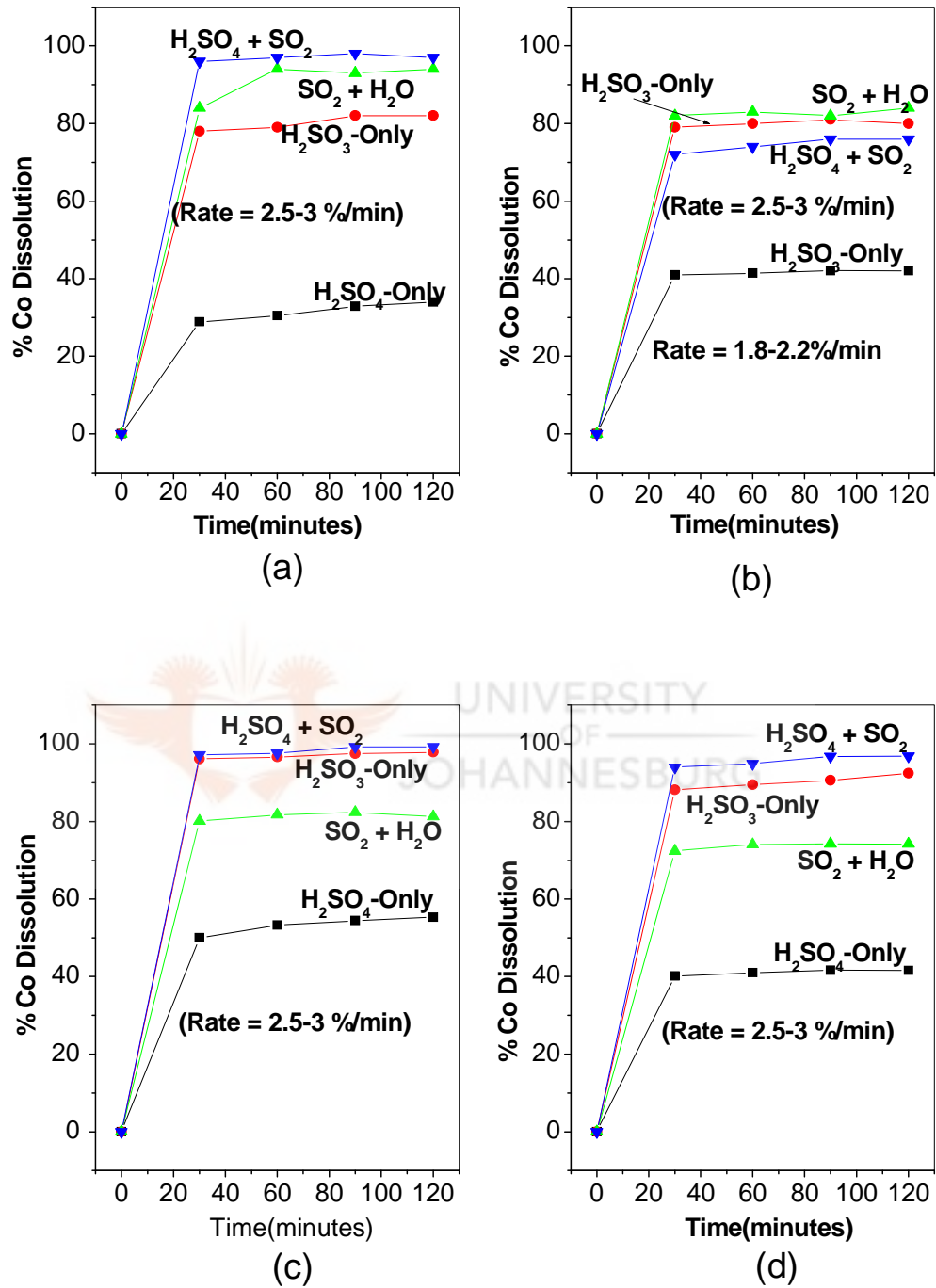
<b>Non microwave-treated samples</b>		<b>Microwave-treated samples</b>	
<b>High cobalt ore</b>		<b>High cobalt ore</b>	
Element	% dissolution	Element	% dissolution
Co	10	Co	34
Cu	94	Cu	94
Fe	11	Fe	11
<b>High copper ore</b>		<b>High copper ore</b>	
Element	% dissolution	Element	% dissolution
Co	31	Co	42
Cu	86	Cu	98
Fe	2	Fe	6
<b>Low cobalt ore with mica</b>		<b>Low cobalt ore with mica</b>	
Element	% dissolution	Element	% dissolution
Co	20	Co	55
Cu	77	Cu	94
Fe	3	Fe	9
<b>Low cobalt ore without mica</b>		<b>Low cobalt ore without mica</b>	
Element	% dissolution	Element	% dissolution
Co	20	Co	42
Cu	95	Cu	99
Fe	2	Fe	8



#### 4.6.2 Leaching behaviour of cobalt from microwave - treated ore samples

The kinetic curves shown in **Figure 4.9** for the microwave-treated samples show an elevated initial rate of cobalt leaching within the first 30 minutes which levels out beyond 30 minutes of leaching time. It was also noted that maximum percentage of cobalt was liberated, in addition to the microwave heating effect, were achieved in admixtures of  $\text{SO}_2$  (i.e.  $\text{H}_2\text{SO}_4 + \text{SO}_2$  and  $\text{SO}_2 + \text{H}_2\text{O}$ ). In comparison, the leaching trend of cobalt in non microwave-treated ores (**Figure 4.2**) is generally similar to that in microwave assisted leaching as illustrated in **Figure 4.9**. The one main difference between the two scenarios is that there is a significant improvement in the leaching efficiency of cobalt from the microwave-treated samples than in non microwave-treated samples.



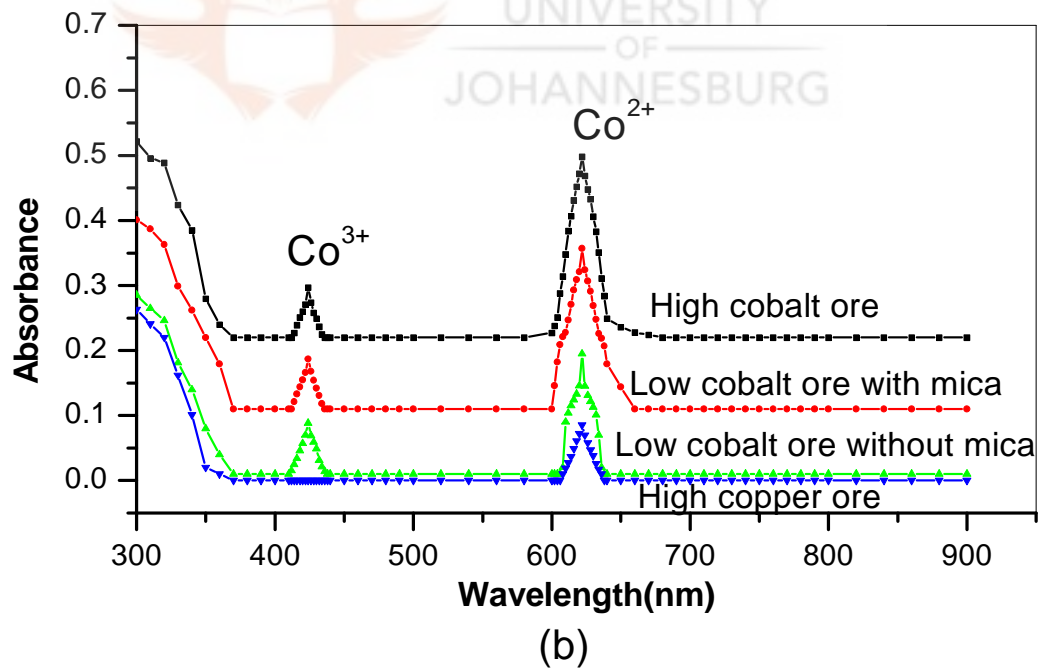
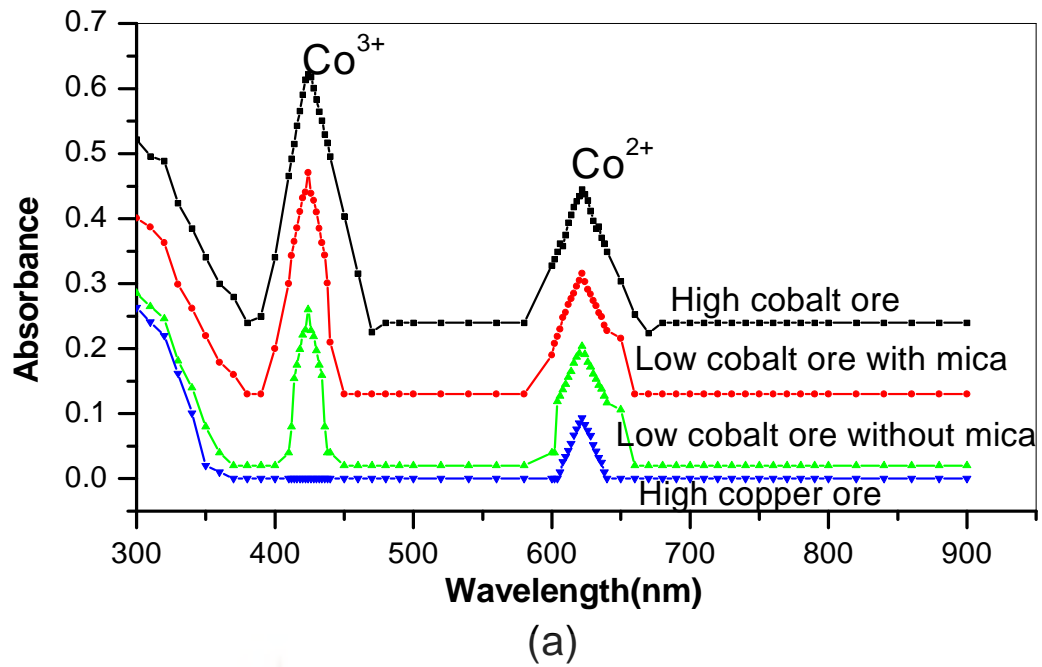


**Figure 4.9:** Leaching behaviour of cobalt from microwave treated samples; (a) High cobalt ore, (b) High copper ore, (c) Low cobalt ore with mica and (d) Low cobalt ore without mica

#### 4.6.3 UV/Vis spectra of $\text{Co}^{2+}$ and $\text{Co}^{3+}$ in microwave-treated samples

UV/Vis experiments were carried out to ascertain the role of  $\text{SO}_2$  in promoting the leaching yield of cobalt from microwave treated samples. The results of these experiments are shown in **Figure 4.10**. Generally, it was observed that the concentration of  $\text{Co}^{3+}$  was higher before  $\text{SO}_2$  treatment and lower after  $\text{SO}_2$  treatment. The concentration of  $\text{Co}^{2+}$  in microwave treated samples before  $\text{SO}_2$  treatment was lower and higher after  $\text{SO}_2$  treatment. It was observed that a relatively short microwave exposure time (up to 30 minutes at 900W) was effective in promoting good cobalt recovery from mixed Co-Cu oxide ores.

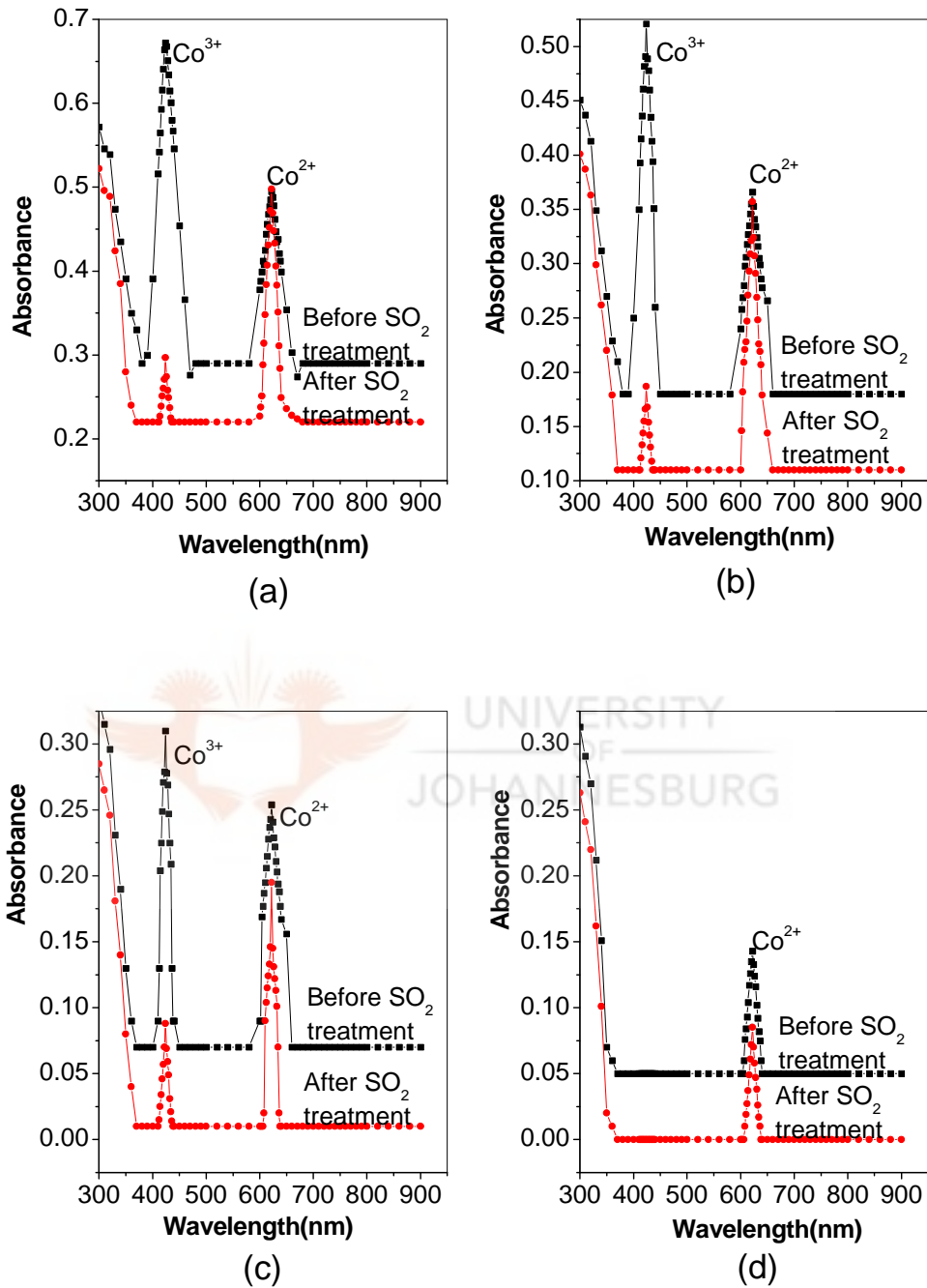




**Figure 4.10:** UV/Vis Spectra for microwave treated samples; (a) Before  $\text{SO}_2$  treatment, (b) After  $\text{SO}_2$  treatment

As can be noted in **Figure 4.11(a)**, **Figure 4.11(b)** and **Figure 4.11(c)** the absorbance of  $\text{Co}^{3+}$  before  $\text{SO}_2$  treatment is high compared with the absorbance of  $\text{Co}^{2+}$ . The reverse trend is observed after leaching microwave treated samples in the presence of  $\text{SO}_2$ . In this case, the absorbance of  $\text{Co}^{3+}$  becomes smaller than that of  $\text{Co}^{2+}$  as shown in **Figure 4.11**. This observation suggests a reduction effect on the  $\text{Co}^{3+}$  with an increase in the  $\text{Co}^{2+}$  as the microwave treated mixed Co-Cu ores are leached in the presence of  $\text{SO}_2$ .



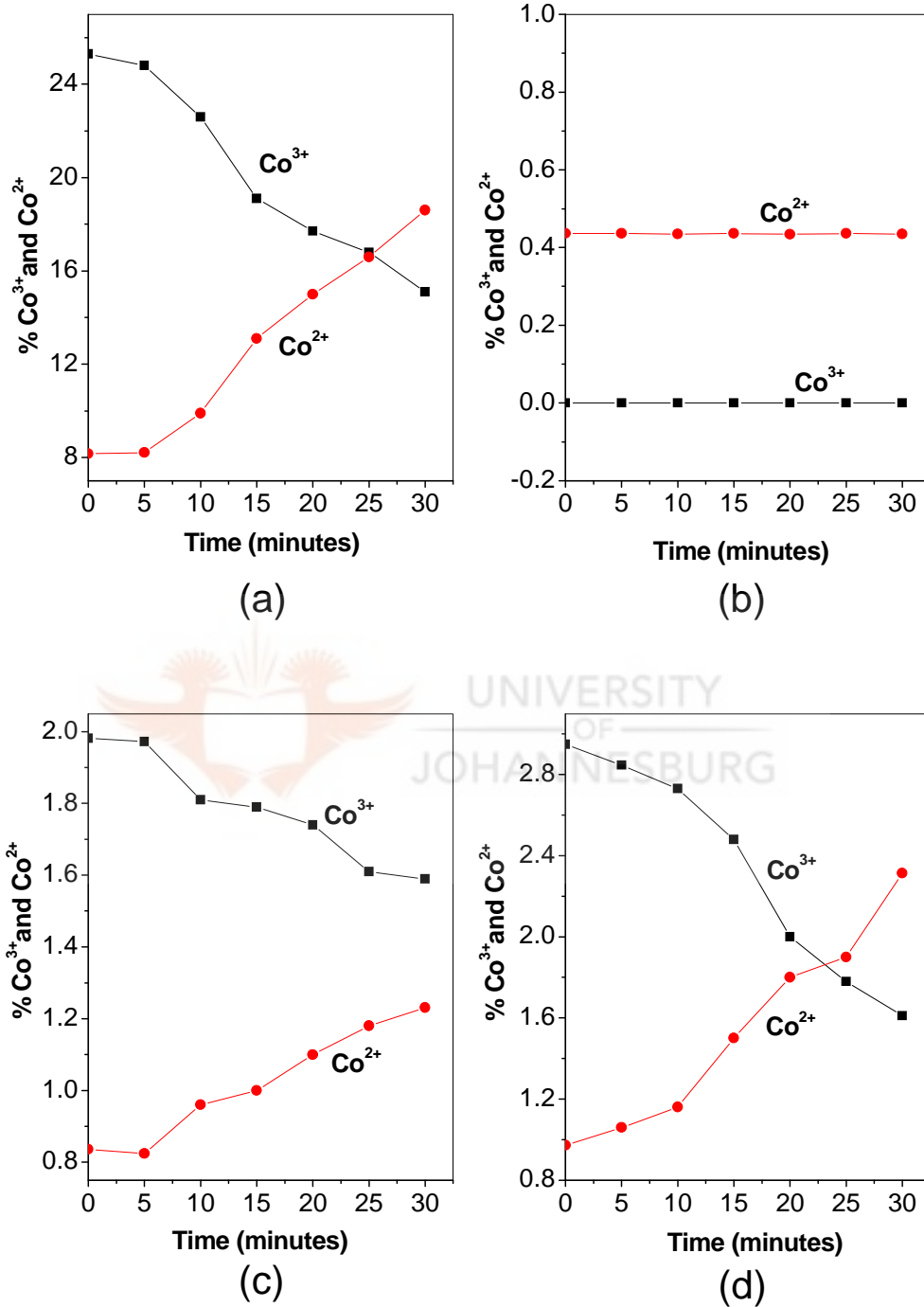


**Figure 4.11:** UV/Visible spectra for microwave treated samples; (a) High cobalt ore, (b) Low cobalt with mica, (c) low cobalt ore without mica, (d) High copper ore

#### 4.6.4 The leaching behaviour of $\text{Co}^{2+}$ and $\text{Co}^{3+}$ in microwave-treated ores

The results shown in **Figure 4.12** illustrate the rate at which  $\text{Co}^{3+}$  decreases with an increase in  $\text{Co}^{2+}$  within the first 30 minutes of leaching the microwave treated samples in aqueous  $\text{H}_2\text{SO}_4$ . As can be noted from **Figure 4.12(b)**, the high copper ore plot is different from the other three plots and this is still subject to further experimentation. However, it was observed that the rate of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  conversion in high cobalt ore (**Figure 4.12(a)**) and low cobalt ore with mica (**Figure 4.12(d)**) was faster compared to low cobalt ore without mica (**Figure 4.12(c)**). This trend is similar to what has been observed in the non-microwave treated samples shown in **Figure 4.5**.





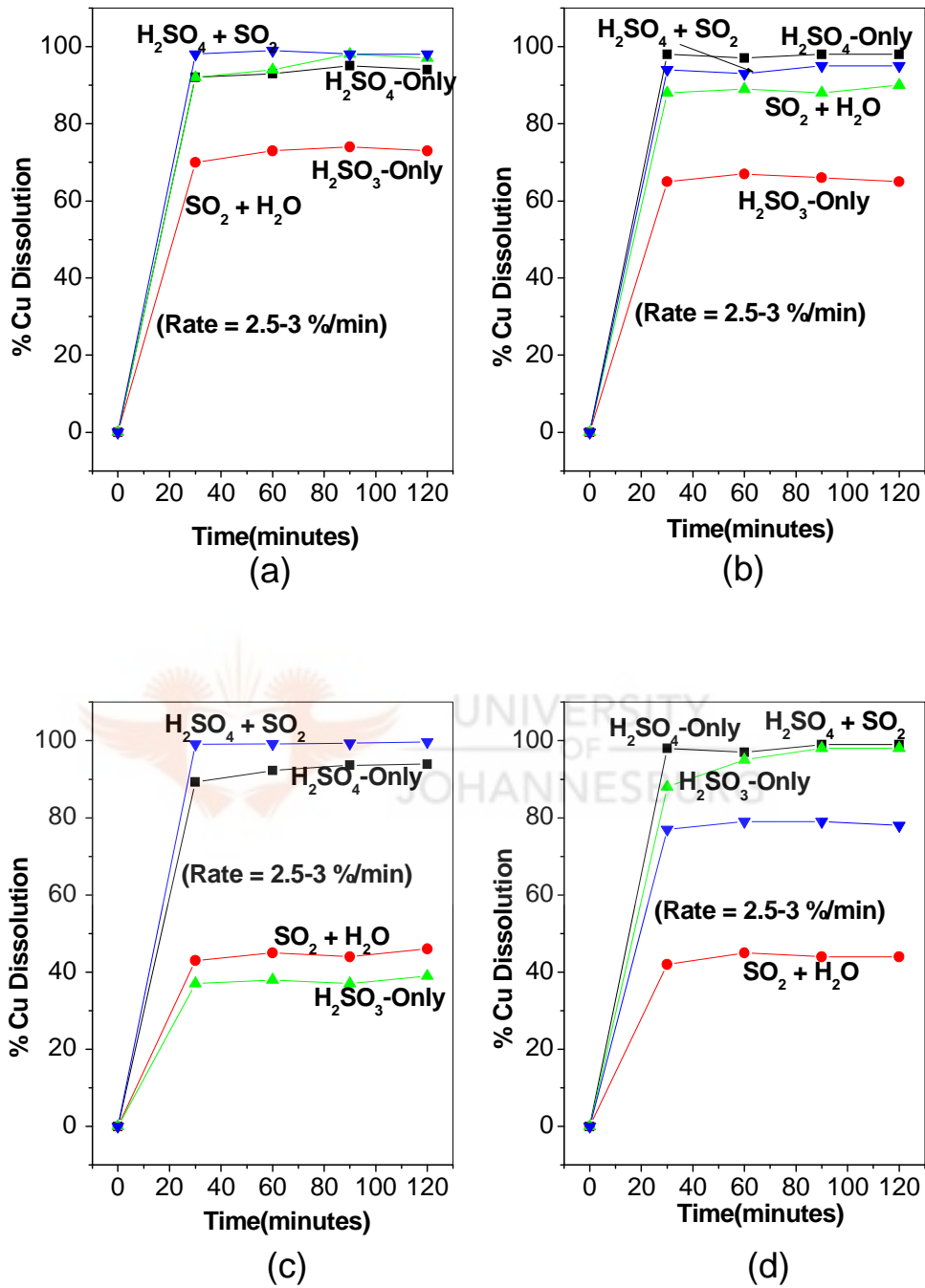
**Figure 4.12:** Behaviour of Co<sup>2+</sup> and Co<sup>3+</sup> during cobalt dissolution; (a) High cobalt ore, (b) High copper ore, (c) Low cobalt without mica and (d) Low cobalt with mica



#### 4.6.5 The leaching behaviour of copper from microwave-treated samples

The plots obtained for the dissolution of copper from microwave-treated samples (**Figure 4.6**) and non-microwave treated samples (**Figure 4.13**) are generally similar. This suggests that microwave treatment of mixed Co-Cu oxide ores for improving the percentage copper yields was not crucial. Admixture of  $\text{H}_2\text{SO}_4 + \text{SO}_2$  for the dissolution of copper from the high cobalt ore (**Figure 4.13(a)**) and low cobalt ore with mica in **Figure 4.13(c)** yield the maximum percentage copper dissolution. The use of  $\text{H}_2\text{SO}_4$  in leaching the high copper ore and the low cobalt ore (without mica) as shown in **Figure 4.13(b)** and **Figure 4.13(d)** resulted in a high percentage copper dissolution. The minimum percentage copper dissolutions from microwave treated samples were obtained when  $\text{H}_2\text{SO}_3$  was used as a leach medium.

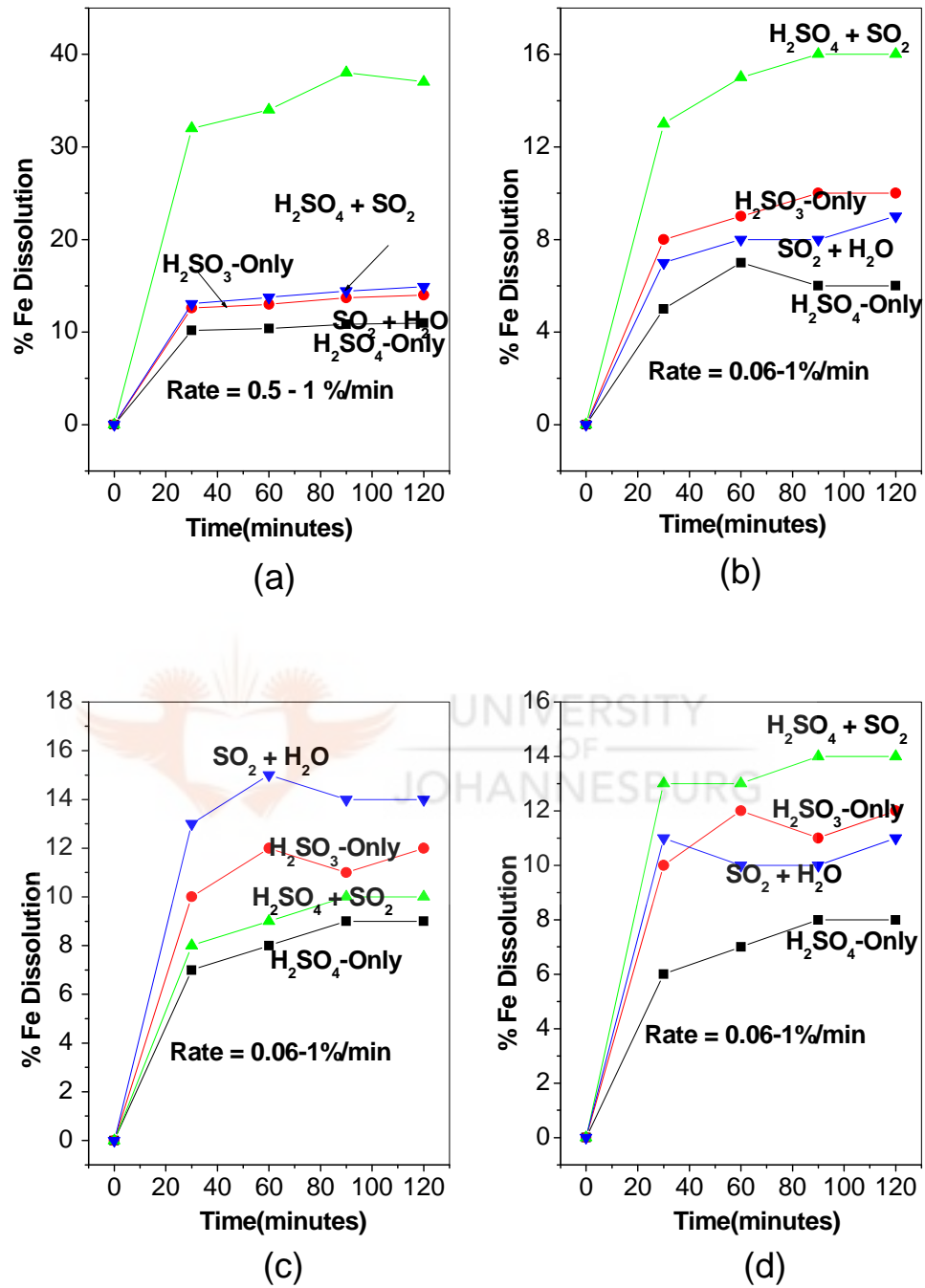




**Figure 4.13:** Leaching behaviour of copper from microwave treated samples; (a) High cobalt ore, (b) High copper ore, (c) Low cobalt ore with mica and (d) Low cobalt ore without mica

#### 4.6.6 Analysis of iron dissolution from microwave-treated samples

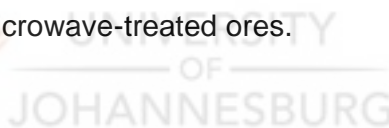
The maximum percentage iron dissolution from microwave-treated ores was also achieved in admixtures of  $\text{SO}_2$ . The plots in **Figure 4.14** reveal that much better iron yields, compared to **Figure 4.7**, were achieved from leaching the microwave-treated ore samples in admixtures of  $\text{SO}_2$ . The additional effect observed in the improved iron dissolution was attributed to microwave heating. As can be inferred in **Figure 4.14(a)**, the maximum percentage iron dissolution (40%) from the high cobalt ore was achieved in admixture of  $\text{H}_2\text{SO}_4 + \text{SO}_2$ , and the minimum percentage iron dissolution (10%) was achieved when  $\text{H}_2\text{SO}_4$  was used as a leaching medium. Similar leaching trends were observed with the high copper ore and the low cobalt ore (without mica) as shown in **Figure 4.14(b)** and **Figure 4.14(d)**, respectively. In contrast, maximum percentage iron dissolution (15%) for the low cobalt ore (with mica) in **Figure 4.14(c)** was achieved in an admixture of  $\text{SO}_2 + \text{H}_2\text{O}$ . These results show that microwave heating of the mixed Co-Cu oxidised ores is important in the dissolution of iron.

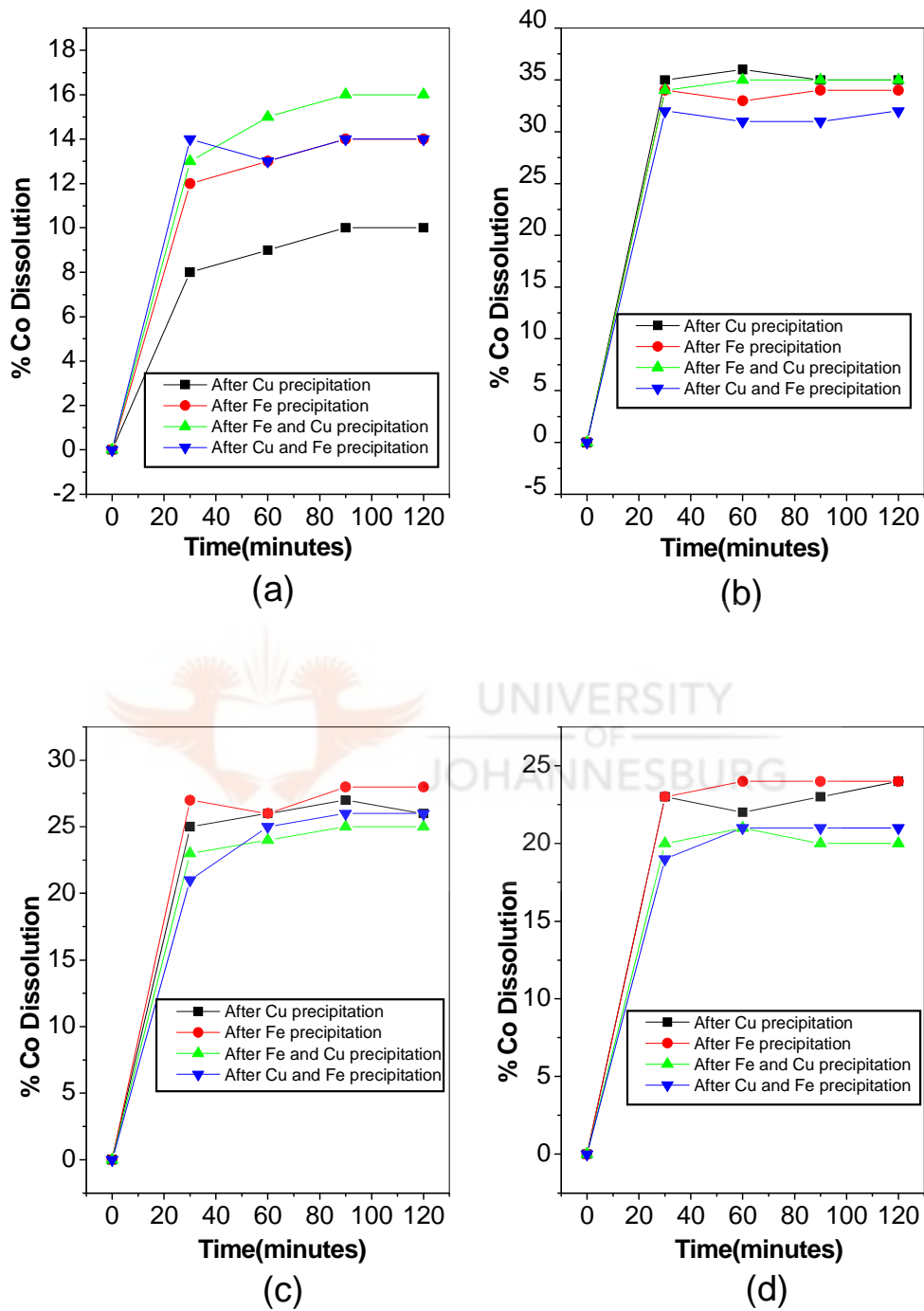


**Figure 4.14:** Leaching behaviour of iron from microwave treated samples; (a) High cobalt ore, (b) High copper ore, (c) Low cobalt ore with mica and (d) Low cobalt ore without mica

#### 4.7 Precipitation of iron and copper from cobalt leach solutions

Generally, as can be noted in **Figure 4.15**, the percentage cobalt dissolution after iron precipitation increased by 3 to 4%. After copper precipitation, percentage cobalt dissolution increased by 2% in all four mixed Co-Cu oxidised ores. As shown in **Figure 4.15(a)**, **Figure 4.15(b)**, **Figure 4.15(c)** and **Figure 4.15(d)**, the maximum percentage cobalt dissolution was achieved after iron precipitation, followed by copper precipitation. Furthermore, precipitation experiments carried out on the leach solutions of microwave-treated ore samples, revealed that a more efficient method of precipitation was to start precipitation from pH 2 to pH 5 (i.e. iron first and then copper) rather than precipitating from pH 5 to pH 2 (i.e. Cu first and then Fe). It was also noted that even with the microwave-treated samples, precipitating from pH 5 to pH 2 always resulted in heavily hydrated iron precipitates that were not easily filtered off by gravity than when precipitating from pH 2 to pH 5. It was noted that precipitation experiments for microwave-treated ores yielded similar results as non microwave-treated ores.





**Figure 4.15:** Cobalt leaching after precipitation; (a) High cobalt ore, (b) High copper ore, (c) Low cobalt ore with mica and (d) Low cobalt ore without mica

#### 4.8 References

1. Whiston C., (1987), X-Ray Methods, UK, John Wiley and Sons, pp 45-66.
2. Mwema, M.D., Mpoyo., M., Kafumbila, K., (2002), Use of sulphur dioxide as a reducing agent in cobalt leaching at Shituru hydrometallurgical plant, Journal of SAIMM,1., pp 1-4.



## CHAPTER 5

# CONCLUSIONS AND RECOMMENDATIONS

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### 5.1 Conclusions

This research study successfully accomplished all the objectives and a summary of the results that have emanated from this study is given in this chapter. The following conclusions were arrived at from the results derived from this project.

- The XRD results confirmed the presence of cobalt, copper and iron bearing minerals in all four mixed Co-Cu oxidised ores investigated. Although not much information pertaining to  $\text{Co}^{2+}$  bearing minerals in mixed Co-Cu oxidised ores was obtained from XRD results, heterogenite minerals ( $\text{CoOOH-2H}$  and  $\text{CoOOH-3R}$ ) which bear cobalt as  $\text{Co}^{3+}$  were noted.
- The results obtained from XRF and AAS confirmed the percentage elemental compositions of cobalt, iron and copper in mixed Co-Cu oxidised ores. Furthermore, all three techniques were successfully proven complimentary with one another in providing information about cobalt, copper and iron present in mixed Co-Cu oxidised ores. However, the use of a more sensitive XRD technique, preferably coupled with microscope, is required to fully characterize  $\text{Co}^{2+}$  bearing minerals in mixed Co-Cu oxidised ores. In addition, the UV/Visible spectroscopy successfully explored and monitored the levels of both  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  before and after leaching mixed Co-Cu oxidised ores in the presence of  $\text{SO}_2$ .
- Exceptional cobalt yields (i.e. 85-95% dissolutions) in solution were achieved when leaching mixed Co-Cu oxidised ores in the presence of  $\text{SO}_2$ . These improved cobalt yields were achieved due to the reduction of  $\text{Co}^{3+}$  to



$\text{Co}^{2+}$  by  $\text{SO}_2$  during the leaching process as confirmed by UV/Visible spectroscopy. Improved cobalt yields were also realised when the mixed Co-Cu oxidised ores were treated with microwaves prior to leaching in the presence of  $\text{SO}_2$ , and this enhancement was attributed to microwave heating characteristics. .

- In general, the rate of cobalt leaching from mixed Co-Cu oxidised ores is faster when admixtures of  $\text{H}_2\text{SO}_4 + \text{SO}_2$  are used as leaching media. In contrast, the slowest rates of cobalt leaching are observed when only aqueous  $\text{H}_2\text{SO}_4$  was used as a leaching medium.
- Precipitation of iron from cobalt leach solutions resulted in higher cobalt recoveries when the residue was re-leached in the iron free solution as compared to the precipitation of copper. In addition, it was observed that precipitating from a lower pH towards a higher was a better method of precipitation than precipitating from a higher pH down to a lower pH. In the former case, co- precipitation of cobalt is minimised substantially.

## 5.2 Recommendations

A few recommendations from this research study based on the results that have been discussed are as follows:

- Further research work must be conducted which should characterise in detail both  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  bearing minerals and both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  bearing minerals in mixed Co-Cu oxidised ores. The findings of these studies could provide better understanding on the effect of the presence of iron on the leaching efficiency of cobalt from mixed Co-Cu oxidised ores.
- Research should be done to investigate if microwave processing of mixed Co-Cu oxide ores, especially the high copper bearing ore, prior to leaching would result in an enhanced cobalt yield in solution. Furthermore, the presence of gangue material such as nimitite1M<sub>11b</sub> in mixed Co-Cu oxidised

ores in promoting or otherwise the leaching efficiency of cobalt also needs to be examined.

- Further experimentation, especially UV/Visible experiments, should be conducted on the high copper ore in order to elucidate the cobalt leaching trend as realised in this research study.



## APPENDIX 1

### Attribution of mineral phases in the XRD plots, Figure 4.1

HIGH COBALT ORE						HIGH COPPER ORE					
High cobalt ore					Reference(33-1161)	High copper ore					Reference(33-1161)
Mineral phase	2(Theta)	dA	rel.Intensity	dA	rel.Intensity	Mineral phase	2(Theta)	dA	rel.Intensity	dA	rel.Intensity
SiO <sub>2</sub>	20.8565	4.259	32	4.257	22	SiO <sub>2</sub>	20.0567	4.259	29	4.257	22
	26.6306	3.347	100	3.342	100		26.7816	3.347	100	3.342	100
	45.9098	1.98	3	1.979	14		43.1968	1.98	2	1.979	14
	75.6514	1.256	4	1.255	1		73.2554	1.256	1	1.255	1
Reference(7-169)						Reference(7-169)					
	2(Theta)	dA	rel.Intensity	dA	rel.Intensity		2(Theta)	dA	rel.Intensity	dA	rel.Intensity
CoOOH-3R	19.8913	4.363	6	4.384	100	CoOOH-3R	19.8343	4.336	2	4.384	100
	36.5341	2.432	6	2.429	12		37.1234	2.447	2	2.429	12
	38.7761	2.312	23	2.314	85		39.3973	2.339	1	2.314	85
	45.7847	1.98	4	1.977	12		46.5847	2.03	1	1.977	12
	77.6477	1.228	1	1.231	2		78.0619	1.218	1	1.231	2
Reference(41-1390)						Reference(41-1390)					
	2(Theta)	dA	rel.Intensity	dA	rel.Intensity		2(Theta)	dA	rel.Intensity	dA	rel.Intensity
Cu <sub>2</sub> (CO <sub>3</sub> )OH <sub>2</sub>	12.4935	7.0852	7	7.37	6	Cu <sub>2</sub> (CO <sub>3</sub> )OH <sub>2</sub>	12.5231	7.381	8	7.37	6
	14.8069	5.9829	4	5.97	84		14.6912	5.971	23	5.97	84
	17.5598	5.0507	4	5.04	96		16.0984	5.039	34	5.04	96
	24.0708	3.6972	3	3.69	100		24.0309	3.692	42	3.69	100
	35.6135	2.5209	2	2.518	55		36.0833	2.519	21	2.518	55
Reference(33-664)						Reference(33-664)					
	2(Theta)	dA	rel.Intensity	dA	rel.Intensity		2(Theta)	dA	rel.Intensity	dA	rel.Intensity
Fe <sub>2</sub> O <sub>3</sub>	24.0708	3.697	3	3.684	30	Fe <sub>2</sub> O <sub>3</sub>	24.7378	3.677	4	3.684	30
	33.2221	2.696	2	2.7	100		34.2921	2.632	2	2.7	100
	35.6135	2.521	2	2.519	70		37.6613	2.515	1	2.519	70
	54.2226	1.69	1	1.694	45		57.2028	1.642	1	1.694	45
Reference(22-712)						Reference(22-711)					
	2(Theta)	dA	rel.Intensity	dA	rel.Intensity		2(Theta)	dA	rel.Intensity	dA	rel.Intensity
Nimite-1M <sub>11b</sub>	6.2292	14.18	5	14.2	25	Willemseite	8.1312	9.231	5	9.4	100
	25.107	3.547	2	3.55	45		27.171	4.348	3	4.57	16
	50.127	1.818	6	1.82	2		51.122	2.511	4	2.503	30
	55.01	1.672	1	1.66	2		56.011	1.664	2	1.7	2

## Attribution of mineral phases in the XRD plots, Figure 4.1

LOW COBALT ORE WITH MICA						LOW COBALT ORE WITHOUT MICA					
Low cobalt ore with mica					Reference(33-1161)	Low cobalt ore without mica					Reference(33-1161)
Mineral phase	2(Theta)	dA	rel.Intensity	dA	rel.Intensity	Mineral phase	2(Theta)	dA	rel.Intensity	dA	rel.Intensity
SiO <sub>2</sub>	21.8113	4.249	12	4.257	22	SiO <sub>2</sub>	20.8565	4.251	11	4.257	22
	25.9856	3.247	100	3.342	100		26.6306	3.249	100	3.342	100
	46.0393	1.978	4	1.979	14		45.9098	1.969	2	1.979	14
	75.9912	1.266	2	1.255	1		75.6514	1.267	3	1.255	1
Reference(7-169)						Reference(7-169)					
	2(Theta)	dA	rel.Intensity	dA	rel.Intensity		2(Theta)	dA	rel.Intensity	dA	rel.Intensity
CoOOH-3R	19.8212	4.218	13	4.384	100	CoOOH-3R	19.8225	4.321	14	4.384	100
	36.2952	2.438	1	2.429	12		36.9523	2.465	2	2.429	12
	38.5862	2.319	7	2.314	85		38.7864	2.322	6	2.314	85
	45.1939	1.972	8	1.977	12		45.8929	1.993	5	1.977	12
Reference(26-1107)						Reference(26-1107)					
	2(Theta)	dA	rel.Intensity	dA	rel.Intensity		2(Theta)	dA	rel.Intensity	dA	rel.Intensity
CoOOH-2H	19.8913	4.367	1	4.39	100	CoOOH-2H	19.9135	4.372	2	4.39	100
	36.5341	2.442	1	2.47	70		36.5544	2.448	1	2.47	70
	38.7761	2.38	2	2.38	50		38.8276	2.361	1	2.38	50
	79.8757	1.186	3	1.199	40		79.6763	1.204	4	1.199	40
Reference(41-1390)						Reference(41-1390)					
	2(Theta)	dA	rel.Intensity	dA	rel.Intensity		2(Theta)	dA	rel.Intensity	dA	rel.Intensity
Cu <sub>2</sub> (CO <sub>3</sub> )OH <sub>2</sub>	12.5236	7.332	3	7.37	6	Cu <sub>2</sub> (CO <sub>3</sub> )OH <sub>2</sub>	12.4993	7.323	4	7.37	6
	14.8271	5.865	2	5.97	84		14.8195	5.902	3	5.97	84
	17.4897	4.987	2	5.04	96		17.5093	4.9772	2	5.04	96
	24.1734	3.683	1	3.69	100		24.2784	3.681	4	3.69	100
Reference(33-664)						Reference(33-664)					
	2(Theta)	dA	rel.Intensity	dA	rel.Intensity		2(Theta)	dA	rel.Intensity	dA	rel.Intensity
Fe <sub>2</sub> O <sub>3</sub>	24.7211	3.652	2	3.684	30	Fe <sub>2</sub> O <sub>3</sub>	25.7108	3.631	3	3.684	30
	33.1432	2.654	2	2.7	100		32.1329	2.633	2	2.7	100
	35.9872	2.523	2	2.519	70		36.7173	2.452	2	2.519	70
	54.5626	1.663	3	1.694	45		55.0229	1.658	1	1.694	45
Reference(22-712)						Reference(22-712)					
	2(Theta)	dA	rel.Intensity	dA	rel.Intensity		2(Theta)	dA	rel.Intensity	dA	rel.Intensity
Nimite-1M <sub>11b</sub>	6.345	13.87	3	14.2	25	Nimite-1M <sub>11b</sub>	6.2932	13.94	4	14.2	25
	25.275	3.546	2	3.55	45		25.147	3.564	5	3.55	45
	52.127	1.812	1	1.82	2		50.138	1.813	3	1.82	2
	55.241	1.657	5	1.66	2		56.031	1.664	6	1.66	2

## APPENDIX 2

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### The least-squares method used for deriving AAS calibration plots.

#### Assumptions:

1. There is a linear relationship between the measured variable (y) and the anion concentration. (ie  $y = mx + c$ , where c is the y-intercept and m the slope of the line).
2. Any deviation of individual points from the straight line results from error in the measurement, not from the calibration standards.

For convenience, three quantities are defined:  $S_{xx}$ ,  $S_{yy}$ , and  $S_{xy}$

Where

$$S_{xx} = \sum x_i^2 - (\sum x_i)^2/N$$
$$S_{yy} = \sum y_i^2 - (\sum y_i)^2/N$$
$$S_{xy} = \sum x_i y_i - (\sum x_i)(\sum y_i)/N$$

Where n is the number of pairs of data used in preparing the calibration curve and (X) and (Y) being the average values for the variables x and y. Five useful quantities were derived from  $S_{xx}$ ,  $S_{yy}$ , and  $S_{xy}$ :

1. the slope of the line  $m$  :

$$m = S_{xy} / S_{xx}$$

2. the intercept  $b$  :

$$b = (Y) - m(X)$$

3. the standard deviation about regression  $S_r$  :

$$S_r = \sqrt{(S_{yy} - m^2 S_{xx}) / (n-2)}$$

4. the standard deviation of the slope  $S_m$  :

$$S_m = \sqrt{S_r^2 / S_{xx}}$$

5. the standard deviation of the intercept  $S_b$  :

$$S_b = S_r \sqrt{[1/n - (\sum x)^2 / \sum x^2]}$$

Product-moment correlation( $r$ ) used to determine the %fit of the calibration graph as follows:

$$\%fit = r^2 \times 100$$

**Calibration data (Absorbance) derived from the AAS instrument for cobalt**

[Co] (ppm)	Absorbance	Statistical treatment		
(x)	(y)	$x^2$	$y^2$	xy
0	0	0	0	0
0.5	0.047	0.25	0.002209	0.0235
1	0.091	1	0.008281	0.091
2	0.161	4	0.025921	0.322
5	0.339	25	0.114921	1.695
10	0.506	100	0.256036	5.06
N=6				
(X)	(Y)	$\Sigma x^2$	$\Sigma y^2$	$\Sigma xy$
3.08333	0.19066	130.25	0.407368	7.1915

$$\begin{aligned} S_{xx} &= \Sigma x_i^2 - (\Sigma x_i)^2/N \\ &= 130.25 - (18.5)^2/6 \\ &= 73.20833333 \end{aligned}$$

$$\begin{aligned} S_{xy} &= \Sigma x_i y_i - (\Sigma x_i)(\Sigma y_i)/N \\ &= 7.1915 - (18.5)(1.144)/6 \\ &= 3.664166667 \end{aligned}$$

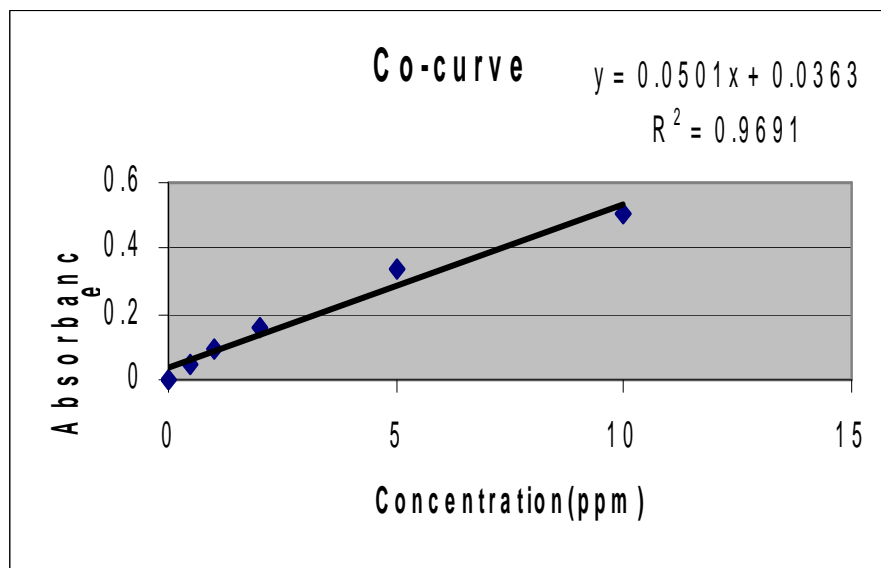
$$\begin{aligned} m &= S_{xy} / S_{xx} \\ &= 0.05005 \end{aligned}$$

$$\begin{aligned} b &= (Y) - m(X) \\ &= 0.190666666 - 0.050051223(3.083333333) \\ &= 0.03634 \end{aligned}$$

**Equation of the straight line derived by method of linear regression**

$$y = 0.0501x + 0.0363$$

### Calibration curve for cobalt analysis using AAS



The same procedure was followed to derive calibration curves for copper and iron.

### Calculations

Weighed 1.025g of finely ground *low cobalt ore (with mica)*, dissolved it completely in aqua-regia, transferred and diluted it into a 250ml volumetric flask. Analysis of the resulting solution after a further 20x dilution using AAS gave Co concentration of 8.124 parts per million (ppm):

- ◆ Calculation of percentage cobalt in the *low cobalt ore(with mica)*

$$8.124\text{ppm} = 8.124 \text{ mg/L}$$

$$8.124 \text{ mg/L} \times 20 = 162.48 \text{ mg/L}$$

$$162.48 \text{ mg/L} \times 0.25 \text{ L} = 40.62 \text{ mg}$$

$$40.62 \text{ mg} = 0.04062 \text{ g of cobalt in solution}$$

$$\begin{aligned}\% \text{ Co in ore} &= \text{grams of Co in solution} \div \text{grams of the ore weighed} \times 100 \\ &= 0.04062 \text{ g} \div 1.025 \text{ g} \times 100 \\ &= 3.963 \% \text{ Co in the low cobalt ore (with mica)}\end{aligned}$$


After leaching the ore for 30 minutes, only 0.5893 % Co was recovered in solution.

◆ Calculating for % Co dissolution with respect to the low cobalt ore :

$$\% \text{ Co in ore} = 3.963$$

$$\% \text{ Co in solution} = 0.5893$$

$$\% \text{ Co dissolution} = \% \text{Co in solution} \div \% \text{Co in ore} \times 100$$

$$\begin{aligned}&= 0.5893\% \text{ Co in solution} \div 3.963\% \text{ Co in ore} \times 100 \\ &= 14.87\%\end{aligned}$$
The logo of the University of Johannesburg is visible in the background, featuring two stylized orange birds with their wings spread, facing each other. To the right of the birds, the text 'UNIVERSITY OF JOHANNESBURG' is written in a light grey, sans-serif font, with 'OF' centered between two horizontal lines.

Calculations for copper and iron in ore and after leaching were carried out in the same fashion.



### APPENDIX 3

#### Data derived from the leaching process of cobalt

NON MICROWAVE TREATED SAMPLES					MICROWAVE TREATED SAMPLES				
Figure 4.2					Figure 4.11				
High cobalt ore					High cobalt ore				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	7	76	79	94	30	28.89	78	84	96
60	8	76	91	93	60	30.42	79	94	97
90	10	77	90	98	90	32.89	82	93	98
120	10	79	86	97	120	33.97	82	94	97
High copper ore					High copper ore				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	28	77	79	70	30	40.94	79	82	72
60	29	75	79	71	60	41.38	80	83	74
90	31	76	80	72	90	42.07	81	82	76
120	31	77	80	74	120	41.98	80	84	76
low co with mica					low co with mica				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	14.87	85.54	77.23	95.53	30	50.04	96.09	80.13	97.12
60	19.1	95.28	78.42	97.5	60	53.24	96.57	81.7	97.58
90	19.44	95.53	79.93	97.8	90	54.4	97.45	82.3	99.19
120	20.23	96.37	78.9	98.31	120	55.29	97.86	81.26	99.22
low co without mica					low co without mica				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	16.54	85.13	69.89	90.57	30	40.14	88.12	72.37	93.97
60	17.43	87.56	70.95	91.99	60	40.98	89.45	74.08	94.89
90	18.68	87.85	72.87	91.78	90	41.67	90.61	74.24	96.73
120	19.97	87.84	73.98	91.86	120	41.58	92.38	74.19	96.81

## Data derived from the leaching process of copper

NON MICROWAVE TREATED SAMPLES					MICROWAVE TREATED SAMPLES				
Figure 4.6					Figure 4.15				
High cobalt ore					High cobalt ore				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	88	71	93	97	30	92	70	92	98
60	90	72	96	97	60	93	73	94	99
90	91	72	97	98	90	95	74	98	98
120	94	72	97	99	120	94	73	97	98
High copper ore					High copper ore				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	82	62	87	92	30	98	65	88	94
60	85	67	85	92	60	97	67	89	93
90	86	69	86	93	90	98	66	88	95
120	86	70	87	92	120	98	65	90	95
low co with mica					low co with mica				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	70	37	34	96	30	89.29	43	37	99.09
60	79	36	33	94	60	92.28	45	38	99.15
90	84	37	34	99	90	93.66	44	37	99.35
120	77	40	34	93	120	93.91	46	39	99.71
low co without mica					low co without mica				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	97	41	85	75	30	98	42	88	77
60	97	44	87	85	60	97	45	95	79
90	99	46	94	91	90	99	44	98	79
120	95	57	98	99	120	99	44	98	78

## Data derived from the leaching process of iron

NON MICROWAVE TREATED SAMPLES					MICROWAVE TREATED SAMPLES				
Figure 4.7					Figure 4.16				
High cobalt ore					High cobalt ore				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	8	0.4	25	21	30	10.18	12.59	32	13.05
60	9	0.4	32	25	60	10.37	13	34	13.74
90	10	1	36	27	90	10.83	13.69	38	14.41
120	11	1	39	29	120	10.97	13.99	37	14.9
High copper ore					High copper ore				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	2	2	8	3	30	5	8	13	7
60	2	2	11	4	60	7	9	15	8
90	2	2	14	5	90	6	10	16	8
120	2	2	14	6	120	6	10	16	9
low co with mica					low co with mica				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	2	3	4	7	30	7	10	8	13
60	2	4	5	8	60	8	12	7	15
90	3	4	5	9	90	9	11	8	14
120	3	4	5	9	120	9	12	8	14
low co without mica					low co without mica				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	2	1	3	3	30	6	10	13	11
60	2	2	3	4	60	7	12	13	10
90	2	2	4	4	90	8	11	14	10
120	2	2	4	4	120	8	12	14	11

## APPENDIX 4

### Data derived from UV/Visible experiments

Non microwave treated samples Figure 4.5			Microwave treated samples Figure 4.14		
<b>High cobalt ore</b>			<b>High cobalt ore</b>		
<b>Time(min)</b>	<b>Co<sup>3+</sup></b>	<b>Co<sup>2+</sup></b>	<b>Time(min)</b>	<b>Co<sup>3+</sup></b>	<b>Co<sup>2+</sup></b>
0	25.3	8.14	0	25.3	8.16
5	25.2	8.26	5	24.8	8.21
10	22.4	11.5	10	22.6	9.9
15	17.4	15.5	15	19.1	13.1
20	12.3	21.1	20	17.7	15
25	7.5	24.9	25	16.8	16.6
30	6.3	28.1	30	15.1	18.6
<b>High copper ore</b>			<b>High copper ore</b>		
<b>Time(min)</b>	<b>Co<sup>3+</sup></b>	<b>Co<sup>2+</sup></b>	<b>Time(min)</b>	<b>Co<sup>3+</sup></b>	<b>Co<sup>2+</sup></b>
0	0	0.436	0	0	0.436
5	0	0.435	5	0	0.436
10	0	0.434	10	0	0.435
15	0	0.435	15	0	0.436
20	0	0.436	20	0	0.434
25	0	0.435	25	0	0.436
30	0	0.435	30	0	0.435
<b>low co with mica</b>			<b>low co with mica</b>		
<b>Time(min)</b>	<b>Co<sup>3+</sup></b>	<b>Co<sup>2+</sup></b>	<b>Time(min)</b>	<b>Co<sup>3+</sup></b>	<b>Co<sup>2+</sup></b>
0	0	1.985	0	1.981	0.836
5	5	1.962	5	1.972	0.824
10	10	1.8	10	1.81	0.96
15	15	1.74	15	1.79	1
20	20	1.51	20	1.74	1.1
25	25	0.92	25	1.61	1.18
30	30	0.619	30	1.589	1.231
<b>low co without mica</b>			<b>low co without mica</b>		
<b>Time(min)</b>	<b>Co<sup>3+</sup></b>	<b>Co<sup>2+</sup></b>	<b>Time(min)</b>	<b>Co<sup>3+</sup></b>	<b>Co<sup>2+</sup></b>
0	2.948	0.977	0	2.949	0.972
5	2.69	1.24	5	2.846	1.06
10	2.26	1.68	10	2.73	1.16
15	1.9	1.76	15	2.48	1.5
20	1.3	2.48	20	2	1.8
25	1	2.95	25	1.78	1.9
30	0.813	3.215	30	1.611	2.314

## APPENDIX 5

### Data derived from precipitation experiments

NON MICROWAVE TREATED SAMPLES					MICROWAVE TREATED SAMPLES				
Figure 4.8					Figure 4.17				
High cobalt ore					High cobalt ore				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	10	14	11	12	30	8	12	13	14
60	12	15	11	11	60	9	13	15	13
90	14	17	12	12	90	10	14	16	14
120	15	17	11	12	120	10	14	16	14
High copper ore					High copper ore				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	33	35	32	31	30	35	34	34	32
60	34	35	33	32	60	36	33	35	31
90	34	35	33	33	90	35	34	35	31
120	34	35	33	33	120	35	34	35	32
low co with mica					low co with mica				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	23	25	21	22	30	25	27	23	21
60	24	26	22	22	60	26	26	24	25
90	24	28	22	22	90	27	28	25	26
120	24	28	22	23	120	26	28	25	26
low co without mica					low co without mica				
Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>	Time(min)	H <sub>2</sub> SO <sub>4</sub> -only	H <sub>2</sub> SO <sub>3</sub> -only	SO <sub>2</sub> +H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> + SO <sub>2</sub>
0	0	0	0	0	0	0	0	0	0
30	20	21	18	18	30	23	23	20	19
60	20	24	19	19	60	22	24	21	21
90	21	25	18	19	90	23	24	20	21
120	21	25	19	19	120	24	24	20	21

