Nickel oxide reduction in CO/CO$_2$ gas mixtures in reverberatory furnaces

V E Quiroz Cabascango and V Yu Bazhin
Department of Automation of Technological Processes and Production, St. Petersburg Mining University, Russia
E-mail: valeritae111@mail.ru

Abstract. This study present laboratory experiments carried out for nickel oxide reduction in a reverberatory furnace at medium pressure and a temperature range of 400°C-1050°C. Analyses were carried out on nickel nanostructures and their partially reduced metallic nickel products using Zeiss Leo Supra 35 SEM. It became evident from the experimental processes that the reduction process of nickel oxide under those given pressure and temperature conditions can result in fractionation of a dense layer of nickel from the melt surface which is in association with continuous growth of gaseous pores in nickel oxide. Therefore thermodynamic processes and temperature conditions are regarded as the most important factors which play a fundamental role in the reduction process of nickel oxide (gas-metal, or/and oxide-metal). The results indicate a positive correlation between formation mechanism and the rate of reduction of metallic nickel phases upon inter. Our research took a step-by-step assessment of technological processes and a scientific observation on nickel reduction at chemical equilibrium state of an ideal gas was made, and an account was taken with regards to limitations of variables and melting parameters.

1. Introduction
The global demand for nickel has grown sharply over the years. This growth is closely related to the production of stainless steel, a sector responsible for 71% of the total demand recorded in 2017. The remaining use of nickel corresponds to steel alloys and non-ferrous alloys, catalysts, chemicals and batteries.

Finished nickel products are mainly used as an alloy agent in the production of stainless steel, high performance alloys and a variety of nickel-copper alloys, as well as plating material in steel and plastics. China is the main producer of stainless steel with 25.9 Mt produced in 2017, equivalent to 51.5% of the total production on the global scale. As a consequence, China represents 53.2% of global nickel consumption, with a total of 1,16 Mt consumed in 2017. Japan is the second largest consumer, but represented only 8.3% of total demand in 2017. This demonstrates the high degree of concentration and hence dependence on global nickel demands to the evolution of the Chinese market.

The countries that offer nickel every day work in technologies that allow them to provide a purer product to their buyers and thus meet their needs. For this we know that nickel usually appears in combination with other metals, mainly copper and cobalt. There are two broad categories of nickel ore, which are sulfide ores and laterite ores. Sulfide minerals have historically provided the majority of primary nickel production; however, these resources have been depleted faster than the rate of discovery of new deposits. Laterite minerals have been exploited for the production of ferronickel for many years;
however, there has recently been a growing need for the industry to exploit laterite for the production of pure nickel.

Historically, most of the sulfide ores have been exploited in countries such as Canada, Russia, Australia, South Africa, Zimbabwe and Botswana. It should be noted that sulfide mines are generally underground. Laterite minerals, meanwhile, consist of a variety of tropical and subtropical soil profiles rich in iron, nickel and cobalt. The main deposits are in Cuba, the Dominican Republic, Brazil, Australia, the Philippines, Indonesia, New Caledonia, Macedonia and Kosovo. Additionally, there are two main types of ore in most laterite deposits, iron-rich minerals, and silica-rich magnesium and garnierite minerals. Limonite is typically of a lower grade (0.9-1.5% Ni) than garnierite (1.5-2.5% Ni). Unlike sulfide ore, laterite mines are generally open pit. In 2017, approximately 40% of the world's nickel supply came from sulphide ores, with the remaining 60% coming from laterite ores. The above shows a clear transition from production to laterite minerals, which are cheaper to extract, being sold directly to the nickel ore processing markets at a lower price.

Cuban nickel ores, for example, are typical laterites formed due to erosion of ultrabasic rocks. Currently, laterite is extracted in four deposits, two of the most important are: the Punta Gorda reserve where the ore is composed of 1.31% Ni and 0.086% Co and the reserves in the city of Moa where the mineral is composed of 1.35% Ni and 0.1% Co. Both reserves contain about 240 million tons.

Currently, nickel plants mainly process two types of minerals, which differ considerably in composition and chemical properties: oxidized nickel and copper-nickel sulphide. The proportion of nickel increases every year and oxidized minerals are increasingly important.

Chemically, nickel is a low activity metal, it has a high resistance to corrosion and water. The marked oxidation of nickel in the air is observed at temperatures above 750-850°C, sulfuric and hydrochloric acids dissolve nickel slowly, and easily dissolve in nitric acid. Nickel forms two basic oxides with oxygen: Nickel oxide (NiO) and nickel trioxide (Ni₃O₅), the latter decomposes on heating to form NiO₃. In metallurgy, nickel carbide (NiC₃) and carbonyl [Ni(CO)₅] are important as they are the basis for the process of purifying nickel from other metals.

Reduction processes of oxidized nickel ores and their concentrates have been well studied. Such processes include but not limited to: smelting of oxidized nickel ores, slag fuming, direct nickel oxide reduction in fire refining, metal production by metallothermic methods. Nickel oxide reduction analysis has proven to be of great scientific and practical interest for global industrial production of nickel in terms of to get better efficiency and decrease environmental greenhouse gas emissions during smelting.

Previously, laboratory tests were carried on the reduction of nickel oxide with hydrogen (H₂) as a reducing agent. However, analysis presented in various publications shows that nickel oxide reduction process in carbon monoxide and carbon dioxide gas mixtures has been poorly studied in terms of chemical reactions, as well as the whole process of nickel industrial manufacturing. The process of gas reduction of oxides is the easiest process for thermodynamic analysis; therefore, generally, the issue can be formulated as a step-by-step reduction of nickel oxide, accompanied by development of intermediate and transition phases of gaseous and solid products. It is necessary to determine the conditions when the oxide is reduced to metal, if carbon products are used as a reducing agent - a mixture of carbon monoxide and carbon dioxide.

The laboratory analyses were carried out at temperatures greater than 400°C, and consisted of exchanging of the reactant gas from H₂ to carbon dioxide (CO), and then back to H₂. It is widely know that carbon monoxide reduction is a limiting stage with Ni₃C development; however, we did not identify this phase clearly.

Galnbek et al., describes reduction nickel oxide granules with porosity of 3.5-38 vol.% in carbon monoxide and carbon dioxide gas mixtures at temperature ranging from 550°C to 750°C. Reaction rates were assessed by initial reduction rates, and they appeared to exhibit a first-order dependence on the partial pressure of nickel oxide. Activation energy between 550°C and 750°C amounts to 190 kJ/mol, and reaction rate constants do not entirely depend on temperature in the range of 650°C to 750°C. Recovery rates of nickel oxide granules in pure CO (101,325 KPa) for temperature range of 850 to
1050°C, resulted in porosity of granules which was approximated to be 0.6. Activation energy of nickel oxide reduction rate constant is about 18 kJ/mol.

Previous studies illustrates that melting in a heterogeneous system does not induce change in nanostructures that occur upon reduction or in relations with chemical in carbon monoxide and carbon dioxide (CO/CO₂) gas mixtures.[2]

The result of changes in reduction of oxidized nickel ores (nickel oxide sample) maybe proved by development of intermittent phases, which form the basis of this subject of this analysis.

2. Experimental methods
Nickel oxide in the industry and science plays a very important role today, and in a short term one of the most important factors which attracts the interest of many scientists is to add layers of nickel oxide to the poles of car batteries, with a ratio of eight parts of nickel to one of cobalt and manganese, the cost of batteries would be reduced by up to 42%. According to the report made by Nickel Institute in 2016, 39% of the batteries contained the metal, and it is estimated that this figure will be equal to 58% in 2025.

Nickel oxide is a green-black crystalline powder similar to sand and turns yellow when heated and soluble. They are produced by calcining nickel carbonate at temperatures not exceeding 550°C. The calcination temperature exerts great influence on the subsequent contamination of the oxide in sulfuric and hydrochloric acids. The content of active oxygen in the oxide (the stoichiometric excess of oxygen) constitutes a carrier of oxidizing properties, which is used for the purification of nickel sulfate solutions from copper and iron impurities.

Before starting to work with nickel oxide in a laboratory it is necessary to take appropriate protective measures. Nickel oxide affects the human being through inhalation, contact and intake.

Reduction of a pressed nickel oxide briquette pressed onto a substrate in a laboratory furnace was studied at temperatures ranging from 400 to 1050°C in an atmospheric pressure (101,325 KPa) of pure carbon monoxide. Figure 1 illustrates the schematic representation of the unit.

To determine the state of the system, the temperature setting can be applied together with the total pressure of a gas component (CO/CO₂). In this case, the reaction occurs without changing the number of moles of gas components, the total pressure does not affect the state of the system, the CO/CO₂ ratio, and the total gas content that determines the equilibrium constant will depend only on temperature, so the system is mono-variant.

![Figure 1. Unit-scheme](image)

1. Gas inlet, 2. Reaction tube, 3. Refractory, 4. Galvanized steel housing, 5. Gas emission from the treatment system, 6. Sample unloading, 7. Type H thermocouple.
At temperatures of 550°C-1050°C, droplets of metallic nickel were detected and observations were made that with the increase of temperature to 950°C a fractionation phase was seen where a dense metallic nickel phase was growing from the nickel oxide groundmass. Growth of intermediate metal nickel phases on the melt surface (crystallized sample) during reduction in monoxide carbon atmosphere can be directly viewed in an optical microscope.

Scientific approach refers to the reduction of errors associated with the following characteristics: initial particles (droplets) size, sample’s porosity and geometry, as well as potential changes upon phase formation together with reduction reaction, taking into account a decreasing density of nickel oxide samples. [3]

In order to heat the reaction tube, an electric-tube furnace was used. A tubular furnace is an electric heating device that is used to perform synthesis and purification of compounds. Its possible design consists of a cylindrical cavity surrounded by heating coils that are embedded in a thermally insulating matrix. The temperature can be controlled by feedback from a thermocouple. Our tubular furnace has two heating zones and digital temperature controllers up to 1800°C.

Recovery experiment was performed in carbon monoxide and carbon dioxide (CO+CO₂) environment. Gas flows were precisely controlled with the use of various pressure gas flow meters, an PCE-TDS 100 flow meter was used, which confirmed stable operation and were completely mixed before being added into the reaction. The PCE-TDS 100 ultrasound flow meter was used to quickly control and detect the flow rate, so it is a transportable measuring system that is easy to install. This flow meter has its basic operating principle, the frequency change (Doppler effect) that occurs when an ultrasonic signal reflects particles suspended in a gas. In our case, the particles contained in a CO/CO₂ flow are taken into account. In addition the meter is able to show us the temperature and pressure of the said flow.

In our unit some samples of nickel oxide were introduced into the hot reduction zone of the tube, through an air inlet at the top of the unit. Once in the reaction tube the sample was constantly lowered thanks to the influence of gravity. A partially reacted sample was removed after a recovery period, necessary for the chemical reactions. Experimental temperatures and gas compositions used in this study are shown in table 1. [4]

| T, °C | Reaction conditions in (CO + CO₂) | Kp | Kp | Kp |
|------|---------------------------------|----|----|----|
|      | P = 101,325 KPa (vol.% CO)      | (NiO+CO→Ni+CO₂) | (2CO→C+CO₂) | (3NiO+3C O→Ni₃C+2CO₂) |
|------|---------------------------------|-----------------|-------------|-----------------|
| 400  | 1,3                             | 86,2            | 98,2        | 628             | 1,18.10         |
| 566-796 | 2,5                           | 82,1            | 96,3        | 182,6           | 1, 5.10⁻¹     |
| 847-1099 | 5,2                          | 79              | 93,9        | 77,9            | 7,45.10⁻²     |
| ΔG (kJ/mol⁻¹ O₂) | -30                        | -120            | -150        |                 |                |

In our study we need to calculate the reversible work of the thermodynamic system at constant temperature ranges and pressures, this will help us define the thermodynamic potential of the work performed by the system based on pressure forces and temperatures. In every case, we used the next formula to calculate Gibbs free energy (ΔG) or the driving force of reduction reaction

$$\Delta G = -2RT \ln \left( \frac{p_{CO}/p_{CO₂}}{p_{CO}/p_{CO₂}} \right)_{\text{gas}} \left( \frac{p_{CO}/p_{CO₂}}{p_{CO}/p_{CO₂}} \right)_{\text{NiO}} J (\text{mol O}_2)^{-1}$$  \hspace{1cm} (1)
Where: \((pCO/pCO_2)_{\text{gas}}\) represent the ratio of carbon monoxide to carbon dioxide in the bulk gas; \((pCO/pCO_2)_{\text{Ni} / \text{NiO}}\) represent the ratio of carbon monoxide to carbon dioxide at Ni/NiO interface, the latter being equal to the equilibrium constant.

The equilibrium constant (K) is expressed as the ratio between the molar concentrations (mol / l) of reagents and products. Its value in a chemical reaction depends on the temperature, so it must always be specified. In our case, when it comes to gas mixtures, it is sometimes more appropriate to describe the composition in terms of partial pressures. The magnitude of the equilibrium constant informs about the state of equilibrium, that is, the extent to which a chemical reaction is carried out. Equilibrium constants for nickel oxide reduction in carbon monoxide and carbon dioxide environment can be defined by the following reaction:

\[
NiO_{(solid)} + CO_{(gas)} \rightarrow Ni_{(solid)} + CO_2_{(gas)}
\]  

A thermodynamic driving force was created with gas mixtures for reduction of 30, 120, and 150 kJ/mol -1 of O2 removed from the nickel oxide (indicated in table 1) at the given temperatures. Precipitation of solid carbon is described by the reaction below:

\[
2CO_{(gas)} \rightarrow C_{(solid)} + CO_2_{(gas)}
\]  

It is understood that the formation of nickel carbide occurs at low temperatures but of metallic nickel occurs from at least 500°C. The formation of nickel carbide (Ni3C) due to the reaction of nickel and carbon monoxide can be described by the reaction underneath:

\[
3Ni_{(solid)} + 2CO_{(gas)} \rightarrow Ni_3C_{(solid)} + CO_2_{(gas)}
\]

With pure solid constituents equilibrium constants at the pressure of 101,325 KPa were obtained.

3. Results analysis

Once the experiments have been carried out at different temperature ranges, we will describe the results obtained after the samples have been analyzed in the Zeiss Leo Supra 35 Scanning Electron Microscope. Zeiss Leo Supra 35 Scanning Electron Microscope is an electronic scanning instrument that gives us the possibility of observing images of nickel oxide samples with high resolution, being able to give us measurements of new formations at the base of the oxide. This microscope works through electron-matter interactions because it uses an electron beam instead of a light beam to form an image.

Taking into account the toxicity of nickel with the use of this instrument, it is not necessary to adapt the samples to be observed, but can be placed in the microscope with very few preparations, the microscope analyzes the surface of the sample point by point. Its operation is based on running the sample with a very concentrated beam of electrons, these electrons are dispersed in the sample and therefore secondary electrons are generated from the latter surface.

As the electron beam disperses throughout the sample, the image of the same is presented on the monitor.

These scanning electron microscopes have the ability to expand objects 250 000 times or more. This type of microscope is very useful in our study because, it has the ability to reproduce realistic three-dimensional images of the surface of our samples.

Next we describe each one of the images obtained with the use of this instrument.

Figure 2 illustrates structures developed in various forms of reduction and under various conditions of reduction at 850-1050°C. It can be observed that a dense nickel metal layer was developed. This analysis involved the first recovery of O2 at \(\Delta G=30\text{kJ/mol}^1\) for 75 s. To create a reduction potential of \(O_2 \Delta G=150 \text{kJ/mol}^1\) the gas mixture was changed.
Figure 2. Nickel oxide is partially reduced in carbon monoxide to carbon dioxide gas mixture to the limits fixed in the range of 850-1050°C, which indicates development of porous nickel.

Figure 3 shows samples of nanostructure developed with reduction potential of $O_2 \Delta G=30 \text{ kJ/mol}^{-1}$ at 550–750°C. It can be noted that after a short reaction time some nickel metal nuclei appear on nickel oxide surface. In 35 s the nuclei grew to 110. In 330 s, nickel oxide surface is covered with a layer of dense metallic nickel, up to 10 nanometers thick. The metal grains have a diameter of 220 nanometers and are coated with a round oxide crust, diameter 25-55 nanometers. [8]

Figure 3. Surface of nickel oxide template upon reduction in carbon monoxide to carbon dioxide gas mixture, with a reduction potential of $O_2 \Delta G=30 \text{ kJ/mol}^{-1}$ at 550-750°C, exposure time 330 seconds, with a dense layer being formed on a metal sample.

Figure 4 indicates nickel oxide sample surfaces after reduction in carbon monoxide to carbon dioxide gas mixture (reduction potential of $O_2 \Delta G=120 \text{ kJ/mol}^{-1}$) at 400°C, 35 s after the reaction. Figure 4 illustrates that the initial smooth and polished surface became faceted due to nickel reaction with the gas phase and appearance of oxygen that resulted from selective removal.

Figure 4. Surface of nickel oxide upon reduction in carbon monoxide to carbon dioxide gas mixture, with a reduction potential of $O_2 \Delta G=120 \text{ kJ/mol}^{-1}$ at 400°C, exposure time 35 s, showing formation of unstable porous phases of metallic nickel.

Experiments performed after having been analyzed under a microscope show that the formation of metallic nickel and the coating of the surface with a nickel product occur in a few minutes, the time must be very well calculated to reach the required condition. Therefore, the maximum recovery rates of dense nickel oxide are studied based on the initial rate, tangent of thickness / time dependence at time $t = 0$. [9]

Figure 5 indicates initial recovery rates as a function of temperature in the range from 400°C to 1050°C for 100% of carbon monoxide and recovery potentials of $O_2 \Delta G=120$, 30 kJ/mol$^{-1}$. Here it is clearly observed that rates increased monotonously with rising temperatures. Actually, there is a decrease in energy from $\Delta G=150 \text{ kJ/mol}^{-1}$ to $\Delta G=120 \text{ kJ/mol}^{-1}$ within temperature range of 400°C and 750°C, while in the range between 850°C and 1050°C, the energy rate again increases with increased temperature. [10]
Figure 5 Initial nickel growth rates as a function of temperature upon nickel oxide reduction in carbon monoxide/carbon dioxide gas mixture (PCO+PCO$_2$=101,325 KPa).

Figure 6 illustrates the initial growth rates as a function of the partial pressure of carbon monoxide for (CO/CO$_2$). It can be analyzed that the initial growth rates tend to be zero with each temperature, but when the transition from solid to porous nickel approaches, the initial growth rates of the product layer increase linearly with an increase in carbon monoxide pressure.

At reduced reduction potentials, rates are all comparatively slow; in fact, no reduction occurs at all temperatures with a reduction potential of 30 kJ/mol, and also in all other conditions where a dense layer of nickel product appears. [11]

These two graphs 6 and 7 have allowed us to observe how nickel oxide acts in environments with CO/CO$_2$ at different temperatures, which will allow us to have a more exhaustive control of nickel oxide in reverberatory furnaces.

4. Conclusions

Studying the behavior of nickel oxide in a CO/CO$_2$ medium has been the objective of this study, based on the importance that this study required in the nickel industry worldwide.

Results on the analysis of nickel oxide reduction in changing components of natural gas of the furnace and various temperature ranges indicated the possibilities of having different structures of the product upon various interactions of carbon monoxide/carbon dioxide gas mixtures.
The structures we have analyzed have been the result obtained by placing the nickel oxide in an atmosphere in contact with CO and CO$_2$, these structures appear gradually, resulting in surfaces with different characteristics.

An exposure of nickel oxide at a temperature of 400°C in a CO/CO$_2$ environment shows us the formation of a smooth surface with small unstable pores of metallic nickel. An exposure of nickel oxide at a temperature between 550°C and 750°C shows the formation of dense layer with nucleus formation. Lastly, an exposure of nickel oxide at a temperature between 850°C and 1050°C shows the formation of a dense layer full of porosities.

Development of a dense layer of nickel occurred under low thermodynamic driving force of reduction, which also coincides with a low partial carbon monoxide pressure in carbon monoxide/carbon dioxide gas mixtures.

The results received from the analysis of samples that were reduced in a short period of reaction time, at the temperatures mentioned above, indicate that in all cases an initial layer of dense nickel is formed and the morphology of a porous product develops in an isolated mechanism, these data help us determine the generalized rate constant of the reactions of recovery of nickel oxide at a multicomponent industrial level. Calculations and graphs help to adequately describe the behavior of basic metals in experiments in slag blowing with a mixture of CO - CO$_2$ gases.

In general, the rate of reduction of oxides naturally decreases when approaching the equilibrium of the gas and liquid source phases, which must be taken into account when organizing continuous slag depletion processes.

This study therefore provides a tangible proof that it is possible to have a multistage or intermittent mechanism of growth reactions of metallic nickel phase if supplying conditions of the gas mixture change in a given temperature range.

The study has demonstrated the influence of the composition of natural gas mixtures on the thermal balance and the work of the reverberatory furnace.

Therefore, we can improve the efficiency of monitoring and controlling of the reverberatory furnaces by optimizing the supply of natural gas and through medium-pressure burners based on algorithms through the automatic process control systems for nickel refining that may be used in any nickel production plant.

References

[1] Galnbek A A, Shalygin L M and Shmonin Yu V 1990 Calculations of pyrometallurgical processes and non-ferrous metallurgy equipment (Chelyabinsk: Metallurgizdat) p 448

[2] Fernández-Tarrazo E, Sánchez-Sanz M, Sánchez A L and Williams F A 2016 A multipurpose reduced chemical-kinetic mechanism for methanol combustion Combustion Theory and Modelling 20(4) 613–31

[3] Diomidovsky D A 1967 Control and automation of processes in non-ferrous metallurgy (Moscow: Metallurgizdat) p 403

[4] Bains P, Psarras P, Wilcox J 2017 CO$_2$ capture from the industry sector Progress in Energy and Combustion Science 63 146-72

[5] Ayoola T B and Mohammed I H 2016 Furnace Modeling for Efficient Combustion Gas Circulation Light Metals 757-61

[6] Fine M E 2017 Correlation between electrical and thermal conductivity in nickel and nickel alloys The Journal of The Minerals, Metals & Materials Society (TMS) 2 951-2

[7] Diomidovsky D A 1961 Metallurgical furnaces of non-ferrous metallurgy (Moscow: Metallurgizdat) p 728

[8] Fetisov V G, Nikolaev A K and Lykov Y V 2018 Aggregative simulation method for implementing mathematical models for gas transmission systems IOP Conference Series: Materials Science and Engineering 327(2) 022033

[9] Shalygin L M and Konovalov G V 2003 Heat generation and heat transfer in autogenous metallurgical apparatuses of various types Non-ferrous metals 10 17–25
[10] Bernhardt W 1977 Combustion technology for the improvement of engine efficiency and emission characteristics *International Symposium on Combustion* **16**(1) 223–32

[11] Liu X and Mancarella P 2016 Modelling, assessment and Sankey diagrams of integrated electricity-heat-gas networks in multi-vector district energy systems *Applied Energy* **167** 336–52

[12] Galnbek A A 1976 The continuous combined process of smelting and converting sour copper-nickel raw materials *Non-ferrous metals* **4** 16–7

[13] Noboru S, Tadashi Ch, Teiriki T 1988 Reduction of Nickel Oxide with Carbon Monoxide Accompanied by Carbon Deposition *J-STAGE* **14**(3) 368–73