MICROWAVE VACUUM CARBOTHERMIC REDUCTION AND SULPHIDATION OF A LOW GRADE NICKELIFEROUS SILICATE LATERITE ORE

by

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Abstract

The international resources of nickel sulphides are quickly diminishing. In order to satisfy forthcoming nickel demands, the feasible mining of nickel laterite deposits is imperative. Nickel laterites cannot be easily treated since the nickel is finely disseminated throughout the ore. Therefore, very expensive leaching and smelting processes are required to process nickel laterite ore. The incentive for the present research was to develop a new carbothermic reduction process for nickel laterite ore that would produce a higher grade of nickel than current industrial techniques.

Microwave Vacuum Reduction Processing (MVRP) of a nickeliferous silicate laterite ore, followed by magnetic separation was performed. The variables investigated included: processing time, microwave power, system pressure, use of argon as an inert gas, charcoal addition, pyrite addition, sample mass, dewatering of the sample and magnetic field intensity.

The optimum conditions were determined to be a processing time of 5 minutes, microwave power of 1100 W, pressure of 11 kPa, 6% charcoal addition, 30 g sample mass and magnetic separation using a WHIMS at 1A. These conditions produced a high grade magnetic concentrate which contained 21.0% nickel with a corresponding nickel recovery of 69.6%. The use of a vacuum atmosphere reduced the partial pressure of oxygen, increased the rate of reaction of the sample, and the lowered the reaction temperature of the process.

When sulphur was added to a sample in the form of pyrite, less microwave energy was used, and a higher maximum temperature was reached than a sample without pyrite. The
use of an argon atmosphere resulted in high nickel grades of 7.16 to 9.24%, with moderate to high nickel recovery values of 37.64 to 88.77%.

Regarding the tests performed in air, a processing time greater than 10 minutes was found to be detrimental to the nickel recovery due to oxidation of the sample. The presence of magnetite, Fe₃O₄, indicated that the reduced sample was oxidized during microwave processing (overheating from a long processing time) or once the sample was removed from the applicator (air exposure). The nickel was recovered as ferronickel, primarily kamacite, α-(Fe,Ni) or taenite, γ-(Fe,Ni) in higher grade concentrates.
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Statement of Originality

I hereby certify that all of the work within this thesis is the original work of the author.

Any published (or unpublished) ideas and/or techniques from the work of others are fully acknowledged in accordance with the standard referencing practices.

(John Forster)

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>Acid Leaching</td>
</tr>
<tr>
<td>BNC</td>
<td>Basic Nickel Carbonate</td>
</tr>
<tr>
<td>EPAL</td>
<td>Enhanced Pressure Acid Leaching</td>
</tr>
<tr>
<td>HL</td>
<td>Heap Leaching</td>
</tr>
<tr>
<td>HPAL</td>
<td>High Pressure Acid Leaching</td>
</tr>
<tr>
<td>MVRP</td>
<td>Microwave Vacuum Reduction Processing</td>
</tr>
<tr>
<td>NPI</td>
<td>Nickel Pig Iron</td>
</tr>
<tr>
<td>RKEF</td>
<td>Rotary Kiln Electric Furnace</td>
</tr>
<tr>
<td>SAL</td>
<td>Sulphation Atmospheric Leaching</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray Fluorescence</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 General Overview

In this thesis the microwave vacuum reduction processing of a clay silicate nickel laterite ore was studied. The incentive for this research was to develop a new carbothermic reduction process for nickel laterite ore that would yield a higher nickel grade in the concentrate than current industrial techniques. In comparison to nickel sulphides, the processing of nickel laterites is more difficult, due to their complex structure, which provides challenges with regards to the upgrading of laterites. The subsequent sections in this chapter will discuss the uses of nickel, resource economics, ore deposit types, the scope of the present research and the organization of this thesis.

1.2 Uses of Nickel

The uses of nickel may be divided into four categories: the production of nickel steels (46%), nonferrous alloys/superalloys (34%), electroplating (14%) and other uses such as coins, batteries, catalyst for hydrogenating vegetable oils, etc. (6%) (Kuck, 2012). Nickel is able to resist corrosion which makes it a very suitable material for use in steels. Nickel use is increasing at a rate of about 4% per year while the use of nickel-containing stainless steel is growing at about 6% per year (Nickel Institute, 2014).
1.3 Nickel Supply, Demand and Price

Figure 1 shows the exports from China in the year 2014 as well as the global supply and demand from 2010 to 2015 (2014 and 2015 are predicted). There was a sharp increase in the quantity of nickel being exported from China from May to June (value nearly tripled). This was caused by the export ban that was placed in January 2014 by Indonesia which prevented the country from shipping its unprocessed nickel ore. As such, the Philippines replaced Indonesia as the number one supplier of nickel ore to China with an increase of 26% in shipments from January to August of 2014 (Hoyle & Mukherji, 2014). Market analysts predict that there will be a market shortage of nickel in 2015 as a result of Indonesia’s export ban. The price of nickel is forecasted to increase to about 23,900 USD a ton in 2015 and 26,500 USD a ton in 2016 (Hoyle & Mukherji, 2014). When Indonesia is able to feasibly refine its own ore prior to shipping, this will lower the overall market
price of nickel. Currently, there exists a pilot plant project which is being conducted by Direct Nickel, a company which claims to have developed a new process that is both cost effective and environmentally friendly and will be implemented in Indonesia. This process is discussed in further detail in section 2.2.4 of this thesis.

With regards to the global supply of nickel ore, the Philippines has the largest supply at about 15%, followed closely by Russia and Canada with approximate quantities of 13% and 12%, respectively. Australia, Indonesia and New Caledonia have about 11%, 10% and 9%, respectively (Morgan, et al., 2014). The Philippines is also considering placing an export ban on its unprocessed ore. If this occurs, then about 10% of the global demand will be at risk and would disrupt the production of NPI in China. However, a grace period of five years has been proposed before this ban takes place (Dela Cruz, 2014).

1.4 Nickel Laterite Ore Deposits

There are two types of nickel ore deposits; nickel sulphides and oxidic nickel laterites. The current global resource distribution for nickel sulphides and nickel oxides is estimated to be about 28% and 72%, respectively (Dalvi, et al., 2004). The depletion of nickel sulphide deposits worldwide has led to an increase in the global demand for the development of nickel laterite deposits. The global resource distribution of nickel laterite ores is shown in Figure 2. It is shown that the majority of the nickel laterite ore deposits are located in tropical areas within 22°N or 22°S of the equator such as Cuba, Columbia, Indonesia and New Caledonia. Greater amounts of precipitation and higher temperatures are suitable requirements for the formation of these types of deposits. Nickel sulphides are
formed from either volcanic or hydrothermal processes, whereas nickel laterite ores are
formed near the surface as a result of weathering and primarily occur in tropical climates
(Mudd, 2009). Nickel laterites may be divided into two primary groups; limonites and
silicates. The global average nickel grade in nickel laterite ore is about 1.3% (Dalvi, et al.,
2004). There are three different profiles of laterite ore and the composition of each is
determined by the predominant mineralogical factors within the profile (Brand et al., 1998;
Elias, 2002). The primary elemental concentrations and the global resource distribution of
these three profiles (A to C) are shown in Table 1. Figure 3 shows the typical lateritisation
profiles for serpentinized ultramafic rocks. Profile A is a limonitic nickel laterite ore and
Profiles B and C are silicate nickel laterites. Most nickel laterite deposits will have both
limonite and silicate ores. Profile A is referred to as limonitic laterites and contains mostly

Figure 2: Global resource distribution of nickel laterite deposits (Butt & Cluzel, 2013).
Table 1: Fe, Ni, and Si:Mg concentrations and global resource distribution of nickel laterite ores (Brand, et al., 1998).

<table>
<thead>
<tr>
<th>Element</th>
<th>Profile A: Limonitic</th>
<th>Profile B: Hydrous Mg-Si</th>
<th>Profile C: Clay Silicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si:Mg</td>
<td>low</td>
<td>2 to 4</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Fe</td>
<td>&gt;40%</td>
<td>&lt;20%</td>
<td>20 to 30%</td>
</tr>
<tr>
<td>Ni</td>
<td>1 to 1.6%</td>
<td>2 to 5%</td>
<td>1 to 1.5%</td>
</tr>
<tr>
<td>Global Resource Distribution</td>
<td>60%</td>
<td>32%</td>
<td>8%</td>
</tr>
</tbody>
</table>

Figure 3: Typical nickel laterite ore profiles: (A) limonitic laterite; (B) hydrous Mg-Si; (C) clay silicate (Butt & Cluzel, 2013).
goethite (FeO·OH). These profiles contain approximately 1 to 1.6% nickel and account for 60% of the world’s resources of nickel laterite. Profile B refers to deposits that consist of hydrated magnesium-nickel silicates that occur in the deeper section of the deposit. Another term for this profile type is garnierite. These profiles have a nickel grade typically ranging from 2 to 5% (Butt & Cluzel, 2013). Profile C refers to clay silicate laterites. These profiles occur in cooler or drier climates and are predominantly comprised of smectite clays. Serpentinized peridotites weather to produce low-grade smectite clay profiles. These profiles generally occur beneath an oxide zone that is thin and lower in nickel grade (1 to 1.5%) as compared to the ore described in Profile B. The Murrin Murrin deposit in Western Australia is an example of a clay silicate laterite profile, which is weathered to a depth of about 40 to 60 m. This ore was used in the present research.

The occurrence of nickel laterites are a function of several parameters such as climate, geomorphology, drainage, lithology and structure (Brand, et al., 1998). Nickel laterites are formed via the emplacement and serpentinization of ultramafic ore. This material is exposed to a humid tropical climate and a deep intensely weathered regolith. Some nickel laterite deposits are formed with tectonic uplift where the water tables started high and were lowered (Butt & Cluzel, 2013). In tropical environments, leaching of the nickel from oxide zones occurs where it gathers in hydrous magnesium silicates deeper in the saprolite. The weathered peridotite rocks are primarily composed of olivine, ((Mg, Fe)_2SiO_4) and a small quantity of pyroxene (Ni,Mg)SiO_3 (Crundwell, et al., 2011). Water percolates through the weathered material and Fe, Ni, Mg and SiO_2 are dissolved. Iron precipitates as goethite, along with the nickel and cobalt and the iron in the goethite can be replaced by either of these two species. This is the limonitic region of the deposit and is
mostly comprised of goethite. The magnesium and silica precipitate near the bedrock, where magnesium silicates of the serpentine group are created. This layer of the profile may be regarded as the saprolitic region (Crundwell, et al., 2011). The overall depth of a lateritic deposit is a direct result of the chemical weathering at the bottom of the deposit versus erosion at the top of the deposit (Elias, 2002).

An example of the ore and compositional distributions for a nickel lateritic regolith corresponding to the New Caledonia deposit is shown in Figure 4. This deposit fits the description for that of Profile B. It is possible to see the different sections relating to the limonitic laterites (pedolith) and the silicate laterites (saprolith). The transition from the pedolith section to the saprolith section results in an increase in average nickel content and this value decreases at the bedrock of the deposit. The concentrations of magnesium oxide (MgO) and silica (SiO₂) increase upon entering the saprolith section of the deposit. The three primary mineralogical phases present in this profile are goethite ((Fe,Ni)O·(OH)), serpentine/lizardite ((Mg,Fe,Ni)₃Si₂O₅(OH)₄), and quartz ((SiO₂)).

Figure 4: New Caledonia nickel laterite deposit (Robb, 2005).
1.5 Research Scope and Objectives of Present Work

In previous research on pyrometallurgical processes, the nickel laterites were usually heated by conventional techniques. However, very few studies using microwave energy have been conducted. Microwave processing is still a relatively new technology and there exists the possibility of incorporating microwave processing as a unit operation in extractive metallurgy. Vacuum processing has also been applied to nickel laterite ores using conventional heating techniques (Luo, 2012). Hence, it would be advantageous to combine the two processes: microwaving and vacuum processing to develop microwave vacuum reduction processing (MVRP).

The primary research objectives in this thesis are to:

(1) Perform an in-depth literature review of current nickel laterite processing technologies, review the research and development studies on the processing of laterites on both the laboratory and industrial scale, research the microwave processing of nickel laterites, and microwave vacuum processing of nickel laterites and other materials.

(2) Investigate the effects of the following variables on the microwave vacuum carbothermic reduction process: processing time, microwave power, pressure of the system, the use of argon for an inert atmosphere, charcoal addition, pyrite addition, sample mass, dewatering of the sample and magnetic field intensity.

(3) Determine the optimum conditions for the carbothermic reduction and sulphation processing of the as-received clay silicate nickel laterite in a microwave vacuum process.

(4) Propose a list of recommendations for future studies regarding this research area.
1.6 Organization of Thesis

This thesis is organized into five chapters:

Chapter 2: An in-depth literature review regarding the mineral processing and extractive metallurgy of nickel laterites. This chapter will discuss the current industrial practices for the processing of nickel laterites. Also included are thermodynamic studies, phase transition studies, and reduction studies. Lastly, there will be a focus on the extractive metallurgy of nickel laterites with microwave energy and a review of current microwave vacuum processing practices.

Chapter 3: This chapter will be a review of microwave fundamentals and their application to this research. This includes the theory of microwaves, with regards to the heating mechanisms, dielectric properties, processing properties and limitations of the technology.

Chapter 4: This chapter provides an explanation of the materials used and methods performed in the laboratory work. This includes the design set-up of the microwave vacuum reactor system, the materials utilized (ore, charcoal and pyrite), a description of the magnetic separation tests and the different instrumentation methods that were employed to analyze the reacted material. Error analysis calculations are also included. Lastly is a brief section on laboratory safety.

Chapter 5: This chapter is the focal point of the thesis. It provides the results of the experiments performed in the laboratory and includes a thorough discussion of the significance of these results. This section will analyze the effects of the different process variables that were utilized in the experiments.

Chapter 6: The significant findings from this research are reported in this section. Also included are recommendations for future work.
Chapter 2
Literature Review

2.1 Overview

In this literature review the three conventional techniques for processing nickeliferous laterites: acid leaching; smelting processes and the Caron process will be discussed. Industrial applications of these processes will be described along with the research that has been performed to improve nickel laterite processing. In addition to these conventional processes, research performed on microwave processing and vacuum processing of nickel laterites will be reviewed.

Figure 158 in Appendix H is a literature review hierarchy diagram which shows four very important research papers on nickel laterites. These papers can be divided into four primary categories: thermodynamics, sulphation roasting, reduction and review papers, and microwaving of laterites. Canterford (1975) was one of the first review papers which proposed a detailed description on both research and industrial processing of nickel laterites. This paper allowed for many important thermodynamics papers to be written which all referenced this paper. Research by Valix and Cheung (2002b) was one of the first studies to investigate the effect of sulphur on the mineral phases of different nickel laterite ores at high temperatures. Dalvi et al. (2004) presented an in-depth report on nickel laterites which included facts and figures regarding the global resource distribution, the pyrometallurgical and hydrometallurgical industrial processes used and the economics of worldwide operations. Pickles (2004) was the first to study the microwaving of nickel laterite ore, in particular, the heating behaviour of a nickeliferous limonitic laterite ore.


2.2 Processing of Nickel Laterites

All nickel laterite deposits are mined via open-pit mining because the deposits are vast and shallow. Consequently, the extraction selected is a function of the depth. As depicted in Figure 5, laterite deposits normally occur in three layers and these layers consist of limonite, transition (smectite) and saprolite (garnierite) ores. Three primary processes are used to extract nickel from laterite ore. Figure 6 presents the general flowsheet of the nickel laterite processes. Conventional preconcentration techniques are not feasible for nickel laterites as the majority of the nickel is distributed in the iron oxides and clays (Whittington & Muir, 2000). This is different from the sulphide ores as the nickel occurs in a discrete mineral. The limonitic ores are processed using acid leaching (hydrometallurgical), the saprolite ores are smelted (pyrometallurgical) and a limonite-saprolite blend can be extracted using the Caron process (pyro/hydrometallurgical). This

![Figure 5: Processing alternatives for nickel laterites (Brand et al, 1998).](image-url)
process is a hybrid of pyrometallurgical and hydrometallurgical methods. The processing of low grade nickel laterites is becoming more expensive via the pyrometallurgical methods (CRU, 2011). Thus, hydrometallurgical methods are projected to be used more in the future. Figure 7 shows the planned nickel laterite production within the next decade. If the current production is to continue without the implementation of additional hydrometallurgical plants then the smelting processes would be the primary method used in the upgrading of nickel laterites. The proposed production eliminates the use of the Caron process while the leaching processes would be used more and the smelting processes used less.
2.2.1 Pyrometallurgical Processing

Current pyrometallurgical processing operations typically involve either the production of ferronickel or the production of matte for further refining. Nickel pig iron (NPI) is another common product from pyrometallurgical processing. For a smelting operation to be economically feasible, the process should involve mildly reducing conditions so as to selectively reduce the nickel. As a result the crude ferronickel grades are in the range of 30 to 40% (Solar, et al., 2008). Nickel laterite ore that is to be pyrometallurgically processed is described in Table 2.

Table 2: Nickel laterite ore composition for pyrometallurgical processing (Oxley & Barcza, 2013).

<table>
<thead>
<tr>
<th>Description</th>
<th>Fe/Ni</th>
<th>Ni/Co</th>
<th>SiO\textsubscript{2}/MgO</th>
<th>Grade/Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical</td>
<td>&lt;12</td>
<td>40</td>
<td>&lt;1.9</td>
<td>Good</td>
</tr>
<tr>
<td>Extended</td>
<td>&gt;12 to &lt;20</td>
<td>20</td>
<td>&gt;3.5 to &lt;7</td>
<td>Lower</td>
</tr>
<tr>
<td>NPI Blend</td>
<td>5 to 30</td>
<td>10 to &gt;40</td>
<td>1.5 to 5</td>
<td>High</td>
</tr>
</tbody>
</table>
2.2.1.1 Rotary Kiln-Electric Furnace (RKEF) Process

In ferronickel production the nickel laterite is first calcined in a rotary kiln in the temperature range of 850 to 1000°C. After this unit operation, the material is smelted between 1500 to 1600°C in an electric arc furnace with carbon as the reducing agent, which separates the nickel/iron phase from the silica/magnesia slag phase. More strongly reducing conditions yield lower grades of ferronickel typically between 10 to 15% nickel, whereas weaker reducing conditions can produce a ferronickel with greater than 30% nickel (Norgate & Jahanshahi, 2011). All of the nickel is reduced, where approximately 60 to 70% of the iron is reduced (Kyle, 2010). The reduction reactions are given below:

\[
\begin{align*}
\text{NiO} + \text{C} & \rightarrow \text{Ni} + \text{CO} \quad (1) \\
\text{NiO} + \text{CO} & \rightarrow \text{Ni} + \text{CO}_2 \quad (2) \\
\text{FeO} + \text{C} & \rightarrow \text{Fe} + \text{CO} \quad (3) \\
\text{Fe}_2\text{O}_3 + 3\text{CO} & \rightarrow 2\text{Fe} + 3\text{CO}_2 \quad (4)
\end{align*}
\]

The ferronickel is refined by removing impurities such as sulphur, silicon, chromium and phosphorus. The refined ferronickel is then used for stainless steel production (Kyle, 2010).

An example of a successful ferronickel smelting process is the one operated by the company Société du Nickel de Nouvelle Calédonie et Corée (SNNC), located in Gwangyang, Korea (Rodd, et al., 2010). This operation includes two rotary kilns and a ferronickel electric smelting furnace. With a production capacity of 30,000 t/yr of nickel, this is the most productive ferronickel smelting furnace in the world. The nickel laterite ore processed by this plant is from New Caledonia with a head nickel grade of
approximately 2.2 to 2.3%. The ferronickel product contains 17 to 18% nickel. The furnace produces 150 t/hr of slag and 21 t/hr of ferronickel. The nickel recovery for this operation is 97%.

2.2.1.2 Production of a Nickel/Iron Sulphide via Matte Smelting

Sulphur is usually added in the form of elemental sulphur, S or pyrite, FeS₂ to the ore (Kyle, 2010). The viscosity of the ore is reduced and facilitates fast development of the reduced ore particles (Canterford, 1975). Also, the addition of sulphur results in the formation of a low liquidus temperature matte. This reduces the required operating temperature of the furnace to about 1350 to 1400°C. A crude matte is formed by blowing air to a final product which contains nickel and sulphur values of 77 to 78% and 21 to 22% respectively, where the iron content is less than 1%. This process is used for ores with a high Fe/Ni ratio (>6) and a SiO₂/MgO ratio from 1.8 to 2.2 (Kyle, 2010).

The reduction of iron oxide will lower the nickel grade to values of about 5 to 15%, which is in the range of nickel pig iron (NPI). A way to improve the ferronickel grade is to use a blend of 5 to 10% calcined NPI to yield a ferronickel product with a grade of over 25% nickel (Oxley & Barcza, 2013).

2.2.2 Hydrometallurgical Processing

This process is effective at extracting the nickel and cobalt which are in the crystal structure of the limonitic ores. In some processes the saprolite ores are treated. There are several types of hydrometallurgical processes which are used to process nickel laterites. The primary process is high pressure acid leaching (HPAL). Four other methods include
atmospheric acid leaching (AL); enhanced pressure acid leaching (EPAL); heap leaching (HL) and sulphation atmospheric leaching (SAL) (Norgate & Jahanshahi, 2011).

2.2.2.1 High Pressure Acid Leaching (HPAL)

High pressure acid leaching (HPAL) involves leaching of the laterite ore with sulphuric acid at high pressures (5.4 MPa), and temperatures in the range of 245 to 270°C (Mudd, 2009). Countercurrent decantation is then used for solid-liquid separation, followed by solvent extraction. The HPAL process works best with limonitic ores, whereas saprolitic ores contain higher aluminum and magnesium contents, thus requiring more acid to be used. Over 95% of the nickel and cobalt are dissolved into solution. The nickel and cobalt are extracted from the liquor to yield mixed sulphides, mixed hydroxides, metals or oxides. Nickel recoveries are in the range of 90 to 92% (Kyle, 2010). A negative aspect of HPAL is the higher environmental cost due to acid consumption (Mudd, 2009).

2.2.2.2 Atmospheric Acid Leaching

Atmospheric acid leaching (AL) involves the leaching of saprolitic and/or limonitic ores at high temperatures but at atmospheric pressure. This process is not yet commercialized. Two important parameters to consider with regards to the processing of nickel laterites via atmospheric acid leaching are the kinetics of nickel extraction and the processing of the liquor (Norgate & Jahanshahi, 2011). Variables such as temperature, leaching time, redox potential, the use of catalysts, and pretreatment options may be modified. AL occurs at a temperature which is slightly less than the boiling point of the slurry (~100°C), for 12 hours (Kyle, 2010). This extended leaching time serves two purposes: it leaches the nickel into the solution and precipitates the iron from the solution.
This process uses both limonitic and saprolitic ores, where the extractions for nickel and cobalt are greater than 90% and 80%, respectively.

2.2.2.3 Enhanced Pressure Acid Leaching (EPAL)

Enhanced pressure acid leaching (EPAL) combines the HPAL and AL methods. This two stage process can treat the two different nickel laterite ores, limonitic or saprolitic, with HPAL followed by AL. Saprolitic ores with high magnesium contents are more reactive in this process, yielding a higher extraction of nickel (Norgate & Jahanshahi, 2011). Saprolite ore is used to neutralize the acidic slurry at the end of the HPAL process (Equation 5). The leaching of the saprolite ore increases the pH and allows for the precipitation of iron from the solution as goethite (Equation 6) (Liu, et al., 2004).

\[
(Mg,Ni)_3SiO_5(OH)_4(s) + 3H_2SO_4 \rightarrow 3(Mg,Ni)SO_4 + 2SiO_2(s) + 5H_2O \quad (5)
\]

\[
Fe_2(SO_4)_3 + 4H_2O \rightarrow 2FeO\cdot OH(s) + 3H_2SO_4 \quad (6)
\]

2.2.2.4 Heap Leaching (HL)

Compared to the other leaching processes used for nickel laterites, heap leaching is the most promising with regards to costs and is the most environmentally friendly (Oxley & Barcza, 2013). This process involves the agglomeration of the ore followed by irrigation with sulphuric acid. The leached material is collected and reacted with acid once again to improve the solution quality before it goes through the metal recovery process. Nickel recoveries are about 65 to 85% over a period of 102 to 150 days, where acid consumptions vary from 200 to 600 kg/tonne of ore (Kyle, 2010).
2.2.2.5 Sulphation Atmospheric Leaching (SAL)

Concentrated sulphuric acid is added to limonitic ore in a pug mill, where there is a sulphation reaction of the nickel and cobalt. The reacted limonitic ore is then mixed with crushed saprolite ore and water before being ground and leached using the AL process. The iron is removed as goethite, where the pregnant liquor undergoes countercurrent decantation (CCD) and solution purification to yield a mixed hydroxide precipitate which is then sold to nickel and cobalt refiners (Verbaan, et al., 2007).

2.2.3 Caron Process

2.2.3.1 Conventional Caron Process

In the Caron process, the nickel is upgraded several times by both pyrometallurgical and hydrometallurgical unit operations. It is primarily used for limonitic laterites, but can also be used for saprolitic ores or blended ores. A flowsheet of the Caron process is shown in Figure 8. Nickel laterite ore is first dried, crushed and ground before being reduction roasted in air. Ammonia leaching is done next followed by solid/liquid separation. This stage yields the pregnant solution and tailings. The ammonia is removed from the tailings and the leftover material is pre-boiled along with the pregnant liquor. Solvent extraction is performed followed by precipitation of the nickel carbonate (done twice). In the first nickel carbonate precipitation, the raffinate is sent for CoS precipitation which produces cobalt. The tailings from this unit operation may be recycled back to the solid/liquid separation step of the Caron process. Lastly, for the second stage of the nickel carbonate precipitation, calcination, reduction, and sintering are done to produce nickel. Some of the
iron is reduced in the kiln and forms an alloy with the nickel, while the remainder forms magnetite (Fe₃O₄). The recoveries of nickel and cobalt decrease as the amount of saprolitic ore increases since the nickel and cobalt are incorporated in a silicate matrix, making it difficult to reduce them at 700°C (Norgate & Jahanshahi, 2011).

Figure 8: Flowsheet of the Caron Process (Caron, 1950).
2.2.3.2 Modified Version of the Caron Process

A modified version of the Caron process was proposed by Rhamdhani et al. (2009a). The unit operations in this process are: beneficiation; blending; reduction roasting; leaching; solvent extraction; precipitation and thermal decomposition.

Firstly, the nickel laterite ore is dried to a moisture content of approximately 8% before being sent to reduction roasters. Heavy fuel oil serves as the reducing agent in this process, where the maximum temperature is in the range of 740 to 750°C. The nickel is selectively leached from the roasted ore. Iron and cobalt are dissolved and the cobalt is extracted in another circuit for further metallurgical refining. The nickel is precipitated as a basic nickel carbonate (BNC) before being reduced in a rotary kiln operating under slightly reducing conditions to partially reduce the BNC to Ni-NiO mixtures. The reactions are as follows:

\[
x\text{NiCO}_3\cdot y\text{Ni(OH)}_2\cdot z\text{H}_2\text{O} \rightarrow x\text{NiCO}_3\cdot y\text{Ni(OH)}_2 + z\text{H}_2\text{O} \quad (7)
\]

\[
x\text{NiCO}_3\cdot y\text{Ni(OH)}_2 \rightarrow (x + y)\text{NiO} + x\text{CO}_2 + y\text{H}_2\text{O} \quad (8)
\]

\[
\text{NiO}_\text{(s)} + \text{H}_2/\text{CO}_\text{(g)} \rightarrow \text{Ni}_\text{(s)} + \text{H}_2\text{O}/\text{CO}_\text{2(g)} \quad (9)
\]

where reaction (7) occurs at 90 to 200°C and reaction (8) at 270 to 420°C to yield a product containing 92% nickel. A reduction furnace is the next stage in the process where the kiln product is upgraded to 97.5% nickel at a temperature of about 900°C in a 3:1 H₂/N₂ atmosphere. This product is crushed and mixed with stearic acid and fed into the sintering furnace which completes the process to produce a concentrate containing 99% nickel.
2.2.4 Direct Nickel Process

Direct Nickel (DNi) developed a new pilot plant scale hydrometallurgical process (Figure 9) in 2013 which can be used to process limonitic or saprolitic laterite ore and any blend of the two types of laterites using the same unit operations (Direct Nickel, 2014). This process is economically viable because it operates at standard atmospheric pressure and does not require high temperatures. It is also environmentally friendly as the majority of the nitric acid reagent is captured and recycled. Nickel recoveries of over 90% have been reported. In addition to producing iron, nickel and cobalt, hematite and magnesium oxide are produced as by-products which can be sold.

![Figure 9: Process flowsheet for the Direct Nickel Process (Direct Nickel, 2014).](image)

Nitric acid (HNO$_3$) is used to leach the nickel laterite ore in stainless steel tanks for 2 to 4 hours (close to boiling point) and the nickel, cobalt, iron, aluminum, and magnesium are dissolved. Any insoluble residue is separated from the pregnant leach solution using solid/liquid separation. Next, the iron hydrolysis unit operation removes iron and
chromium from the solution. Upon completion of this step, MgO is added to the solution to precipitate out the aluminum. More MgO is added to create a mixed hydroxide precipitate. After filtration the product contains approximately 35 to 45% nickel and 2% cobalt and can be further upgraded to nickel and cobalt metal using conventional processes. The last step of the Direct Nickel Process is the recycling of the magnesium nitrate (Mg(NO$_3$)$_2$) left in the solution. This involves the use of evaporation vessels followed by thermal decomposition to produce MgO and NO$_x$ gases. However, these gases can be captured and recycled again as nitric acid which decreases the amount of material required for processing. The treatment costs for the Direct Nickel Process are estimated to be about 2 to 3 USD per pound which is about half the cost associated with current HPAL processes (de Landgraft, 2014).

2.3 Thermodynamic Studies

Thermodynamic studies have been performed by Canterford and Turnbull (1980), Valix et al. (1995) and Hallet (1997). Thermodynamic calculations were also conducted by Rhamdhani et al. (2009c), which have shown that the optimum conditions for the reduction roasting of the limonitic and saprolitic nickel laterites are different. Pickles et al. (2014) conducted a thermodynamic analysis of the carbothermic reduction roasting of a nickeliferous limonitic laterite ore which was found to be in general agreement with the experimental results that have been reported in the literature. For the limonitic ore it has been observed that there is an optimum reduction at 600°C. Carbothermic reduction can be carried out by the following reactions:

\[
C + CO_2 \rightarrow 2CO \quad (9)
\]
\[
3\text{Fe}_2\text{O}_3 + \text{C} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO} \quad (10)
\]
\[
\text{Fe}_2\text{O}_3 + \text{C} \rightarrow 2\text{FeO} + \text{CO} \quad (11)
\]
\[
\text{NiO} + \text{C} \rightarrow \text{Ni} + \text{CO} \quad (12)
\]
\[
\text{CoO} + \text{C} \rightarrow \text{Co} + \text{CO} \quad (13)
\]

With regards to the Ellingham Diagram (Figure 10), it is noted that at standard atmospheric pressure, the minimum temperature for the reduction of nickel oxide by carbon is 440°C.

Figure 10: Ellingham diagram for the reactions of NiO, C and CO (Li & Wei, 2011).

DTA studies were performed by Kukura et al. (1979) on a saprolitic ore. An endothermic peak was reported to occur within the temperature range from 500 to 750°C which was the dehydroxylation of the nickel laterite. An exothermic peak occurred at
820°C, which was the recrystallization of the silicate phase to olivine. For complete reduction of the nickel in the saprolitic ore, a temperature of 780°C was necessary to ensure that there was complete dehydroxylation. A lower heating rate of 5°C/minute over the temperature range corresponding to dehydroxylation was reported to significantly improve the nickel extracted. It was proposed that during dehydroxylation, the nickel oxide became unstable and could be incorporated into the olivine phase if not reduced. The addition of reagents such as sulphur and chlorides would stop the production of olivine, thus increasing the degree of nickel metallization.

Canterford and Turnbull (1980) were among the first researchers to conduct a thermodynamic study of the reduction of nickeliferous laterites. This work was for the ideal system, NiO-Fe₂O₃-H₂(g)-CO(g)-H₂O(g)-CO₂(g). It was concluded that it was not possible to completely reduce all of the nickel oxide, and that for acceptable reduction, a temperature greater than 600°C was necessary. The three variables investigated were: the effects of temperature (350 to 850°C), the composition of the reducing atmosphere (H₂, CO, H₂O and CO₂) and the ratio of oxide to reductant. The amount of nickel present in the ferronickel alloy was studied for the different reducing conditions. The model calculations indicated that for a hydrogen reducing atmosphere, the product was ferronickel. For weakly reducing atmospheres the product was wüstite and for strongly reducing atmospheres the product was magnetite.

Work performed by Kawahara et al. (1988) reported that for the saprolitic nickel laterite ores with high magnesia to silica ratios, there was a lower percentage of nickel recovery at higher temperatures due to the conversion of the magnesium silicates to olivine.
For nickel laterites with low ratios (limonitic) the conversion of magnesium silicates to olivine was not a problem, and the nickel recovery was high.

Valix et al. (1995) conducted a thermodynamic analysis of the reduction of nickel laterite ores with the purpose being to optimize the reduction of nickel and cobalt oxides and minimize the reduction of iron. Three factors which affected the yield of cobalt and nickel were temperature, the type of reducing atmosphere used and the quantity of reductant used. The temperature ranged from 350 to 850°C, while the atmospheres studied included: CO; CO$_2$; H$_2$ and H$_2$O (independently and in combination). The results showed that if only pure CO or pure H$_2$ were to be used, they should not exceed the stoichiometric values for nickel in order to achieve high metal grades. As the amounts of CO$_2$/CO and H$_2$O/H$_2$ were increased, the selective reduction increased but the recovery of nickel to the alloy phase was decreased. The effect of the different reducing agents and their influence on the formation of carbon was also considered, as reported in Figure 11. It is shown that the formation of carbon was greatest at lower temperatures (less than 800°C) and higher quantities of CO. Lastly, it was reported that the optimum values for nickel were different than those for cobalt and it was recommended that the most economically viable reduction condition should be used depending on the current demands for nickel and cobalt.
Figure 11: Carbon formation for different reducing atmospheres (Valix, et al., 1995).

Hallet (1997) derived stability diagrams for the two systems Fe-Ni-O and Ni-Mg-Si-O. Two of these diagrams are shown in Figure 12 and Figure 13, where the former is for a limonitic laterite ore and the latter is for a saprolitic laterite ore. These systems allow for one to calculate the amount of metallic nickel that can be produced as a function of temperature and CO/CO$_2$ ratio. For a given CO/CO$_2$ ratio, it is shown that when both the temperature and the reducing conditions are increased, the nickel metallization is not improved. Therefore, it is necessary to choose the appropriate CO/CO$_2$ ratio that is required to yield the maximum nickel extraction percentage depending on the reducing temperature.
Figure 12: The Fe-Ni-O stability diagram for goethite containing of 1.2% Ni with Ni metallization curves of 0%, 10%, 50%, 90% and 95% (Hallet, 1997).

Figure 13: Ni-Mg-Si-O stability diagram for olivine (0% Ni, 20% Ni and 50% Ni) and pyroxene (0% Ni, 20% Ni and 50% Ni) from a decomposed garnierite containing 4% Ni (Hallet, 1997).
It was reported that the reduction of nickel in silicate-bearing minerals was more complicated than that of the limonitic ore. For most compositions of garnierite \((\text{Ni, Mg})_3\text{Si}_2\text{O}_7\cdot2\text{H}_2\text{O}\), the decomposition will result in the formation of either olivine, \((\text{Ni, Mg})_2\text{SiO}_4\) or pyroxene, \((\text{Ni, Mg})\text{SiO}_3\). Stronger reducing conditions are required for olivine as compared to pyroxene. Figure 14 is a ternary phase diagram for the MgO-NiO-SiO\(_2\) system. Based on the amount of nickel present in the garnierite, it is possible to use this diagram to determine the resulting phases once the garnierite has decomposed.

\[\text{SiO}_2\]

\[\text{Pyroxene + Silica}\]

\[\text{Pyroxene + Olivine + Silica}\]

\[\text{Pyroxene + Olivine}\]

\[\text{MgSiO}_3\]

\[\text{Olivine + Silica}\]

\[\text{Mg}_2\text{SiO}_4\]

\[\text{Ol}\text{ivine + (Mg}_{\text{1-x}}\text{Ni}_x\text{O Solid Solution)}\]

\[\text{MgO}\]

\[\text{Ni}_2\text{SiO}_4\]

\[\text{NO}\]

\[\text{mol \%}\]

**Figure 14: Phase equilibria in the MgO-NiO-SiO\(_2\) system (Shiirane, et al., 1987).**

Rhamdhani et al. (2009c) performed a thermodynamic study of the phase transformations that occurred during the reduction roasting of nickel laterite ore. The proportion of phases, the nickel distribution in the phases and the nickel in phases at
equilibrium were calculated at a temperature of 740°C. This temperature was regarded as the maximum for the Yabulu Operation, a commercial process which utilized the ore. The goethite present in the material was reported to be converted into hematite (oxidation) or magnetite (reduction) according to reactions (14) and (15), respectively.

\[
2\text{FeO} \cdot \text{OH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \quad (14)
\]

\[
6(\text{Fe,Ni})\text{O} \cdot \text{OH} \rightarrow 2(\text{Fe,Ni})_3\text{O}_4 + 3\text{H}_2\text{O} + 0.5\text{O}_2 \quad (15)
\]

EMPA (electron micro probe analysis) and SXRD analysis confirmed that the nickel was contained within these two species. The ferronickel was formed from the magnetite. It was suggested by the authors that the formation of ferronickel was limited by chemical equilibrium. The increase in temperature from 700 to 740°C resulted in an increase in the recovery of metallic nickel from 46 to 92%, for a \( p_{\text{O}_2} \) of 3.2 \( \times 10^{-15} \) Pa. This showed that a small increase in temperature had a dramatic effect on the nickel recovery.

Swinbourne (2014) developed a thermodynamic model to analyze the smelting of calcined nickel laterites to produce ferronickel. The program HSC Chemistry\textsuperscript{®} 7.1 was used to predict the grade and recovery of the nickel as well as the wüstite content in the slag. The modelling temperature was 1550°C which is between the two tapping temperatures for the ferronickel (1480°C) and the slag (1580°C) used in a typical plant operation. The amount of carbon addition (5 to 35 kg/tonne) and its effect on the metal recoveries for iron, nickel, cobalt and the grade of ferronickel were investigated. The iron recovery was found to increase at a linear rate with increasing carbon content. It was found that the Fe/Ni ratio of the ore did not have a significant effect on the amounts of nickel and iron in the ferronickel product. However, the amounts of silicon and carbon were greatly affected as shown in Figure 15. At a carbon addition of about 26 kg/tonne of calcine, the
silicon and carbon content of the ferronickel rapidly increased. At a Fe/Ni ratio of 10, the silicon present in the ferronickel was calculated to be negligible while the carbon content was 30 times less than that for a calcine with a Fe/Ni ratio of 5. The calculated carbon and silicon concentrations in the ferronickel were plotted as a function of iron recovery to ferronickel. The industrial plant data was also included. It was found that the thermodynamic model was accurate for the low iron reduction smelters. However, the model was not accurate in predicting the carbon and silicon values for the high iron smelters. The difference was that in the model the higher slag amounts occurred at an iron recovery of about 90%, whereas industrially this occurred at about 55 to 65%. This inconsistency could not be taken into account with the model. It was suggested that this

Figure 15: Composition of ferronickel versus carbon in calcine feed with Fe/Ni = 5 (Swinbourne, 2014).

recovery of about 90%, whereas industrially this occurred at about 55 to 65%. This inconsistency could not be taken into account with the model. It was suggested that this
problem was not related to thermodynamics as the amount of iron being reduced did not have a significant effect on the concentrations of carbon and silicon.

Pickles et al. (2014) conducted a thermodynamic analysis of the carbothermic reduction roasting of a limonitic nickel laterite ore. They studied the effects of the following variables: temperature, reductant to ore ratio, use of nitrogen and calcination of the ore on the grade of the ferronickel and nickel recovery. This thermodynamic analysis did not assume ideal behaviour with regards to the phases wüstite, magnetite and ferronickel, whereas previous models had. The software HSC Chemistry® 6.1 was used for this work with four phases: gases, oxides, the ferronickel alloy and carbon. The maximum nickel recovery was 93% and occurred at a temperature of about 600°C. The nickel grade decreased from a value of approximately 93 to 67% over the temperature range corresponding to 400 to 600°C. After this, it decreased at a steady rate before leveling off. In contrast, the iron grade increased from about 7.5 to about 25% from 400 to 600°C. It was thus concluded that the formation of pure nickel was not thermodynamically possible as iron formed simultaneously with nickel. Figure 16 shows the nickel grade versus the nickel recovery for temperatures of 600, 800, 1000, and 1200°C at carbon additions between 0.2 and 0.5kmole/100 kg of ore. It can be seen that the nickel grade decreased with increasing recovery. The nickel grade descended slowly at low recoveries but more quickly at higher recoveries.
Figure 16: Nickel grade versus recovery for temperatures of 600 to 1200°C (Pickles, et al., 2014).

The use of a nitrogen atmosphere resulted in an increase in the maximum nickel recovery values which occurred at lower temperatures and over a wider range than in the absence of nitrogen. Grades were not significantly affected. Calcination of the ore yielded a maximum nickel recovery of about 99% with a nickel grade of 18% at 700°C. The maximum nickel recovery for the uncalcined ore was lower at 93%, but the grade was higher at 70% nickel and occurred at a lower reduction temperature of about 600°C. Finally, the researchers compared the thermodynamic data calculated using their model to the experimental data from De Graaf (1979). The results were in general agreement with one another.
2.4 Phase Transition Studies

Hayashi (1961) studied the effects of phase transitions on the reductive roasting of the nickel-bearing serpentine ores lizardite (Mg₃(Si₂O₅)(OH)₄) and antigorite ((Mg,Fe²⁺)₃(Si₂O₅)(OH)₄). XRD analysis showed that the decomposition temperatures varied for the two different serpentines. Lizardite became amorphous between 500 to 550°C, transforming into forsterite and enstatite between 800 to 850°C. On the other hand, the antigorite decomposed to an amorphous phase at the same time that forsterite and enstatite were formed over the range 600 to 750°C. The optimum roasting temperature was reported to be between 525 and 700°C. Higher temperatures had negative effects on nickel extraction. Low nickel extraction occurred when the nickel oxide present in the serpentine was not reduced in the amorphous state, and when fast heating lead to the recombination of the magnesia and silica phases.

Brindley and Hayami (1965) studied the mechanism of the dehydroxylation of powdered serpentine to the minerals forsterite and enstatite. It was proposed that the magnesium and silicon ions liberated in the reaction zones (where water was formed) diffused into areas where forsterite was produced by the following reaction:

\[
3\text{MgO} \cdot 2\text{SiO}_2 \rightarrow 3\text{MgO} \cdot 0.5\text{SiO}_2 + 0.5\text{SiO}_2
\]  

(17)

It was assumed for this reaction that all of the MgO in the serpentine formed forsterite, leaving behind an excess of amorphous silica. The experimental studies involved reacting serpentine that was 90% dehydroxylated at a temperature of 570°C in air within the temperature range of 650 to 800°C for varying times up to 100 hours. It was found that the forsterite appeared to be fine grained upon recrystallization. The conversion percentage of serpentine to forsterite reached a maximum of about 75 to 80%, as shown in Figure 17.
A study of phase transformations of nickel laterite ores (limonitic and saprolitic) at temperatures in the range of 100 to 800°C was conducted under reducing conditions by Valix et al. (2002a). For the limonitic ore, it was reported that the mineralogical phases formed at a temperature of 800°C were irreversible. XRD peaks corresponding to the ferronickel phase (taenite) were reported to initially increase with increasing temperature, but decreased at temperatures greater than 700°C. With regards to the saprolitic ore, the transformation of magnesium hydrosilicate to forsterite occurred in the uncalcined ore at a temperature of 700°C. The same behaviour was not observed for the uncalcined saprolitic
ore. Thus, it was recommended to use the reducing gas once the dehydroxylation reaction had begun.

Rhamdhani et al. (2009b) studied the microstructure and characterized the phases during the reduction roasting and leaching processes for a blend of limonitic and saprolitic ore (70:30 wt. %) provided by the BHP Billiton Yabulu refinery. This research included the study of the nickel laterite blend at three stages of the process: ore feed, reduced ore and leached ore, where the EMPA, SEM and SXRD techniques were utilized. SXRD analysis of the reduced ore revealed the presence of a mixture of magnetite and silicate minerals. These results also confirmed the presence of taenite in the reduced ore sample. SEM analysis was used to investigate the surface of a magnetite particle. Ferronickel alloy nuclei ranging in size from 15 to 20 nm in diameter were found as shown in Figure 18. Regarding the olivine particles, the amounts of magnesium and iron varied, indicating that

![Figure 18: Surface of a magnetite particle showing the formation of ferronickel alloy nuclei (Rhamdhani, et al., 2009b).](image)
the mineralogical phases forsterite and fayalite existed in various amounts in the different olivine particles. The leached ore samples were found to contain less ferronickel alloy as compared to the reduced ores, confirming that the ferronickel alloy was dissolved in the leaching process. The nickel distribution of the ore feed was found to be 59.6% in the limonitic ore and 35.2% in the saprolitic ore. These values changed to 65.1% and 32.2%, respectively once the ore was reduced. Greater than 90% of the nickel was extracted.

Chen et al. (2013) studied the recovery of ferronickel from a saprolitic ore containing 1.41% nickel. The as-received serpentine ore was pulverized to a particle size passing 38 µm. The authors investigated the microstructural and phase transformations that occurred in reduced samples as well as the nickel recoveries for the different processing conditions. The samples were reduced at fixed temperatures ranging from 500 to 800°C for reduction times of 15, 30 and 60 minutes in an atmosphere containing 15% H₂ in N₂. HRSEM (high resolution scanning electron microscopy) and TEM (transmission electron microscopy) were utilized to analyze the reduced and leached samples. HRSEM found that ferronickel particles began to form at reduction temperatures of 700 and 800°C. With regards to TEM, the reduced samples revealed that the formation of spherical particles increased with increasing temperature. EDS (energy dispersive X-ray spectroscopy) analysis was performed in conjunction with TEM and ferronickel particles were found to be present in the precipitates. Final confirmation of a ferronickel alloy phase was completed with a selected area diffraction (SAD) pattern, where the geometry of the analyzed particle was representative of a ferronickel alloy particle. Figure 19 depicts the nickel recovery with respect to increasing temperature for the three reduction times. The nickel recovery increased with increasing reduction temperature and a maximum occurred
in the temperature range of about 700 to 750°C at a reduction time of 30 minutes. Beyond this temperature range, the nickel recovery decreased. At elevated temperatures, longer reduction times decreased the overall recovery of the nickel. The sharp increase in nickel recovery from 500 to 600°C was attributed to the destruction of the serpentine lattice. Once a critical temperature was reached (>750°C), the reduced ferronickel alloy become encapsulated in the forsterite thereby preventing effective leaching of the reduced sample resulting in a lower nickel recovery.
2.5 Conventional Reduction and Sulphation Studies

2.5.1 Reduction Studies

De Graaf (1979) studied the reduction of three nickel laterite ores; one was limonitic (Manuran) and the other two were saprolitic ores (Gag I and Gag II). The chemical composition for these ores is given in Table 3 and the results for the reduction tests are shown in Figure 20. Variables of interest were the reduction temperature (500 to 900°C), gas composition (H₂, CO, CO mixed with H₂) and retention time. It was reported that fine grinding of the saprolitic ore was required to promote higher nickel extraction. The optimum reduction temperature for the limonitic laterite ore was reported to occur from 600 to 650°C, whereas, the optimum reduction temperature for the saprolitic laterite ore was at 650°C (independent of gas composition) and 900°C (where finer grinding was used) for samples Gag I and Gag II, respectively.

<table>
<thead>
<tr>
<th>Element/Compound</th>
<th>Manuran Limonitic Ore</th>
<th>Gag I Saprolitic Ore</th>
<th>Gag II Saprolitic Ore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1.3</td>
<td>2.2</td>
<td>5.6</td>
</tr>
<tr>
<td>Fe</td>
<td>48.7</td>
<td>25.8</td>
<td>14.0</td>
</tr>
<tr>
<td>Cr</td>
<td>2.2</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.1</td>
<td>26.6</td>
<td>32.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.6</td>
<td>3.6</td>
<td>2.4</td>
</tr>
<tr>
<td>MgO</td>
<td>0.6</td>
<td>14.7</td>
<td>21.3</td>
</tr>
<tr>
<td>LOI</td>
<td>13.7</td>
<td>13.4</td>
<td>13.5</td>
</tr>
</tbody>
</table>
Purwanto et al. (2001) studied the reduction rate of a cement bonded laterite briquette under one of two possible CO/CO$_2$ reducing conditions: 30% CO/70% CO$_2$ or 90% CO/10% CO$_2$ with temperature ranges of 700 to 1000°C and 900 to 1000°C, respectively. The nickel laterite ore was ground to a size fraction of 44 µm and then mixed with Portland cement and water. The mechanical mixture contained 5% Portland cement and 10% water. The cement served as a binder and also increased the strength of the mixture so that a compressive force of 300 MPa could be applied to produce a briquette. The surface of the sample was coated with alumina cement to prevent it from being exposed to reducing gases. For the first reducing condition, at a temperature of 900°C and a time...
of 3 hours, the iron was recovered as magnetite, Fe$_3$O$_4$ with nickel and cobalt being recovered in their metallic states. The second reducing condition produced metallic iron, nickel and cobalt for a temperature of 1000°C and a time of 5 hours, 50 minutes. It was indicated that the reduction of hematite, Fe$_2$O$_3$ was responsible for the weight loss of the briquette (masses of nickel and cobalt oxides were very small). For a briquette reduced under 30% CO/70% CO$_2$, there was an overall weight loss of 2.5%. For the reaction under 90% CO/10% CO$_2$, the corresponding weight loss was 21.9%. The large increase in weight loss was primarily a result of an increase in the reduction degree of the iron. For the treatment with less CO (30%), the hematite was reduced to magnetite (Equation 18) whereas for the treatment with more CO (90%) (Equation 19) the hematite was reduced to metallic iron, resulting in a far greater loss of oxygen from the sample. The reduction rate was calculated for both treatment options, and it was found that it increased with increasing temperature. The measured rate for the reduction of hematite to magnetite was higher than the reduction rate of hematite to metallic iron. Figure 21 shows a cross-section of a reduced laterite briquette for each treatment option. The rectangular section in the middle of the briquette is the unreacted material. For the briquette reduced under 30% CO (left), there was a fractional reduction of 0.5. In comparison, the briquette reduced under 90% CO (right) had a fractional reduction of 0.2 where 0.8 of the briquette is unreacted hematite. This was explained by the fact that the coated sample surface did not react with the reducing gases. A mathematical model was then used to predict the fractional reduction of the
laterite briquettes and the model was in general agreement with the measured experimental values.

![Image of partially reduced briquettes. The sample on the left was reduced under 30% CO at a temperature of 700°C and the sample on the right was reduced under 90% CO at a temperature of 900°C (Purwanto, et al., 2001).]

Kim et al. (2010) performed wet magnetic separation tests on calcined nickel laterite ore. The focus of this research was to change the composition of the iron oxide and hence its magnetic response. The as-received ore was ground to a size fraction of 37 µm and then calcined for a time of 1 hour at a given temperature. After calcination, the sample was magnetically separated and then analyzed with SEM where EDS elemental maps of iron, silicon, magnesium and nickel were produced. The three variables studied included the calcination temperature (200°C, 500°C and 800°C), applied magnetic field strength (0.1T, 0.2T and 0.5T) and the pulp density of the calcined ore (5%, 10%, 15% and 20%) as it was passed through the magnetic separator. From this research it was determined that the optimum values were: a calcination temperature of 500°C, a magnetic field strength of
0.5T and a pulp density of 20%. At these settings, the grade of nickel in the magnetic fraction was 2.9%, with a recovery of about 48%. It was suggested that the transformation of hematite to magnetite was partly responsible for the increase in grade. Regarding the EDS elemental maps, the authors reported that the nickel was equally dispersed throughout the sample and had a very small particle size. They recommended that a longer grinding time was necessary in order to reduce the size of the sample to free the nickel particles.

Li et al. (2010) investigated the effects of selective reduction and magnetic separation of nickel laterite ore containing 0.97% nickel to produce a high grade nickel concentrate. With regards to temperature, the nickel grade and the recovery greatly improved over the range of 1100 to 1250°C and then the nickel recovery leveled off. The effect of the amount of reductant is depicted in Figure 22, where the grade of the nickel decreased with increasing reductant, while the recovery increased up to 97.7% and then leveled off. Fayalite was found to be a dominant mineral phase in the reduced sample as well as taenite, which is a ferronickel alloy high in nickel content. The optimum grades were reported to be 5.1% nickel and 82.7% iron with recoveries of 98.8% nickel and 41.5% iron. This was achieved by using a reduction temperature of 1250°C, a reduction time of 1 hour, a coal additive of 3%, a basicity of 0.07 and an additive addition of 3% calcium sulphate. It was proposed that the calcium sulphate additive improved the reduction and enhanced the growth of the ferronickel particle.
Figure 22: Effect of reductant addition on the grade and recovery of nickel and iron with 3% calcium sulphate addition (Li, et al., 2010).

Li et al. (2011) studied the reduction of nickel laterite ore while investigating the following parameters: temperature, reduction time, CO content of the gas, carbon content and CaO content. By increasing the CO content of the gas, the carbon content of the feed and the temperature, there was an increase in metallization. For reduction time and CaO content, initial increases were noted in the reduction rate, with decreasing reduction rates after a time of about 1.25 hours and CaO contents in excess of 10%. XRD analysis revealed the presence of taenite, which indicated good nickel recovery. The authors stated that the CaO sped up the decomposition of the silicate according to the equation:

$$\text{CaO} + 2\text{NiO} \cdot \text{SiO}_2 \rightarrow \text{CaO} \cdot \text{SiO}_2 + 2\text{NiO}$$  \hspace{1cm} (20)
Too much CaO was detrimental to the reduction as it caused the specific surface area to decrease, lowering the nickel recovery.

Bunjaku et al. (2011) conducted thermogravimetric analysis and differential scanning calorimetry on three hydrous nickel-magnesium silicate ores. These three ores had nickel contents of 0.76% (Columbia-1, CMSA deposit), 2.3% (Columbia-2, CMSA deposit), and 2.6% (Mirabela deposit, Brazil), respectively. DSC (differential scanning calorimetry) analysis of the three samples found that three endothermic reactions occurred at temperatures of about 100°C, 250°C and 600°C corresponding to the loss of free water, decomposition of goethite and the dehydroxylation of the crystalline water, respectively. With regards to the thermogravimetric data, the crystalline water corresponded to a weight loss of about 8%. According to the XRD and SEM studies, the nickel was reported to be predominantly present in the crystal lattice of the serpentine minerals. It was also reported that the antigorite present in the Columbia-1 ore facilitated the dehydroxylation of the magnesium silicate and recrystallization of forsterite and enstatite. The other two ores, Columbia-2 and Mirabela did not contain antigorite and this resulted in the formation of intermediate phases.

The effect of ore mineralogy and the type of reducing agent was examined for several saprolitic ores by Bunjaku et al. (2012). The same ore was used as described above in the research performed by Bunjaku et al. (2011). The authors compared the use of two different reducing atmospheres: CO/CO₂ (72%:28%) and H₂/N₂ (72%:28%) at fixed reduction temperatures of 750°C and 900°C for times of 90 minutes. In addition, a thermobalance furnace was used to permit the constant measurement of the mass change
of the sample being reduced in order to calculate the degree of oxygen removal. For the Columbia-1 ore, reduction under the different process conditions resulted in the formation of forsterite and enstatite which were difficult to reduce. However, for the Columbia-2 ore, the degree of reduction increased with increasing temperature for the H₂/N₂ atmosphere as a result of the different mineralogy. It was suggested that the reduction of wüstite to metallic iron was one of the rate controlling steps in this process. Furthermore, the authors recommended that a CO/CO₂ gas mixture should be used as the reducing agent to produce the highest degree of nickel metallization.

Zhu et al. (2012) performed selective reduction and magnetic separation tests on a nickel laterite ore. The effects of processing time and temperature were investigated. Calcium sulphate (CaSO₄) was added as a source of sulphur and coal was the reducing agent. When the temperature was increased from 1000 to 1100°C the nickel recovery increased from 70.8 to 92.3% and the grade increased from 1.9 to 5.9%. The highest grades and recoveries achieved were 6.0% and 92.1% respectively, where over 75% of the reduced sample was rejected as tailings. With calcium sulphate in the reduction process, coarser ferronickel particles (taenite) were obtained. The mean size of the ferronickel particles increased from 5.8 to 16.1µm.

Fa-tao et al. (2013) performed an experimental study of the reduction and magnetic separation of a nickel laterite ore containing 1.63% nickel. They studied the effects of reduction temperature, percentage of CaO used as a flux and the C/O (carbon/oxygen) ratio. After the reduction roasting operation, magnetic separation was performed with an applied magnetic field strength of 100 mT to yield a high grade ferronickel concentrate. XRD
analysis of the as-received ore showed that the four main phases were goethite (FeO·OH), garnierite ((Ni,Mg)₃Si₂O₅(OH)₄), kaolinite (Al₂Si₂O₅(OH)₄) and clinochrysotile (Mg₃Si₂O₅(OH)₄). To observe the effect of temperature, fixed temperatures of 1325, 1350, 1375 and 1400°C were used with a C/O ratio of 1.4 and a CaO flux amount of 12%. The authors observed an increase in grade and recovery with increasing temperature which was attributed to the higher temperature range used for these reduction tests. This allowed for improved kinetics and better agglomeration of the ferronickel particles thus enriching the magnetic concentrate. The optimum reduction temperature was 1375°C with a nickel recovery of 92.5%. The effect of C/O ratio was determined by using different values of 1.0, 1.2, 1.4 and 1.6 with the reduction temperature fixed at 1375°C and the CaO flux amount at 12%. An increase in the C/O ratio resulted in a lower recovery where the optimum ratio was reported to be 1.2. Lastly, the effect of CaO on the nickel grade and recovery was studied. CaO in the amounts of 8, 12, 16 and 20% were used. The maximum nickel recovery was 94.5% at a CaO percentage of 12%. The researchers also measured the change in volume fractions of CO and CO₂ gases as a function of increasing temperature as shown in Figure 23. It is seen that both direct reduction with carbon and indirect reduction with CO occur during the reduction process. At lower temperatures carbon serves as the primary reducing agent during direct reduction, but at higher temperatures CO has a greater benefit over carbon as there is a greater amount of CO₂
produced compared to CO gas. Consequently there is both direct and indirect reduction.

![Graph showing volume fraction of CO and CO₂ as a function of temperature](image)

**Figure 23:** Volume fraction of CO and CO₂ as a function of temperature (Fa-tao, et al., 2013).

Li et al. (2013) studied the reduction mechanisms of a nickel laterite ore containing 2.26% nickel using coal-based reduction in a muffle furnace and a C/O ratio of 2.5. The reduction temperature tests were carried out within the range of 1200 to 1300°C at a time of 40 minutes. The reduction time tests were performed at 20, 40, 60 and 80 minutes at a fixed temperature of 1275°C. The reduced samples were quenched after being removed from the furnace to allow for rapid cooling and to limit oxidation of the reacted sample. With regards to the reduction time, the amount of the impurities, namely calcium, silicon, and aluminum decreased with increasing reduction time, while the peak value for nickel increased. However, it was suggested by the authors that too much reduction lead to a
lower reducing atmosphere causing the reduced metallic particles to oxidize. The proposed reduction mechanism was that the nickel oxide was primarily reduced by CO at elevated temperatures (>1000°C). The reduction process damaged the olivine lattice. The iron and nickel combined with one another to form spherical ferronickel particles which grew in size with increasing reduction time and temperature.

Ma et al. (2013) carried out a study of limonitic laterite ore via initial screening to remove some silicate minerals followed by reduction roasting and ammonia-carbonate leaching. The metal recoveries of the processed screened ore were compared to the values for the processed as-received ore. The four parameters studied in this work were: reduction roasting temperature, time, bitumite dosage and the cooling method utilized. The overall goal of this study was to determine the optimum conditions for these variables that would yield high nickel and cobalt extractions as well as improved iron recoveries. The optimum reduction temperature was determined to be 825°C, where the nickel and cobalt metal extractions decreased after this temperature. It was proposed that lower reduction temperatures resulted in a slower reaction rate and the incomplete selective reduction of metal oxides. Conversely, higher reduction temperatures caused a faster reaction rate and the oxides were over-reduced. A reduction time of 90 minutes was understood to be the optimum value because it was at this time when the extraction percentages for nickel and cobalt levelled off. With regards to the reductant dosage, the optimum amount of bitumite was reported to be 8% which yielded a nickel recovery of 88.1% compared to 81.7% when only 6% bitumite was used. Three different cooling methods were used in this work: slow cooling, quenching and inert gas cooling. Slow cooling allowed the sample to cool to room temperature after being reduced. Quenched cooling consisted of cooling the sample in 13...
L of boiled cooling water to prevent reoxidation of the roasted ore. Lastly, inert gas cooling was used and this method produced the highest extractions as the reoxidation of the ore was kept to a minimum. However, quenched cooling was determined to be the best method due to the application of future commercial projects. Once the optimum conditions were determined, a series of tests were performed to be able to effectively compare the as-received ore to the ore where the silicate minerals had been removed. The as-received ore returned cobalt and nickel extractions of 35.5% and 84%, respectively, compared to the other ore which produced cobalt and nickel values of 47.4% and 87.9%, respectively. The researchers attributed this to the fact that the removal of silicates and magnesium reduced the amount of forsterite formation.

Li et al. (2014) investigated the effects of a flux catalyst, amount of coal, reduction temperature, reduction time, and magnetic field intensity in order to optimize the reduction and magnetic separation process for nickel laterites. It was found that the sample should contain 4% coal, as further additions (8% and 12%) resulted in a decrease in the grade of the nickel product. A high reduction temperature of 1200°C improved the kinetics of the reaction between the metal oxides and the reducing agent. Both the nickel grade and the nickel recovery were increased with temperature. With regards to the reduction time, three values were used in the tests: 60, 120 and 180 minutes. The increase in processing time from 60 minutes to 120 minutes improved the grade from 3.5 to 5.5% and the recovery from 64.3 to 82.4%. However, for a reduction time of 180 minutes the nickel grade only increased to 5.6%. Finally, with regards to the value of magnetic field intensity, a value of about 3027 Oe was found to be the optimum value.
2.5.2 Sulphation Studies

The addition of sulphur and its effect on the reduction processing of nickel laterites has been investigated by many researchers. Valix and Cheung (2002b) used synchrotron radiation based X-ray powder diffraction (SRXRPD) to investigate the effect of elemental sulphur. It was found that the addition of sulphur helped improve the nickel and cobalt recoveries in both the limonitic and the saprolitic ores (fresh and weathered). A reducing atmosphere consisting of CO, CO$_2$ and N$_2$ was used for this work. It was reported that the serpentine phase transformed into fayalite (Fe$_2$SiO$_4$) and amorphous magnesium silicate at a temperature of about 500°C. At a temperature of 700°C, the magnesium silicate transformed to forsterite (Mg$_2$SiO$_4$). The nickel present in the forsterite phase could neither be reduced nor extracted (Stevens, et al., 1975). The calcined weathered saprolitic ore could be reduced between 500 to 600°C as this prevented forsterite from forming. It was reported that in order to achieve maximum recovery of nickel and cobalt, the dehydroxylation of saprolite ore was necessary at temperatures of between 400 and 800°C.

Harris et al. (2011) investigated the selective sulphidation of a nickeliferous limonitic ore within the temperature range 450 to 1000°C, and for sulphur additions from 25 to 900 kg S/tonne of ore. This work involved the processing of the limonitic laterite to yield a Ni-Fe-S phase and particles large enough for physical separation from the gangue material. Temperatures greater than 550°C produced the best grade and recovery values of up to 10% and 90%, respectively. It was concluded that for higher sulphur additions there was an increase in iron sulphidation which may have prevented the reaction between sulphur and hematite, resulting in a decrease in sulphur utilization. Thermogravimetric analysis (TGA), differential thermal analysis (DTA) and evolved gas analysis (EGA) were
utilized to analyze the effect of sulphur on the phase changes occurring during the processing of the sample. The as-received ore and also the ore with sulphur additions of 100 kg S/tonne and 700 kg S/tonne were compared. With regards to the TGA data the temperature range for the first reaction (dehydroxylation) was similar for all the samples. The DTA data showed that liquid formed at 917°C for the 100 kg S/tonne sample compared to 977°C for the 700 kg S/tonne sample. This indicated that a nickel sulphide formed at lower sulphur additions. This research showed that nickel extractions of up to 90% were possible and the extraction increased with increasing temperature. For sulphur additions of less than 300 kg S/tonne, a pyrrhotite phase was dominant, as compared to higher sulphur additions, where pyrite was more prevalent.

Li et al. (2012) tested the beneficiation of nickel laterite ore with sodium sulphate (Na₂SO₄) additions using a two-step process involving reduction roasting, then magnetic separation. The as-received material was reported to primarily consist of the following mineralogical phases: lizardite ((Mg, Fe)₃Si₂O₅(OH)₄), goethite (FeO·OH) and maghemite, (γ·Fe₂O₃). To understand how these phases reacted under reduction roasting, TG/DSC analysis was performed. The results are shown in Figure 24. From room temperature up to about 100°C there was a negative peak (endothermic) corresponding to the removal of free water. The dehydroxylation of goethite and lizardite occurred at higher temperatures of 269.4°C and 597.9°C, respectively. The recrystallization of forsterite occurred at 805.8°C. Sodium sulphate was reported to restrict the metallization of the iron leading to an improved upgrading of the nickel. Also, reduction tests performed with sodium sulphate did not contain undesirable mineralogical phases such as forsterite and enstatite. The grades and recoveries of both the iron and nickel increased as a function of
temperature from 800 to 1100°C. The optimum processing temperature with sodium sulphate as an additive was reported to be 1100°C. The ferronickel grains produced from the tests with sodium sulphate were found to be larger in size than those without sodium sulphate, with average particle sizes of 5 to 10 µm and 50 µm, respectively. This is important because a larger ferronickel particle size will lead to improved magnetic separation. The formation of troilite (FeS) allowed for faster ferronickel particle aggregation to occur due to the eutectic in the Fe-FeS system.

Jiang et al. (2013) also investigated the effect of sodium sulphate as an additive in the reduction roasting processing of a nickel silicate laterite ore. Na$_2$SO$_4$, Na$_2$S, Na$_2$O and S were mixed with the nickel laterite ore in a series of tests to examine their specific effects on the reduction process. The experiments were performed at a temperature of 1200°C for 50 minutes with a coal addition of 2% as the reducing agent and an additive addition of

Figure 24: TG/DSC plots for nickel laterite ore (Li, et al., 2012).
10% corresponding to one of the additives (Na₂SO₄, Na₂S, Na₂O and S). The nickel grade of the ferronickel concentrate was increased from 3.7 to 9.5% and the nickel recovery increased to 84.0% when 7% Na₂SO₄ was used. The effects of the different additives were reported to be as follows: Na₂O improved the nickel recovery, and Na₂S and S were helpful in enriching the nickel in the magnetic separation process due to the formation of FeS (nonmagnetic). SEM-EDS analysis established that the metallic particles formed a shell on the surface of the roasted ore. Two phases of ferronickel were found to exist in the ferronickel concentrate; taenite (γ·(Fe,Ni)) and kamacite (α·(Fe,Ni)). Other phases included forsterite ((Mg,Fe)₂SiO₄), wüstite (FeO), nepheline (Na₃MgAl(SiO₄)₂) and troilite (FeS). The mineralogical phases found in this analysis were confirmed by XRD analysis.

2.6 Microwave Reduction of Nickel Laterites

Nickel laterite ore contains a significant amount of iron oxide. Standish and Worner (1990) conducted one of the first reduction studies which compared conventional heating and microwave heating of hematite and magnetite with carbon. Conventional heating was performed at a temperature of 1000°C, whereas microwave heating was conducted at a power of 1.3 kW. The microwave reduction process was stopped after the sample reached a temperature of 1000°C. Figure 25 illustrates the mass loss as a function of time for the two methods. From this data it is seen that the rate of mass loss is higher in microwave processing and that the reduction time is less. These results showed that higher reductions could be obtained in microwave processing.
Figure 25: Comparison of carbothermic reduction by microwave heating and conventional heating (Standish & Worner, 1990).

Regarding the microwave processing of nickel laterites, several areas of research have been investigated in previous studies including: phase transformations (Chang, et al., 2008), segregation processing (Ma & Pickles, 2002; Ma & Pickles, 2005), heating behaviour (Pickles, 2004), drying behaviour (Pickles, 2005a), microwave assisted atmospheric leaching (Xiaokui, et al., 2010), and carbothermic reduction (Pickles, 2005b; Yi, et al., 2011; Samouhos, et al., 2012; He, et al., 2013).
2.6.1 Microwave Phase Transformations

Chang et al. (2008) investigated the effects of charcoal content and processing time on the mineralogical phases of the processed laterite ore at a fixed power of 800 W. Charcoal contents of 1.9%, 5.2% and 7.6% were used with a maximum processing time of 12.5 minutes. These researchers found that for the limonitic ore used in their research, after the sample was heated, the governing mineralogical phase, goethite, was converted to hematite, then magnetite thus improving the heating behaviour of the sample. The magnetite would then convert to wüstite and then iron. The transformations are as follows:

\[
\text{FeO} \cdot \text{OH} \rightarrow \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe} \tag{21}
\]

It was reported that a higher charcoal content (7.6%) led to a lower stabilized temperature when a longer processing time was used. XRD analysis was conducted on the processed samples. At 1.9% charcoal addition, hematite and magnetite were the major phases present. For 5.2% charcoal addition, the phases were magnetite and wüstite. Lastly, for 7.6% charcoal addition, a ferronickel phase was found to be present at the longer processing times of 8 to 12 minutes.

2.6.2 Microwave Segregation Processing

Microwave segregation processing was performed by Ma and Pickles (2002). This involved the processing of a silicate nickel laterite ore with charcoal and calcium chloride in excess of 30 wt. %. The nickel grade in the ferronickel product was found to be higher for the microwaved product as compared to the conventional product. For the conventional work, the nickel grades were reported as 44% and 13% at reaction temperatures of 750°C and 1050°C, respectively. For two microwave experiments at 2 and 5 minutes, the grades
were 50% and 55%, respectively. The researchers suggested that the substantial decrease in the nickel grade for conventional tests was because of the increased reduction of the iron oxide. An important finding from their work was that the silicate laterite ore became a good microwave absorber at temperatures greater than 500°C.

2.6.3 Microwave Heating Behaviour

The heating behaviour of a limonitic laterite ore was investigated by Pickles (2004). Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTGA) were performed on the limonitic laterite ore. Free water was removed by about 100°C and the conversion of goethite to hematite occurred at 230°C. Permittivity measurements were made in order to understand the heating behaviour of the limonitic laterite ore. From this research it was possible to relate the values for the real permittivity \( \varepsilon' \), to that of the temperature \( T \). The values for the permittivities, \( \varepsilon' \) and \( \varepsilon'' \) started off low, followed by a rapid increase in the temperature range of 600 to 800°C. The conversion of goethite to hematite occurred in the temperature range of 250 to 400°C as follows:

\[
2\text{FeO} \cdot (\text{OH}) \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \quad (22)
\]

Preheating the sample in a conventional furnace improved the microwave heating behaviour. As a final point, susceptors such as charcoal and the use of a fireclay crucible also helped with the heating process.

2.6.4 Microwave Drying

Research was carried out on the microwave drying of a nickeliferous limonitic laterite ore (Pickles, 2005a). This involved a comparison between conventional drying and microwave drying. It was found that the microwave drying rates were at least twice those
of the conventional values. The variables investigated included: microwave power; sample mass; briquette aspect ratio (l/d ratio); specific surface area and compaction pressure. When the permittivity and TGA/DTGA were plotted together, it was found that the removal of free water resulted in a decrease in the values of the real and the imaginary permittivities. A sample with a higher moisture content had a higher dielectric loss factor, which resulted in faster heating. An increase in microwave power resulted in faster drying rates. Regarding the aspect ratio, as it was increased, the specific surface area decreased, while the sample mass increased. This increase in sample mass led to enhanced microwave absorption and faster heating rates. For greater compaction pressures, the density of the material was increased, hence lowering the porosity of the sample and the drying rate decreased.

2.6.5 Microwave Assisted Atmospheric Leaching

Microwave assisted atmospheric leaching was performed by Xiaokui et al. (2010). This work involved the leaching of a nickel laterite ore while varying the following parameters: H$_2$SO$_4$ concentration, processing time, microwave power and reaction temperature. The reported optimum parameters for this research were also tested using conventional heating. The experiments conducted with microwave assisted leaching had a maximum nickel recovery of 90.8%, while the work performed by the conventional method had a maximum nickel recovery of only 79%. Optimum values for this research for the sulphuric acid concentration, leaching time, microwave power, and reaction temperature were 25 vol. %, 1.5 h, 600 W, and 90°C, respectively.
A similar study was conducted by Zhai et al. (2010), where the maximum value for nickel recovery was reported to be approximately 92% for a microwave reaction time of 6 minutes at a microwave power setting of 800 W, for an acid to ore mass ratio of 2:1. A higher acid to ore mass ratio caused the goethite and hematite to completely dissolve leaving behind iron sulphate and nickel sulphate which were dissolved in the water leaching process (done at 90°C for 90 minutes).

Zhao et al. (2013) performed microwave testing on a saprolitic laterite ore and investigated the effects of leaching time and temperature on the recoveries of Ni\(^{2+}\) and Co\(^{2+}\). For a temperature of 70°C and a leaching time of 60 minutes, recoveries were reported as 89.19% and 61.89% for the Ni\(^{2+}\) and Co\(^{2+}\), respectively. A second stage of separation was performed to extract the Ni, Co, Fe, and Mg from the leaching solution by using a NaOH solution. Final recoveries were reported to be 77.3%, 65.9%, 95.4%, and 92.2% for the Ni, Co, Fe, and Mg, respectively.

### 2.6.6 Carbothermic Reduction Processing

Pickles (2005b) investigated the microwave reduction of a high grade nickeliferous silicate laterite ore. The process parameters that were investigated included: power input; processing time; sample mass; and charcoal additions. TGA/DTGA analysis was also conducted on this material in order to investigate the removal of moisture. With this analysis, it was possible to understand relevant phase changes such as the decomposition of goethite and lizardite at 240°C and 500°C, respectively. The permittivity testing proved that the charcoal improved the heating behaviour of the material. The values for the absorbed microwave power versus time improved with microwave power, sample mass
and charcoal addition. The maximum values for grade and recovery were found to be 13% and 90%, respectively. This work suggested that if microwave heating was combined with conventional heating as a hybrid process, the benefits of both processes could lead to an improved overall process.

Yi et al. (2011) performed an experimental study of reduction roasting and magnetic separation of a nickeliferous laterite ore by microwave heating. For the microwave heating process, the effects of processing time and coal blending ratio were studied. A power level of 2 kW was used for the microwave tests. The reduced material was then subjected to grinding at different times before being magnetically separated at various magnetic field intensities. With regards to the effect of microwave processing time, an increase from 30 to 90 minutes did not significantly affect the nickel grade as it was found to remain relatively constant in the range of 3.5 to 3.8%. However, an increase in time from 30 to 45 minutes resulted in a nickel recovery increase from about 22 to 31.8%. A further increase in reduction time led to a decrease in the nickel recovery. Thus, a time of 45 minutes was proposed to be the ideal roasting time. A coal blending ratio of 22.7% corresponded to a nickel grade of 5.2% and a recovery of 72%. This was regarded as the “optimum separation point”. The authors stated that shorter grinding times were necessary to ensure that no valuable minerals were lost with the tailings. This would lead to an increase in the grade and recovery of the nickel. Hence, a grinding time of approximately three minutes was proposed. The fourth variable, the effect of magnetic field strength, was studied between the ranges of 1300 to 2500 Oe. In general, an increase in the magnetic field strength resulted in a gradual decrease in the nickel grade. The nickel recovery increased from 72% at 1300 Oe to 82.4% at 1900 Oe before decreasing to 62% at 2500 Oe.
However, at 1900 Oe, the grade was only 3.9%, which was lower than the grade of 5.2% at a field strength of 1300 Oe. The results from microwave processing were compared to tests run in a conventional furnace within the temperature range of 850 to 1200°C. The optimum reduction temperature for the conventional tests was reported to be 1150°C. Microstructure analysis established that larger ferronickel grains formed as a result of microwave processing compared to conventional heating. This was attributed to the “electromagnetic field effect” where growth and diffusion of the ferronickel was enhanced.

Samouhos et al. (2012) studied the microwave reduction of a nickeliferous laterite ore. They investigated the same variables as Pickles (2005b). However, in their research, powdered samples were used instead of briquettes. The three power levels used were: 200, 400 and 800 W. Figure 26 is an image of a spherical ferronickel particle that was formed during an experiment. The authors stated that the addition of carbon altered the dielectric properties of the sample. The study also showed that both power and carbon addition increased the reduction degree. This study recommended that future work to improve this process would include matching the sample mass to the microwave power used.
He at al. (2013) varied the amount of activated carbon used as a reducing agent for the microwave processing of a nickel laterite ore. They studied the effect of carbon on the final temperature of the powdered sample after the reduction process. Three amounts of carbon were used: 1.9, 5.2 and 7.6%. Figure 27 shows the effect of carbon content on sample temperature with respect to time. The graph confirms that the as-received laterite ore is initially not a good microwave absorber. With no carbon, at 5 minutes, the temperature was only about 330°C. However, for the same time, with carbon additions of 1.9% and 5.2%, the corresponding temperatures were 687°C and 922°C, respectively. The temperature rapidly increased as the newly formed hematite and magnetite phases were better microwave absorbers than the goethite originally present in the laterite ore. TGA was also performed on the ore. Weakly bound water was removed at temperatures up to about 180°C, while the mineral goethite decomposed up to 300°C. A time of
approximately 12.5 minutes was necessary for the desirable reduction of the laterite ore, as it was this time where the maximum temperature of the material began to level off for all of the tests. Lastly, it was found that for the lowest carbon content explored, the iron oxide was only reduced to magnetite which suggested that more carbon was needed.

![Figure 27: Temperature versus time for different carbon contents (He, et al., 2013).](image)

### 2.7 Vacuum Processing of Nickel Laterites

Research has been performed on the carbothermic reduction of a low grade saprolitic laterite ore in a vacuum atmosphere using a furnace (Luo, 2012). After the reduction process, magnetic separation was performed in order to extract the ferronickel and silicon. A thermodynamic analysis indicated that the reduction temperature for iron oxide and nickel oxide were less than 433°C when the pressure was less than 0.1 kPa. The
nickel laterite ore contained three different types of water: free water, crystalline water and structural water. They were removed at temperatures of 103.4, 587.1 and 794.2°C, respectively. The microstructure of the nickel laterite ore transformed when it was heated above 700°C. A peak in the DSC plot at a temperature of 817.7°C indicated the crystallization of the forsterite phase. Increasing the temperature, carbon content and reaction time resulted in an increase in the reduction ratio of magnesium and an increase in the nickel grade. The addition of CaO or CaF$_2$ improved the rate of reduction of nickel, and promoted the agglomeration of the ferronickel particles. Particle size and the magnetic field intensity had an impact on the grades and recoveries of the iron and nickel. A particle size of -400 mesh and a magnetic field intensity of 4A yielded grades of 5.21% nickel, 53.5% iron and recoveries of 87.7% nickel and 88.5% iron in the magnetic fraction. Approximately 70% of the silicon was recovered in the nonmagnetic fraction. For future work, the author recommended that leaching tests should be performed as opposed to magnetic separation to determine the effect of leaching on the nickel grade.

2.8 Microwave Vacuum Processing

2.8.1 Microwave Vacuum Processing of Materials

To date, there are no industrial applications involving the microwave processing of ores in a vacuum environment. However, considerable work has been conducted in the food industry, regarding the drying of fruits, vegetables, pharmaceuticals and polymers. Although nickel laterite has been processed under vacuum conditions, the present work is the first to investigate microwave vacuum processing of nickel laterite ores. While the
objectives of using this type of process in the food industry are different than those intended for mineral processing and extractive metallurgy, similar principles apply.

The first of many food studies involved the microwave drying of cranberries. For this work, two methods of microwaving were compared: microwave vacuum and microwave-convective (Sunjka, et al., 2004). Drying performances were found to be better for the microwave vacuum process. In this work, the researchers investigated the use of operating with a pulsed mode where the drying efficiencies were even higher. This work concluded that the efficiency of microwave vacuum drying was higher than microwave-convective drying.

Work performed by Changrue et al. (2007) involved the investigation of drying strawberries. The experimental set-up was such that if either the reflected power or the product temperature reached the maximum set points, then the microwave reactor would shut down. This allowed for more efficient processing as the material was not overheated or reacted for too long. The researchers also investigated the mass loss of the material with respect to time, which helped provide a better understanding of the process. One finding reported in this study was the effect of the incident power on the absorbed microwave power. It was recommended that for future studies, if the incident power was reduced, this would lead to improved energy absorption. Two different pressures were used for this work; 6.5 kPa and 13.3 kPa. Although the value for the second pressure setting used was twice that of the first, it was determined that the change in vacuum pressure did not have any significant effect on the process drying time.

A study on optimizing the drying conditions for the drying of enzymes (de Jesus & Filho, 2011) found that when the microwave power and vacuum strength were increased,
the water activity decreased. The amount of water present in the air was decreased, which increased the speed at which the water molecules were removed from the surface of the sample, thus leading to improved drying of the water molecules.

Another food study involved the microwave vacuum processing of thin layers of sour cherries. There are many models regarding thin-layer drying for microwave processing, however, only a select few of these models involved the use of microwave vacuum processing. It was reported by Motavali et al. (2013) that for tests conducted at a uniform power, where the pressure was increased, the drying time increased. For constant pressure and increasing power, the drying time decreased. From this, it may be deduced that if both the power was increased while decreasing the pressure, then the reaction should occur even more quickly.

The use of microwave vacuum processing to help improve the quality of contaminated soil was investigated by several researchers over two decades ago (George, et al., 1992). As found with other researchers, this work concluded that as the power level was increased, there was a greater removal of material (toluene and xylene in this case) with increasing time. The material volatilized at a greater rate when the vacuum pressure was increased. Further to this, it was reported that the effect of increasing vacuum was a reduction in the power intensity and time required to remove the hydrocarbons from the soil. It was also found that for soils with greater moisture content, the required microwave exposure time was shorter. This was explained by the dielectric loss factor for water being higher than those for the hydrocarbons being removed from the material. With regards to particle size, particles of a smaller size absorbed more microwave power because there was a larger surface area.
2.8.2 Rationale

Since water evaporation will occur at lower temperatures under a vacuum, the product processing temperature will also be lower (Sunjka, et al., 2004). The removal of moisture is accelerated, where this improved mass transfer process may be attributed to the low water vapour pressure at the reduced evaporation temperature (Mousa & Farid, 2002).

With regards to the use of a vacuum atmosphere for industrial applications, volumetric heating is imperative as it is necessary to dry bulk viscous products which have a low thermal conductivity. For microwave processing in a vacuum atmosphere, an important point to note is that if there are peaks in the electric field intensity, it is possible to produce plasma if the breakdown field strength is exceeded. A vacuum atmosphere will reduce this effect. For industrial drying processes, the normal vacuum pressure is typically in the range of 1 to 5 kPa (Puschner Microwave Power Systems, 2013). The lower pressure exhibited by a vacuum atmosphere in conjunction with the use of microwave processing, will lower the operating temperature, as well as the time it takes to react the material. Decreasing both the temperature and time of a process will improve the efficiency of the process. It is very difficult to efficiently process materials in a conventional furnace under a vacuum atmosphere as the heat can only be transferred via convection or conduction. However, because microwaves can pass through a vacuum as radiation, it is possible to heat the material of interest. For the purposes of the experimental work carried out in this thesis, when the term ‘vacuum’ is used, it refers to a low vacuum which is defined as a pressure in the range of 3 to 100 kPa (National Physical Laboratory, UK, 2010).
Chapter 3

Microwave Fundamentals

3.1 Background on Microwaves

A diagram of an electromagnetic wave is shown in Figure 28. An electromagnetic wave consists of two oscillating fields which are a magnetic field and an electric field and they are perpendicular to one another. The wavelength, $\lambda$ determines what type of wave it is. Microwaves are a part of the electromagnetic spectrum with wavelengths in the range of 1 mm to 1 m, corresponding to a frequency range of 300 MHz to 300 GHz. The two most commonly used microwave frequencies are 915 MHz and 2450 MHz, where the former applies to industrial applications, and the latter is normally for commercial and/or domestic use. Microwave energy is not a type of thermal energy. Rather, the heating resulting from microwave processing is a product of the electromagnetic energy created from the interaction of the dielectric properties of a material and the applied electromagnetic field. There are two types of microwave heating mechanisms; dipole rotation and ionic conduction.

Figure 28: Diagram of an electromagnetic wave (Leger, 2014).
The reaction of microwaves on the dipoles in liquids is regarded as dipole rotation. Dipole rotation involves microwave energy being absorbed by the water present in the material being heated, where heat is generated when the rotation of these water molecules is out of phase with the applied electric field (Jones & Rowley, 1996). The positive and negative poles change at a frequency of 2.45 GHz. The friction between the dipole molecules and the surrounding molecules produce heat.

The interaction of microwaves and ions is referred to as ionic conduction. Free ions or ionic species can interact with the same electric field as the water dipoles. When a charged atom tries to arrange itself in an electromagnetic field, the movement of ions generate heat and the transfer of energy. As the temperature of the sample being reacted increases so does the energy transfer.

3.2 Microwave Theory

Before microwaves can be applied to an extractive metallurgy procedure, it is imperative to have a critical understanding of four essential parameters governing the dielectric properties of the material being utilized. They are: i) the relative dielectric constant; ii) the relative dielectric loss; iii) the loss tangent and; iv) the half-power depth. The first two variables, the relative dielectric constant, \( \varepsilon' \), and the relative dielectric loss, \( \varepsilon'' \), are functions of the complex permittivity of the material, \( \varepsilon \). It was reported by Mudgett (1982), that the dielectric properties of a material microwaved are proportionally related to the moisture content of the material. The equation for the complex permittivity is as follows:

\[
\varepsilon = \varepsilon_0 \cdot (\varepsilon'_r - j\varepsilon''_r)
\]

(23)
In the above equation, \( \varepsilon_0 \) is a constant, which is the permittivity of free space with a corresponding value of \( 8.85 \times 10^{-12} \text{ m}^{-3} \text{ kg}^{-1} \text{ s}^{-4} \text{ A}^{2} \). The dielectric constant is a measure of the potential ability of a material to absorb microwaves, or become polarized by the electric field (Michael, et al., 1997). The dielectric loss factor measures the ability of the material to dissipate microwave energy (Lovás, et al., 2011). That is, the efficiency of the electromagnetic radiation to be converted into heat. It is the dielectric loss factor which determines the heating rate of the process for any given material. Materials with high values of the dielectric loss factor will absorb energy more rapidly than materials with low loss factors.

Several variables which influence the dielectric properties of a material include: the temperature; the moisture content; the frequency of the electric field; the material density; and the structure of the material (Nelson & Karszewski, 1990). The dielectric loss factor for a material with water will be greater than for the same material without water. Free water, is removed at 100°C, whereas bound water is removed at greater temperatures. In addition to these aforementioned parameters, the dielectric loss factor should be between one and one hundred for optimum processing using microwave energy. If the values for \( \varepsilon' \) and \( \varepsilon'' \) are known, then the value of the loss tangent (\( \tan\delta \)) can be calculated, using the ratio of the dielectric loss to the dielectric constant:

\[
\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\delta}{2\pi f \varepsilon' \varepsilon_0}
\]  

This relationship describes the dielectric losses, where \( \delta \) represents the conductivity of the material, and \( f \) is the frequency of the incident wave. The half-power depth (or
penetration depth) is important as it is the distance where the microwave power is
decreased by one-half. This value conforms to the following relationship:

\[ D_p = \frac{\lambda_0}{2\pi (2\varepsilon'_r)^{\frac{1}{2}}} \left\{ \sqrt{1 + \left( \frac{\varepsilon''_r}{\varepsilon'_r} \right)^2} - 1 \right\}^{-\frac{1}{2}} \]  (25)

where \( \lambda_0 \) is the wavelength of the incident radiation. The heating rate of a material is a
function of its electromagnetic properties. The average power absorbed by a given material
is the summation of the electric and magnetic losses:

\[ P_{av} = 2\pi f\varepsilon_0 \varepsilon''_{eff} E^2 + 2\pi f\mu_0 \mu''_{eff} H^2 \]  (26)

where \( E \) is the root mean square (rms) electric field intensity measured in V/m, \( \varepsilon''_{eff} \) is the
effective relative dielectric loss factor, \( \mu_0 \) is the permeability of free space \((2\pi \times 10^{-7} \text{ H/m})\),
\( \mu''_{eff} \) the effective relative magnetic loss factor, and \( H \) is the root mean square (rms) of the
magnetic field. Lastly, the rate of temperature increase is defined by:

\[ \frac{dT}{dt} = \frac{0.239 p_d}{(C_p \rho)} \]  (27)

where \( C_p \) and \( \rho \) are the respective values for the specific heat and specific gravity of the
material. This equation indicates that the heating rate is directly proportional to the
material’s dielectric properties, and inversely proportional to the specific heat and specific
gravity of the material. Research conducted by Soysal et al. (2006) reported that when the
material load being processed was greater, more microwave energy was required for
evaporating moisture from the material. In contrast, when the material load was less, the
drying efficiency decreased. Hence, the expected result was an increase in the specific
energy consumption for the process.
3.3 Microwave Processing Properties

Microwave heating differs from conventional heating. Microwaves generate inner heat via radiation, where this property depends on the penetration depth for the given material. This creates an inverse temperature gradient, causing the inside of the material to be hotter than the outside. This phenomenon is depicted in Figure 29 where A (T₁) is the outer part of a sample and B (T₂) is the inner part (temperature of B > temperature of A). This allows for great improvements with regards to the processing time and heat transfer. Since microwave absorption is enhanced with certain materials, (dielectric properties vary for each material), this feature can be used to help improve the process and lead to more efficient heating of the material. This process is known as selective heating, where certain parts of the sample can be heated while other parts remain unheated. Once a critical temperature, T_{crit} is reached (Figure 30) the dielectric loss factor and loss tangent will rapidly increase with respect to temperature. This effect is regarded as thermal runaway, which may benefit (rapid heating rates) or obstruct (detrimental hot spots) a

![Figure 29: Microwave heating showing higher interior temperature (Gupta & Leong, 2007).](image)
process. Several variables affecting thermal runaway include: sample size, geometry, relative density, composition, thermal conductivity and the temperature. Materials with high dielectric loss factors have smaller values for penetration depth. The interaction of an electromagnetic field with different materials is depicted in Figure 31. As the dielectric loss factor of a material increases, the material becomes more reflective. For materials with very low dielectric values, the opposite is true. These materials may be regarded as transparent in nature. Hence, to have the greatest efficiency, it is necessary to process materials that have intermediate dielectric loss factors, where this range is understood for several materials in Figure 32.
Figure 31: Interaction of electromagnetic fields for various materials (Gupta & Leong, 2007).

Figure 32: Absorbed microwave power versus dielectric loss factor (Thostenson & Chou, 1999).

3.4 Magnetron Operation

The magnetron is a high-powered vacuum tube, working as a microwave oscillator, where the primary components are the anode, cathode, magnets, and filament. A section view of a typical magnetron unit is shown in Figure 33. In the magnetron, the cathode produces electrons which form a cloud, moving outwards. The movement of electrons in a magnetron is displayed in Figure 34. The electrons are affected by the magnetic field
produced by the magnets located above and below the tube. This magnetic field is perpendicular to the applied electric field and causes the electrons to move around the circle of the magnetron. This produces the natural resonant frequency of the cavities. The current

Figure 33: Section view of a magnetron (Toshiba Hokuto Corporation, 2014).

Figure 34: The movement of electrons in a magnetron (Gallawa, 1989).
surrounding these cavities radiates them producing electromagnetic energy, which is sent to the applicator via the waveguide (Beverly Microwave Division, 2014). The resonant frequency \( F_R \) of a microwave reactor is a function of the capacitance \( C \) and the inductance \( L \) according to the following equation:

\[
F_R \approx \frac{1}{(2\pi)} \cdot \sqrt{\frac{1}{LC}}
\]

(28)

3.5 Limitations of Microwave Processing

The primary drawback of microwave processing is that the operating costs are very high because microwave processing is not as efficient as conventional heating techniques. Hence, scaling up from a laboratory process to an industrial process is not necessarily feasible. For example, a laboratory process typically involves batch testing in a closed system whereas industrial processing is continuous and must make use of a conveyor system, which is an open system. This would change the process design parameters which would affect the feasibility of a given process.

Another problem with the microwave processing of materials is that microwave radiation will cause materials to undergo certain physical and structural phase transformations, which will change the dielectric properties of the material with respect to time. Since these dielectric properties are not constant, and the temperature of the system is not regulated, it would be more difficult to predict the experimental process in the laboratory (i.e., when \( T_{\text{crit}} \) is reached).
Chapter 4

Experimental

4.1 Materials

4.1.1 Nickel Laterite Ore Composition

The nickel laterite ore used for this research was from Minara’s Murrin Murrin nickel and cobalt operation located in Western Australia. Both the low grade and high grade material were assayed using XRF. The elemental assay data for the ore is in Table 4 and the compound analysis is in Table 5. Table 6 includes the common phases/minerals that are referenced throughout this thesis along with their chemical formulas.

Table 4: Elemental analysis of the as-received nickel laterite ore using XRF.

<table>
<thead>
<tr>
<th>Element</th>
<th>Assays (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low Grade (LG)</td>
</tr>
<tr>
<td>Ni</td>
<td>1.09</td>
</tr>
<tr>
<td>Co</td>
<td>0.06</td>
</tr>
<tr>
<td>Si</td>
<td>17.9</td>
</tr>
<tr>
<td>Al</td>
<td>2.1</td>
</tr>
<tr>
<td>Fe</td>
<td>21.5</td>
</tr>
<tr>
<td>Mg</td>
<td>4</td>
</tr>
<tr>
<td>Ca</td>
<td>0.66</td>
</tr>
<tr>
<td>Na</td>
<td>0.51</td>
</tr>
<tr>
<td>K</td>
<td>0.1</td>
</tr>
<tr>
<td>Ti</td>
<td>0.13</td>
</tr>
<tr>
<td>P</td>
<td>0.01</td>
</tr>
<tr>
<td>Mn</td>
<td>0.06</td>
</tr>
<tr>
<td>Cr</td>
<td>0.4</td>
</tr>
<tr>
<td>V</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Table 5: Compound analysis of the as-received nickel laterite ore using XRF.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Assays (wt. %)</th>
<th>Low Grade (LG)</th>
<th>High Grade (HG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td></td>
<td>1.39</td>
<td>1.51</td>
</tr>
<tr>
<td>CoO</td>
<td></td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>SiO₂</td>
<td></td>
<td>38.3</td>
<td>39.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td></td>
<td>3.95</td>
<td>2.87</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td></td>
<td>30.8</td>
<td>30.6</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td>6.57</td>
<td>5.08</td>
</tr>
<tr>
<td>CaO</td>
<td></td>
<td>0.93</td>
<td>0.32</td>
</tr>
<tr>
<td>Na₂O</td>
<td></td>
<td>0.69</td>
<td>0.52</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
<td>0.12</td>
<td>0.09</td>
</tr>
<tr>
<td>TiO₂</td>
<td></td>
<td>0.21</td>
<td>0.13</td>
</tr>
<tr>
<td>P₂O₅</td>
<td></td>
<td>0.03</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>MnO</td>
<td></td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td></td>
<td>0.58</td>
<td>0.58</td>
</tr>
<tr>
<td>V₂O₅</td>
<td></td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>LOI</td>
<td></td>
<td>16.3</td>
<td>19.6</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td>100.03</td>
<td>100.53</td>
</tr>
</tbody>
</table>

Table 6: Common mineralogical phases and their ideal chemical formula.

<table>
<thead>
<tr>
<th>Phase/Mineral Name</th>
<th>Ideal Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Serpentine</td>
<td>(Mg,Fe,Ni,Al)₂(Al,Si)₂O₅(OH)₄</td>
</tr>
<tr>
<td>Fayalite</td>
<td>Fe₂SiO₄</td>
</tr>
<tr>
<td>Forsterite</td>
<td>Mg₂SiO₄</td>
</tr>
<tr>
<td>Enstatite</td>
<td>MgSiO₃</td>
</tr>
<tr>
<td>Goethite</td>
<td>FeO·OH</td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>Wüstite</td>
<td>FeO</td>
</tr>
<tr>
<td>Kamacite</td>
<td>α(Fe,Ni)</td>
</tr>
<tr>
<td>Taenite</td>
<td>γ(Fe,Ni)</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al₂Si₂O₅(OH)₄</td>
</tr>
<tr>
<td>Troilite</td>
<td>FeS</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
</tr>
</tbody>
</table>
Two XRD plots of the as-received high grade ore are shown in Figure 35 and Figure 36. Three primary mineralogical phases were identified to be goethite (FeO·OH), hematite (Fe₂O₃) and lizardite ((Mg,Al)₃(Si,Fe)₂O₅(OH₄)). From the elemental and compound analysis and the XRD data, the nickel laterite ore may be classified as a silicate laterite ore. The Si:Mg ratio for the low grade and high grade ores are 4.48 and 5.9, respectively. The average iron content is 21.4% and 21.5% for the low grade and high grade ores respectively. The average nickel content is 1.09% and 1.19% for the low grade and high grade ores respectively. This analysis categorizes the nickel laterite ore as Profile C, which is the clay silicate group.

Figure 35: XRD plot of the as-received high grade ore showing goethite and hematite.
Figure 36: XRD plot of the as-received high grade ore showing lizardite.

The as-received nickel laterite ore was first ground using a ring pulverizer and then screened using a series of sieves to separate the sample into the appropriate size fractions. A plot of sieve size versus the corresponding Tyler Mesh Equivalent size is given in Figure 157 in Appendix G. The particle size distribution and weight percent distribution values are provided in Table 7 and plotted in Figure 37. The values were averaged from two individual screening tests performed which used 750 g of pulverized low grade nickel laterite ore. The same size distribution was assumed for the high grade nickel laterite ore.
Table 7: Particle size and cumulative wt. % distribution of low grade nickel laterite ore.

<table>
<thead>
<tr>
<th>Particle Size (Sieve Aperture, mm)</th>
<th>Weight (g)</th>
<th>Weight (%)</th>
<th>Cumulative (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.680</td>
<td>41.41</td>
<td>5.56</td>
<td>5.56</td>
</tr>
<tr>
<td>1.270</td>
<td>94.87</td>
<td>12.75</td>
<td>18.31</td>
</tr>
<tr>
<td>0.726</td>
<td>66.95</td>
<td>9.00</td>
<td>27.30</td>
</tr>
<tr>
<td>0.405</td>
<td>229.97</td>
<td>30.90</td>
<td>58.20</td>
</tr>
<tr>
<td>0.182</td>
<td>56.69</td>
<td>7.62</td>
<td>65.82</td>
</tr>
<tr>
<td>0.128</td>
<td>81.45</td>
<td>10.94</td>
<td>76.76</td>
</tr>
<tr>
<td>0.090</td>
<td>44.39</td>
<td>5.96</td>
<td>82.73</td>
</tr>
<tr>
<td>0.075</td>
<td>128.57</td>
<td>17.27</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Figure 37: Particle size and cumulative wt. % distribution of low grade nickel laterite ore.
4.1.2 Activated Charcoal

Activated charcoal from Ward’s Science was used as the reducing agent for the microwave reduction tests. Proximate analysis of the activated charcoal found that the amounts corresponding to the fixed carbon, ash, volatile matter, and moisture contents were 44.11%, 9.69%, 35.4% and 10.8%, respectively. These values were determined according to the procedures outlined in Pradhan (2011). The charcoal was ground using a ring pulverizer before being mechanically mixed with the appropriate amounts of nickel laterite ore and pyrite. A particle size distribution analysis of the pulverized charcoal was conducted using a Fritsch particle size analyzer. The results are shown in Figure 38.

Figure 38: Particle size distribution of activated charcoal used for microwave tests.
5.1.3 Pyrite

Pyrite (FeS$_2$) was used as the source of sulphur for this research. A sample of pyrite was ground using a ring pulverizer before being sieved to a size fraction corresponding to -50 +200 mesh (Tyler Mesh Equivalent). An XRD plot of the pyrite is in Figure 39.

![XRD analysis plot of the as-received pyrite.](image)

**Figure 39:** XRD analysis plot of the as-received pyrite.

4.2 Sample Preparation

The sample preparation and experiments performed were done according to Figure 40. The material was mechanically mixed with charcoal as the reducing agent, where the appropriate mass of the three constituents was utilized (nickel laterite ore, charcoal and pyrite). Next, this now homogenous mixture was compacted into a briquette by use of a hydraulic jack pellet press which was used at a pressure of about 48,260 kPa, and held for
a time of 10 seconds. The dimensions of the briquette were a height of 23.5 mm and a diameter of 31.75 mm. This procedure was performed to ensure sample consistency for all of the tests. A briquette will increase the contact between charcoal and the ore and increase the microwave absorption due to the higher density of the sample compared to a powered sample. The prepared sample was microwaved at either 101 kPa (standard atmospheric pressure) or at a reduced pressure, typically 11 kPa (41 and 71 kPa were also used). For the tests performed at a pressure of 101 kPa, the briquetted sample was placed inside a quartz crucible measuring 38 mm in diameter and 87 mm in height. The sample was bounded by powdered alumina (20 g in total) from Acros Organics (99% extra pure). The

![Flowsheet of the experimental process.](image)

Figure 40: Flowsheet of the experimental process.
powdered alumina served as insulation for the sample during processing, minimizing any heat loss to the surroundings. It also prevented the sample from reacting with the quartz crucible. Six tests were performed in an argon atmosphere as a comparison. The argon was purged into the crucible before the test was started to ensure that the crucible was full of argon. For the samples performed under a reduced atmosphere (<101 kPa), glass wool was placed on top of the sample inside of the crucible to prevent the alumina powder from being drawn into the vacuum pump. Lastly, a quartz crucible was placed inside of a quartz vacuum chamber that was attached to the vacuum pump. Transparent alumina material (SALI™) was used as the platform for all of the tests. The height of this platform was measured to be 37 mm. The composition of this material is approximately 80% Al₂O₃ and 20% SiO₂. Both quartz and SALI™ are transparent to microwaves under the present experimental conditions. A typical reacted briquette is presented in Figure 41. The top view of the sample indicates that the upper portion of the sample reacted very well. However, the side view of the sample shows that the bottom part of the sample contains an unreacted portion which is brownish in colour. This unreacted material was removed in order to prevent it from affecting the nickel grade of the magnetic concentrate. The unreacted material was weighed and the mass was subtracted from the original sample mass. Therefore, only the reacted sample was pulverized and magnetically separated.
Figure 41: Top view (A) and side view (B) of a nickel laterite sample processed at 1000 W for a time of 15 minutes with 6% charcoal addition.

4.3 Microwave System

Figure 42 shows the experimental set-up for this research. The microwave system was supplied by the Conversion Technology Corporation (CTC). The 3000 V DC magnetron operated at a frequency of 2450 MHz. The input power could be continuously varied from 0 to 2000 W. The dimensions of the applicator were 40 cm in length, 40 cm in width, and 26 cm in height. The magnetron was connected to the microwave applicator via an aluminum waveguide. In order to prevent damage to the magnetron, any reflected power from the applicator travelling back through the waveguide was dissipated in the water load contained in the circulator. Two power meters were used to measure the forward (incident) and reverse (reflected) power. The percent absorbed microwave power was calculated from the difference between these two values. The absorbed microwave power would increase rapidly at a certain processing time. Once this happened, this meant that the internal temperature of the sample was equal to the critical temperature for that material. This was seen by a rapid increase in the permittivity values.
Figure 42: Schematic diagram of the experimental set-up.
4.4 Reactor Design

The vacuum chamber design is depicted in Figure 43. A General Electric rotary vane vacuum pump (Model # 5KC37PG433X) with 250 W nominal power was connected to a valve in order to obtain the desired reduced pressure of the system. The quartz chamber was situated in the applicator and connected to the rotary vacuum pump.

![Figure 43: Schematic diagram of the reaction chamber.](image)

4.5 Limitations

For samples that used a vacuum chamber during processing, it was not possible to measure the temperature of the sample. However, for some samples run at 101 kPa it was possible to measure the temperature of the sample immediately after removing it from the
microwave applicator. This was done using a HH309A Omega® data logger type K thermocouple. The sample was placed inside of a vacuum chamber, which was placed on top of an alumina platform, preventing the recording of mass change of the sample versus time. Hence, the output variables that were measured were the percent absorbed microwave power and the grades and recoveries of the magnetic concentrates of the reacted material.

4.6 Magnetic Separation Tests

Once the material was pulverized and screened to the appropriate size fraction, typically -100 µm, it was passed through a wet magnetic separator. Initially, a Davis Tube Tester (DTT) was used. Subsequently, a wet high-intensity magnetic separator (WHIMS) was used to yield a lower mass of concentrate.

4.6.1 Davis Tube Tester

The microwaved sample was pulverized for 40 seconds, then passed through the DTT for a time of 240 seconds. Figure 44 shows the set-up of the DTT. First, the hose outlet was clamped, and then the glass tube was filled with water such that the magnetic poles were covered. The magnet was turned on before introducing the sample into the glass tube where wash water was then added to ensure that the entire sample was a slurry mixture. A rubber stopper was placed on the inlet end of the tube, and then the sample was agitated for 240 seconds. This process allowed for the nonmagnetic material to be collected in a pan. The flow rate of water used was 1.2 L/min, with a stroke rate of 73 strokes/min. Once the discharge water from the outlet end of the tube was clear, the agitation was

88
stopped, and a new pan was placed underneath the outlet of the tube so that the magnetic material could be collected.

![Diagram of DTT](image)

**Figure 44: Schematic of the DTT.**

After taking losses into account, the nickel recovery was calculated using the equation:

\[
R_{\text{Ni}}(\%) = \frac{Cc}{Ff} \cdot 100\% = \frac{(\text{Mass of concentrate}) \cdot (\% \text{ Ni in the concentrate})}{(\text{Mass of ore}) \cdot (\% \text{ Ni in the ore})} \cdot 100\%
\] (29)

### 4.6.2 Wet High Intensity Magnetic Separator (WHIMS)

A wet high intensity magnetic separator (WHIMS) was used for the additional magnetic separation tests. This was Outokumpu Technology’s Carpco WHIMS Model 3x4L (Serial number 227-05). The magnetic media used was 64 mm iron spheres, where the magnetic field intensity could be varied from 0 to 17.49 kG (Figure 45). The maximum allowable particle size was 1 mm (16 mesh) but there was no limit to the minimum particle size that was used. It was recommended that the pulp density should be in the range of 20
to 30% solids (Outokumpu Technology, 2004). A value of 20% solids was used for all tests with the WHIMS as this was found to be the optimum amount for the work performed by Kim et al. (2010). A wash water flow rate of about 2.7 L/min was used to complete the magnetic separation unit operation.

![Graph](image)

**Figure 45: Magnetic field intensity versus amps for WHIMS.**

Single variable analysis was used for the different process parameters in order to find the optimum conditions. This included eight different input variables: processing time, microwave power, atmosphere (air at 101 kPa, vacuum atmosphere or argon at 101 kPa), charcoal addition, pyrite addition, sample mass, dewatering of the sample, and magnetic field intensity. By varying the different input parameters, $i_p$, and testing the different output parameters, $o_p$, (absorbed microwave power and grade and recovery of the magnetic concentrate) it was possible to determine the effects of these different parameters ($i_p$ on $o_p$).
4.7 Instrumental Methods Utilized

4.7.1 X-ray Diffraction (XRD) Analysis

X-ray Diffraction (XRD) analysis was used to determine the different mineralogical phases present in the as-received nickel laterite ore (low grade and high grade) and the reacted samples. The powdered material was tested using an Xpert Pro Philips powder diffractometer (Cu Kα radiation). In different materials, diffraction of X-rays of a known wavelength occur at specific angles. A diffraction pattern is collected according to Bragg’s Law as follows:

\[ n\lambda = 2dsin\theta \]  

(30)

Where:
- \( n \) = depth where diffraction occurs; = 1 for XRD and XRF purposes
- \( \lambda \) = wavelength of X-ray (fixed in XRD); usually in Angstroms or nanometres
- \( d \) = spacing between atomic planes (fixed in XRF); usually in Angstroms or nanometres
- \( \theta \) = angle at which X-rays hit the sample

4.7.2 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

A schematic diagram of the ICP-OES analysis instrument is shown in Figure 46. To accurately use the XRF technique, samples were first analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Processed samples were analyzed for iron, cobalt and nickel. This method involved pumping an aqueous solution into a nebulizer via a peristaltic pump. The nebulizer generated an aerosol mist and injected humidified argon gas into the chamber along with the sample. This mist accumulated in the spray chamber, where the largest mist particles settled out as a waste and the finest particles were subsequently swept into the torch assembly. The fine aerosol mist containing argon gas and sample were injected vertically up the length of the torch assembly into the plasma (Hou & Jones, 2000). The radio frequency (RF) generator
produced an oscillating current in an induction coil that travels around the tubes, thereby creating a magnetic field allowing for the ions and electrons to transfer energy to other atoms to create a high temperature plasma which can be up to 10,000 K (Tissue, 2000). When the electrons returned to their ground state at a certain spatial position within the plasma, they emitted energy at the specific wavelengths particular to a sample’s elemental composition. Thus, by determining which wavelengths were emitted by a sample and by determining their intensities, the operator was able to quantify the elemental composition of the given sample relative to a reference standard.

### 4.7.3 X-ray Fluorescence (XRF)

X-ray Fluorescence (XRF) analysis was performed on the as-received material and the magnetic concentrate using an Oxford Instruments X-Supreme 8000. This analytical technique is shown in Figure 50. The numerical values used for calibration were originally
calculated using the ICP-OES technique. The different grades for iron, cobalt and nickel determined with ICP-OES were input into the XRF machine and a plot of the calculated concentration versus the given concentration was produced. The plots for the iron, cobalt and nickel are provided in Figure 47, Figure 48 and Figure 49, respectively. For samples with concentrations that were outside of the range of the XRF, ICP-OES was used.

![XRF calibration curve for iron.](image)

Figure 47: XRF calibration curve for iron.
Figure 48: XRF calibration curve for cobalt.

Figure 49: XRF calibration curve for nickel.
XRF uses a similar principle as XRD but allows the chemical composition of the sample being analyzed to be determined. In XRD, primary X-rays from the sample are used. However, in XRF the secondary X-rays for a crystal with a known d spacing are utilized. The number of X-rays pertaining to a certain element striking the detector is proportional to the amount of that element present in the sample. This allows one to determine the amount of an element that exists within a sample.

![Diagram of XRF analytical technique]

**Figure 50:** Depiction of the XRF analytical technique.

### 4.7.4 Scanning Electron Microscope

Portions of several samples were studied with a scanning electron microscope (SEM). The samples were mounted in epoxy and polished. A depiction of how an SEM operates is shown in Figure 51. A SEM uses electrons to form an image of a sample. A beam of electrons is formed at the top of the microscope by an electron gun. The beam is passed through the microscope where it travels through electromagnetic fields and lenses focusing the beam down toward the sample. The beam hits the sample causing the
electrons (backscattered and secondary) and X-rays to eject from the sample, which are detected and converted to a signal producing an image of the sample.

![Diagram of SEM operation](image)

**Figure 51: Theory of how an SEM operates.**

### 4.7.5 Cavity Perturbation Technique

The values pertaining to the dielectric properties of the nickel laterite ore with 6% charcoal (real and imaginary permittivities, loss tangent and half-power depth) used for this research were calculated using the cavity perturbation technique. A schematic of the cavity perturbation technique is shown in Figure 52. This system was capable of measuring the dielectric properties of a material up to temperatures of about 1400°C at frequencies of 912 MHz and 2466 MHz. This method measured the difference of the microwave cavity response between an empty sample holder and a sample holder with a sample (Hutcheon, et al., 1992). A cylindrical cavity was connected to a network analyzer and conventional furnace. A small cylindrical sample mounted in a sample holder tube was heated and then inserted into the cavity which was heated up in steps. The difference in the cavity resonant frequency values and Q factor allowed one to determine the dielectric constants.
Figure 52: Schematic of the cavity system which used the cavity perturbation technique to measure the dielectric properties of the nickel laterite ore (Hutcheon, et al., 1992).

4.7.6 Carbon-Sulphur Determinator

An Eltra CS 2000 carbon-sulphur determinator was used to test for the amounts of carbon and sulphur present in several of the processed samples. A separate calibration step was required for sulphur and carbon by using suitable standards containing known amounts of these elements in a powder form (4.07% for sulphur and 12% for carbon). This machine measured the sulphur and carbon contents by combustion of the sample in an oxygen-rich atmosphere in the combustion tube. The resulting combustion gases involving SO$_2$ and/or CO$_2$ from the ore sample passed through a narrow band optical filter. The concentration of sulphur and/or carbon was determined by measuring the SO$_2$ and/or CO$_2$ content of the gas through infrared (IR) absorption spectroscopy. The IR unit utilized a specific detector
for absorption of IR radiation, which was already adjusted at the characteristic wavelengths for these two gases. The process took approximately 3 minutes per sample.

4.7.7 TGA/DTA

Nickel laterite ore, ore plus charcoal and ore plus carbon plus pyrite were tested using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques. A schematic of the Netzsch STA 449 is provided in Figure 53. TGA measures mass loss versus time (temperature increases at a linear rate), whereas DTA measures the heat of reaction by comparing the sample under study to an inert reference. The use of these two techniques simplified the characterization of chemical reactions, including decomposition, sulphation, melting and crystallization as a function of the three variables: time, temperature and atmosphere (Perkin Elmer, 2010). The procedure involved weighing

![Figure 53: Schematic diagram of Netzsch STA apparatus.](image-url)
out 30 mg of sample into an alumina crucible, which was then placed inside the Netzsch STA apparatus along with an empty crucible (inert reference). A heating rate of 10°C/min was used up to a temperature of 1200°C. Nitrogen gas was continuously purged through the system at a rate of 80 mL/min to prevent oxidation of the sample from occurring. All of the tests were measured with respect to a correction file which accounted for buoyancy of the reaction atmosphere (which may have occurred during the heating process).

4.8 Variables Investigated

Table 8 provides a summary of the variables investigated for this research as well as their respective values. The most important input variables were the effects of processing time, microwave power, the absolute pressure of the system and the addition of activated charcoal and pyrite. The output variables analyzed were the absorbed microwave power versus time and the grade and recovery of metallic nickel (iron, and cobalt in some cases) in the magnetic concentrate. Phase transformations were also investigated through the use of XRD and SEM analysis.

Table 8: Variables and conditions for microwave vacuum reduction processing tests.

<table>
<thead>
<tr>
<th>Variable</th>
<th>*Primary Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processing Time (minutes)</td>
<td>5, 10, 15</td>
</tr>
<tr>
<td>Microwave Power (W)</td>
<td>800, 900, 1000, 1100, 1200</td>
</tr>
<tr>
<td>Absolute Pressure (kPa)</td>
<td>11, 41, 71, 101</td>
</tr>
<tr>
<td>Charcoal Addition (wt. %)</td>
<td>6, 9</td>
</tr>
<tr>
<td>Pyrite Addition (wt. %)</td>
<td>2, 4, 6</td>
</tr>
<tr>
<td>Sample Mass (g)</td>
<td>10, 30</td>
</tr>
<tr>
<td>Calcination Temperature (°C)</td>
<td>150</td>
</tr>
<tr>
<td>Magnetic Field Intensity</td>
<td>4500 Gauss (DTT), 1A (WHIMS)</td>
</tr>
</tbody>
</table>

*NOTE: The vast majority of the experiments were conducted using these parameters.
4.9 Error Analysis

Assuming that there was equal variance for the different sample populations, the pooled variance statistical test was used in order to produce a more precise estimate of the variance for the iron and nickel grade and recovery values. Three different sets of tests were used to calculate the pooled variance according to the equation:

\[
s_p^2 = \frac{\sum_{i=1}^{k} (n_i - 1)s_i^2}{\sum_{i=1}^{k} (n_i - 1)} \tag{31}
\]

Where \(n_i\) is the sample size of population \(i\), and the variance for a sample set \(i\) is given by:

\[
s_i^2 = \frac{1}{(n - 1)} \sum_{i=1}^{n} (y_i - \bar{y})^2 \tag{32}
\]

The results for the pooled variance statistical tests for the iron and nickel grades are provided in Table 9 and Table 10, respectively. The pooled variance statistical test data pertaining to the iron and nickel recoveries are provided in Table 11 and Table 12, respectively. All three sample sets used in this statistical analysis were processed using a nickel laterite ore briquette sample weighing 30 g with 6% charcoal addition, 0% pyrite addition, and a particle size of -100 mesh. They were all magnetically separated using the DTT. The three sample sets (A to C) differed in operating parameters with regards to power, processing time, and pressure which was necessary in order to produce a statistically significant set of variances for the iron and nickel grade and recoveries. Sample set A consisted of four samples which were processed at a power level of 1100 W and a time of 15 minutes at 101 kPa. Sample set B used three tests which were processed at a power level of 1000 W and a time of fifteen minutes, also at 101 kPa. Lastly, sample
set C had two samples which were processed at a power level of 1000 W, processing time of five minutes and a pressure of 41 kPa.

Table 9: Statistical test data used to calculate the pooled variance for iron grade.

<table>
<thead>
<tr>
<th>Sample set</th>
<th>Sample ID</th>
<th>Iron Grade (yi)</th>
<th>(yi − ŷ)^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>T21</td>
<td>20</td>
<td>5.23</td>
</tr>
<tr>
<td></td>
<td>T46</td>
<td>20.511</td>
<td>3.152</td>
</tr>
<tr>
<td></td>
<td>T47</td>
<td>19.112</td>
<td>10.077</td>
</tr>
<tr>
<td></td>
<td>T76</td>
<td>29.523</td>
<td>52.367</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>ŷ_1 = 22.29</td>
<td>s_1^2 = 23.61</td>
</tr>
<tr>
<td>B</td>
<td>T14</td>
<td>58</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>T19</td>
<td>38</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>T20</td>
<td>42</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>ŷ_2 = 46.00</td>
<td>s_2^2 = 112.00</td>
</tr>
<tr>
<td>C</td>
<td>T41</td>
<td>29.264</td>
<td>5.192</td>
</tr>
<tr>
<td></td>
<td>T70</td>
<td>24.707</td>
<td>5.192</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>ŷ_3 = 26.99</td>
<td>s_3^2 = 10.38</td>
</tr>
</tbody>
</table>

Table 10: Statistical test data used to calculate the pooled variance for nickel grade.

<table>
<thead>
<tr>
<th>Test Group</th>
<th>Sample ID</th>
<th>Nickel Grade (yi)</th>
<th>(yi − ŷ)^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>T21</td>
<td>1.9</td>
<td>0.000676</td>
</tr>
<tr>
<td></td>
<td>T46</td>
<td>1.301</td>
<td>0.391</td>
</tr>
<tr>
<td></td>
<td>T47</td>
<td>1.283</td>
<td>0.413</td>
</tr>
<tr>
<td></td>
<td>T76</td>
<td>3.220</td>
<td>1.674</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>ŷ_1 = 1.93</td>
<td>s_1^2 = 0.826</td>
</tr>
<tr>
<td>B</td>
<td>T14</td>
<td>2.3</td>
<td>0.111</td>
</tr>
<tr>
<td></td>
<td>T19</td>
<td>3.6</td>
<td>0.934</td>
</tr>
<tr>
<td></td>
<td>T20</td>
<td>2</td>
<td>0.401</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>ŷ_2 = 2.63</td>
<td>s_2^2 = 0.723</td>
</tr>
<tr>
<td>C</td>
<td>T41</td>
<td>2.045</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>T70</td>
<td>2.620</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>ŷ_3 = 2.33</td>
<td>s_3^2 = 0.165</td>
</tr>
</tbody>
</table>

101
The pooled variances for the iron and nickel grades are calculated below:

\[
s_p^2 (\text{iron grade}) = \frac{(3 \cdot 23.61) + (2 \cdot 112) + (1 \cdot 10.38)}{(3 + 2 + 1)} = 50.868
\]

\[
s_p (\text{iron grade}) = 7.13
\]

\[
s_p^2 (\text{nickel grade}) = \frac{(3 \cdot 0.826) + (2 \cdot 0.273) + (1 \cdot 0.165)}{(3 + 2 + 1)} = 0.682
\]

\[
s_p (\text{nickel grade}) = 0.83
\]

Table 11: Statistical test data used to calculate the pooled variance for iron recovery.

<table>
<thead>
<tr>
<th>Test Group</th>
<th>Sample ID</th>
<th>Iron Recovery (yi)</th>
<th>((y_i - \bar{y})^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>T21</td>
<td>44.91</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>T46</td>
<td>52.89</td>
<td>60.14</td>
</tr>
<tr>
<td></td>
<td>T47</td>
<td>52.93</td>
<td>60.74</td>
</tr>
<tr>
<td></td>
<td>T76</td>
<td>29.80</td>
<td>234.99</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>(\bar{y}_1 = 45.13)</td>
<td>(s_1^2 = 118.64)</td>
</tr>
<tr>
<td>B</td>
<td>T14</td>
<td>9.09</td>
<td>20.95</td>
</tr>
<tr>
<td></td>
<td>T19</td>
<td>18.53</td>
<td>23.65</td>
</tr>
<tr>
<td></td>
<td>T20</td>
<td>13.38</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>(\bar{y}_2 = 13.66)</td>
<td>(s_2^2 = 22.34)</td>
</tr>
<tr>
<td>C</td>
<td>T41</td>
<td>57.98</td>
<td>106.96</td>
</tr>
<tr>
<td></td>
<td>T70</td>
<td>37.29</td>
<td>106.96</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>(\bar{y}_3 = 47.63)</td>
<td>(s_3^2 = 213.92)</td>
</tr>
</tbody>
</table>
Table 12: Statistical test data used to calculate the pooled variance for nickel recovery.

<table>
<thead>
<tr>
<th>Test Group</th>
<th>Sample ID</th>
<th>Iron Recovery ($y_i$)</th>
<th>($y_i - \bar{y})^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>T21</td>
<td>76.74</td>
<td>97.55</td>
</tr>
<tr>
<td></td>
<td>T46</td>
<td>62.98</td>
<td>15.07</td>
</tr>
<tr>
<td></td>
<td>T47</td>
<td>66.71</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>T76</td>
<td>61.03</td>
<td>34.05</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>$\bar{y}_1 = 66.87$</td>
<td>$s_1^2 = 48.90$</td>
</tr>
<tr>
<td>B</td>
<td>T14</td>
<td>6.50</td>
<td>101.07</td>
</tr>
<tr>
<td></td>
<td>T19</td>
<td>31.67</td>
<td>228.47</td>
</tr>
<tr>
<td></td>
<td>T20</td>
<td>11.49</td>
<td>25.62</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>$\bar{y}_2 = 16.56$</td>
<td>$s_2^2 = 177.58$</td>
</tr>
<tr>
<td>C</td>
<td>T41</td>
<td>72.87</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>T70</td>
<td>71.13</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>$\bar{y}_3 = 72.00$</td>
<td>$s_3^2 = 1.52$</td>
</tr>
</tbody>
</table>

The pooled variances for the iron and nickel recoveries are calculated below:

$$s_p^2 (\text{iron recovery}) = \frac{(3 \cdot 118.64) + (2 \cdot 22.34) + (1 \cdot 213.92)}{(3 + 2 + 1)} = 102.42$$

$$s_p (\text{iron recovery}) = 10.12$$

$$s_p^2 (\text{nickel grade}) = \frac{(3 \cdot 48.90) + (2 \cdot 177.58) + (1 \cdot 1.52)}{(3 + 2 + 1)} = 83.90$$

$$s_p (\text{nickel recovery}) = 9.16$$

4.10 Laboratory Safety

The power supply was always turned off before the applicator door was opened (either before or after processing a sample). However, a failsafe was installed as a precautionary measure in order to guarantee the safety of the experimenter from exposure to microwave irradiation. This failsafe consisted of a door switch that connected the
applicator unit to the water circulator. This safety mechanism served two functions. First, if the applicator door was opened at any time during microwave processing, this action alone would turn off the switch and cut the power to the magnetron preventing any microwaves from being produced. Secondly, if the required minimum flow rate of water travelling from the sink to the water circulator was not met, then the power supply would not turn on. This was imperative, because if the unit was operated without the appropriate quantity of water then the magnetron would be damaged.

To ensure that the reaction experiments were carried out safely, both sulphur dioxide (SO$_2$) and carbon monoxide (CO) meters were used in the laboratory. The threshold limit values for SO$_2$ and CO are 25 ppm and 2 ppm, respectively (Matheson Tri-Gas, 2014). If these values were exceeded, the experimenter would safely exit the premises. A lab coat, safety glasses and nitrile gloves were worn at all times while working in the laboratory. When using the ring pulverizer, steel toe boots were worn to protect the worker’s feet. A dust mask was worn to prevent the inhalation of any pulverized material. Heat resistant gloves were worn to remove samples from the applicator once the reduction procedure was completed.
Chapter 5

Results and Discussion

5.1 Heating Behaviour of Nickel Laterite Ore

In order to effectively determine the heating behaviour of the nickel laterite ore, the maximum temperature of the samples processed at 101 kPa was recorded with a type K thermocouple. The maximum temperatures of twelve samples processed under various conditions are provided in Figure 54 with the accompanying parameters in Table 13. For tests 1 to 5, which were processed for times of 15 minutes, the maximum interior temperatures of these samples ranged from 606 to 1029°C, which corresponds to a wide temperature range. At 1000 W, with 6% charcoal, the values were lower at 642 and 606°C (average temperature of 624°C). Increasing the microwave power to 1100 W resulted in an average temperature of 868°C which was greater than the two tests done at 1000 W. Adding pyrite additions of 2% or 4% to the nickel laterite samples resulted in elevated interior temperatures of the reduced samples. It was possible to compare the four samples with pyrite additions at 1000 W (tests 7, 8, 10 and 11). For an increase in pyrite content from 2 to 4%, at 1000 W and a charcoal addition of 6%, there was a decrease in the maximum temperature from 1177 to 989°C (test 7 to 10). The same trend was observed going from test 8 to test 11 which were both run at charcoal additions of 9% where the temperature decreased from 1149 to 1018°C. At a power level of 1200 W, the maximum recorded temperatures were 1319°C for a sample with 2% pyrite and 6% charcoal, and 1384°C for the sample with 4% pyrite and 9% charcoal. The higher recorded temperatures
when pyrite was added may be attributed to the improved microwave absorption of the sample, thereby increasing the reaction temperature of the sample.

Figure 54: Maximum interior temperatures recorded for selected samples at 101 kPa.

Table 13: Maximum interior temperatures recorded for selected samples at 101 kPa.

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Microwave Energy (kJ)</th>
<th>Maximum Temperature (°C)</th>
<th>Charcoal Addition (%)</th>
<th>Pyrite Addition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>900</td>
<td>642</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>900</td>
<td>606</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>990</td>
<td>840</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>990</td>
<td>735</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>990</td>
<td>1029</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>480</td>
<td>1060</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>600</td>
<td>1177</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>600</td>
<td>1149</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>720</td>
<td>1319</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>989</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>11</td>
<td>600</td>
<td>1018</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>12</td>
<td>720</td>
<td>1384</td>
<td>9</td>
<td>4</td>
</tr>
</tbody>
</table>
5.2 TGA/DTA and Permittivities

The TGA results and the real permittivity for the high grade ore are shown in Figure 55. The TGA plot showed that the mixture lost all of its free water at a temperature of 145°C, causing the real permittivity to decrease as a function of decreasing moisture content. As the temperature was increased from about 145 to 563°C, the real permittivity value exhibited a steady linear increase, as the goethite decomposed to hematite. Once the critical temperature (563°C) of the nickel laterite ore/charcoal mixture was reached, the real permittivity increased rapidly with temperature up to a value of about 770°C (Curie temperature for iron). This may be attributed to the fact that the sample temperature was increasing and some magnetite formed.

Figure 55: TGA and real permittivities (2466 MHz) for the high grade nickel laterite ore with 6% charcoal) at a heating rate of 10°C/min.
TGA/DTA analysis was performed on the as-received ore and ore plus carbon and/or pyrite. Plots of the results are shown for TGA in Figure 56, DTA in Figure 57 and TGA/DTGA in Figure 58. With reference to Table 14, it is seen that when either charcoal or a mixture of charcoal with pyrite were added to the as-received nickel laterite ore, the total mass loss increased due to the reduction process. As shown in Figure 56, the as-received ore exhibited a mass loss of about 14.8% and the mixtures had mass losses in the range of 21.8 to 24.0%. Figure 57 displays the DTA data for the as-received ore and mixtures. It was observed that the maximum DTA value for the as-received ore occurred at a temperature of about 1008°C. The maximum DTA value for the mixtures occurred at lower temperatures than the as-received ore. The temperature of the peak mV/mg value for the 6% charcoal blend occurred at 856.1°C, and this was interpreted to be the crystallization of the forsterite phase (Flavio, 1992; Tartaj, et al., 2000; Kim, et al., 2010; Li, et al., 2012). The samples containing 6% charcoal and 2 or 4% pyrite followed the same DTA curve suggesting that the small increase in pyrite from 2 to 4% had no effect on the results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass Loss(%)/Temperature Range</th>
<th>DTGA Minimum (°C)</th>
<th>DTA Maximum (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30-112 (°C) 112-223 (°C) 223-276 (°C) 276-1200 (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-Received</td>
<td>2.48  5.36  1.36  5.55</td>
<td>130</td>
<td>1008</td>
</tr>
<tr>
<td>6% Charcoal</td>
<td>2.91  5.29  1.55  14.29</td>
<td>116</td>
<td>856</td>
</tr>
<tr>
<td>9% Charcoal</td>
<td>3.13  5.48  1.41  13.01</td>
<td>118</td>
<td>689</td>
</tr>
<tr>
<td>6% Charcoal with 2% Pyrite</td>
<td>2.6   5.32  1.36  12.48</td>
<td>120</td>
<td>602</td>
</tr>
<tr>
<td>6% Charcoal with 4% Pyrite</td>
<td>2.89  5.34  1.36  13.22</td>
<td>116</td>
<td>581</td>
</tr>
</tbody>
</table>
Figure 56: TGA of different mixtures of high grade ore up to 1200°C at a heating rate of 10°C/min.

Figure 57: DTA of different mixtures of high grade ore up to 1200°C at a heating rate of 10°C/min.
The DTGA result and the TGA results for the as-received nickel laterite ore were compared to the results for ore sample containing 6% charcoal in the temperature range of 30 to 1200°C as shown in Figure 58. The two samples followed the same DTGA trend up to about 600°C where there are two main inflection points to consider. From 116 to 130°C the free water was removed. Goethite decomposed to hematite and water over the temperature range 276 to 280°C. At about 600°C, the TGA and DTGA of the as-received ore leveled off as there was no further reaction. On the contrary, for the sample containing 6% charcoal, the sample continued to lose mass from 600 to 1200°C at an increasing rate due to the reduction process.

![Graph showing TGA and DTGA results](image)

Figure 58: Comparison of the TGA and DTGA for the as-received nickel laterite ore and ore with 6% charcoal over the temperature range 30 to 1200°C at a heating rate of 10°C/min.

Figure 59 shows the real and the imaginary permittivities (at 2466 MHz) and the DTGA of a nickel laterite ore sample containing 6% charcoal. Initially the free water was
removed and there was a dramatic decrease in the real and the imaginary permittivities, where there was an increasing rate of mass loss down to a value of about -1.1%/min. As the weakly bounded water was removed from the sample, the dielectric properties of the material decreased. At the end of this stage, the rate of mass loss decreased to a value of about -0.2%/min at 200°C. From about 200 to 590°C, the real permittivity increased from 9.40 to 11.26 and the imaginary permittivity increased from 3.32 to 5.67. The critical temperature of the sample was reached at about 600°C, and the sample permittivities increased rapidly. The real permittivity reached a maximum of 18.46 at a temperature of 763°C before decreasing with increasing temperature. It was at this point when the nickel laterite ore would have absorbed the maximum amount of microwave energy. From 732 to 763°C, the imaginary permittivity decreased before increasing once again from 763 to

Figure 59: DTGA data and real and imaginary permittivities (2466 MHz) for nickel laterite ore with 6% charcoal at a heating rate of 10°C/min.
828°C. One possibility for this drop could be the crystallization of the forsterite phase. Figure 60 shows the real and the imaginary permittivity data for the nickel laterite ore at two frequencies: 912 MHz and 2466 MHz. The real and imaginary permittivities at 912 MHz followed the same trends at 2466 MHz. The permittivities were higher at 912 MHz than at 2466 MHz.

Figure 60: Real and imaginary permittivities versus temperature for high grade nickel laterite ore with 6% charcoal in an argon atmosphere at a heating rate of 10°C/min.

The loss tangent for the nickel laterite ore is shown in Figure 61. The value for the loss tangent, which is the ratio of the imaginary permittivity to the real permittivity was
between 0.3 and 0.8 for the entire temperature range. There was a sharp decrease in the loss tangent at about 800°C, which is again likely due to the formation of forsterite.

Figure 61: Loss tangent versus temperature for high grade nickel laterite ore with 6% charcoal in an argon atmosphere at a heating rate of 10°C/min.

Figure 62 shows the half-power depth for the nickel laterite ore with a 6% charcoal addition. The plot may be divided into two stages: the primary stage (26 to 681°C) and the secondary stage (681 to 1030°C). In the primary stage, the half-power depth decreased rapidly from 84.3 to 19.5 mm. In the secondary stage, the half power depth increased from 19.5 to 28.7 mm. For the briquette dimensions used in the present work (height of 23.5 mm and diameter of 31.75 mm) the half power depth was greater than half of the diameter or greater the height. Thus, the middle of the sample would not have problems being
penetrated by the microwaves whether they entered from either the top or the sides of the sample.

Figure 62: Half-power depth versus temperature for high grade nickel laterite ore with 6% charcoal addition in an argon atmosphere at a heating rate of 10°C/min.
5.3 Absorbed Microwave Power versus Time

To understand the significance of the absorbed microwave power versus time data, consider Figure 63. This graph provides a typical plot of absorbed microwave power versus time for the four different stages of processing. Stage 1 corresponds to the initial removal of free water from the sample. The amount of absorbed microwave power is very high in this stage due to the dielectric properties of water. The free water is completely removed from the sample at a temperature of 100°C. Stage 2 represents the gradual heating of the sample where the temperature increases until it reaches a critical temperature, $T_C$, which is the point at which the amount of microwave energy being absorbed increases rapidly (this is on the border of Stage 2 and Stage 3). Stage 3 corresponds to the rapid heating of the sample up to a maximum quantity of absorbed microwave power. In this stage the charcoal is being combusted and the sample is undergoing phase transformations, thereby more microwave power is being absorbed. Stage 4 is the last stage where there is a decrease in the absorbed microwave. This decrease is due to the charcoal being used up and the phase transformation of magnetite to iron. The trend for the absorbed microwave power versus time is similar to the data pertaining to the real permittivity in Figure 55.
Figure 63: Typical plot of absorbed microwave power versus time.

It was possible to calculate the approximate value of microwave energy that was absorbed by the sample during the reduction tests by calculating the area under the absorbed microwave power versus time curves, which was done using the trapezoidal rule. Figure 64 depicts the total microwave energy absorbed by the sample as a function of microwave power for the different system pressures. From this data, it is evident that less microwave energy was absorbed by the sample when run under standard atmospheric pressure (101 kPa). It is worth mentioning that the tests at a pressure of 101 kPa were processed for 15 minutes. The energy was calculated for the first five minutes of the tests so that a comparison could be made with the vacuum tests.
Figure 64: Energy absorbed versus microwave power for different pressures for processing times of 5 minutes and 6% charcoal addition.

The absorbed microwave power versus time data for samples microwaved at fixed charcoal and pyrite amounts of 6% and 2%, respectively is provided in Figure 146 in Appendix E. This data was used to produce two plots regarding the change in absorbed microwave power as a function of time. There are two important slopes to consider: the first is the decrease in absorbed microwave power due to the removal of free water; and the second pertains to the rapid increase in absorbed microwave power (critical temperature of sample was obtained). The data in Figure 65 depicts the change in absorbed microwave power versus time corresponding to the removal of free water. For a pressure of 101 kPa, the slope of the 1000 W test was steeper than the 1200 W test. The same observation regarding the two power levels could be made for the tests performed at a reduced pressure of 11 kPa. However, the tests conducted at 11 kPa did not exhibit the same degree of
linearity as those at standard atmospheric pressure as the two tests run at standard atmospheric pressure had higher R² values.

Figure 65: Absorbed microwave power versus time for the water removal stage at a charcoal content of 6% and pyrite content of 2%.

Figure 66 displays the absorbed microwave power relating to the critical temperature of the sample being reached. The results show a rapid increase in the slope of the curve. This data shows that the tests run under reduced pressure experienced a faster increase in absorbed microwave power compared to those at standard atmospheric pressure. The 1000 W test took off before the 1200 W test at 11 kPa. However, for the tests at 101 kPa, the 1200 W test reached its critical temperature first. This concludes that for this set of tests, the reduced pressure facilitated a faster reaction at a power level of 1000 W but a slower reaction at a higher power of 1200 W. The reduced partial pressure
of oxygen created a more reducing atmosphere leading to an improved reaction at 1000 W. However, for 1200 W, the higher power level yielded a slower reaction of the nickel laterite ore. This indicates that as the microwave power was increased, the effect of pressure on the absorbed microwave power was decreased. The tests performed under a reduced atmosphere also reached greater values of maximum absorbed microwave power (Figure 146).

![Graph showing absorbed microwave power versus time](image)

**Figure 66:** Absorbed microwave power versus time for the critical temperature stage at a charcoal content of 6% and pyrite content of 2%.

The absorbed microwave power data for a test run in an argon atmosphere for a time of 6.25 minutes is shown in Figure 67. This graph follows the same trend as a typical test as outlined in Figure 63. The sample lost its free water from 15 to 150 seconds as understood by the decrease in absorbed microwave power from about 55.6 to 13.9%. The
temperature and absorbed microwave power increased during the interval corresponding to 150 to 300 seconds up to a value of 33.3%. Lastly, at approximately 300 seconds, the critical temperature of the sample was reached and thus the absorbed microwave power increased rapidly to 76.1% in 75 seconds. The average rates of change for the curves A, B and C were calculated to be -0.309, 0.296 and 0.571%/sec, respectively. It is seen that the initial heating stage, A, conformed to a 2nd order polynomial curve and stages B and C were linear.

![Figure 67: Absorbed microwave power versus time for nickel laterite sample processed for 6.25 minutes at a power of 900 W in an argon atmosphere at 101 kPa with 6% charcoal addition, 30 g sample mass, -200 mesh particle size and HG ore.](image)

5.4 Effect of Processing Time

Initial reduction tests were conducted for 15 minutes. This value was found to be too long and oxidation of the nickel laterite ore often occurred as a result. Thus, a series
of 5 minute tests were performed, followed by 10 minute tests. Other time increments were also used. However, these three times (5, 10 and 15 minutes) were used the most often. It was determined that once the microwaved sample reached its critical temperature, the absorbed microwave power increased rapidly up to a maximum value before decreasing. The optimum reduction time could not be determined under the given conditions, as the processing temperature of the sample was unknown.

Figure 68 and Figure 69 provide the XRD plots of the processed magnetic concentrates of two reduction tests performed at times of 10 and 12 minutes, respectively. The processing conditions were a microwave power of 1100 W, 6% charcoal addition, particle size of -100 mesh, sample size of 30 g, and dehydration of the samples at 150°C before processing to remove the free water. Lastly, the DTT was used to magnetically separate the reduced sample. In the first test (Figure 68), which was 10 minutes in processing time, three mineralogical phases were found: pigeonite, cristobalite and iron. The formation of iron in the sample without ferronickel present suggests that oxidation of the sample occurred. For the second test which was 12 minutes, (Figure 69), three mineralogical phases were formed: pigeonite, cristobalite and magnetite. The fact that the third test was longer in duration where magnetite was yielded as opposed to iron, indicates that the sample was not fully reduced and is a result of the microwave variability. In comparison, a sample was reacted under the same process conditions as mentioned above, with two differences being that the sample was not dehydrated prior to reduction processing and the processing time was shortened to a time of 6 minutes. XRD analysis of this test is shown in Figure 70, which revealed the presence of corundum and kamacite along with cristobalite and pigeonite. These results conclude that in order to achieve ferronickel at the
above mentioned conditions, either the presence of free water in the sample is required in order to speed up the reaction process (and thus improve the absorbed microwave power) or a shorter reduction time for these conditions is required to prevent oxidation of the sample form occurring.

Figure 68: XRD analysis of the magnetic concentrate of a dehydrated sample reduced for 10 minutes.
Figure 69: XRD analysis of the magnetic concentrate of a dehydrated sample reduced for 12 minutes.

Figure 70: XRD analysis of the magnetic concentrate of a sample reduced for 6 minutes.
5.4.1 Grade versus Recovery Data

Six samples were processed at different times at a power level of 1100 W, pressure of 101 kPa, fixed charcoal content of 6%, sample mass of 30 g and a particle size of -100 mesh. The sample was separated into a magnetic fraction (concentrate) and nonmagnetic fraction (tailings) using the DTT. The results for the nickel grades and recoveries are shown in Figure 71. The iron grades and recoveries are in Figure 72. A processing time of seven minutes resulted in a nickel grade of about 1.5%. Increasing the processing time to ten minutes improved the nickel grade to 3.8%. When the laterite ore was processed for 11 minutes the nickel grade decreased to 2.8%. The nickel recovery benefited with processing times of 9 and 10 minutes with respective recoveries of 97.7% and 95.5%. Increasing the time above ten minutes was detrimental to the nickel recovery which plummeted to 19.5% and 30.4% when processing times of 10.5 and 11 minutes were used. The iron recovery followed a similar trend as the nickel. The maximum value was 46% and occurred at a time of 9 minutes.
Figure 71: Effect of processing time on nickel grade and recovery for 30 g samples in air at 1100 W, 6% charcoal addition, 101 kPa, -100 mesh particle size with HG ore and separated with the DDT.

Figure 72: Effect of processing time on iron grade and recovery for 30 g samples in air at 1100 W, 6% charcoal addition, 101 kPa, -100 mesh particle size with HG ore and separated with the DTT.
Table 15 reports the grade and recovery values for iron, cobalt and nickel at a reduced pressure of 41 kPa. At a microwave power level of 800 W, as the time was increased from 5 to 10 minutes, the nickel grade increased from a value of 2 to 3.5%. The recovery also increased from 10.7 to 94.5%. When the time was doubled from five to ten minutes for a power level of 1000 W, the nickel grade did not change and the recovery decreased by 5.2%. These results conclude that for these four samples, the processing time had a profound effect on the nickel grade and recovery values at a power level of 800 W, but almost no effect when a higher power level of 1000 W was used. The cobalt followed the same trend as the nickel with regards to the grade and recovery values. The iron recovery increased when the processing time was increased from 5 to 10 minutes at 800 W was used but the corresponding grade decreased by about 50%.

Table 15: Effect of pressure of 41 kPa on metal grade and recovery values for 6% charcoal addition.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Processing Time (min)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>800</td>
<td>5</td>
<td>0.08</td>
<td>49.0</td>
</tr>
<tr>
<td>800</td>
<td>10</td>
<td>0.13</td>
<td>24.1</td>
</tr>
<tr>
<td>1000</td>
<td>5</td>
<td>0.11</td>
<td>27.0</td>
</tr>
<tr>
<td>1000</td>
<td>10</td>
<td>0.09</td>
<td>19.2</td>
</tr>
</tbody>
</table>

Table 16 reports the nickel grade and recovery values for six tests run at a pressure of 11 kPa for powers of 800, 900 and 1000 W in order to compare the effect of processing time on the nickel grade and recovery values for a reduced pressure. The WHIMS was used for the magnetic separations. Analyzing the two tests run at 800 W, it is noted that there was a decrease in both the nickel grade and the nickel recovery when the time was increased from 5 to 10 minutes. At a power of 900 W, the nickel grade decreased from
18.8 to 17.9% when the time was increased from 5 to 10 minutes. However the recovery increased from 11.0 to 55.7%. Lastly, for the tests at 1000 W, the nickel grade decreased by 2% from 17.2 to 15.2% and the recovery increased from 23.4 to 71.4%. Hence, it is concluded that for a low microwave power of 800 W, a time of 5 minutes is preferred, whereas for higher microwave powers of 900 and 1000 W, a time of 10 minutes is favoured.

Table 16: Nickel grades and recoveries for tests at times of 5 and 10 minutes, powers of 800, 900, and 1000 W at a pressure of 11 kPa and a charcoal addition of 6%. Magnetic separation was done with the WHIMS.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Power (W)</th>
<th>Ni Grade (%)</th>
<th>Ni Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>800</td>
<td>14.4</td>
<td>34.7</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>18.8</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>17.2</td>
<td>23.4</td>
</tr>
<tr>
<td>10</td>
<td>800</td>
<td>4.8</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>17.9</td>
<td>55.7</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>15.2</td>
<td>71.4</td>
</tr>
</tbody>
</table>

5.5 Effect of Microwave Power

Increasing the input power will increase the electric field intensity which will lead to a greater amount of absorbed microwave power. Preliminary test work involved processing a briquetted sample weighing 30 g, with a charcoal content of 6%, in the microwave reactor for a time of 15 minutes. The forward power was held constant for each test and the data is shown in Figure 73. All five tests began with the same trend, where the absorbed microwave power decreased rapidly, corresponding to the removal of free water from the sample. Next, the absorbed microwave power leveled off and the sample temperature started to increase. It is important to note that three of these tests did not reach the critical temperature necessary for the reduction process to take place. However, for the test conducted at a power of 1100 W, once the critical temperature was reached, the
absorbed microwave power increased rapidly from value of about 57 to 90%. This was attributed to the phenomenon of thermal runaway which is caused by non-uniform heating and creates hotspots within the sample. This effect is problematic as the sample will become too hot and ignite typically resulting in oxidation of the nickel laterite ore and thus decreasing the nickel grade of the sample. A similar occurrence was observed for the sample processed at a power of 1200 W. As mentioned previously, the microwave variability is another factor to consider when comparing the absorbed microwave power data for these five samples. Worth mentioning is that the maximum interior temperatures for the tests at 1050 W and 1150 W were 836°C and 849°C, respectively. Studying Figure 73, it is evident that these two tests absorbed the same amount of microwave power. To test the use of a blend of alumina powder and charcoal as an insulator, three tests were done with charcoal mixed with alumina powder at a ratio of 1:2. The results are presented in Figure 74. A total mass of 45 g of material was used to insulate the briquette inside of the crucible, with 15 g of the blend on the bottom half of the sample and 30 g placed on the top half. As the microwave power was increased from 1000 to 1200 W, the absorbed microwave power curve shifted to the left which showed that the critical temperature of the sample was reached earlier at a higher power.
Figure 73: Absorbed microwave power versus time for 30 g samples with 6% charcoal at 101 kPa.

Figure 74: Absorbed microwave power versus time for 30 g samples with 6% charcoal mixed with alumina powder (1:2 ratio) at 101 kPa.
Figure 75 shows the relationship between the absorbed microwave power versus time for powers of 500, 750 and 900 W. Three tests were performed at each power setting using 30 g samples with a 6% charcoal addition and processing times of 10, 12.5 and 15 minutes, respectively. The tests at 500 W were more efficient as a lower percentage of forward power was reflected back into the waveguide. However, for all tests (nine in total), the sample did not become hot enough to facilitate a reaction. It was concluded that higher microwave powers were needed to promote a reaction. The production of plasma was attained for several reduction tests indicating that the breakdown field strength was exceeded for the sample. The breakdown field strength is the strongest electric field that a material can be exposed to without the polarization forces becoming too strong and causing electrons to break free from atoms, causing to the formation of plasma. Pulsed microwave

![Figure 75: Absorbed microwave power versus time for 30 g samples with 6% charcoal addition and processing times of 10 minutes (A), 12.5 minutes (B) and 15 minutes (C) at powers of 500, 750 and 900 W, respectively.](image-url)
vacuum drying would help with reducing the possibility of plasma arcing, as the energy dissipated in the magnetron would be decreased (Meredith, 1998). When plasma was produced, most of the microwave energy was absorbed by the plasma and not the sample, leading to poor processing of the material.

It was originally expected that the greater the microwave power, the greater the maximum absorbed microwave power would be. However, this was not the case as can be realized in Figure 76. The results indicate that when either 2 or 4% pyrite was added to the sample, the maximum absorbed microwave power values were less than the values for the tests conducted without the addition of pyrite. Of note are the values for 1000 W. For the test run at 41 kPa, a maximum value of 96.5% was obtained which was much greater than the tests performed at a lower power level of 800 W; which reached a maximum absorbed microwave power at 72.3%, and at a higher power level of 1200 W; which reached a maximum value of 86.6%. Conversely, with regards to the test performed at a pressure of 101 kPa and a power setting of 1000 W, the opposite effect occurred. The maximum absorbed microwave power was only 64.4%, which was less than both of the values at 800 W and 1200 W which were 84.7% and 82.8%, respectively. The results for tests at a pressure of 101 kPa with 2% pyrite addition followed a similar trend as those at 4% pyrite, where 1000 W exhibited the lowest maximum absorbed microwave power value.
Figure 76: Effect of microwave power on maximum absorbed microwave power for different pressures at 6% charcoal addition and a processing time of 10 minutes.

Figure 77 displays the absorbed microwave power data for three samples containing 9% charcoal, a pressure of 101 kPa and pyrite content of 2%. A power level of 800 W yielded the greatest absorbed microwave power, followed by 1200 W, then 1000 W. Figure 78 comprises of the absorbed microwave power data for three samples which used 9% charcoal, a pressure of 101 kPa and pyrite content of 4%. This data followed a similar trend as the samples with 2% pyrite. A power of 800 W does not remove the water quickly enough whereas 1200 W removes the water very quickly. However, at 1000 W, there was a greater change in the decrease of absorbed microwave power indicating that there was also a greater amount of free water removed from the sample than at 800 and 1200 W.
Figure 77: Effect of microwave power for a charcoal addition of 9%, pyrite addition of 2% and pressure of 101 kPa.

Figure 78: Effect of microwave power for a charcoal addition of 9%, pyrite addition of 4% and pressure of 101 kPa.
5.5.1 Grade versus Recovery Data using the DTT

The high grade ore was used for the tests that were magnetically separated with the DTT. The grade versus recovery plots for nickel at different processing conditions were compared to one another in order to determine the optimum conditions for the different input variables studied in this thesis. Figure 79 shows that as the microwave power was increased from 1000 to 1500 W, the nickel grade decreased. However, the nickel recovery increased when the power was increased from 1000 to 1100 W which was followed by a decrease in recovery as the power was increased from 1100 to 1500 W. One reason for the low nickel grades at higher microwave powers was due to oxidation of the sample. Further reduction tests (after this batch) were performed between power levels of 800 and 1200 W to mitigate this problem. With regards to the nickel recovery, it increased from a value of 19.1 to 63.6% when the microwave power was increased from 1000 to 1100 W. This is a large increase in value which could be the result of the greater sample temperature that was reached at 1100 W (without oxidation occurring). The grade and recovery plots for cobalt and iron are in Appendix C. The cobalt grades and recoveries followed the same trends as the nickel. The iron grade and recovery plots were different, because as the grade was increased, the recovery decreased.
Figure 79: Effect of microwave power on nickel grade and recovery for processing times of 15 minutes, 6% charcoal addition, 30 g sample size, -100 mesh particle size, pressure of 101 kPa with HG ore.

Figure 80 shows the effect of an operating pressure of 71 kPa on the nickel grade and recovery when a processing time of only 5 minutes was used. Comparing this to the tests at 101 kPa, it is seen that at a power level of 1000 W, a grade of 2.6% and recovery of 55.8% was attainable when using a reduced pressure. This is an improvement in the nickel recovery, which was 19.1% at 101 kPa. The nickel grade decreased to from 3.0% at 101 kPa to about 2.6% at 71 kPa.
5.5.2 Grade versus Recovery Data using the WHIMS

The WHIMS was used for the remaining tests to yield a lower mass of concentrate. This section comprises of four sets of reduction tests at atmospheric pressure (Figure 81, Figure 83, Figure 84 and Figure 85) and one set of tests at a reduced pressure of 11 kPa (Figure 86). The input power was varied between tests while all other input parameters were held constant. The tests performed at atmospheric pressure were quenched immediately after processing to prevent reoxidation of the sample from occurring. The tests under a vacuum atmosphere were allowed to cool under a vacuum after the reduction process. These two cooling methods were found to yield better results than slow cooling in air. From Figure 81, it is evident that the nickel grade and nickel recovery curves followed a similar trend. An increase in microwave power from 800 to 900 W resulted in

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Figure 80: Effect of microwave power on nickel grade and recovery for a processing time of 5 minutes, 6% charcoal addition, 30 g sample size, -100 mesh particle size, pressure of 71 kPa with HG ore.
an immediate decrease in the grade and recovery of nickel, which may be attributed to poor reduction for this particular test. At a power of 1200 W, the maximum nickel grade was 5.0% with a corresponding nickel recovery of about 30%. The decrease in recovery from 1100 W to 1200 W may be attributed to oxidation of the sample.

![Graph showing nickel grade and recovery vs. microwave power](image)

**Figure 81**: Effect of microwave power on nickel grade and recovery for processing times of 10 minutes, 6% charcoal addition, 30 g sample size, -100 mesh particle size, at 101 kPa with LG ore.

SEM analysis was carried out on the magnetic concentrate of the sample processed at a power level of 800 W (orange points in Figure 81). The corresponding nickel grade and recovery values were 3.40% and 25.3%. Figure 82 shows the elemental maps of the Si, Mg, Ni, Fe and Co. The iron and nickel are closely associated with one another to form a ferronickel bead in the bottom left side of the image labelled as A. Next, the magnesium and silicon from a magnesium silicate phase which could be either enstatite or forsterite.
Figure 82: Elemental map of Si, Mg, Ni, Fe and Co for magnetic concentrate of sample processed for a time of 10 minutes, 6% charcoal addition, 30 g sample size, -100 mesh particle size, at 101 kPa with LG ore.

A series of tests was completed under the same conditions as those in Figure 81, with the exception being the addition of 2% pyrite. The results are in Figure 83. It is seen that the addition of 2% pyrite resulted in a higher nickel grade for all powers except for 1100 W. This is because the sulphur in the pyrite promotes ferronickel particle growth resulting in a higher grade of nickel in the ferronickel. The nickel recovery increased for all powers except 1200 W, where it decreased. However, the increase in the recovery of nickel going from 0 to 2% pyrite for the powers of 1000, 1100 and 1200 W was not substantial. The tests in Figure 84 were processed under the same conditions as the tests in Figure 83, but with a charcoal addition of 9% instead of 6%. Very low nickel grade and
recovery values resulted from this set of tests. The nickel grade also remained relatively constant throughout the tests which was unexpected as this did not occur in the previous set of reduction tests. For the last set of tests performed at standard atmospheric pressure (Figure 85), which used a pyrite addition of 4%, there was an improvement in the nickel grade for 1000 and 1200 W compared to the tests done with only 2% pyrite. The nickel grade essentially doubled at 1000 W and increased by about 41% at 1200 W. When the pyrite content was increased from 2 to 4% at a power of 800 W, the nickel recovery was reduced by about a half from 13 to 6.8%. However, the on other hand, the opposite was true for higher powers of 1000 and 1200 W, where the recovery was doubled. It was concluded that doubling the quantity of pyrite at a power of 1000 W doubled the nickel grade and recovery and doubled the recovery at 1200 W as well.
Figure 84: Effect of microwave power on nickel grade and recovery for processing times of 10 minutes, 9% charcoal addition, 2% pyrite, 30g sample size, -200 mesh particle size, pressure of 101 kPa with HG ore.

Figure 85: Effect of microwave power on nickel grade and recovery for processing times of 10 minutes, 9% charcoal addition, 4% pyrite, 30g sample size, -200 mesh particle size, pressure of 101 kPa with HG ore.
The highest reported nickel grades in the present work were obtained when a reduced pressure of 11 kPa was used for a processing time of 5 minutes, as shown in Figure 86. For powers from 800 to 1200 W the nickel grades ranged from 14.4 to 21%. This indicates that the ferronickel for these reduction tests was taenite. The nickel grade followed an increasing trend from 14.4 to 18.8% when the power was increased from 800 to 900 W. Then the grade slightly decreased to 17.2% for a power of 1000 W. The grade then increased once again to 21% (at 1100 W) before decreasing to 18.1% at 1200 W. With regards to the nickel recovery, it started off at 34.7% decreased to 11.0% then increased to a value of about 70.0% at 1100 W where it remained constant at up to 1200 W. A power level of 1100 W was found to be the optimum condition for the process parameters used in Figure 86. The energy consumption at the optimum conditions would be about 3250.6 kWh/tonne ore. The carbothermic reduction of nickel laterite ore in a vacuum atmosphere yielded high nickel grade and recovery values due to the reduced partial pressure of oxygen in the system, thereby increasing the reduction potential of the process and also accelerating the rate of reaction. It is also understood that these tests were reduced at a lower temperature and that the ferronickel product was easily separated from the slag phase (which was less abundant) via magnetic separation.
5.6 Effect of Pressure

There exists a critical pressure $p_c$, in every system. Xiong et al. (2012) studied the preparation of metal zinc via vacuum carbothermic reduction. They found that when the critical pressure, $p_c$ was less than the system pressure, the rate of evaporation decreased with increasing system pressure. As the value for $p_c$ became larger than that of the system pressure, the rate of evaporation remained constant (for both an increase and decrease in the system pressure). For the present research, in order to facilitate the reduction of nickel, (improve the reduction rate) a lower system pressure would be preferred. The reduction of NiO with charcoal is understood by the following equation:
\[
\text{NiO}(s) + C(s) \rightarrow \text{Ni}(s) + \text{CO}(g)
\] (33)

As the pressure of the system is decreased, so is the required reduction temperature to facilitate the above reaction. At standard atmospheric pressure, a temperature of about 440°C is needed, whereas at a very low pressure of 0.01 kPa, a temperature of only 226°C is needed (Luo, 2012). The test work in the lab was done at both 101 and 11 kPa, so the required operating temperature is somewhere in this temperature range. Figure 87 shows the standard free energy as a function of temperature for the seven reactions relating to iron reduction, serpentine decomposition, fayalite formation and the two stability diagram lines corresponding to carbon and carbon monoxide at 101 kPa. At about 700°C, the reduction of magnetite to iron is more favourable than the reduction of wüstite to iron.

![Figure 87: Standard Free Energy as a function of temperature for relevant species at 101 kPa.](image)

When comparing the physical appearance of samples processed under a vacuum atmosphere compared to those at standard atmospheric pressure, it was found that the
vacuum atmosphere yielded better results. This was visually determined by Figure 88 (standard atmosphere) and Figure 89 (vacuum atmosphere), where it is apparent that the samples processed under a vacuum atmosphere were reduced more efficiently. The parameters for these tests are summarized in Table 17. Reviewing Figure 89, it is seen that

![Figure 88](image1.png)  ![Figure 89](image2.png)

**Figure 88**: Samples processed at 101 kPa that are not fully reacted.

**Figure 89**: Samples processed in a vacuum atmosphere that reacted well.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Power (W)</th>
<th>Time (min)</th>
<th>Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1100</td>
<td>10</td>
<td>101</td>
</tr>
<tr>
<td>2</td>
<td>1100</td>
<td>12</td>
<td>101</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>5</td>
<td>41</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>5</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>800</td>
<td>10</td>
<td>71</td>
</tr>
<tr>
<td>6</td>
<td>1200</td>
<td>5</td>
<td>41</td>
</tr>
</tbody>
</table>

**Table 17**: Tests at 101 kPa versus tests in a vacuum atmosphere with 6% charcoal addition.
for an increase in power from 1000 to 1200 W, there was a better reduction of the sample. Also, for an increase in time from 5 to 10 minutes, there was also an enhanced reaction. This would initially suggest that processing the sample in a vacuum atmosphere for a longer period of time and at a higher power level should result in a greater reaction of the sample. However, this was not found to always be the case as indicated by the results from Table 16 and Figure 86. Regarding the data in Table 16, an increase in time from 5 to 10 minutes decreased the nickel grade at powers of 900 and 1000 W but improved the recovery. And from Figure 86, an increase in microwave power from 1100 W to 1200 W decreased the nickel grade.

Two reduction tests were performed in order to compare the effect of processing at a reduced atmosphere. The XRD results for these two tests are shown in Figure 90 and Figure 91. Figure 90 is for a sample processed at 1000 W, a time of 5 minutes, pressure of 71 kPa, and charcoal addition of 6%. Figure 91 is for a sample processed at 1000 W, a time of 5 minutes, pressure of 41 kPa, and charcoal addition of 6%. The magnetic concentrates in both of the samples contained the following mineralogical phases: magnetite, fayalite, pigeonite and cristobalite. However, the sample processed at a greater pressure also contained some iron as well as lizardite, which was found in the as-received material. The results indicate that a lower pressure of 41 kPa resulted in an improved reduction as there was no lizardite in the final product but there was still magnetite. Also, the fact that iron was not found to exist by itself indicates that the sample was not oxidized as much as the sample tested at 71 kPa.
Figure 90: XRD analysis of a sample processed at a power of 1000 W, time of 5 minutes, pressure of 71 kPa and charcoal addition of 6%.
Figure 91: XRD analysis of a sample processed at a power of 1000 W, time of 5 minutes, pressure of 41 kPa and charcoal addition of 6%.

The nickel grade versus pressure and nickel recovery versus pressure plots are shown in Figure 92. The parameters for this set of tests were a processing time of 10 minutes, a power of 1000 W, 6% charcoal, 30 g sample size, -200 mesh particle size, with high grade ore used in the blend. The samples were separated using the WHIMS at a setting of 1A. The results indicate that an increase in the pressure of the system from either 11 to 41 kPa or from 11 to 101 kPa led to a decrease in the nickel grade and recovery. It is interpreted that the lower operating pressure of the system decreased the partial pressure of oxygen and improved the reducing atmosphere. The lower pressure also decreased the required temperature needed to facilitate the carbothermic reduction of the ore.
Figure 92: Effect of pressure on nickel grade and recovery for a processing time of 10 minutes, power of 1000 W, 6% charcoal addition, 30 g sample size, -200 mesh particle size, with HG ore and separated with WHIMS at 1A.

5.7 Effect of Argon

Six reduction tests were performed in an argon atmosphere with a fixed input power of 900 W. The processing time was varied at 5, 6.25, 7.5, 8.75, 10 and 12.5 minutes, respectively. Plots of the nickel grades and recoveries are shown in Figure 93. The nickel grade decreased from about 9.2% at a processing time of 5 minutes to 7.2% at 8.75 minutes. The nickel grade then increased back to about 9.2% at a processing time of 12 minutes. This downward parabolic curve trend was not expected and may be attributed to the variability microwave processing. These results were different than the tests performed in air (Figure 71), because for those tests the nickel grade increased from a value of about
1.5% to a maximum of 3.8% before decreasing to 2.8%. Of particular importance is the fact the tests in air were done at 1100 W and magnetically separated with the DTT, whereas the tests in argon were done at 900 W and magnetically separated with the WHIMS. The amount of oxidation of the sample was limited in the argon atmosphere thereby preventing the sample from being reoxidized after the reduction process, which resulted in a higher nickel grade. The nickel recovery started off low at about 43.8% at 5 minutes which decreased to 37.6% before it reached a maximum of 88.8% at 12 minutes. A processing time of 12 minutes resulted in the best nickel grade and nickel recovery values of 9.2% and 88.8%, respectively.

Figure 93: Effect of processing time on nickel grade and recovery in an argon atmosphere at 101 kPa for a microwave power of 900 W, 6% charcoal addition, 30 g sample size, -100 mesh particle size, with HG ore and separated with WHIMS at 1A.
SEM analysis was performed on the sample that was reduced in the argon atmosphere for a time of five minutes. An image of a section of the sample is provided in Figure 94. The two phases numbered as 1 and 2 correspond to the spot scans provided in Figure 95 and Figure 96, respectively. Spot 1 is interpreted to consist of fayalite, due to the high peaks of iron and silicon, whereas spot 2 contains peaks of magnesium and silicon as well as iron. This phase is expected to be magnesium silicate.

Figure 94: SEM analysis of the magnetic concentrate for a reduction test in an argon atmosphere. Parameters were a microwave power of 900 W, processing time of 5 minutes, and 6% charcoal addition using the HG ore. The reduced sample was magnetically separated with the WHIMS at 1A.
Figure 95: Spot 1 of SEM analysis showing the presence of fayalite.

Figure 96: Spot 2 of SEM analysis showing the presence of a magnesium silicate phase.
5.8 Effect of Charcoal

Three different amounts of activated charcoal were used in this research, corresponding to either 3, 6 and 9% charcoal present in the briquetted sample. Most of the tests were run with a charcoal addition of 6%. Since charcoal has a higher permittivity value compared to that of nickeliferous silicate laterite ore, it was expected that the absorbed microwave power would increase as the amount of charcoal in the sample was increased. Preliminary testing involved the addition of varying amounts of charcoal in a 30 g sample of nickel laterite, where the following amounts of charcoal were used: 6, 18, 21 and 24%. A trend of the data is shown in Figure 97, where it was perceived that the absorbed microwave power increased rapidly for the samples that reacted.

![Figure 97: Absorbed microwave power versus time for 30 g samples with varying charcoal additions at a power setting of 1000 W, and a processing time of 15 minutes.](image-url)
The corresponding nickel grades and recoveries are plotted against the charcoal addition in Figure 98. These samples were magnetically separated with the DTT. As the charcoal content was increased from 6 to 18% the recovery decreased from 31.7 to 22.6% while the grade increased slightly from about 3.6 to 4.0%. The recovery increased from 18 to 21% charcoal addition while the grade decreased. For a charcoal addition of 24%, both the nickel grade and nickel recovery decreased. This data can be compared to the absorbed microwave power data above where it is seen that the test with 18% charcoal addition only achieved a maximum absorbed microwave power level of about 51% indicating that the sample did not fully react. This helps explain why the nickel grade and recovery values for this test were very low.

Figure 98: Nickel grade and nickel recovery versus charcoal addition for 30 g samples at 1000 W, and a processing time of 15 minutes, 101 kPa, -200 mesh particle size with HG ore.
The quantity of activated charcoal used and its corresponding effect on the amount of absorbed microwave power was investigated for several tests run at a reduced pressure. This series of tests included two sets of three samples containing a charcoal addition of 3, 6 and 9%, respectively. The first three tests were conducted at a pressure of 71 kPa and the next three were performed at 41 kPa. A power setting of 1000 W was used for all six tests. The results of these tests are shown in Figure 99 and Figure 100. Analyzing these two graphs, it is evident that a charcoal addition of 3% was not effective as the sample did not readily absorb microwaves once the free water has been removed from the sample. Instead, the absorbed microwave power rapidly decreased and did not show a dramatic increase in value like the other tests.

The addition of 6% charcoal yielded a curve that is described in four stages. Firstly, the absorbed microwave power decreased rapidly as a result of the free water being removed from the sample. The second stage corresponded to the increase of absorbed microwave power which may be attributed to the combustion of the charcoal within the briquette as this material is a very good microwave absorber. The charcoal reduced the hematite present in the nickel laterite to produce magnetite, which is also a very good microwave absorber due to its magnetic properties. The third stage of the reduction test occurred once the critical temperature of the sample was reached. Eventually, the carbon was all used up and either the compound wüstite or iron was formed (not good microwave absorbers). The quantity of microwave power being absorbed by the sample decreased then leveled off which is seen as the fourth stage of the curve. The tests performed with 6% and 9% charcoal conducted at a pressure of 71 kPa resulted in smoother curves compared to the tests at a reduced pressure of 41 kPa under the same conditions. Increasing
the charcoal addition from 6% charcoal to 9% charcoal decreased the time required to transition from the first stage of processing to the second stage. For an operating pressure of 71 kPa, the critical temperature (which occurred at the beginning of the third stage) for 6% charcoal was about 130 s and 80 s for 9% charcoal addition.

![Graph showing absorbed microwave power vs. time for different charcoal concentrations](image)

**Figure 99:** Effect of activated charcoal on the absorbed microwave power at a power of 1000 W and a pressure of 71 kPa.

In Figure 100 however, the test with 6% charcoal did not experience the same behaviour as in Figure 99. Once all of the free water was removed from the sample, the second stage of heating did not result in a rapid increase in absorbed microwave power as was expected. Instead, there was a gradual increase from a time of about 43 to 186 seconds which are the times corresponding to the minimum and maximum absorbed microwave powers respectively. Worth mentioning, was that at a lower operating pressure of 41 kPa
with a 9% charcoal addition, the absorbed microwave power leveled off shortly after reaching its maximum. This was different than the test performed at a pressure of 71 kPa which quickly decreased after achieving its maximum absorbed microwave power.

![Graph showing absorbed microwave power over time for 3%, 6%, and 9% charcoal additions.]

**Figure 100:** Effect of activated charcoal on the absorbed microwave power at a power of 1000 W and a pressure of 41 kPa.

Two XRD plots in Figure 101 and Figure 102 compare two of the initial reduction tests, where the magnetic concentrates of the samples were analyzed. Both plots showed the presence of cristobalite (SiO$_2$) and magnetite (Fe$_3$O$_4$). The XRD plot in Figure 101 contains a magnesium silicate slag phase known as enstatite (MgSiO$_3$), and the sample presented in Figure 102 contains magnesium iron catena-silicate (clinoenstatite, Mg$_{0.54}$Fe$_{0.46}$SiO$_3$). The significance of the species magnetite in the magnetic concentrate is that it suggests that the reacted laterite sample has reoxidized from wüüstite, FeO after...
processing. For both tests, there exists a mineralogical phase which may be regarded as kamacite, a ferronickel species which has an Fe:Ni ratio between that of 90:10 to 95:5. A second ferronickel species that has been reported to occur in the literature is taenite, which has an Fe:Ni ratio between 80:20 and 35:65. This is imperative, because it is not thermodynamically possible to produce pure nickel by itself as a quantity of iron will come along with it (Canterford and Turnbull, 1980; Utigard and Bergman, 1992; Li, 1999).

Figure 101: XRD plot of the magnetic concentrate of a high grade nickel laterite ore sample processed at a power of 1000 W, time of 15 minutes and charcoal addition of 21%.
Figure 102: XRD plot for the magnetic concentrate of a high grade nickel laterite ore sample processed at a power of 1000 W, time of 15 minutes and charcoal addition of 6%.

5.9 Effect of Sulphur

Sulphur was added via a small quantity of pyrite, FeS$_2$ in the amounts of either 2% or 4% to the nickel laterite ore and activated charcoal and mechanically mixed to produce a mixture of the three materials. The effects of pyrite addition were analyzed by examining several data sets. Firstly, TGA/DTA was performed on samples with and without pyrite to determine its effect on the mass loss and also the heats of reaction of the process. This was shown in Figure 56 in section 5.2. Next, it was possible to compare the quantity of sulphur remaining in the processed sample with a carbon-sulphur determinator. An analysis of the absorbed microwave power versus time plots was necessary to effectively determine how the addition of pyrite changed the process. It was possible to analyze the mineralogical
phases present in the processed material using XRD and SEM analysis. Lastly, the nickel grade and nickel recovery data was compared.

Table 18 shows the data from the carbon and sulphur determinator analysis. For test NVS6, while 73% of the sulphur was used, only 81.8% of the carbon was. However, for the two tests at 101 kPa (NVS5 and NVS7), over 95% of the carbon reacted. The amount of sulphur present in sample NVS6 was twice that for samples NVS5 and SSV7. For the samples processed under the same conditions, with the exception of the reduced pressure the same observation did not apply. Less sulphur reacted for the samples with 6% charcoal, but more sulphur reacted for the samples processed with a charcoal addition of 9%. This may be attributed to the fact that as more charcoal was added, there was a greater proportion of charcoal compared to that of the pyrite in the briquette. Upon heating, the carbon in the sample was heated where almost all of it had reacted, leaving behind a larger fraction of sulphur which had not reacted.

Table 18: Carbon and sulphur determinator data for selected processed samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (mg)</th>
<th>FeS₂ (%)</th>
<th>Initial Amount (%)</th>
<th>Final Amount (%)</th>
<th>Amount Reacted (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sulphur</td>
<td>Charcoal</td>
<td>Sulphur</td>
</tr>
<tr>
<td>NVS5</td>
<td>88.2</td>
<td>2</td>
<td>1.07</td>
<td>6</td>
<td>0.5097</td>
</tr>
<tr>
<td>NVS6</td>
<td>91.4</td>
<td>4</td>
<td>2.14</td>
<td>6</td>
<td>0.5778</td>
</tr>
<tr>
<td>NVS7</td>
<td>96.2</td>
<td>2</td>
<td>1.07</td>
<td>9</td>
<td>1.0158</td>
</tr>
<tr>
<td>MVRPS1</td>
<td>128.9</td>
<td>2</td>
<td>1.07</td>
<td>6</td>
<td>0.8198</td>
</tr>
<tr>
<td>MVRPS2</td>
<td>88.6</td>
<td>4</td>
<td>2.14</td>
<td>6</td>
<td>1.5405</td>
</tr>
<tr>
<td>MVRPS5</td>
<td>117.2</td>
<td>2</td>
<td>1.07</td>
<td>6</td>
<td>0.7501</td>
</tr>
<tr>
<td>MVRPS6</td>
<td>101.6</td>
<td>4</td>
<td>2.14</td>
<td>6</td>
<td>1.612</td>
</tr>
<tr>
<td>MVRPS7</td>
<td>82.9</td>
<td>2</td>
<td>1.07</td>
<td>9</td>
<td>0.9748</td>
</tr>
</tbody>
</table>

The absorbed microwave power data may be studied to determine if the addition of pyrite to the nickel laterite ore helped improve the amount of absorbed microwave power.
Figure 103 shows the absorbed microwave power data for samples containing 6% charcoal that were processed at a pressure of 11 kPa and a time of 10 minutes. At this pressure and charcoal content, it was possible to conclude that at 1000 W there was a negligible difference in absorbed microwave power for the water removal stage and the time to reach the critical temperature of the sample. However, towards the end of the test, there was a noticeable difference. At a processing time of about 500 seconds, the test with 2% pyrite steadily increased reaching a maximum of 93.8% while the test at 4% pyrite decreased until the end of the test. For the 1200 W tests, there was a significant improvement in the absorbed microwave power when the pyrite content was increased from 2 to 4%. The reaction occurred at an earlier time where the rapid increase in absorbed microwave power started at a time of 156 seconds compared to 282 seconds for the sample with only 2% pyrite. The maximum absorbed microwave power values for 2% and 4% were 91.7% and 90.6%, respectively. Figure 104 illustrates the visual difference between a sample tested at 101 kPa and a sample tested under the same process parameters with the exception of the pressure, which was 11 kPa. The parameters for these two tests were a processing time of 10 minutes, power setting of 1200 W, with a charcoal addition of 6% and a pyrite addition of 2%. The respective pressures were 101 kPa (NVS5) and 11 kPa (MVRPS5). Sample NVS5 was greenish in colour compared to sample MVRPS5 which was dark grey in colour. The temperature of NVS5 was measured immediately after the reduction test was finished and the maximum recorded temperature was 1319°C, indicating that the sample was smelted. However, as seen in Figure 105, the ferronickel phase kamacite was still formed.
Figure 103: Effect of pyrite addition on absorbed microwave power at 11 kPa and 6% charcoal.

Figure 104: Processed samples (101 kPa (left) versus 11 kPa (right)) with 6% charcoal addition and 2% pyrite addition.

The mineralogical phases present in the tests NVS5 and MVRPS5 are presented in Figure 105 and Figure 106. Both tests NVS5 and MVRPS5 contained three of the same phases: corundum, cristobalite and pigeonite. They differed with regards to their iron containing phases, where NVS5 contained kamacite but MVRPS5 contained iron and
wüstite. It was originally thought that a lower operating system pressure would result in a better reducing atmosphere due to the reduced partial pressure of oxygen. Perhaps the higher microwave power of 1200 W was not as effective compared to a lower power at a reduced pressure.

Figure 105: XRD analysis of NVS5 showing the presence of kamacite.
Figure 106: XRD analysis of MVRPS5 showing the presence of wüstite and iron.

Figure 107 is an optical microscope image of a ferronickel bead. This bead is from the sample MVRPS4, which was processed at a power level of 1000 W, time of 10 minutes, pressure of 11 kPa, and charcoal and pyrite additions of 9% and 4%, respectively. SEM analysis was conducted to effectively determine the distribution of the elements Si, S, Co, Ni, Fe and Mg for a section of this bead (depicted in Figure 108). The corresponding elemental mapping images are provided in Figure 109. The iron and nickel are closely associated with one another as expected because they form a ferronickel alloy bead predominantly composed of nickel and iron. Next, the cobalt elemental map is closely associated with the ferronickel. The magnesium is uniformly distributed throughout the sample. The sulphur corresponds to the light greyish phase in Figure 108, and is located
between the ferronickel particles throughout the sample. It is associated with iron as an iron sulphide phase, FeS. Lastly, is the silicon phase which is represented by the dark grey circles in Figure 108. This is confirmed by the elemental map in Figure 109. The silicon is expected to be associated with the magnesium and iron to form the two mineralogical species, forsterite and fayalite, respectively.

Figure 107: Micrograph of a FeNi bead at 200x magnification for sample processed at 1000 W, 10 minutes, pressure of 11 kPa, with charcoal and pyrite additions of 9% and 4%, respectively.
Figure 108: SEM image of sample MVRPS4. FeNi is labelled as 1, magnesium silicate slag phase as 2, and iron sulphide phase as 3.

Figure 109: SEM elemental maps of Si, S, Co, Ni, Fe, and Mg for sample MVRPS4.
SEM was performed on two other samples, NVS5 and MVRPS5. For sample NVS5, two sections (which were removed from the reacted sample) were analyzed. The SEM images for NVS5 are in Figure 110. The first (A) was a ferronickel bead which could be compared to the ferronickel bead from sample MVRPS4. There exists the presence of a ferronickel phase and a sulphur phase, but no clear silicon phases are seen in this section of sample NVS5. The second piece (B) is a slag which was expected to contain high concentrations of magnesium and silicon as the phases cristobalite and pigeonite were reported in the XRD analysis for this sample. The bright circular dots represent ferronickel particles and the dark background was interpreted to comprise of higher concentrations of magnesium, silica and alumina. The slag from sample MVRPS5 was analyzed in order to compare to the slag in sample NVS5. Figure 111 is the SEM image for this sample. MVRPS5 is similar to that of NVS5 as it contains trace amounts of ferronickel. However, what MVRPS5 does not have is the third phase that sample NVS5 has. This is interpreted to be the mineralogical phase forsterite as it is greenish in colour, whereas MVRPS5 is dark in colour (Figure 104).

![Figure 110: SEM images of NVS5. Image A shows a section of the ferronickel bead and image B is a section of the slag phase.](image-url)
Figure 111: SEM image of slag from MVRPS5 containing a small concentration of ferronickel.

5.9.1 Grade versus Recovery Data for a Pressure of 101 kPa

Four sets of tests with pyrite added to the nickel laterite ore were conducted. The first set of tests was done at a power level of 800 W with 6% charcoal and the second set of tests was done at 800 W but with 9% charcoal. The third set of tests was performed at 1100 W with 6% charcoal and the fourth set of tests used a power level of 1000 W with 9% charcoal. For all of the tests, the amount of pyrite used was either 0, 2 or 4% (6% was also used for third set). All of the reacted samples were quenched in a beaker containing 250 mL of water (at room temperature) immediately after processing. The pulverized samples were then magnetically separated using the WHIMS at a setting of 1A. The grade and recovery results for these tests are in Figure 112, Figure 113 and Figure 114, respectively.

Figure 112 shows the nickel grade and recovery values for the first two sets of tests. At an operating microwave power of 800 W, a lower charcoal addition of 6% was favoured over an addition of 9% as this amount yielded higher nickel grades. At a charcoal addition
of 6%, when pyrite was added, the nickel increased from 3.4% (no pyrite) to 5.7% (2% pyrite) and 5.8% (4% pyrite). The nickel recovery remained relatively constant. At 9% charcoal addition, the nickel grade remained relatively constant while the recovery first decreased when 2% pyrite was added then increased when 4% pyrite was used.

The results for the third set of tests (Figure 113) show that at a pyrite addition of 4%, a nickel grade of about 5.0% and nickel recovery of 62% may be obtained. These values are superior to those above which is understood by the increase in microwave power from 800 W to 1100 W. Increasing the quantity of pyrite from 0 to 4% resulted in an increase in both the nickel grade and nickel recovery. However, increasing the pyrite amount from 4 to 6% resulted in a decrease in the nickel grade and recovery.
Figure 113: Effect of pyrite addition on nickel grade and recovery for processing times of 10 minutes, a power of 1100 W, pressure of 101 kPa, 6% charcoal addition, 30 g sample size, -200 mesh particle size, with HG ore.

The fourth set of tests used 9% charcoal and a power of 1000 W. It was confirmed that a pyrite addition of 4% yielded the highest nickel grade at 5.2%. The nickel grade when no pyrite was used was 2.46%. An increase of pyrite from 0 to 2% content did not affect the nickel grade which was 2.45% at 2% pyrite. When no pyrite was used, the nickel recovery was 37.7% which was similar to 4% pyrite, which yielded a recovery of 39.2%.
Figure 114: Effect of pyrite addition on nickel grade and recovery for processing times of 10 minutes, a power of 1000 W, 101 kPa, 9% charcoal, 30 g sample, -200 mesh particle size, with HG ore.

5.9.2 Grade versus Recovery Data for a Pressure of 11 kPa

Four reduction tests were performed at a reduced pressure of 11 kPa for a time of 10 minutes. The high grade nickel laterite ore was used and the particle size was -200 mesh with a sample size of 30 g. The WHIMS was used for magnetic separation at 1A. The grade and recovery values are shown in Table 19. Pyrite was added at either 2% or 4%, charcoal at 6% or 9% and a power of 1000 W was used for the first test while a power

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Microwave Power (W)</th>
<th>Charcoal (%)</th>
<th>Pyrite (%)</th>
<th>Metal Grade (%)</th>
<th>Metal Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>MVRPS3</td>
<td>1000</td>
<td>9</td>
<td>2</td>
<td>0.265</td>
<td>61.64</td>
</tr>
<tr>
<td>MVRPS5</td>
<td>1200</td>
<td>6</td>
<td>2</td>
<td>0.269</td>
<td>61.50</td>
</tr>
<tr>
<td>MVRPS6</td>
<td>1200</td>
<td>6</td>
<td>4</td>
<td>0.270</td>
<td>65.00</td>
</tr>
<tr>
<td>MVRPS7</td>
<td>1200</td>
<td>9</td>
<td>2</td>
<td>0.108</td>
<td>29.44</td>
</tr>
</tbody>
</table>
of 1200 W was used for the last three tests. This way it was possible to compare the effects of pyrite, charcoal, and power on the grades and recoveries of the magnetic material. The best nickel grade and recovery values occurred at a power of 1200 W, charcoal addition of 6% and pyrite addition of 4%, and were 8.1% and 62.6%, respectively (MVRPS6). Decreasing the pyrite to 2% while keeping the other variables constant resulted in a slight decrease in nickel grade to 7.96% and a noticeable decrease in the nickel recovery down to 47.7% (MVRPS5). The 3% increase in charcoal content going from sample MVRPS5 to MVRPS7 resulted in a decrease in nickel grade from 7.96 to 5.7% but a 10.9% increase in nickel recovery from 47.7 to 58.5%. The grade of iron was decreased by more than half while the cobalt grade decreased from 0.27 to 0.11%.

Thus, it can be concluded that the addition of pyrite from 2 to 4% was beneficial with regards to the improvement of the nickel recovery with very little effect on the nickel grade. However, the addition of charcoal resulted in a less desirable nickel grade with only a slight increase in nickel recovery. Samples MVRPS3 and MVRPS7 showed the effect of microwave power on the nickel grades and recoveries. For a charcoal content of 9% and a pyrite content of 2%, an increase in power from 1000 to 1200 W resulted in a very slight decrease in nickel grade and a very minor increase in nickel recovery. The metals cobalt and iron did not benefit from an increase in microwave power, as both the grade and recovery values of the cobalt and iron decreased with increasing microwave power. For a system operating at a reduced pressure, when pyrite was used, an increase in microwave power had an overall negative effect with 9% charcoal addition. A possible by-product when pyrite is used as a sulphation reagent is troilite, FeS. When this mineralogical species forms, there is a faster ferronickel particle accumulation as a result of the eutectic in the
Fe-FeS system (Li, et al., 2012). In addition, since troilite is nonmagnetic, less iron would be reported to the magnetic stream during magnetic separation, thus decreasing the recovery of iron in the concentrate (Jiang, et al., 2013). Established by the results in Table 19, a pyrite content of 4%, charcoal content of 6% and microwave power of 1000 W would be expected to produce the best results for future tests.

5.10 Effect of Sample Mass

Ma and Pickles (2002) found that briquettes with smaller sample masses had a shorter height and greater heat losses. The internal temperatures of the samples were found to be lower resulting in a lower nickel recovery. Hence, for this work, the majority of the samples were 30 g in mass. Preliminary testing used a smaller mass of 10 g to investigate the effects it had on the absorbed microwave power. It is worth mentioning that samples with a lower surface area to volume ratio should reduce the heat loss of the sample. As seen in Figure 115 (smoothed data), the absorbed microwave power was very low for tests weighing only 10 g. These three tests were conducted without the use of alumina powder.

Five reduction tests were performed at a pressure of 11 kPa to examine the effect of charcoal addition on a 10 g sample with a power level of 1000 W. No alumina powder was used for these reduction tests. The absorbed microwave power data as a function of processing time is shown in Figure 116. As with the results at 101 kPa, it is understood by the absorbed microwave data that a sample mass of 10 g is not large enough for the sample to react under microwave irradiation. Hence, a much larger sample mass of 30 g (with alumina powder around the sample) was used for the remainder of the reduction tests carried out in this work.
Figure 115: Absorbed microwave power versus time for 10 g samples processed at 101 kPa for 15 minutes with 6% charcoal at different power settings.

Figure 116: Absorbed microwave power versus time for 10 g samples processed at 11 kPa for 15 minutes at 1000 W for different charcoal additions.
5.11 Effect of Magnetic Field Intensity

Two types of magnetic separators were used for this research. The first, the Davis Tube Tester (DTT), had a fixed magnetic field intensity at a value of about 4500 Gauss. The WHIMS however, had an adjustment knob allowing the magnetic field intensity to be varied. A series of tests were performed to calibrate the WHIMS to determine the approximate range corresponding to the highest grades and recoveries achieved. The following is plotted in Figure 117. As seen below, the best setting is 1A which yielded a nickel grade and recovery of 17.9% and 52.3%, respectively. A value of 0.5A produced a grade of 17.8% but only a recovery of 45.1%. Increasing the magnetic field intensity decreased the nickel grade to 9.6% and 7.1% for 2A and 3A, respectively. The nickel recovery also demonstrated a decreasing trend where it went from 52.3% at 1A to values of 40.4% and 14.8% at 2A and 3A, respectively. Therefore, a setting of 1A was used for the majority of the tests in this thesis.
Figure 117: Effect of WHIMS setting on the nickel grade and nickel recovery. The process parameters were a time of 10 minutes, power of 900 W, pressure of 11 kPa, 6% charcoal, 30 g sample mass, -200 mesh particle size with LG ore.
5.12 Effect of Dehydration

A series of tests was conducted with the free water removed from the nickel laterite ore prior to testing. This was done by weighing out 1 kg of both the high and low grade ores. The two 1 kg samples were placed in a drying oven for 24 hours at a temperature of 150°C to remove the free water. The high grade material had a mass loss of about 23.5% and the low grade ore experienced a mass loss of about 19.6%. The samples were very close in composition where the majority of the tests made use of the high grade ore. However, tests were conducted on both ores involving the removal of free water to determine its effect on microwave processing.

In conventional nickel laterite processing, the free water is removed prior to reduction roasting. However, in microwave heating, free water is known to improve the heating of the material as it increases its dielectric properties. A series of tests was performed on a blend of dehydrated (as described above) high grade and low grade laterite ore (50:50) ratio. The process parameters included a power of 1100 W, a sample size of 30 g, and 6% charcoal addition. The absorbed microwave power versus time plot is shown in Figure 118. It is apparent that the data is more variable for the dehydrated ore compared to that of the hydrated (shown previously in thesis). This could be attributed to the fact that without the free water increasing the dielectric properties of the ore, the microwave irradiation affects the ore differently. There is no initial loss of free water from the sample either.
Figure 118: Absorbed microwave power for nickel laterite ore dehydrated at 150°C. Process parameters were a power of 1100 W, sample mass of 30 g and 6% charcoal addition.
Chapter 6

Conclusions and Recommendations

6.1 Conclusions

MVRP of a nickeliferous silicate laterite ore was performed in numerous laboratory tests which investigated the effects of the following input variables: processing time, microwave power, system pressure, use of argon as an inert gas, charcoal addition, pyrite addition, sample mass, dewatering of the sample and magnetic field intensity. The optimum conditions were determined to be a processing time of 5 minutes, microwave power of 1100 W, pressure of 11 kPa, 6% charcoal addition, 30 g sample size and magnetic separation using the WHIMS at 1A. These variables produced a high grade magnetic concentrate which contained 21% nickel with a corresponding recovery of 69.58%. This corresponds to an energy consumption of about 3250.6 kWh/tonne ore.

When sulphur was added to a sample in the form of pyrite, less microwave energy was used to achieve a higher maximum temperature than a sample without pyrite. This was likely due to the improved microwave absorption of the sample when pyrite was added to it. For example, one test run in air at 101 kPa with 6% charcoal addition used 900 kJ of energy and reached a maximum temperature of 642°C, whereas a second test under the same conditions, with 2% pyrite added achieved a temperature of 1060°C while only using 480 kJ of microwave energy. In addition to this, the use of a vacuum atmosphere enhanced the nickel grade and recovery values for the pyrite tests. This provides further support regarding the proposed reduction mechanism associated with the use of vacuum atmosphere, which is that a lower system pressure will yield higher nickel grade and
recovery values due to the reduced partial pressure of oxygen, increased rate of reaction, and the lower required reaction temperature.

The use of an argon atmosphere also reduced the partial pressure of oxygen in the system and resulted in high nickel grades of 7.16 to 9.24%, with moderate to high nickel recovery values of 37.64 to 88.77%. Although the results in the argon atmosphere were satisfactory, with the vacuum system, the speed of the reaction was increased and the reduction temperature was also lowered, making it a more favourable process.

For the tests performed in air, a processing time greater than 10 minutes was found to be detrimental to the nickel recovery. A series of tests was performed at a pressure of 41 kPa and a charcoal content of 6%. At a low power level of 800 W, increasing the processing time from 5 to 10 minutes had a significant effect on the nickel grade which increased from 2.0 to 3.4%, and also the nickel recovery, which increased from 10.7 to 94.5%. However, for a higher power level of 1000 W at the same conditions, there was a very small change in nickel grade (2.6 to 2.7%) and nickel recovery (55.8 to 61.0%).

When 9% charcoal addition was used, the absorbed microwave power achieved the critical temperature before the tests that used 6% charcoal addition. This was attributed to the fact that when more charcoal was mixed with the sample, there was an increase in the dielectric properties of the material thus leading to a greater amount of absorbed microwave power versus time and thus a faster rate of reaction of the nickel laterite briquette.

Three mineralogical species to consider that were revealed by XRD analysis on several of the magnetic concentrates are: magnetite, pigeonite/enstatite, and kamacite. The presence of magnetite indicated that the reduced sample was oxidized either during
microwave processing (overheating from a long processing time) or once the sample was removed from the applicator (exposed to air). Pigeonite/enstatite are slag phases in the nickel laterite ore, which are undesirable phases. The presence of kamacite was expected for most of the magnetic concentrates as this is the desirable ferronickel phase. For the vacuum tests with very high nickel grades, the ferronickel phase taenite was formed and recovered via grinding followed by magnetic separation.

6.2 Recommendations

The following are recommendations for advancing this area of research:

(1) The development of a thermodynamic model in order to determine the optimum process parameters at equilibrium: temperature, pressure, charcoal addition and pyrite addition.

(2) Temperature measurements of the sample with respect to time would allow the researcher to understand the time at which certain reactions occur during the reduction process.

(3) Measuring the mass loss versus time would be beneficial as this would allow the researcher to determine the reaction kinetics of the microwave vacuum reduction process when using charcoal or charcoal plus a sulphation agent.

(4) The investigation of microwave pulsing in a vacuum atmosphere, as this would decrease the amount of energy required and might help prevent overheating of the sample from occurring.
(5) The investigation of different additives and sulphation agents. Possible additives are CaF₂ and CaO. Sulphation agents include Na₂SO₄, CaSO₄, and elemental sulphur.

(6) The use of different laterite ores (limonitic and magnesium-hydrous silicate) would be useful as a comparison to the clay silicate nickel laterite ore data.

(7) The measurement of the dielectric properties of the nickel laterite ore when pyrite is added in various amounts (2, 4 and 6%).

(8) An economic analysis of the microwave vacuum carbothermic reduction and sulphidation process should be conducted to determine the feasibility of this research.

(9) If the process is economically feasible, pilot plant test work should be conducted in the future. Instead of using a batch process as done in the laboratory in this thesis, a continuous process would be utilized.
References


Li, Q. et al., 2010. Study on Selective Reduction and Magnetic Separation of Low-Grade Nickel Laterite Ore to Produce High Nickel Concentrate. *XXV International Mineral Processing Congress*, pp. 1549-1556.


Luo, Q., 2012. *Low-grade Nickel Laterite Vacuum Carbothermal Reduction Mechanism and Experimental Studies*, Kunming, P.R. China: Kunming University of Science and Technology.


Nickel Institute, 2014. *Where and Why Nickel is Used*. [Online] Available at:


Appendix A
DTT Experimental Data

Table 20: Effect of microwave power on grade and recovery for a processing time of 15 minutes, 6% charcoal addition, 30 g sample size, -100 mesh particle size, pressure of 101 kPa with HG ore.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>1000</td>
<td>0.12</td>
<td>48.00</td>
</tr>
<tr>
<td>1100</td>
<td>0.09</td>
<td>23.54</td>
</tr>
<tr>
<td>1200</td>
<td>0.09</td>
<td>38.00</td>
</tr>
<tr>
<td>1300</td>
<td>0.10</td>
<td>52.00</td>
</tr>
<tr>
<td>1400</td>
<td>0.07</td>
<td>43.00</td>
</tr>
<tr>
<td>1500</td>
<td>0.07</td>
<td>41.00</td>
</tr>
</tbody>
</table>

Table 21: Effect of microwave power on grade and recovery for a processing time of 5 minutes, 6% charcoal addition, 30 g sample size, -100 mesh particle size, pressure of 71 kPa with HG ore.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>800</td>
<td>0.08</td>
<td>49.00</td>
</tr>
<tr>
<td>1000</td>
<td>0.11</td>
<td>26.98</td>
</tr>
<tr>
<td>1200</td>
<td>0.16</td>
<td>26.32</td>
</tr>
</tbody>
</table>

Table 22: Effect of charcoal addition on grade and recovery for a processing time of 15 minutes, 1000 W microwave power, 30 g sample size, -100 mesh particle size, pressure of 101 kPa with HG ore.

<table>
<thead>
<tr>
<th>Charcoal (%)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>6</td>
<td>0.13</td>
<td>38.00</td>
</tr>
<tr>
<td>18</td>
<td>0.19</td>
<td>42.00</td>
</tr>
<tr>
<td>21</td>
<td>0.18</td>
<td>47.00</td>
</tr>
<tr>
<td>24</td>
<td>0.12</td>
<td>49.00</td>
</tr>
</tbody>
</table>
Table 23: Effect of processing time on grade and recovery for 6% charcoal addition, 1000 W microwave power, 30 g sample size, -100 mesh particle size, pressure of 101 kPa with HG ore.

<table>
<thead>
<tr>
<th>Processing Time (min)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>7</td>
<td>0.06</td>
<td>23.11</td>
</tr>
<tr>
<td>9</td>
<td>0.12</td>
<td>21.30</td>
</tr>
<tr>
<td>10</td>
<td>0.13</td>
<td>20.90</td>
</tr>
<tr>
<td>10.5</td>
<td>0.10</td>
<td>37.39</td>
</tr>
<tr>
<td>11</td>
<td>0.09</td>
<td>30.22</td>
</tr>
</tbody>
</table>
Appendix B

WHIMS Experimental Data

Table 24: Effect of microwave power on nickel grade and recovery for a processing time of 10 minutes, 6% charcoal addition, 30 g sample size, -100 mesh particle size, pressure of 101 kPa with LG ore.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>800</td>
<td>0.06</td>
<td>44.11</td>
</tr>
<tr>
<td>900</td>
<td>0.09</td>
<td>27.96</td>
</tr>
<tr>
<td>1000</td>
<td>0.20</td>
<td>30.38</td>
</tr>
<tr>
<td>1100</td>
<td>0.23</td>
<td>38.25</td>
</tr>
<tr>
<td>1200</td>
<td>0.24</td>
<td>42.32</td>
</tr>
</tbody>
</table>

Table 25: Effect of microwave power on nickel grade and recovery for a processing time of 10 minutes, 6% charcoal addition, 2% pyrite, 30 g sample size, -100 mesh particle size, pressure of 101 kPa with HG ore.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>800</td>
<td>0.25</td>
<td>46.49</td>
</tr>
<tr>
<td>1000</td>
<td>0.19</td>
<td>60.40</td>
</tr>
<tr>
<td>1100</td>
<td>0.20</td>
<td>32.53</td>
</tr>
<tr>
<td>1200</td>
<td>0.222</td>
<td>76.4</td>
</tr>
</tbody>
</table>

Table 26: Effect of microwave power on nickel grade and recovery for a processing time of 10 minutes, 9% charcoal addition, 2% pyrite, 30 g sample size, -200 mesh particle size, pressure of 101 kPa with HG ore.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>800</td>
<td>0.30</td>
<td>86.92</td>
</tr>
<tr>
<td>1000</td>
<td>0.29</td>
<td>73.52</td>
</tr>
<tr>
<td>1200</td>
<td>0.26</td>
<td>54.77</td>
</tr>
</tbody>
</table>
Table 27: Effect of microwave power on grade and recovery for a processing time of 10 minutes, 9% charcoal addition, 4% pyrite, 30 g sample size, -200 mesh particle size, pressure of 101 kPa with HG ore.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>800</td>
<td>0.34</td>
<td>95.00</td>
</tr>
<tr>
<td>1000</td>
<td>0.16</td>
<td>76.00</td>
</tr>
<tr>
<td>1200</td>
<td>0.27</td>
<td>62.97</td>
</tr>
</tbody>
</table>

Table 28: Effect of pyrite addition on grade and recovery for a processing time of 10 minutes, 6% charcoal addition, 800 W microwave power, 30 g sample size, -200 mesh particle size, pressure of 101 kPa with HG ore.

<table>
<thead>
<tr>
<th>Pyrite (%)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>0</td>
<td>0.06</td>
<td>44.11</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>46.49</td>
</tr>
<tr>
<td>4</td>
<td>0.33</td>
<td>95.74</td>
</tr>
</tbody>
</table>

Table 29: Effect of pyrite addition on grade and recovery for a processing time of 10 minutes, 9% charcoal addition, 800 W microwave power, 30 g sample size, -200 mesh particle size, pressure of 101 kPa with HG ore.

<table>
<thead>
<tr>
<th>Pyrite (%)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>0</td>
<td>0.30</td>
<td>86.92</td>
</tr>
<tr>
<td>2</td>
<td>0.34</td>
<td>95.00</td>
</tr>
<tr>
<td>4</td>
<td>0.09</td>
<td>19.15</td>
</tr>
</tbody>
</table>
Table 30: Effect of pyrite addition on grade and recovery for a processing time of 10 minutes, power of 1100 W, 101 kPa, 6% charcoal, 30 g sample, -200 mesh particle size, with HG ore.

<table>
<thead>
<tr>
<th>Pyrite (%)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>0</td>
<td>0.20</td>
<td>32.53</td>
</tr>
<tr>
<td>2</td>
<td>0.31</td>
<td>88.97</td>
</tr>
<tr>
<td>4</td>
<td>0.26</td>
<td>52.50</td>
</tr>
<tr>
<td>6</td>
<td>0.23</td>
<td>38.25</td>
</tr>
</tbody>
</table>

Table 31: Effect of pyrite addition on grade and recovery for processing times of 10 minutes, power of 1000 W, 101 kPa, 9% charcoal, 30 g sample, -200 mesh particle size, with HG ore.

<table>
<thead>
<tr>
<th>Pyrite (%)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>0</td>
<td>0.16</td>
<td>24.55</td>
</tr>
<tr>
<td>2</td>
<td>0.29</td>
<td>73.52</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>76.00</td>
</tr>
</tbody>
</table>

Table 32: Effect of processing time on nickel grade and recovery for a power of 900 W, argon atmosphere at 101 kPa, 6% charcoal, 30 g sample, -200 mesh particle size, with LG ore.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Processing Time (min.)</th>
<th>Ni Grade (%)</th>
<th>Ni Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR1</td>
<td>5</td>
<td>9.24</td>
<td>43.82</td>
</tr>
<tr>
<td>AR5</td>
<td>6.25</td>
<td>8.29</td>
<td>37.64</td>
</tr>
<tr>
<td>AR2</td>
<td>7.5</td>
<td>7.37</td>
<td>83.30</td>
</tr>
<tr>
<td>AR4</td>
<td>8.75</td>
<td>7.16</td>
<td>79.71</td>
</tr>
<tr>
<td>AR3</td>
<td>10</td>
<td>7.67</td>
<td>74.70</td>
</tr>
<tr>
<td>AR6</td>
<td>12.5</td>
<td>9.15</td>
<td>88.77</td>
</tr>
</tbody>
</table>

Table 33: Effect of pressure on grade and recovery for a processing time of 10 minutes, power of 1000 W, 6% charcoal, 30 g sample, -200 mesh particle size, with LG ore.

<table>
<thead>
<tr>
<th>Pressure (kPa)</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
</tr>
<tr>
<td>11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>41</td>
<td>0.14</td>
<td>21.43</td>
</tr>
<tr>
<td>101</td>
<td>0.20</td>
<td>30.38</td>
</tr>
</tbody>
</table>
Appendix C
Selected Cobalt and Iron Grade and Recovery Plots

Figure 119: Effect of microwave power on cobalt grade and recovery for a processing time of 15 minutes, 6% charcoal addition, 30 g sample size, -100 mesh particle size, pressure of 101 kPa with HG ore.
Figure 120: Effect of microwave power on iron grade and recovery for processing times of 15 minutes, 6% charcoal addition, 30 g sample size, -100 mesh particle size, pressure of 101 kPa with HG ore.
Appendix D
Magnetron Calibration

The percent absorbed microwave power (ABMP) was computed by calculating the difference between the forward and the reverse power and then dividing this value by the forward power according to the following equation:

\[
\text{ABMP} = \left( \frac{(FP - RP)}{FP} \right) \times 100\% \quad (34)
\]

The calibration data for the forward and reverse microwave power is presented in Table 34. Figure 121 provides the calibration curve for the forward power and Figure 122 provides the calibration curve for the reverse power. Detector crystals were used for this calibration.

Table 34: Calibration values for forward and reverse microwave power using detector crystals
(Gerling Applied Engineering, 2010).

<table>
<thead>
<tr>
<th>Waveguide Power (W)</th>
<th>Output Voltage (mVDC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Forward Power</td>
</tr>
<tr>
<td>40</td>
<td>-4</td>
</tr>
<tr>
<td>60</td>
<td>-5</td>
</tr>
<tr>
<td>80</td>
<td>-6</td>
</tr>
<tr>
<td>100</td>
<td>-8</td>
</tr>
<tr>
<td>200</td>
<td>-15</td>
</tr>
<tr>
<td>400</td>
<td>-30</td>
</tr>
<tr>
<td>600</td>
<td>-43</td>
</tr>
<tr>
<td>800</td>
<td>-57</td>
</tr>
<tr>
<td>1000</td>
<td>-69</td>
</tr>
<tr>
<td>2000</td>
<td>-123</td>
</tr>
<tr>
<td>4000</td>
<td>-208</td>
</tr>
<tr>
<td>6000</td>
<td>-277</td>
</tr>
</tbody>
</table>
Figure 121: Forward power calibration curve.

Figure 122: Reverse power calibration curve.
The calibration data for the magnetron is presented in Table 35 and the corresponding absorbed microwave power plots are shown in Figure 123. The microwave system was initially calibrated using a 200 mL sample of water at three power settings: 1000, 1100 and 1200 W. A beaker containing 200 mL of water was microwaved in the bottom centre of the applicator for 1 minute at the three different power settings. The efficiency of the system at the different power settings was calculated according to the equation:

\[
\text{Efficiency} = \frac{q}{\text{TM}} \quad (35)
\]

Where:

\[
\begin{align*}
q &= \text{Amount of heat lost or gained (J)} \\
\text{TM} &= \text{Theoretical maximum of energy produced (J)}
\end{align*}
\]

The value q is computed according to the equation:

\[
q = mc\Delta T \quad (36)
\]

Where:

\[
\begin{align*}
m &= \text{mass of object heated (g)} \\
c &= \text{specific heat capacity of water (J/g°C)} \\
\Delta T &= \text{change in temperature (°C)}
\end{align*}
\]

Table 35: Table of data for calibrating the microwave unit. The mass of the sample was 200 g with a processing time of 1 minute.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Theoretical Max. (J)</th>
<th>T₁ (°C)</th>
<th>T₂ (°C)</th>
<th>ΔT</th>
<th>c (J/g°C)</th>
<th>q (J)</th>
<th>Eff. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>60000</td>
<td>22.5</td>
<td>83.1</td>
<td>60.6</td>
<td>4.18</td>
<td>50661.6</td>
<td>84.44</td>
</tr>
<tr>
<td>1100</td>
<td>66000</td>
<td>23.1</td>
<td>93.2</td>
<td>70.1</td>
<td>4.18</td>
<td>58603.6</td>
<td>88.79</td>
</tr>
<tr>
<td>1200</td>
<td>72000</td>
<td>22.3</td>
<td>84.5</td>
<td>62.2</td>
<td>4.18</td>
<td>51999.2</td>
<td>72.22</td>
</tr>
</tbody>
</table>
Figure 123: Absorbed microwave power versus time for the water calibration tests.

To test the variability of the reduction tests, an experiment was repeated several times where the sample’s parameters were held constant. The series of tests that were performed to fulfill this requirement used a 30 g sample with a charcoal addition of 6%. Two typical absorbed microwave power versus time tests conducted are plotted in Figure 124. These tests were performed with a 50:50 blend of high grade ore and low grade ore. The test highlighted by the red curve was surrounded by 30 g of alumina powder. It is seen that for this test there was a sharp increase in the absorbed microwave power at a time of about 200 seconds. The other sample did not start to react until a time of about 375
202 seconds. This suggests that when alumina powder was not used, the sample was not insulated as well and did not heat as efficiently.

Figure 124: Absorbed microwave power data used to analyze the reproducibility of microwave testing using a microwave power of 1100 W and 6% charcoal addition.
Appendix E

Absorbed Microwave Power versus Time Data

Figure 125: Effect of microwave power with 6% charcoal at 71 kPa.
Figure 126: Effect of microwave power with 6% charcoal at 41 kPa.

Figure 127: Effect of microwave power with 6% charcoal at 11 kPa.
Figure 128: Effect of microwave power with 6% charcoal at 11 kPa.

Figure 129: Effect of microwave power with 6% charcoal and 2% pyrite.
Figure 130: Effect of microwave power with 6% charcoal and 4% pyrite.

Figure 131: Effect of microwave power with 9% charcoal and 2% pyrite.
Figure 132: Effect of microwave power with 9% charcoal and 4% pyrite.

Figure 133: Effect of charcoal addition on absorbed microwave power at 101 kPa and 2% pyrite.
Figure 134: Effect of charcoal addition on absorbed microwave power at 11 kPa and 2% pyrite.

Figure 135: Effect of charcoal addition on absorbed microwave power at 101 kPa and 4% pyrite.
Figure 136: Effect of charcoal addition on absorbed microwave power at 11 kPa and 4% pyrite.

Figure 137: Effect of pyrite addition on absorbed microwave power at 101 kPa and 6% charcoal.
Figure 138: Effect of pyrite addition on absorbed microwave power at 11 kPa and 6% charcoal.

Figure 139: Effect of pyrite addition on absorbed microwave power at 101 kPa and 9% charcoal.
Figure 140: Effect of pyrite addition on absorbed microwave power at 11 kPa and 9% charcoal.

Figure 141: Effect of pressure on absorbed microwave power for 6% and 9% charcoal at 800 W.
Figure 142: Effect of pressure on absorbed microwave power for 6\% charcoal at 1000 W.

Figure 143: Effect of pressure on absorbed microwave power for 9\% charcoal at 1000 W.
Figure 144: Effect of pressure on absorbed microwave power for 3% charcoal at 1000 W.

Figure 145: Effect of pressure on absorbed microwave power for 6% charcoal at 1200 W.
Figure 146: Effect of pressure on absorbed microwave power for 6% charcoal and 2% pyrite.

Figure 147: Effect of pressure on absorbed microwave power for 6% charcoal and 4% pyrite.
Figure 148: Effect of pressure on absorbed microwave power for 9% charcoal and 2% pyrite.

Figure 149: Effect of pressure on absorbed microwave power for 9% charcoal and 4% pyrite.
Appendix F
Selected Sample Photos

Figure 150: Briquetted sample measuring 23.5 mm in height and 31.75 mm in diameter. The nickel laterite, charcoal and pyrite used was mechanically mixed before being compressed in a mold with a hydraulic jack for 10 seconds at a pressure of about 48,260 kPa.

Figure 151: Partially reacted sample showing unreacted surface. The process parameters were a time of 11 minutes, power of 1100 W, pressure of 101 kPa, charcoal addition of 6%, sample mass of 30 g, particle size of -100 mesh, and magnetic separation with the DTT. The nickel grade was 3.2% and the recovery was 47.3%.
Figure 152: Part of a reacted sample showing ferronickel beads and slag. The process parameters were a time of 10 minutes, power of 1000 W, pressure of 11 kPa, charcoal addition of 9%, pyrite addition of 2%, sample mass of 30 g, particle size of -200 mesh, and magnetic separation with the WHIMS. The nickel grade was 5.93% and the recovery was 57.98%.

Figure 153: Sample was processed in an argon atmosphere for a time of 10 minutes, power of 900 W, charcoal content of 6%, sample mass of 30 g, and a particle size of -200 mesh. The interior of the sample shows the presence of ferronickel beads (B).
Figure 154: Sample was processed in an argon atmosphere for a time of 7.5 minutes, power of 900 W, charcoal content of 6%, sample mass of 30 g, and a particle size of -200 mesh. The interior of the sample shows the presence of ferronickel beads and magnesium silicate slag (greenish phase in photo (B)). The surface temperature of the reacted sample was 467°C.

Figure 155: Top view of a microwaved sample glowing red hot. The cracked opening allowed for the carbonaceous gases to escape from the sample’s interior. The process parameters were a power of 1400 W, time of 15 minutes and charcoal content of 6%.
Figure 156: The sample was processed for a time of 10 minutes, power of 1000 W, pressure of 101 kPa, charcoal addition of 6%, pyrite addition of 2%, sample mass of 30 g, particle size of -200 mesh, and magnetically separated with the WHIMS. The maximum recorded temperature was 1177°C (left) the top of the sample did not react (middle) and the bottom half of the reacted sample contained ferronickel beads (right). The nickel grade was 6.85% and the nickel recovery was 41.98%.


Appendix G

Conversion from Tyler Mesh Equivalent to Sieve Screen Size

Table 36: Tyler Mesh Equivalent and corresponding Sieve Screen Size

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Figure 157: Sieve screen size versus corresponding Tyler mesh equivalent size.
Appendix H

Literature Review Hierarchy Diagram

Figure 158: Literature review hierarchy diagram for nickel laterite ores.
## Appendix I

### Wave Separation Technologies LLC Patents

Table 37: Wave Separation Technologies LLC patents for different countries.

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<tr>
<th>Country</th>
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