Reduction of Nickeliferous Laterite Ores by Liquefied Petroleum Gas (LPG)

GEVELYN B. ITAO
NATHANIEL M. ANACLETO

Abstract

Laterite ores, in which the nickel occurs in oxide form, represent a significant potential resource of metallic nickel. Since nickel-containing sulfide ores has high environmental effects due to acid waste disposal, it is necessary to develop new processing techniques of laterite ores. In the present research, reduction of Palawan limonitic laterite ore ((Fe,Ni)O(OH).nH2O) using liquified petroleum gas (LPG) as reductant was investigated in a fixed bed laboratory reactor. Advantages in utilizing LPG as a reductant in recovering nickel from laterite ores by pyrometallurgical operation are as follows: allows as to operate at a lower temperature, and minimizes the cost of electrical energy and environmental concerns associated with production of metallurgical coke and pelletised ores. Firstly, since the ore contains considerable moisture, both free and combined, it was calcined at 800°C for 2 hours prior to crushing and sizing. The reduction experiments were carried out in a temperature range of 500°C to 700°C and reaction times from 10 to 60 min. Phases of raw materials and reduced samples were analyzed by XRD.

The percent nickel reduced was highest at particle size of 150 μm. The reduction rate of laterite ore increased with increasing temperature. Nickel and iron oxides in the ore were reduced to metallic nickel and iron at 700°C. No metallic carbide was formed due to the propane/butane cracking and carbon deposition.

ITAO is an Assistant Lecturer II, College of Engineering, MSU-Iligan Institute of Technology, Iligan City. She has a Masters of Engineering in Material Science degree (Nov. 2010) from MSU-IIT, and a B.S. Metallurgical Engineering from MSU-IIT. ANACLETO is a Professor VI, Materials Science & Engineering Technology, School of Engineering Technology, MSU-Iligan Institute of Technology, Iligan City. He obtained his Doctor of Philosophy at the University of New South Wales, Australia, his Masters of Science degree at University of Queensland, and his Bachelor of Science in Metallurgical Engineering at Mapua Institute of Technology.

Introduction

Nickel is an important industrial catalyst and is typically formed in situ via the reduction of NiO (Twigg, 1996). It also exhibits potential as an oxygen carrier in chemical looping combustion (CLC), which is a novel approach for power generation that offers inherent $\mathrm{CO2}$ capture (Mattisson et al., 2006; Erri, 2007). Because of its valuable properties and numerous industrial uses, nickel is very desirable to have a practical process for separating and recovering of its metal from the ore deposits in which it occurs.

It is worth emphasizing that 72% (161Mt) of the world's mineral resources occur in laterite ores while the balance is obtained from sulphur containing ores (Figure 1). Today, about 42% of the new nickel supply is produced from lateritic sources, while the balance originates from sulphide sources (Gleeson et al., 2003; Sudol, 2005). Although, sulfides are still the primary source of nickel and cobalt, increasing underground costs and decreasing the grades of the sulfide ores attract more attention towards the exploitation of laterite ores (Dalvi et al., 2004; Pickles, 2004). One of the major economic factors, which limit the development of the laterite ores, is that the energy costs for processing these ores are two to three times higher than that for the sulfide ores (Thomas, 1995).

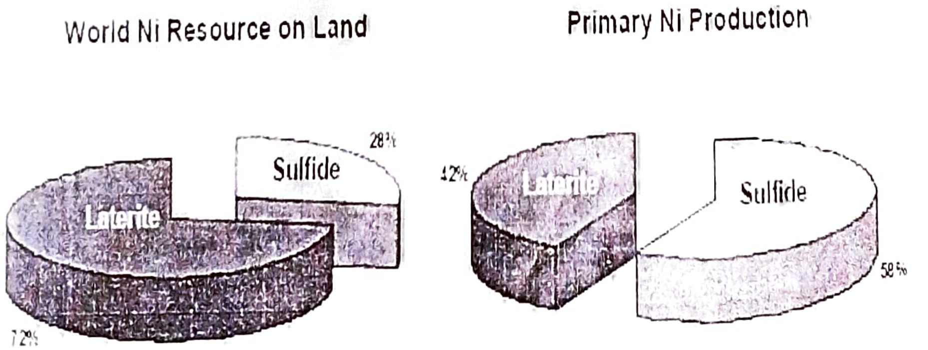

Figure 1. World's Land Based Nickel Resources and Primary Nickel Production (Resources Distribution by Contained Nickel)

Since 1950, nickel production and demand has continued to increase (Figure 2). As forecasted, the total increase in production from 1950 to 2003 has been about 8 fold from about 140 kt/yr in 1950 to 1200 kt/yr in 2003 (USGS Bureau of Mines, INCO Limited). In 1950 laterite source nickel formed only a small fraction of the production (<10%). In 2003, nickel from laterite sourced accounted for 42 % or about 510 kt Ni. By 2012 the share of laterite source nickel is expected to rise to 51 %. The growth in nickel supply has followed economic cycles and other world events. However on the whole nickel production has risen at a rate of about 4% p.a. This is higher than the average increase in the World GDP. Thus, there is a need of processing laterite ores.

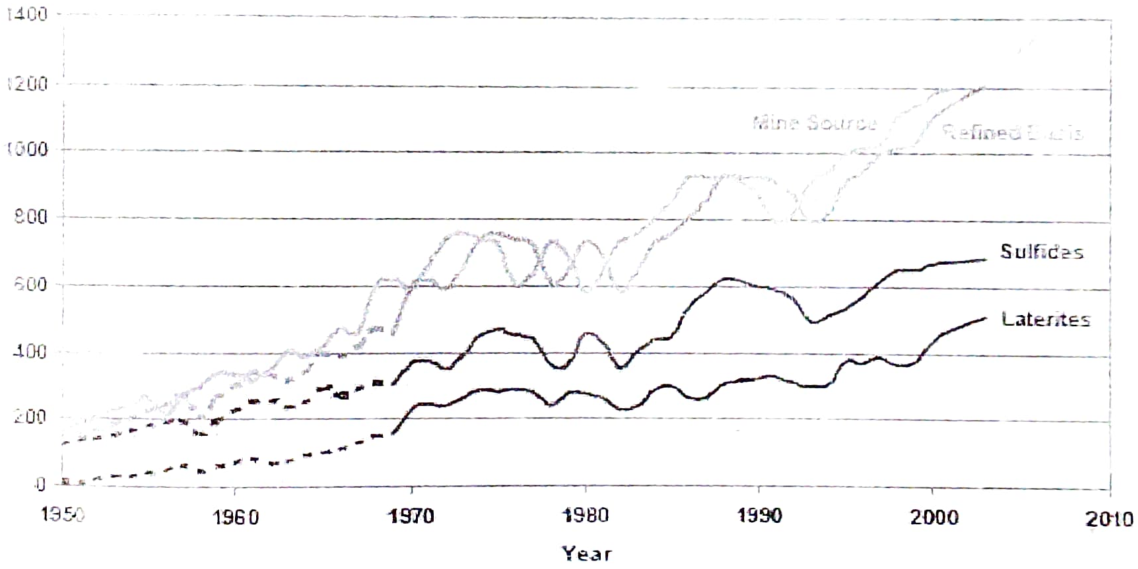

Figure 2. Expected Nickel Production.

Several metallurgical processes have been adopted to recover metallic nickel from lateritic ores. It can be processed by hydrometallurgical or pyrometallurgical methods. Processes for the extraction of nickel values and other metal values associated from nickeliferous oxide ore by leaching with ammoniacal solution is relatively well known as exemplified by the disclosures of the United States Patents (Caron, M.H., 1920; Caron, M.H., 1942; Brogdon, V.H., 1946; Hills, R.C., 1946). But in High Pressure-Acid leaching (HPAL), preparation of ore requires a very delicate technique, leaching process cannot be done at ordinary temperature and at atmospheric pressure, the leaching system has high corrosive characteristics, and there is necessity of sealing the leaching system against escape of volatile gases. On the other hand, pyrometallurgical route of ferronickel production, nickel oxide smelting, has practical disadvantage due to high power consumption (Green, G.E., 1964). Therefore, in the long term, it will be necessary to develop new and more processing techniques suitable for reduction of nickeliferous lateritic ores.

To increase the recovery of the metal by hydrometallurgical methods, prior art method of pretreating ores by reduction roasting at an elevated temperature is improved by employing as the reductant a saturated or unsaturated, substituted or unsubstituted, hydrocarbon having at least 2 carbon atoms to about 8 carbon atoms and, which, is a gas at the roasting temperature. The fuel/reductant may be coal, fuel oil, natural gas, LPG or other suitable material as exemplified by the disclosures of the United States Patents (Albrethsen, A. E., et. al, 1988; Baldock, B.R., et.al, 2004).

In this process, an attractive route to recover nickel from laterite ores by pyrometallurgical operation at a lower temperature is conducted using liquefied petroleum gas (LPG) as a reducing agent. Specifically, this study aimed to determine the effect of particle size on the percent nickel from the reduced laterite ores, determine the effect of reduction time on the percent nickel from the reduced laterite ores, and determine the effect of reduction temperature on the reduction rate of laterite ore.

Reduction of laterite ore was done using liquefied petroleum gas (LPG). The gas was composed of 60% propane (C_3H_8) and 40% butane (C_4H_{10}). Gas flowrate employed was 170 ml/min. Magnetic separation after reduction was conducted to determine the percent nickel recovered. Process conditions in terms of varying the particle size, reduction temperature, and reduction time had been investigated.

Methodology

aterials and Equipment

1.1. Laterite Sample

The limonitic laterite sample from Palawan was used in this study. Chemical composition of the ore used was determined by XRF (Table 1).

Table 1. XRF Analysis of Nickeliferous Limonitic Ore.

Constituent	Chemical Compound	Mass, %
Silicon Dioxide	SiO_2	20.97
Aluminum Oxide	Al_2O_3	1.85
Ferric Oxide	Fe_2O_3	47.30
Chromium Oxide	Cr_2O_3	2.01
Magnesium Oxide	MgO	6.81
Sulfur Trioxide	SO_3	0.06
Chloride	Cl	0.24
Phosphorus Pentoxide	P_2O_5	0.03
Manganese Oxide	MnO	0.62
Nickel Oxide	NiO	2.28
Bromide	Br	1.35
Loss on Ignition	LOI	16.10

1.2. Gas Reductant

A commercial liquified petroleum gas (LPG), gasul, was used as the gaseous reductant. Proximate analysis of the reducing gas mixture was 60% propane (C_3H_8) and 40% butane (C_4H_{10}).

1.3. Chemicals and Reagents

Chemicals and reagents used were all of analytical grade. Preparation of Chemicals and reagents:

Citric Acid Solution

- Dissolve 250 g citric acid and dilute to 1 lit. Shake.

Bromothymol Blue Indicator

- Dissolve 0.1 g bromothymol blue in 100 ml ethyl alcohol.

Dimethyl Glyoxime Solution

- Dissolve 10 g NaOH in about 400 ml H_2O. Add 10 g of dimethyl glyoxime and heat to dissolve. Cool and dilute to 1 lit.

Ammonium Acetate Solution

- Dissolve 500 g ammonium acetate in H_2O and dilute to 1 lit.

Buffer Solution

- Dissolve 85 g sodium acetate anhydrous in 420 ml acetic acid and dilute to 1 lit.

Copper-pan Indicator

- Dissolve 1 g Cu-pan in 50 ml dioxane. Dilute to 100 ml. filter and store in colored dropping bottle.

Ammonium Hydroxide Solution (1+1)

- Mix 100 ml ammonium hydroxide in 100 ml H_2O.

Acetic Acid Solution (1+1)

- Mix 100 ml acetic acid in 100 ml H_2O.

Nitric Acid Solution (1+1)

- Mix 100 ml nitric acid in 100 ml H_2O.

Hydrochloric Acid Solution (1+9)

- Mix 100 ml hydrochloric acid in 900 ml H_2O.

1.4. Tube Furnace

Experiments were conducted by using a fixed bed reactor having a vertical electric resistance furnace with an alumina working tube allowed for heating the samples. There were facilities for thermocouples (either B type or C type) for measurement of the sample temperature. The furnace was programmable with the desired reduction temperature and reduction time could be set.

1.5. Manometer

The flow rate of the reducing gas to the apparatus was primarily controlled using a manometer flow controller. It was first calibrated with the gas reductant before using.

2. Experimental Procedure

2.1. Ore Preparation

Naturally, laterite ore would hold a large content of free moisture, commonly 25 to 30% H_2O, although, sometimes it would contain even 40% or more. In addition to this, combined water would not be driven off until a temperature of 700 to 800°C was reached; its amount was up to 15% based on the dry ore weight. Because of the quantity of water present, and because water requires so much energy to evaporate and heat up, it was clear that some pretreatment of the ore (at least drying and calcining) was necessary.

Thus, prior to crushing and sizing, the ore was calcined at 800°C under air in a muffle furnace for 2 hours to remove combined water, volatiles and decompose compounds such as carbonates. This procedure was undertaken to ensure that experimental mass loss is solely due to the reduction reaction. Then it was cooled, crushed, and sieved to 150, 180, 425, 600 and 850 μm size ranges.

2.2. Calibration of the Tube Furnace

Temperature measurements were done using a thermocouple. To determine the temperature profile of the tube furnace, equilibrium temperatures at different distances from the base of the tube furnace were taken. The temperature profile of the tube furnace is shown in Figure 3. The temperature change varied as the distance from the bottom of the furnace increases.

The temperature of the furnace increased from 156°C to 715°C, as the distance from the base of the furnace increased from 0 to 12 inches, respectively. The temperature decreased slightly to 713°C at 13 inches from the base of the furnace and decreased further with increasing distance. The maximum temperature obtained was 715°C at 12 inches from the base of the furnace.

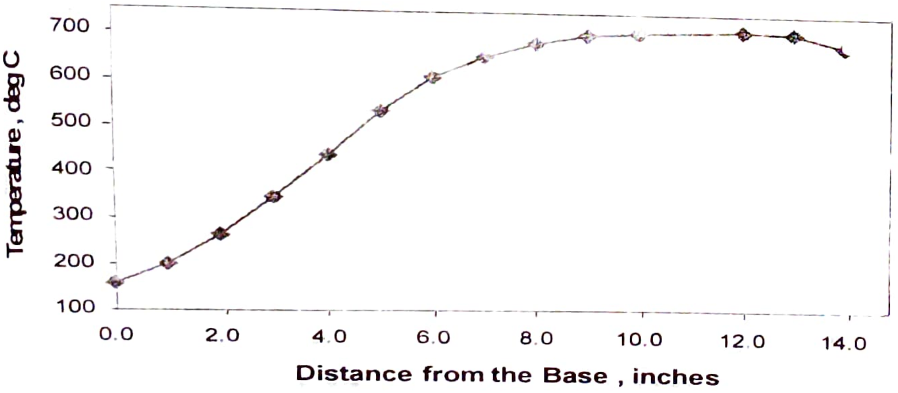

Figure 3. Variation of Temperature with Distance from the Base of the Furnace.

2.3. Calibration of the LPG Flowmeter

The flowrate of the LPG which was used as the reducing gas was measured in a manometric type of flowmeter using soap bubble as the manometric fluid. The flowmeter was calibrated by passing LPG into a calibrated 50-ml test tube with soap bubble. The gas passing into the graduated test tube displaced the soap bubble in the test tube. The time interval that has displaced the soap bubble from 0 to 50 ml was noted. Five trials were conducted for different rotameter setting of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0. The flowrate was then calculated using the average time. Figure 4 shows the flowrate of the LPG at different rotameter setting.

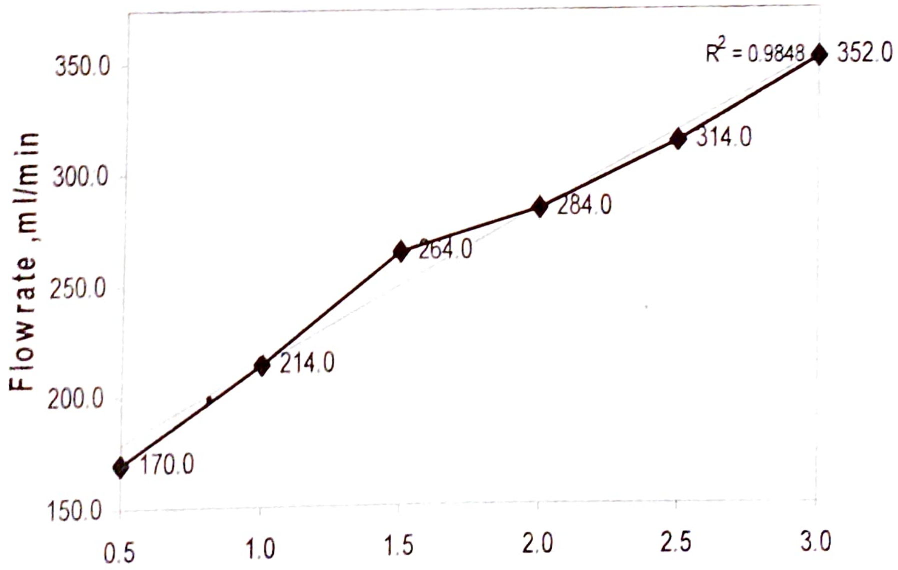

Figure 4. Flowrate Measured at Different Rotameter Setting.

2.4. Reduction Process

Isothermal reduction experiments were conducted on pre-screened calcined ore sample with a mass of 2.000 g (±0.003) placed in a reaction crucible at a temperature range of 500-700°C. The reducing gas was then fed when the appropriate reducing temperature was reached. The total gas flow was kept constant at 170 ml/min for all runs. After the reducing time was obtained, the alumina tube with the crucible was gradually lowered enough that the distance of the crucible from the bottom of the furnace was zero. The reducing gas was still applied after dwelling to avoid oxidation of the reduced ore. After cooling, the crucible was then transferred into a dessicator to prevent oxidation of the reduced sample with air.

Figure 5 shows the schematic diagram of the experimental assembly made in this study.

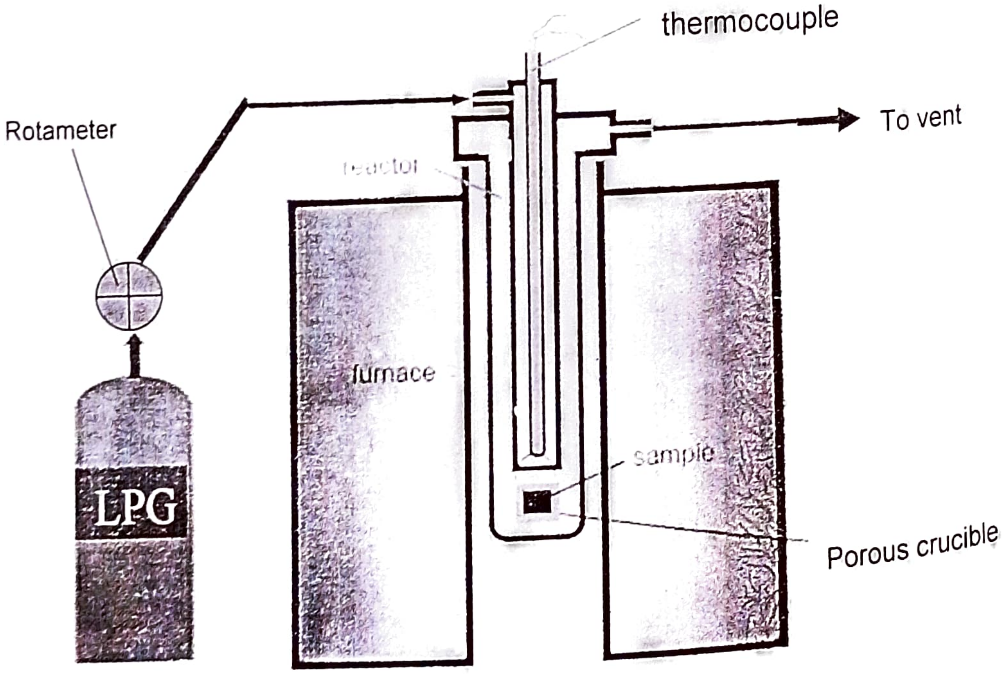

Figure 5. Schematic Diagram of the Experimental Set-Up.

3. Dry Magnetic Separation

After reduction, each of the reduced ore samples was weighed using the analytical balance. The weights of the reduced limonitic ore were recorded. It was then spread in a clean and dust-free piece of bondpaper. Magnetic separation was conducted on reduced ore sample using a permanent magnet, which was enclosed with cellophane. The concentrate was then placed in another sheet of clean bondpaper. Magnetic separation was repeated several times (more than 5 times) until no more particles adhered to the magnet. The magnetic particle was then weighed and recorded.

4. Wet Analysis

The magnetic particle was analyzed for nickel content by wet analysis. EDTA (Ethylenedinitrilo Tetraacetic Acid) Titration was employed.

5. Product Analysis

The extent of reduction was primarily investigated using XRD analysis and optical microscopy. XRD analysis was carried out in a Maxima-X Shimadzu 7000 X-Ray Diffractometer with monochromator and a copper Kα x-ray source at the National Institute of Geological Sciences (NIGS), College of Science, University of the Philippines. Samples were prepared by crushing to a fine powder and then placed into the specimen holder for X-ray diffraction. Scanning range was from 1.5° to 75° at a speed of 2.0°/min, with a step of 0.02°. The voltage and current used was 40kV and 30mA, respectively.

Results and Discussion

1. Effect of Particle Size on Percent Nickel Reduced

The following settings of parameters were kept constant: gas flowrate = 170 ml/min, reduction temperature = 600 °C, and reduction time = 10 min. The analysis of nickel in the limonitic laterite ore at different particle size is shown in Table 2. There was an increasing trend of percent nickel reduced as the particle size decreases as shown in Figure 6. The optimum percent nickel reduced was at 150μm. This is in accordance with the kinetics of reduction that smaller particle size is easily reduced than larger particle size.

Table 2. Percent Nickel at Different Particle Size.

Particle size, μm	% Nickel
150	1.91
180	1.88
425	1.84
600	1.83
850	1.76

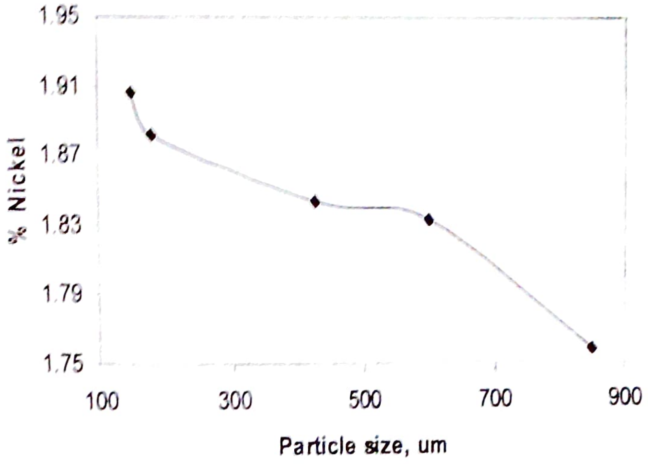

Figure 6. Effect of Particle Size to Percent Nickel.

2. Effect of Reduction Time on Percent Nickel Reduced

The influence of reduction time on percent nickel reduced is shown in Table 3 and Figure 7. Holding the particle size equal to 150μm and gas flowrate equal to 170 ml/min for all runs since percent nickel reduced was highest at 150μm.

As shown, percent nickel reduced was highest at 10 mins. reduction time at 700°C, 20 mins. at 600°C, and 30 mins. at 500°C. It increased gradually as reduction time increases and decreased abruptly further at a certain reduction time. Immediately after the most significant amount of percent nickel reduced was reached, an abrupt decrease was observed. This decrease is due to the reason that there is enough time for carbon deposition.

Table 3. Percent Nickel Reduced at Different Reduction Time.

Reduction time, mins.	% Nickel		
	500 °C	600 °C	700 °C
10	1.88	1.91	1.99
20	1.93	1.97	1.87
30	1.94	1.89	1.68
40	1.87	1.83	
60	1.81	1.59	

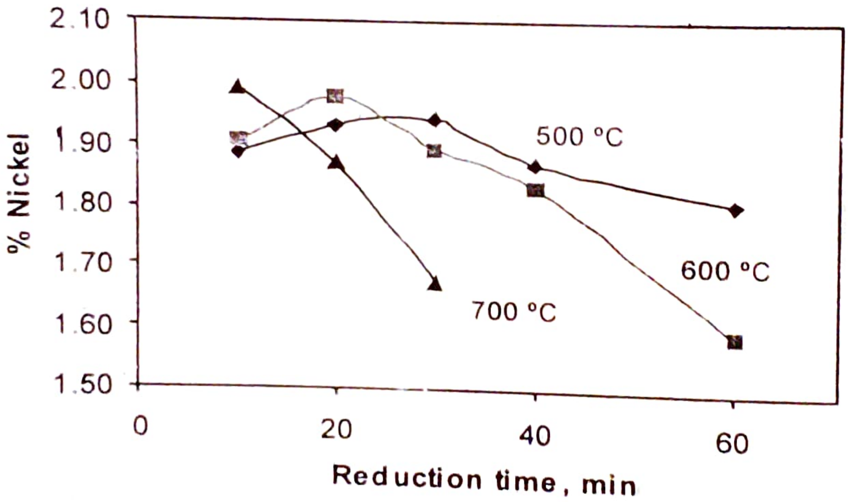

Figure 7. Effect of Reduction Time to Percent Nickel.

3. Effect of Reduction Temperature on Reduction Rate

Generally, increasing reduction temperature increased the reaction rate as depicted by reaction kinetics. As the reaction rate increased, the rate of carbon deposition would definitely increase.

The reduction of nickel oxide by propane and butane to nickel carbide occurs in accordance with the following reaction and their corresponding standard Gibbs free energies:

$$\begin{array}{ll}
<NiO> \leftrightarrow <Ni> + \frac{1}{2}(O_2), & \Delta G^{o} = 56{,}310 - 20.57T,\ (cal/gmol) \\
[(C_3H_8) \leftrightarrow 3<C> + 4\ (H_2), & \Delta G^{o} = 24{,}820 - 64.51T,\ (cal/gmol)]4/9 \\
[3<Ni> + <C> \leftrightarrow <Ni_3C>, & \Delta G^{o} = \ \ 9{,}500 - \ \ 4.1T,\ (cal/gmol)]\ 1/3 \\
<C> + \frac{1}{2}\ (O_2) \leftrightarrow (CO), & \Delta G^{o} = -27{,}340 - 20.5T,\ (cal/gmol) \\
\hline
<NiO> + 4/9(C_3H_8) \leftrightarrow 1/3<Ni_3C> + (CO) + 16/9(H_2) &
\end{array}$$

(1)

$\Delta G^{o} = 43,\ 168 - 71.11T$, (cal/gmol)

$$\begin{array}{ll}
<NiO> \leftrightarrow <Ni> + \frac{1}{2}(O_2), & \Delta G^{o} = 56{,}310 - 20.57T,\ (cal/gmol) \\
[(C_4H_{10}) \leftrightarrow 4<C> + 5\ (H_2), & \Delta G^{o} = 29{,}810 - 74.10T,\ (cal/gmol)]\ 1/3 \\
[3<Ni> + <C> \leftrightarrow <Ni_3C>, & \Delta G^{o} = \ \ 9{,}500 - \ \ 4.1T,\ (cal/gmol)]\ 1/3 \\
<C> + \frac{1}{2}\ (O_2) \leftrightarrow (CO), & \Delta G^{o} = -27{,}340 - 20.5T,\ (cal/gmol) \\
\hline
<NiO> + 1/3(C_4H_{10}) \leftrightarrow 1/3<Ni_3C> + (CO) + 5/3(H_2) &
\end{array} \quad (2)$$

$\Delta G^{o} = 42,\ 074 - 67.14T$, (cal/gmol)

where < > and ( ) denote solid and gas phase, respectively.

At standard conditions, reactions (1) and (2) will proceed spontaneously at temperatures 334°C and 353°C, respectively. These indicate that the temperature of NiO reduction to nickel carbide with propane-butane-containing gas is much lower compared to the existing carbothermal process in the FeNi production where smelting temperature reaches up to 1600°C. Figure 8 compares reduction of nickel oxide with different gaseous reductant. Reduction by propane-butane-containing gas resulted to a more negative values of the Gibbs energies than carbon monoxide and hydrogen gas.

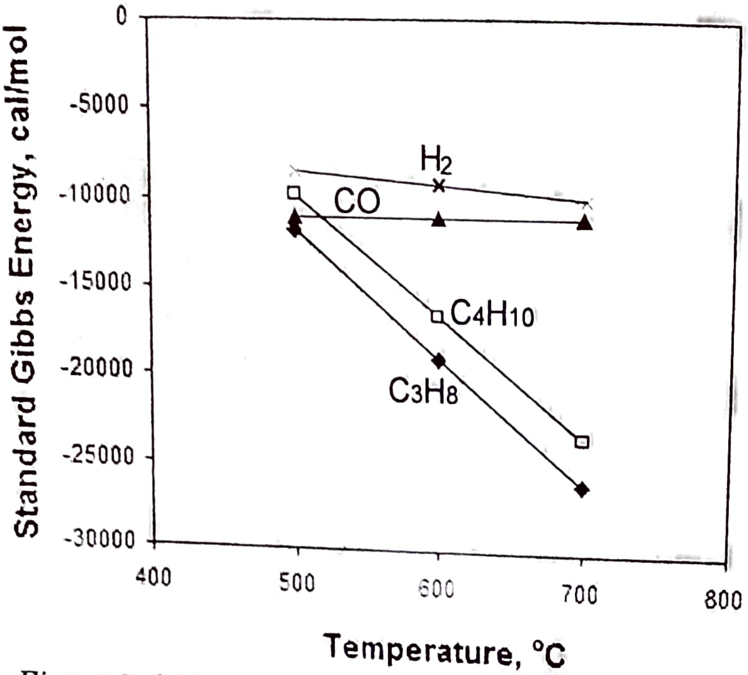

Figure 8. Gibbs free energies for NiO reduction with CO, H_2*,* C_4H_{10} *and* C_3H_8 *at different temperatures*

4. XRD and SEM Analyses

In accordance with XRD analysis, nickel and iron in laterite raw ore was mainly in the form of goethite, (Fe,Ni)O(OH)_nH_2O as shown in Figure 9. Other phases detected are serpentine with the general formula $(Mg,Al,Fe,Mn,Ni)_{2\text{-}3}(Si,Al,Fe)_2O_5(OH)_4$ and silica (SiO_2). A separate SiO_2 phase was detected in both microscopic and XRD analysis. SEM image of the raw laterite ore matrix is shown in Figure 10.

5. Reduced samples were subjected to XRD analysis. The phases formed at different stages of reduction is presented in Table 4. It shows that metallic iron is formed after reduction at 700°C. Figure 4 also shows

that trevorite, $NiFe_2O_4$ forms after reduction. Silica is not reduced even at 700°C.

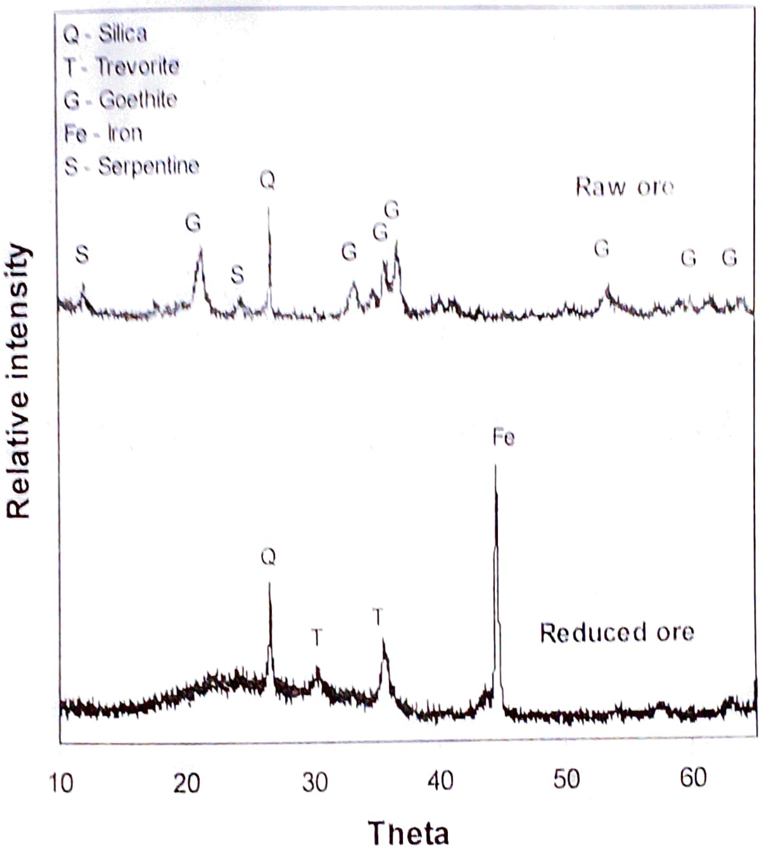

Figure 9. *X-ray diffraction patterns of raw laterite ore and reduced ore by liquefied petroleum gas at 700°C.*

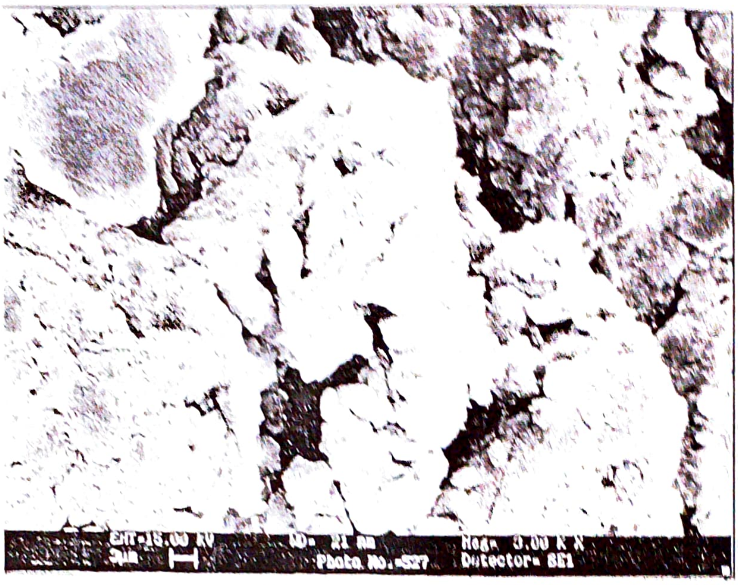

Figure 10. SEM image of raw laterite

Table 4. Phases formed at different stages of reduction.

		Compound/Element present
Raw Ore		Goethite, Serpentine, SiO_2
Calcined ore		Fe_2O_3, SiO_2
Reduced At 500°C	10 min	Fe_2O_3, Fe_3O_4, SiO_2
	20 min	Fe_3O_4, Fe_2O_3, SiO_2
	30 min	$Ni_{0.4}Fe_{2.6}O_4$, Fe_3O_4, SiO_2
	40 min	Fe_3O_4, SiO_2
Reduced At 600°C	10 min	$Ni_{1.25}Fe_{1.85}O_4$, SiO_2
	20 min	Fe_3O_4, SiO_2
	30 min	Fe_3O_4, SiO_2
	40 min	Fe_3O_4, SiO_2
Reduced At 700°C	10 min	$NiFe_2O_4$, SiO_2
	20 min	Fe, $NiFe_2O_4$, SiO_2
	30 min	Fe, $NiFe_2O_4$, SiO_2
	40 min	Fe, $NiFe_2O_4$, SiO_2

Conclusion and Recommendation

In this paper the results from the samples taken indicate that the reduction rate of laterite ore increased with decreasing particle size and increasing temperature. Nickel and iron oxides in the ore were reduced to metallic nickel and iron. No metallic carbide was formed due to the butane/propane cracking and carbon deposition.

It is recommended to study further the extent and kinetic analysis of the recovery of nickel from the reduced laterite ore including the carbon deposition.

Acknowledgment

The realization of this research would not be possible without the guidance, strength, and blessings of our **Almighty God** who has always shown His love by providing the author's needs directly and indirectly through giving her the following who have helped, inspired, and contributed to the success of this project.

To **Dr. Nathaniel M. Anacleto**, her adviser for his motivation and patience in extending his knowledge and ideas. He had extended help selflessly with all that he could, emotionally and financially as well. The author is so thankful to him and words are not enough to express her deepest gratitude and appreciation;

To the **Department of Mechanical Engineering, COE, MSU-IIT,** her second family, **Dr. Jonathan C. Maglasang, Dr. Eliseo P. Villanueva, Prof. Deuel H. Allen, Prof. Vannie Joy T. Resabal, Prof. Rolando Uy,** and **Dean Dr. Feliciano Alagao** for giving her the opportunity, understanding and consideration to work on this research project; and,

Finally, to her husband **Ruben**, and her sons, **Karlbein Reyman** and **Kent Rayjhon**, for the love and understanding they showed her during those times when she had no time for them, and during those nights she was not around for them due to laboratory work.

References

Albrethsen, A.E., (1988). *Reduction Roasting of Metals.*

Anacleto N, Ostrovski O. and Ganguly S., *ISIJ Int.* 44, 1480, (2004)

Anacleto N. and Ostrovski O., *Metall Mater Trans B,* 35B, 609, (2004)

Atkins, P., de Paula, J. *Physical Chemistry.* 7th ed. Oxford New York: University Press Inc., 2002.

Baldock, B.R., et.al., (2004). *Smelting Process for the Production of Iron.*

Brogdon, V.H., (1946). *Recovery of Nickel and/or Cobalt from Ores.*

Caron, M.H., (1942). *Process for separating Nickel and Cobalt in Solutions.*

Dalvi, A. D., Bacon, W. G., Osborne, R. C. (2004). *The Past and the Future of Nickel Laterites.* PDAC 2004 International Convention, Trade Show and Investors Exchange.

Gleeson, S.A.. C.R.M. Butt, and M. Elias. "Nickel Laterites: A Review." *SEG Newsletter* 54 (2003): 9–16.

Hills, R.C., (1946). *Recovery of Nickel and Ammonia.*

Knacke, O., O. Kubaschewski, and K. Hesselmann *Thermochemical Properties of Inorganic Substances.* 2nd ed. Berlin: Springer Verlag, 1991.

Mattisson, T., M. Johansson, and A. Lyngfelt. "The Use of NiO as an Oxygen Carrier in Chemical-Looping Combustion." *Fuel* 85 (2006): 736.

Moskalyk, R.R., and A.M. Alfantazi. "Nickel Laterite Processing and Electrowinning Practice." *Minerals Engineering* 15 (2002): 593–605.

Thomas, F. T. "Comparative Costs of Nickel Sulphides and Laterites." *Resources Policy* 21.3 (1995): 179-187.

Twigg, M. V. *Catalyst Handbook*. 2nd ed. London: Manson Publishing, Ltd., 1996.