Optimization of Magnesium Removal from Hydrometallurgical Leach Liquors by Struvite Formation

by

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Abstract

Nickel is a vital metal which occurs in two types of ore: laterites and sulfides. Historically sulfide ores have been the primary source of nickel however due to their limited resources and the vast occurrence of laterites, laterite processing has gained a great deal of attention. Nickel in laterite ores is accompanied by impurities such as magnesium and iron, due to their similarity in ionic radii and their capability in replacing one another in crystal lattices. Magnesium compounds are highly soluble, therefore, magnesium impurity in nickel processing leads to the production of non-recyclable process water which results in high water consumption and negative environmental impact due to the wastewater being discarded to the environment.

An approach has been derived at the University of British Columbia which involves the removal of magnesium compounds from nickel plant wastewater streams as struvite. Struvite, MgNH₄PO₄·6H₂O, is a valuable fertilizer which provides three important nutrients of magnesium, phosphorus and nitrogen to plants.

This study confirms the ability of the proposed flowsheet to successfully remove magnesium as struvite from nickel laterite plants from both aspects of the magnesium removal efficiency and the produced struvite purity; with the experiments conducted at the base conditions having magnesium removal efficiency of above 95 percent and the produced struvite purity being above 97 percent.

This study focuses on the optimal conditions leading to the maximum magnesium removal and therefore struvite precipitation. Struvite precipitation is affected by many parameters. The most influential factors affecting struvite crystallization are mixing intensity, seeding and the seeding technique, pH, temperature, crystal retention time, magnesium to phosphate ratio,
supersaturation level and the impurities present in the system. This study verifies that each of these parameters affect struvite precipitation differently. For instance, variations in supersaturation level and pH have greater effect on struvite precipitation than variations in temperature and mixing intensity. Additionally, this study confirms that the optimum condition for struvite precipitation is the same as the existing conditions of the effluent solution such as ambient temperature and pH; therefore, no further adjustment is required; however, solution seeding with struvite powder does improve the magnesium removal efficiency.
Preface

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TO

My Amazing Parents

&

My Lovely Sister
1 Introduction

1.1 Background

Nickel, the silvery-white metal, is one of the most essential metals produced. Its extensive applications are a result of its capability to produce heat and corrosion resistant alloys i.e. stainless steel [1].

Land-based nickel occurrences are classified into two major groups of laterite and sulfide deposits. Despite the 70 percent nickel occurrence in laterite ores, only 40 percent of worldwide nickel production is from laterite ores. This is due to laterites incapability of being pre-concentrated by routine gravity separation methods and therefore increasing the operational costs [2]. However due to the vast occurrence of laterites and limited sulfide resources, options for economical laterite processing are being significantly considered.

Nickel laterite deposits consist of mixtures of hydrated iron oxides and hydrated magnesium silicates. Due to the similarity of magnesium, iron and nickel ionic radii these ions may replace one another in crystal lattices such as silicates; thus both the iron oxide and magnesium silicate present in laterite deposits can contain various concentrations of nickel. Depending on the nickel concentration and distance from the earth’s surface, laterite deposits are divided into three zones [3].

The zone furthest from the earth surface which contains the highest concentration of nickel is the garnierite zone. The garnierite zone is fairly heterogeneous and in addition to high concentrations of nickel it contains high concentrations of magnesium silicate; therefore, the nickel extraction is primarily done by pyrometallurgical methods where the profit associated
with the amount of nickel production will balance the cost of smelter operations. Additionally, since the whole ore is smelted the high concentration of impurities is not of issue.

Conversely, the zone closest to the earth surface which contains the lowest concentration of nickel is the limonite zone. The intermediate zone which contains intermediate concentrations of nickel is called the serpentine zone. The limonite and the serpentine zones are fairly homogeneous and contain sufficiently low concentrations of impurities to be treated with hydrometallurgical methods such as the Caron process and the high pressure acid leach process.

The Caron process consists of four main steps; ore drying and grinding, reduction roasting, and ammonium carbonate leaching followed by metal recovery. The typical nickel recovery of this process is 75 percent. Recovery from the high pressure acid leach process is about 95 percent. The main step in this process is an autoclave where the ore is directly treated with sulfuric acid at high temperature and pressure which will lead to the selective separation of nickel and cobalt from the iron impurities present in the ore. The subsequent steps are countercurrent decantation of the leach solution, neutralization and mixed sulfide precipitation.

1.2 Problem Definition

Due to the similarity of magnesium, iron and nickel ionic radii, these ions are capable of replacing one another in crystal lattices. This leads to nickel present in laterite ores to be accompanied by various concentrations of magnesium and iron impurities. The main hydrometallurgical methods for nickel extraction are the Caron process and the high pressure acid leach process; both of which focus on separation of nickel from magnesium and iron. The impact of the presence of magnesium on hydrometallurgical processes is categorized into two groups. The first group of impact is the general effect of magnesium presence on hydrometallurgical processes. This group is caused by the high solubility of magnesium
compounds (magnesium sulfate has a solubility of 35.1 g/100 mL water at 20°C [4]) and results in two negative outcomes. The first outcome is reduction of nickel recovery which results in lower profits and the second outcome is the production of non-recyclable process water which results in high water consumption and negative environmental impact due to waste water being discarded to the environment. The second group of impact is dependent on the specific hydrometallurgical process used to extract nickel. The Caron process is affected by magnesium in the reduction roasting step. This step typically operates at temperatures above 850°C; while at temperatures between 750 to 850°C amorphous magnesium silicates recrystallize to form forsterite where any nickel not reduced to the metallic state will co-crystallize with the forsterite and therefore will be insoluble in the proceeding leaching step.

The high pressure acid leach process generally accepts ores with magnesium content between 3 and 10 percent; where higher magnesium content leads to excessive acid consumption. This is because magnesium competes with nickel for the acid. However, lower magnesium content requires additional neutralization [3; 5].

1.3 Project Objective

The objective of this study is to examine the removal of magnesium from laterite process liquors by precipitating it as struvite. This is done in order to eliminate the production of non-recyclable process water in nickel plants. This project proposes a process in which magnesium present in the process water stream is recovered as struvite. Therefore, as opposed to dumping water solutions contaminated with magnesium solutions to the environment, magnesium is used to produce an efficient, slow release fertilizer. Struvite, MgNH₄PO₄·6H₂O, is a valuable fertilizer which provides three important nutrients of magnesium, phosphorus and nitrogen for plants. Therefore, future nickel plants, as opposed to having a negative impact caused by magnesium
dumping to the environment, can produce a valuable by-product that is able to justify the added costs and also have a positive impact on the environment.

Additionally, this study is done in order to discover the optimum conditions which will lead to the maximum magnesium removal from the waste water stream.
2 Literature Review

2.1 Nickel

Nickel is a silvery white metal with the atomic number 28 which belongs to the transition group metals. Due to nickel’s strength and corrosion resistance it is primarily used for alloy production, where about 60 percent of the worldwide produced nickel is being used in the nickel-steel industry (predominantly stainless steel). Other applications of nickel include coin production, electroplating, alnico magnets, rechargeable batteries, fuel cells and microphone capsules [6; 7].

Although nickel is the sixth most abundant element in the universe [5]; it only forms about 0.016 percent of earth’s crust [3]. Universally the rocks that contain the highest concentration of nickel are basic and contain high amounts of iron and magnesium. The reason for the correlation between the nickel content and the iron and magnesium content is that the ionic radii of the three divalent metals are very similar; therefore, they can replace one another in some crystal lattices, mainly silicates.

2.2 Nickel Deposits

Nickel generally occurs in two types of land based ores, sulphide and laterite, and a third type of deep-sea manganese nodule, which could be a resource in the future. Land based nickel resources are estimated to be about 47 million tons; from which about 72 percent are present in nickel bearing laterite ores and the remainder are present in sulphide ores. Additionally, the sea-based manganese nodules are estimated to bear about 25-40 million tons of nickel [3].
Although 72 percent of world land based nickel resources are present in laterites, only 40 percent of world nickel production is from laterites. This arises from the fact that the nickel distribution through the molecular structure of laterites prevents them from being upgraded in pre-concentration processes by routine gravity separation methods. Nevertheless, laterites have the advantage of being amenable to open pit mining [2; 5].

Nickel laterite ore formation is based on the laterization process of “peridotite” rocks; in which the peridotite rock undergoes a weathering process under specific chemical conditions that occur predominantly in the tropical regions which leads to repeated dissolution and precipitation of metals.

Conversely, nickel sulphide ore is a result of the ascending liquid magma from below the earth’s crust forming an intrusive volume of liquid and subsequently solidifying within the existing rock [3].

### 2.3 Mineralogy of Nickel Laterites

Nickel laterite deposits contain heterogeneous mixtures of hydrated iron oxides and hydrated magnesium silicates; both can contain low concentrations of nickel and cobalt. These deposits are formed by weathering of serpentine and peridotite rocks, and are often found in areas with an abundance of rainfall such as tropical or subtropical regions. Olivine is an iron and magnesium silicate \([\text{Fe}_2\text{Mg}_2\text{Si}_4\text{O}_{10}]\) and is one of the main constituents of peridotite rocks. Olivine usually contains low concentrations of nickel; since \(\text{Fe}^{2+}, \text{Mg}^{2+}\) and \(\text{Ni}^{2+}\) have similar ionic radii and nickel may substitute for either magnesium or iron in the olivine structure.

A typical nickel laterite deposit is divided into the following three zones:

1. Limonite zone (L ore): This zone primarily consists of goethite, FeOOH, and is the closest zone to the surface. Nickeliferous limonite contains relatively low concentrations
of nickel and is quite uniform in both mineralogical and chemical composition and has very poor crystallinity and fine grain size.

2. Serpentine zone (S ore): This zone is a transition zone which occurs beneath the limonite zone and usually consists of various magnesium silicates. The serpentine zone contains intermediate amounts of nickel, iron, magnesium and silica and is fairly heterogeneous.

3. Garnierite zone (G ore): Just above the bed rock the nickel rich hydrated magnesium silicates form the garnierite zone. This zone usually contains the highest concentration of nickel but is extremely heterogeneous [3].

The chemical compositions and typical extraction methods for laterite deposits depending on different zones are demonstrated in Table 2-1.
Table 2-1: Chemical composition of laterite ores [8].

<table>
<thead>
<tr>
<th>Common name</th>
<th>Approximate analysis (%)</th>
<th>Extraction method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Co</td>
</tr>
<tr>
<td>Red limonite</td>
<td>&lt;0.8</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Yellow limonite</td>
<td>0.8–1.5</td>
<td>0.1–0.2</td>
</tr>
<tr>
<td>Transition</td>
<td>1.5–2</td>
<td>0.02–0.1</td>
</tr>
<tr>
<td>Serpentine/Garnierite</td>
<td>1.8–3</td>
<td>0.02–0.1</td>
</tr>
<tr>
<td>Fresh rock</td>
<td>0.3</td>
<td>0.01</td>
</tr>
</tbody>
</table>

2.4 Laterite Ore Processing Options

The two principal zones in a laterite ore, limonite and garnierite, are so different in heterogeneity and nickel content that they are treated by different methods.

The garnierite ores, having high nickel content and high heterogeneity, is typically treated by pyrometallurgical methods, including:

1. Smelting to ferronickel
2. Production of nickel matte with addition of sulfur or pyrite

In these processes the whole ore is smelted, so the heterogeneity of the ore is not an issue but the nickel concentration should be high enough to justify the energy consumption and costs.

The limonite ores are fairly homogenous and contain too much iron and too little nickel to be economically smelted to ferronickel; therefore, they are treated by hydrometallurgical methods. The hydrometallurgical methods go about selectively leaching the nickel and cobalt into the leach solution while the iron is removed in the solid leach residue. The two processes that are industrially used are [3]:

1. The Caron process
2. The high pressure acid leach process (HPAL)

### 2.4.1 The Caron Process

The Caron process was developed in the 1920s by M.H. Caron. This process consists of four main steps including:

1. Ore drying and grinding
2. Reduction roasting
3. Leaching with ammonium carbonate solutions
4. Metal recovery from solution

Figure 2-1 illustrates the Caron process flowsheet [3].
Figure 2-1: Caron process flowsheet [3].
In this process the ore drying and grinding is used to decrease the raw ore moisture content from 30–50 percent to 2–3 percent which requires a considerable amount of energy. Typically, about 60 percent of the total process energy input is consumed in this step.

The next step in the process is the reduction roasting with the purpose of selectively reducing nickel and cobalt to the metallic state while minimizing iron reduction. Nevertheless, typically about 10 percent of the iron is also reduced producing a nickel-iron alloy. The reduction roasting reaction can therefore ideally be written as:

\[
\text{NiO} + 2 \text{Fe}_2\text{O}_3 + 3 \text{H}_2 \rightarrow \text{FeNi} + \text{Fe}_3\text{O}_4 + 3 \text{H}_2\text{O}
\]  

(1)

This process usually takes place at temperatures above 850°C to ensure selective reduction. Subsequently the hot reduced ore is first cooled down to about 150°C under reducing conditions and afterwards undergoes an ammonia leaching step under oxidizing conditions causing nickel and cobalt to be selectively dissolved as ammine complexes. The leaching process occurs at about pH 10 according to the following reaction:

\[
\text{FeNi} + \text{O}_2 + 8 \text{NH}_3 + 2 \text{H}_2\text{O} \rightarrow [\text{Ni(NH}_3)_6]^{2+} + [\text{Fe(NH}_3)_2]^{2+} + 4 \text{OH}^-
\]  

(2)

At pH 10 the affinity of nickel and cobalt to form ammine complexes prevents them from hydrolyzing. Conversely, iron will oxidize to the ferric state and hydrolyze and precipitate as ferric hydroxide which will leave the process in the leach residue. The iron hydrolysis reaction is as follows:

\[
4 [\text{Fe(NH}_3)_2]^{2+} + \text{O}_2 + 8 \text{OH}^- + 2 \text{H}_2\text{O} \rightarrow 4 \text{Fe(OH)}_3 + 8 \text{NH}_3
\]  

(3)

Consequently, the pregnant leach liquor and the barren solids are separated by countercurrent decantation in a series of thickeners.
The last step of the process is metal recovery, where nickel and cobalt are recovered. This is typically done in two consecutive steps:

1. Cobalt and nickel sulphide mixed precipitation
2. Basic nickel carbonate precipitation

After filtration and clarification, the pregnant leach liquor is mixed with ammonium sulphide solution or hydrogen sulphide gas; this is usually done in a pipeline reactor and will cause cobalt to precipitate as cobalt sulphide. The pregnant leach liquor typically contains 20 times more nickel than it does cobalt; therefore, the sulphide precipitate is in fact a mixture of nickel and cobalt sulphide with a nickel to cobalt ratio of 2:1. The mixed precipitate is thickened, washed, dried, and sold as a nickel/cobalt sulphide mixture.

Afterwards the cobalt free solution proceeds to the nickel precipitation stage; where the ammonia and carbon dioxide are removed and recycled to the leaching circuit while the nickel precipitates as basic nickel carbonate. The reaction for this step is as follows:

\[
5 [\text{Ni(NH}_3\text{)}_6]^{2+} + 5 \text{CO}_3^{2-} + 7 \text{H}_2\text{O} \rightarrow 2 \text{NiCO}_3 \cdot 3\text{Ni(OH)}_2 \cdot 4\text{H}_2\text{O} + 3 \text{CO}_2 + 30 \text{NH}_3
\]  

The basic nickel carbonate is then treated with one of the following methods:

1. Producing nickel oxide powder by calcination of the basic nickel carbonate to drive off carbon dioxide and water.
2. Producing nickel powder by dissolving the basic nickel carbonate in an ammonium sulfate solution and precipitating it using hydrogen gas.
3. Electrowinning of pure nickel cathodes by re-dissolution spent electrolyte and purifying it with sulphide precipitation.

The important advantages of the Caron process are that, theoretically, all of the leaching reagents are recycled and only the process losses have to be made up, and that corrosion
problems are minimal in ammonia systems. On the other hand, the main disadvantage of the Caron process is that the overall metal recovery is only about 75–80 percent for nickel and about 40–50 percent for cobalt. Moreover, the energy consumption of the drying and grinding processes is very high [3].

2.4.2 The High Pressure Acid Leaching Process

The first high pressure acid leach process was built in Cuba for the Moa Bay laterite deposits. The Moa Bay laterite deposits have high iron content and are moderately rich in cobalt. Their low magnesium content makes them suitable for direct attack with sulfuric acid at high temperature and pressure. This focuses on improving the major disadvantages of the Caron process which are low metal recovery and high energy consumption. In this process the raw ore is directly treated, therefore eliminating the energy intensive drying and grinding processes. Furthermore, the metal recovery is more than 90 percent for both nickel and cobalt.

The high pressure acid leach process uses the propensity of ferric iron to hydrolyze at high temperatures to form hematite, goethite and jarosite (in sulfate solutions) to achieve selective separation of nickel and cobalt from iron. This is done by leaching the ore with sulfuric acid at temperatures of about 250°C with less than 1 g/L iron reporting in the pregnant leach solution. The leaching is typically carried out in a series of vertical autoclaves where concentrated sulfuric acid is pumped co-current to the ore flow, however, the leaching process has been revised in more recent high pressure acid leach plants to be carried out in series of horizontal autoclaves where all the acid is added to the first autoclave. Subsequently the leach slurry goes through a heat exchanger and then into a flash tank where the pressure will be decreased to atmospheric pressure. The cooled low pressure liquid is then washed in a countercurrent washing stage to separate the solid from the pregnant leach solution. This is followed by the metal recovery stage.
where hydrogen sulfide gas is added to co-precipitate nickel and cobalt as sulfides. The sea floor coral mud from Moa Bay sea is used to neutralize the free acid in the leach solution before the sulfide precipitation is done, since it contains high calcium carbonate content and a large surface area which makes it an effective neutralizing agent. The neutralized solution having a pH of about 2.4 is heated to 120°C and is treated with hydrogen sulfide gas at pressures as high as 1034 kPa. These conditions will result in the following reactions and recovery of 99 percent of the nickel and 98 percent of the cobalt.

\[
\begin{align*}
\text{Ni}^{2+} + \text{H}_2\text{S} & \rightarrow \text{NiS} + 2 \text{H}^+ \\
\text{Co}^{2+} + \text{H}_2\text{S} & \rightarrow \text{CoS} + 2 \text{H}^+
\end{align*}
\]

The progression of these reactions results in acid production and lowering the solutions pH which will cause the reaction rate to decrease. Therefore, recycling of the precipitates is used to control the particle size of the precipitates and to achieve high metal recoveries. Upon the completion of these reactions the resulting slurry is then cooled and the excess hydrogen sulfide gas is recovered in an atmospheric pressure flash tank. The final product is washed and concentrated to about 65 percent solids in a thickener and is then ready for shipment.

Figure 2-2 demonstrates the flowsheet of HPAL process [3].
Figure 2-2: The HPAL process flowsheet.


2.5 Goro Plant Operation

The Goro nickel plant, located on the south pacific island of New Caledonia, treats one of the richest laterite ores in the world, with an estimated value of 55 million tons of mineral reserve and an annual production capacity of 60,000 tons of nickel and 4,700 tons of cobalt [9].

The Goro plant is based on the high pressure acid leach process where both limonite and serpentine ores are accepted as feed. The deposit undergoes open-cut mining and after screening and pulping is sent to the high pressure acid leach process. After thickening, the ore slurry is acid leached in a pressurized autoclave which is followed by countercurrent decantation, purification and solvent extraction. The final products are nickel oxide and cobalt carbonate [10].

2.5.1 Mining

The first step of the Goro plant is the mining of the ore. The deposit characteristic involve it being a distinct, continuous thick layer which allows for an open-cut mining operation. Hence several surfaces will be opened horizontally and vertically allowing the extraction of the entire profile from the surface limonite layer to the further down serpentine layer. The Goro deposit mine has been estimated to have a life of 29 years [9].

2.5.2 Nickel Extraction

Initially after the mining operation, the whole limonite and serpentine ore is screened where the large rocks are separated. Afterwards the ore is pulped by water addition and stirring. The ore slurry is then conveyed to the plant situated below the mine via pipes. The pulp is then subjected to decantation where thickened pulp is produced and the water is recycled back to the pulping process.
The thickened pulp is then sent to the high pressure acid leach process where before treating with acid the pulp is gradually heated up to 260°C at a pressure of 4.5 MPa which inhibits water from reaching its boiling point.

The pulp is then injected in an autoclave where it is mixed with sulfuric acid; this causes nickel and cobalt to leach into the acid solution while impurities such as iron remain in a solid state in the pulp. Each autoclave processes 200 tons of ore per hour and consumes 67 tons of sulfuric acid per hour. Upon exiting the autoclave, the solution is cooled to atmospheric pressure and is subsequently decanted in a thickener. This step leads to the settlement of solids in the bottom of the thickener and their separation from the decanted solution. The decanted solution now comprises nickel, zinc, chrome, cobalt, aluminum, magnesium, copper and manganese and trace amounts of iron and a low concentration of unconsumed sulfuric acid.

The following step is the separation of nickel and cobalt from the decantation solution which is done by the addition of limestone causing the precipitation of gypsum. The gypsum precipitation is caused by the reaction occurring between the residual sulfuric acid and the limestone. This reaction also results in solidifying and co-precipitation of aluminum, chromium, iron and copper along with the gypsum. The mineral-rich gypsum is then treated for discharge.

The residual solution containing nickel, cobalt and copper, zinc, magnesium and manganese impurities is then treated through several solvent extraction columns to separate nickel and cobalt from the impurities. The impurities are then sent to a waste treatment center and the nickel and cobalt rich solution is treated through a second solvent extraction unit to separate nickel from cobalt into two distinct solutions.
The nickel solution is heated up to a temperature of 800°C which causes the water to evaporate and nickel oxide grains to form. This nickel oxide is the main product of the Goro plant.

Additionally, the cobalt solution is subjected to sodium carbonate addition which will result in the formation of cobalt carbonate which is the Goro plant secondary product for export [11].

Figure 2-3 shows a picture of the Goro plant at New Caledonia [10].

Figure 2-3: Goro plant operation at south pacific island, New Caledonia.

2.6 Magnesium in Laterite Processing

Most rocks that contain high concentrations of nickel are basic or mafic and contain high concentrations of magnesium and iron. This is due to the similarity of the ionic radii of nickel, magnesium and iron which enables them to replace one another in crystal lattices such as
silicates [3]. Therefore, the primary objective of any nickel extraction plant is to separate iron and magnesium from the nickel.

The impact of magnesium on the nickel extraction plant is dependent on the ore nickel content and the process used for nickel extraction. Typically, high nickel content ores are treated pyrometallurgically where the whole ore is smelted therefore the impurity content and the heterogeneity of the ore are not of high importance. Although the nickel content should be significantly high to justify the melting energy requirement.

Nevertheless, magnesium presence in low nickel grade ores operations such as the Caron process and the HPAL process affects the extraction process. The impact of magnesium on each process is different, although in both the cases of the Caron process and the HPAL process magnesium is known to reduce the nickel recovery. Additionally, magnesium compounds are highly soluble and the ore treatment will lead to magnesium laden solutions which are non-recyclable and are typically dumped to the environment.

The Caron process is affected by magnesium in the reduction roasting step. This step typically operates at temperatures above 850°C; while at temperatures between 750 to 850°C amorphous magnesium silicates recrystallize to form forsterite where any nickel not reduced to the metallic state will co-crystallize with the forsterite and therefore will be insoluble in the proceeding leaching step.

The high pressure acid leach process can generally accept ores with magnesium content between 3 and 10 percent; where higher magnesium content will lead to excessive acid consumption since magnesium will compete with the nickel for the acid, on the other hand lower magnesium content will require additional neutralization [3; 5].
2.7 Struvite a Magnesium Based Fertilizer

Struvite or magnesium ammonium phosphate hexahydrated is a white crystalline substance which is formed according to the reaction: [12]

\[ \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6 \text{H}_2\text{O} \rightarrow \text{NH}_4\text{MgPO}_4\cdot6\text{H}_2\text{O} \]  

(7)

Struvite consists of equal stoichiometric ratios of magnesium, ammonium and phosphate in addition to six waters of hydration. Struvite is believed to have an orthorhombic crystalline shape with the internal structure consisting of regular \( \text{PO}_4^{3-} \) tetrahedral, distorted \( \text{Mg(H}_2\text{O)}_6^{2+} \) octahedral and \( \text{NH}_4^+ \) groups, which are all held together through hydrogen bonding. Struvite crystal habit is variable; depending on the growth conditions it can be equant, wedge shaped, short prismatic or thick tubular [13].

Struvite is one of the best fertilizers since in addition to containing magnesium, ammonium and phosphate which are important nutrients for soil fertility, it is a concentrated, easy to apply, non-odorous and slow release fertilizer [14]. The advantage of struvite being a slow release fertilizer is that it allows lower application rates, which is beneficial due to the increase in fertilizer prices [15].

2.8 Struvite History

Undesired struvite precipitation has been reported to occur in pipelines and equipment for anaerobic digestion and post digestion processes in several waste water treatment plants since the 1960s. These struvite precipitates are hard and difficult to extricate, therefore causing a decrease in plant capacity and damage to the pumping equipment and plugging of the sludge pipes. Solutions to this problem include acid washing, heat treating and mechanical jet washing, however these methods are costly. The reported annual cost associated with this problem for a mid-size treatment plant (25 million gallons per day) exceeds US$100,000. The most effective
and cost efficient method to solve this problem is to initiate intentional struvite precipitation from the supernatant stream in a crystallization reactor [13].

2.9 Struvite Shape and Size

Struvite is known to be a sparingly soluble substance and its dissolution is dependent on its particle size. Smaller particles with greater surface area to volume ratio dissolve more readily than larger particles. The dissolution rate is an important parameter for struvite application. Struvite usage as fertilizer demands lower dissolution rates and hence larger sizes for slow release onto the land to avoid overload or crop burning. The additional advantage of this is that it allows lower application rates. Conversely smaller pellets are used in stream nutrient enhancement to provide relatively faster nutrient release [15].

As opposed to larger struvite crystals being more desirable; most crystallization plants produce fine struvite crystals that form powder when dried. To produce larger crystals high control over the process conditions is essential to achieve the required supersaturation ratio. Additionally, large struvite crystal formation is highly dependent on reactor type and design often requiring high flow rates and high energy consumption. Thus to produce smaller struvite crystals simpler processes are used [16].

Crushing strength is another important parameter in struvite application. Stronger crystals are easier to transport and apply to the field whereas crushed or fine crystals can cause material loss during the manufacturing and application processes.

Therefore, the struvite quality is described with both composition/purity and crushing strength; where the requirements vary for different applications [15].
2.10 Factors Affecting Struvite Precipitation

Struvite crystal growth, morphology and size is dependent on many factors including mixing intensity, seeding and the seeding technique, pH, temperature, crystal retention time, magnesium to phosphate ratio, supersaturation level and the impurities present in the system. Variations in each of these parameters effects struvite precipitation in a different manner.

2.10.1 Stirring Speed

The stirring speed or the mixing intensity is defined as the speed at which the stirrer mixes the solution. Mixing of the solution is done in order to achieve uniform distribution of all of the components present in the solution.

Stirring speed is known to effect struvite precipitation; it is believed that the stirring intensity is responsible for controlling struvite growth rate and crystal habit [17]. However, several researchers have established that the mixing intensity has little effect on the struvite precipitation. It is believed that the reason for this is the existence of mixing energy in excess amount in comparison to its optimum value corresponding to the set base parameters. Furthermore, excessive mixing may result in crystal breakage, thereby reducing process efficiency and stability [12].

2.10.2 Seeding

Seeding is a parameter that does not affect struvite precipitation directly; however, it has been used by many researchers as a method to enhance struvite precipitation. Moreover, it is believed that the seed crystal size and structure impact struvite precipitation. Therefore, seed material that mimics the precipitate crystal structure is used. Additionally, seed material with smaller size and therefore larger specific area is used to promote struvite precipitation [12; 18].
2.10.3 pH

The pH is one of the most influential parameters that affects struvite precipitation. This is due to the fact that the availability of struvite constituent ions (Mg$^{2+}$, NH$_4^+$ and PO$_4^{3-}$) is dependent on the pH. However, at different pH the actual ions present in the solution may differ. As in the case of struvite all of the reacting ions display complex equilibria in aqueous solutions. For instance, the amount of ammonium ion present in the solution is reliant on the equilibrium between ammonia and ammonium ion which is highly dependent on the pH. Likewise, for phosphate ion; because of the triprotic nature of phosphoric acid, numerous phosphate species exist in an aqueous solution which result in different quantities of phosphate ion at different pHs. Similarly, in the case of magnesium; magnesium hydrolysis leads to the formation of magnesium hydroxide which only occurs at high pHs. Therefore, in the presence of ammonia, phosphate and magnesium numerous complexes form based on the pH of the solution; hence, the speciation of the components and the struvite solubility are also pH dependent.

Typically, it is seen that within the operating pH interval of 7 to 8.5 struvite solubility increases with decreasing pH. This is due to the fact that as the pH increases the ammonium concentration decreases whereas the phosphate concentration increases; this leads to a pH at which the struvite solubility is minimum.

2.10.4 Temperature

Temperature is an important factor in struvite precipitation. Struvite formation and morphology are both influenced by temperature changes; this is caused by the fact that struvite crystal growth is dependent on the temperature [17].

Various salts correspond to temperature changes differently. The impact of temperature change is mainly determined by the amount of heat absorbed or released upon solute dissolution.
Heat absorption or release is dependent on the amount of energy required to break the crystal structure of the solute and on the amount of energy released when the solute particles interact with the solvent. If the energy that is required to break the solute particles is more than the energy gained from the interaction of the solvent and the solute particles, heat will be absorbed and the dissolution will be called endothermic and the enthalpy change is positive; conversely, if the energy gained from the solute-solvent interaction is more than the energy requirement for the crystal breakage of the solute, heat will be released and the dissolution will be called exothermic and the enthalpy change is negative.

Most salts dissolutions are supplemented with heat absorption and are endothermic reactions. Therefore, upon raising the temperature of a saturated solution the reaction of solid dissolution where the solid particles enter the solvent solution is more favorable in comparison to the solid precipitation from the solution. Therefore, the salts solubility increases with temperature. Contrariwise if the solid precipitation is favored over the solid dissolution, the dissolution reaction is exothermic and the solid solubility will decrease upon temperature increase.

Several researchers have investigated the effect of temperature on struvite solubility. Their observations indicate a steady increase in struvite solubility with an increase in temperature over the range of 10–65°C. It is seen that at the temperature of 30°C struvite solubility is maximum. However, a sudden transition occurs at the temperature of 55°C which is believed to be due to the phase change from struvite with six waters of hydration to magnesium ammonium phosphate monohydrate. The presence of more waters of hydration in struvite causes it to be more soluble.

Simplified struvite crystallization reaction is according to reaction (7) and the change in the enthalpy of formation for struvite precipitation is calculated to be -89.9 KJ/mol and therefore struvite crystallization is slightly exothermic [19].
The temperature effect on struvite solubility could also be demonstrated using struvite thermodynamic solubility product. The logarithmic thermodynamic solubility product of struvite is reported to be in the range of 14.36 to 14.01 for the temperature interval of 10 to 60°C where the minimum value is 13.17 at the temperature of 30°C [20].

2.10.5 Residence Time

Another parameter that affects struvite precipitation is the crystal residence time which refers to the time that a single crystal precipitate spends in the reactor. The residence time is typically used to determine the precipitate crystal size. It is seen that precipitate crystal size increases with increasing residence time. However, upon achieving the maximum crystal size, a further increase in the residence time will lead to a decrease in the crystal size [17].

2.10.6 Magnesium to Phosphate Ratio

Magnesium to phosphate ratio is the molar ratio of magnesium ion to phosphate ion present in the reactor. Several researchers have indicated that higher magnesium concentrations result in larger crystal precipitation by favoring crystal agglomeration [17].

2.10.7 Impurity

A parameter that is known to have a drastic effect on struvite precipitation and struvite crystal growth is the presence of impurities in the reactor. The impurities can be classified into three distinct groups. The first group of impurities improve crystal growth; the second group of impurities suppress crystal growth completely; the third group of impurities apply a selective effect where they only act on certain crystallographic faces and suppress or accelerate crystal growth solely on those faces [17].
2.10.8 Supersaturation

Supersaturation is the most important factor in struvite precipitation. It is believed that the crystal habit development is dependent on the supersaturation level. Furthermore, a solution supersaturation level effects the precipitate crystal size where high supersaturation level will lead to the formation of small crystals [17].

To fully understand the concept of supersaturation, the concept of conditional solubility product and supersaturation ratio are defined.

2.10.8.1 The concept of conditional solubility product

Conditional solubility product is a quantitative parameter introduced in order to determine the precipitation potential of a certain solution. The conditional solubility product is in close relation with the solubility product. However, the solubility product is only accurate at a specific pH value; therefore, in order to overcome this fact, the conditional solubility product is introduced as the equilibrium constant which is consistent under a fixed set of conditions.

The solubility product is defined by Equation 8 where \{\} describes the activity of each component; likewise, the conditional solubility product is defined by Equation 9 where [ ] represent the molar concentration of each component [21].

\[
K_{sp} = \{Mg^{2+}\} \{NH_4^+\} \{PO_4^{3-}\} \quad (8)
\]

\[
P_S = [Mg^{2+}]_{total}[NH_4^+]_{total}[PO_4^{3-}]_{total} \quad (9)
\]

2.10.8.2 The concept of supersaturation and supersaturation ratio

In terms of aquatic chemistry; supersaturation ratio is defined as the quantitative representation of struvite precipitation potential increase, associated with an increase in struvite constituent concentrations. The supersaturation ratio is described using Equation10 [21].
\[
SSR = \frac{P_s}{P_{s-eq}}
\]  

(10)

Where the \(P_{s-eq}\) is the equilibrium value of the conditional solubility product.

Theoretically, supersaturation ratio values larger than one imply that the solution is supersaturated and that precipitation is possible. Conversely if the supersaturation ratio value is less than one the solution is unsaturated and precipitation is not possible. Supersaturation values equal to one indicate that the solution is at equilibrium.

However, in crystallization processes the concept of supersaturation ratio is defined differently. Crystallization researchers offer refinements to the supersaturation ratio concept. It is believed that the crystallization process involves two consecutive stages. The first stage is the nucleation stage which is controlled by solubility chemistry and the second stage is the growth stage which is controlled by the mixing energy in the crystallizer.

2.10.8.3 Supersaturation and metastable region

A supersaturated solution refers to a solution which contains higher concentrations of solute than its saturation concentration at a certain temperature. Typically, a supersaturated solution is prepared by cooling the unsaturated solution [22].

From a thermodynamic point of view, supersaturated solutions are unstable; however up to a certain concentration the solution appears to be stable and its properties are constant. The interval from the saturation state up to the concentration in which the supersaturated solution is no longer stable is defined as the metastable region [20]. From a crystallization viewpoint, the metastable region is the critical region in which the crystallization process is not governed by nucleation and the nucleation rate is very small in comparison to the growth rate [21];
consequently, crystallization processes are typically carried out in the metastable zone since the desired process control could solely be achieved in this region.

2.11 Struvite Mechanism

Phosphorus is one of the main nutrients that struvite provides. Phosphorus is a crucial macro nutrient for plants and crop growth. Typical phosphorus fertilizers are highly soluble in water and upon application dissolve rapidly into the soil profile. The issue with the conventional fertilizers is that plants are unable to absorb all of the applied phosphorus. It is known that the maximum phosphorus that plants absorb is only 25 percent of the applied phosphorus in one year. The remainder 75 percent phosphorus reacts with iron, aluminum or calcium and becomes unavailable to the plant. Therefore, it is possible for a soil to have a high concentration of phosphorus but still have phosphorus deficient plants. Additionally, excess amounts of phosphorus can leach or run off resulting a nutrient overload in the nearby water ways.

In contrast to conventional fertilizers; struvite offers a phosphorus delivery mechanism that minimizes nutrient loss and the risk of nutrient run off to adjacent water ways. Typical plants release organic acids such as citrates when they require nutrients. Struvite is a citrate soluble fertilizer and will dissolve slowly into the soil solution and provide nutrients whenever the plant roots require them. Furthermore, as the plants’ nutrient requirements decrease, the nutrient release from struvite decreases as well, thereby reducing the risk of nutrient leaching and run off [23].
2.12 Struvite Nutrients

Plants require food for growth and development. It is established that plants need 16 essential elements for survival. From these 16 elements carbon, oxygen and hydrogen are delivered by the atmosphere and soil water, and are therefore not required in a fertilizer [24].

The remaining 13 essential elements include nitrogen, phosphorus, magnesium, potassium, sulfur, calcium, zinc, iron, copper, manganese, molybdenum, boron and chlorine, and must be supplied via soil minerals or fertilizers. These 13 elements are categorized into three groups. Nitrogen, phosphorus and potassium are categorized as the primary nutrients; whereas magnesium, calcium and sulfur are the secondary nutrients and the remainder of the elements are categorized as the micronutrients. The primary nutrients are described as the nutrients that are largely utilized by the plants; the secondary nutrients are defined as the nutrients which plants require in smaller concentrations than the primary nutrients and the micronutrients are the nutrients that plants require in very small doses [25].

Each plant nutrient requirement is unique and has a distinct minimum and maximum value. Low levels of nutrients will cause nutrient deficiency and high levels of nutrients will be toxic to the plants and will cause poor growth. Therefore, application of nutrients within the optimum range is necessary [24].

2.12.1 Nitrogen

Amongst the three primary nutrients, plants demand nitrogen in the largest quantities. Plants consume nitrogen as nitrate and ammonium ions. Nitrogen is used in order to stimulate rapid growth, improve leaf quality and size, accelerate crop maturity and endorse fruit and seed development. Additionally, nitrogen in biological combination with carbon, hydrogen, oxygen and sulfur form amino acids which are the protein blocks used to build protoplasm and therefore
help with plant growth and development. Other uses of nitrogen are promoting plant enzymatic reactions and facilitating photosynthesis [24; 25].

2.12.2 Phosphorus

The other primary nutrient plants require for their growth is phosphorus which is available to plants as the orthophosphate ion. Phosphorus is used to enhance seed development, stimulate plant blooming, accelerate maturity, reduce disease incidence in plants and offer winter resilience for crops planted during late fall [24; 25].

2.12.3 Magnesium

The final component of struvite which is also a secondary nutrient to plants is magnesium. Magnesium is an essential component for photosynthesis. Additionally, it is used in order to regulate other nutrients uptake, transport phosphate ions throughout the plant, and increase oil and fat production [25].

2.13 Struvite in Comparison to Other Fertilizers

The most common parameters used to compare the effectiveness of fertilizers are the phosphorus uptake and the isotopically exchangeable phosphorus also known as IEP. A comparison between typical triple super phosphate fertilizer also known as TSP and struvite verifies that struvite is equally as effective as TSP [26].
3 Methodology

3.1 Introduction

The removal of magnesium to form struvite is based on the simplified reaction presented in Equation 7.

Since hydrometallurgical solutions typically involve soluble magnesium as magnesium sulfate, the magnesium solutions used in this study are synthetic magnesium sulfate solutions. However, as the experiments progressed the magnesium sulfate solution was enhanced to contain typical impurities found in hydrometallurgical plants. The compositions used for these solutions were based on solutions available from Vale Inco’s Goro plant. Additionally, the required ammonium feed is supplied using an ammonium hydroxide solution whereas phosphoric acid is used to supply the required phosphate feed.

3.2 Magnesium Removal Process Flowsheet

An approach for magnesium recovery from nickel laterite plants has been developed at the University of British Columbia. The premise of this approach involves recovering soluble magnesium as struvite which is a valuable, environmentally friendly byproduct. The production of a valuable by-product will marginally reduce the plants dependence on nickel prices. Therefore, the overall process will be less vulnerable to market fluctuations. Additionally, this method will cause an increase in resource recycling and reduces solution dumping to the environment.

Figure 3-1 shows the proposed flowsheet for removing magnesium from nickel laterite leach solutions. The flowsheet starts with nickel recovery in the solvent extraction stage. The flowsheet involves lime addition to the solution exiting the solvent extraction unit in order to
increase the pH to a value near neutral. Furthermore, the lime addition causes the majority of metals in the solution to precipitate as hydroxides; subsequently the mixed precipitate which is mainly gypsum is collected for disposal. The solution is then pumped to the precipitation tank where phosphoric acid and ammonia are added to the solution. The addition of these reagents will provide stoichiometry and pH control and will cause struvite to precipitate. The precipitated struvite is then filtered and sent for drying and sale. The solution which is now predominantly ammonium sulfate is subjected to further lime addition. This is done in order to precipitate the sulfate as gypsum and prepare the solution for ammonia stripping. The second gypsum product is pure enough for sale mitigating some of the additional lime cost. The ammonia solution is then sent to an ammonia stripping unit where the ammonia is separated from the leach liquor and is recycled back to the struvite precipitation stage. The purified leach liquor is then ready for recycling and is sent to the front end of the nickel leaching stage.
Figure 3-1: Proposed flowsheet for magnesium removal from nickel laterite leach solutions.
This flowsheet offers a simple method for recovering magnesium with a straightforward chemistry. To precipitate struvite; ammonium and phosphate are added to the feed magnesium sulfate solution. The stoichiometric ratio of reagents in this stage is 1 Mg$^{2+}$: 3 NH$_4^+$: 1 PO$_4^{3-}$. Although struvite does precipitate at any reagent stoichiometric ratio the minimum suggested stoichiometric ratio is unity. In this study the additional ammonium is added to maintain a pH control and to form ammonium sulfate for the consecutive stage.

$$\text{MgSO}_4 + 3 \text{NH}_3 + \text{H}_3\text{PO}_4 + 6 \text{H}_2\text{O} \rightarrow \text{NH}_4\text{MgPO}_4\cdot6\text{H}_2\text{O} + (\text{NH}_4)_2\text{SO}_4 \quad (11)$$

The next stage involves lime addition to the remainder ammonium sulfate solution leading to the precipitation of gypsum and the removal of sulfate.

$$(\text{NH}_4)_2\text{SO}_4 + \text{Ca(OH)}_2 \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O} + 2 \text{NH}_3 \quad (12)$$

This will lead to the conversion of ammonium to ammonia which is then sent to a stripping stage in which the solution is heated and agitated to liberate the dissolved gas. After the stripping stage the ammonia is recycled back to the struvite precipitation step.

### 3.3 Process of Magnesium Recovery as Struvite

Struvite precipitation is a relatively simple process and is carried out in accordance with Equation 7. Table 3-1 illustrates the baseline concentrations at which the experiments were carried out.

Prior to the addition of ammonium and phosphate solutions, these solutions are mixed in a separate mixing tank. This mixing will lead to the formation of an ammonium phosphate solution. This mixing reaction is highly exothermic and will cause the solution temperature to rise. Any decrease in the temperature will lead to the formation of ammonium phosphate crystals which can block the pumping tubes. Therefore, this solution is typically maintained at temperatures higher than ambient temperature. However the amount of increase in the
temperature is dependent on the solution volume and the amount of water present since water has a high heat capacity and it could be exposed to heat without affecting the temperature greatly.

Subsequently to the mixing of the ammonium and phosphate solution, the solution is pumped to the magnesium sulfate solution. These concentrations are considerably higher than the supersaturation concentration of struvite precipitation. Therefore, upon the addition of struvite constituents the precipitation occurs immediately.

The pumping duration is reliant on the volume of the ammonium phosphate solution and the pumping speed; however, due to the high concentration of struvite constituents the pumping speed did not have any effect on struvite precipitation; since struvite precipitates immediately after the first drop of ammonium and phosphate solution is poured into the magnesium sulfate solution. Following the pumping the residence time is measured; this time is the time required for the solution and the precipitated struvite to reach equilibrium, where any additional time had no additional impact on the pH or struvite mass precipitated. After equilibrium is reached the mixing is stopped and the solution is left overnight so that the solid precipitate can separate from the liquid. This is done in order to simplify the following filtration step and to decrease the liquid input to the filtration step.

The filtration step is carried out in order to separate the solution from the solid precipitate. In this step the solution containing the precipitate is pumped through a filter paper with mesh size of about 10 µm to obtain a clear solution. Additionally the filtered precipitate is washed with deionized water to rinse off any residual solution. After the filtration step the filtered precipitate, which is predominantly struvite, is dried at a temperature of 40°C for 24 hours after which it is weighed and stored.
To identify the composition of the precipitate, the precipitated solids are analyzed by X-ray diffraction analysis. This method is further explained in section 3.7.1.

3.4 Optimization of Struvite Precipitation

The extent of struvite precipitation is dependent on many factors; the most influential parameters include: supersaturation level, magnesium to phosphate ratio, pH, mixing strength, seeding technique, the presence and concentration of impurities, the magnesium salt used, temperature and residence time.

Each of these parameters were examined to obtain the optimum condition for struvite precipitation. To find the optimum level of each parameter, other parameters were held constant at the baseline conditions chosen for the experiments, while the parameter of interest was changed to find a value which corresponds to maximum struvite precipitation and magnesium removal.

The base conditions for the set of experiments in this study are presented in Table 3-1:
Table 3-1: Base conditions for struvite precipitation reaction.

<table>
<thead>
<tr>
<th>General Conditions</th>
<th>Synthetic Solution Concentrations</th>
<th>Goro Plant Solution Concentrations</th>
<th>Replicated Goro Plant Solution Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>28</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Stirring Speed (rpm)</td>
<td>340</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stoichimetric Ratio</td>
<td>1Mg$^{2+}$ : 1PO$_4^{3-}$ : 3NH$_4^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration of Magnesium (M)</td>
<td>0.25</td>
<td>0.0612</td>
<td></td>
</tr>
<tr>
<td>Concentrations of Impurities (M)</td>
<td>Cl = 0.035</td>
<td>Na = 0.033</td>
<td>Ca = 0.019</td>
</tr>
<tr>
<td>Concentrations of Ammonium (M)</td>
<td>0.75</td>
<td>0.183</td>
<td></td>
</tr>
<tr>
<td>Concentrations of Phosphate (M)</td>
<td>0.25</td>
<td>0.0612</td>
<td></td>
</tr>
</tbody>
</table>

### 3.5 Chemicals

To evaluate the effectiveness of struvite precipitation and removal of magnesium from laterite plant effluents, two sets of experiments were carried out. The first set of experiments used synthetic magnesium sulfate solution to replicate plant effluent solution since the main constituent of the effluent stream is magnesium sulfate. The second set of experiments used solutions with compositions analogous to the Goro plant effluent stream. Both sets of experiments aimed to find the optimum conditions for maximum magnesium removal.
The magnesium salt used to replicate the effluent solution was commercial grade magnesium sulfate and in the case of the Goro plant solution commercial grade magnesium sulfate, calcium sulfate and manganese sulfate were used.

To supply the ammonium, a solution of 14.5 percent ammonium hydroxide was used. The required phosphate was supplied using an 8.5 percent phosphoric acid solution.

The pH adjustments were made using either 1 normal sulfuric acid or 1 mole per liter sodium hydroxide solutions depending on the adjustment requirements towards more acidic or basic conditions.

3.6 Setup

The basic experimental setup used for this study is shown Figure 3-2. A peristaltic pump is used to pump the solution of ammonium and phosphate to the magnesium sulfate solution and a pH meter is used to measure the solution pH.
Figure 3-2: (a) Schematic illustration of struvite precipitation set-up (b) Actual Struvite precipitation set-up.

3.7 **Product Quality Test**

Struvite quality is determined by its purity/composition, size and crushing strength. The struvite produced in this study was solely tested for its composition and purity through XRD analysis.

The dissolution of struvite, a sparingly soluble material, is generally controlled by surface reactions. Therefore, the size of the struvite pellets influences the dissolution kinetics. Smaller pellets, having a greater surface area to volume ratio, are more easily dissolved than larger ones. These dissolution rates are important for struvite application. The use of struvite as an agricultural fertilizer may demand lower dissolution rates for slow release into the land, thus avoiding overload or crop burning. In contrast, small pellets are desirable for stream nutrient enhancement that will provide relatively faster slow release of nutrients. In addition to the size requirements, the formation of pellets with higher crushing strengths is desirable for transport and application of struvite in the field. The pellets also have to be durable, because fine or crushed struvite may lead to loss of material during manufacture, collection, and application. The
quality of struvite formed can be described in terms of both composition/purity and crushing strength, and the requirements are different for varying applications. [15]

3.7.1 X-Ray Diffraction Analysis

In order to determine the composition and purity of the produced struvite, qualitative X-ray diffraction (XRD) analysis was done. This analysis was carried out by the Department of Earth, Ocean & Atmospheric Sciences at the University of British Columbia. For this analysis the sample grain size is required to be reduced to less than 10 μm which is done by grinding under ethanol in a vibratory micronizing mill. The powder XRD data for the sample were gathered over a range of 3−80°2θ with CoKα radiation on a diffractometer.

The International centre for diffraction database and Bruker search-match software were used to analyse the X-ray diffractogram. Furthermore, the powder XRD data were refined using a Rietveld program.

3.8 Terminology

The extent of magnesium recovery as struvite is estimated using the following equation.

\[
\text{Theoretical Reaction Recovery} = \frac{\text{Actual mass of precipitate}}{\text{Theoretical mass of struvite precipitate}} \times 100
\]  

(13)
4 Results and Discussion

4.1 General Observations of Magnesium Removal Process

For both the synthetic magnesium sulfate experiments and the replicated Goro plant experiments the response of the set-up is very encouraging, both in terms of magnesium removal and hence the struvite recovery and the produced struvite purity. The base condition experiments gave an average of 95 percent magnesium removal with struvite purity of 97.5 percent for the synthetic magnesium sulfate experiments, and 96.13 percent magnesium removal with struvite purity of 99.8 percent for the replicated Goro plant experiments.

The overall results confirm the ability of the magnesium removal flowsheet to recover magnesium with recoveries above 90 percent. One of the advantages of this process, which is due to the high concentrations of struvite constituents, is that struvite precipitation occurs immediately after the constituents are mixed, so that equilibrium is achieved reasonably rapidly and therefore struvite removal can be completed within as little as 10 minutes time.

The most important advantage of the flowsheet is that the existing conditions of the effluent solution such as ambient temperature and pH are the conditions at which the optimum results occur; therefore no further adjustment in any of the conditions is required.

In all of the experiments, the resulting struvite precipitate was powdery with relatively low hardness since in all cases the precipitate could be crushed by hand. The struvite powder image, both with no magnification and with 1.5K magnification using scanning electron microscopy (SEM), is presented in Figure 4-1; this figure shows that the precipitated struvite is a white powder with poor crystallinity.
The purity of the struvite is determined using XRD analysis which shows to be typically more than 98 percent. The XRD result for the base experiment using magnesium sulfate solution is presented in Figure 4-2.

In several cases such as the synthetic magnesium sulfate solution the final product is 97.54 percent struvite and the remainder 2.33 percent is Newberyite, Mg(PO\textsubscript{3}OH).3(H\textsubscript{2}O), which is a fertilizer; therefore, its precipitation with struvite is not of issue.
Figure 4-2: XRD analysis results for magnesium sulfate solution experiment under base conditions.

4.2 Factors Affecting the Magnesium Removal Process

Struvite precipitation, in terms of the extent of precipitation, the kinetics of the precipitation process and the precipitate morphology and size, is dependent on many factors, as noted above.

Each of these parameters were examined to obtain the optimum condition for struvite precipitation. To find the optimum level of each parameter, other parameters where held constant at the values set to be the base conditions for the experiments, while the original parameter was changed to find the value which corresponds to maximum struvite precipitation and magnesium removal. The degree of effectiveness of each of these parameters is different; while supersaturation level and pH have great impact on the extent of magnesium removal, temperature and mixing intensity are less influential.
4.2.1 The Effect of Stirring Speed on Magnesium Removal

To achieve uniform concentration distribution in all of the experiments, magnetic stirrers are used. The mixing intensity of the solutions is quantified by measuring the stirrer speed in revolutions per minute (rpm).

The magnesium removal efficiency is anticipated not to be highly dependent on the mixing intensity. However, it is seen that, depending on the impurities present in the magnesium sulfate solution, the effect of mixing intensity is different. As shown in Figure 4-3, in the case of synthetic magnesium sulfate feed with no impurities present, the impact of stirring speed is negligible. Therefore, lower stirring speeds could be used to decrease the energy consumption and the crystal breakage probability. Conversely, in the case of replicated Goro plant solution, lower stirring speed led to insufficient mixing and the co-precipitation of struvite and gypsum.

Figure 4-3 illustrates the changes in reaction efficiency at different stirring speeds.

![Graph: Reaction efficiency vs. stirring speed](image)

Figure 4-3: The effect of stirring speed on the reaction efficiency.
In the case of the replicated Goro plant solutions the reaction efficiencies are higher than 100 percent. This is due to the co-precipitation of gypsum and struvite in the final precipitate which is a result of insufficient mixing. The results from XRD analysis confirm the co-precipitation of gypsum and struvite in the final product. The XRD results are presented in Table 4-1, Figure 4-4 and Figure 4-5.

The quartz present in the XRD results is most likely contamination from the grinding pellets in the XRD analysis laboratory.
Table 4-1: XRD results for replicated Goro plant solution at 80 and 100 rpm stirring speeds.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>R-Goro 80 rpm</th>
<th>R-Goro 100 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite</td>
<td>(NH₄)MgPO₄·6H₂O</td>
<td>91.2</td>
<td>92.5</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>8.7</td>
<td>7.4</td>
</tr>
<tr>
<td>Quartz*</td>
<td>SiO₂</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Figure 4-4: XRD result for replicated Goro plant solution with 80 rpm stirring speed.
The Effect of Seeding and Seeding Technique on Magnesium Removal

Seeding of the feed solution is used to increase the magnesium removal efficiency by providing reaction surface that promotes struvite crystal formation and precipitation. Typically, seeds with larger specific surface area and thus smaller size enhance magnesium removal. Additionally, both seeding and the size and crystal structure of the seeds used affect the magnesium removal process. The seeds used should be of sufficient size and crystal structure to simulate the precipitating substance [12; 18].

The results for both seeded synthetic magnesium sulfate solution and seeded replicated Goro plant solution confirm the predictions and show an improved recovery of more than 98 percent. The results for the seeding experiments are presented in Figure 4-6.
Although the results are very promising in the case of powder seeding, other seeding techniques seem to decrease the magnesium removal efficiency. The seeding methods used for the synthetic magnesium sulfate solution include addition of 3 times more seed than the expected struvite precipitation amount (3:1 seed), seeding the magnesium feed solution with recycled seed (second seeding) which are seeds that have already been used in a seeding experiment, and using the precipitated struvite without filtering and drying it (decantation); all of these cases correspond to recoveries lower than the recovery of the reaction without seeding.

Furthermore, often seeding is used to increase the size of struvite precipitate along with increasing the reaction recovery. In the case of our experiments no difference in the appearance of the precipitate is observed in both cases of seeded and unseeded. Although the seeded precipitates seem to be harder to crush, since no exact experiment exists to evaluate precipitate hardness, this observation is made by crushing the struvite precipitate by hand.

Figure 4-6: The effect of seeding and seeding technique on magnesium removal efficiency.
4.2.3 Impurity Effect on Struvite Precipitation and Magnesium Removal

The addition of impurities to the feed solution affects the magnesium removal process both in terms of the extent of magnesium removal and the precipitated struvite quality and purity. The impurity addition effect may be positive or negative; in the case where the effect is positive the impurity acts as a seed and facilitates the precipitation [27], but in the case where the effect is negative the impurity can compete with the magnesium to consume ammonia and/or phosphate and therefore decrease the reaction recovery. It is also reported that impurities could absorb on the crystal surface and retard struvite formation. Furthermore, impurities can prevent the increase of crystal size by blocking active growth sites [28].

The results of the impurity tests for this study show that struvite precipitation is dependent upon the concentration of impurities present. Higher concentrations of impurities affect both the reaction recovery and the precipitate purity.

The impurities with the most effect on the system are manganese and calcium. This is confirmed by the negligible difference between the recovery and the product purity of the tests replicated Goro plant solution containing only magnesium sulfate, manganese sulfate and calcium sulfate and the case containing magnesium sulfate, sodium sulfate, calcium sulfate, potassium sulfate and magnesium chloride which contains all components present in the actual Goro plant solutions. In both of these cases the recovery is about 96 percent and the product purity analyzed by XRD is 99.8 percent. The reaction recovery and the XRD analysis results are presented in Table 4-2 and Table 4-3.
Table 4-2: Reaction recovery results comparing solutions replicated Goro plant solutions containing various impurities.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>MgSO₄, MnSO₄, CaSO₄</th>
<th>MgSO₄, MnSO₄, CaSO₄, MgCl₂, K₂SO₄, Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction Recovery (%)</td>
<td>96.14</td>
<td>96.94</td>
</tr>
</tbody>
</table>

Table 4-3: XRD analysis results comparing solutions replicated Goro plant solutions containing various impurities.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>MgSO₄, MnSO₄, CaSO₄</th>
<th>MgSO₄, MnSO₄, CaSO₄, MgCl₂, K₂SO₄, Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite</td>
<td>(NH₄)MgPO₄·6H₂O</td>
<td>99.8</td>
<td>99.8</td>
</tr>
<tr>
<td>Quartz*</td>
<td>SiO₂</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Furthermore, the effects of manganese sulfate addition and calcium sulfate addition have been studied separately in magnesium sulfate solutions, and the results are presented in Figure 4-7. It is seen that the presence of manganese sulfate in the solution results in an appearance change of struvite where the struvite color changes from white to light brown. Additionally, the presence of manganese sulfate decreases the recoveries by a small factor but it also decreases the struvite purity; it is seen that the mineral newberyite, Mg(HPO₄)·3H₂O, co-precipitates with struvite.

XRD analysis results for the pure magnesium sulfate solution and the sample containing 1 mg/L manganese sulfate are presented in Table 4-4 and show a decrease in struvite purity from 97.5 percent to 96.3 percent.
Figure 4-7: Impurity addition effect on magnesium removal efficiency; the comparison of cases containing either manganese sulfate or calcium sulfate as impurities to synthetic magnesium sulfate solution containing no impurity.

Table 4-4: XRD analysis results comparing struvite formed in solutions with pure magnesium sulfate and solution containing 1 mg/L manganese sulfate.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>Pure MgSO₄</th>
<th>1 mg/L MnSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite</td>
<td>(NH₄)MgPO₄·6H₂O</td>
<td>97.5</td>
<td>96.3</td>
</tr>
<tr>
<td>Newberyite</td>
<td>Mg(HPO₄)·3H₂O</td>
<td>2.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Quartz*</td>
<td>SiO₂</td>
<td>0.1</td>
<td>–</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

As for the case of the calcium sulfate impurity; where high concentrations such as 137 mg/L of calcium sulfate are used, in addition to a decrease in both reaction recovery and the precipitate purity it could be seen that calcium sulfate tends to co-precipitate with struvite therefore resulting in apparent higher recoveries where the actual precipitate is in fact a mixture of struvite and gypsum. However, where only 33 mg/L calcium sulfate is used both the reaction recovery and the struvite purity improve. The XRD analysis comparing the product purity of the magnesium
sulfate solution containing no calcium sulfate to 33 mg/L CaSO₄ to 137 mg/L CaSO₄ is presented in Table 4-5.

Table 4-5: XRD analysis results comparing struvite formed in solutions with pure magnesium sulfate and solution containing 33 mg/L and 137 mg/L calcium sulfate.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>Pure MgSO₄</th>
<th>33 mg/L CaSO₄</th>
<th>137 mg/L CaSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite</td>
<td>(NH₄)MgPO₄·6H₂O</td>
<td>97.5</td>
<td>99.3</td>
<td>96.4</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td></td>
<td>0.7</td>
<td>3.2</td>
</tr>
<tr>
<td>Newberyite</td>
<td>Mg(HPO₄)·3H₂O</td>
<td>2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz*</td>
<td>SiO₂</td>
<td>0.1</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Figure 4-8 compares the cases where either calcium sulfate or manganese sulfate impurity exist in the solution to the case where both impurities are present. It can be seen that the addition of both impurities together will cause improvement in the reaction recovery and the struvite purity.

Figure 4-8: Impurity effect on magnesium removal and struvite precipitation.
4.2.4 The Effect of Initial and Final pH on Magnesium Removal and Struvite Formation

Solution pH is one of the most important parameters that affect struvite precipitation since the availability of the reactants changes with the pH of the solution. As the solution pH increases the ammonium and magnesium ion concentrations decrease while the phosphate ion concentration increases [12].

Furthermore, struvite solubility changes at a pH of about 7; above pH 7 struvite is insoluble whereas below pH 7 struvite solubility increases sharply. The ammonium phosphate solution resulting from the mixing of ammonium and phosphoric acid solutions is a basic solution and its addition to the magnesium sulfate solution increases the magnesium sulfate solution pH, typically to values higher than 7. However, if the solution initial pH is too acidic the solution final pH would be below 7. Therefore, both the initial and final pH of the solution affect struvite precipitation conditional to the final pH being above or below 7.

The results of the experiments confirm that solutions with final pH below 7 have the lowest recoveries. The results of the experiments indicate that the optimum final pH of both the synthetic magnesium sulfate solution at 9.43 and the replicated Goro plant solution at 9.63 are their natural, unaltered final pH’s.

Additionally, in the case of the synthetic solution the natural initial pH of 7.36 results in the maximum recovery. However, in the case of the replicated Goro plant solution, the solution with the initial pH of 7.81 has the highest recovery of 96.93. It is also noteworthy that the replicated Goro plant solution natural initial pH is 6.71 and will lead to a slightly lower recovery of 96.13.

Additionally, the Goro plant solution has an initial pH of 8 where the addition of ammonia and phosphate (ratio of 3:1) will result in an increase in the pH causing the final solution to have pH of above 9 where the reaction recovery is observed to be at the maximum.
The results of the pH experiments are presented in Figure 4-9 and Figure 4-10.

**Figure 4-9**: Effect of the initial pH of the solution on struvite reaction efficiency.

**Figure 4-10**: Effect of the final pH of the solution on struvite reaction efficiency.

### 4.2.5 Residence Time Impact on Struvite Precipitation

In this study residence time refers to the time that the solution requires to reach equilibrium with the precipitated struvite. In this practice the residence time is the time interval between the
time which the addition of ammonium and phosphate solution to the magnesium sulfate solution has ended to the time when the stirring of the solution stops.

Furthermore, in the case of struvite crystallization, the residence time is referred to the time that an individual struvite crystal spends in the crystallization reactor. In this case the residence time is used to determine the crystal size [17]. Typically, longer retention time is used to allow the crystals to reach larger sizes thus making them more prone to harvesting [18]. However, it is reported that struvite crystals reach a maximum size after a certain residence time and further increase in the residence time initiates a decrease in the crystal size [17].

The base experiments for this study involve reactants in higher than supersaturation ratios leading to struvite precipitation as soon as all of the reactants are mixed. Hence it is anticipated that lower residence time is more efficient since it leads to less energy requirement for the mixing and less crystal breakage probability. The experimental results confirm this assumption; for the synthetic solution the increase in the residence time decreased the reaction recovery. Nevertheless in the case of the Goro plant solution increasing the residence time did lead to a small increase in the reaction recovery which, depending on the required extent of magnesium removal, may be justified to use. However, the appearance of the precipitated struvite in all of the residence time experiments is white powder with no obvious increase in the crystal size or the crystal hardness.

XRD analysis was used to determine the struvite purity for the replicated Goro samples with longer residence times; Table 4-6 compares the purity of struvite precipitated from the replicated Goro plant solutions with different residence times.

The results for the residence time tests are presented in Figure 4-11.
Table 4-6: XRD analysis results comparing the purity of struvite precipitated from the Goro plant solutions with different residence times.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>Goro 10 min</th>
<th>Goro 7 hr</th>
<th>Goro 3 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite</td>
<td>(NH₄)MgPO₄·6H₂O</td>
<td>99.8</td>
<td>99.7</td>
<td>99.5</td>
</tr>
<tr>
<td>Strunzite</td>
<td>Mn²⁺(Fe³⁺)₂(PO₄)₂(OH)₂·6H₂O</td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>Quartz*</td>
<td>SiO₂</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Figure 4-11: Effect of residence time on struvite reaction efficiency

### 4.2.6 Temperature Change Impact on Struvite Precipitation

Various salts correspond to temperature change differently. The change in a salt’s solubility with temperature change is determined by the amount of heat liberated or absorbed when the salt dissolves. The liberation or absorption of heat is dependent on the energy required to break the salt’s crystal structure and on the energy released when the salt interacts with the solvent. A
dissolution is called endothermic when more heat is required to break the salt particles than the heat gained from the interaction of the salt’s component ions and the solvent; in this case heat is absorbed and further heat addition and increasing the temperature will increase the salt’s solubility. Conversely a dissolution is called exothermic when the heat gained from salt and solvent interaction is more than the heat required to break the salt’s crystal structure; in this case heat is gained and the solution temperature rises and further increase in the temperature will decrease the salt’s solubility. The dissolution of most salts and also struvite have been reported to be endothermic; therefore struvite is less soluble at lower temperatures [18; 20].

The results of this study confirm that the struvite recovery is highest at lower temperatures. The lowest temperature examined in this study is the ambient temperature which led to maximum struvite recovery for the replicated Goro plant solution; this fact demonstrates that this process is optimum at ambient temperature and no further temperature adjustment is required. However the synthetic solution has a higher recovery at temperature about 28°C.

![Figure 4-12: Effect of temperature of the solution on struvite reaction efficiency.](image)
4.2.7 Supersaturation Effect on Struvite Precipitation

A solution is said to be saturated when further addition of the soluble compound will lead to its precipitation. Conversely a region exists where a solution has dissolved more soluble compound than its saturation state this is called the supersaturation state. By thermodynamics this state is assumed to be unstable. However, up to a certain concentration the solution appears to be stable; this is the metastable region, which is typically used to suppress crystal nucleation and hence to increase crystal size [29].

The results for the supersaturation experiments show that struvite recovery in the metastable region is significantly lower than recovery from solutions in the supersaturated region. Furthermore the precipitate size remained unchanged, powdery and breakable by hand pressure. It is worth mentioning that in addition to the region in which the precipitation is carried out the stoichiometric ratio of struvite constituents has an important effect on the reaction recovery since under similar conditions in the metastable region a stoichiometric ratio of 1 magnesium: 1 phosphate: 1 ammonium led to no precipitation, while increasing the ammonium concentration so that the stoichiometric ratio is 1:1:3 leads to 84 percent magnesium recovery.

The metastable region curve and the results for the supersaturation tests are presented in Figure 4-13 and Figure 4-14.
Figure 4-13: Metastable region for struvite precipitation [29].

Figure 4-14: Supersaturation and struvite constituent stoichiometric ratio effect on struvite precipitation reaction recovery.
4.2.8 Optimum Mg:P Ratio for Magnesium Removal

In practice, struvite precipitation can occur at any stoichiometric ratio. However, theoretically, for intentional struvite precipitation the stoichiometric ratio of the struvite constituents Mg$^{2+}$, PO$_4^{3-}$ and NH$_4^+$ should at least be 1:1:1. Furthermore, at a specific pH, increasing the Mg:P ratio causes an increase in the degree of supersaturation with respect to struvite precipitation which predicts higher magnesium recoveries [12].

The effect of addition of magnesium and phosphate ion in stoichiometric ratios of 1:1.1 and 1.1:1 is examined while the concentration of the ammonium is held constant. The results show that addition of magnesium and phosphate at higher than stoichiometric ratios will decrease the reaction recovery compared to the base experiment where the stoichiometric ratio is unity. Furthermore, in the case of the replicated Goro plant solution addition of magnesium at higher than the unity stoichiometric ratio led to co-precipitation of struvite and gypsum; and the addition of phosphate ion at higher than the unity stoichiometric ratio caused the precipitation of an amorphous phase which was undetectable by XRD analysis.

Figure 4-15: Mg: P stoichiometric ratio effect on struvite precipitation reaction efficiency.
Table 4-7: XRD analysis results comparing different magnesium to phosphate stoichiometric ratios for Goro plant solutions.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>1 Mg:1 P</th>
<th>1.1 Mg:1 P</th>
<th>1 Mg:1.1 P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite</td>
<td>(NH₄)MgPO₄·6H₂O</td>
<td>99.8</td>
<td>93.5</td>
<td>99.4</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td></td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>Quartz*</td>
<td>SiO₂</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

4.2.9 Additional Environmental Parameters and their Effect on Struvite Precipitation

An approach for producing struvite pellets has been developed at the University of British Columbia Department of Civil Engineering which is able to produce struvite pellets as large as 3.5 mm; in this approach magnesium chloride is used as the source of magnesium [30]. Therefore, in an attempt to produce struvite pellets, an experiment was carried out using synthetic solution of magnesium chloride instead of synthetic magnesium sulfate. This led to a small increase in the recovery, increasing it from 95.06 to 96.08 percent. However, the appearance of the precipitated struvite remained unchanged.

Additionally, a series of tests was carried out using magnesium chloride under various conditions in pursuit of producing struvite pellets. The results of these experiments are reported in Table 4-8. Although the recovery of several of these tests is higher than the baseline experiment, none of these tests were able to produce struvite pellets.
Table 4-8: Results of effect of using magnesium chloride as source of magnesium under various conditions.

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Conditions</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MgCl₂·6H₂O</td>
<td>96.08</td>
</tr>
<tr>
<td>2</td>
<td>MgCl₂·6H₂O, Stirring Speed: 100 rpm</td>
<td>99.83</td>
</tr>
<tr>
<td>3</td>
<td>MgCl₂·6H₂O, 5 g seed</td>
<td>51.07</td>
</tr>
<tr>
<td>4</td>
<td>MgCl₂·6H₂O, Final pH: 7.9</td>
<td>96.24</td>
</tr>
</tbody>
</table>

Based on the results of these tests it is concluded that the struvite appearance is dependent on the reactor type and the continuous conditions under which the reactor operates.

4.3 Conclusion

This study confirms the ability of the proposed flowsheet to successfully remove magnesium as struvite from nickel laterite plants from both aspects of the magnesium removal efficiency and the produced struvite purity, with the experiments conducted at the base conditions having magnesium removal efficiency of 95 percent for the synthetic solution and 96.13 percent for the replicated Goro plant solution. Additionally, the produced struvite is 97.5 percent pure in the case of the synthetic solution and 99.8 percent pure in the case of the replicated Goro plant solution.

The main advantages of this process are the immediate formation of struvite due to the high concentrations of struvite constituents and achieving equilibrium in as little as 10 minutes residence time. The most important advantage is the optimum magnesium removal condition being the same as the existing conditions of the effluent solution such as ambient temperature and pH, with no further adjustment required.
Conversely, all of the experiments resulted in the formation of struvite powder as opposed to struvite pellets which will lead to a more difficult filtration step and require additional product handling downstream.

The extent of struvite precipitation and the final crystal size is dependent on many factors. The most influential factors affecting struvite crystallization are mixing intensity, seeding and the seeding technique, pH, temperature, crystal retention time, magnesium to phosphate ratio, supersaturation level and the impurities present in the system.

Each of these parameters affect struvite precipitation differently, the extent of their impact is also different. For instance, variations in supersaturation level and pH have greater effect on struvite precipitation then variations in temperature and mixing intensity.

Solution stirring is done in order to maintain a uniform concentration of reagents throughout the solution. Where low stirring intensity leads to inadequate mixing and high stirring intensity causes crystal breakage. In the case of struvite precipitation, the mixing intensity impact is dependent on the presence of impurities in the solution; the solution of synthetic magnesium sulfate was unaffected by the stirring speed and the replicated Goro plant solution required high mixing intensities to avoid insufficient mixing.

Solution seeding is a common method to increase reaction efficiency by providing a reaction surface that stimulates the precipitation reaction. Typically seeds with larger specific surface area and thus smaller size enhance magnesium removal. This study confirms the positive effect of using struvite powder as seed for both the synthetic magnesium sulfate solution and the replicated Goro plant solution.

The existence of impurities in actual plant operations is unavoidable. The presence of impurities in the synthetic magnesium sulfate solution effects both the magnesium removal
efficiency and precipitated struvite quality and purity. This study confirms that the impurities with the most impact on struvite precipitation are manganese and calcium; where the addition of manganese leads to the co-precipitation of struvite and newberyite and the addition of calcium leads to the co-precipitation of struvite and gypsum. However, the addition of both manganese and calcium at levels replicating the Goro plant solution shows an improvement in the reaction efficiency and struvite purity in comparison to the synthetic magnesium sulfate solution.

Struvite solubility is highly dependent on the pH of the solution being above or below 7; since struvite is insoluble at pH above 7 but struvite solubility increases sharply at pH below 7.

The results of the experiments indicate that the optimum final pH of both the synthetic magnesium sulfate solution at pH 9.43 and the replicated Goro plant solution at pH 9.63 are their natural, unaltered final pH. Additionally, in the case of the synthetic solution, the natural initial pH of 7.36 results in the maximum recovery. However, in the case of the replicated Goro plant solution, the solution with the initial pH of 7.81 has the highest recovery of 96.93 which is slightly higher than the replicated Goro plant solution natural initial pH at 6.71 resulting in a reaction recovery of 96.13.

In this study residence time refers to the time required for the solution and the precipitated struvite to reach equilibrium. This study involves reactants at higher ratios than struvite supersaturation ratio leading to struvite precipitation upon mixing of all of the reactants; therefore, lower residence times are used in order to lower the energy requirement for the mixing and to lower the crystal breakage probability. Additionally, increasing the residence time is seen to reduce the reaction recovery in the case of the synthetic magnesium sulfate solution. However, increasing the residence time from 10 minutes to 3 days for the case of the replicated Goro plant
solution resulted in an increase in the reaction recovery from 96.13 percent to 98.66 percent however the struvite purity decreased from 99.8 to 99.5 percent.

The dissolution of most salts such as struvite are endothermic. This study confirms that struvite is less soluble at lower temperatures and that the reaction recovery is highest at lower temperatures. The lowest temperature examined in this study is the ambient temperature which led to maximum struvite recovery for the replicated Goro plant solution. This confirms that the solution at ambient temperature leads to the maximum reaction recovery and therefore no further temperature adjustment is required.

Struvite constituent concentrations in this study are well above the supersaturation level for struvite precipitation, which leads to immediate precipitation of struvite upon mixing the constituents and also high values of reaction recovery. This study also verifies that the reaction recovery in the metastable region is significantly lower than recovery from solutions in the supersaturated region.

Furthermore, it is seen that the stoichiometric ratio of struvite constituents has a significant effect on the reaction recovery; where under similar conditions in the metastable region a stoichiometric ratio of 1 magnesium: 1 phosphate: 1 ammonium led to no precipitation, while increasing the ammonium concentration so that the stoichiometric ratio is 1:1:3 led to 84 percent magnesium recovery.

Struvite is formed according to Equation 7 and theoretically struvite precipitation occurs at any reactant stoichiometric ratio; however, this study verifies the optimum stoichiometric ratio of magnesium to phosphate to be 1:1.
5 Future Work

This study is the initial step of the proposed flowsheet for magnesium recovery from nickel plants. This study verifies the possibility of magnesium removal and the fast production of struvite with efficiencies higher than 90 percent.

However the remainder of the flowsheet is yet to be examined. Future work on this subject should both involve examination of the performance and optimization of all the individual steps, and also their ability to work in continuous mode to remove magnesium, produce struvite, remove sulfate, produce gypsum and recycle ammonia and process water.

Furthermore, the remainder of the flowsheet may be altered to recover sulfuric acid and ammonia from the ammonium sulfate solution. Sulfuric acid would be a valuable byproduct which may be recycled to the nickel recovery section or be sold for additional profit and reagent cost justification.

Additionally this study was unable to produce large struvite pellets. The struvite pellet size is thought to be dependent on the struvite crystallization reactor. Future work should authenticate this hypothesis and make an effort in production of large struvite pellets. Large struvite pellet production will lead to the production of more easily harvestable struvite with longer application period.
References


