SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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AN INVESTIGATION ON THE COUPLED GAS-SOLID REACTIONS USING MATLAB: NICKEL OXIDE REDUCTION BY CARBON

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled: **“An Investigation on the Coupled Gas-Solid Reactions Using MATLAB: Nickel Oxide Reduction by Carbo**n**”**. I also declare that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body or university.

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Date : 22 June 2017

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LIST OF SYMBOLS

A	Reactant Gas
B	Product Gas
C_p	Specific Heat Capacity
D_{AB}	Binary Diffusivity of Gas A and B
σ	Stefan-Boltzmann Constant
ε	Thermal Emissivity
E_a	Activation Energy
G	Gas Flow Rate
H	Standard Enthalpy of Reaction
I_D	Collision Integral of Diffusion
k	Thermal Conductivity
K_{eq}	Equilibrium Constant
M_A	Molecular Weight of Component A
M_B	Molecular Weight of Component B
Nu	Nusselt Number
P_A	Partial Pressure of A
P_B	Partial Pressure of B
Pr	Prandtl Number
R	Gas Constant
R_{wp}	Weighted Profile Factor
ρ	Density

ρ_A	Density of Species A
ρ_B	Density of Species B
ρ_c	Density of Species C
n_A	Molar Rate Transport for Component A
n_B	Molar Rate Transport for Component B
n_C	Molar Rate Transport for Component C
r_{AB}	Collision Diameter
r_i	Position of Reaction Interface
Re	Reynold Number
R_o	Radius of Pallet
q_{conv}	Convective Heat Transfer
q_{sens}	Sensible Heat Transport
q_{rad}	Radiation Heat Transfer Coefficient
Sc	Schmidt Number
Sh	Sherwood Number
T_o	Initial Temperature
$T^{(c)}$	Core Temperature
$T^{(g)}$	Gas Temperature
$T^{(p)}$	Product Temperature
$T^{(s)}$	Surface Temperature
e_p	Porosity of Product
e_r	Porosity of Reactant
X_R	Extent of Reduction
X_o	Percentage of Weight Reduction

W_i	Initial Weight
W_f	Final Weight
μ	Viscosity
Ʈ	Tortuosity Factor

LIST OF ABBREVATIONS

ANOVA	Analysis of Variance
Ar	Argon
C	Carbon
CHNS	Carbon Hydrogen Nitrogen Sulphur
CMC	Carboxy methyl Cellulose
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DOE	Design of Experiments
EDX	Energy Dispersive X-Ray
ICSD	Inorganic Crystal Structure Database
Ni	Nickel
NiO	Nickel Oxide
PSA	Particle Size Analysis
RSM	Response Surface Methodology
SCM	Shrinking Core Model
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

SUATU PENYIASATAN TENTANG DUA REAKSI GAS-PEPEJAL MENGGUNAKAN MATLAB: PENURUNAN NIKEL OKSIDA DENGAN KARBON

ABSTRAK

Nikel adalah satu pemangkin perindustrian yang mempunyai beberapa aplikasi penting. Oleh itu, adalah penting untuk menghasilkan suatu proses penurunan yang lebih mudah dan berkesan dalam penghasilan nikel. Dalam kajian ini, penurunan nikel oksida dengan karbon dilakukan dengan menggunakan rekabentuk eksperimen (DOE) untuk parameter yang berlainan. Parameter yang dikaji termasuk suhu penurunan (800^{o}C ke 1000^{o}C), masa penurunan (1 jam ke 2 jam) dan nisbah molar C kepada NiO (0.5 ke 1.5). Model pengecutan teras untuk keadaan isoterma dan keadaan bukan isoterma telah dibentuk dengan menggunakan perisian MATLAB untuk mengkaji pemodelan kinetik proses penurunan untuk mendapatkan tahap penurunan dan kadar tindak balas. Model-model ini dibentuk daripada sifat-sifat fizikal dan sistem tindak balas termodinamik yang tidak bersandar, dan sifat-sifat yang diukur melalui eksperimen. Tahap penurunan yang diramal daripada hasil penerbitan pemodelan kemudiannya dibanding dengan keputusan eksperimen. Berdasarkan analisis DOE, masa penurunan berbanding dengan parameter lain menunjukkan kesan paling ketara ke atas peratusan pengurangan berat dan tahap penurunan. Analisis SEM dan XRD juga dilakukan untuk memastikan proses penurunan telah dijalankan dengan berkesan. Daripada kajian ini, tahap penurunan meningkat dengan peningkatan suhu penurunan, masa penurunan dan nisbah molar C kepada NiO. Tahap penurunan tertinggi dalam kajian ini adalah 77.88%. Hasil ini dicapai dengan suhu penurunan pada 1000^{o}C selama 2 jam penurunan dan nisbah molar C kepada NiO pada 1.5. Daripada keputusan pemodelan kinetik, didapati bahawa model pengecutan terus untuk keadaan isoterma dan keadaan bukan isoterma menunjukkan aliran yang serupa dan tahap penghampiran bererti yang berkesan dengan keputusan eksperimen.

AN INVESTIGATION ON THE COUPLED GAS-SOLID REACTIONS USING MATLAB: NICKEL OXIDE REDUCTION BY CARBON

ABSTRACT

Nickel is an important industrial catalyst and has several important applications. Thus, it is important to discover a simpler and more effective reductive process to produce nickel. In this study, nickel oxide reduction by carbon is performed experimentally using Design of Experiment (DOE) in variation of parameters. The parameters studied are reduction temperature (800^{o}C to 1000^{o}C), reduction time (1 hour to 2 hours) and molar ratio of C to NiO (0.5 to 1.5). Shrinking core model for isothermal and non-isothermal conditions is employed using MATLAB programming for the kinetic modelling of reduction process to determine the extent of reduction and the reaction rate. The models are developed from independently measured physical and thermodynamic properties of the reaction system, and experimentally measured properties. The predicted extent of reduction is then compared with the experimentally measured results. From the DOE analysis, as compared to other parameters, reduction time shows most significant effect on the percentage of weight reduction and extent of reduction. SEM and XRD analysis are also done to ensure the reduction process has taken place effectively. From the study, the extent of reduction increases with increasing reduction temperature, reduction time and molar ratio of C to NiO. The highest extent of reduction in this study is 77.88%, which is achieved at reduction temperature of 1000^{o}C, 2 hours of reduction time and molar ratio of C to NiO

at 1.5. From the result of kinetic modelling, both isothermal and non-isothermal shrinking core model show similar trend and significant closeness to the experimental result.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Nickel is an important industrial catalyst and has been used over a long period due to its properties such as thermal resistance, chemical activity and magnetism (Manukyan et al., 2015, Kim et al., 2011). Some of the important application of nickel include stainless steel production, superalloys for high temperature application, batteries, catalysts and fuel cells (Manukyan et al., 2015, Kim et al., 2011, Richardson et al., 2003, Rodriguez et al., 2002, Alizadeh et al., 2007). In general, nickel is typically produced from reduction of nickel oxide. Nickel oxide is a green cubic crystal with density of 6.72 g/cm^3 and insoluble in water (Patnaik, 2002).

Many methods to produce nickel powder has been proposed and studied but many of them are not economically feasible (Kim et al., 2011, Utigard et al., 2005). Hence, it is important to develop a less expensive and more effective process in nickel oxide reduction. In this study, the method used is reduction of nickel oxide by carbon as carbon is relatively cheap and easily available. Many types of mechanism for nickel oxide reduction by carbon has been proposed. According to Lin (1975), Sharma et al. (1997), Jagtap et al. (1992), the reaction start initially with solid state reaction between nickel oxide and carbon. As the reaction proceed and CO and CO_2 gas has been produced, coupled gas solid reaction between NiO and CO and between C and CO_2 will be the predominant reaction.

For the kinetic modelling of nickel oxide reduction by carbon, coupled gas solid reactions is being investigated. Gas solid reaction system is the interaction of a solid particle with a moving gas stream. This type of reaction is very common to chemical engineering process and process metallurgy (Lin, 1975). In the formulation, the kinetics for both of the reactions, porosity and gas diffusion are being taken into consideration.

In this study, there are 3 parameters being studied using Design of Experiment (DOE) which are reduction temperature, reduction time and molar ratio of C to NiO. The reduction process is carried out at temperature range between 800^{o}C to 1000^{o}C for period of 1 hour to 2 hours under atmospheric pressure. Kinetic models are employed to determine the kinetic mechanisms of reduction of nickel oxide at different parameters in order to examine the feasibility of reducing nickel oxide using carbon powder.

1.2 Problem Statement

Nickel is used extensively in stainless steel production (more than 60% of primary nickel consumption in the world), superalloys for high temperature applications, aerospace alloys, high temperature nickel-chromium alloys, electrolytic plating, electroless plating, cupronickel alloys and naval brasses (Alizadeh et al., 2007). Some researchers have studied to make metal powder of Ni using various methods, but many of them are not economically feasible. Therefore, there is a need to develop simpler and more efficient reductive process for NiO powders (Kim et al., 2011).

Reduction of nickel oxide (NiO) by carbon has been studied by a number of researchers, and several theories have been put forth to explain the mechanism and kinetics of the reaction. However, the mechanism and kinetics of the reaction between nickel oxide and carbon are not completely understood as there are conflicting views (Sharma et al., 1997). Besides, most of the mathematical models proposed to explain behavior of these systems are based on restrictive assumptions, such as overall reaction controlled by one slow reaction (Lin, 1975). Hence, the mechanisms and kinetics of the reaction need to be concretely worked out using effective mathematical modelling and simulation.

In this study, NiO powder was reduced to Ni using pellet of NiO mixed with carbon powder at selected parameters: reduction temperature, reduction time and molar ratio of carbon to nickel oxide. It was thought of interest to study the changes produced in NiO and carbon during the reaction of their powder mixture, in order to get a deeper insight into the factors influencing the mechanism of the reaction. By using appropriate kinetic modelling, the reaction can be mathematically modelled and simulated with advance simulation programming tools and this will ease future lab work.

1.3 Objectives

The objectives of this project are:

- To determine the best combination of treatment for parameters such as reduction temperature, reduction time and molar ratio of carbon to nickel oxide using Design of Experiment (DOE).
- To model mathematically the kinetic mechanisms of nickel oxide reduction by carbon with different parameters: reduction temperature, reduction time and molar ratio of carbon to nickel oxide using kinetic modelling software.
- To compare and investigate the predicted results of analytical kinetic modelling with DOE experimental results for different parameters.

1.4 Scope of Project

In this study, several parts including experimental work, statistical analysis and kinetics simulation are being done. First, the raw NiO and graphite powder are being sent for raw material characterization such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX), Particle Size Analyzer (Sympetec), X-Ray Fluorescence (XRF) and Thermogravimetric Analysis (TGA) for determination for sample morphology, purity and other properties. Then the samples will undergo carbothermal reduction in a tube furnace and the weight loss and extent of reduction are recorded and calculated. After that, the reduced product are sent for characterization such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) and CHNS Elemental Analyzer. Any changes in the phases and morphology will be determine. For statistical analysis and kinetic simulation, Design Expert v8.0.6 is used to construct the matrix of DOE and study on the equations and parameters are being conducted. After that, the predicted extent of reduction and experimentally measured results of the carbothermal reduction of nickel oxide are compared and analyzed.

1.5 Outline

In this thesis, the brief introduction and overview of the study will be discussed in Chapter 1, which include problem statements, project objectives and scope of the project. Chapter 2 will be the literature review in which related researches and studies that has been done are discuss in relate to current study. In Chapter 3, methodology and kinetic model with some calculations for the constants are discussed. The results and analysis from the experimental work will then discussed in Chapter 4. Next, conclusion and recommendations are highlighted in Chapter 5 while references will be in Chapter 6.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Nickel oxide or also known as nickelous oxide, is green in colour, and occurs in nature in the mineral, bunsenite. Nickel oxide is green cubic crystals, has density of 6.72 g/cm^3, Mohs hardness 5.5 and melting point of 1955^{o}C. It is used mainly in ceramic industry for making frit, ferrites and colouring porcelain. It is also important in preparation of many nickel salts and as electrode in fuel cells. Elemental composition of nickel oxide is around 78.58% nickel and 21.42% oxide (Patnaik, 2002).

By heating nickel oxide with hydrogen, carbon or carbon monoxide, it can be reduced to metallic nickel. Nickel is an important industrial catalyst and is typically produced by reduction of nickel oxide. The most important applications of nickel involve its alloys which are used to in various reaction vessels, aerospace components and plumbing parts (Patnaik, 2002). Nickel containing products has an advantages over other materials as it possess better corrosion resistance, greater toughness, more strength and a range of special magnetic and electronic properties. Due to these properties, the use of nickel is extensive in the production of stainless steel (more than 60% of primary nickel consumption in the world) (Alizadeh et al., 2007).

The literature reviews on the kinetics and mechanism of reduction of nickel oxide by carbon and other reducing gases and the possible parameters that affect the reduction is discussed in this chapter. Besides, Boudouard reaction and its mechanism for the study is also being discussed. In this chapter, the literature review also include the study on the model construction and the kinetic models employed in gas-solid reactions.

2.2 Reduction of Nickel Oxide

Nickel can be synthesized or produced from nickel oxide by reduction with various reductants. Lin (1975) studied the reaction between nickel oxide and carbon monoxide in the temperature range 847 – 1099^{o}C and separate experiments are conducted to study the effect of reaction temperature, pellet size, molar ratio of carbon to nickel oxide and other parameters on the overall conversion. From the study, the reaction of nickel oxide with carbon monoxide at high temperature was diffusional controlled and the reaction rate constant was found to be given by $k = 4.057 \times 10^{-3} \exp(-4168/R_gT)$ cm/sec (Lin, 1975).

Sharma et al. (1997) studied on the reduction of nickel oxide by carbon and kinetic studies on their interaction. From their study, reduction of nickel oxide is described by first order plots, and have an activation energy of 75 kcal/mol. They also found out that the rate of diffusion of carbon atoms through nickel is not the rate controlling step in the reduction of nickel oxide. The activation energy for diffusion of carbon atoms through nickel is about 33 kcal/mol (Sharma et al., 1997), which is much lower compared to the activation energy for the reduction reaction.

Nickel Oxide Reduction by Hydrogen: Kinetics and Structural Transformations is studied by Manukyan et al. (2015). The reduction kinetics of bulk NiO crystals by hydrogen and the corresponding structural transformation is studied in the temperature range 543 – 1593K. From their study, at lower temperature (543 – 773K), non-complete reduction results in product with complex porous networked structure due to low nucleation rates and slow outward diffusion of water molecules. At high temperature (above 1173K), instantaneous nucleation of Ni on the NiO crystal surface is caused by the increased nuclei density, followed by rapid growth of Ni phase. The kinetics of the process shows some distinctive features and the activation energy over the large temperature difference varies by an order of magnitude, between 10 and 150 kJ/mol. The large variation in activation energy may be explained by the lack of consistency between NiO samples, characterization techniques and other experimental parameters (Manukyan et al., 2015).

Krasuk and Smith (1972) studied on the kinetics of reduction of nickel oxide with CO. The initial rates were measured at atmospheric pressure and temperatures from 566 to 796^{o}C. The reaction appeared to be first order in carbon monoxide and the rate constants indicated an activation energy of 47 kcal/g-mol.

Reduction of nickel oxide powder and pellet by hydrogen is studied by Chatterjee et al. (2012). The kinetic of reduction of NiO powder and pellets were studied at temperature range of 573K to 973K and hydrogen flow rate of 100 to 200 cc/min. The reduction of NiO powder reaches 70-80% reduction while reduction of NiO pellet reaches 95% reduction. The activation energy for reduction of NiO powder and pellet is 20.14 kJ/mol and 19.21 kJ/mol respectively.

Utigard et al. (2005) studied the reduction kinetics of Goro nickel oxide using hydrogen. In the temperature range from 400 to 600^{o}C, the rate of reduction increased with increasing temperature and the activation energy was found to be 90 kJ/mol. The reduction rate decreased noticeably above 600^{o}C and suddenly becoming extremely fast above 950^{o}C. They suggested that the reduction process stopped at some point, followed by the penetration of hydrogen deeper into the NiO particle. According to Utigard et al. (2005), the slowdown in the rate may be due to grain growth of the nickel formed.

Besides carbon, carbon monoxide and hydrogen, methane is also used in study of nickel oxide reduction. In 2007, Alizadeh et al. (2007) carried out kinetic study of nickel oxide reduction by methane at the temperature range of 600 – 725^{o}C at atmospheric pressure. Based on the study, the reduction of nickel oxide by methane is first order reaction with respect to methane concentration, and the activation energy is found to be 63.9 kcal/g-mol.

2.3 Boudouard Reaction

The Boudouard reaction, which is discovered by Octave Leopold Boudouard in 1905, is the redox reaction of a chemical equilibrium mixture of carbon dioxide and carbon monoxide at a given temperature. It is the disproportionation of carbon dioxide and graphite into carbon monoxide or vice versa. The Boudouard Reaction is described in the Equation 2.1.

$$CO_2 + C \rightleftharpoons 2CO \qquad \text{(Equation 2.1)}$$

The reaction is highly endothermic, thus equilibrium lies far to the left, with CO_2 being the more favored product. However, at high temperature (above 700^{o}C), the free energy becomes negative, which favors the formation of CO from CO_2 (Hunt et al., 2013, Ergun, 1956, Marchon et al., 1988). The Boudouard reaction is an important process in blast furnace. As an example, as the reaction between solids are typically very slow, thus the reduction or iron oxide is not achieved by carbon but by carbon monoxide. Then, most of the carbon dioxide produced in the reduction of oxides will be converted back to carbon monoxide by the Boudouard reaction if equilibrium is obtained (Lindstad et al., 2004). Similarly, in this study, the reduction of nickel oxide is performed at temperature range of 800 – 1000^{o}C. At this temperature range, carbon dioxide produced by reduction of nickel oxide will react with graphite and produce carbon monoxide as a reactant gas for nickel oxide reduction.

The Boudouard reaction has been studied by many researcher and various reaction mechanism has been proposed, but the Langmuir-Hinshelwood type rate expression is generally accepted (Rao and Jalan, 1972, Ergun, 1956, Gadsby et al., 1946). The expression is shown in Equation 2.2:

$$Rate\ of\ reaction = \frac{k_1 P_{CO_2}}{1+k_2 P_{CO}+k_3 P_{CO_2}} \qquad \text{(Equation 2.2)}$$

Where P_{CO2} = partial pressure of CO_2

P_{CO} = partial pressure of CO

$k_{1,}$ $k_{2,}$ k_3 = reaction rate constants, function of one or more than one primary rate constant

2.4 Experimental Parameters

2.4.1 Effect of Reduction Temperature

From the previous work on nickel oxide reduction, it is shown that the reduction rate and extent of reduction increases as temperature increases (Sharma et al., 1997, Lin, 1975, Budarin et al., 1998, Manukyan et al., 2015, Kim et al., 2011).

Lin (1975) studied the reaction of nickel oxide and carbon in the carbon dioxide – carbon monoxide environment at the temperature range of 850^{o}C to 954^{o}C. The experimental curves shows that higher temperature has a higher reaction rate but once the conversion is greater than 60%, the experimental results show a decrease in reaction rate, especially at higher temperatures. Lin (1975) also suggested that rate constant, k in the study is related to the reaction temperature by Equation 2.3 below. From the equation, it can be seen that as the temperature increases, the rate constant will also increase.

$$k = 272205\,\exp\left(-\frac{49142}{RT}\right) \qquad \text{(Equation 2.3)}$$

Manukyan et al. (2015) investigated on the kinetics and structural transformation on nickel oxide reduction by hydrogen in the temperature range of 543 – 1593K. They have found that there are two distinctive temperature intervals where the reaction kinetics and product microstructures are different. At low temperatures (543 – 773K), the kinetic curves have long induction times and result in incomplete conversion due to formation of complex polycrystalline Ni/NiO porous structure. On the other hand, for high temperatures (1173 – 1593K), no induction period was observed and full reduction of NiO to Ni is achieved within seconds.

According to Budarin et al. (1998), there is a dependence of the rate of reduction of NiO on the temperature with different extents of reduction of the sample. They suggested that the increase in the rate with increasing temperature may be related to the increase in the entropy of activation and increase in the number of active sites in the nickel oxide samples.

2.4.2 Effect of Reduction Time

From the study of Kim et al. (2011) on preparation of Ni powders fabricated by various reductive gas, the reduction rate of NiO was found to be increased with increasing reaction time, and the rate was sharply increased for 1 hour, but the slope was shown to be slowing down after that. Figure 2.1 shows the graph on the reduction rate of NiO as a function of temperature and reaction time.

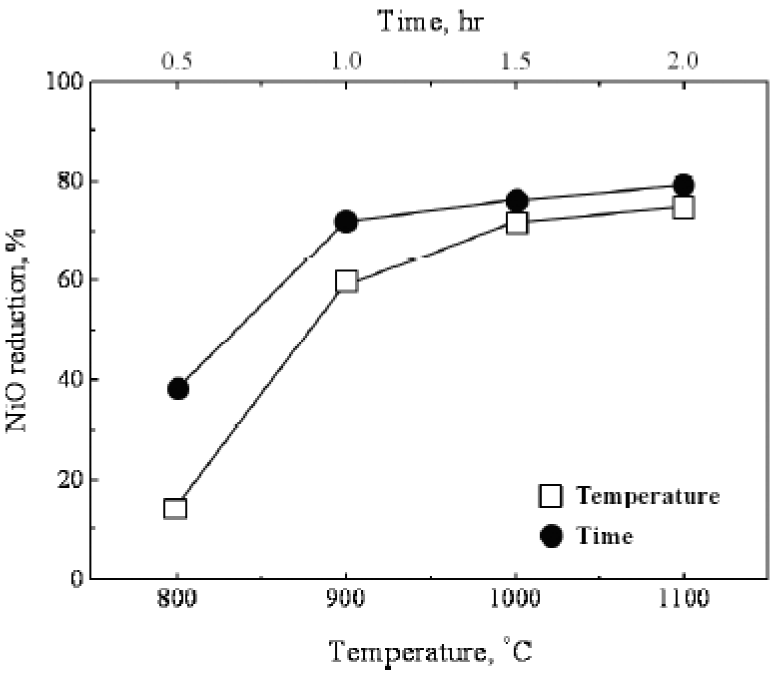


Figure 2.1: NiO reduction as a function of time and temperature (Kim et al., 2011)

According to Lin (1975), at the initial stage of nickel oxide reduction, the reaction is very slow. This is due to the temperature of the pellet lower than that of the environment. As the pellet reaches its environment temperature, the reaction will proceed quickly but at conversion of NiO to Ni greater than 60%, a decrease in reaction rate will occur. The decrease in reaction rate is attributed to the sintering of metal product which reduces the effective diffusivity (Seth and Ross, 1966, Szekely and Evans, 1970). The temperature at which a material starts to sinter for nickel oxide and nickel is 933K and 1223K respectively. Thus, under experimental conditions, sintering of nickel is much more extensive than sintering of nickel oxide.

2.4.3 Effect of Reductant and its Molar Ratio

The effect of molar ratio of carbon to nickel oxide in reduction of nickel oxide is studied by Lin (1975) and Kim et al. (2011). In both of the studies, increasing molar ratio of carbon led to increase reduction ratio of NiO. In the study by Kim et al. (2011), molar ratio of carbon of carbon is altered from 0.7 to 1.5. At carbon molar ratio of 0.8, the reduction ratio of NiO was around 60% while carbon molar ratio of 1.5 shows an increase of NiO reduction up to 90%.

Similarly, Lin (1975) studied the effect of carbon molar ratio to the NiO reduction at molar ratio of 0.1, 0.2, 0.3 and 0.5 with other parameters kept constant. From the study, it is shown that for carbon molar ratio of 0.1, the overall conversion of NiO to Ni was only 60% after 450 seconds while for molar ratio of 0.5, the overall conversion reached 90% at 200 seconds.

As discussed in previous section and as proposed by Lin (1975), the nickel oxide reduction by carbon occur through the following reaction scheme:

$$CO_2 + C = 2CO \qquad \text{(Equation 2.4)}$$

$$2CO + 2NiO = 2CO_2 + 2Ni \qquad \text{(Equation 2.5)}$$

Hence, an increase in the molar ratio of carbon to nickel oxide will increase the concentration of carbon monoxide close to pellet center and consequently, the reduction rate of nickel oxide is enhanced. Nevertheless, to obtain a higher reduction rate, the carbon content should only be increased up to a certain limit as when the carbon content is larger than a certain limit, the pellet will collapse during the reaction (Lin, 1975).

Besides molar ratio, types of carbon source will also have different effect on the reduction of nickel oxide as each of the carbon sources has different activation energy and works at different temperature range. Table 2.1 below shows a summary of materials used and their respective activation energies.

Table 2.1: Summary of carbon source used in reduction (Lin, 1975)

Researcher	**Activation energy (kcal/g-mol)**	**Carbon source**	**Temperature range (ºC)**
(Gadsby et al., 1946)	28.7	Coconut shell charcoal	700 – 830
(Lewis et al., 1949)	54.3	New England coke	802 – 1093
(Long and Sykes, 1950)	56.8	Coconut shell charcoal (impurities free)	700 – 884
(Wu, 1949)	56.6	Electron carbon	871 – 1085
	67.8	New England coke	817 – 1058
(Ergun, 1956)	59	Activated carbon	700 – 1400
		Activated graphite	
		Ceylon graphite	
(Grabke, 1973)	78	Graphite	900 – 1100
(Rao and Jalan, 1972)	79.6	Carbon black	839 – 1050
(Walker et al., 1959)	88 (Average value)	Graphitized carbon black graphite "wear dust"	N/A
(Lin, 1975)	63	Carbon black	890 – 1098

2.4.4 Effect of Gas Flow Rate

The gas flow rate has significant effect toward the extent of reduction. If the consumption of gas for reduction process is higher than the flow of the gas provided, the extent of reduction will be limited by the gas flow. Thus, gas flow rate need to be high enough to overcome the gas diffusion resistance (Bardi et al., 1987).

Study by Chatterjee et al. (2012) on reduction of nickel oxide powder and pellet by hydrogen shows that for both powder and pellet, the rate and extent of reduction increased with increasing hydrogen flow rate from 100 to 200 cc/min. This indicates that there was some difficulties of the reducing gas to diffuse through the powder sample, due to the gas stagnation in the crucible. Thus, the removal of product gas and increasing of reducing potential of reacting gas is enhanced by the increase in the hydrogen gas flow rate. The increase in flow rate supports a rate controlled by diffusion through gas film (Chatterjee et al., 2012).

According to Feinman et al. (1965), gas flow rate has a significant effect on the kinetics of reduction of iron oxide pellets with hydrogen. From the study, it can be seen that the rate of reduction increases with increasing flow rate until above a flow rate of about 6 g-mole/cm^2-h where the effect of flow rate on the reduction is less significant. The effect of flow rate on the reduction is shown on Figure 2.2.

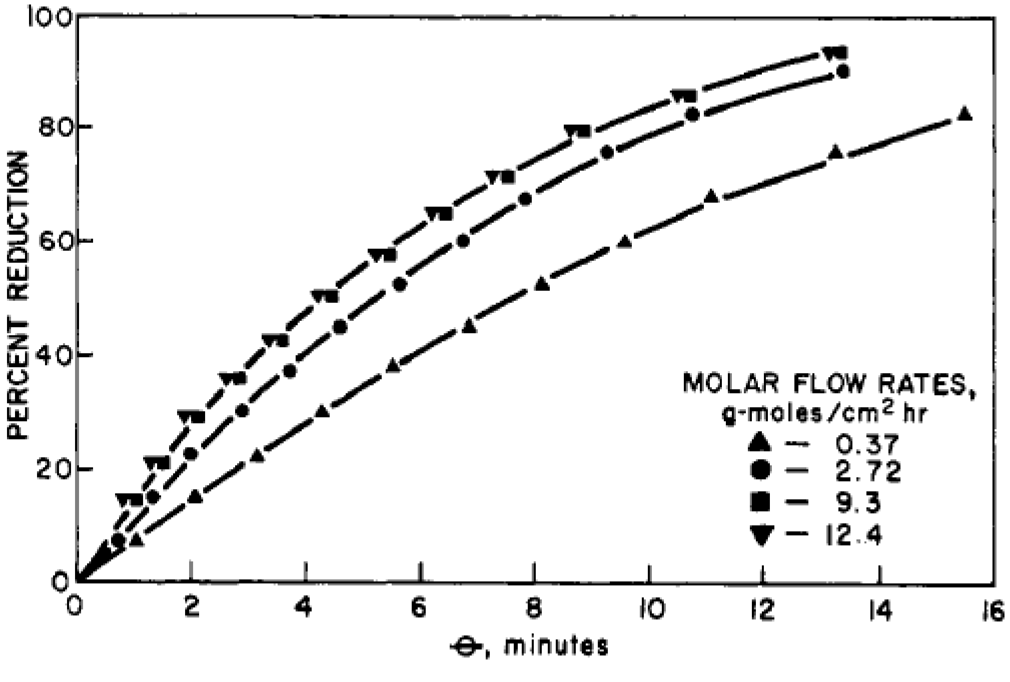


Figure 2.2: Effect of flow rate on reduction curve at 927°C (Feinman et al., 1965)

2.4.5 Effect of Pellet Size

In the study by Lin (1975), the pellet size was incorporated into the modified Thiele modulus where it is shown that pellet size has a proportionality relationship with Thiele modulus. Thus, it is said that the effect of pellet size on the overall conversion is similar to that of Thiele modulus. As pellet size decreases, the value of Thiele modulus decreases and the concentration profile of CO and CO_2 become less steep and as a result, the reduction rate of nickel oxide is increased. By this, the net effect of reducing pellet size is to increase the overall conversion rate. Thus, in order to obtain the highest rate of reduction of nickel oxide, the pellet size of the sample should be reduced as much as possible (Lin, 1975). Figure 2.3 shows the effect of pellet size on overall conversion studied by (Lin, 1975).

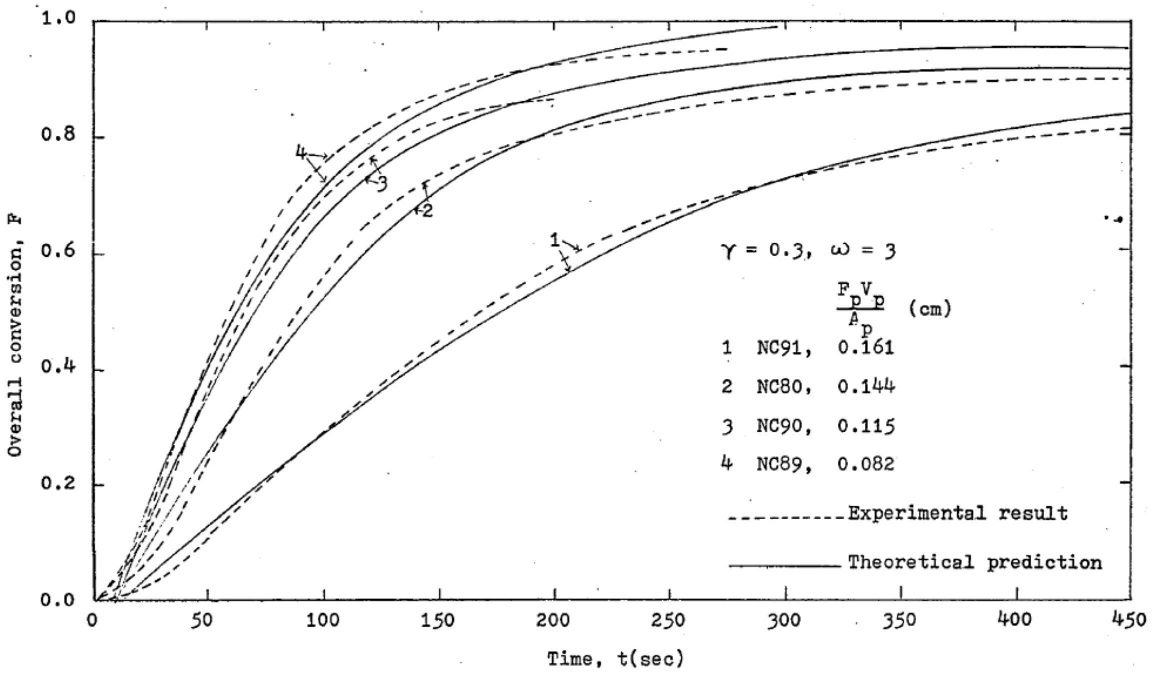


Figure 2.3: Effect of pellet size on overall conversion as a function of time (Lin, 1975)

2.5 Chemical Kinetic

Chemical kinetics is the study and discussion of chemical reactions with respect to reaction rates, effect of various variables, rearrangement of atoms, formation of intermediates and so forth. It can be used to determine how quickly a reaction will occur under certain given circumstances. Study of chemical kinetic is important as it can be applied to enhance the reaction rate of desired chemical reaction and to retard the rate of undesired reactions. By this, prediction from theory can be done to enable the development of more rapid and efficient reaction scheme and eliminate costly and time consuming experimental work (Gower, 1971).

Generally, chemical reaction can be divided into homogeneous and heterogeneous reactions. Homogeneous reaction are those which take place in one phase while heterogeneous reactions involve reaction between two or more phases. Both of the reaction type can be catalyzed or not catalyzed (Gower, 1971).

In this study, nickel oxide reduction by carbon is a heterogeneous reaction although both nickel oxide and carbon are solid phase. This is because the main reaction in this study is the reaction between nickel oxide and carbon monoxide and between carbon and carbon dioxide. According to Gower (1971), in heterogeneous reactions, contact between phases is an important consideration where properties of the boundary separating the phases and any changes occurring to this boundary during the reaction must be considered.

2.5.1 Heterogeneous Gas-Solid Reaction

Gas-solid reactions play a major role in the technology of most industrialized nation including extraction of metals from their ores. The typical gas-solid reaction of a single particle with a moving gas stream can be represented by:

$$aA(g) + bB(s) = cC(g) + dD(s) \qquad \text{(Equation 2.6)}$$

where a, b, c and d are the stoichiometric coefficients.

In this study, the reaction scheme would be:

$$CO(g) + NiO(s) + CO_2(g) + Ni(s) \qquad \text{(Equation 2.7)}$$

Szekely et al. (1973), Szekely et al. (1976) suggested that the overall reaction process of a gas-solid reaction may involve the following individual steps:

1. Gas phase mass transfer of the gaseous reactant from the bulk gas stream to the external surface of the solid particle.
2. Interfacial reaction between gas and solid:
    a) Diffusion of gaseous reactant through the pores of the solid particle
    b) Adsorption of gaseous reactant onto the surface of solid particle
    c) Chemical reaction at the surface of the solid matrix
    d) Desorption of the gaseous product from the surface of solid particle
    e) Diffusion of gaseous product away through the pores of solid particle
3. Gas phase mass transfer of gaseous product from external surface of solid to bulk gas stream.

According to Gower (1971), the interfacial reaction between gas and solid and be divided into six types as follow:

1. Adsorption
2. $\text{Solid} + \text{Gas}_1 = \text{Gas}_2$
3. $\text{Gas}_1 = \text{Solid} + \text{Gas}_2$
4. $\text{Solid}_1 + \text{Gas} = \text{Solid}_2$
5. $\text{Solid}_1 = \text{Solid}_2 + \text{Gas}$
6. $\text{Solid}_1 + \text{Gas}_1 = \text{Solid}_2 + \text{Gas}_2$

In this study reaction 2 and 6 are involved in which the reaction involved are represented by Equation 2.4 and Equation 2.7 respectively.

$C(s) + CO_2(g) = 2CO(g)$ (Equation 2.4)

$CO(g) + NiO(s) + CO_2(g) + Ni(s)$ (Equation 2.7)

For exothermic or endothermic reactions the diffusional and reaction steps will also involve convective heat transfer between gas stream and solid surface and conduction heat transfer within solid reactant-product matrix (Szekely et al., 1976). A schematic representation of gas-solid reaction is shown in Figure 2.4 below.

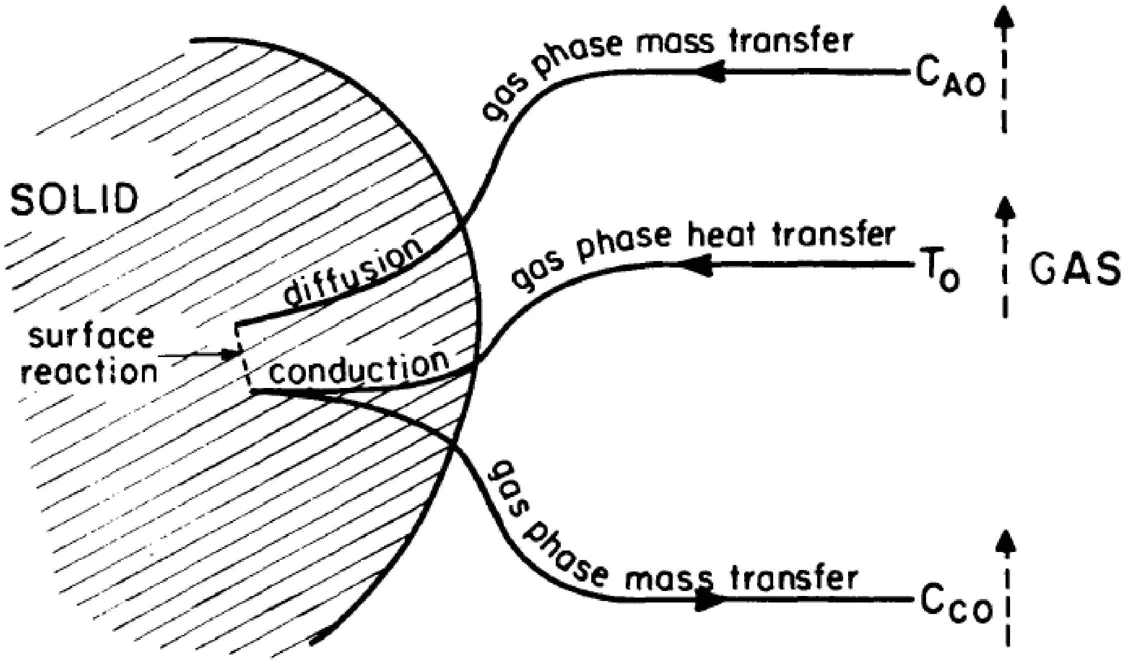


Figure 2.4: Schematic representation of gas solid reaction (Szekely et al., 1976)

2.5.2 Model Construction

There are two main sections in the model developed in this study, in which prediction of reaction rate is done from known temperature and vice versa. This enables simultaneous prediction of reaction rate and pellet temperature as a function of time to be done under various experimental conditions. For the purpose of calculation, the reactant sphere is divided into a larger number of concentric shells and each shell is assumed to react uniformly throughout its volume. Besides, each shell is also assumed to be completely consumed throughout the reaction and all heat of reaction is dissipated before the next shell start to react (Gower, 1971). In previous studies on reduction of nickel oxide, the model construction are mainly based on grain model, shrinking core model and nucleation model (Alizadeh et al., 2007, Chatterjee et al., 2012, Foran, 2014, Krasuk and Smith, 1972, Lin, 1975, Manukyan et al., 2015, Sakai et al., 1989, Utigard et al., 2005). Details and literature reviews of shrinking core model is discussed in next section.

2.5.3 Shrinking Core Model

In gas-solid reaction system, a solid with a certain radius is in contact with a flowing stream and throughout the solid product forms an "ash" layer around the non-porous reactant solid. As the reaction proceed, the unreacted solid core will reduce or shrink in size and that is how the name "Shrinking Core Model" from. However, the overall size of the solid may or may not change, depending on the relative densities of the solid product and reactant. The reaction occurs at the interface region between the unreacted core and the product or ash layer. Thus, it is important that the gaseous reactant be able to diffuse through the product layer to the interface for the reaction to occur (Szekely et al., 1976).

This model was first developed by Yagi and Kunii (1955), Yagi and Kunii (1961a), Yagi and Kunii (1961b), Yagi and Kunii (1961c), where five steps are being visualized to occur in succession during the reaction. Representation of concentration of reactants and products in shrinking core model is shown in Figure 2.5.

The five steps illustrated by Yagi and Kunii (1955), Yagi and Kunii (1961a), Yagi and Kunii (1961b), Yagi and Kunii (1961c) include:

i. Diffusion of gaseous reactant through the film surrounding the particle to the surface of the solid.
ii. Diffusion and penetration of gaseous reactant through the blanket of ash to the surface of the unreacted core.
iii. Reaction of gaseous reactant with solid at the reaction surface.
iv. Diffusion of gaseous products through the ash back to exterior surface of the solid.
v. Diffusion of gaseous products through the gas film back to the main body of fluid.

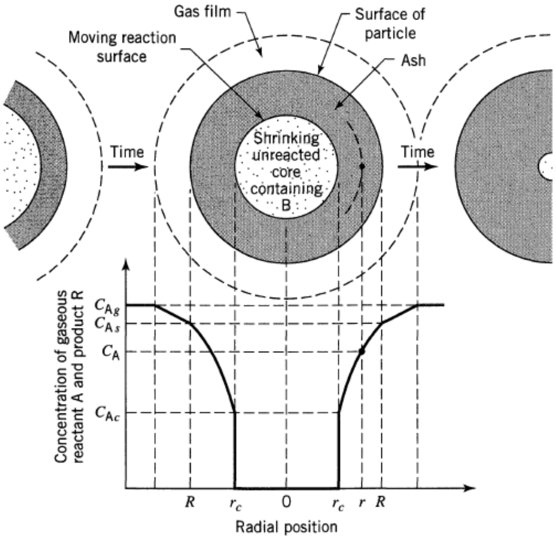


Figure 2.5: Illustration of concentration of reactants and products in shrinking core model (Levenspiel, 1999)

According to Levenspiel (1999), the shrinking core model is the best representation for majority of the gas-solid reaction systems. However, there are some limitations of the shrinking core model as the assumptions of the model may not match reality precisely. As an example, the reaction may occur along a diffuse front rather than along a sharp interface between ash and fresh solid, giving behavior intermediate between shrinking core and continuous reaction models. Besides, in fast reactions, the rate of heat release may be high enough to cause significant temperature gradients within the particles or between particle and the bulk fluid (Levenspiel, 1999).

Alizadeh et al. (2007) has constructed a kinetic model based on grain model and shrinking core model for the kinetic study of nickel oxide reduction by methane. The solid reactant is visualized as being composed of large number of grains and these grains individually reacts according to the unreacted shrinking core model. Utigard et al. (2005) also constructed shrinking core model in the study on reduction kinetics of Goro nickel oxide using hydrogen. Macroscopic analysis is done on the samples and it showed that in the temperature range the reaction followed the shrinking core model.

Table 2.2: Summary of previous studies on the gaseous reduction of nickel oxide

Author	**Reducing Gas**	**Model**
(Lin, 1975)	CO	Grain Model
(Krasuk and Smith, 1972)	CO	Shrinking Core Model
(Manukyan et al., 2015)	H_2	Avrami Nucleation Model
(Chatterjee et al., 2012)	H_2	Nucleation model
(Utigard et al., 2005)	H_2	Shrinking Core Model, Grain Model
(Alizadeh et al., 2007)	methane	Grain Model, Shrinking Core Model
(Foran, 2014)	H_2	Grain Model, Shrinking Core Model
(Sakai et al., 1989)	H_2-CO	Shrinking Core Model

CHAPTER 3

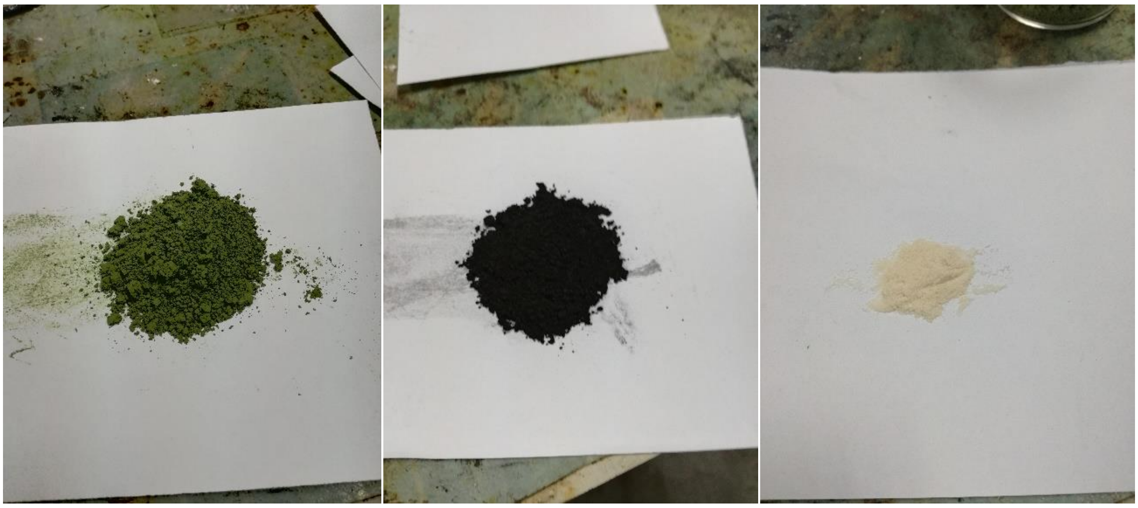
MATERIALS AND METHODOLOGY

3.1 Introduction

In this chapter, nickel oxide reduction by carbon is studied by using Design of Experiment (DOE) and kinetic models are developed using MATLAB software. In this research, the parameters such as reduction temperature, reduction time and molar ratio of carbon to nickel oxide are used in studying the kinetic reaction behavior of the reduction of nickel oxide by carbon. Pellets are prepared and tested at different combination of parameters to determine the effect of these parameters on the extent of reduction. The DOE experimental results for different parameters are then compared with the predicted results from kinetic modelling.

3.2 Raw Materials

Raw materials that are used in this study of nickel oxide reduction by carbon include nickel oxide, graphite and carboxymethyl cellulose (CMC). The properties and other details of the raw materials are discussed in the following parts. The appearance of raw materials is shown in Figure 3.1 below.



(a) (b) (c)

Figure 3.1: The appearance of raw materials (a) nickel oxide (b) graphite (c) CMC

3.2.1 Nickel Oxide

The main material used in this study is nickel (II) oxide powder. It is a fine powder which is green in colour. Some of the general properties of nickel oxide powder are shown in Table 3.1 below.

Table 3.1: General properties of nickel oxide powder

Properties	**Description**
Phase	Crystalline Solid
Colour	Green
Density, g/cm3	6.67
Molecular Weight, g/mole	74.69
Melting Temperature, °C	1955

3.2.2 Graphite

Graphite is a crystalline form of carbon which is black in colour. It is used in this study to reduce nickel oxide to nickel. General properties of graphite are shown in Table 3.2.