Investigating the effect of counter-current precipitation of cobalt hydroxide on its quality and MgO consumption rate

by

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7th March 2023

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ABSTRACT

In this work, a different configuration for precipitating cobalt hydroxide is investigated and presented in order to enhance the cobalt hydroxide quality and maximize the utilization of magnesium oxide. The proposed configuration includes a precipitation step in presence of sodium sulphate using magnesium oxide to recover cobalt from cobalt-bearing solution, followed by a cobalt hydroxide washing step to fully utilize the excess or residual magnesium oxide using acidic cobalt-bearing solution. The results of precipitation experiments showed that using 4g/L of sulphate ions at 25°C, a magnesia dosage of 1.10g of MgO/g Co, and precipitation duration of 4 hours, approximately 99% of cobalt can be recovered in the precipitation step while leaving 87% of the manganese in solution. The equilibrium pH at precipitation stage was 8.42. The washing experiments' findings demonstrated that the cobalt hydroxide quality could be significantly improved by using an acidic cobalt sulphate solution as the washing solution, with cobalt upgrading of approximately 8% at 45°C, a washing solution volume of 350ml, and a washing time of 4 hours. The equilibrium pH at washing stage was 7.36. The ability of cobalt sulphate solution to lower or remove the excess or undissolved magnesium oxide which enhances the upgrading of cobalt hydroxide while maximizing the MgO usage was demonstrated. A reduction in magnesium oxide consumption rate of roughly 18% was evaluated as the effect of washing.

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NOMENCLATURE

MgO: magnesium oxide

AAS: Atomic Absorption Spectroscopy

LECO: Laboratory Equipment Corporation

ICP-AES: Inductively Coupled Plasma Atomic Emission Spectroscopy

Wt.%: weight percent

HCO_3^-: bicarbonate

Na_2SO_4: sodium sulphate

Ks: solubility product

$NaOH$: caustic soda

Mn: manganese

SMBS: sodium metabisulphite

Mg: magnesium

Co: cobalt

MHP: mixed hydroxide precipitates

EW: electrowinning

ORP: redox potential

$Co(OH)_2$: cobalt hydroxide

SO_2: Sulphur dioxide

g: gram

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

Cobalt is a valuable metal that is extensively considered in industrial applications. In the past years, cobalt was only used as a pigment in glass manufacture. It is also employed in super-alloys production as an additive. Super alloys containing cobalt have special properties that allow them to maintain their properties at high temperatures, including corrosion resistance, strength, and magnetic properties. This makes them ideal for use in the production of gas turbine engines and spare parts for spacecraft, petroleum, and chemical plants, as well as rechargeable batteries (Boland and Kropschot, 2011).

In combined copper-cobalt ores contained in quartz (SiO_2) or dolomite ($MgCO_3.CaCO_3$) gangue, cobalt minerals are found in association with copper in the Central African Copperbelt region, which stretches from Zambia to the Democratic Republic of the Congo. As a result, the paths for extracting copper and cobalt from their ores are linked in this area. The hydrometallurgical route for processing oxidized copper-cobalt ores requires a leaching step using sulphuric acid in combination with a reducing agent such as sulfur dioxide (Mwema et al., 2002; Ferron, 2008), ferrous ions (Apua and Mulaba-Bafubiandi, 2011), sodium metabisulphite (Crundwell et al., 2011). Welham et al. (2015) used sodium sulphite and ammonium sulphite and thiosulphate to leach off the trivalent state cobalt, which is insoluble in aqueous solution. On the other hand, some unwanted metallic species are simultaneously dissolved into solution notably, iron, manganese, zinc, and aluminum. Copper can be extracted from the pregnant liquor solution by use of solvent extraction and some impurities metals can be lowered or removed from the solution in sequence driven by their solubility products using a multi-stage selective precipitation method before cobalt recovery.

Cobalt hydroxide precipitation using magnesium oxide (MgO) is increasingly being used to recover the cobalt as a valuable by-product of the processing of copper ores. On another point, cobalt precipitation in form of cobalt hydroxide compound is widely used in hydrometallurgy processes as a purification method in the processing of nickel ores to produce mixed hydroxide precipitates (MHP) and as a means of upgrading the cobalt concentration before cobalt electrowinning (White, 2009).

Hydrolytic precipitation using magnesia (MgO) as a precipitating agent is the predominant method currently employed to effectively recover cobalt from purified acidic sulphate leach liquors (Jones & Miller, 2002). However, this technique tends to result in significant unreacted magnesium and high co-precipitation of manganese in the cobalt hydroxide produced. Moreover, the undissolved magnesium oxide in the final product represents an inefficient use of a relatively expensive reagent and increases the operating cost in downstream processing and transport.

1.2 PROBLEM IDENTIFICATION

The classic technique employed to recover cobalt from purified cobalt-containing aqueous solution using magnesium oxide as an alkaline agent to raise the pH of the solution, and then precipitate the cobalt as cobalt hydroxide results in significant presence of unreacted magnesia as well as co-precipitation of manganese in precipitates. This, however, affect the quality of cobalt hydroxide produced when high cobalt recovery is targeted. Secondly, the residual magnesium oxide in the cobalt hydroxide represents an inefficient utilization of a costly precipitating agent and increases the operating cost in downstream processing and transport. These problems have been observed in most of the mines producing cobalt hydroxide using magnesium oxide in the Central African Copperbelt region. Although the cobalt hydroxide quality could be enhanced by preferentially precipitating the majority of cobalt in the first step and minimizing manganese precipitation by adding a predetermined amount of magnesia, this requires a further increase of pH using mainly lime to recover the remaining cobalt in the second step as a contaminated solid which can then be recycled back to maintain the overall recovery. This however leads to extra input flow rate and cost of lime used.

To ensure a high quality of cobalt hydroxide while maximizing the cobalt recovery and magnesia utilization, it is becoming important to investigate an alternative technique of hydrolytic precipitation that can eliminate or control the difficulties associated with the classic technique of cobalt hydroxide precipitation using magnesium oxide as the pH-modifying agent. Therefore, this research investigates the effect of counter-current precipitation in presence of sodium sulphate as an alternative technique.

The counter-current precipitation technique consists of precipitating cobalt from purified sulfate aqueous solution via a series of two precipitation stages coupled with solid-liquid separation steps which are arranged to give counter-current flows of solid (MgO) and the feed solution to maximize the utilization of pH-modifier agent while expecting to re-dissolve impurities into solution. In this configuration, the fresh solution is contacted with impure cobalt hydroxide so that at each end the strongest stream is acting upon the most depleted stream of the other.

By washing the cobalt hydroxide precipitates with a cobalt-bearing solution, the equilibrium pH is lowered to remove the residual magnesium oxide from cobalt hydroxide precipitates. Thermodynamic data indicates that at basic pH and in presence of sodium sulphate, manganese sulphate complexes are stable in an aqueous solution. This means that when precipitating cobalt from a cobalt-bearing solution containing traces of leached manganese, this can be discarded into the effluent without contaminating the cobalt hydroxide precipitates.

This approach fully utilizes the neutralizing potential of magnesia added in the first stage and lowers the level of different contaminants in the final cobalt hydroxide produced. This work investigates the benefit of using the counter-current precipitation technique to ensure a suitable cobalt recovery, and magnesium oxide utilization and improves the cobalt hydroxide quality.

1.3 RESEARCH OBJECTIVE (S)

This research aims at investigating an alternate setup for cobalt hydroxide precipitation in order to improve the quality of precipitates generated while also maximizing cobalt recovery, minimizing manganese co-precipitation, and utilizing magnesium oxide to the fullest extent possible. The specific objectives are:

- To optimize the precipitation conditions which maximize the cobalt recovery while leaving manganese in solution by varying MgO dosage, sodium sulphate concentration and temperature.

- To investigate the feasibility of washing the recovered cobalt hydroxides with cobalt feed solution at various washing volume and temperature to maximize the usage of magnesium oxide while upgrading cobalt hydroxide precipitates.
- To assess the cost-savings potential in term of magnesium oxide consumption rate related to the effect of washing the cobalt hydroxide precipitates.
- To assess the precipitation and washing processes in order to propose a potential substitute method for precipitating cobalt as hydroxide using magnesium oxide.

1.4 RESEARCH QUESTIONS

The following are some questions that this study needs to address:

- Which precipitation conditions will maximize the cobalt recovery?
- To what extent can manganese be prevented from hydrolysis and precipitation in solution when precipitating in excess of sulphate ions?
- Which washing conditions will result in a significant reduction of MgO content in hydroxide precipitates?
- To what percentage can MgO consumption be reduced when precipitation and washing processes are combined.

1.4.1. Research approach

To arrive at a meaningful answer to the research questions, the following methodology is necessary:

- Analysis of feed solution for cobalt, manganese, and magnesium using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).
- Run the cobalt precipitation tests at varied operating conditions such as magnesia dosage ratio to determine the optimum parameters resulting in a maximum recovery of the cobalt.
- Conduct the cobalt precipitation tests in presence of sodium sulphate ions to investigate the effects of sulphate ions on the rate of the manganese co-precipitation.

- Re-contact the resultant precipitates at optimum conditions with a varied volume of feed solution to determine the optimum wash solution volume expected to improve the cobalt hydroxide quality by re-dissolving the maximum of magnesia and manganese.
- Conduct the cobalt precipitation experiments on intermediate effluent generated at the washing stage at various MgO dosage ratios to evaluate the reduction in MgO consumption rate. This can be realized at plant scale by counter-current precipitation configuration.
- Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) were used to analyse the resulting precipitates and solutions for cobalt, manganese, and magnesium.
- Making use of the information from ICP-AES to calculate the effectiveness of the tested conditions' precipitation.

1.5 DISSERTATION LAYOUT

The report is divided into five chapters. These are:

- Chapter I: Introduction and research motivation.
- Chapter II: Literature review.
- Chapter III: Experimental methodology
- Chapter IV: Results and discussions
- Chapter V: Conclusions and recommendations.

CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

The goal of this literature study is to explore the methods currently being utilized in industry to extract cobalt specifically through hydrometallurgy processing techniques. Furthermore, this section will debate the previously published research works done on the hydrolytic precipitation of cobalt to see how their findings can benefit this study.

2.2 PROCESSING COBALT-BEARING ORES IN AFRICAN COPPERBELT

Cobalt occurs in the Central African Copperbelt region either as sulphide (carrolite: Co_2CuS_4) or oxide (heterogenite: CoOOH) minerals in association with copper minerals respectively hosted in dolomite or silica gangue (Crundwell et al, 2011; Cailteux et al., 2005 and Dewaele et al., 2006). The sulphide cobalt-bearing materials are generally processed through flotation to discard the unwanted minerals before roasting. Cobalt and copper are usually extracted from oxidized ores or roasted concentrate materials via a hydrometallurgical processing route in which the materials are preferentially leached in sulfuric acid under reducing conditions using sulphur dioxide, ferrous ions, sodium metabisulphite, ammonium thiosulphate, and sodium sulphite to bring trivalent cobalt (Co_2O_3) into solution. Sodium metabisulfite is commonly used for this purpose.

Leaching in sulphuric acid is commonly used due to its availability and relatively cheaper cost (Mwema et al, 2002; Crundwell et al, 2011). The indiscriminate nature of acid leaching results in the co-extraction of numerous undesired elements notably, Mn, Mg, Al, Ca, Fe, and Si necessitating a subsequent step of purification to remove these unwanted elements from cobalt-bearing solution before recovery of the cobalt as cathodic cobalt or cobalt hydroxide (Welham et al., 2009).

Copper is selectively and effectively extracted using copper solvent extraction followed by electrowinning to produce high-grade copper cathodes. The most commonly used method of removing the remaining impurities from cobalt-bearing solution is selective precipitation steps. In this method, iron, aluminum, and some manganese are simultaneously precipitated by the injection of a combination of air and sulfur dioxide to maintain the potential above 600mV and the addition of an alkaline reagent, such as quick lime, hydrated lime, or ground limestone slurry to bring the pH up to between 3.0 to 3.5. The oxidative precipitation of manganese using an air/sulfur dioxide mixture is a relatively cheap method of removing manganese from cobalt-bearing solution and offers the best selectivity at a lower pH range of 3 to 6 (Zhang et al, 2007). The excess acid from the leach discharge solution and the generated acid at the solvent extraction is also neutralized at this step.

In the following step, the residual copper is removed by further addition of an alkaline reagent to raise the pH to between 5.0 to 5.2 to precipitate most of the copper content in the aqueous solution (Crundwell and al, 2011). Since the sequence of hydrolytic precipitation of metals is governed by their solubility product, magnesium and manganese will remain in the cobalt-bearing solution. The purified aqueous solution is then processed through a final precipitation step to recover cobalt as a hydroxide using magnesium oxide to bring up the pH to about 8.2. The precipitates obtained are settled, filtered, and dried before shipment. In mining engineering 2/1984, Schiller and Khalafaller described the use of magnesium oxide and its advantages over lime for the precipitation of metals from an aqueous solution. The effect of ageing of magnesium oxide slurry, its efficiency, and the filterability of hydroxide product obtained have been mentioned as well.

A typical process flowsheet for cobalt extraction from oxidized ores using the hydrometallurgical process route is shown in Figure 2.1 below:

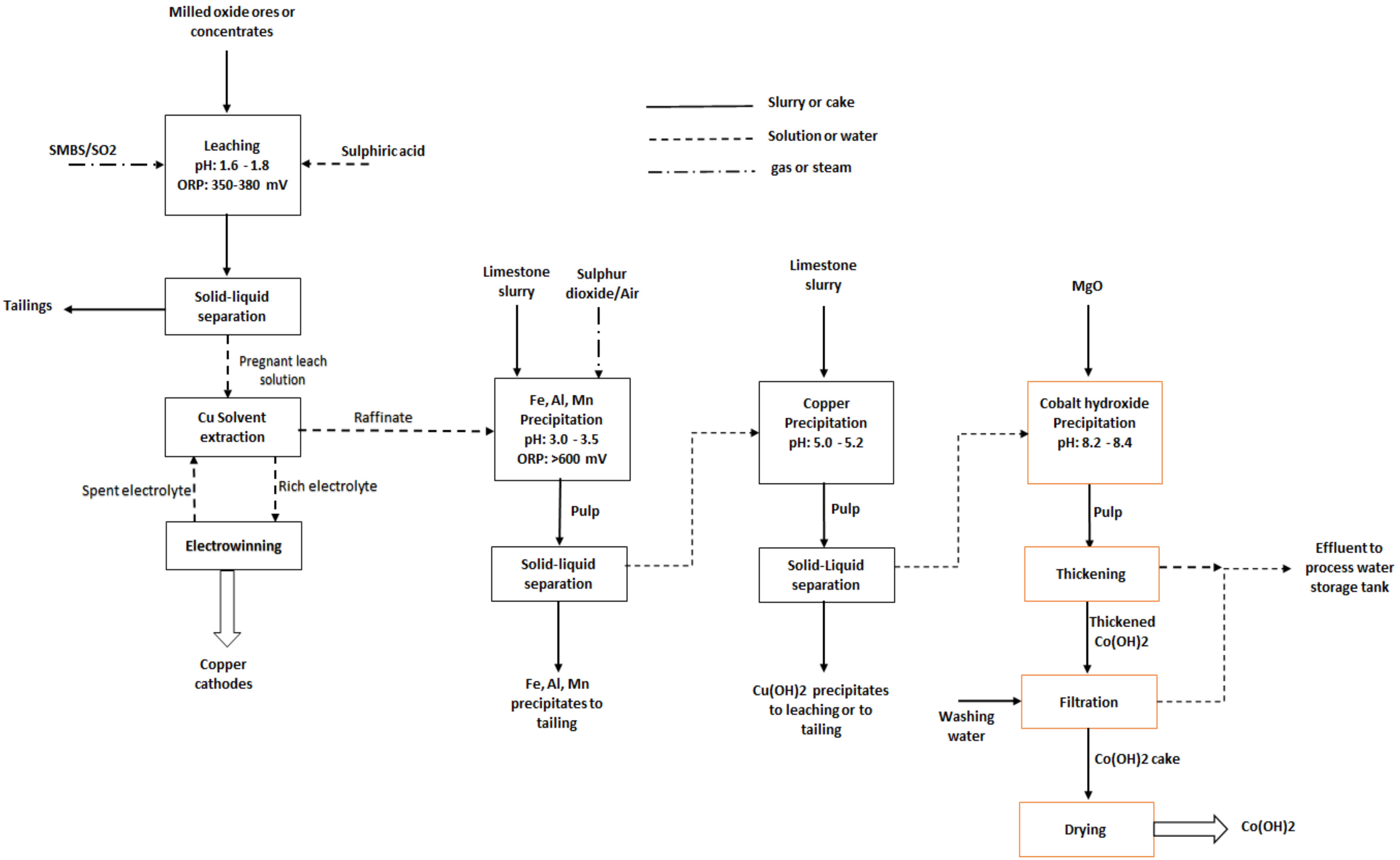

Figure 2.1: Typical hydrometallurgical process flowsheet for cobalt extraction from oxidized ores

Because cobalt tends to slag with iron during smelting, Crundwell et al. (2011) and Fischer (2011) claim that the pyrometallurgical procedures pathway for extracting cobalt results in large losses to slag between 25 to 80%. For this reason, the hydrometallurgical process route for cobalt extraction seems to be more attractive compared to the smelting process route. However, it is possible to lose significant amounts of cobalt up to 50% during the multi-stage precipitation steps, therefore rigorous process control is necessary (Welham et al, 2015).

In the aqueous treatment of cobalt, the purified cobalt-bearing aqueous solution is either subjected to final precipitation as cobalt hydroxide precipitates using alkaline reagent to raise the pH to at least 8.2 to precipitate cobalt as hydroxide or followed by re-leaching with sulphuric acid which aims at achieving an adequate cobalt concentration in rich electrolyte before electrowinning for cobalt metal (Louis, 2009; Roux et al, 2009). This results in an uneconomical high consumption rate of sulphuric acid.

2.3 THERMODYNAMICS OF THE HYDROLYTIC PRECIPITATION

2.3.1 Principles of hydrolytic precipitation

Precipitation is a physical-chemical process in which soluble metals and inorganics are transformed into relatively insoluble metals and inorganic salts (precipitates) by the addition of a precipitating agent. The precipitation of finely sparingly soluble component MA in water is governed by the solubility product, the soluble cations in solution precipitate up to attaining the equilibrium state of the reaction. For a given reaction in a diluted solution, the activities of ions are equal to a unit. The solubility product K_s can be expressed by:

$$[M]^m \times [A]^n = Ks \qquad \text{(Eq. 2.1)}$$

Where:

- $[M]$ and $[A]$ are the concentration of ions.
- m and n are stoichiometric numbers.

If $[M]^m \times [A]^n < K_s$, the solid compound will dissolve up to attaining the saturation state of the reaction.

If $[M]^m \times [A]^n > K_s$, the solid compound will precipitate up to attaining the equilibrium state of the reaction.

Metals hydroxides and hydrated ions are the most common forms of precipitation salts and can be represented by the following general equations (Hydrometallurgical fundamentals course notes, chapter 9, Minerals Council of Australia, Murdoch university),

$$M^{n+} + nOH^- \Leftrightarrow M(OH)_n \qquad \text{(Eq. 2.2)}$$

$$M^{n+} + nH_2O \Leftrightarrow M(OH)_n + nH^+ \qquad \text{(Eq. 2.3)}$$

The equilibrium constant can be written as:

$$K_1 = \frac{1}{[M^{n+}] \times [OH^-]^n} = \frac{1}{K_s} \qquad \text{(Eq. 2.4)}$$

$$K_2 = \frac{[H^+]^n}{[M^{n+}]} = Kw \times K_1 = \frac{Kw}{K_s} \qquad \text{(Eq. 2.5)}$$

Where Ks is the solubility product and Kw is the ionic product of water (Kw= 10^{-14} at 25°C).
The most convenient method to graphically represent this equilibrium is the solubility diagram or Monhemius precipitation diagram which consists of expressing the above equations in the following form.

$$\log[M^{n+}] = \log K_s - n \times \log Kw - n \times pH \qquad \text{(Eq. 2.6)}$$

This results in a linear relationship $\log[M^{n+}]$ as shown below for several metal ions. This describes the basics of selective precipitation.

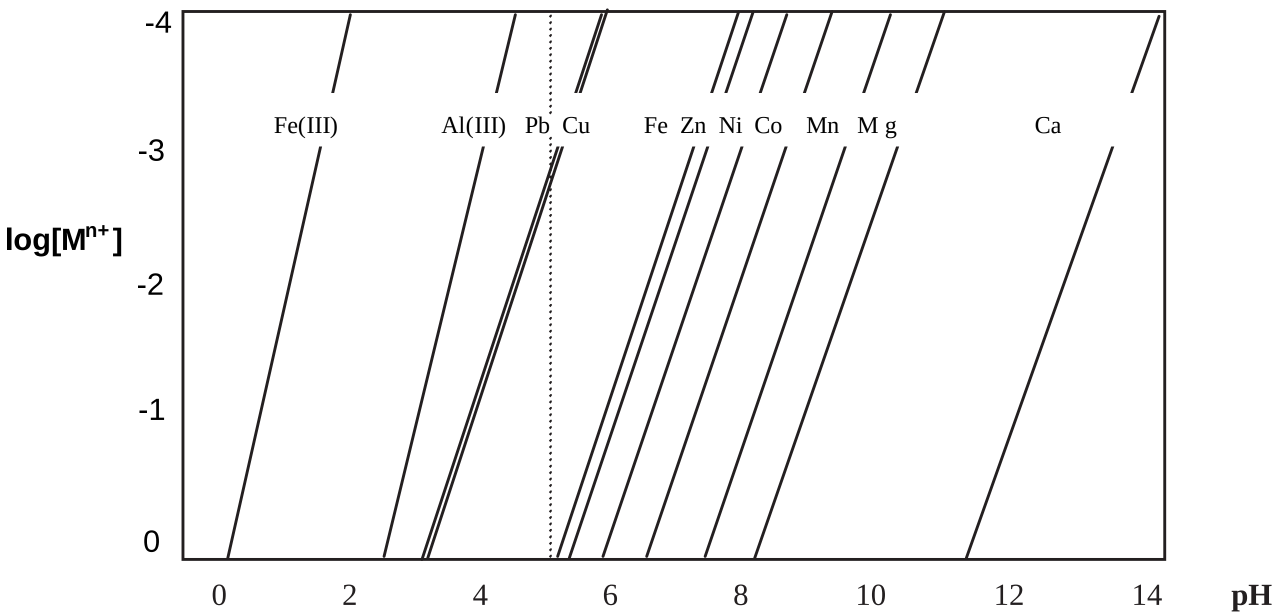

Figure 2.2: Hydroxide precipitation diagram, 25˚C (adapted from Monhemius, 1977)

In this diagram, the elements on the left side of the dotted line will undergo precipitation whereas those on the right side remain stable at pH shown by the dotted line. This means iron and aluminum will be quantitively precipitated while copper and lead will be partially precipitated with a residual ionic concentration in a solution of about 10^{-3} M, and all other metal ions to the right side will be soluble.

2.3.2 Factors influencing the solubility of soluble salts

a) Effect of the concentration of hydrogen ions

The solubility of salt formed from alkali or weak acids is influenced by the concentration of hydrogen ions in the solution. One we can consider the following reaction:

$$MA_n \leftrightarrow M^{n+} + nA^- \qquad \text{(Eq. 2.7)}$$

Since A^- comes from a very weak acid, the following can be written after substitution:

$$K_s = [M^{n+}] \times \alpha^n \times (C_A)^n \qquad \text{(Eq. 2.8)}$$

$$C_A = [A^-] + [HA] \qquad \text{(Eq. 2.9)}$$

C_A represents the total concentration of the ions A^- in solution. The dissociated fraction of the ions A^- can be expressed by the following equation.

$$\alpha = \frac{K_A[HA]}{[H^+]\left(\frac{K_A[HA]}{[H^+]}+[HA]\right)} \quad \text{(Eq. 2.10)}$$

This can be used to determine the solubility of the salt at a given concentration of hydrogen ions.

b) Effect of identical ions

if the concentration of the residual ions is significantly higher than the concentration given by the solubility of the compound, then the solubility is negligible.

$$S = \sqrt[n]{\frac{K_S}{C_M^m \times n^n}} \quad \text{(Eq. 2.11)}$$

Where m and n are the corresponding stoichiometric coefficients of the dissociated cation and anion. Residual concentration of the ions M^+ is denoted by C_M.

c) Effect of hydrolysis of the cation

The precipitated salt's solubility is affected by the extent to which the metals' cations are hydrolyzed in an aqueous solution. The cation hydrolyses in an aqueous solution according to the following equations:

$$M^{n+} + H_2O \leftrightarrow MOH^{n-1} + H^+ \quad \text{(Eq. 2.12)}$$

$$K_1 = \frac{[H^+][MOH^{n-1}]}{[M^{n+}]} \quad \text{(Eq. 2.13)}$$

$$MOH^{n-1} + H_2O \leftrightarrow M(OH)_2^{n-2} + H^+ \quad \text{(Eq. 2.14)}$$

$$K_2 = \frac{[H^+][M(OH)_2^{n-2}]}{[MOH^{n-1}]} \quad \text{(Eq. 2.15)}$$

From the above equation, the total concentration of the cation M is denoted by C_M can be expressed as follows:

$$C_M = [M^{n+}] + [MOH^{n-1}] + [M(OH)_2^{n-2}] \tag{Eq. 2.16}$$

And then the fraction of M which is in the ionic state M^{n+} denoted by α can be expressed as follows:

$$\alpha = \frac{[M^{n+}]}{[M^{n+}]+[MOH^{n-1}]+[M(OH)_2^{n-2}]} \tag{Eq. 2.17}$$

The solubility product for MA_n salt is defined as

$$K_S = [A^-]^n \times C_M \times \alpha \tag{Eq. 2.18}$$

K$_1$ and K$_2$ are the constants of progressive hydrolysis. In hydrometallurgy, the iron can undergo hydrolysis to form $Fe(OH)^{2+}$, $Fe(OH)_2^+$, and $Fe(OH)_2^{4+}$. The hydrolysis of Al^{3+} is more complex, in addition to the ions $Al(OH)^{2+}$ and $Al(OH)_2^+$, we can find in the solution the polymeric anions $Al_2(OH)_4^{4+}$, $Al_3(OH)_6^{3+}$ and larger complexes. For instance, $Al_{13}(OH)_{32}^{7+}$ (Bard A.J; Faulkner L.R, 2000).

d) Effect of the formation of complexes

The metal ion might not precipitate in the solid phase if a stable complex is present. This is mainly determined by the ratio of complex constant and solubility product. Considering the below reaction:

$$MA \leftrightarrow M + A \qquad K_S = [M][A]$$

In presence of a complexing agent, we can get the following reactions.

$$M + L \leftrightarrow ML \qquad \beta_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \leftrightarrow ML_2 \qquad \beta_2 = \frac{[ML_2]}{[ML][L]}$$

$C_M = [M] + [ML] + [ML_2]$ represents the total concentration of M. Therefore, the fraction of ions M not bounded in the complex is denoted by α.

$$\alpha = \frac{[M]}{[C_M]} = \frac{1}{1+\beta_1[L]+\beta_1\beta_2[L]^2} \qquad \text{(Eq. 2.19)}$$

The following equation can be used to express the solubility product K_S:

$$K_S = [M] \times [A] = \alpha \times C_M \times [A] \qquad \text{(Eq. 2.20)}$$

2.3.3 Overview and significance of $Mn - H_2O$ diagram

A stability-field or Pourbaix diagram is a graphical means of representing the relative stabilities zone of specified soluble ions or solid-phase species of an element in presence of water as a function of electrode potential and hydrogen-ion concentration of the system at equilibrium. In other words, the Pourbaix diagram shows in clear form the prevailing species of an element that can be found under certain conditions of the system. The tables of thermodynamics data can be used to establish if reactions are thermodynamically feasible and define the approximate conditions under which reactions are likely to take place. The diagrams are generally established for a pressure of 1 atm and a temperature of 25°C and any deviations below or above or below the above-mentioned conditions will introduce minor or serious errors. This should be kept in mind when interpreting. $Mn - H_2O$ diagram is depicted in Figure 2.3.

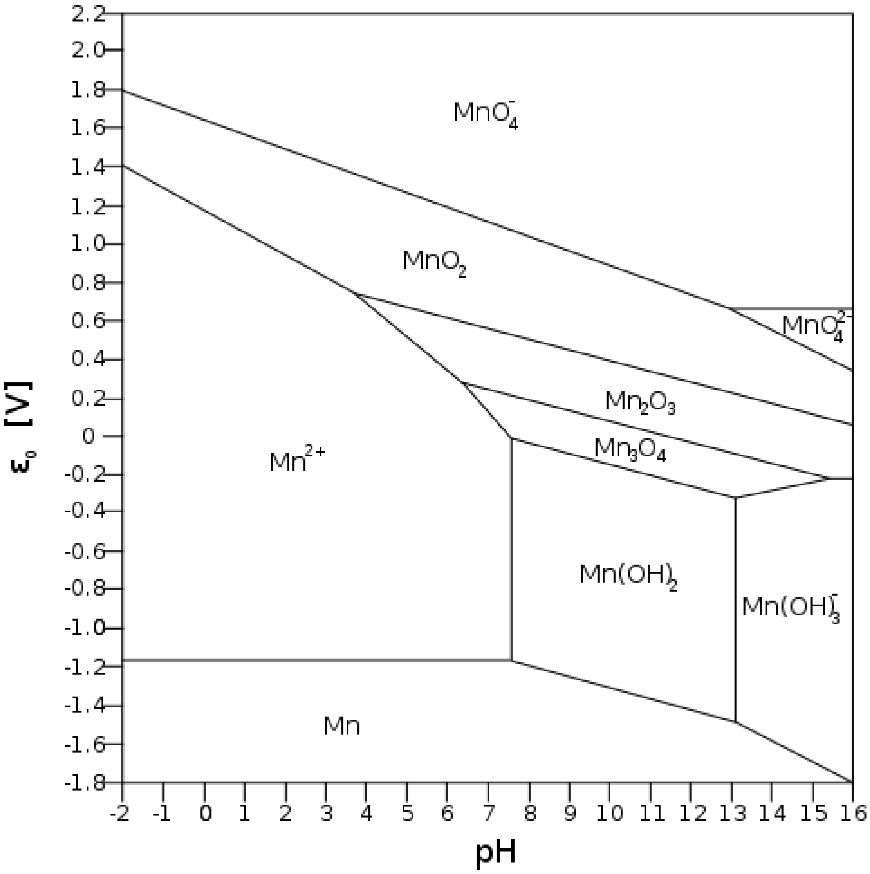

Figure 2.3. Pourbaix diagram Mn-H_2O

When considering the cobalt hydroxide precipitation pH range, as can be observed, at a pH range between 7.5 to 13 and a potential of stability of water, manganese is not stable in aqueous solution and co-precipitate together with the cobalt under the same conditions. The stability-field or Eh-pH diagram of manganese indicates the presence of four solids phases of manganese, notably MnO_2, Mn_2O_3, Mn_3O_4 and $Mn(OH)_2$ and the fields of the dominance of dissolved species of manganese considered are Mn^{2+}, $MnOH^+$ and the anionic form $HMnO_2^-$. All of these are varieties of divalent manganese. Within the water-stability area and a pH above 8, MnO_2, Mn_2O_3, Mn_3O_4 and $Mn(OH)_2$ solid species are stable depending on potential. The only solid of divalent manganese variety is $Mn(OH)_2$ which is amphoteric hydroxide. As pH decreases, the equilibrium shift to the right.

$$Mn(OH)_2 + H^+ \leftrightarrow MnOH^+ + H_2O \qquad \text{(Eq. 2.21)}$$

$$K = 4.9 \times 10^4$$

Bjerrum, Schwarzenbatch, and Sillen (1958) report the existence of manganese complexes with the formula $MnSO_4$. It is stated that 1.9×10^2 is the equilibrium constant for the process that creates this compound. It was discovered that this followed the equation:

$$Mn^{2+} + SO_4^{2-} \leftrightarrow MnSO_4 \qquad \text{(Eq. 2.22)}$$

As a result of its stability, the manganese sulphate complex is significant in natural water. In a solution where the activity of sulphate ions is 2000 ppm, about 80 percent manganese would be complexed.

$$\frac{[MnSO_4]}{[Mn^{2+}][SO_4^{2-}]} = 1.9 \times 10^2 \qquad \text{(Eq. 2.23)}$$

$$\frac{[MnSO_4]}{[Mn^{2+}]} = 1.9 \times 10^2 \times 2.1 \times 10^{2-} = 4 \qquad \text{(Eq. 2.24)}$$

The apparent percentage of manganese which would be stable in the solution for the indicated concentration of sulphate ions values will be as follows.

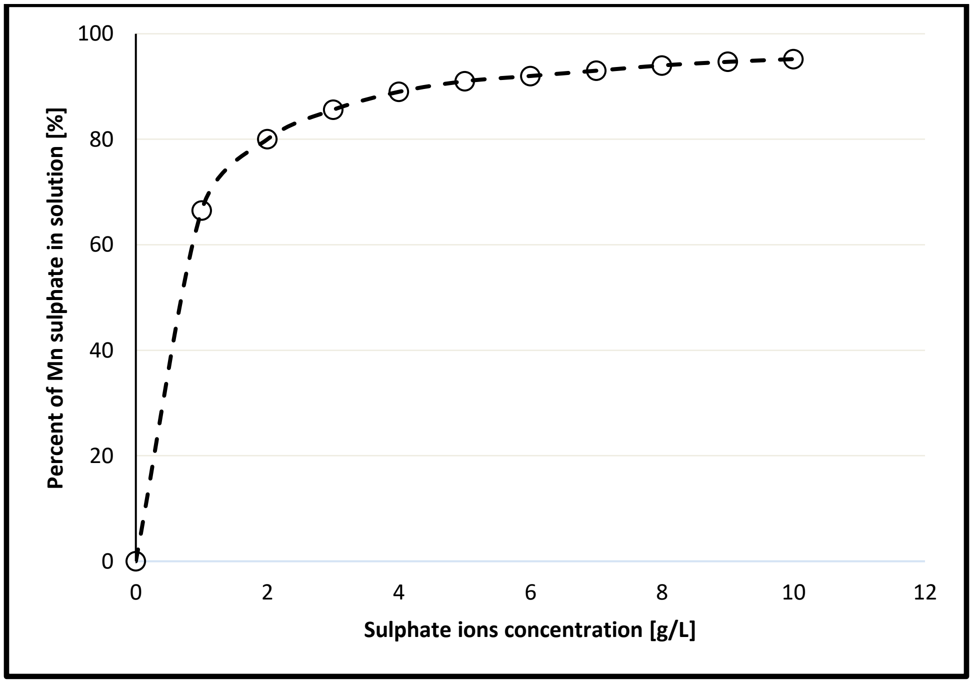

Figure 2.4. Percent of Mn in solution as a function of the sulphate ions concentration.

It can be deduced from Figure 2.4 that there is no significant change of percent of manganese stable when the sulphate ions concentration is beyond 4g/L.

2.4 KINETICS OF PRECIPITATION

The kinetics of precipitation reactions are complex and involve several steps which are simultaneously homogeneous and heterogeneous. These processes are described by the following concepts:

- Any substance can have its usual solubility surpassed without undergoing a phase shift (Supersaturation of solution).
- There must also be a reduction in free energy for a stable solid phase to emerge spontaneously from a solution (Growth).

There are several approaches to define the degree of supersaturation in a solution, but the most relevant one is:

$$S = (C-Ce)/Ce \qquad \text{(Eq. 2.25)}$$

where Ce represents the saturated or equilibrium solubility and C represents the solute concentration.

The ions of the solute have a greater propensity to associate with one another as S increases. The formation and dispersal of such groups is ongoing. These clusters will develop into new, and stable solid particles if S increases to a certain level. A decrease in free energy is necessary for the homogeneous nucleation process, also known as spontaneous nucleation. The change in free energy is equal to the sum of the surface and volume free energies.

The volume free energy comes from the interaction between the ions in the crystal lattice, while the surface free energy is connected to the production of new surface area. The critical free energy of nucleation is the point at which the net free energy reaches its highest as the cluster size grows. The formation of stable nuclei is feasible when this threshold is exceeded. Despite the fact that the critical size varies from solute to solute, it frequently does not exceed the crystalline solid's unit cell. The relationship between a spherical nucleus's critical radius (R_c) and supersaturation is given by the equation:

$$R_c = \frac{A \times T \times M}{\rho \times ln\left(\frac{1}{S}\right)} \qquad \text{(Eq.2.26)}$$

where M is the molecular mass, ρ is the solid's density, and T is its temperature.

This equation demonstrates that when supersaturation rises, the size of a crucial nucleus shrinks.The following relationship describes the rate of homogeneous nucleation (B).

$$B = A_1 \times exp\left\{-\frac{A_2}{T^3 S^2}\right\} \qquad \text{(Eq.2.27)}$$

A_1 and A_2 being constants. The rate of nucleation is exponentially strongly correlated with temperature and supersaturation level, as shown by this equation.

The two relationships above demonstrate that, when S is raised, the quantity and size of the nuclei produced by homogeneous nucleation grow and decrease, respectively. For instance, the chemical reaction progresses quickly, and extremely high levels of supersaturation can be reached in the precipitation of a metal hydroxide by the addition of alkali, making homogeneous nucleation the predominant mechanism of crystallization (nucleation).

Other secondary mechanism for nucleation is feasible and frequently more significant in the majority of hydrometallurgical applications. These include nucleation on tiny, suspended solids, which might be the same solid's seed material for precipitation. In these situations, the rate of nucleation often follows a linear relationship with S.

Once nucleation has occurred, the smaller nuclei may expand to greater sizes to further lower their free energy. Growth continues until the solution's supersaturation is removed and the equilibrium solubility is reached. It has also been discovered that the growth rate is a linear function of S. Bigger crystals typically outgrow smaller ones because the smaller ones are more soluble, and the solution is supersaturated in comparison to the larger ones. The process of precipitate aging, which aims to improve the solid's filterability, is based on this.

The above observations can be summarized in Figure 2.4 below.

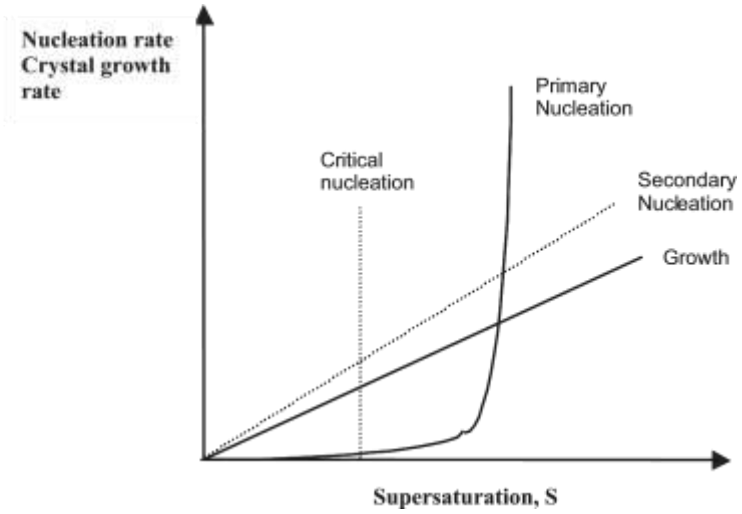

Figure 2.4. Effects of supersaturation on nucleation rate and crystal growth rate

Induction of secondary nucleation (seed) in a precipitation process becomes more and more employed in several precipitation processes to promote crystal growth while improving precipitant utilization and precipitate filterability (Miller, 2009; Kuyucak et al, 2007).

The pH and any additional ions that may be present have an impact on how quickly manganese oxidizes and precipitates out of aerated solutions, according to Hem and John D (1961). The presence of SO_4^{2-} and HCO_3^- is said to slow the rate down, whereas elevating the pH is said to speed it up.

2.5 HYDROLYTIC PRECIPITATION OF COBALT USING MAGNESIA

The use of hydrolytic precipitation of cobalt was firstly employed by California Nickel to produce a mixed nickel-cobalt hydroxide to eliminate the usage of H_2S as a precipitating agent and to obtain hydroxide precipitate which is rapidly soluble in dilute sulphuric acid and ammonia before solvent extraction and electrowinning steps (Taylor, 1995).

An industrial pilot application of hydrolytic precipitation of cobalt-nickel in two steps using magnesium oxide was developed by Adams et al (2004). In which, in the first stage, 95% of nickel and 98% of cobalt were recovered at a pH of around 7.5 for 200-300 minutes. The magnesia dosage was 0.68kg/kg (Ni+Co) fed into the solution. In the second step, the residual cobalt and nickel were recovered using lime at pH 8 which precipitated 94% of the residual nickel, and simultaneously 20 to 45% of manganese was co-precipitated.

The industrial use of mixed nickel-cobalt hydroxide precipitation was more thoroughly explained by White et al. in 2006. Magnesium was used at 0.82 kg MgO/kg of nickel precipitate with a 3 hours residence duration at pH 7.4. The chemical composition of the solid obtained was 40.4% of Ni, 2.8% of Mn, 2.5% of Mg, 1.7% of Co, 0.7% of Ca, 0.4% of Si, 0.1% of Fe, 0.02% of Al, and the remainder 17% includes hydroxide, sulfate, and chloride.

High recoveries of 99% were obtained by Oustadakis et al (2006) in mixed nickel-cobalt precipitation when using magnesium oxide as precipitating agent. The tests were conducted at room temperature and the pH was maintained at 9. The resultant solid contained 26% of magnesium hydroxide due to poor utilization of magnesia.

Hydroxide solids enrichment by contacting the precipitates with feed solution was studied by Miller and Jones (2002). The aim was to enhance the quality of nickel and cobalt hydroxide recovered while also fully utilizing the magnesium oxide used initially. The initial purpose was to eliminate the use of the second precipitation step by fully recovering the nickel and cobalt in the first step and upgrading the hydroxide obtained by contacting them with a feed solution. This was achieved by dividing the feed solution into two fractions. The solid composition was said to contain 35.6% Ni, 1.4% Co, 3.1% Mn, and 7.3% Mg. After contacting with the second fraction, it was upgraded to 47.6% Ni, 2.32% Co, 1.46% Mn, and 0.75% Mg It was also claimed that because there is less of a propensity for particle coalescence, the filtration properties of the resulting precipitates are superior than those of single contact precipitation.

Harvey et al (2011) found that re-contacting the mixed nickel-cobalt precipitates with feed solution significantly increase nickel, cobalt, sulphate, and chloride content in resultant solids while substantially reducing magnesium level and manganese to a lesser extent. This can be considered a potential drawback if the manganese hydroxide is mixed with cobalt and nickel hydroxides. The reason is that when aged together the presence of manganese inhibits the re-dissolution of nickel and cobalt species in ammonia-ammonium carbonate solution as described by Miller and Jones (2002).

The majority of the investigations centered on the nickel-cobalt aqueous sulfate system. The development of a precipitation technique for the sulphate solution containing high cobalt and manganese concentration is undoubtedly an important topic in the precipitation of cobalt from an aqueous cobalt system. Moreover, each situation is specific thus requires a specific technique and application. Conditions that may have an impact on one process might not have an impact on another.

Having considered different problems associated with the aforementioned approaches especially relating to nickel-cobalt precipitation using magnesium oxide, it is becoming useful to study the feasibility of implementing the use of the counter-current precipitation technique of cobalt from cobalt-bearing solution with manganese content, as many cobalt hydroxides production plant still use selective precipitation as a recovery method. This is the route we will follow in this project.

CHAPTER 3: MATERIALS AND METHODS

3.1 REAGENTS

Magnesium oxide (MagChem 40) used in this experiment was sourced from Magnesia Solutions (Axis House branch) in Mauritius. MagChem 40 was selected due to its relatively high purity, and it is extremely efficient in chemical processes where ease of conversion is a factor. It is produced from magnesium-rich brine and dolomitic lime. This fine white powder has a very high reactivity index and low bulk density.

MagChem 40 is 97% MgO (minimum as per specification sheet) with a typical composition of 98.2% MgO (ignited basis), 0.8% CaO, 0.35% SiO_2, 0.15% Fe_2O_3, 0.10% Al_2O_3, 0.30% Cl, 0.05% SO_3 and the loss on ignition is estimated at a 3% maximum. Chemical analysis was performed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). LECO was utilized to determine the total sulphur content, and titrimetric methods were employed to determine the total chloride content.

In addition to this, MagChem 40 is characterized by a typical median particle size of between 3 to 6 microns, the surface area above $4m^2/g$, the activity is 9 seconds, and 99 percent of particles passing through 325 mesh. Melvern Mastersizer 2000 was used to determine size the particle distribution. The loosely bound aggregates were spread out over a period of one minute at the Martin Marietta laboratory using a moderate ultrasonic frequency.

The solution used in the study was a cobalt precipitation feed solution from Mutanda Mines in the Lualaba region of DRC in the Central African Copperbelt region. The sample of solution was sent for chemical analysis using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) at the Mutanda Mines analytical laboratory. Table 3.1 details the composition of the post-neutralization and copper removal solution tested in these experiments.

Table 3.1: Feed solution composition

Feed solution assays (pH=6.19)

Elements	**Co^{2+}**	**Cu^{2+}**	**Mn^{2+}**	**Mg^{2+}**	**Fe^{2+}**	**Ni^{2+}**	**Zn^{2+}**
Concentration [g/L]	4.34	0.03	2.73	2.16	0.001	0.06	0.02
Molarity [Mol/L]	0.0796	0.0005	0.0497	0.0889	0.00002	0.0010	0.0003

3.2 EXPERIMENTAL EQUIPMENT AND PROCEDURE

To simulate the counter-current precipitation configuration in the laboratory, cobalt was initially precipitated from aqueous solution by use of magnesium oxide to raise the pH of the solution. Next, the resultant precipitates were washed with cobalt feed solution to improve the cobalt grade and fully utilize the magnesium oxide that had been previously employed. The intermediate effluent generated from washing stage was subjected to precipitation process stage to further precipitate the remaining cobalt and the impure cobalt hydroxide precipitates produced were recycled back to washing stage. Cobalt recovery and quality was used as a proxy to investigate the effect of different parameters.

Preliminary tests were intended to assess how long it would take to completely precipitate cobalt and reduce the excess of reacting magnesium oxide at cobalt precipitation and washing stages respectively. pH of the slurry was used as a proxy to ensure that the equilibrium was reached. Baffled beakers holding 1000 mL were used for the experiment. For the tests conducted at elevated temperatures, electrical stoves with temperature controls were used.

3.2.1 Effect of MgO dosage ratio on cobalt feed solution

The first investigation was to determine the optimum MgO dosage ratio that could maximize cobalt recovery from feed solution. This was done at room temperature by comparing the cobalt recovered and quality at various MgO/Co ratios. A preset amount of dry magnesia was added to start the precipitation reaction. The matrix for the batch precipitation tests is shown in Table 3.2.

Table 3.2: Investigation parameters on the effect of MgO dosage ratio on cobalt recovery and quality at 25°C

Tests	Temperature [°C]	Agitation [rpm]	Running time [hours]	Dosage (MgO/Co) [g/g]
1	25	600	4	0.90
2	25	600	4	1.00
3	25	600	4	1.10
4	25	600	4	1.20

500mL of the feed solution was mixed with a predetermined amount of dry MgO to get the desired dosage ratio. Before collecting the sample, the agitation was stopped, and the slurry was left for 5 minutes to allow solids to settle. 5ml of the solution samples were collected at various time intervals syringe filtered through a 0.22µm syringe filter, diluted with deionized water to make 25 mL, and then booked for chemical analysis.

All tests were conducted for 4 hours as per preliminary tests findings, and the stirring speed was maintained at 600 rpm using a digital controller. After precipitation, the equilibrium pH was recorded and, the slurry was vacuum filtered in Buchner funnel using a Whatman filter paper (0.45µm), dried, weighed, and submitted for chemical analysis. Solids and solution samples were analyzed using Atomic Adsorption Spectroscopy (AAS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

3.2.2 Effect of sulphate ions concentration

Thermodynamics data from the literature, which are illustrated by equation 2.23, show that divalent manganese sulphate ($MnSO_4$) is sufficiently stable in excess of sulphate ions in aqueous solution at basic pH. Theoretically, this means that precipitating cobalt hydroxide in presence of sulphate ions will result in less co-precipitation of manganese in solid-phase and therefore improve cobalt hydroxide quality. The batch cobalt precipitation tests in the presence of sulphate ions were performed following the conditions given in Table 3.3.

Table 3.3: Investigation parameters on the effect of sulphate ions concentration on Mn co-precipitation and cobalt hydroxide quality.

Tests	**Temperature [°C]**	**Agitation [rpm]**	**Running time [hours]**	**Dosage [MgO/Co]**	**Na_2SO_4 [g/l]**
1	25	600	4	Optimum	0.00
2	25	600	4	Optimum	2.00
3	25	600	4	Optimum	3.00
4	25	600	4	Optimum	4.00

For each experiment undertaken, 500 mL of the feed solution was mixed with a predetermined amount of MgO that corresponding to optimum dosage ratio and with a preset amount of sodium sulphate was added at the start of the precipitation to obtain the desired concentration in term of sulphate ions. The stirring speed was maintained at 600 rpm using a digital controller throughout all tests, which were carried out for a total of 4 hours in accordance with the results of the preliminary testing. Before collecting the sample, the agitation was stopped, and the slurry left for 5 minutes to allow solids to settle. 5ml of solution samples were collected at various time intervals, syringe filtered through a 0.22µm syringe filter, diluted with deionized water to make 25 mL, and then booked for chemical analysis.

3.2.3 Effect of temperature on cobalt precipitation

It is commonly known that the rate of precipitation reaction increases with increasing in the temperature. Since this research aims to maximize cobalt recovery and improve the cobalt hydroxide quality, it became necessary to investigate a trade-off temperature where both aims are met. The experimental conditions for the investigation of the effect of temperature on the precipitation rate of cobalt are given in Table 3.4.

Table 3.4: Investigation parameters on the effect of temperature on cobalt precipitation.

Tests	**Temperature [°C]**	**Agitation [rpm]**	**Running time [hours]**	**Dosage [MgO/Co]**	**Na_2SO_4 [g/l]**
1	25	600	4	Optimum	Optimum
2	35	600	4	Optimum	Optimum
3	45	600	4	Optimum	Optimum

For each test performed, 500 mL of the feed solution was mixed with predetermined amount of MgO and sodium sulphate that corresponded to optimum dosage ratio of MgO and sulphate ions concentration respectively. According to the results of the preliminary tests, all tests were carried out for 4 hours while utilizing a digital controller to keep the stirring speed at 600 rpm. Before collecting the sample, the agitation was stopped, and the slurry left for 5 minutes to allow solids to settle. 5ml of solution sample was collected at various time intervals, syringe filtered through a 0.22µm syringe filter, diluted with deionized water to make 25 mL, and then booked for chemical.

3.2.4 Effect of washing at 25°C

Having determined the optimum dosage ratio, ions sulphate concentration, and optimum temperature to work at, the resultant cobalt hydroxide precipitates were washed with cobalt feed solution at different wash solution volumes. This was performed to investigate the effect of washing volume on cobalt hydroxide enrichment. The different washing batch set-ups to investigate the effect of wash solution volume are tabulated in Table 3.5.

Table 3.5: Investigation parameters on the effect of washing on cobalt quality at 25°C.

Tests	Temperature [°C]	Agitation [rpm]	Running time [hours]	Wash solution volume [mL]
1	25	600	4	250
2	25	600	4	300
3	25	600	4	350

For each washing test, the resultant cobalt hydroxide precipitates obtained at optimum conditions were thickened and subsequently mixed with cobalt feed solution. The volume of the wash solution was equal to discarded effluent to maintain the total volume of 500 mL. The stirring speed was maintained at 600 rpm using a digital controller throughout all tests, which were carried out for a total of 4 hours in accordance with the results of the preliminary testing.

After washing, the equilibrium pH was recorded and, the slurry was vacuum filtered in Buchner funnel using a Whatman filter paper (0.45µm), dried, weighed, and submitted to chemical analysis. Solids and solution samples were analyzed using atomic adsorption spectroscopy (AAS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

3.2.5 Effect of temperature on the washing

Washing cobalt hydroxide precipitates at elevated temperature was also investigated in order to assess whether the quality of cobalt hydroxide could be enhanced by washing at elevated temperature. In an attempt to optimize the temperature, tests were carried out under conditions tabulated in Table 3.6.

Table 3.6: Investigation parameters on the effect of temperature on washing.

Tests	**Temperature [°C]**	**Agitation [rpm]**	**Running time [hours]**	**Wash solution volume [mL]**
1	25	600	4	Optimum
2	45	600	4	Optimum
3	55	600	4	Optimum

For each batch test, the resultant cobalt hydroxide precipitates were mixed with the optimum volume of wash solution. The stirring speed was maintained at 600 rpm using a digital controller throughout all tests, which were carried out for a total of 4 hours in accordance with the results of the preliminary testing. After washing, the equilibrium pH was recorded, and the slurry was vacuum filtered in Buchner funnel using a Whatman filter paper (0.45µm), dried, weighed, and submitted for chemical analysis. Solids and solution samples were analyzed using Atomic Adsorption Spectroscopy (AAS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

3.2.6 Effect of washing on MgO consumption rate

To further investigate the impact of washing on magnesium oxide consumption rate, three precipitation tests were conducted on intermediate effluent generated at washing stage. This was achieved at room temperature by comparing the cobalt recovered at various MgO/Co ratios in the presence of sulphate ions. A preset amount of dry magnesia and sodium sulphate were added to start the precipitation reaction. The matrix for the batch precipitation tests is shown in Table 3.7.

Table 3.7: Investigation parameters on the effect of washing on MgO consumption rate.

Tests	**Temperature [°C]**	**Agitation [rpm]**	**Running time [hours]**	**Dosage [MgO/Co]**	**Na_2SO_4 [g/l]**
1	25	600	4	0.85	Optimum
2	25	600	4	0.90	Optimum
3	25	600	4	0.95	Optimum

For each experiment carried out, 500 mL of the intermediate effluent from washing stage was mixed with a predetermined amount of magnesium oxide. Sodium sulphate was added at the start of the precipitation to obtain the desired concentration in term of sulphate ions. The stirring speed was maintained at 600 rpm using a digital controller throughout all tests, which were carried out for a total of 4 hours in accordance with the results of the preliminary testing.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 COMPOSITION OF FEED SOLUTION

The chemical composition shown in Table 3.1 indicates that the solution is a high-grade cobalt content solution with some traces of copper, nickel, and zinc. A significant presence of manganese and magnesium was identified. The data in Table 3.1 will be used in this work to calculate the precipitation efficiencies. The chemical composition analysis was performed using Atomic Adsorption Spectrometer and the cobalt exists in a divalent oxidation state.

4.2 EFFECT OF MgO DOSAGE RATIO ON PRECIPITATION

The first investigation examined the impact of MgO dosage ratio on the extent of cobalt precipitation. The precipitation was conducted using the operating conditions tabulated in Table 3.2. Under these conditions, the running duration, temperature, and agitation were unchangeable, but the MgO dosage ratio was raised from 0.9 to 1.2 times of the stoichiometric needed to precipitate all cobalt in solution. The results of these experiments are shown in Figure 4.1 and Figure 4.2.

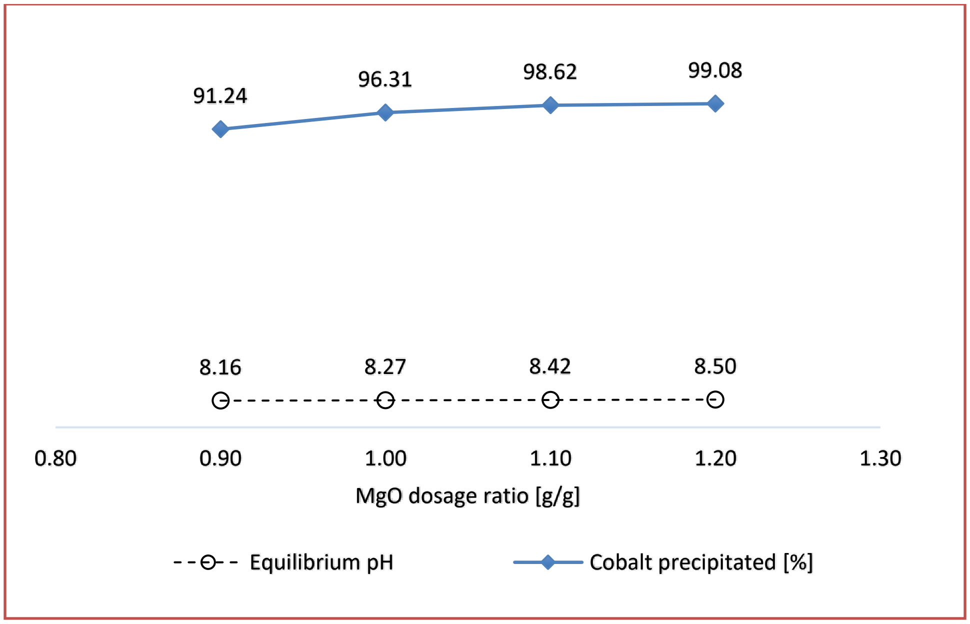

Figure 4.1: Effect of MgO dosage ratio on cobalt precipitation extent and equilibrium pH

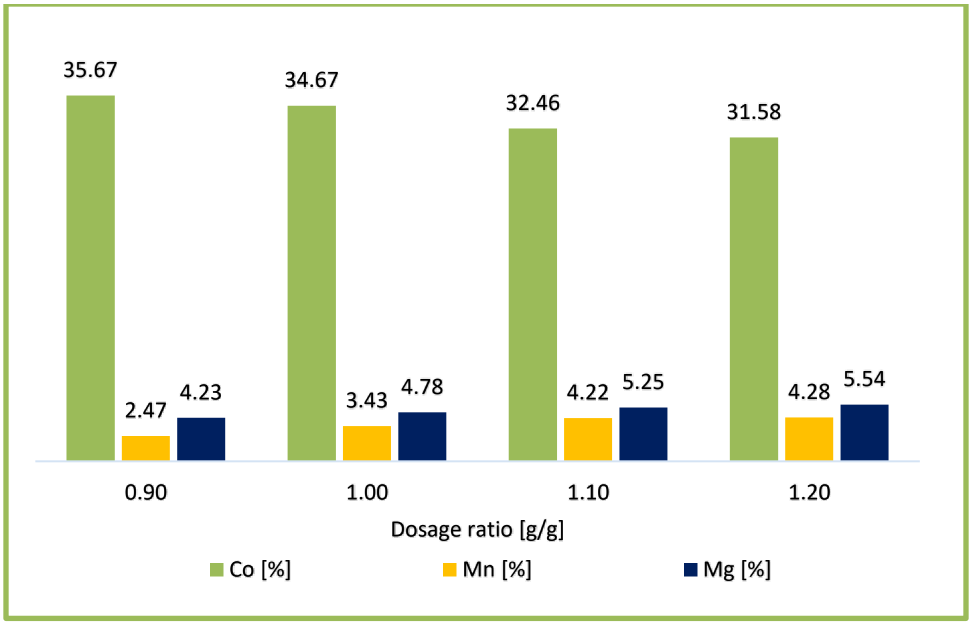

Figure 4.2: The effect of MgO dosage ratio on cobalt hydroxide quality

Figure 4.1 illustrates the results of cobalt precipitation extent as a function of dosage ratio at ambient temperature. It can be seen that cobalt recovery increases with MgO dosage ratio. The cobalt was almost completely precipitated (99%) at 1.10 g of MgO/g Co after 4 hours, resulting in an equilibrium pH of 8.42. However, Figure 4.2 indicates that an increase in MgO dosage ratio tends to reduce the cobalt grade in resultant cobalt hydroxide precipitates due to manganese and magnesium contamination. The possible reason for magnesium presence is that the proportion of residual MgO increases with MgO dosage ratio and then reports in precipitate. The reason for manganese presence in precipitates is that the manganese in solution could be getting oxidized and co-precipitated when the pH increases. (Hem, J.D.,1981) reported that the rate at which manganese is oxidized and co-precipitated by the effect of air increases by raising the operating pH which is consistent with the observations made in this study.

4.3 EFFECT OF SULPHATE IONS CONCENTRATION ON Mn CO-PRECIPITATION

The experiment in Section 4.2 evaluated the effect of MgO dosage ratio on cobalt precipitation efficiency. Since the presence of sulphate ions in solution retards the rate of oxidation of manganese (Hem, J.D.,1981), subsequent experiments investigated the effect of sulphate ions concentration on manganese co-precipitation extent. The operating conditions presented in table 3.3 were used to conduct the experiment. In these experiments, the dosage ratio was maintained at optimum (1.10 gram of MgO/g Co) and the sulphate ions concentration was varied from 0 to 4g/L. It should be noted that beyond 4g/L the effect of sulphate ions concentration becomes less relevant, as demonstrated in Figure 2.4. The results showing the effect of sulphate ions on manganese co-precipitation are shown in Figures 4.3 and 4.4.

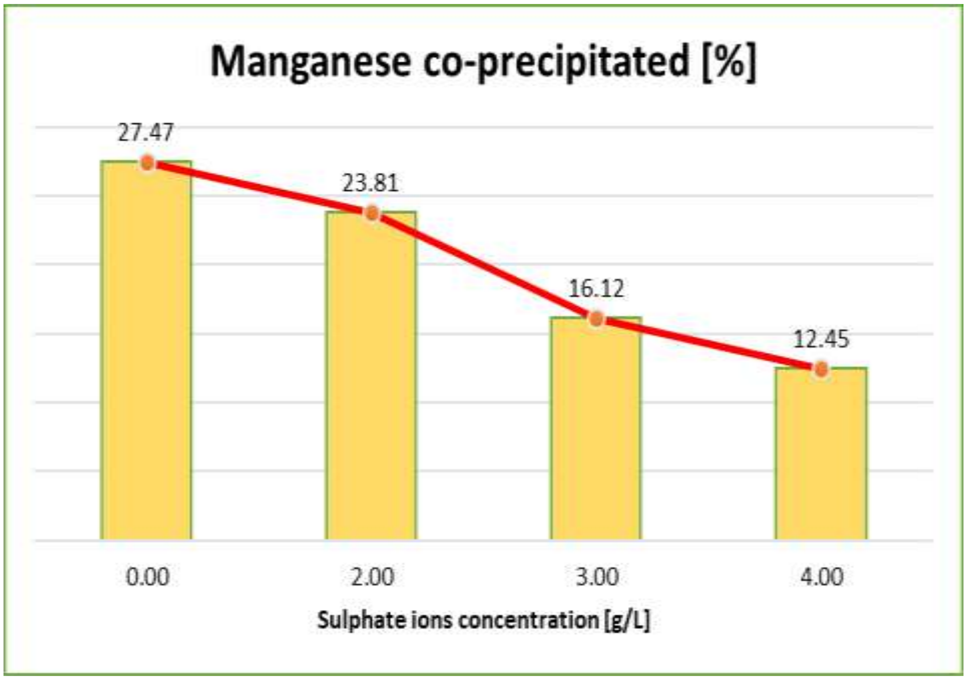

Figure 4.3: Effect of sulphate ions concentration of Mn co-precipitation extent

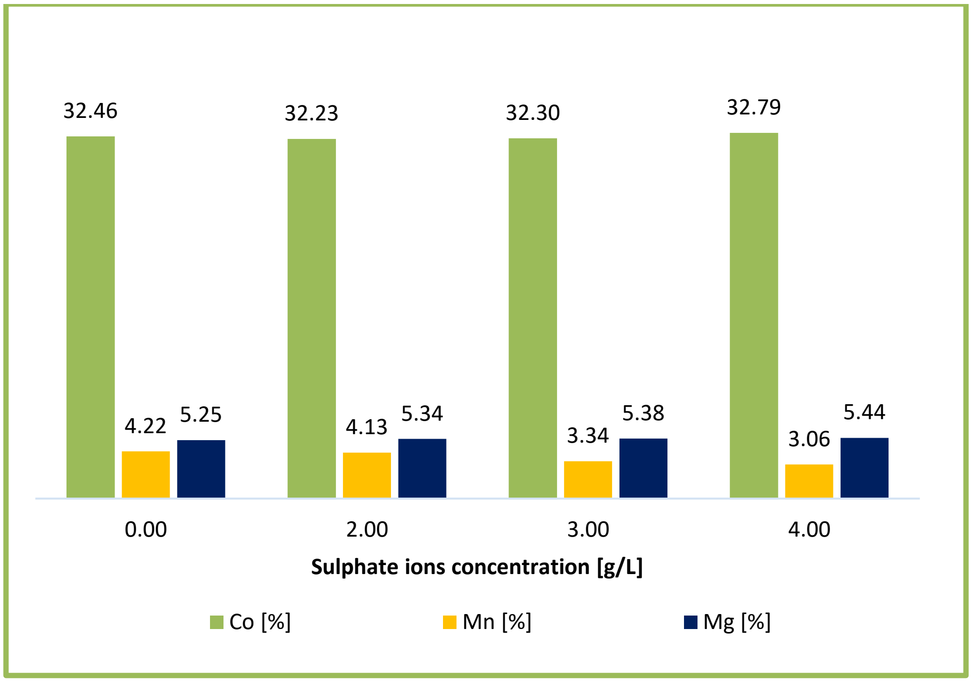

Figure 4.4: Effect of sulphate ions concentrations on cobalt hydroxide quality

The results in Figure 4.3 and Figure 4.4 showed that there is a significant reduction of manganese co-precipitation when sulphate ions are added at room temperature. The best and most affordable results were attained at 4g/L of sulphate ion where the co-precipitation of manganese decreases to about 12.45% which resulted in 32.79 Co, 3.06% Mn, and 6.44% Mg. The equilibrium pH was approximately 8.55. Nonetheless, a small rise in Mg was seen. The reason could be that the presence of sodium ions acts as a neutralizing agent by the formation of NaOH in an aqueous solution and contribute to cobalt precipitation.

4.4 EFFECT OF TEMPERATURE ON PRECIPITATION

To evaluate the role that temperature plays in cobalt precipitation rate and quality, supplementary series of experiments were performed using the operational parameters tabulated in table 3.4. In these experiments, the dosage ratio and sulphate ions concentrations were kept at the optimum values (1.10g/g Co and 4g/L respectively), but the temperature of precipitation was raised from 25°C to 45°C. The results of these experiments are shown in Figure 4.5 and Figure 4.6.

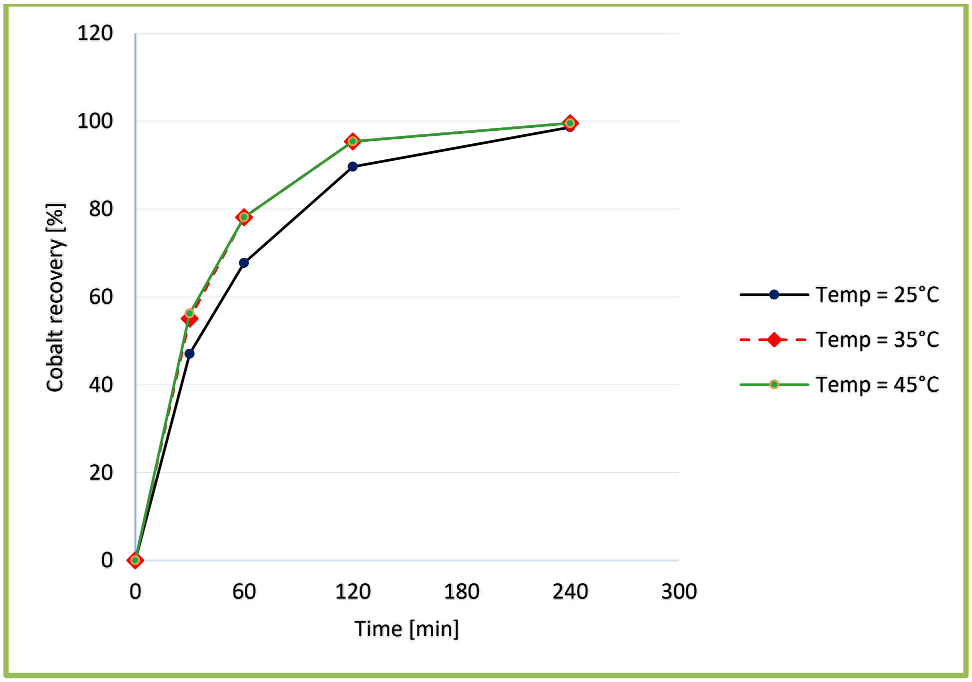

Figure 4.5: Effect of temperature on precipitation rate

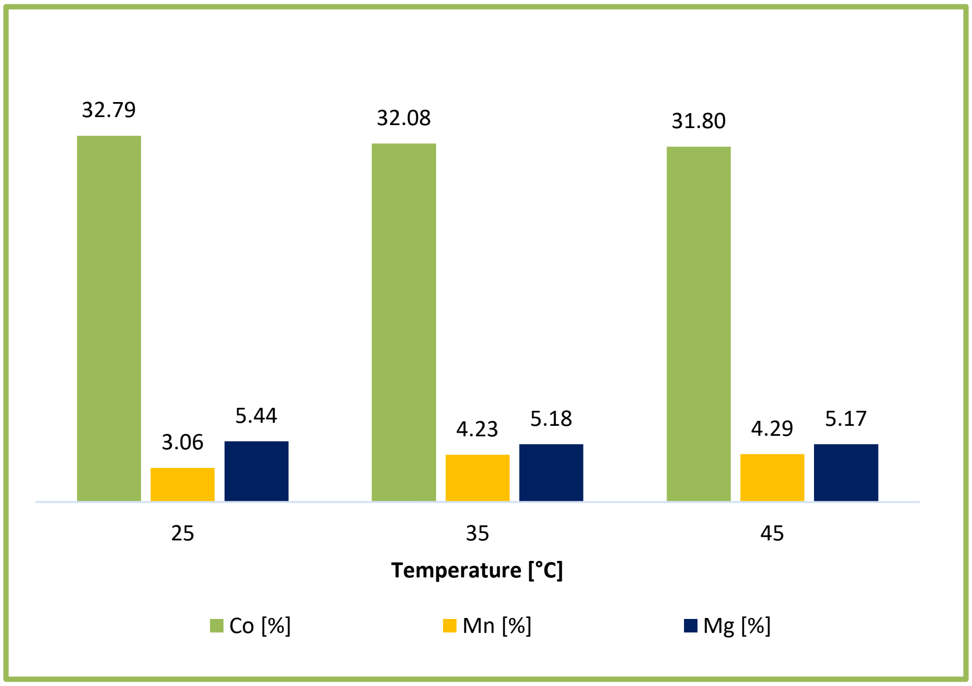

Figure 4.6: Effect of temperature on cobalt hydroxide quality

Figure 4.5 illustrates the cobalt precipitation extent as a function of time at different temperatures. It can be deduced that when raising the temperature at optimum dosage ratio and optimum sulphate ions concentration, a faster cobalt precipitation rate was observed up to 35^{o}C. At higher temperature of 45^{o}C, cobalt recovery and precipitation rate were almost similar to those observed at 35°C. Figure 4.6 shows that precipitating at elevated temperature results in nearly similar cobalt grade and a little reduction in terms of magnesium content in precipitates compared to the experiment at ambient temperature. However, raising in temperature tends to further contaminate the precipitates in term of manganese. This could be explained by the increase of pH of the solution. These observations demonstrate that the quality and recovery of cobalt are not significantly impacted by temperature.

4.5 EFFECT OF WASHING ON COBALT HYDROXIDE QUALITY AT 25°C

Once the optimum MgO dosage ratio, sulphate ion concentration, and temperature have been established, the next experiment carried out was to evaluate the impact of washing on the quality of the recovered cobalt hydroxide precipitates at room temperature. The washing tests were performed using the operational parameters tabulated in table 3.5. Under these conditions, the washing duration was 4 hours as per preliminary test results, temperature and agitation were maintained constant; however, the washing solution volume was varied from 0 to 350mL which was achievable in real-world situations. The cobalt feed solution was used as a washing solution at different volumes as a replacement for discarded effluent to maintain the total volume of 500mL. The results of these tests are tabulated in Table 4.1.

Table 4.1: Effect of washing on precipitates chemical composition (T=25°C)

Washed precipitates chemical composition (T=25°C)

Elements [%]	**Co**	**Cu**	**Mn**	**Mg**	**Fe**	**Ni**	**Zn**	**Final pH**
0 mL	32.79	0.13	3.06	5.44	0.11	0.47	0.14	8.45
250 mL	36.78	0.18	2.97	2.20	0.08	0.53	0.17	7.70
300 mL	37.78	0.20	3.03	2.15	0.08	0.55	0.19	7.66
350 mL	38.55	0.21	2.99	2.08	0.07	0.57	0.20	7.62

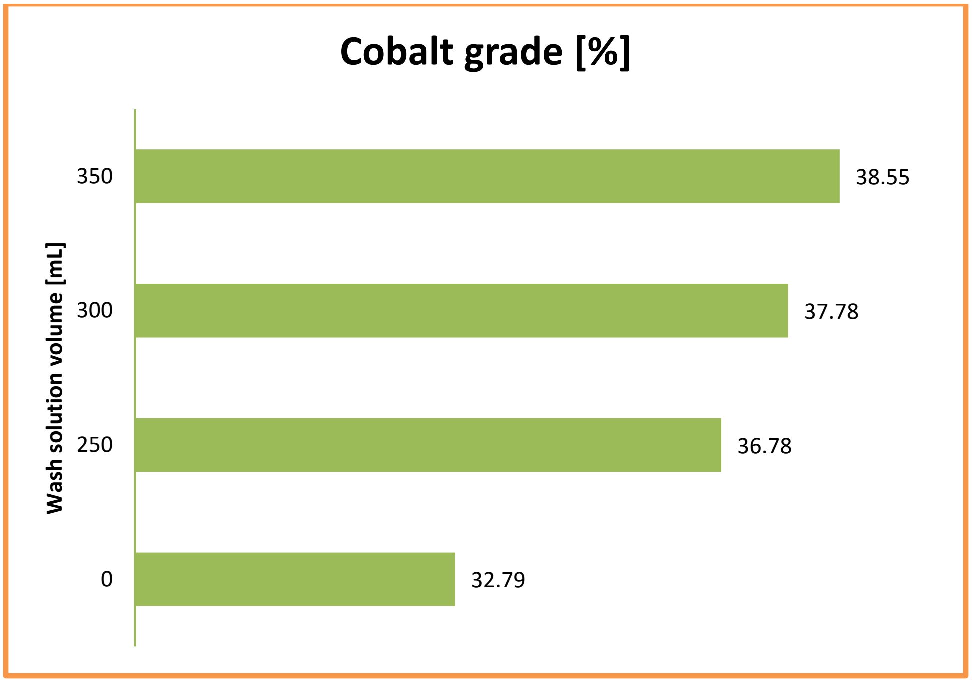

Figure 4.7: Wash solution volume on cobalt grade

Figure 4.7 shows that re-contacting the precipitates with cobalt feed solution substantially improves the quality of cobalt hydroxide and the cobalt grade in washed precipitates rises with wash solution volume. Table 4.1 indicates that the best results was recorded at 350 mL of wash solution where the following assays results of cobalt hydroxide precipitates were obtained (wt.%) 38.55 Co, 2.99 Mn, 2.08 Mg, 0.21 Cu, 0.07 Fe, 0.57 Ni, and 0.20 Zn. The equilibrium pH was 7.62. This is due to the fact that by re-contacting the cobalt hydroxide precipitates with cobalt feed solution, the residual magnesium oxide in precipitates is redissolved, and additional cobalt is precipitated into cobalt hydroxide (Jones, E.M., Miller, M.J., 2002). It can also be noted that increasing the wash solution volume beyond 300 mL does not significantly improve the cobalt hydroxide quality.

4.6 EFFECT OF TEMPERATURE ON WASHING

These investigations were performed by keeping the washing solution volume at 350 mL and sequentially changing the temperature. These tests investigated the effect of washing at elevated temperature on cobalt hydroxide upgrading. The tests were conducted using the operational parameters tabulated in table 3.6. The results of these tests are shown in Table 4.2.

Table 4.2: Effect of temperature on washed precipitates chemical composition

Washed precipitates chemical composition at varying temperature (wash solution volume = 350mL)

Elements [%]	Co	Cu	Mn	Mg	Fe	Ni	Zn	Final pH
25°C	38.55	0.21	2.99	2.08	0.07	0.57	0.20	7.62
45°C	40.97	0.22	2.92	1.59	0.07	0.55	0.20	7.49
55°C	41.71	0.21	3.35	0.97	0.05	0.56	0.20	7.40

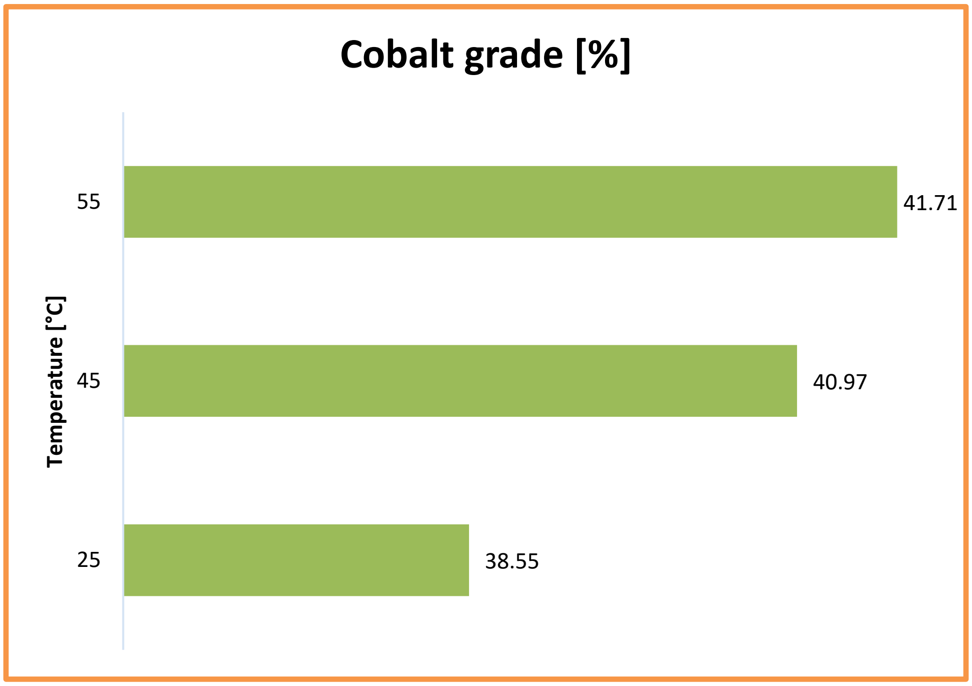

Figure 4.8: Effect of temperature on cobalt grade

Table 4.2 shows that when the washing solution volume was fixed at 350 mL, an increase in temperature further improves the quality of cobalt hydroxide precipitates produced. Figure 4.5 clearly indicates the cobalt grade increases with the temperature. The highest cobalt quality was observed at 55°C where the following cobalt hydroxide precipitates composition were obtained (wt.%) 41.71 Co, 3.35 Mn, 0.97 Mg, 0.56 Ni, 0.05 Fe, and 0.21 Cu. The equilibrium pH was 7.40. The optimum cobalt quality was found to be at a temperature of 45 °C, where the following cobalt hydroxide precipitates composition (wt.%) were found: 40.97 Co, 2.92 Mn, 1.59 Mg, 0.55 Ni, 0.07 Fe, and 0.22 Cu. The equilibrium pH was 7.36.

4.7 EFFECT OF WASHING ON MgO CONSUMPTION RATE

The last investigation assessed the impact of washing on MgO consumption rate. The precipitation was conducted on intermediate effluent generated at washing stage and using the operating conditions presented in Table 3.7. Under these conditions, the running duration, temperature, sulphate ions concentration and agitation were unchangeable, but the MgO dosage ratio was raised from 0.85 to 0.95 times of the stoichiometric needed to precipitate all cobalt in solution.

Table 4.3: Effect of MgO dosage ratio on cobalt precipitation from intermediate effluent.

Ratio [g of MgO/g Co]	Equilibrium pH	Co recovery [%]
0.85	8.30	95.77
0.90	8.40	99.26
0.95	8.60	99.76

Table 4.3 indicates that cobalt was almost completely precipitated (99%) at 0.90g of MgO/g Co after 4 hours, resulting in an equilibrium pH of 8.40. This shows that by washing the cobalt hydroxide precipitates with cobalt feed solution prior to final precipitation, the consumption rate was lowered by 18% (from 1.10 to 0.90g of MgO/g of Co).

Summary

On the whole, the performed experiments investigated firstly the effect of magnesium oxide dosage ratio on cobalt precipitation extent and cobalt hydroxide quality at ambient temperature followed by the effect of sulphate ions concentration on manganese co-precipitation. Thereafter the effect of temperature on cobalt precipitation rate and cobalt hydroxide quality was explored. The effect of washing solution volume on quality of cobalt recovered at room and elevated temperature was also investigated and lastly the effect of washing on MgO consumption was evaluated.

In the first set of experiments performed, the effect of MgO dosage ratio was evaluated at 25°C. MgO/Co ratio was varied to determine the corresponding cobalt precipitation extent. The ratio resulting in nearly maximum cobalt recovery was 1.10 gram of MgO/g Co. It was also found in this experiment that increasing the MgO dosage decreased the cobalt grade and increased the magnesium and manganese content in precipitates. This means that it is difficult to get high cobalt recovery with lower magnesium content when using magnesium oxide as precipitating agent.

The next experiments were carried out to investigate the impact of precipitating cobalt in the presence of sulphate ions on manganese co-precipitation at the optimal MgO dose ratio. The sulphate ions concentration of 4g/L was found to reduce the manganese co-precipitation by approximately 54%. It should be emphasized that beyond 4g/L the effect of sulphate ions concentration becomes less relevant, as demonstrated in Figure 2.4. It was found that the cobalt grade was almost similar at different sulphate ions concentrations and a slight increase in terms of magnesium contamination was observed.

The next experiments were carried out to investigate the effect of temperature on cobalt precipitation rate and quality of precipitates produced at optimum MgO dosage ratio and optimum sulphate ions concentration. Nearly identical results were observed in terms of cobalt hydroxide quality and recovery when precipitating at various temperatures. It was suspected that the slight manganese and magnesium contamination observed when precipitating at elevated temperatures was caused by the rapid in pH increase experienced. These findings demonstrate that the quality and recovery of cobalt are not significantly impacted by temperature.

The following series of experiments were conducted to investigate the effect of washing the resultants cobalt hydroxides with cobalt feed solution on cobalt quality and magnesium oxide utilization at both ambient and elevated temperatures. The results obtained showed that re-contacting the precipitates with cobalt feed solution substantially improves the quality of cobalt hydroxide and the cobalt grade in washed precipitates rises with wash solution volume. Washing the precipitates at elevated temperature further improves the quality of cobalt hydroxide precipitates produced. The washing solution volume and the operating temperature resulting in optimum cobalt quality and magnesium oxide utilization were 350 mL and 45°C respectively. This enhanced the precipitation of additional cobalt and redissolved the residual magnesium in the precipitates. After washing, the cobalt was upgraded by about 8% and the magnesium content was decreased by approximately 3.8%.

The last experiments were performed to investigate the effect of washing prior to precipitation on magnesium oxide consumption rate at room temperature. The results indicated that there is a substantial reduction in term of MgO consumption when precipitating cobalt from the intermediate effluent generated at washing stage. The reduction of magnesium oxide consumption rate was evaluated at approximately 18%.

The economic study presented in Table 4.3 shows the benefit of precipitating cobalt as hydroxide using magnesium oxide followed by washing the resultants precipitates with cobalt containing solution.

Table 4.3: Economical benefit of washing cobalt hydroxide precipitates.

Precipitation methods	**MgO consumption rate [t/t]**	**Estimated MgO price [USD/Mt]**	**Cost of MgO per ton of cobalt produced [USD/ton]**	**Benefit on MgO consumed [USD/ton of cobalt produced]**
Precipitation without washing	1.10	$ 1,280.00	$1,408.00	-
Precipitation with washing	0.90	$ 1,280.00	$1,152.00	$256.00

According to the findings of this research, the configuration of cobalt precipitation can be altered to maximize cobalt recovery and upgrade the quality of hydroxide produced while maximizing the MgO utilization.

An illustration of how to operate the counter-current precipitation circuit to facilitate contact between the cobalt feed solution and the precipitated solids is shown in Figure 4.9. The incoming iron, copper and aluminum free solution containing essentially cobalt, manganese, and magnesium typically at pH 5 to 6 is reacted with the underflow slurry from thickener 1 in order to re-dissolve the unreacted magnesium oxide and precipitate additional cobalt as hydroxide in reactors vessel 2. Steam is injected into reactors vessel 2 to obtain the desired temperature of 45°C.

After washing, the slurry is thickened wherein the underflow is subjected to filtration prior to drying. The overflow from thickener 2 is reacted with sodium sulphate and magnesium oxide under pH control to precipitate maximum cobalt as hydroxide in reactors vessel. The pH is controlled by the addition of MgO to reach a value of approximately 8.5. The resulting slurry is thickened wherein the underflow is recycled back to washing stage while the overflow constitutes the final effluent.

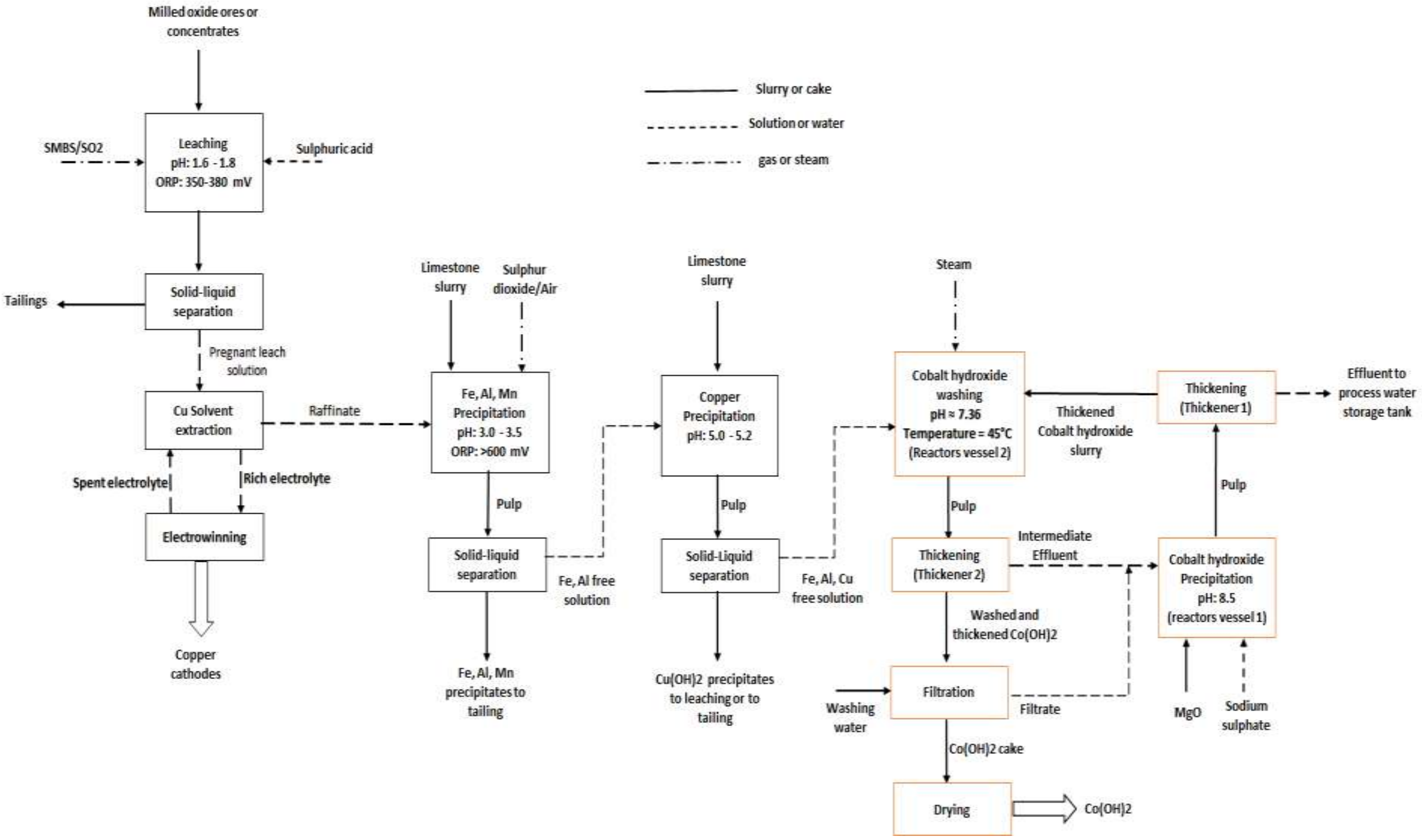

Figure 4.9: Proposed configuration for cobalt precipitation as per findings.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

The objective of this research was to investigate the benefit of precipitating cobalt hydroxide in presence of sulphate ions followed by washing of resultant precipitates with cobalt feed solution as an alternative technique to the well-known and established classic cobalt precipitation configuration using magnesium oxide. This way of precipitating cobalt can be realized at plant scale by operating in counter-current configuration as proposed in Figure 4.9. This research highlights the hydrolytic precipitation of cobalt using magnesium oxide as a precipitating agent in presence of sulphate ions followed by washing of resultant cobalt hydroxide precipitates with cobalt feed solution at different temperatures.

The effect of MgO dosage ratio, the effect of sulphate ions concentration, and the effect of temperature were evaluated for their ability to maximize cobalt recovery and minimize manganese co-precipitation. The effect of washing solution volume and temperature were also investigated for their ability to improve cobalt grade while maximizing the MgO usage.

5.1 Effect of MgO dosage ratio

Raising the MgO dosage ratio increases cobalt precipitation extent and reduces cobalt grade in precipitates produced due to manganese co-precipitation and magnesium contamination. The nearly maximum cobalt recovery (≈98.6%) was obtained when adding 1.10 gram of MgO/g Co at 25°C. The equilibrium pH was about 8.45.

5.2 Effect of sulphate ions concentration

In the previous tests, the optimum cobalt recovery was obtained at 1.10 gram of MgO/g Co. But there was a significant presence of manganese in the precipitates produced. This was due to the high pH experienced at the aforementioned MgO dosage (≈8.45). To mitigate this co-precipitation, cobalt precipitation was performed at different concentrations of sulphate ions for 4 hours. It was found that the optimum sulphate concentration was 4g/L where manganese co-precipitation was reduced by about 54%. It should be underlined that beyond 4g/L the effluence of sulphate ions concentration becomes less relevant as demonstrated in Figure 2.4.

5.3 Effect of temperature on cobalt precipitation

The results of this experiment showed that the cobalt precipitation rate, extent, and quality were not significantly affected by the temperature. Cobalt recovery and grade remained constant at about 99% and 32% respectively throughout the tested temperature range. Manganese was, however, slightly affected by the temperature. It has been found that the cobalt can successfully be precipitated at 25°C.

5.4 Effect of washing on cobalt quality

These experiments aimed to determine the best volume of washing solution and temperature that would result in the best cobalt hydroxide quality while maximizing the MgO utilization. The optimum cobalt grade (≈40.97%) was obtained at 350 mL of washing solution and 45°C while reducing the magnesium content at 1.59%.

5.5 Effect of washing on MgO consumption rate

After washing the cobalt hydroxide precipitates with cobalt feed solution, precipitation experiments were undertaken on resultant effluent or intermediate effluent to evaluate the MgO consumption rate. The cobalt recovery was almost at its maximum (99%) when 0.90 g of MgO/g Co was added at 25 °C. Its pH at equilibrium was around 8.4. Therefore, a magnesium oxide saving of approximately 18% could be realized.

It can be concluded that cobalt can be precipitated from an aqueous solution using magnesium oxide by counter-current precipitation configuration in presence of sulphate ions. The circuit requires 2 stages of 4 agitated tanks coupled with solid-liquid separation steps as proposed in Figure 4.9.

5.6 Recommendations

Based on the results and conclusions the followings can be recommended that for future work on this research:

- Possible way to fully mitigate or further lower the manganese co-precipitation in cobalt hydroxide precipitates produced be investigated. This can be achieved by adding bicarbonate ions (HCO_3^-) in conjunction with sulphate ions (SO_4^{2-}) to further decrease the rates of manganese oxidation as the effluence of sulphate ions concentration becomes less relevant beyond 4g/L.

- Additional precipitation and washing tests to assess the magnitude of uncertainty in the results obtained (error bars) followed by a statistical analysis in comparing results.

- The scope of this work was limited to investigating the effect of counter-current precipitation of cobalt as hydroxide (precipitation coupled to washing) on its quality and MgO consumption in batch set-ups. The further investigations should focus on dynamic cobalt precipitation and washing tests at pilot plant scale to determine the realistic MgO consumption rate and cobalt upgrading ratio.

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Appendices

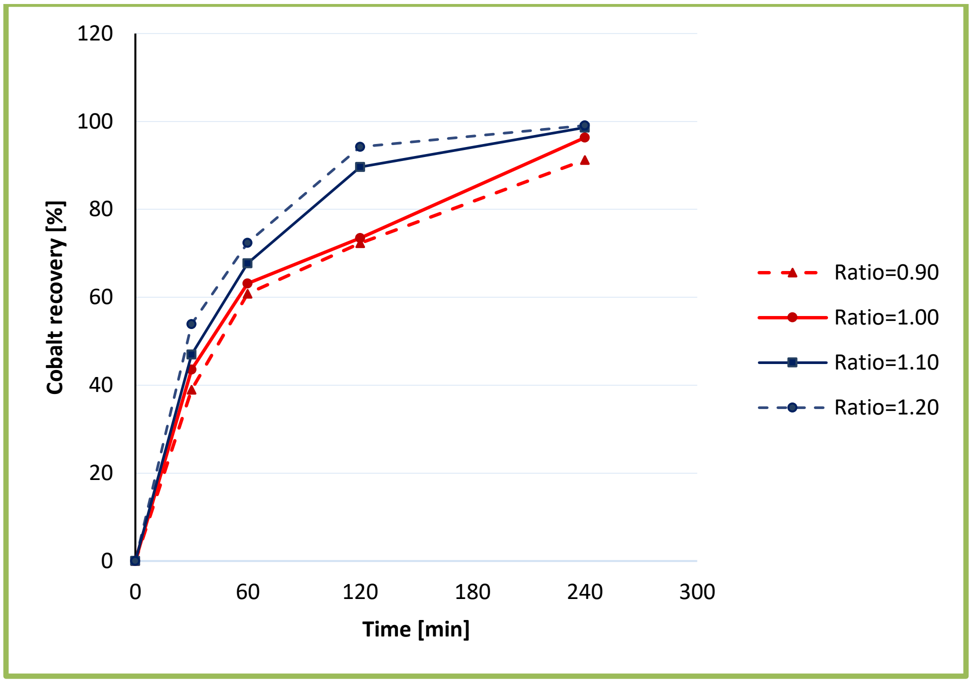
Raw preliminary pH profile at precipitation

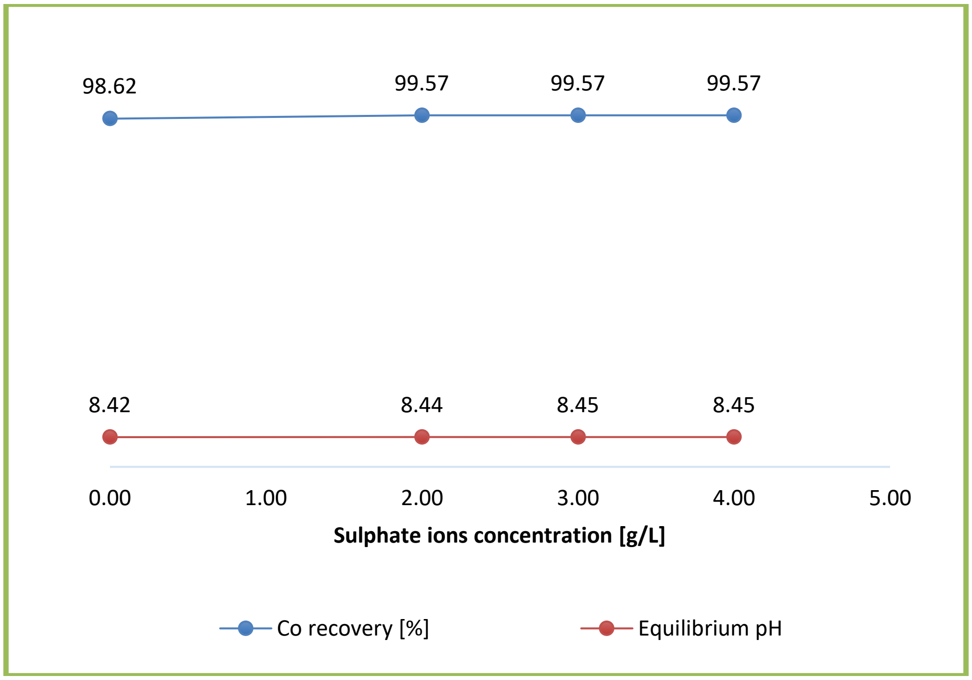
Time [min]	Ratio [g of MgO/g Co]			
	0.90	**1.00**	**1.10**	**1.20**
0	6.19	6.19	6.19	6.19
30	7.47	7.41	7.46	7.40
60	7.68	7.73	7.78	7.80
120	7.73	7.80	8.01	7.95
180	8.09	8.10	8.20	8.30
240	**8.16**	**8.24**	**8.32**	**8.40**
300	8.17	8.24	8.32	8.41

Raw preliminary pH profile at washing

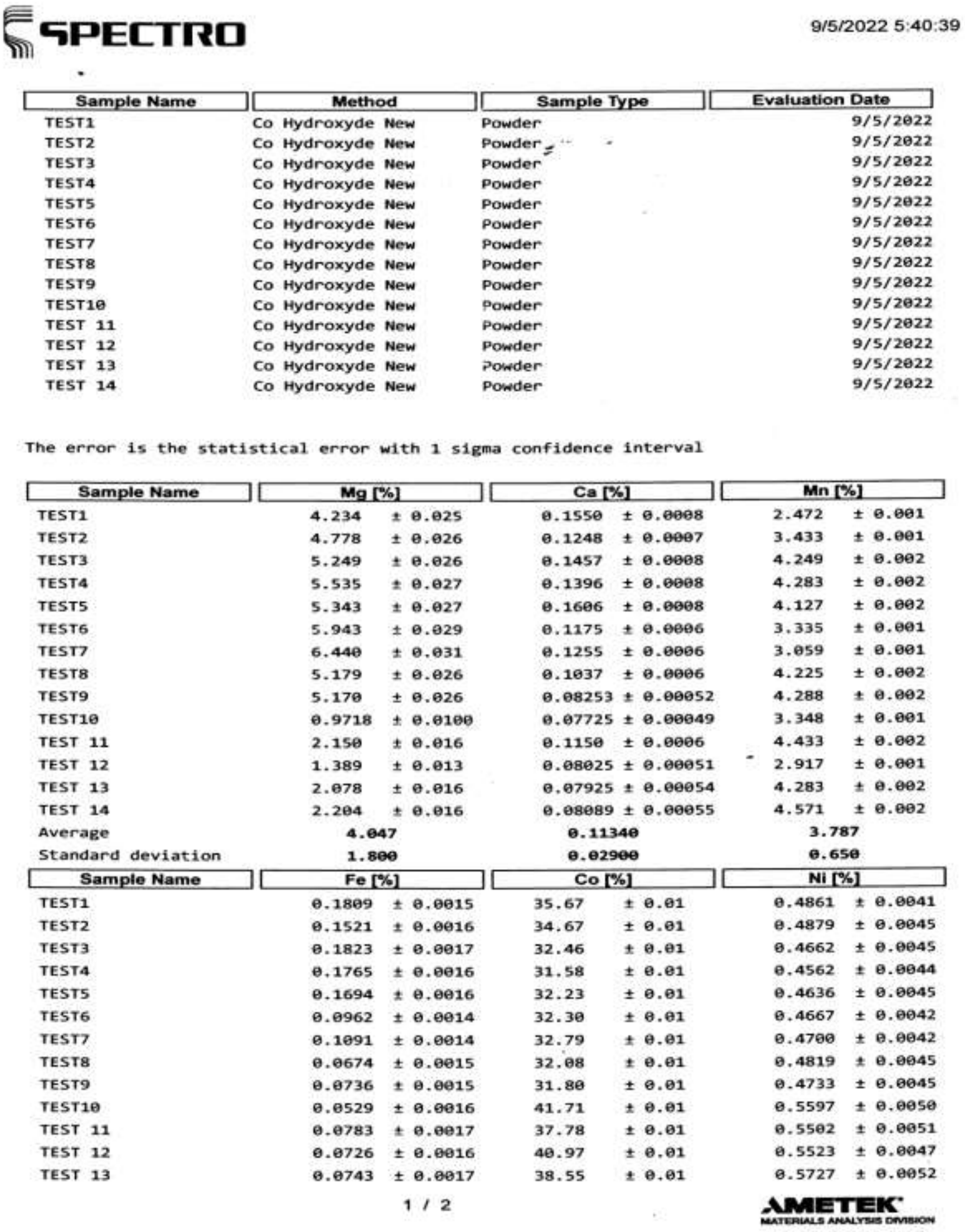
Time [min]	Washing volume at 25°C [mL]		
	250	**300**	**350**
0	8.45	8.45	8.45
30	7.16	7.11	7.07
60	7.21	7.16	7.11
120	7.26	7.19	7.14
180	7.30	7.20	7.16
240	**7.33**	**7.23**	**7.18**
300	7.34	7.23	7.19

Detailed precipitation kinetics





Detailed ICP-AES results for solids



SPECTRO

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Sample Name	Method	Sample Type	Evaluation Date
TEST1	Co Hydroxyde New	Powder	9/5/2022
TEST2	Co Hydroxyde New	Powder	9/5/2022
TEST3	Co Hydroxyde New	Powder	9/5/2022
TEST4	Co Hydroxyde New	Powder	9/5/2022
TEST5	Co Hydroxyde New	Powder	9/5/2022
TEST6	Co Hydroxyde New	Powder	9/5/2022
TEST7	Co Hydroxyde New	Powder	9/5/2022
TEST8	Co Hydroxyde New	Powder	9/5/2022
TEST9	Co Hydroxyde New	Powder	9/5/2022
TEST10	Co Hydroxyde New	Powder	9/5/2022
TEST 11	Co Hydroxyde New	Powder	9/5/2022
TEST 12	Co Hydroxyde New	Powder	9/5/2022
TEST 13	Co Hydroxyde New	Powder	9/5/2022
TEST 14	Co Hydroxyde New	Powder	9/5/2022

The error is the statistical error with 1 sigma confidence interval

Sample Name	Mg [%]	Ca [%]	Mn [%]
TEST1	4.234 ± 0.025	0.1550 ± 0.0008	2.472 ± 0.001
TEST2	4.778 ± 0.026	0.1248 ± 0.0007	3.433 ± 0.001
TEST3	5.249 ± 0.026	0.1457 ± 0.0008	4.249 ± 0.002
TEST4	5.535 ± 0.027	0.1396 ± 0.0008	4.283 ± 0.002
TEST5	5.343 ± 0.027	0.1606 ± 0.0008	4.127 ± 0.002
TEST6	5.943 ± 0.029	0.1175 ± 0.0006	3.335 ± 0.001
TEST7	6.440 ± 0.031	0.1255 ± 0.0006	3.059 ± 0.001
TEST8	5.179 ± 0.026	0.1037 ± 0.0006	4.225 ± 0.002
TEST9	5.170 ± 0.026	0.08253 ± 0.00052	4.288 ± 0.002
TEST10	0.9718 ± 0.0100	0.07725 ± 0.00049	3.348 ± 0.001
TEST 11	2.150 ± 0.016	0.1150 ± 0.0006	4.433 ± 0.002
TEST 12	1.389 ± 0.013	0.08025 ± 0.00051	2.917 ± 0.001
TEST 13	2.078 ± 0.016	0.07925 ± 0.00054	4.283 ± 0.002
TEST 14	2.204 ± 0.016	0.08089 ± 0.00055	4.571 ± 0.002
Average	**4.047**	**0.11340**	**3.787**
Standard deviation	**1.800**	**0.02900**	**0.650**

Sample Name	Fe [%]	Co [%]	Ni [%]
TEST1	0.1809 ± 0.0015	35.67 ± 0.01	0.4861 ± 0.0041
TEST2	0.1521 ± 0.0016	34.67 ± 0.01	0.4879 ± 0.0045
TEST3	0.1823 ± 0.0017	32.46 ± 0.01	0.4662 ± 0.0045
TEST4	0.1765 ± 0.0016	31.58 ± 0.01	0.4562 ± 0.0044
TEST5	0.1694 ± 0.0016	32.23 ± 0.01	0.4636 ± 0.0045
TEST6	0.0962 ± 0.0014	32.30 ± 0.01	0.4667 ± 0.0042
TEST7	0.1091 ± 0.0014	32.79 ± 0.01	0.4700 ± 0.0042
TEST8	0.0674 ± 0.0015	32.08 ± 0.01	0.4819 ± 0.0045
TEST9	0.0736 ± 0.0015	31.80 ± 0.01	0.4733 ± 0.0045
TEST10	0.0529 ± 0.0016	41.71 ± 0.01	0.5597 ± 0.0050
TEST 11	0.0783 ± 0.0017	37.78 ± 0.01	0.5502 ± 0.0051
TEST 12	0.0726 ± 0.0016	40.97 ± 0.01	0.5523 ± 0.0047
TEST 13	0.0743 ± 0.0017	38.55 ± 0.01	0.5727 ± 0.0052

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TEST 14	0.0799 ± 0.0017	36.78 ± 0.01	0.5270 ± 0.0050
Average	**0.1118**	**35.10**	**0.5010**
Standard deviation	**0.0470**	**3.40**	**0.0400**

Sample Name	Cu [%]	Zn [%]	Al [%]
TEST1	0.1613 ± 0.0009	0.1672 ± 0.0007	0.1526 ± 0.0017
TEST2	0.1543 ± 0.0008	0.1558 ± 0.0007	0.07029 ± 0.00078
TEST3	0.1336 ± 0.0007	0.1339 ± 0.0006	0.00313 ± 0.00003
TEST4	0.1159 ± 0.0007	0.1290 ± 0.0006	0.00464 ± 0.00005
TEST5	0.1258 ± 0.0007	0.1323 ± 0.0006	0.01995 ± 0.00022
TEST6	0.1374 ± 0.0007	0.1366 ± 0.0006	0.0954 ± 0.0011
TEST7	0.1324 ± 0.0007	0.1413 ± 0.0006	0.1183 ± 0.0013
TEST8	0.1448 ± 0.0007	0.1344 ± 0.0006	0.01287 ± 0.00014
TEST9	0.1338 ± 0.0007	0.1318 ± 0.0006	0.00200 ± 0.00002
TEST10	0.2106 ± 0.0011	0.1951 ± 0.0009	0.02946 ± 0.00033
TEST 11	0.1998 ± 0.0010	0.1853 ± 0.0008	< 0.00020 -
TEST 12	0.2167 ± 0.0011	0.2024 ± 0.0009	0.07572 ± 0.00084
TEST 13	0.2110 ± 0.0010	0.2015 ± 0.0008	< 0.00020 -
TEST 14	0.1775 ± 0.0009	0.1667 ± 0.0007	< 0.00020 -
Average	**0.1611**	**0.1581**	**0.04176**
Standard deviation	**0.0340**	**0.0270**	**0.04900**

Sample Name	U [ppm]	Sum [%]
TEST1	22.0 ± 2.9	43.68
TEST2	15.5 ± 2.8	44.03
TEST3	16.7 ± 2.6	43.02
TEST4	16.5 ± 2.5	42.42
TEST5	15.5 ± 2.6	42.77
TEST6	15.1 ± 2.5	42.63
TEST7	16.7 ± 2.6	43.39
TEST8	15.2 ± 2.5	42.43
TEST9	15.7 ± 2.5	42.16
TEST10	27.1 ± 3.7	47.16
TEST 11	21.4 ± 3.3	45.49
TEST 12	26.9 ± 3.6	46.48
TEST 13	24.1 ± 3.4	46.05
TEST 14	16.6 ± 3.1	44.59
Average	**18.9**	
Standard deviation	**4.3**	