Effect of the Composition, Nickel Sulfate Addition, and Reduction Temperature on the Morphology of Nickel Oxide through Reduction

by

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ABSTRACT

EFFECT OF COMPOSITION, NICKEL SULFATE ADDITION, AND REDUCTION TEMPERATURE ON THE MORPHOLOGY OF NICKEL OXIDE THROUGH REDUCTION

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University of Guelph, 2015

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The morphology of nickel oxide through reduction under various, controlled conditions was investigated. The reduction process increased the specific surface area of samples from 0.03 to >2 m²/g linearly until ~80% completion, when it plateaued. Nickel oxide samples with varying concentrations and types of impurities, most notably copper (0.13-5.18%) and sulfur (0.005-0.36%) were analyzed to determine their effects on product morphology. The presence of copper impurities had the greatest impact specific surface area, which ranged from 2-6 m²/g between samples after being reduced at 400 °C.

The addition of nickel sulfate also increased the specific surface areas by a factor of 1.5-2 by decreasing the rate of sintering. Each type of nickel oxide had a temperature range where the nickel/nickel oxide’s porous network was in a way maintained that depended on the concentration of the sulfate.
Acknowledgements

Many people have contributed to the completion of this project. While thanking them all properly would be a great undertaking, I’d like to highlight a few who have helped me with my master’s project.

First, the group. Paul made this project possible, and has shaped my scientific and philosophical thinking through the last four years. Stuart and Alina patiently put up with my frequent pestering during my fourth year research project, and inspired me to take up winemaking and read some classics (respectively). Nathan made an interesting addition to the already interesting Vale team, bringing solid scientific fundamentals, and could reduce nickel oxide with the best of them. All of the members of the group helped to whittle away my incompetence and doubt through their advice and questioning.

I’d also like to give a special mention to Dan Thomas, who was one of the reasons I came to the University of Guelph back in 2008, and who improved my understanding of atomic-scale phenomena in my first semester of university. I’m excited to begin my PhD with him on chemical education.

Finally, G-Force needs a shoutout. Gabrielle was a (usually) amiable research partner, welcome baker, and delightful friend. She has been such a positive influence on my life. Through knowing Gabrielle, I feel that I have become a more understanding person, learned that there is certainly a time for stubbornness (and patience), become more physically fit, and have tried many new things (trampoline dodgeball, TENS!) that I otherwise would not have.
My family has supported me through all of my schooling, and my master’s project was no exception. I always found myself explaining what I’d done that week to them over Skype, which made elevator and poster conversations much easier.

Last, Emily deserves recognition. She is an enabler in the best sense: without her, it’s unlikely that I would take the stairs, have done a master’s project, started a PhD, taken up winemaking, become the Canadian representative for the International Jugglers’ Association, and much more. Her encouragement, support, and patience has allowed all this to happen.

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5.5.2 FWHM values of nickel 111 peaks for SR and DR TNO through reduction.
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<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
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<tr>
<td>DR</td>
<td>doubly roasted</td>
</tr>
<tr>
<td>ECSA</td>
<td>effective cross sectional area</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
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<tr>
<td>MC</td>
<td>Monte Carlo</td>
</tr>
<tr>
<td>NOVA</td>
<td>no void analysis</td>
</tr>
<tr>
<td>SR</td>
<td>singly roasted</td>
</tr>
<tr>
<td>STP</td>
<td>standard temperature and pressure</td>
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<tr>
<td>TNO</td>
<td>Tokyo nickel oxide</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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1. Introduction

1.1 – Industrial Context of Nickel Purification

Over two million tonnes of nickel were produced worldwide in 2012, about 10 % of which came from Canada. It is used for many applications, including construction, aerospace, and automotive industries. Nickel’s alloying properties (increasing hardness and corrosion resistance) complement iron well, resulting in ~60 % of mined nickel to eventually be used in the production of stainless steel.

For most types of stainless steel, nickel must only be >75 % pure, depending on the types of impurities. Mined nickel used for this application is referred to as class II nickel, and is used after reduction (see section 1.1.2) without further purification. Class I nickel refers to a product that is ≥ 99.7 % pure, and is necessary for the manufacturing of pure nickel powders, discs and briquettes. These purer products are essential for the electrochemical, pharmaceutical, and fine chemical industries. Efficiency improvements to the post-reduction purification steps would decrease manufacturing costs and environmental impact.

1.1.1 Preparation of Nickel Sulfide Ore

Nickel is mined as either laterite or sulfide ores (see Table 1 for compositional information), the latter of which accounts for over 60 % of the currently mined nickel. The first step in their treatment is typically roasting. In this step, the ore is heated to 600-700 °C in the presence of oxygen, causing most of the sulfur and some iron to be oxidized and sulfur dioxide to be driven off. The metals (mostly present as oxides) are then poured into the smelter.
Table 1 – Typical elemental composition of laterite\textsuperscript{5,6} and sulfide\textsuperscript{2,7} nickel ores. The remainder of the ore contains varying amounts of magnesium, aluminum, and calcium oxides. Trace amounts of gold, silver, and platinum are also present.\textsuperscript{2}

<table>
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<th>Ore type</th>
<th>Nickel</th>
<th>Copper</th>
<th>Iron</th>
<th>Sulfur</th>
<th>Silicon</th>
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<td>Laterite</td>
<td>0.3-1.4 %</td>
<td>&lt;150 ppm</td>
<td>10-45 %</td>
<td>0.05 %-trace</td>
<td>5-25 %</td>
</tr>
<tr>
<td>Sulfide</td>
<td>0.4-2.0 %</td>
<td>0.2-2.0 %</td>
<td>10-30 %</td>
<td>5-20 %</td>
<td>20-35 %</td>
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Following roasting, the product is further refined by a sequential smelting process. This involves flowing silica through the system to bind with iron oxide and other gangue (commercially useless minerals), allowing \(2\text{FeO} \cdot \text{SiO}_2\) to float to the top of the liquid as a slag layer, which is removed. The remaining material is a copper- and nickel-rich matte. This process is normally done in two steps to decrease the iron in the matte to < 1 % while maintaining > 95 % total nickel and copper. The slag undergoes a conversion process where oxygen-enriched air is flowed through the system with silica, resulting in further extraction of iron. Reaction of oxygen with the other metal sulfides forms their respective metal oxides. Finally, the nickel oxide is reduced at 350-450 °C by hydrogen to yield >85 % pure nickel.\textsuperscript{2} A summary of these preparatory processes is shown in Figure 1.
Figure 1 – A summary of industrial processes: sulfide ores are mined, roasted, and smelted to generate >90% purity nickel oxide.
1.1.2 The Mond Process

Approximately 7% of worldwide mined nickel ore is eventually converted into high-purity (>99.9%) nickel using a method of gaseous carbonyl refining called the Mond process.\textsuperscript{1} In all variations of this process, carbon monoxide is flowed through a system containing >85% nickel, forming the volatile nickel tetracarbonyl. This is flowed into a second, hotter chamber where the nickel tetracarbonyl decomposes on nickel seed pellets, depositing >99.9% pure nickel.\textsuperscript{2} A summary of the Mond process is shown in Scheme 1.

\[
\text{Ni}_{(s)} + 4\text{CO}_{(g)} \xrightarrow{50 \degree \text{C}} \xrightarrow{200 \degree \text{C}} \text{Ni(CO)}_4_{(g)}
\]

Scheme 1 – A summary of carbonylation and decarbonylation reactions for nickel.

A facility made to operate the Mond process at atmospheric pressure was originally built in 1902 (only 4 years after the Mond process was discovered) in Clydach, Wales\textsuperscript{2} that produced over 42 000 tons of nickel in 2013.\textsuperscript{9} In it, ~92% pure nickel is fed into a 50 m long, 50 °C, water-cooled kiln through which carbon monoxide is flowed (Figure 2).\textsuperscript{2} Industrially, the rate of this reaction is kinetically limited and depends on the surface area of the nickel feed of the process.
Figure 2 – A summary of the methodology of the Mond process industrially implemented by Vale in Wales.

The decomposition takes place in a 180-240 °C chamber standing 3 m tall, where nickel is deposited onto nickel seeds and the carbon monoxide is recycled. Nickel spheres exit through the bottom of the decomposer, where they are screened. Spheres that have a diameter >1 cm are removed from the process and sold, while smaller spheres are recycled and delivered to the top of the decomposer again. The yield of purified nickel is ~90 %, but can vary, and the remaining feed is further processed as outlined below.²

A high pressure Mond reaction plant was completed in Sudbury, Canada in 1972, and operates at ~70 atm of carbon monoxide. Operating at higher pressures increases the rate of the carbonylation reaction (Figure 3), and this refinery typically produces 70 000 tons of 99.99 % pure nickel per year.² The high pressure carbonylation is a batch process, unlike the low pressure process. Notably, it extracts ~97.5 % of nickel from the post-reduced material, in
addition to being more versatile: the high pressure process operates well down to an 80 % pure nickel feedstock.²

The drawbacks to the high pressure process are industrial, not chemical: more energy is required for the high pressure process, and poses greater potential hazards. Carbon monoxide and nickel tetracarbonyl are both very toxic, with LC₅₀ values of 3760 ppm¹⁰ and 35 ppm,¹¹ respectively, for rats with a 30 minute exposure. The high pressure process uses 70 atm carbon monoxide in each carbonylation chamber and is a batch process, resulting in higher concentrations of both of these toxic species.

Early in the development of the Mond process, the addition of sulfur-containing compounds was found to increase the reaction rate.³ A chemical understanding of the mechanism in which sulfur-containing compounds enhance the rate of reaction is currently missing from the literature. While some sources consider it to be a catalyst, it seems more likely that sulfur adsorption to specific sites on a nickel/nickel oxide surface block deleterious side reactions, maintaining the carbonylation rate.¹² Unlike a catalyst, sulfur does not take part in the mechanism of the volatilization of nickel with CO. Jeppe et al. reported that sulfur preferentially binds to step edges in Ni(111) surfaces at 400 K at atmospheric pressure, similar conditions to those in the atmospheric carbonylation cylinders. Once adsorbed, these sulfur species were found to block irreversible carbon deposition¹³, which can nucleate at step edges and spread across the surface. This work aims to find if the addition of sulfur prior to the reduction step increases the surface area of the product, which would in turn be expected to increase the initial carbonylation rate.
1.1.3 – Proposed Mechanisms of Carbonylation

The mechanism of formation of nickel tetracarbonyl from a nickel surface being exposed to carbon monoxide is not well established – many mechanisms have been proposed.\textsuperscript{14,15} Two mechanisms, proposed by Liang and De Groot, are shown in Figure 3. Both require the establishment of a certain quantity of adsorbed carbon monoxide species.

![Potential mechanisms for the carbonylation of nickel proposed by De Groot\textsuperscript{14} (top) and Liang\textsuperscript{15} (bottom).](image-url)

Liang \textit{et al.} investigated the addition of carbon monoxide to a nickel surface at $10^{-6}$ - $3 \times 10^{-2}$ Pa and 270-420 K, and measured the quantities of nickel tetracarbonyl and its subcarbonyl species via pulsed field desorption mass spectrometry. They proposed a carbonylation mechanism that required the formation of a monolayer of carbon monoxide molecules to establish a “compression structure”, which favourably oriented the surface for further carbonylation from neighbouring adsorbed CO (Langmuir-Hinshelwood process). Each of the subcarbonyl species were detected ($\text{Ni(CO)}_x$, $x=1$-3), which indicated that the addition of carbon monoxide molecules
was sequential. Liang et al. proposed the rate-limiting step to be the addition of the second carbon monoxide molecule, and identified this to be the step where a nickel atom is removed from its surrounding lattice.

De Groot et al. measured reaction rates at 50-140 °C under atmospheric pressure on (111), (110), and (100) crystallite faces. They found that on any crystallite face, nickel was rapidly removed preferentially to form the (111) face. In the proposed mechanism by De Groot, a complete monolayer is not necessary for the reaction to proceed, but does increase the rate of reaction. A minimum of three adjacent nickel atoms bound to carbon monoxide molecules is required. One carbon monoxide molecule shifts to an already occupied nickel site, and the carbon monoxide molecule that was occupying that site shifts to a third occupied nickel site. This results in one carbon monoxide molecule bridging two nickel sites, and two carbon monoxide molecules binding to a single nickel site. The third and fourth carbon monoxide molecules further bind to this nickel atom sequentially.

While it is not known exactly how this sequential addition takes place, De Groot et al. also propose that the latter two carbon monoxide molecules bind via a Langmuir-Hinshelwood mechanism. This is because the rate of a Langmuir-Hinshelwood process depends only on the surface area, rather than its morphology. This is consistent with the findings of De Groot et al., and rules out the alternative Eley-Rideal (reaction between adspecies and gaseous species) process.
1.2 – Relevant Results of Reduction Work

Several of the results found in a complementary, concurrent study of reduction kinetics conducted by Foran affected the interpretation of the gas-sorption data. The reduction times varied from 30-580 minutes due to differences in types of nickel oxides (labelled FRM, FEN, DR TNO, SR TNO, which will be explained in section 2.1), reduction temperatures, reduction percentages and quantities of additives varied. Reduction times always increased as reduction temperature decreased: samples reduced at 350 °C required 3-4 times longer to reduce completely compared to the same type of sample reduced at 450 °C. Samples with higher concentrations of nickel sulfate showed required ~10 % longer reduction times than samples without nickel sulfate when reduced at 350 °C, but there was little difference in reduction times at 450 °C.¹⁶
Figure 4 – Summary of reduction times for nickel oxide samples. Times for FRM samples are slightly artificially low, as they were reduced to ~80 % completion, while the other types of nickel oxide were reduced to >95 % completion.

All of the nickel oxide samples’ reductions were found to follow a chemical-interface-limited model, in which the reduction rate depended primarily on the number of reactive surface sites on the sample. The best geometric approximation of the nickel oxide’s grain-shape varied depending on the type of nickel oxide, the concentration of nickel sulfate present, and the reduction temperature. FRM nickel oxide was best approximated as having spherical grains when no nickel sulfate was added, but rodular otherwise. FEN nickel oxide and SR TNO were both best described as having rodular grains through reduction under all conditions. DR TNO
exhibited rodular grains under all conditions except when reduced at 450 °C with nickel sulfate, in which case using spherical grains yielded a better fit. The differences in applicable models were attributed to morphological changes that occur through reduction\textsuperscript{16} the spherical model tended to apply to more sintered samples.

1.3 – Research Objectives

The goals of this research are driven by industrial necessity and academic curiosity. Purification using the Mond process under atmospheric conditions results in the unreacted portion of the batch containing $>5\%$ nickel, which is then further refined. Currently, $\sim3500$ tons of nickel contained in residue is reshipped annually to Canada for this purpose, where it is refined under higher temperatures. While this is still economically more favourable than discarding the remaining feed, it is not as economically or ecologically favourable as achieving a more complete separation of nickel from the impurities in the atmospheric process.

Industrial experience shows that the addition of sulfur-containing additives increased the rate of reaction in the reduction process, and the rate and completion of the Mond process. Yields were found to vary between feeds, indicating that these refining processes are sensitive to the compositional and/or morphological variations within them. Detailed mechanistic understandings of both the reduction of nickel oxide and the Mond process on nickel are missing from the literature, as are the exact chemical effects of added sulfur-containing compounds and impurities within the nickel oxide.

Industrial experience and preliminary work in this project revealed that the specific surface areas of the products of reduction varied depending on the reduction temperature (350-450 °C), concentration of nickel sulfate (0-1 %) added to them, and types and quantities of impurities.
These differences in specific surface areas were suspected to contribute to the variability of carbonylation completion seen in the following purification step. By determining the effects of each variable on the specific surface area of the nickel oxide through reduction, reduction conditions could be varied to maximize the product’s specific surface area, thus optimizing the carbonylation rate and completion.

Thus, the questions that this project aims to answer are:

1 – How does added nickel sulfate affect the specific surface area of reduced nickel oxide?
2 – How do varying concentrations of impurities within industrially-relevant nickel oxide affect the specific surface areas of their reduced products?
3 – Do these two factors influence the specific surface area independently?

We aim to answer these three questions by reducing industrially-sourced samples of nickel oxide under industrially-relevant conditions, and determining surface characteristics including specific surface areas and pore-size distributions using gas sorption analysis.

1.4 – Gas Sorption Analysis

Gas sorption analysis is frequently used for surface area/pore characterization of a wide variety of solids including oxides, carbons, and zeolites, and is of particular interest in catalyst surface characterization, where a high surface area is often of the utmost importance. It is more accurate than methods such as sieving, optical attenuation measurements, and permeametric methods for particles that would be poorly approximated as spheres. Approximating nickel oxide particles as spheres that are 0.5 mm in diameter and have a density of 6.67 g/cm$^3$, the specific surface was calculated to be $9 \times 10^{-4}$ m$^2$/g. This is much lower than the observed specific surface areas of the nickel oxide, and reduced nickel oxide (see table 2 for a comparison). Gas sorption
analysis also allows for an entire sample to be analyzed (provided the sample can fit into a sample tube), compared to microscopy techniques (e.g. scanning electron microscopy) which directly measure only a subset of a sample.\(^\text{18}\)

Table 2 – Specific surface areas determined by approximating the particles as spheres (estimated particle diameter 0.5 mm for nickel oxide) compared against values obtained through gas sorption analysis.

<table>
<thead>
<tr>
<th>Spherical Approximation</th>
<th>Nickel Oxide</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 x 10^{-4} m^2/g</td>
<td>(\sim 0.03) m^2/g</td>
<td>2-8 m^2/g</td>
</tr>
</tbody>
</table>

Gas sorption analysis admits small, known quantities of gas into sample tubes that are under vacuum and often at low temperatures and monitoring the pressure of the system. There are two ways of generating an isotherm: discrete relative pressure measurements, and continuous-measurement. Discrete relative pressure measurement observes the pressure of the system at many relative pressure values that are set by the user. Relative pressure is the pressure of the system (assuming no adsorption) divided by the vapour pressure of the adsorbate, and is denoted \(P/P_0\).\(^\text{18}\)

Continuous-measurement systems are an alternative, and involve slowly increasing the pressure and establishing quasi-equilibria. While more accurate, this method is much slower, not as commonly available, and limits the analysis to one sample at a time.

In both types of analysis, adsorbates adsorb preferentially to micropores (radii < 1 nm). Micropores fill first because they are near the order of a molecular dimension; an adsorbate can interact appreciably with both walls of the pore simultaneously. Mesopores (radii 1-25 nm) fill
second for similar reasons, though the interactions with multiple walls are weaker. Macropores (radii >25 nm) are practically indistinguishable from planar surfaces, and fill at about the same rate as planar multilayers.

Schematic chemical potentials ($\varepsilon$) between an adsorbate and the walls of a pore are shown in Figure 4. In macropores or near a mostly planar surface, an adsorbate interacts significantly with only one area. Similarly, in a mesopore, an adsorbate interacts mostly with only one area, but has a small, significant interaction with other walls. Conversely, an adsorbate experiences significant interaction with both walls (or many walls, depending on the geometry of the pore), near the middle of a micropore. If the pore is relatively large compared to the adsorbate size, this can result in multilayer formation within the pore before a monolayer is formed on the rest of the sample (capillary condensation). If the pore is small or near the size of the adsorbate, these pores will be inaccessible to the adsorbate, and not be measured.

![Chemical potential graph](image)

Figure 4 – Chemical potential of an adsorbate interacting with a macropore (left) a mesopore (middle) and a micropore (right). 18
Typically, adsorbate-substrate interactions are more attractive than adsorbate-adsorbate interactions, resulting in micropore filling, then monolayer formation prior to multilayer formation. Following monolayer formation, multilayers form, with mesopores filling first. As the relative pressure approaches 1, an increasing number of multilayers form until the surface is indistinguishable from a bulk liquid of the adsorbate. This process is summarized in Figure 5.11

Figure 5 – A summary of the preferential adsorbing sites in an isotherm.
1.5 – Types of Isotherms

A sorption isotherm describes the equilibrium between an adsorbed phase and a gaseous phase of a species at constant temperature. This can be generated by varying the pressure of the adsorbate in a system containing the sample. Different isotherm profiles indicate specific types of surface morphologies and strengths of adsorbate-surface interactions. Six common profiles as characterized by IUPAC are shown in Figure 6.²⁰

![Isotherm Diagram](image)

Figure 6 – IUPAC classifications of isotherms.²⁰ For the isotherms exhibiting hysteresis, thin arrows are used to indicate the direction of the isotherm. S denotes the point at which a monolayer is established.

Type I isotherms show little to no hysteresis: their isotherms show no significant deviation between the adsorption and desorption isotherms. This kind of isotherm is a result of an adsorbate-substrate combination where little/no multilayer formation occurs. The amount adsorbed increases and asymptotically approaches a value.¹⁸ An example of a system where very little multilayer formation occurs is carbon monoxide on nickel at room temperature, where
carbon monoxide chemisorbs to nickel to form a monolayer, and negligible further adsorption occurs. Microporous samples can also yield this type of isotherm, as adsorbate would quickly fill micropores (due to a high adsorption potential) and multilayer formation is minimal and/or comparatively small.

Type II isotherms also show little to no hysteresis, and are indicative of non-porous or macroporous substrates. The approximately linear growth with relative pressure indicates that unrestricted multilayer formation can occur. The slight knee marked by S in the diagram indicates a complete monolayer formation, and multilayer formation beginning.

Type III isotherms also show little to no hysteresis effect, and are similar to type II isotherms but without a knee. It is indicative of a relatively weak adsorbate-substrate interaction, as shown by little adsorption at low relative pressures. Non-porous or macroporous substrates give rise to this type of isotherm. An example of a system that is known to yield this isotherm shape is nitrogen on a polyethylene substrate.

Type IV isotherms are observed from analysis of mesoporous materials. It also exhibits a shoulder (marked with an S) similar to type II isotherms, which is indicative of complete monolayer coverage and the onset of multilayer formation. The hysteresis loop shows more adsorption at lower relative pressures. Hysteresis can be caused by a number of sources, which will be further explored after figure 7.

Type V isotherms also show hysteresis, but is otherwise similar to type III isotherms. They are indicative of weak adsorbate-substrate interaction, and imply the presence of micropores, mesopores, or large pores with narrow openings.
Type VI isotherms show no hysteresis effects, and are indicative of the sequential formation of multilayers. This occurs when there is a significant difference in adsorption potential between each layer of adsorption. Uniform, non-porous surfaces analyzed by isotropic adsorbates yield this kind of isotherm.\(^\text{18}\)

Depending on the sample-adsorbent interaction strength and morphology of the sample, hysteresis may be seen by a difference in the adsorption and desorption isotherms at a specific relative pressure. IUPAC classifications of hysteresis loops are shown in Figure 7.

![Hysteresis Loops](image)

Figure 7 – Summary of hysteresis loops characteristic of different pore shapes and distributions.\(^\text{18}\) The adsorption and desorption isotherms do not always meet - the dashed line refers to low-pressure hysteresis.
The presence of hysteresis is indicative of the morphology (e.g. pore size distribution, geometry, connectivity), rather than composition, of the surface. H1 hysteresis shows near-vertical and parallel sorption branches, which implies rapid adsorption/desorption at a particular relative pressure. This high degree of relative pressure sensitivity indicates the surface is relatively uniform, and this kind of hysteresis loop is typical for surfaces with well-defined cylindrical pores or agglomerates of uniform spheres.

Conversely, H2 hysteresis shows comparatively low relative pressure sensitivity during the adsorption isotherm, but high relative pressure sensitivity on the desorption isotherm. This behaviour is indicative of a surface where the pores sizes and shapes are heterogeneous. Isotherms with H3 hysteresis do not exhibit a plateau at high relative pressures, which is observed with non-rigid aggregates of disk-like particles that cause the formation of slit-shaped pores. H4 hysteresis also shows the presence of slit-shaped pores, but shows the presence of micropores of this type as well.

Low-pressure hysteresis is observable to very low relative pressure, and is associated with a change in the volume of the adsorbent. This can be caused by the swelling of non-rigid pores or irreversible adsorption. A leak in the system can also cause similarly shaped isotherms, so reproducibility tests are essential before an interpretation is drawn based on low-pressure hysteresis.
1.6 – BET Theory

To find specific surface areas of samples in this investigation, the BET (named after the authors on the original paper, Brunauer, Emmett, and Teller) method was used. Developed in 1938, it was among the first methods of measuring the surface area of powders using gas sorption techniques, and is still in wide use today. The theory is based on a generalization of the Langmuir model, treating each adsorption site as a separate film, allowing for multilayer formation. For more background information on Langmuir films, see reference 23.

BET theory uses the heats of adsorption and condensation of an adsorbate to derive what is now known as the BET isotherm equation (equation 1, note that some variable assignments have been updated to be consistent with more recent literature):\(^1\)

\[
\frac{1}{V_a(P_0P)^{-1}} = \frac{1}{V_mC} + \frac{(C-1)}{V_mC} \cdot \frac{P}{P_0}
\]

[1]

Where:

P≡Equilibrium partial vapour pressure of adsorbate

P₀≡Vapour pressure of adsorbate

Vₐ≡Molar volume of gas adsorbed at STP

Vₘ≡Required volume of gas adsorbed at STP for the formation of a monolayer

C≡BET constant, which is related to the enthalpy of adsorption of the adsorbate on the substrate

Equation 1 can be plotted as \(\frac{1}{V_a(P_0P)^{-1}}\) against the relative pressure, \(P/P_0\), to yield a line of slope \(\frac{(C-1)}{V_mC}\) and y-intercept \(\frac{1}{V_mC}\). From these values, the required volume for monolayer formation
(\(V_m\)) and the BET constant (C) are solved for. From \(V_m\), the surface area of the sample, \(SA\), is calculated using known properties of the adsorbate as shown in equation 2.\(^{18}\)

\[
SA = \frac{V_m N s}{V_a}
\]

[2]

Where:

\(SA\)≡Surface area of the sample

\(N\)≡Avogadro’s number

\(s\)≡effective cross-section of the adsorbate on the substrate

The BET method makes several assumptions. First, it assumes the formation of an infinite number of adsorbate layers at the vapour pressure of the adsorbate (at its normal boiling point) in order to simplify a more general equation to Equation 1.\(^{18}\) This is reasonable for our analysis, as gaseous nitrogen was used as the adsorbate and liquid nitrogen was used as the cooling bath. Thus, at the vapour pressure of the adsorbate, there will be many layers of adsorbed nitrogen.

The BET method also assumes that the layer farthest from the substrate is at equilibrium with the surrounding gas, meaning the rate of adsorption is equal to that of desorption. Additionally, for any desorption to occur, an energy equivalent to that lost by adsorption must be provided.\(^{18}\)

Implicit within the mathematics of the BET method is the packing structure of an adsorbed multilayer. Only single adsorbate-substrate and adsorbate-adsorbate interactions are considered; an adsorbate interacting with multiple particles on the surface is not considered. Thus, adsorption is assumed to be to only one atom on the substrate, not bridged between several.\(^{18}\)

In this work we use BET analysis only to find the surface areas of the samples, which does not extend into an appreciable multilayer formation regime. As such, only the linear portions of
adsorption isotherms were used (typically P/P₀ between 0.01 and 0.4, referred to as the BET region), as this corresponds to the relative pressures before significant multilayer formation. Thus, the assumption about packing structure has little effect on the interpretation of this work’s results.

An alternative to using the multi-point BET method is the use of a single-point BET calculation. This makes the assumption that the y-intercept of a BET plot is very close to 0 (valid for very high C values,) and therefore requires the measurement of volume at only one relative pressure. The specific surface area of the sample can then be calculated using Equation 3.

\[
V_a = n^a \left( 1 - \frac{p}{p_0} \right)
\]  

[3]

In this work, no single-point BET calculations were used. While they allow for much greater throughput, they do not allow for the calculation of C, which was used here to determine approximate error values in surface area values. Additionally, C was monitored across samples to ensure the applicability of the BET method – analyses resulting in C values of less than 15 were outgassed again and rerun. In measuring the volume at only one pressure, no characteristics of the pore distributions can be inferred by visual isotherm analysis or by computational methods.

Other types of analysis, such as density functional theory (DFT) and Monte Carlo (MC) methods can be used to determine specific surface areas. These methods often have greater accuracy than the BET method, especially for microporous substrates. DFT and MC have a quantum-mechanical basis, which typically outperform models based on the Kelvin equation, such as the BJH method. However, these methods are still relatively new, and are substrate- and adsorbate-dependent, and have only been commercially implemented for very common substrates, such as
carbon and silica. Collecting full adsorption and desorption isotherms would allow for their use immediately if they were to be developed for nitrogen adsorption on macroporous nickel, without necessitating further experiments.

1.7 – BJH Theory

BJH theory is used to determine pore-size distributions and was first proposed in 1950 by (and named after) Barrett, Joyner, and Haledna.\textsuperscript{24} It was based on the Kelvin equation (equation 4), which describes changes in vapour pressure due to a liquid-gas meniscus.\textsuperscript{18}

\[
\ln \left( \frac{P}{P_0} \right) = -\frac{2\gamma V_l}{rRT} \tag{4}
\]

Where:

- $\gamma$=surface tension of an adsorbate
- $V_l$=molar volume of the adsorbate liquid
- $r$=radius of the meniscus of the liquid-gas interface
- $R$=ideal gas constant
- $T$=temperature (in Kelvin)

To make the Kelvin equation useful for determining pore distributions, the BJH method assumes that all pores are cylindrical, and that all pores with the same radius will respond identically. It also assumes preferential adsorption against adsorbate-adsorbate interaction, resulting in the complete wetting (monolayer formation) of pores before pore filling occurs. Making these modifications, and acknowledging a non-zero thickness of adsorbate layers prior to capillary condensation taking place, the Kelvin equation becomes equation 5.\textsuperscript{25}
\[ \ln \left( \frac{P}{P_0} \right) = -\frac{2\gamma \cos(\theta)}{RT\Delta \rho (r_p - t_c)} \]  

[5]

Where:

\( \theta \equiv \) angle of meniscus of the adsorbate from the surface normal to the capillary wall

\( \Delta \rho \equiv \) difference between the orthobaric density (density of the adsorbed and not adsorbed phase at equilibrium)

\( r_p \equiv \) radius of the pore

\( t_c \equiv \) statistical thickness of the multilayer prior to capillary condensation

Note that \( r_p - t_c \) yields the effective inner radius of the pore with some quantity of adsorbent present. This is the radius of a pore that incoming adsorbate interacts with. Statistical thickness is the thickness of an adsorbate layer assuming a uniform film thickness for the entirety of the sample. This assumption is not reasonable for micropores, where capillary condensation fills pores before a monolayer forms, and therefore the BJH method should not be used for the characterization of microporous samples.

Originally (and typically for modern work)\(^{18}\), the desorption branch from \( P/P_0 \) of 0.99 to 0.4 was used in this work. This range encompasses multilayer evaporation/desorption of the adsorbate from the surface and meso-macropores. This relative pressure region does not typically include relative pressures where only a monolayer is present or adsorbate has desorbed from micropores, as these occur at \( P/P_0 < 0.4 \).
1.8 - Choice of Adsorbate

Many adsorbates can be used in gas sorption analysis. Nitrogen, argon, krypton, carbon monoxide, carbon dioxide and many more are used for different purposes in the literature.\textsuperscript{25,26} A potential adsorbate must be stable under the analysis pressure range and when in contact with the substrate. In most cases, physisorption is preferred, as a reversible process allows for both an adsorption and desorption isotherm to be measured. Similarly, isotropic polarizability is preferred for general use, as the orientation of the bound adsorbate will be more consistent between substrates.

Vapour pressure and cross-sectional area are more complex factors that contribute to an adsorbate’s ubiquitous or niche use. These factors and the uses of nitrogen, argon, krypton, and carbon monoxide will be discussed here.

1.8.1 – Vapour Pressure

The vapour pressure (sometimes called saturation pressure, or saturation vapour pressure) of an adsorbate must be sufficiently low to allow for significant adsorption to the substrate to occur. A lower vapour pressure causes more of the adsorbate to adsorb rather than exist as a gas. This increases the signal to noise of a pressure measurement – a small change in pressure can be detected more precisely at low pressure than high pressure. Thus, to minimize error due to void volume error, a low vapour pressure is advantageous.\textsuperscript{27}

The vapour pressure of an adsorbate is related to the relative chemical potentials of the adsorbate in the adsorbed ($\mu_a$) and bulk liquid ($\mu_0$) phases (equation 6). A greater vapour pressure indicates a smaller (more negative) chemical potential of the adsorbed phase. This means that, other parameters held constant, the adsorbate will more preferentially adsorb to the substrate instead of
previously adsorbed species, which is advantageous in gas sorption analysis. In this regard, an adsorbate with a high vapour pressure is advantageous.\textsuperscript{18} For practical gas-sorption analysis, the vapour pressure of an adsorbate under the temperature of analysis must not be too high, nor too low. Examples of such adsorbates are discussed in sections 1.6.3-1.6.6.

\[
\mu_a - \mu_0 = RT \ln \left( \frac{P}{P_0} \right) \tag{6}
\]

\begin{itemize}
  \item $R \equiv$ ideal gas constant
  \item $T \equiv$ temperature in Kelvin
  \item $P \equiv$ pressure of the system
  \item $P_0 \equiv$ vapour pressure of the adsorbate at the system’s temperature
\end{itemize}

1.8.2 – Effective Cross-Sectional Area

Most analysis methods using gas sorption data rely on knowing the cross-sectional area of the adsorbate on the substrate at the system’s temperature to a high degree of accuracy,\textsuperscript{18} the error in specific surface area is proportional to the error in the effective cross-sectional area value (recall equation 2).

Finding effective cross-sectional areas for potential adsorbates is a non-trivial task. While related properties such as van der Waals and covalent radii are well known, effective cross-sectional areas depend strongly on not only temperature, but the adsorbate-substrate chemical potential. This potential depends on the properties of the substrate, making knowing exactly the effective cross-sectional area exactly on a novel substrate impossible.\textsuperscript{28}
The magnitude of variation in cross-sectional area due to adsorbate-substrate potential depends on the adsorbate. A high polarizability (especially anisotropic polarizability) contributes to large variations effective cross-sectional areas across different substrates.\textsuperscript{18} Tables 3 shows the observed effective cross-sectional areas (ECSA) on carbon and glass-based substrates for a number of adsorbates, which illustrates these adsorbates’ variability due to substrate composition/structure.

Table 3 – Assorted adsorbates and their ECSA on carbon- and glass-based substrates. Each analysis was done at a temperature typical for its adsorbate.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>ECSA on carbon (Å\textsuperscript{2})</th>
<th>ECSA on glass (Å\textsuperscript{2})</th>
<th>Temperature (K)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>16</td>
<td>13.1</td>
<td>77</td>
<td>18, 29</td>
</tr>
<tr>
<td>Kr</td>
<td>22.1</td>
<td>21.5</td>
<td>77-78</td>
<td>30, 31</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>7.9</td>
<td>19.5</td>
<td>298-299.5</td>
<td>32, 33</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>24.4</td>
<td>16.0</td>
<td>192-195</td>
<td>34, 35</td>
</tr>
<tr>
<td>Xe</td>
<td>20.2</td>
<td>28.5</td>
<td>78</td>
<td>36, 37</td>
</tr>
</tbody>
</table>

1.8.3 – Nitrogen as an Adsorbate

Due to its low cost and favourable physical properties nitrogen is generally the first choice for gas sorption analysis. The ubiquity of liquid nitrogen also provides for a convenient method of cooling samples to a useful analysis temperature simply by filling a small dewar. Nitrogen has a relatively low, consistent effective cross-sectional area on most surfaces.\textsuperscript{18}

The application of nitrogen as an adsorbate also has two fundamental limitations: the presence of a quadrupole moment and a relatively high (1 atm) vapour pressure under analysis conditions (77
The presence of a quadrupole moment allows for an adsorbate molecule’s adsorption orientation to vary: on very polar (especially hydroxylated) substrates, nitrogen’s effective cross-sectional area has been found to decrease from 16 to 13 Å². This change is shown in Figure 7, and attributed to a change in orientation of the nitrogen adsorbates from having the molecular axis perpendicular to the surface (left) to having the molecular axis parallel with the surface (right).  

Figure 7 – The difference in orientation of molecular nitrogen on polar (left) and nonpolar substrates (right)

Another criticism of nitrogen is its preferential adsorption to certain sites of some adsorbates, resulting in deviation from its accepted effective cross-sectional area. For example, adsorption on carbon black yields a specific surface area that is only consistent with those found from benzene, n-hexane, and ethyl chloride analyses if nitrogen’s effective cross-sectional area is 20 Å² instead of 16.2 Å² on that substrate. This change is attributed to the localization of adsorbed nitrogen at lattice sites, shown in Figure 8.
Figure 8 – Schematic showing the preferential adsorption of nitrogen (blue) to a graphite (black) surface. Note that while there are significant uncovered areas of graphite between nitrogen molecules, there is insufficient area for more nitrogen to adsorb, resulting in an artificially low measured specific surface area.

The most important surface-independent property of nitrogen as an adsorbate is its high vapour pressure. This causes a relatively high void volume error, as a particular quantity of gas admitted into the sample tube does not result in as much adsorption as it would with other adsorbates. This results in a smaller pressure decrease (comparing the theoretical pressure where no adsorption occurred to the measured pressure after adsorption has taken place), and therefore less usable signal. This limits nitrogen adsorption isotherms to measuring surface areas >0.5 m² and prevents measuring pore size distributions for micropores.¹⁸
1.8.4 – Krypton as an Adsorbate

For samples with a surface area of ≤0.5 m², the quantity of nitrogen adsorbate in the void volume is greater than those adsorbed to the sample by about a factor of 5 (depending on adsorbate-substrate interaction strength) due to its high vapour pressure, causing a smaller signal to noise ratio. This issue can sometimes be mitigated by increasing the amount of sample, but only to an extent: often sample availability or the volume of the tube is limited.

To mitigate error due to void volume effects, an adsorbate with a lower vapour pressure at liquid nitrogen temperatures can be used. Krypton can be supercooled to maintain liquid-like characteristics at pressures above its typical sublimation point (1.6 torr at 77.4 K), resulting in a vapour pressure of 2.63 torr at 77.4 K. Vapour pressure is proportional to the number of adsorbate particles that occupy the void volume at a given temperature, and krypton has a factor of ~290 fewer unadsorbed particles than nitrogen would under similar conditions. This drastically decreases the noise due to void volume error, and allows for the measurement of samples with ≤0.05 m².

There are some properties of krypton that make it less suitable for higher surface area samples. First, due to its low vapour pressure, the system must achieve far lower absolute pressure for the same P/P₀ value. This necessitates the use of a second pump, usually a turbomolecular pump. Additionally, multiple pressure transducers are required for a full range of pressure measurements. Systems capable of krypton adsorption analysis are usually equipped with 0.1 or 1, 10, and 1000 torr transducers, compared against a single 1000 torr transducer contained in other gas sorption analyzers. These additions result in a substantial price increase for the system.
A second, more fundamental problem with krypton adsorption at liquid nitrogen temperature is our limited understanding of its thermodynamic state of adsorbed species. BET analysis assumes the complete wetting of an adsorbed phase, but it is unclear whether krypton acts as a liquid, solid, or supercooled liquid at ~77 K, which is 39 K below its triple point temperature. This behaviour is dependent on the adsorbate-substrate interactions, and thus changes between sample types. Nitrogen wetting behaviour is better understood, and while krypton measurements agree well with nitrogen measurements, no direct comparisons can be made for samples with very low surface areas.18

A third problem with using krypton for surface area analysis is its more variable effective cross-sectional area. Its two-dimensional supercooled liquid density is 15.2 Å², though effective cross-sectional areas have been observed between 17.6-22.8 Å².18 In this investigation, we assume an effective cross-sectional area of 20.5 Å², as this is the standard value used, as recommended by the International Organization for Standardization.39

1.8.5 – Argon as an Adsorbate

Argon at normal boiling liquid argon temperatures (~87 K) can be used to characterize microporous substrates much more precisely than nitrogen or krypton. In microporous samples, equilibration times become prohibitive for nitrogen at 77 K because micropore filling requires very low relative pressures ($P/P_0 = 10^{-7}$-$10^{-5}$).18 Because of the low pressures required, characterization of microporous samples with nitrogen also requires very sensitive pressure transducers. Conversely, the use of argon for micropore characterization at 87 K necessitates relative pressures of only $10^{-5}$-$10^{-3}$, allowing for a much faster equilibration.40 Figure 9 shows the relative pressures that micropore filling occurs at for nitrogen and argon at their respective boiling points for a standard, microporous zeolite.21
Figure 9 – Comparison of adsorption isotherms using nitrogen and argon as adsorbates.\textsuperscript{21}

A further advantage for argon use over nitrogen in pore-size determination is its isotropic polarizability. Nitrogen analysis at \(\sim\,77\) K, shows variable micropore filling pressures, as this occurs due to the specific interactions between nitrogen and the substrate. These specific interactions vary depending on the composition and structure of the substrate.\textsuperscript{21} Argon does not exhibit those specific interactions, and has a more reliable micropore-filling pressure. This also allows for very high resolution of micropore characterization, down to 0.1 nm in diameter.\textsuperscript{21}

It is important to note that for micropore characterization, the samples should be immersed in liquid argon (\(T = 87\) K), not liquid nitrogen (\(T = 77\) K). The decrease in bath temperature of only \(\sim\,10\) K results in a shift of the adsorption isotherm to lower relative pressures, mitigating the advantages obtained by using argon. This is because 77 K is below argon’s triple point, resulting in a low saturation pressure (230 torr for supercooled liquid argon at 77 K, 205 torr for solid argon). This also limits the use of argon for characterization of pores <15 nm, as pore
condensation cannot be observed at this temperature. Liquid argon is more expensive and less convenient than liquid nitrogen, which makes pore analysis using argon less logistically appealing.

1.8.6 – Carbon Monoxide as an Adsorbate

Carbon monoxide is also sometimes used as an adsorbate for gas sorption analysis due to its selective binding to certain surfaces. While it has a similar vapour pressure to nitrogen at 78 K (~0.8 atm) it does not adsorb well to nickel oxide at 78 K, but chemisorbs to nickel. By comparing surface areas as determined by carbon monoxide against those with nitrogen, one can find not only the total surface area of the sample, but deconvolute the contributions from nickel and nickel oxide. This would allow for the determination of active surface area (i.e. surface area available for reaction) in a partially reduced sample, and could further corroborate reduction completion values.

1.9 – Mean Crystallite Size Determination

X-ray diffraction (XRD) detects the diffraction of X-rays from crystallites. By modelling different 2D crystallite phases as reflective sheets and bombarding the sheets with X-rays, one can obtain a series of Bragg angles (θ) of incidence at which the X-rays were reflected. Bragg’s law (equation 7) describes the relationship between the distance between crystalline layers, the Bragg angle, and the wavelength of the X-rays.
\[ n\lambda = 2dsin(\theta) \]  \[7\]

Where:

\( n \)≡ path length of X-rays between crystalline layers

\( d \)≡ distance between crystalline layers

For a particular index, the relationship between \( d \) and the Miller indices is shown in Equation 8, and this allows Equation 10 to be made in terms of the Miller indices.\(^\text{42}\)

\[ d = \frac{na}{\sqrt{h^2+k^2}} \]  \[8\]

Where:

\( a \)≡ lattice parameter of the unit cell

\( h, k, l \)≡ Miller indices of the crystallographic plane

\[ \lambda = \frac{2asin(\theta)}{\sqrt{h^2+k^2}} \]  \[9\]

The Bragg angles of nickel and nickel oxide peaks are well-known and are summarized in Table 5. Peak widths are dependent on several factors, including stacking faults, microstresses, grain boundaries, which are related to small crystallite sizes.\(^\text{42}\) The last factor is used by the Scherrer equation (Equation 10) to determine mean crystallite size based on the shapes of the peaks.\(^\text{43}\)
Table 4 – XRD peaks for nickel oxide and nickel\textsuperscript{44}

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>[hkl]</th>
<th>Relative intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.26</td>
<td>111</td>
<td>63</td>
</tr>
<tr>
<td>43.29</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>62.88</td>
<td>220</td>
<td>48</td>
</tr>
<tr>
<td>75.42</td>
<td>311</td>
<td>17</td>
</tr>
<tr>
<td>79.41</td>
<td>222</td>
<td>12</td>
</tr>
</tbody>
</table>

Nickel

| 44.50  | 111   | 100                    |
| 51.86  | 200   | 44                     |
| 76.39  | 220   | 19                     |

\[
\tau = \frac{K \lambda}{(\beta - \beta_0) \cos(\theta)} \tag{10}
\]

Where:

\(\tau\) = mean crystallite size

\(K\) = shape factor

\(\beta\) = full width half maximum of the peak

\(\beta_0\) = full width half maximum caused by instrumental broadening
This equation assumes that sample-specific peak broadening other than that due to small crystallite size is insignificant, and therefore only works on crystallite sizes $<\sim 100$ nm. Peak broadening due to other factors results in the mean crystallite size determined by the Scherrer equation is a lower bound, but for crystallite sizes $<100$ nm the error is typically low. The shape factor depends on the shape of the crystallites and method of analysis; for a rigorous explanation on its determination, see reference 45.
2 – Methodology

2.1 – Materials

Most nickel oxide samples were provided by our industrial partners, Vale. DR (doubly roasted) and SR (singly roasted) TNO (Tokyo Nickel Oxide) is mined in Indonesia from laterite ores and initially refined by fluid bed roasting nickel sulfide pellets, yielding a product with a true density of 6.65 g/cm³ in both cases. SR TNO only undergoes this process once, resulting in a much higher sulfur content than DR TNO. FRM and FEN nickel oxides are both mined from sulfide ore in Ontario, Canada. They have a true density (density of a particle) of 6.7 g/cm³ and differ in the floatation treatment, resulting in different elemental compositions, most notably having a higher copper content. Typical elemental compositions of all of the nickel oxide samples used in this study are shown in Table 6. Nickel (II) sulfate hexahydrate was provided both from Vale and Fisher Scientific, with the former having larger, coarser crystals than the latter.

In investigating observed specific surface areas varying with mass dependence (section 4.2), > 99 % pure commercial nickel oxide was used as provided from Fisher Scientific.

Table 5 – Typical elemental composition of DR TNO, SR TNO, FRM, and FEN NiO.

<table>
<thead>
<tr>
<th>NiO type</th>
<th>Ni (%)</th>
<th>Cu (%)</th>
<th>Fe (%)</th>
<th>Co (%)</th>
<th>O (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR TNO</td>
<td>75.9</td>
<td>0.13</td>
<td>0.49</td>
<td>1.29</td>
<td>20.5</td>
<td>0.005</td>
</tr>
<tr>
<td>SR TNO</td>
<td>75.2</td>
<td>0.13</td>
<td>0.49</td>
<td>1.28</td>
<td>20.3</td>
<td>0.36</td>
</tr>
<tr>
<td>FRM</td>
<td>73.3</td>
<td>0.86</td>
<td>0.48</td>
<td>1.13</td>
<td>20.2</td>
<td>0.008</td>
</tr>
<tr>
<td>FEN</td>
<td>68.9</td>
<td>5.18</td>
<td>0.61</td>
<td>1.11</td>
<td>19.8</td>
<td>0.13</td>
</tr>
</tbody>
</table>
Nitrogen and helium used in gas sorption analysis were obtained from Linde and were 99.998 and 99.995 % pure, respectively.

2.2 – Reduction of Nickel Oxide

In this investigation, nickel oxide samples were reduced in a home-built machine named Vulcan (Figure 10), which was capable of reducing up to seven samples simultaneously. Samples from 0.5-2.0 g were dried to constant mass at ~50 °C. This low temperature was chosen in order to maintain the hydration of the added nickel sulfate hexahydrate, which decomposes at 103 °C.46 The samples were inserted into the furnace, and the temperature of Vulcan was ramped to the reduction temperature (350 - 450 °C) over 15-20 minutes under argon flow. During this time, the quantity of released water vapour was measured by a mass spectrometer. The mass spectrometer monitored each sample in sequence for 29 seconds, and then the line was disconnected from the sample tube and flushed with argon for 16 seconds. This process was cycled through each sample and repeated until the analysis was complete. Once the nickel sulfate hexahydrate had completely decomposed to anhydrous nickel sulfate (as measured by the m/z = 18 signal decreasing to its baseline level) a gaseous mixture of 10 mL/min of hydrogen and 200 mL/min of argon was continuously flowed through the system. This was considered the starting time of the reduction.16
Figure 10 – A schematic diagram of the gas flow process through sample holders in Vulcan. Blue arrows represent reactant gas, magenta arrows represent product gas.\textsuperscript{16}

The reduction was stopped when water production (from the reaction outline in Scheme 2) decreased again to its baseline level. The mass of the reduced sample was used to calculate the completeness of the reaction, which agreed well with completeness as calculated by integrated water signal with the mass spectrometer and the known mass of NiO.\textsuperscript{16}

\[
\text{NiO}_{(s)} + \text{H}_2(g) \rightarrow \text{Ni}_{(s)} + \text{H}_2\text{O}(g) 
\]

In this investigation, a “reduced” sample refers to one that was 90-100 % reduced as measured in this way, with most samples being > 95 % reduced.
2.3 – Gas Sorption Analysis

Prior to analysis, samples were added to dry, 11” long, 6 mm diameter, large-bulbed sample cells of known mass provided by Quantachrome. These samples were outgassed using a commercially available Quantachrome Flovac Degasser at 150 °C at < 10 mtorr for typically 12-20 hours. The sample cells were weighed before addition of the sample and after outgassing (heating the sample under vacuum to remove physisorbed contaminants) to determine the mass of the added sample.

Samples were analyzed using nitrogen gas sorption surface analysis using a Quantachrome NOVA 4200e Surface Area and Pore Size Analyzer. Depending on the number of samples being run concurrently and the estimated surface areas of each sample (which influences the duration of the analysis), different numbers of data points were collected: these ranged from 20 evenly-spaced points to 13 and 9 selected points on the adsorption and desorption isotherms, respectively. Priority was given to points predicted to be in the BET \((P/P_0 = 0.01 – 0.4\) on the adsorption isotherm) and BJH \((P/P_0 = 0.99 - 0.4\) on the desorption isotherm) regions, but points outside of these ranges were still collected to allow for different analyses if necessary and to monitor any changes to isotherm shape.

Void volume was determined by the no volume analysis (NOVA) method prior to each run. To find the volume of the sample tubes, helium was admitted into the manifold, its pressure was measured, and the valve connecting the manifold and the sample tube was opened. The equilibrium pressure was measured, and assuming no adsorption, the volume of the sample tube was calculated.
Other parameters used for the analysis are listed in Table 7. Some parameters (e.g. maximum equilibrium time) were varied to determine whether sufficient time was being provided for the system to equilibrate. For example, the maximum equilibrium time was lowered from 30 minutes to 17 minutes. If the total analysis time changed when that change was made, this would indicate that system equilibration for at least one relative pressure took longer than 17 minutes. Since no total analysis times changed when varying any experimental parameters within the limits in Table 7, sufficiently long equilibration time and sufficiently low pressure variation tolerance was allowed.

Table 6 - Summary of experimental parameters used in gas sorption analysis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure variation tolerance</td>
<td>0.15-2.0 torr</td>
</tr>
<tr>
<td>Minimum equilibrium time</td>
<td>500-600 s</td>
</tr>
<tr>
<td>Maximum equilibrium time</td>
<td>1000-1800 s</td>
</tr>
<tr>
<td>Bath temperature</td>
<td>77.35 K</td>
</tr>
<tr>
<td>Adsorbate cross sectional area</td>
<td>16.200 Å</td>
</tr>
<tr>
<td>Adsorbate molecular weight</td>
<td>28.013 g/mol</td>
</tr>
<tr>
<td>Adsorbate liquid density</td>
<td>0.808 g/cc</td>
</tr>
</tbody>
</table>
2.4 – Measurement of Adsorption

While variations on gas sorption measurement methods exist, the method employed by the instrument used in this investigation for all nickel samples was typical of nitrogen adsorption. Nickel oxide samples were sent to LabQMC for analysis with krypton. The details of the former process are outlined below.

During installation, the volume of the inlet manifold was determined and the pressure transducer was calibrated. The vacuum integrity was checked and any easily removed adsorbed species were removed from the sample by pumping the system down to < 10 mtorr and pressurizing with nitrogen to 800 torr through several cycles at room temperature.

During analysis, the sample tubes are immersed ~3 cm into liquid nitrogen by the movement of a small elevator lifting an open dewar. A slight excess of nitrogen is admitted into the room-temperature manifold from a gas cylinder. A precise, specified quantity of nitrogen is achieved via the rapid opening and closing of a valve connected to a fine vacuum line. This pressure is selected to match an input relative pressure \((P/P_0)\) where \(P_0\) is saturation vapour pressure of the adsorbate once the valve between the manifold and the sample tube is opened, assuming no adsorption. Once equilibrium has been reached, the system’s pressure is measured for that relative pressure and the tube is again pumped down to <0.1 torr. These steps are repeated for each relative pressure in ascending then descending order to generate an adsorption and desorption isotherm, respectively.
3 – Development/changes to the method

Throughout this work, a number of changes to the initial procedure have been made in response to experimental problems or in an effort to improve throughput. Each change was tested against previous work to ensure that there would be negligible change to the results if they were to be compared. The changes and experimental data supporting these changes are reviewed below.

3.1 – Outgassing

It is important to outgas (also known as degas) samples before gas sorption analysis in order to remove physisorbed material from the sample. Outgassing mitigates the effects of the storage environment on the measured surface area and pore distribution, which is essential for ensuring reproducibility for a given sample and for reliable comparison between samples.\textsuperscript{18}

Vacuum outgassing was used instead of flow outgassing in this work for several reasons. It prepares the sample in a similar environment to that which it experiences during analysis. This limits the types of stresses the sample undergoes, which simplifies troubleshooting. Vacuum outgassing is also faster than flow outgassing (where an inert gas is flowed through the system) because it decreases the pressure in the system. Desorbed material would, on average, encounter fewer other particles between it and the opening of the tube (\textit{i.e.} it has a longer mean free path) causing it to leave the sample tube more quickly. Elutriation (loss of sample into the vacuum system) is the primary shortcoming of vacuum outgassing with powder samples,\textsuperscript{18} but none was observed for any of the industrially-provided samples which had sufficient particle masses to be unaffected.
3.1.1 – Outgassing Time and Temperature

Several experiments were run on samples with 2-4 times the sample mass of a typical sample, with varying outgassing times and temperatures, starting at 85 °C and increasing to 200 °C. Samples were weighed both between outgassing and analysis and after analysis. By weighing samples after analysis instead of before, the atmospheric exposure of a sample changed from approximately 5 minutes to 30-90 seconds. This allowed for the effect of atmospheric exposure time to be tested. A summary of the isotherms from samples prepared in these ways is shown in Figure 10.

Figure 10 – Total (left) and low relative pressure region (right) isotherm measurements on commercially obtained nickel oxide outgassed at varying temperatures and times. Note that the second 200 °C run was transferred from degassing to analysis station quickly (< 90 seconds).

A difference in detected volumes of gas between the adsorption and desorption branches or a desorption isotherm that appears to have less noise (having a better fit to a type III isotherm) than the adsorption isotherm can both be indicative of incomplete desorption. No correlation is evident between degas time or temperature and difference between tail points (Figure 10, right). Noise levels between adsorption and desorption isotherms are comparable by visual inspection.
For a semi-quantitative analysis of noise on the adsorption isotherm, the correlation of the points in the BET region against a BET fit was found. This region corresponds to the relative pressure regions where a monolayer forms, and is expected to be linear for samples without significant contribution to surface area from micropores. The results of this analysis are shown in Figure 11.

Figure 11 – Plots of the transformed isotherms in the BET regions (left) where a linear trend would be expected and the correlation coefficients (right) which were used as a measure of outgassing quality.

BET plots \( \frac{1}{V_a \left( \frac{P_0}{P} - 1 \right)} \) against relative pressure) identical samples outgassed at different temperatures for different times showed variable noise levels. The noise was quantified as a correlation coefficient between the data and a BET fit (a linear line of best fit). Based on these data, an outgassing temperature of 85 °C for 6.5 hours is insufficient, as a sample outgassed in this way had a lower correlation coefficient than any of the other methods.

Correlation coefficients for outgassing at 150 °C for 24 hours and 200 °C for 10 hours were similar, with the latter being slightly lower. Conversely, when a sample was outgassed at 200 °C
for 10 hours but transferred to the analyzer quickly, the correlation coefficient was similar to that of the sample outgassed at 150 °C for 24 hours. This was unsurprising, as the formation of a monolayer on a substrate occurs in well under one second in atmospheric conditions. This indicated that the difference in correlation coefficients in the samples outgassed at ≥150 °C for ≥10 hours is likely insignificant. Based on these findings and logistics, samples considered in this study were outgassed overnight (12-20 hours) at 150 °C.

3.1.2 – Change in Outgassing Instrument

For the analysis of FRM and FEN samples, the outgassing stations on the analyzer were used. The analyzer was not able to outgas and analyze samples simultaneously, so in an effort to increase throughput, an independent outgasser was obtained. To ensure that the new outgassing procedure yielded a similarly outgassed product to the analyzer’s outgassing stations, commercially available nickel oxide samples were outgassed using both instruments and analyzed using the analyzer. The samples were outgassed for the same durations as outlined in the previous section, and the same comparison was used to compare the data. The results are shown in Figure 12.
Figure 12 – Comparison of correlation coefficients of a BET plot against linearity of samples outgassed using an analyzer’s outgassing stations against samples outgassed using an independent outgasser.

A sample outgassed at 85 °C for 6.5 hours had a higher correlation coefficient to linearity in a BET plot when the independent outgasser was used instead of an outgassing station on the analyzer. This may have been caused by the designated outgasser having a more direct pumping configuration and a lower ultimate outgassing pressure. At degassing temperatures ≥160 °C, there was no significant differences between samples outgassed on the two instruments. Based on these findings, comparisons between analyses of samples outgassed with different instruments was deemed acceptable.
3.2 – Use of Filler Rods

When analysis of SR TNO and DR TNO began, many of the isotherms were noisier than those of FRM and FEN. Both TNO-type reduced nickel oxides showed lower specific surface areas than FEN and FRM, which had already been close to the limit of quantification for the method and instrument. Filler rods were used to partially (~ 70 %) fill the analysis tubes’ empty space, thereby decreasing the void volume error. Two samples (both fully reduced DR TNO with 0.1 % commercial NiSO₄, reduced at 450 °C, varying by 16 minutes of oven time) were analyzed including and excluding filler rods. With filler rods the specific surface areas of the samples agreed within experimental error. The error was also decreased through the use of filler rods: the specific surface areas of the samples were 2.16±0.2 and 2.16±0.1 m²/g with filler rods and 8.1±3.7 and 4.5±1.3 m²/g without. The inconsistency in the values in the latter two measurements and the much higher uncertainties imply that there was significant error caused by void volume error, and therefore should not be used. The fit to the BET model (as measured by the correlation coefficient on a BET plot) was also improved through the use of filler rods, as shown in Figure 13. Based on these findings, all DR and SR TNO samples were analyzed using the filler rods.
The observed specific surface areas for FEN and FRM samples depended much less on the inclusion/exclusion of filler rods (see Figure 14). This is attributed to a higher signal to noise ratio in these samples, resulting in higher correlation coefficients and percent errors being improved by a factor of ~2 compared to TNO samples. The void volume error is expected to remain approximately consistent between samples (<1 % change in void volume due to changes in sample volume) while the observed surface area increased due to greater mass and specific surface area of the sample.
Figure 14 – Comparison of correlation coefficients (data compared against a linear fit on a BET plot) and percent error for FRM (sample 1) and FEN (sample 2) reduced nickel samples.

3.3 – Measurement or Calculation of $P_0$

It is recommended in the literature that the reference saturation pressure, $P_0$, be measured frequently in order to minimize error in its value.$^{17}$ While saturation pressure measurements can be made directly, doing so requires an empty sample tube that nitrogen can be admitted into. In an effort to increase throughput, calculating the saturation pressure of nitrogen based on an assumed temperature of liquid nitrogen was tested using a porous aluminum oxide standard. The specific surface areas of the standard as determined when the saturation pressure was measured every five data points and when it was calculated were $111.6 \pm 2$ and $114.6 \pm 2$ m$^2$/g, respectively, which agree within experimental error.

This method is not viable for systems with much temperature fluctuation, as an increase of only 0.2 K near the boiling point of liquid nitrogen causes a saturation pressure increase of ~20 torr. Impurities, such as dissolved oxygen and water vapour cause the temperature of the boiling liquid nitrogen to increase by 0.1-0.2 K. This small temperature change increases the saturation pressure of nitrogen at ~77 K by 10-20 torr.$^{18}$
A change in saturation pressure of up to 20 torr does not have a strong influence on observed specific surface areas as measured using BET analysis. Because the ordinate and abscissa of the BET plot \(\frac{1}{V_a\left(\frac{P_0}{P}-1\right)}\) and relative pressure, respectfully) deviate in the same direction, a 15 torr error in the saturation pressure of nitrogen corresponds to an error on the order of 1% in observed specific surface area. However, this is not true for BJH analysis, which is based on the modified Kelvin equation. In this case, the same error of 20 torr yields an error of 10% in pore size analysis.
4 – Determination of the Viability of Results

The reliability of the output isotherms was constantly scrutinized, and several features were found to indicate flawed results. Any samples that showed any of these indicators were analyzed up to twice more, which was sufficient to obtain an isotherm with none of the indicators.

4.1 – Indicators within an Isotherm

The first indicator of an erroneous isotherm is an adsorption isotherm with a negative slope, usually in the low to mid (P/P₀ = 0.05-0.7) relative pressure regimes (Figure 15). This phenomenon was found to be independent of sample type, though samples with much higher specific surface areas than measured in this investigation may render this error insignificant.¹⁸

Figure 15 – The effect of a negative slope in an adsorption isotherm (left) on multi-point BET plots (right).

This can occur because the system is pumped to its baseline pressure, then a pressure measurement is recorded to be used as a reference pressure. If a sample were not fully outgassed, species would desorb from it during and after the system was pumped down. This would cause an artificially high pressure measurement to be used as the baseline pressure. The
small amounts of nitrogen added to the system to achieve the $P/P_0$ setpoints would have been small compared to the amount of gas from desorbed species for most of the $P/P_0$ range. This would result in a decreasing, $<0$ pressure reading for the first section of the isotherm, as seen in figure 15.

The second indicator of a misleading isotherm is the early and/or deep crossing of the desorption branch with the adsorption branch (Figure 16). This can be attributed to hysteresis: a greater volume of gas is detected at a relative pressure during the increase in relative pressure than the decrease. Since equilibrium is established at each point, the only differences between a relative pressure on the adsorption branch compared to the desorption branch of the isotherms are time and the previous state.

The two physical phenomena that contribute to isotherms crossing are very small or bottlenecked pores and insufficient degassing. Micropores are pores that have a diameter under 2 nm, which is on the order of the molecular dimension of the adsorbate. In both micropores and small mesopores an adsorbate experiences a significant potential from more than one side, which can...
result in preferential adsorption to these sites, such that multilayers form in these pores before a global monolayer is established.

Based on the isotherm shape micropores and bottlenecked pores do not have a significant contribution to the samples’ surface areas. Eliminating these two possibilities, the crossing of an isotherm could be attributed to either a leak in the system or incomplete degassing of the sample. Thus, these isotherms should not be used for surface area or pore size analysis, and the samples should be re-analyzed.

This phenomenon is most likely caused by a slow leak of air into the system. The vacuum integrity test that is performed automatically by the instrument prior to every analysis seems to be insufficiently sensitive to detecting leaks that cause significant error in the ~1-3 m² samples. Figure 17 shows excerpts from the same sample run thrice. The first run showed a suspected small leak. To test this, the second run was conducted immediately afterward, without any adjustment, and the third run was conducted after removing the sample and remounting it.
Figure 17 – Three trials of analyzing the same sample. The first (red) and second (blue) trials were done without modification, while the third (black) trial was done after remounting the sample tube.

The isotherm shape of the first two runs were similar: both show adsorption branches of the isotherms that initially decrease with increasing relative pressure, which could have been caused by faulty pressure calibration at the beginning of the analysis, caused by a leak or incomplete outgassing. Additionally, the desorption branch has much lower volumes at STP than its respective adsorption branch at relative pressures below 0.5. This could be indicative that the first issue was (at least partially) due to incomplete outgassing instead of a leak, as the sample may have reached an appropriate level of outgassing part-way through the analysis. These isotherm shapes contrast that of the third trial, which exhibits a typical type III isotherm.
These contrasting data show that the presence of features indicating flawed results depended on the sample mounting, and likely, the vacuum integrity. An o-ring is used to seal the system from atmosphere, and leaks were no longer measurable (by isotherm shape) when its position was changed. Thus, the leaks were likely caused by the poor orientation of the o-ring. Attempts were made to diagnose these slight leaks prior to analyses included the automatic vacuum integrity tests, slight tugging of the sample tube to ensure a snug fit, further tightening the connection, but no correlation between leaks and any of these variables were found.

4.2 – Indicators between Samples

One indicator of flawed results was only apparent when comparing multiple analyses of the same sample. When any kind of nickel oxide was analyzed, a different, but still potentially valid, isotherm was observed (Figure 18). The adsorption branch of the isotherm was still a type III isotherm, but the desorption branch showed higher measured volumes at STP than the adsorption branch by up to a factor of 3.

Figure 18 – Isotherm and BET plot of FRM nickel oxide prior to reduction.
This difference in isotherm shape between nickel oxide and nickel samples could be rationalized by hysteresis: nickel oxide samples seemed to adsorb nitrogen much more strongly, or have significant surface area contributions from ink-pot pores (pores with large bodies but narrow necks). This was unexpected, as type III isotherms do not typically show such strong hysteresis\textsuperscript{18}. However, these isotherms were not expected to have identical shape to those from nickel samples, as the sample composition and morphology may have been different. The BET regions were slightly shorter than those from reduced samples, but still had a linear portion. Based on the isotherm shape and BET regions alone, excluding these isotherms from the analysis would have been unjustified.

When several of these runs were compared, the specific surface area was inconsistent between samples of different masses, but identical composition and morphology. Figure 19 shows a summary of these findings across a wide range of masses and between types of nickel oxide. For each type of nickel oxide, the data follow a curve proportional to $1/\text{mass}$. A curve proportional to $1/\text{m}$ would be expected if the samples had surface areas below the limit of detection of the instrument; there would be a constant amount of measured total surface area as a result of noise, and an increasing mass. To find the specific surface area, the total surface area is divided by the mass.
When analyzed using krypton as an adsorbate, it was found that DR TNO had a specific surface area of \(0.027 \pm 0.004 \text{ m}^2/\text{g}\), which indicated that it would have a total surface area near or under the detection limit of nitrogen adsorption with completely full sample tubes (~15 g). This finding is in conflict with work by Plascencia et al., which reports the specific surface area of unreduced TNO to be \(0.071 \text{ m}^2/\text{g}\). Correspondence with this group confirmed that they had not analyzed samples of different masses in their study, and thus would not have seen this mass dependency. The other types of nickel oxide have been submitted for analysis, and are likely to have similarly low specific surface areas, as nitrogen adsorption analysis shows a mass dependency for those as well. With 15 g of sample, in order to have a total surface area of less than \(0.5 \text{ m}^2/\text{g}\), the specific surface area values must be under \(0.033 \text{ m}^2/\text{g}\).

If only noise were measured, one would expect the proportionality constant in the \(1/m\) curves to be consistent between types of nickel oxides. Since they are different, nitrogen adsorption analysis was capable of discerning between sample types. This indicates that despite these samples having less surface area than is quantifiable using this method (especially at low sample...
masses) the data are sample-specific. Once the specific surface areas are known from krypton analysis, it could be determined whether these proportionality constants could be related to the specific surface areas of these samples.
5 – Results and Discussion

5.1 – Isotherm Shape

The analyzed nickel samples (Figure 20) showed type III isotherms, which are indicative of macroporous substrates with relatively weak affinity for adsorption and little to no microporosity. The near-linearity for \( \frac{P}{P_0} < 0.8 \) is also indicative of monolayer formation occurring over a wide range of relative pressures. Additionally, since there are no distinct points of inflection in the low pressure regime, micropores have little contribution to the overall surface area.

![Figure 20 – A representative isotherm of FEN nickel oxide reduced at 420 °C.](image)

Care must be taken when analyzing type III isotherms: the validity of using BET analysis depends on the C constant, which represents the adsorbate-sample interaction strength. The literature states consistently that low C values (< 20 typically, but with acceptable values as low
as 10) indicate that the interaction is too weak for the application of the BET model. The applicability of the model for samples with high (>150) C values is somewhat controversial, and while IUPAC recommends its use, Sing warns against the use of such isotherms. C values on nickel samples in this study ranged between 20-100.

While type III isotherms typically do not exhibit hysteresis, small, reproducible differences between the adsorption and desorption isotherms were observed for both the nickel and nickel oxide samples. For the nickel samples, isotherms best fit hysteresis type H3. This is indicative of a sample with slit-shaped pores, where one width dimension of a pore is much larger than a second width dimension. Additionally, an H3 hysteresis type indicates the absence of ink-pot pores, which is a necessary consideration: if they were present, equilibria could take over an hour to be established, if it were reached at all. Varying allowed equilibration times (see section 2.3) across several reduced FRM samples and finding no difference in total analysis time corroborated the absence of ink-pot pores.

While typical hysteresis loops have desorption branch isotherms above their respective adsorption branch, measured isotherms for nickel samples often showed branch crossing at low relative pressures. A greater volume of gas at STP measured in the adsorption branch than the desorption branch could be caused by contaminants adsorbed to the sample surface prior to analysis. While outgassing removes most of these contaminants, it is possible that additional contaminants (such as water) from the atmosphere had adsorbed to the sample during transfer from the outgasser to the analysis station.
5.2 – Specific Surface Area and Structure through Reduction

The specific surface areas and pore distributions of samples were monitored through the reduction process by removing samples from reduction conditions before complete reduction had occurred. The results of these analyses are summarized in Figures 21 and 22.

Figure 21 - Specific surface area of an FRM sample through several stages of reduction completion at 420 °C.

The specific surface area of nickel/nickel oxide samples increased approximately linearly with reduction progress until ~80 % completion (Figure 21). After this point, the specific surface area did not continue to increase, and was approximately constant or exhibited a slight decrease. The total specific surface area increase was over two orders of magnitude.

The initial increase in specific surface area is attributed to oxygen atoms leaving their lattice sites following reaction with hydrogen, which would leave behind a vacancy with a radius of
approximately that of the covalent radius of oxygen (0.7 Å). These newly-formed pores would have low stability under all reduction conditions considered in this study. Isotherm shape also indicated the absence of micropores, but the presence of mesopores. This indicates that while pore collapse did occur, the net effect of reduction was pore (and therefore surface area) generation.

The pore distribution of the sample was measured at several points through its reduction for a more detailed description of the morphological changes that occurred and is shown in Figure 22. The 46% reduced sample had relatively high surface area contribution from small mesopores (radii < 25 Å) and pores with radii of 45-100 Å. The FRM sample reduced to 66% completion showed the greatest quantity of pores for every radius < 150 Å, with most of the surface area caused by pores of radii 45-120 Å. The sample that was completely reduced had some small mesopores and a large surface area contribution from pores with radii > 150 Å.
Figure 22 – Pore distributions of FRM nickel oxide reduced at 420 °C through several stages of reduction.

This evolution of pore distribution illustrates the generation and destruction of pores through the reduction process. Between the 44 % and 66 % reduced samples, there was a small increase in 50-75 Å radii pores, but a large increase in the number of larger pores. This was caused by these smaller pores being formed, but collapsing into the larger pores. In this stage of the reduction, the net effect of these two factors is an increase in the specific surface area.

In samples that were 66 and 100 % reduced, the total surface area was approximately constant while the pore distribution continued to evolve. The pore distribution decreased for radii under ~180 Å, while increasing for larger pores. Since the total surface area was constant, but the surface area contribution from the measured pores was decreasing, this indicated that pores were being formed that were larger than the limit of quantification of the system. In the 65-100 %
reduction regime, the rate of surface area loss (due to sintering) was approximately equal to the rate of surface area generation (due to oxygen loss).

This shift in relative rates was caused by two factors: slowing reduction rate and the production of a more easily sintered material. Beyond ~80 % reduction, the reaction enters a “trailing off period”, in which the rate of reaction slows. For the reduction of FRM at 420 °C, the trailing off period takes ~20 % of the total 430 minute reduction time. This causes surface area generation to slow, allowing more time for sintering to take place. Additionally, nickel is more malleable than nickel oxide, which implies it will also sinter more readily than nickel oxide.

To decouple the effects of pore collapse due to oxygen loss and those due to sintering, two FRM samples were reduced at 420 °C. At that point (which corresponded to a reduction completion of 54 %), one sample was removed, and the second of each sample remained in the oven at 420 °C for an additional two hours with only argon flowing through the system (no hydrogen). The sample that was reduced then removed had a specific surface area of (1.93±0.14) m²/g and the sample that was heated for an additional two hours had a specific surface area of (1.69±0.08) m²/g.

To further characterize the changes occurring during this secondary heating, pore size analysis was run on each of the samples and is shown in Figure 23.
Over the additional heating, the pore distribution changed slightly, with similar pore distributions from 25-40 Å pore radii. The sample that did not undergo an additional 2 hours of heating showed a higher specific surface area contribution from pores with radii ~20 Å and >40 Å. The higher surface area contribution of the sample reduced without additional heating from > 50 Å radius pores may be surprising based on the Figure 22, which shows larger pore formation as a result of sintering. However, the samples that did not undergo additional heating were still heated for a total time of 6.2 hours. Since the latter was heated for two hours longer, it is likely that sufficient sintering occurred to merge the pores sufficiently to be larger than what could be detected by this method.
5.3 – Effect of Impurities in NiO

In this investigation the surface areas and pore structures of reduced nickel oxide samples with different impurities were compared. Each type of nickel oxide was a current or potential nickel oxide source for our industrial partner. The specific surface area trends of the nickel oxide types in industrially-relevant temperature ranges are shown in Figure 24.

![Figure 24 - Comparison of post-reduction specific surface areas of nickel oxide samples with varying impurities as a function of reduction temperature.](image)

FRM nickel oxide (which is composed of 0.86 % copper and 0.008 % sulfur) samples showed a 19 % decrease in specific surface area between reduction temperatures of 375-400 °C, but little change was observed when the sample was reduced above 400 °C. These findings were also largely independent of time in the ranges examined: the samples reduced at 375 and 420 °C were held at their respective temperatures for 9.5 hours, while the sample reduced at 400 °C was
maintained at that temperature for 3 hours. These findings indicate that most of the sintering FRM nickel oxide samples occurred in the first three hours of reduction.

The specific surface areas of the FEN (which is composed of 5.18 % copper and 0.13 % sulfur) samples were greater than those of FRM samples reduced at the same temperatures. Additionally, the specific surface area of FEN nickel oxide decreased somewhat linearly with reduction temperature. FEN and FRM untreated nickel oxides showed similar relative specific surface area reductions over the 375-420 °C span tested (17 and 19 %, respectively). FEN nickel oxide lost 13 % of its initial specific surface area between 375-400 °C, while FRM nickel oxide samples’ specific surface areas decreased 17 % in the same temperature range. This further indicates that FEN better resists sintering.

SR and DR TNO had indistinguishable specific surface areas at all temperatures measured. These types of nickel oxides differ mostly in sulfur concentration: SR TNO is 0.36 % sulfur by mass, and DR TNO is 0.005 %. This observation indicates that sulfur (in the form of impurities, as found in industrial samples) has no observable effect on the specific surface area of the reduced product over the range of conditions tested.

Both FEN and FRM nickel oxides had greater specific surface areas than SR and DR TNO when reduced at temperatures between 375-420 °C. The greatest difference between SR and DR TNO samples against FRM and FEN nickel oxides is the quantity of copper. Both TNO samples contain 0.13 % copper, whereas FRM and FEN nickel oxide samples contain 0.86 and 5.13 % copper, respectively. Thus, it appears that copper impurities play the greatest role in maintaining or increasing surface area through reduction.
To corroborate the effect of copper without other metallic impurity concentration differences, the specific surface areas of reduced FRM nickel oxide and DR TNO can be compared. Both types of nickel oxide have \( \leq 0.005 \% \) sulfur, and comparable quantities of other impurities. The factor of ~2 increase of specific surface area from DR TNO to FRM can be attributed to the greater copper concentration in the latter. Additionally, FEN nickel oxide has a factor of ~6 higher copper concentration than FRM, and shows a ~1 m\(^2\)/g increase in specific surface area. This indicates that, while copper impurities lead to greater specific surface areas in the reduced products, this increase diminishes at higher copper content (Figure 25).

Figure 25 – The specific surface areas of SR TNO (0.13 % copper), DR TNO (0.13 % copper), FRM nickel oxide (0.86 % copper), and FEN nickel oxide (5.18 % copper).
The reason for samples with larger quantities of copper impurities having larger specific surface areas in the reduced product is unclear. Copper oxide is more easily reduced than nickel oxide, which would lead to a more rapid establishment of oxygen vacancy sites in the nickel oxide lattice. Oxygen vacancies (i.e. small areas of metallic nickel) are necessary for the reduction of nickel by hydrogen. Industrially, this could result in reduced reduction times, which would decrease the amount of time the sample spends under high temperatures, decreasing the amount of sintering that would take place, improving energy efficiency.

These findings are in contrast with findings reported by Barcicki et al., who found that beyond 0.025% copper addition, higher copper concentrations in nickel oxide samples resulted in lower specific surface areas of the reduced (from 350-500 °C) materials. Samples with 2.5% added copper converged to a specific surface area of ~ 2 m²/g, regardless of reduction temperature. This disagreement may be due to whether the copper is assimilated into the nickel oxide lattice or not: Barcicki et al. added copper as an ion (in copper nitrate) whereas the copper in our samples was present primarily as copper oxide. That we observed enhanced specific surface areas at higher concentrations of copper supports the theory that copper oxide must be integrated into the nickel oxide lattice. In this latter case, the rapid reduction of copper oxide would cause the formation of oxygen vacancies, decreasing the induction period. The addition of copper nitrate would not have an effect on the generation of oxygen vacancies, and therefore not increase the rate of reduction in this way.

With all types of nickel oxides, increased temperature resulted in decreased specific surface areas. This was unsurprising, as sintering rate increases exponentially with temperature. Reaction times for samples reduced at higher temperatures were faster: to achieve the same reduction completion (>95%), 1 g FRM and FEN samples were reduced for ~9 hours at 375 °C,
compared to ~2.5 hours at 420 °C. Similarly, 0.5 g samples of DR and SR TNO reduced at 350 °C required ~6.5 hours, and those reduced at 450 °C required ~2 hours.

The two factors considered in the determination of specific surface area for a reduced sample have been surface area generation through reduction and surface area loss through sintering. In an effort to decouple these two factors, specific surface areas through the reduction process were compared (Figure 27). FRM and FEN nickel oxides have oxygen concentrations of 20.2 and 19.8 %, respectfully. Since surface area generation is caused by the removal of oxygen, if the extent of sintering were constant between these two samples, a reduced FRM nickel oxide sample would have slightly (imperceptibly, to our instrument and method) more specific surface area than an FEN one. Thus, if the sintering rate were constant between the two samples, very similar specific surface areas of the reduced products would be expected.

Comparing the specific surface areas of untreated FRM and FEN during reduction at 420 °C, there is little difference in the net rate of specific surface area generation during the early (pre 80 % completion) stages of reduction (Figure 25). After 80 % reduction completion, the specific surface areas of the FRM nickel oxide samples begin to deviate from linearity. This indicated that the rate of sintering was increasing relative to the rate of surface area generation in the late stages of reduction.
Since FEN nickel oxide was found to have slightly higher specific surface areas throughout the reduction than FRM, and the gross amount of specific surface area generated was about constant, there must have been a difference in the extent of sintering. Based on only these data, it is inconclusive whether this difference was due to sintering rate or sintering time: the most reduced FRM sample above required 580 minutes under reducing conditions to become 100 % reduced, while the most reduced FEN sample (98 %) required only 430 minutes.

Based on the specific surface area evolution of FRM nickel oxide, there would be little change in specific surface areas between 430-580 minutes. Thus, the difference in specific surface area was likely due to either the different reduction extents (though at >~80 % reduction, the specific surface areas were found to plateau for FRM nickel oxide) or resistance to sintering (due to the
compositional difference). In an industrial setting, both of these possibilities favour FEN over FRM nickel oxide.

5.4 – Effect of Nickel Sulfate

Certain sulfur-containing additives are known to increase the yield of the Mond process, and in this investigation, the effect of nickel sulfate on specific surface area through reduction was tested. The same experiment outlined in section 5.1 involving additional heating of a fully reduced sample was conducted for samples treated with 0.1, 0.4, and 1.0 % (by mass sulfur) commercially-purchased NiSO₄, and the results are summarized in Figure 26.

![Figure 26 - Specific surface areas for FRM samples reduced at 420 °C with varying sulfate addition.](image-url)
As seen in section 5.1, there is a small but significant increase in specific surface area between samples reduced to 56 % completion without any added sulfates at 420 °C compared to an identical sample that spent an additional 2 hours at 420 °C. Through the addition of 0.1 % NiSO₄, the specific surface area of a completely reduced product was higher. Further addition of nickel sulfate continued to increase the specific surface area of the fully reduced samples, though beyond a concentration of 0.4 %, the increase became close to experimental uncertainty.

The effect of added sulfates on sintering was also considered. With no sulfate added, there was little difference between the sample reduced with the standard procedure and the one with additional heating. This was likely because sintering happened sufficiently quickly that most of the pores that were able to collapse at 420 °C had already done so, and an additional two hours did not have a significant effect.

When comparing these data, it is important to note that the rate of reduction for the sample without any nickel sulfate was about half of that for the sample with 1 % NiSO₄ added. This resulted in it having a much lower reduction percentage (56 %) than the others, which all had reduction percentages > 80 %. Thus, the much smaller absolute specific surface area is artificial. Had the untreated sample been reduced to completion, a larger decrease in specific surface area is expected between the only reduced sample and the additionally heated sample.

The difference in specific surface areas between samples with 0.1 % nickel sulfate added with and without additional heating was over 1 m²/g, with the reduced sample losing about 25 % of its specific surface area from two hours of additional heating. Samples with 0.4 % nickel sulfate added showed a smaller difference in both absolute and relative terms: additional heating decreased the specific surface area by 0.7 m²/g, or 10 %. Samples treated with 1.0 % nickel
sulfate had slightly higher specific surface areas than those treated with 0.4 % nickel sulfate, and showed little change after two additional hours of heating.

These findings indicate that samples with sulfate addition resisted sintering better in the two hour span after reduction completion, and maintained their pores’ structural integrity better during the reduction. The added nickel sulfate was found to decompose at ≥400 °C and form nickel sulfides.¹⁶

To determine in greater detail the surface structural changes that occurred over the additional two hours of heating, the pore distributions of the samples were analyzed. Figure 29 shows the pore distributions of each sample as they were after reduction, with no additional heating. While there is some surface area contribution resulting from ~20-25 Å pores, the bulk of the surface area comes from the 50-250 Å radius region. Even the sample with 0.1 % nickel sulfate addition had a large increase in the number of pores in that range compared to the sample with no added sulfates (a factor of 5 increase for pore radii ~70 Å), though there were diminishing returns with the addition of more nickel sulfate.

The differences in pore distribution between the samples treated with 0.4 and 1.0 % nickel sulfate are small, though there is a slight shift to larger pore radii. These trends indicate that added nickel sulfate helps to maintain the structure of mesopores, and omitting nickel sulfate allows for these pores to collapse sufficiently to become macropores (which are outside of the region studied) or effectively become planar.
Figure 27 – Specific surface area contributions by pores of various sizes for FRM samples reduced at 420 °C.

The pore distributions of samples heated for an additional two hours (Figure 30) showed the influence of added nickel sulfate more clearly: increased sulfate concentration caused greater specific surface area contribution from pores throughout the mesopore region. Comparing Figures 27 and 28, the specific surface area contribution by mesopores in samples treated with 0.1 and 0.4 % nickel sulfate decreased, with the former decreasing more. The sample with 1.0 % sulfate addition showed very little change in porosity. These findings indicate that when an FRM nickel oxide sample is reduced at 420 °C, adding ~0.4 % nickel sulfate is sufficient to mitigate sintering, provided the samples are removed from the reduction conditions shortly after completion. If the samples are to remain in the reduction conditions for longer than is necessary for the reaction completion, there is an advantage to the addition of more than 0.4 % nickel sulfate.
Figure 28 – Specific surface area contributions by pores of various sizes for FRM samples reduced at 420 °C, then heated at 420 °C for an additional 2 hours.

The specific surface area evolution through reduction of FRM samples is shown in Figure 29. The specific surface areas of samples treated with 0.4 % nickel sulfate were higher than the untreated samples at each reduction percentage, with larger differences seen for more reduced samples. This indicates that sintering occurs through the entirety of the reduction process, but decreases surface area more rapidly per percent reduction at higher reduction temperatures.
Figure 29 – Specific surface area generation of FRM with and without 0.4 % added nickel sulfate through reduction at 420 °C.

The effect of nickel sulfate addition with nickel oxides with different types and quantities of impurities was also tested. The specific surface area of each was measured for each type of nickel oxide after being treated with 0.1, 0.4, and 1.0 % nickel sulfate and reduced at temperatures between 350-450 °C.

The specific surface area of FRM nickel oxide showed a 2-3.5 m²/g increase in specific surface area between samples reduced with and without 0.4 % nickel sulfate addition. The magnitude of the specific surface area enhancement was found to depend on temperature (see Figure 30).
Figure 30 – Specific surface areas of FRM nickel oxide reduced between 375-420 °C.

The specific surface areas of the reduced product that had 0.4 % nickel sulfate added to it were indistinguishable when reduced at 375 and 400 °C. Over this temperature range, it appeared that the nickel sulfate was effective in mitigating sintering over the course of reduction, as the untreated samples showed a decrease in specific surface area over that range. At 420 °C, the specific surface area of the sample treated with nickel sulfate was 17 % lower than when reduced at 375 and 400 °C. This decrease was similar in quantity to the relative specific surface area decrease of 16 % exhibited by the untreated FRM samples reduced at 375-420 °C.

Nickel sulfate was also added to FEN nickel oxide prior to reduction, and the specific surface areas of the reduced products are summarized in Figure 31. The results were similar to those found with FRM nickel oxide: samples treated with nickel sulfate had higher specific surface areas than those that weren’t treated at every reduction temperature tested. Additionally, little sintering was evident in samples that had nickel sulfate added to them when reduced at 375-
420 °C for 3-8.5 hours. Comparing these results to Figure 30, every reduced FEN nickel oxide sample had a greater specific surface area than its corresponding (same temperature and quantity of nickel sulfate addition) FRM sample.

![Figure 30 - Specific surface areas of FEN nickel oxide reduced between 375-420 °C.](image)

The ability of incorporated copper to mitigate sintering, especially when paired with nickel sulfate was observed in comparison between nickel samples with varying quantities of copper (FRM and FEN). While two-thirds of a melting point is often used to estimate sintering temperatures, copper-nickel alloys all have lower melting points than pure nickel.\(^5\) Thus, this approximation does not accurately predict these findings. This deviation from the general trend of ease of sintering being inversely related to melting point may be due to the different types of bonding at play: in a strictly nickel lattice, there are only metallic bonds, whereas nickel sulfide lattices exhibit dipolar interactions.
Additionally, the sulfur in added in the form of sulfates were found by Raman spectroscopy to exist as nickel sulfides (not copper sulfides) in fully reduced samples.\textsuperscript{16} Like the above, nickel-sulfur species have lower melting points than nickel for all compositions (except for ~75-95 % sulfur, which is unreasonable in this environment)\textsuperscript{52} yet nickel oxide samples with nickel sulfate added to them have more rigid pores that resist sintering.

Based on the findings in Figures 29 and 30, the presence of copper did not completely prevent sintering. The specific surface area of FEN nickel oxide still increased as a result of the addition of nickel sulfate, despite its high copper content. The addition of nickel sulfate yielded a greater specific surface areas of fully reduced products, indicating that neither nickel sulfate addition nor copper impurities make these materials fully stable under the reduction conditions studied.

Impurity concentration and type were found to affect the reduction kinetics and surface structure of the product of nickel oxide samples. The sensitivity to added nickel sulfate species was found to vary with the concentration of impurities of the nickel oxide. Comparing FEN (5.18 % copper and 0.13 % sulfur) to FRM (0.86 % copper and 0.008 % sulfur) nickel oxide, FEN samples consistently show greater specific surface area in comparable conditions. Additionally, the most effective temperature range over which added sulfates mitigate sintering is greater in FEN. This was shown by no significant decrease in specific surface area beyond experimental error across 375-420 °C when treated with 0.4 % sulfates (Figure 24).

Analysis of the pore structure of FRM and FEN nickel oxide samples reduced at 400 and 420 °C (Figure 31) indicates that despite the specific surface area not changing appreciably, there are still surface changes occurring. The pore distribution of the FEN samples do show a shift toward large pore radii with increasing temperature, indicating that some sintering is taking place, but not sufficiently to show a significant decrease in specific surface area. Conversely, in the FRM
sample, the shift toward large pores is more substantial, which is reflected in the decreased specific surface area. This further indicates the significance of copper, which extended the temperature range over which added sulfates effectively maintain specific surface area.

Figure 31 - Specific surface area contributions by pores of various sizes for FRM samples treated with 0.4 % nickel sulfate.

Nickel sulfate was also added to SR TNO, and its effect on specific surface area of post-reduced samples is summarized in Figure 32. Since SR TNO was a potential new nickel oxide source for industry and therefore did not have a standard operating procedure for its treatment and reduction environment, a greater range of nickel sulfate concentrations (0, 0.1, 0.4, 1.0 % nickel sulfate, by mass sulfur) and reduction temperatures (350, 400, 450 °C) were used.
As also shown in section 5.1, the specific surface area of SR TNO decreased approximately linearly with reduction temperature from 350-450 °C. This trend differs from that exhibited by samples treated with nickel sulfate. When reduced at 350 °C, the samples treated with 0.1 % nickel sulfate show a greater specific surface area than untreated samples by ~1 m²/g. When the reduction temperature was 400 °C instead of 350 °C, the specific surface area of the SR TNO treated with 0.1 % nickel sulfate decreased by ~1.1 m²/g; this was a greater change than the untreated samples showed (0.2 m²/g). At 400 °C, the specific surface areas of the untreated sample and the sample treated with 0.1 % nickel sulfate differ by only 0.1 m²/g. When both samples were reduced at 450 °C, the SR TNO samples treated with 0.1 % nickel sulfate showed no significant change compared to when similar samples were reduced at 400 °C, but the untreated samples showed a decrease in specific surface area by 0.5 m²/g.

Figure 32 - Specific surface areas of SR TNO reduced between 350-450 °C.
This implies that interaction with nickel sulfate causes a dichotomy of pore stability: pores that are less stable and pores that are more stable, with little population in between. While untreated samples showed a linear decrease in specific surface area, the decrease for samples treated with 0.1 % nickel sulfate occurred as a step, with little change at reduction temperatures beyond 400 °C.

Similar tests were also done with DR TNO, and the results are summarized in Figure 33. As with SR TNO, DR TNO was a potential new nickel oxide source for industry, and therefore these tests were run over a wider range of sulfate additive concentrations than for FRM and FEN nickel oxides.

Figure 33 - Specific surface areas of DR TNO reduced between 350-450 °C.

As with SR TNO, DR TNO samples showed increasing specific surface areas when greater concentrations of nickel sulfate were added to them. At every comparable temperature,
increasing the concentration of nickel sulfate in the sample yielded a product with a greater specific surface area.

Also like the other nickel oxide types, the specific surface areas of reduced DR TNO decreased with increasing reduction temperature for all concentrations of nickel sulfate. Unlike the other types of nickel oxide, however, the trend is approximately linear for all nickel sulfate concentrations except for 0.1 %. This deviation is due to the specific surface areas of nickel oxide reduced at 400 °C: these values are lower than comparable ones from SR TNO samples. Reduced SR TNO samples showed constant (within experimental error) specific surface areas between 350-400 °C when treated with 0.4-1.0 % nickel sulfate, while the specific surface areas for reduced DR TNO samples were 15 and 18 % lower when reduced at 400 than 350 °C, respectively.

The difference between SR and DR TNO was that DR TNO was roasted a second time. This resulted in the sulfur composition of DR TNO to be 0.005 %, compared to SR TNO, which contains 0.36 % sulfur. However, the discrepancy between a linear decrease with temperature and a stepwise one (implying a dichotomy of pores) cannot be attributed only to sulfur composition, as FRM nickel oxide also has very low (0.008 %) sulfur concentration, and shows a stepped decrease of specific surface area with reduction temperature. A complicating factor is that laterite (SR and DR TNO) and sulfide ores (FEN and FRM) are refined differently to produce nickel oxides. Future work should be done to determine if these refining processes have an effect on factors other than composition, such as which types of crystalline species form.
5.5 – Effect of Sintering on Crystallinity

XRD spectral intensities for characteristic peaks of nickel and nickel oxide correlated well with reduction completion: through reduction, the intensities of nickel oxide peaks diminished, while those of nickel peaks increased. Comparing a spectrum taken of an FEN nickel oxide sample that had been reduced to 28 % completion against one that had been reduced completely, the nickel oxide peaks become barely visible while the nickel peaks become sharper (Figure 34).

Figure 34 - Comparison between FEN nickel oxide samples that were 28 and 100 % reduced.

Black lines above spectra mark NiO peaks, red lines mark Ni peaks.
5.5.1 – XRD analysis of DR TNO

To estimate the average grain sizes of different nickel and nickel oxide crystallites in the samples, FWHM values of various XRD peaks for DR TNO through the reduction process were found. Figure 35 illustrates the trends of many of the nickel oxide peaks as DR TNO was reduced at 450 °C without nickel sulfate additional.

![Figure 35](image)

Figure 35 – FWHM values of XRD peaks of different crystallographic faces of nickel oxide as a function of reduction percentage for DR TNO reduced at 450 °C with no nickel sulfate added. Values are an average of FWHM from the spectra of three granules of each type of sample.

For every crystallographic plane, the FWHM values increased with further reduction. This indicates that the average nickel oxide grain sizes are decreasing in size, causing broader peaks. This was unsurprising, as oxygen is being removed from the nickel oxide lattice, resulting in shrinking and fragmenting nickel oxide grains.
The FWHM values for peaks corresponding to nickel crystallites were also examined, and are summarized in Figure 36.

![Graph showing FWHM values of XRD peaks of different crystallographic faces of nickel as a function of reduction percentage.](image)

Figure 36 - FWHM values of XRD peaks of different crystallographic faces of nickel as a function of reduction percentage for DR TNO reduced at 450 °C with no nickel sulfate added.

These results show shrinking FWHM values with reduction percentages for every crystal face, indicating larger average grain sizes. This indicates that through the reduction process, more crystalline nickel was formed. If nickel atoms were unperturbed by the removal of oxygen from the nickel oxide lattice, none of the examined nickel peaks would have changed. That we do see changes (in the form of decreased FWHM values, or increased average crystallite size) indicates that through the reduction, nickel atoms are mobile, and move together to form crystals. This corroborates the interpretation of sintering throughout this process there were based on surface area measurements.
To determine the effect of added nickel sulfate on crystallite evolution, a similar analysis was done for samples treated with 1.0 % nickel sulfate, and the results are summarized in Figure 37.

Figure 37 – FWHM values of XRD peaks of different crystallographic faces of nickel oxide as a function of reduction percentage for DR TNO reduced at 450 °C with 1.0 % nickel sulfate added prior to reduction. Untreated samples are shown with a grey border, for comparison.

Like nickel oxide samples without nickel sulfate addition, these samples showed increasing FWHM values with increasing reduction percentages, indicating decreasing average grain sizes for each crystal face. While this trend is almost identical to that shown in Figure 35, the FWHM values for the nickel sulfate-treated samples are generally higher when fully reduced. This indicates smaller average grain size, but the cause of this may be due to reduction completion, rather than nickel sulfate addition: the untreated sample was 97 % reduced, while the nickel sulfate-treated sample was 100 % reduced.
The FWHM values for nickel in the DR TNO sample treated with 1.0 % nickel sulfate were also analyzed, and are summarized in Figure 38.

Figure 38 – FWHM values of XRD peaks of different crystallographic faces of nickel as a function of reduction percentage for DR TNO reduced at 450 °C with 1.0 % nickel sulfate added. Untreated samples are shown with a grey boarder, for comparison.

The addition of nickel sulfate had little effect on the grain sizes of all of the crystal faces observed, as Figure 38 is very similar to Figure 36.
5.5.2 – XRD analysis of SR TNO

The effect of intrinsic sulfur on grain size evolution was examined by analyzing SR TNO using the same method as outlined in the previous section. The FWHM values for nickel oxide and nickel peaks in SR TNO without nickel sulfate-addition reduced at 450 °C are outlined in Figures 39 and 40.

Figure 39 – FWHM values of XRD peaks of different crystallographic faces of nickel oxide as a function of reduction percentage for SR TNO reduced at 450 °C without any nickel sulfate addition.

The grain size evolution trends for SR TNO without nickel sulfate appears very similar to those from DR TNO: decreasing grain size through reduction due to shrinking and splitting of nickel oxide crystals.
Figure 40 – FWHM values of XRD peaks of different crystallographic faces of nickel as a function of reduction percentage for SR TNO reduced at 450 °C without any nickel sulfate addition.

The FWHM values for nickel in SR TNO without nickel sulfate-addition are also similar to their DR TNO counterparts. However, the continuous grain size growth that was evident in DR TNO samples is less obvious here: instead, the average grain sizes of each nickel face increased until ~30 % reduction, at which point they remained constant. This is attributed to the additional sulfur impurity present in SR TNO (0.36 %, compared to 0.005 %), which would interrupt nickel crystallite formation.
The effect of nickel sulfate addition to SR TNO on crystallite evolution was also tested, and the results are summarized in Figures 41 and 42.

Figure 41 – FWHM values of XRD peaks of different crystallographic faces of nickel oxide as a function of reduction percentage for SR TNO reduced at 450 °C without any nickel sulfate addition. Untreated samples are shown with a grey boarder, for comparison.

The trend of average nickel oxide grain size decreasing with reduction remained for the SR TNO sample with nickel sulfate added. However, the addition of nickel sulfate caused the FWHM values to increase higher for a completely reduced sample. Unlike the DR TNO comparison in section 5.3.1, both of these samples were reduced to 100 % completion (as determined by mass loss). This implies that the addition of nickel sulfate does cause nickel oxide grains to become smaller.
There are two potential causes for this. Nickel sulfate may allow for nickel oxide samples to reduce further in a given amount of time – mass loss measurements would not be able to discern a 99.9 %-reduced sample from a 99.99 %-reduced sample. Since nickel sulfate is thought to maintain porous networks within the sample, it is feasible that these pores would better facilitate reduction in the late stages of the reaction. A second way that nickel sulfate could be responsible for the smaller nickel oxide grain sizes would be through integration within the lattice. Nickel sulfate decomposes into nickel sulfide at these temperatures, which may interrupt the nickel oxide lattice.

If the latter case were true, one would expect the nickel sulfide to also interrupt the nickel lattice, causing grain sizes of nickel to decrease with the addition of nickel sulfate. To test this, a similar analysis was done on the peaks resulting from nickel crystallites, and is shown in Figure 42.
Figure 42 – FWHM values of XRD peaks of different crystallographic faces of nickel as a function of reduction percentage for SR TNO reduced at 450 °C without any nickel sulfate addition. Untreated samples are shown with a grey boarder, for comparison.

The grain sizes of SR TNO with 1.0 % nickel sulfate added are very similar to when no nickel sulfate was added. Coupled with Figure 41, this implies that the nickel oxide grain size decrease in these samples was caused by further reduction, and not by nickel sulfate interrupting nickel oxide lattices. Like Figure 40, Figure 42 also shows an initial decrease in FWHM values, followed by relatively constant values. This further implies that the intrinsic sulfur in SR TNO interrupts nickel crystal formation.

For ease of comparison, the FWHM values corresponding to the 111 peaks for nickel oxide are shown in Figure 43. The 111 peak was chosen because of its high intensity on these XRD spectra and relatively good reproducibility.
Figure 43 – FWHM values of nickel oxide 111 peaks for SR and DR TNO through reduction.

At < 40 % reduction completion, all of the FWHM values were low, and experimentally indistinguishable from each other, increasing by an average of <1 % from 0-10 % to 25-40 %.

From 25-40 % to 65-70% reduction, the average FWHM increased by 6 %, and the average standard deviation between samples of the same kind (measured in triplicate) increased by 16 %.

The final four points show a different trend: samples reduced to 97-99 % showed a small increase in FWHM values compared to those reduced to 65-70 % completion. Conversely, samples that were reduced to 100 % completion showed an increase of an average of ~40 %, with greater variability between samples. This demonstrates that the greatest changes in nickel oxide crystallinity occur in the final % of reduction. It also implies that, through reduction, nickel oxide crystallite islands are consumed in a relatively sequential way: nickel oxide islands are lost completely before others begin reducing.
A similar analysis was done on the nickel 111 FWHM values to determine whether the formation of nickel crystallites occur differently than the loss of nickel oxide crystallites, and is shown in Figure 44.

![Figure 44](image.png)

Figure 44 – FWHM values of nickel 111 peaks for SR and DR TNO through reduction.

Like the nickel oxide 111 FWHM values, there is little change observed in the middle part of the reduction. This indicates that nickel crystallites grow to a certain size, then remain at that size through the remainder of the reduction process. A slightly higher average FWHM value occurs at 5-10 % reduction, indicating that the ratio of small to full-size crystallites was still fairly large.

An alternative interpretation of the constant Ni FWHM values at more complete reductions, and NiO FWHM values for less complete reductions, is that the FWHM is due to mostly instrumental broadening. Currently, our method cannot distinguish between these two possibilities. Analysis with an instrument/setup with less instrumental broadening would answer this question.
6 – Conclusions

The specific surface areas of nickel oxides with varying impurity percentages and elemental compositions were analyzed at varying reduction completions, reduction environments, and nickel sulfate addition. These final surface areas increased with nickel sulfate addition (from 0.1-1.0 \% by mass sulfur), decreased with increasing reduction temperature, and increased with increasing intrinsic copper content.

The specific surface area of samples increased by approximately two orders of magnitude during the reduction process. This was caused by oxygen atoms leaving the nickel oxide lattice, causing the initial generation of micropores. Gas sorption isotherms indicated a lack of micropores for samples of any reduction percentage. This indicates that pore collapse and/or merger was taking place, and occurred at a sufficient rate to cause an unmeasurably small surface area contribution from micropores. This was further tested by reducing samples, then continuing to heat a subset of them for two additional hours. The samples heated for additional time exhibited lower specific surface areas by 10, 40, 10, and 2 \% for samples treated with 0, 0.1, 0.4, and 1.0 \% NiSO\textsubscript{4}, respectively. This supported the theory of sintering being a mechanism for micropore elimination.

Through the addition of nickel sulfate to nickel oxide samples before reduction, nickel sulfide was formed during reduction, and was found to increase the specific surface areas of these samples. Through pore analysis, it was found that this occurred due to a greater surface area contribution from smaller (d = 10-40 nm) mesopores, indicating that less sintering occurred. This also indicates that the nickel sulfate, initially present as a coating about 100-1000 layers thick on the nickel oxide, was mobile – the sulfur was found not to be concentrated on the surface of the sample after reduction\textsuperscript{16} Since sulfur had such a large effect on the specific
surface area, it is very likely that the sulfur was mobile, and mitigated sintering throughout the sample, rather than just near the surface present prior to reduction.

Lower reduction temperatures were also found to yield higher specific surface areas. Although the reduction process occurred slower for lower temperatures, less sintering also occurred: FRM and FEN nickel oxides decreased from an average of 7.1 to 6.1 m²/g, and DR and SR TNO from 4.5 to 3.2 m²/g. This was expected, as sintering varies linearly with time, but exponentially with temperature.\textsuperscript{53}

The presence of copper impurities was also found to yield greater specific surface areas. This was surprising, as copper-nickel mixtures all have lower melting points (which is often correlated with sintering temperature) than pure nickel. Copper impurities may have disrupted the formation of nickel crystals via sintering, increasing the surface’s roughness, thus increasing the specific surface area. The pore size distributions of samples with included copper impurities showed a greater surface area contribution from small (50-200 nm) pores than comparable samples with little copper composition.

The presence of sulfur impurities did not have a noticeable effect on specific surface areas. The specific surface areas of fully reduced DR and SR TNO had mean difference of only 0.2 m²/g across all reduction conditions, despite the large difference in sulfur concentrations (0.005 % and 0.36 %, respectively). XRD analysis showed that grain sizes of nickel on reduced SR TNO were smaller than DR TNO, which indicated that intrinsic sulfur did mitigate the formation of longer-range crystalline nickel.

There are several studies that would be useful in further characterizing the reduced nickel oxide samples, thus improving our understanding of the reduction process. XRD analysis of FRM and
FEN nickel oxides would be able to determine whether the copper in FEN has a similar effect on nickel crystallite formation through reduction. Additionally, elemental analysis of reduced DR and/or SR TNO sample with and without nickel sulfate addition would determine whether nickel sulfate facilitates more complete reduction. The answer to this would be useful in interpreting the average grain size measurements, to determine whether the larger grain sizes evident when nickel sulfate was added were caused by more complete reduction or another factor.

There were some questions that appeared over the course of this work that have yet to be answered. Experimental specific surface areas that varied with mass for the same sample would imply that only noise was being measured. However, FRM, FEN nickel oxides and DR TNO all showed different decaying functions with mass (specific surface area = x/m, where x = 2.1, 1.2, and 0.7, respectively). This implies that sample-specific information is still being measured. Analyzing these samples using krypton gas-sorption analysis would allow for their specific surface areas (which are too low for nitrogen gas-sorption analysis to measure) to be determined. A correlation between x and the samples’ true specific surface areas may allow for low samples with surface areas to be measured with nitrogen adsorption analysis.

Evaluation of the available, reactive surface area of nickel oxide during reduction would also be useful. By determining the total surface area of a sample via nitrogen adsorption analysis, then determining the surface area of only the nickel portion of the sample, the surface area of the available nickel oxide could be found. This is the area that limits the reduction reaction, and if certain reduction conditions enlarge this area, the reduction could be completed more quickly. This would be of great interest industrially, as faster reduction times would mean not only faster turnover at that step, but also less sintering. The latter would cause a faster turnover during the carbonylation/decarbonylation stage.
7 - References


<http://www.vale.com/canada/EN/business/mining/nickel/Pages/default.aspx>


14 - De Groot, P.; Coulon, M.; Dransfeld, K. *Surf. Sci.* 94, 204, **1980**.


21 - Quantachrome. *Powder Tech Note* 52. **2011**.


25 - Pierce, C.; Ewing, B. *J. Phys. Chem.* 68, 2562, **1964**.


28 - McClellan, A.; Harnsberger, H. *J. Colloid Inter. Sci.* 23, 577, **1967**.


49 - Richardson, J.; Scates, R.; Twiff, M. *App. Cat. A: Gen.* 246, 137, **2003**.


52 - Okamoto, H. *J. Phase Eq. Diff.* 30, 123, **2009**.