

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

Foreword

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Mining industry provides the necessary supply of valuable metallic and non-metallic materials for global consumptions. Metallurgical industry processes the ore for distribution to different industrial plant. The existence of these two significant industries is imperative to the benefit of the general public, especially here in the Philippines where the land is rich of mineral resources.

The three technical papers presented in this issue feature some of the important applications in the field of mining and metallurgical engineering. The two articles written by Professor Enrique Ostrea tackle the potential benefits of the gold refinery and the proposed metallurgical treatment in the production of pig iron for steel manufacturing in the country. Professor Ostrea, who played an active part in the development of mining and metallurgical engineering in the Philippines, strongly believed that these kinds of undertakings will be profitable and essential to the government. Unfortunately, we are not able to fully capitalize this kind of proposition. The article written by Dr. Manolo Mena described the reduction behavior of nickel in high-iron.

The pioneering role of mining and metallurgical engineering in national development is inevitable. With the mandate of corporate social responsibility and the advocacy of sustainability, the mining and metallurgical industries will provide economic benefits and at the same time follow compliance in the other aspects at stake on the operation such as environmental, social, health and safety. It is therefore a challenge for every sectors involved; the government, the mining and metallurgical industries, the engineers, the local government units and the socio-civic organizations to fully maximize the use of our resources.

The Reduction Behavior of Nickel in High-Iron Laterites Under CO/CO₂/N₂ Atmospheres

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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 Sudbury 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 become 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 represent 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.

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Lacerites 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 found most abundantly in the tropics. They are of two varieties, the oxides and the silicates. In the oxide-type, most of the nickel is associated with hydrated iron oxide or goethite 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 favorable 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/CO₂/N₂ atmospheres. It also seeks to determine the response of metallized nickel in ammoniacal leaching.

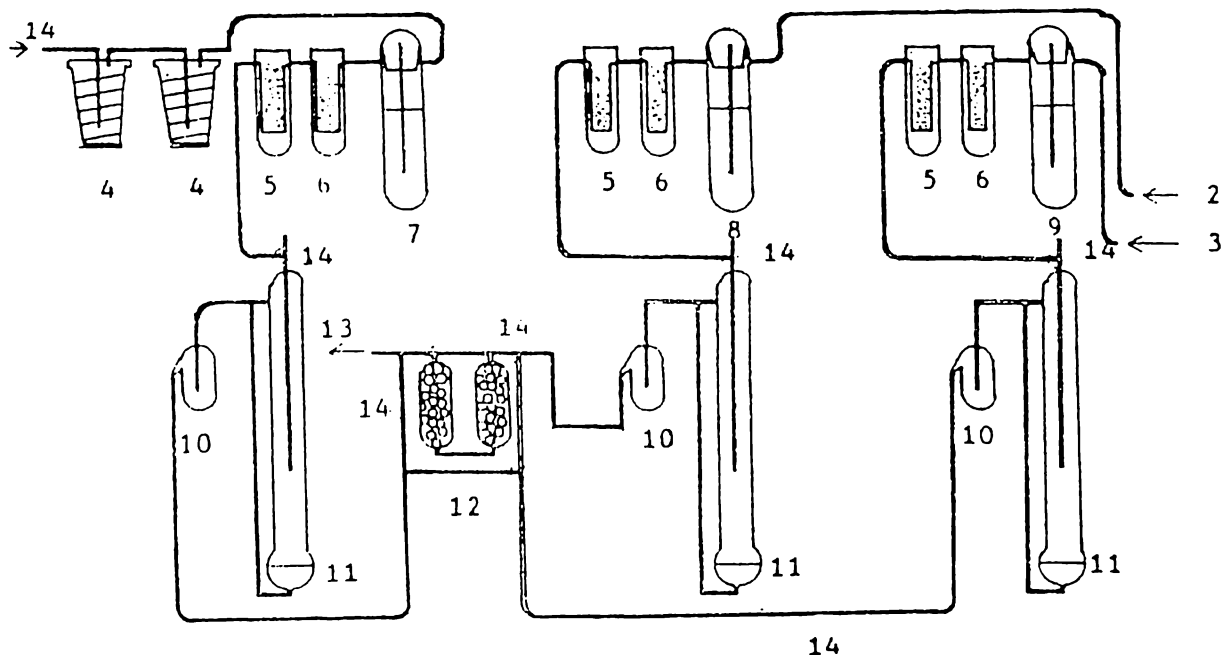
MATERIALS AND METHODS

The laterite sample used was 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 oven-drying. The pellets analyzed 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 CO₂ and later on with N₂. 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 McDanel 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.

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 CO₂ and N₂, 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/CO₂ 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 terminated by immediately raising the pellet to the cold section of the furnace where it was allowed to cool for



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 Stopcock.

Figure 1: Details of Gas Flow System.

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 metalization.

All solution assays were performed using a Varian Techtron Atomic Absorption Spectrophotometer. 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.

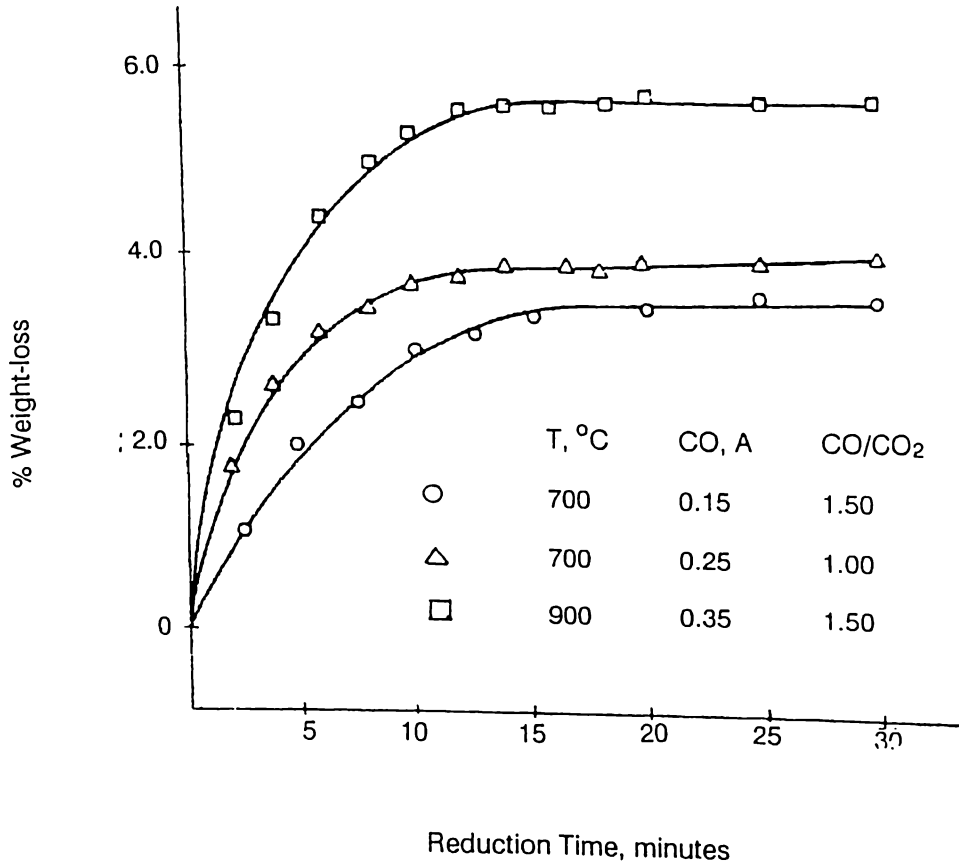


FIGURE 2 : Typical Reduction Curves at Various Conditions.

Figure 3 shows the effect of increasing CO partial pressure on nickel metallization at various CO/CO₂ ratios and constant temperature. It can be noted that the

metallization initially increases up to some peak values but thereafter, it started to decline.

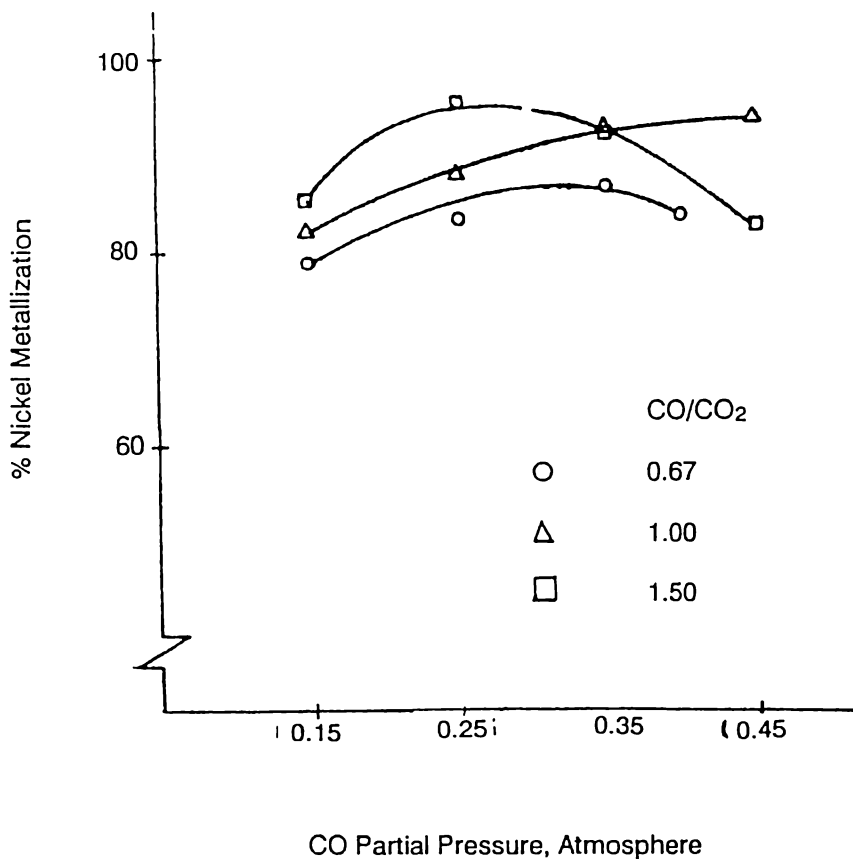


Figure 3: Influence of CO Partial Pressure and CO/CO₂ Ratio on Nickel Metallization at 700 C.

Shown in Figure 4 is the influence of temperature on nickel metallization at various CO partial pressures and constant

CO/CO₂ ratio. The same "inverted U" trend is once again noticeable.

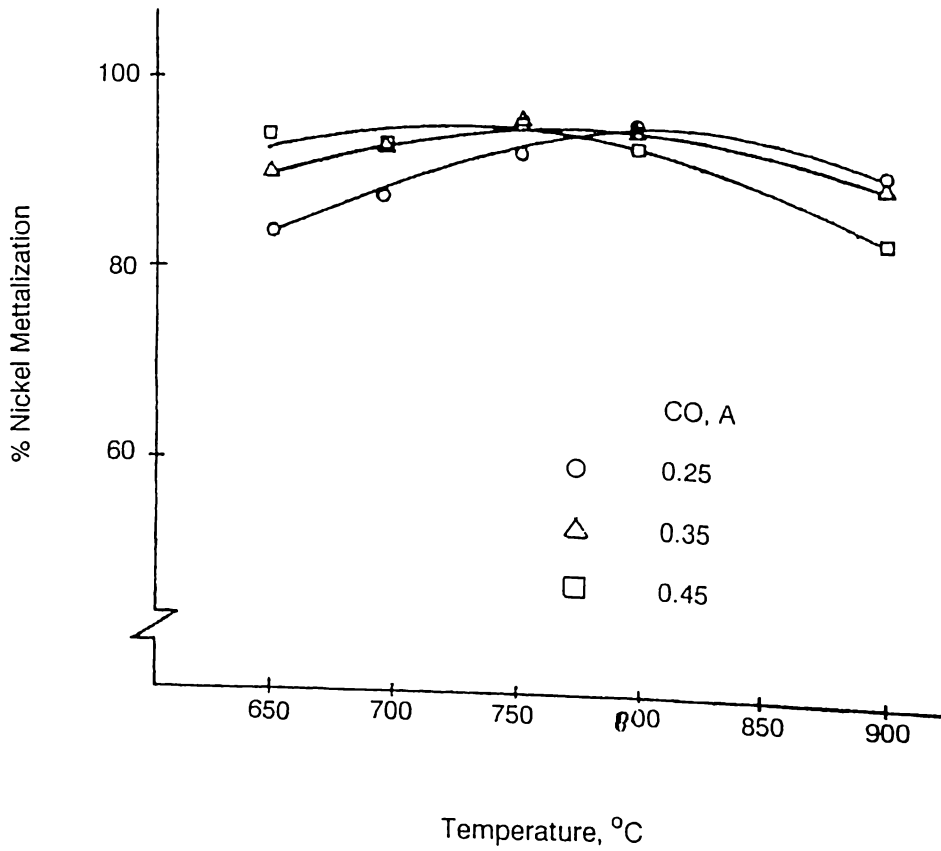


Figure 4: Influence of Temperature and CO Partial Pressure on Nickel Metallization at 1.0:1.0 CO/CO₂ Ratio.

Shown in Figure 5 is the effect of increasing CO/CO₂ ratio on nickel metallization at various CO partial pressures and constant temperature. Except for the

one obtained at the lowest CO partial, all curves exhibit the now familiar "inverted U" trend.

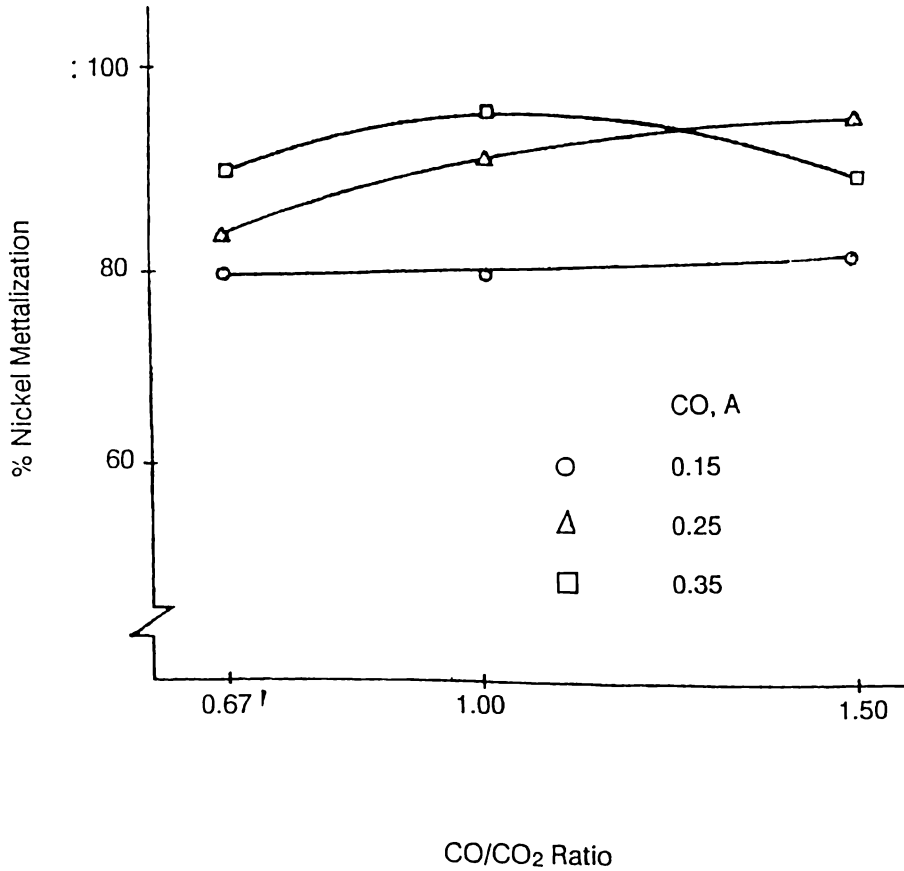


Figure 5: Influence of CO/CO₂ Ratio and CO Partial Pressure on Nickel Metallization at 750°C.

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.

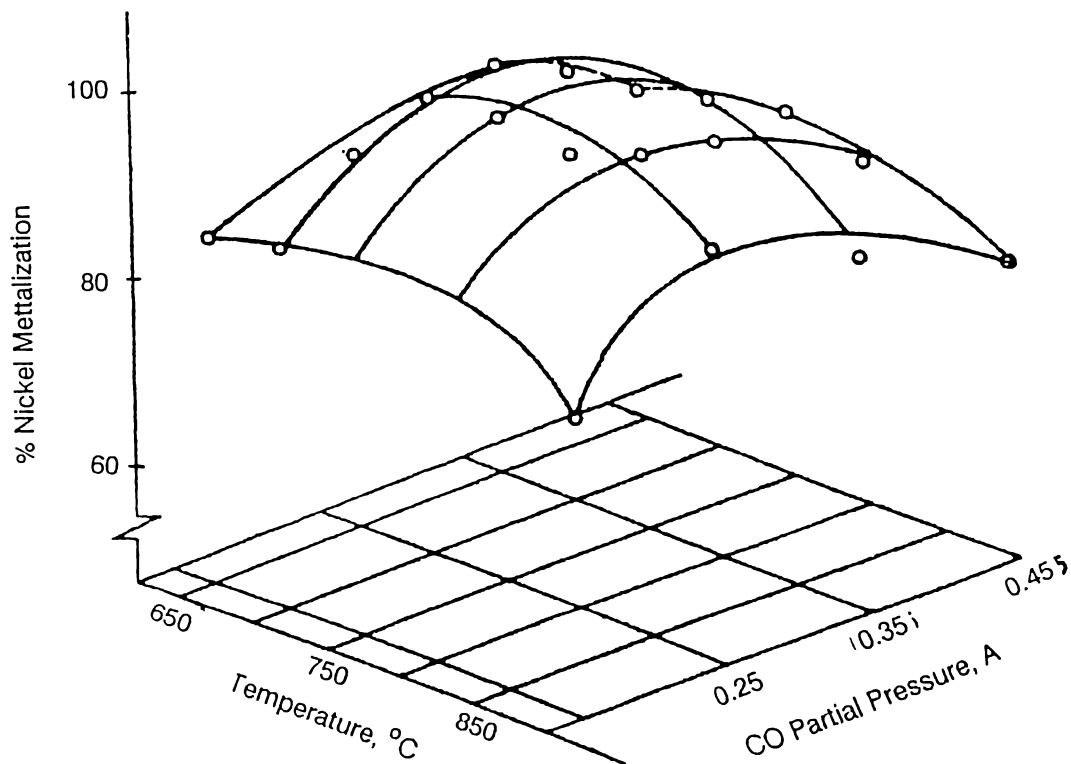


Figure 6: 3-dimensional Plot Showing the Combined Influence of Temperature and CO Partial Pressure on Nickel Metallization at 1.50:1.00 CO/CO₂ Ratio.

Table 1. Optimum Reduction Conditions and Results

| | |
|--------------------------|-----------|
| 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 |

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.

The inverted U" trend in nickel metallization is a familiar observation in laterite reduction studies (De Graaf, 1979) and this behavior is explained by Canterford (private communication) in terms of recrystallization theory. Accordingly, as the goethite fraction of the laterite recrystallizes or reduces to lower forms, some nickel is inevitably trapped into their lattice structures, thereby making this fraction inaccessible to the leach liquor. A more detailed discussion of this theory is presented elsewhere (Golecruz, 1987).

Table 2. Results of Ammoniacal Leach Tests

| | | |
|-------------------------------------------------------------------|----------------------------------------|-----------------------------------------|
| Temperature, °C | , 50 . | |
| [NH ₃] _T to [CO ₂] molar ratio | , 4.0 : 1.0 | |
| | % Nickel Recovery | |
| Leaching Time, hrs | 75 gpl [NH ₃] _T | 120 gpl [NH ₃] _T |
| 0.5 | 74.6 | 85.3 |
| 1.0 | 80.8 | 88.6 |
| 1.5 | 76.5 | 84.2 |
| 2.0 | 82.9 | 92.9 |
| 3.0 | 84.0 | - |
| 4.0 | 86.5 | 93.9 |

The results of ammoniacal leach tests are given in Table 2. The test pellets used were those reduced at the optimum conditions.

As can be noted, the maximum overall nickel recovery at 75 gpl total ammonia was 86.5% and this was achieved after 4 hours leaching. At 120 gpl total ammonia, the recovery improved to 88.6% in 1 hour leaching time and to 92.9% in 2 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.

CONCLUSION

The results of the tests showed that over a wide range of reduction conditions, nickel metallization follows an "inverted U" trend. That is, it increases initially up to some peak values and then it decreases thereafter. The results also proved that Nonoc laterite is responsive to CO/CO₂ reduction roast/ammoniacal leach process. an overall nickel recovery of about 94% was demonstrated to be possible at the following conditions:

1. Reduction

| | |
|---------------------------------|---------|
| Temperature, °C | 750 |
| Reaction Time, minutes | 30 |
| CO Partial Pressure, atmosphere | 0.35 |
| CO/CO ₂ Ratio | 1.0:1.0 |
2. Leaching

| | |
|----------------------------------------------|---------|
| Temperature, °C | 50 |
| Reaction Time, hours | 2 |
| Total Ammonia Concentration, gpl | 120 |
| Total Ammonia to CO ₂ Molar Ratio | 4.0:1.0 |

ACKNOWLEDGEMENT

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

REFERENCES

1. Canterford, J.H., "The Treatment of Nickeliferous Laterites," *Min. Sci. Eng.*, Vol. 4, No. 1, 1975, p.17.
2. De Graaf, J.H., "The Treatment of Lateritic Nickel ores - A Further Study of the Caron Process and Other Possible Improvements, Part I: Effect of Reduction Conditions," *Hydrometallurgy*, Vol. 5, No. 1, 1979, pp. 47-65.
3. Golecruz, R.B., "The Reduction Behavior of Nickel in High-Iron Laterites Under $Co/CO_2/N_2$ Atmospheres," Masteral Thesis, University of the Philippines, 1987.
4. Iwasaki, I., Takahasi, 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.
5. Kinson, K., Dickenson, 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.
6. Platon, R.J., "Hydrogen Reduction of Philippine Limonites," Masteral Thesis, University of the Philippines, 1971.
7. 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.