Trans. Nat. Acad. Science & Tech. (Phils) 1988: 10: 63-70

THE REDUCTION BEHAVIOR OF NICKEL IN HIGH-IRON LATERITES UNDER CO/CO₂/N₂ ATMOSPHERES

R.B. Golecruz and M.G. Mena, Ph.D.

Department of Metallurgy College of Engineering University of the Philippines

ABSTRACT

The reduction behavior of nickel in high-iron Nonoc laterite was studied by varying the reduction temperature, reaction time and gas composition. It was observed that over a wide range of conditions, the degree of metallization increases with increasing level of any process variable, reaches some peak values, and then decreases with further increase in severity of reduction conditions. It was also noted that no more than 96.6% nickel can be metallized from the test sample. Ammoniacal leaching of pre-reduced pellets demonstrated that the Nonoc laterite is responsive to the treatment. An overall nickel recovery of about 94% is possible with this process.

Introduction

Nickel is a soft, ductile, extremely tough, nearly white and easily polished metal. It gained commercial prominence in the late 19th century when substantial reserves were discovered in New Caledonia and at Sadbury and the world's naval powers adapted nickel-bearing armors. Following World War I, research on its industrial applications was greatly increased and henceforth, the metal has became very vital in the production of several types of alloys for different industries.

Nickel has two land-based deposits of commercial importance, namely sulfides and laterites. Presently, the former represents the largest single source of production but for two reasons, effort is being made to shift the supply base to laterites. One reason is the increasing mining cost and the declining grade of sulfide deposits. The second and more important consideration is that the nickel and iron in laterites account for over 75% (Roorda and Queneau, 1973) and 20% (Iwasaki *et al.*, 1966), respectively, of the world's known reserves.

Laterites are indurated red formations which are rich in sesquioxides and silicates of iron, aluminum, magnesium and even manganese. They are essentially the products of weathering and natural leaching processes and hence, are found most abundantly in the tropics. They are of two varieties, the oxides and the silicates. In the oxide-type, most of nickel is associated with hydrated iron oxide or goetlite but in the silicate-type, the association is with iron-magnesium silicate minerals known collectively as garnierite. It was reported (Canterford, 1975) that nickel can be easily separated and recovered from oxide-type laterites but not from silicate-type.

The choice of metallurgical process in the treatment of a given laterite deposit is dependent to a large extent on its average mineralogical composition. If it is oxide-type, the treatment procedure involves acid leaching but if it is silicate-type, the preferred route is smelting. When the deposit contains comparable amounts of the two types, a pyro-front/leaching-end process was developed to take into consideration both the nickel recovery and the process economy. The ore is selectively reduced and then the metallized nickel is extracted by ammoniacal leaching. This was the process adapted by our Surigao nickel plant in Nonoc Island.

Selective reduction involves the preferential reduction of nickel over iron oxides. It aims to maximize nickel metallization and minimize iron production in order to cut down the ore's reductant and lixiviant or fluxes requirements. It is traditionally carried out in H_2/H_2O atmospheres due to favourable process kinetics but because of the rising prices of the hydrogen sources, the use of gas mixtures containing CO/CO₂ couple is now being considered. It is well-known that carbon monoxide can be cheaply generated from carbonaceous solids like coal.

This study aims to investigate the reduction behavior of nickel in high-iron laterite under $CO/CO_2/N_2$ atmospheres. It also seeks to determine the response of metallized nickel in ammoniacal leaching.

Materials and Methods

The laterite sample used was provided by Surigao Nickel Refinery of Nonoc Island. It was a cut of the mill's roasters feed and hence the as-received material was already ground to 93.6% passing 325 mesh. It was pelletized to a uniform diameter of about 1.24 cm by hand rolling and then the pellets were cured by ovendrying. The pellets anlayzed 1.05% nickel, 0.11% cobalt, 51.5% total iron and 13.5% chemically-combined water.

Carbon monoxide was generated by passing a metered stream of carbon dioxide in hot ipil-ipil charcoal bed. The reductant was purified and then it was mixed with CO_2 and later on with N_2 . The composition of the gas mixture was maintained to the desired levels by controlling the flowrates of its constituents. Figure 1 shows the schematic diagram of the gas flow system.

Reduction was carried out in an electrically-heated McDaniel refractory tube. Its temperature was maintained to within 2°C of the desired temperature and this was monitored with an API temperature recorder and a Leads and Northrup millivolt potentiometer Model 8690 thru chromel-alumel thermocouples. The progress of reduction was monitored with a Mettler balance Model H10w mounted above the furnace.



1. CO In, 2. N₂ In, 3. CO₂ In, 4. KOH Solution, 5. Silica Gel, 6. Sodium Carbonate, 7. KBr Solution, 8. Alkaline Pyrogallol, 9. Sulfuric Acid, 10. Oil Trap, 11. Flowmeter, 12. Gas Mixer, 13. Gases Out, 14. 3-way of Stopcock.

Figure 1. Details of gas flow system.

A typical test run was conducted as follows. As soon as the temperatures of the CO generator and the reduction furnace had stabilized, both were flushed with CO_2 and N_2 , respectively, for about one hour. Then a pellet was introduced in the reduction furnace via a wire-mesh basket whose one end was attached to the balance. It was freed of its combined water and soaked at the process temperature under flowing nitrogen. After constant pellet weight was achieved, the CO/CO_2 couple was admitted to the furnace and reduction commenced. Reduction was performed for 30 minutes and a weight-loss reading was taken regularly. The run was teminated by immediately raising the pellet to the cold section of the furnace where it was allowed to cool for some time. Cooling was done in a slightly reducing atmosphere in order to protect the metallics from back-oxidation (Platon, 1971). Finally, the reduced pellet was digested in 5% bromine-methanol solution (Kinson *et al.*, 1968) or, as in some instances, in ammoniacal solution to estimate the degree of metallization.

All solution assays were performed using a Varian Techtron Atomic Absorption Spectrophotomer. An internal standard solution consisting of laterite digested in aqua regia was used as a basis in recovery calculations.

Results and Discussion

Figure 2 shows the typical reduction curves at various conditions. The curves exhibit relatively high initial reduction rates but they ultimately tapered off after

about 20 to 25 minutes. This observation was made the basis in fixing the reaction time of the test runs at 30 minutes.



Figure 2. Typical reduction curves at various conditions.

Figure 3 shows the effect of increasing CO partial pressure on nickel metallization at various CO/CO_2 ratios and constant temperature. It can be noted that the metallization initially increases up to some peak values but thereafter, it started to decline.



Figure 3. Influence of CO partial pressure CO/CO₂ ratio on nickel metallization at 700°C.

Shown in Figure 4 is the influence of temperature on nickel metallization at various CO partial pressures and constant CO/CO_2 ratio. The same "inverted U" trend is once again noticeable.



Figure 4. Influence of temperature and CO partial pressure on nickel metallization at 1.0:1.0 CO/CO₂ ratio.

Shown in Figure 5 is the effect of increasing CO/CO_2 ratio on nickel metallization at various CO partial pressures and constant temperature. Except for the one obtained at the lowest CO partial pressure, all curves exhibit the now familiar "inverted U" trend.



Figure 5. Influence of CO/CO₂ ratio and CO partial pressure on nickel metallization at 750°C.

Three-dimensional plots involving two process variables and nickel metallization were also prepared and a typical plot is presented in Figure 6. The position of the "hump" of the response surface indicates that the optimum reduction conditions are intermediate of the values of the variable studied. The same information can be drawn from the other plots.



Figure 6. 3-dimensional plot showing the combined influenced of temperature and CO partial pressure on nickel metallization at 1.50:1.00 CO/CO₂ ratio.

Table 1 summarizes the optimum conditions and results. It shows that the maximum nickel that can be metallized from the test sample used was 96.6%. The corresponding values for cobalt and iron were 81.9% and 8.8% respectively.

Table 1.	Optimum	reduction	conditions	and results
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Temperature, °C	750
Reaction Time, minutes	30
CO Partial Pressure, A	1.00
CO/CO ₂ Ratio	1.0:1.0
% Nickel Metallization	96.6
% Cobalt Metallization	81.9
% Iron Metallization	8.8

The "inverted U" trend in nickel metallization is a familiar observation in laterite reduction studies (De Graaft, 1979) and this behavior is explained by Canterford (private communication) in terms of recrystallization theory. Accordingly,

mum overall nickel recovery at 75 gpl total ammonia was 86.5% and this was achieved after four hours leaching. At 120 gpl total ammonia, the recovery improved to 88.6% in one hour leaching time and to 92.9% in two hours. It is possible that further improvement in results can be analyzed by simply varying together both the reduction and leaching conditions but this is already beyond the scope of the present work.

Acknowledgments

The authors wish to tank The U.P. Engineering Research and Development Foundation, Inc. for funding this research study and the Surigao Nickel Refinery for providing the test material.

Literature Cited

- Canterford, J.H., "The Treatment of Nickeliferous Laterites," Min. Sci. Eng. Vol. 4, No. 1, 1975, p. 17.
- De Graaft, J.H., "The Treatment of Lateritic Nickel Ores A Further Study of the Caron Process and Other Possible Improvements, Part I: Effect of Reduction Condition, "Hydrometallurgy, Vol. 5, No. 1, 1979, pp. 47-65.
- Golecruz, R.B., "The Reduction Behavior of Nickel in High-iron Laterites Under CO/CO₂/N₂ Atmospheres," Masteral Thesis, University of the Philippines, 1987.
- Iwasaki, I., Takasahi, Y., and Kahata, H., "Extraction of Nickel from Iron Laterites and Oxidized Nickel Ores by a Segregation Process," Trans. A.I.M.E., Vol. 236, 1966, pp. 308-320.
- Kinson, K., Dickeson, J.E., and Belcher, C.B., "The Determination of Metallic Iron, Nickel, and Cobalt in Reduced Ores and Oxides," Anal. Chim. Acta, Vol. 41, 1968, pp. 107-112.
- Platon, R.J., "Hydrogen Reduction of Philippine Linionites," Masteral Thesis, University of the Philippines, 1971.
- Roorda, H.J. and Queneau, P.E., "Recovery of Nickel and Cobalt from Limonites by Aqueous Chlorination in Sea Water," Trans. Instn. Min. Met., Vol. 82, 1973, pp. C79-C87.