Some Hydrometallurgical Studies on Indonesian Low-Grade Nickel Laterite

KATSUYOSHI MITSUTOMI, DJOEWITO ATMOWIDJOJO and YUSUF

National Institute for Metallurgy, LIPI, Bandung, Indonesia

(Accepted for publication April 29, 1986)

ABSTRACT

Mitsutomi, K., Atmowidjojo, D. and Yusuf, 1987. Some hydrometallurgical studies on Indonesian low-grade nickel laterite. *Int. J. Miner. Process.*, 19: 297–309.

The hydrometallurgical processes used on low-grade nickel laterite from the Pomalaa mine have been investigated for several years. The results of various investigations showed that the depression of the solubility of the iron and magnesium constituents in the reduction-roasted ore is difficult. In order to depress the solubility of the iron constituent, iron oxide, especially wustite which remains in the roasted ore, needs to be oxidized to magnetite, maghemite, and hematite. Because of this, we studied the oxidation process after the reduction-roasting process. However, a large part of the iron constituent in the oxidized ore seemed to be wustite, and the solubility of the iron constituent under ambient pressure remained on a high level. In order to overcome its disadvantages, the high-pressure-high-temperature leaching procedures with the autoclave were carried out on the reduction-roasted ore, and the solubility of the iron constituent could be depressed perfectly by these procedures. To obtain a low solubility of the magnesium constituent, the additive silica sand was used before the reduction-roasting-autoclave leaching procedure was carried out. As the result of these investigations, the iron oxide produced by the reduction of goethite in limonitic ore could play a role as the substitutional reagent, and the utilization of the additive silica sand and the reduction-roasting-autoclave leaching procedures were most effective in depressing the solubility of the iron and magnesium constituents.

INTRODUCTION

The addition of iron powder and then two mixing times during the roasting stage contributed to the increase in nickel extraction without the increase in iron and magnesium extraction.

Iron powder was used generally as the substitutional reagent in the mixed serpentinic and limonitic ores. In this case, the autoclave leaching procedure on the roasted ore contributed toward the remarkable improvement in the iron and magnesium solubilities.

However, this process did not succeed in the perfect depression of the solubility of the iron constituent, which remained considerable.

The positive utilization of iron oxide (wustite and magnetite) which is produced from goethite by the reduction procedure allows the possibility of the substitution of the nickel constituent in forsterite and the autoclave leaching procedure after the roasting process is most effective in the depression of iron dissolution. After the reduction-steam roasting procedure, the roasted ore was directly leached by diluted sulfuric acid under high pressure and high temperature with the autoclave.

These procedures allow the dissolution of the iron constituent to be depressed perfectly.

However, the dissolution of the magnesium constituent could not be depressed.

After several discussions we tried adding silica beach sand to fix the magnesium constituent as magnesium silicate hydrate and basic magnesium silicate. The addition of silica beach sand and reduction-roasting–autoclave-leaching brought about an effective depression of the iron and magnesium dissolution.

In this paper, we would like to describe our experimental procedures concerning two stage processes – the first stage, the reduction process for the formation of magnetite and/or wustite from goethite in limonitic ore with a reduction gas such as hydrogen and the second stage, the substitution between nickel elements and iron oxides by the steam roasting leaching procedure under ambient pressure and high-temperature–high-pressure method.

PREPARATION OF THE TEST SAMPLE AND EXPERIMENTAL PROCEDURE

Serpentinic and limonitic ores from the Pomalaa mine were prepared as the experimental ore samples. These ore samples were crushed to 100% -200 mesh with a pulverizer. Every test used 10 g, which contained laterite and other additive substances mixed thoroughly.

The ore sample was charged into the ceramic boat and then charged into the combustion tube made from stainless steel. The ore sample was submitted to rising temperature and reduction roasting simultaneously.

The mixed reduction gas (H_2 plus steam) and/or roasting gas (N_2 plus steam) were prepared by the injection of either hydrogen or nitrogen gas into hot water at 90°C with the water temperature being controlled automatically with a temperature control unit. The roasted ore sample was then leached immediately with diluted sulfuric acid or kept in a desiccator filled with carbon dioxide gas to prevent the passive formation of nickel oxide.

The leaching test under ambient pressure was carried out with a $(1+25)$ concentration of sulfuric acid, and that under 11 kg/cm^2 with the autoclave was the $(1+50)$ sulfuric acid concentration.

The leaching conditions with diluted sulfuric acid under ambient pressure were as follows: (a) leaching pulp density 4%; (b) leaching pulp temperature

TABLE 1

Chemical component

	Grade (%):				
	Ni	Fe	MgO	SiO$_2$	CaO
Serpentinic ore	1.10	8.40	15.20	49.52	0.26
Limonitic ore	0.97	26.92	5.71	20.76	0.01

90°C; (c) leaching time 20 min; and (d) the leached pulp was filtrated to separate the solid residue and liquid, and these were analyzed by a SHI-MADZU AA–640–12 atomic absorption spectrophotometer.

CHARACTERISTICS OF THE ORE

The chemical analysis of the ores is shown in Table 1.

The results obtained from an ethylene glycol leaching test, a heating test at 550°C and an X-ray diffraction applied to limonitic ore, clarified that the clay minerals in limonitic ore consisted of halloysite, chlorite and montmorillonite. Clay minerals in serpentinic ore were so scanty that they can be neglected. The main minerals in limonitic and serpentinic ores are shown in Table 2.

The results of a heating test, X-ray diffraction and an infrared absorption spectrum, indicated that antigorite was decomposed and that recrystallization to forsterite began at 870° – 900°C.

THE LEACHING TEST ON MIXED RAW ORE WITH DILUTED SULFURIC ACID UNDER AMBIENT PRESSURE AND HIGH PRESSURE (AUTOCLAVE)

We studied the characteristics of mixed ore (serpentinic and limonitic ores) in sulfuric acid before the reduction-roasting test. The results obtained from

TABLE 2

Main minerals in serpentinic and limonitic ores

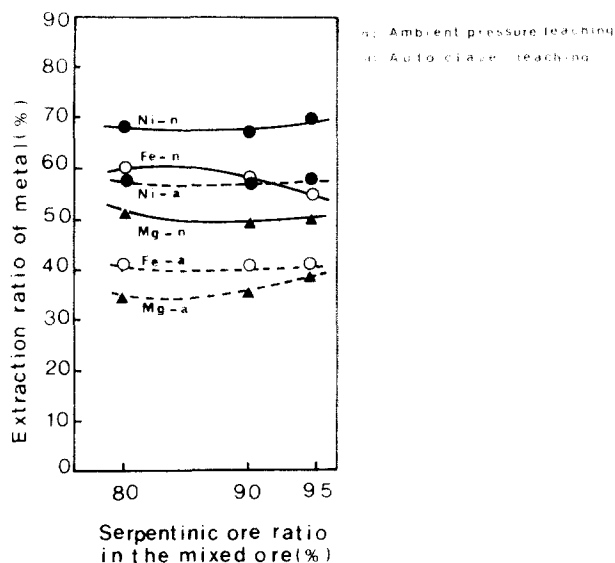| Limonitic ore		Serpentinic ore	
Goethite	Halloysite	Antigorite	
Hematite	Chlorite	α-quartz	
Magnetite	Bayerite	Clino-enstatite	
α-quartz		Magnetite	
Gibbsite		Chrysotile	

Fig. 1. Relation between the metal extraction and serpentinic ore rate in the mixed ore.

laboratory tests are shown in Fig. 1. The nickel extraction was expected to be about 30–70%, the iron and magnesium extractions were estimated to be higher than 50%.

Sulfuric acid leaching with high-pressure–high-temperature (called auto-clave leaching in the following) seems to be a possibility in order to decrease the sulfuric acid concentration which creates a similar nickel extraction and lower the iron and magnesium extraction.

THE LEACHING TEST WITH SULFURIC ACID ON THE MIXED ORE AFTER THE CALCINATION PROCEDURE

In order to investigate the solubility of metals after the calcination procedure of the mixed ore, we carried out the calcination of the mixed ore with a muffle furnace and the leaching test with sulfuric acid under ambient pressure. The mixed ore was charged into the muffle furnace and left for 1–3 h at temperatures between 800° and 1,000°C.

The calcined ore was cooled slowly in the atmosphere. After cooling it was leached with sulfuric acid under ambient pressure. The experimental results are shown in Fig. 2.

The nickel extraction increased until a calcination temperature of 900°C. As can be seen from the X-ray diffraction test on serpentinic ore, the initial recrystallization temperature of forsterite was 870° – 900°C, and the maximum temperature for nickel extraction coincides with the initial recrystallization temperature of forsterite from antigorite. An increase of nickel extraction
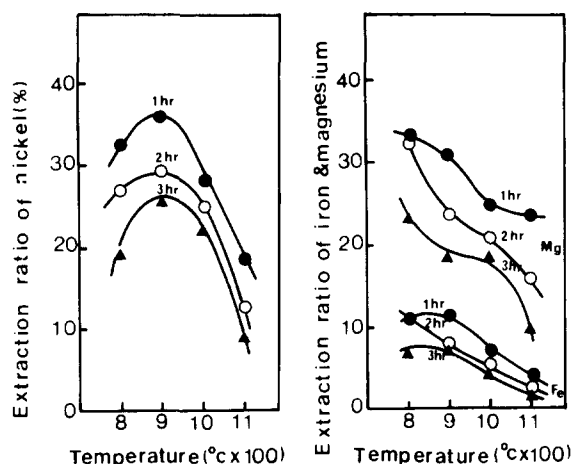
Fig. 2. Relation between the calcination temperature and the metal extraction ratio.

up to that temperature will result from the dehydration–decomposition of antigorite, and then substitution by iron oxide.

The longer the retention time, the lower the nickel extraction.

The decrease of nickel extraction seems the excessive oxidation of nickel oxide. The nickel extraction decreased rapidly at temperatures higher than 900°C, at the initial recrystallization of forsterite.

Ten percent of the nickel extraction was shown at 1,100°C, at a calcination temperature for three hours.

The iron extractions were depressed effectively, and show only a few percents at 1,100°C for one to three hours.

It seems that the iron constituent tends to be easily fixed as forsterite (ferroan) and fayalite. On the other hand, the magnesium extraction could not be depressed to lower than 10%.

From these experimental results, it may be expected that the sulfuric acid leaching process applied to nickel laterite ore with a high magnesia content will cause public discussion.

EFFECT OF THE MIXING TIME DURING THE STEAM-ROASTING STAGE

As Shirane et al. (1) have already mentioned, the reaction during steam-roasting in the secondary stage is the substitution of iron oxides and the nickel element in forsterite and/or enstatite. The rate of the reaction depends upon the probability of contact between magnetite and/or wustite and forsterite, and that contact probability will be proportional to the mixing time.

From this point of view, we carried out an experiment by drawing out the sample from the tube furnace and putting it into a mixing box, which was filled
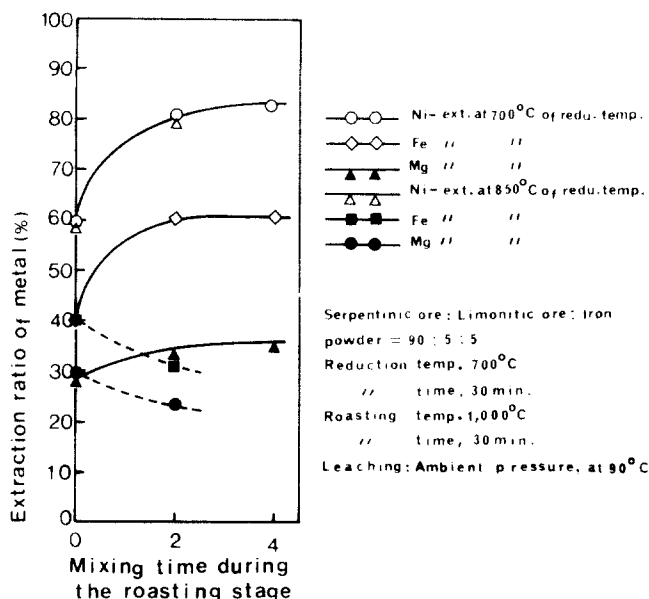
Fig. 3. Effect on the metal extraction of the mixing procedure during the steam roasting stage.

with carbon dioxide gas, then grinding and mixing in a porcelain mortar and feeding it back into the combustion tube.

The experimental results after two and four mixings of the roasted ore are shown in Fig. 3. The nickel and iron extractions at a 700°C reduction temperature were proportional.

The first reduction stage seems to occupy the Fe–MgO–Ni range in the equilibrium constitutional diagram of the Fe–Ni–Mg metal oxide (2).

Metallic iron produced in the first reduction stage will be roasted with steam in the secondary stage and hydrogen gas will be then produced.

$$Fe^0 + H_2O = FeO + H_2 \tag{1}$$

$$3Fe^0 + 4 H_2O = Fe_3O_4 + 4H_2 \tag{2}$$

The secondary steam-roasting stage will, therefore, become a weak reduction atmosphere. That is, the metallic iron which was formed at 700°C in the first reduction stage, where hydrogen or mixed gas was used as the reduction gas, will be changed to wustite and/or magnetite at the 1,000°C of the secondary steam-roasting temperature and metallic nickel which was reduced from goethite will change to nickel oxide due to the electrostatic neutrality in the secondary steam-roasting stage and the substituted nickel element from forsterite will finally form nickel oxide. This nickel oxide may have a high probability of precipitation on the contact surface between forsterite and wustite or magnetite. On the other hand, antigorite is decomposed and will be changed
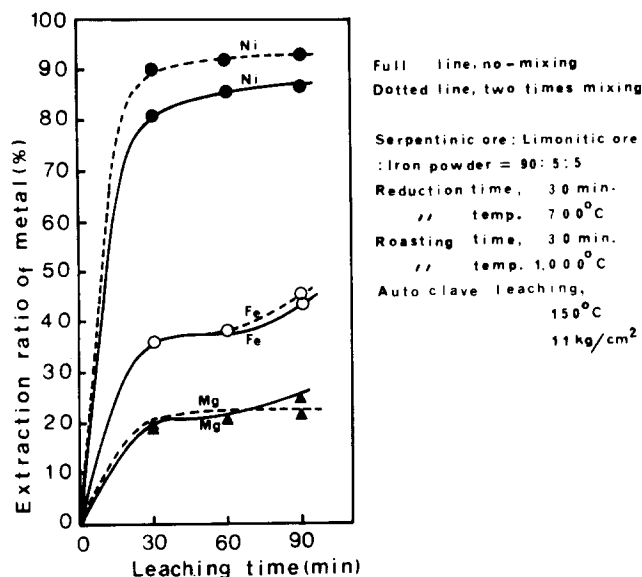
Fig. 4. Relation between the autoclave-leaching time and metal extraction ratio.

to forsterite and amorphous silica at 800°C (3, 4). The iron minerals will, therefore, consist of wustite and/or magnetite, and iron silicate.

Nickel oxide which coexists with wustite may be dissolved by the hot diluted sulfuric acid. At temperatures greater than 850°C in the first reduction stage, the main iron minerals will be forsterite (ferroan), enstatite (ferroan) and metallic iron.

Some of the iron elements will be consumed in the formation of iron olivine in the first reduction stage. The iron will change mainly to magnetite and to wustite in the secondary roasting stage. The wustite content will become less than that at 700°C in the first reduction stage and the iron extraction ratio may be reduced as a result.

When iron powder was added, two mixing times were enough to improve nickel extraction.

After reduction-roasting procedures, autoclave leaching tests were carried out and the mixing effects were compared. These results are shown in Figs. 4 and 5.

When the added iron powder was used as a substitutional reagent, the iron extraction ratios were higher than that of magnesium. This caused the formation of a large amount of wustite.

Nickel extractions were improved by the mixing procedure, but iron and magnesium extractions were unchanged. The optimum leaching time by the autoclave was 30 to 60 min. Iron extraction ratios increased suddenly at leach-
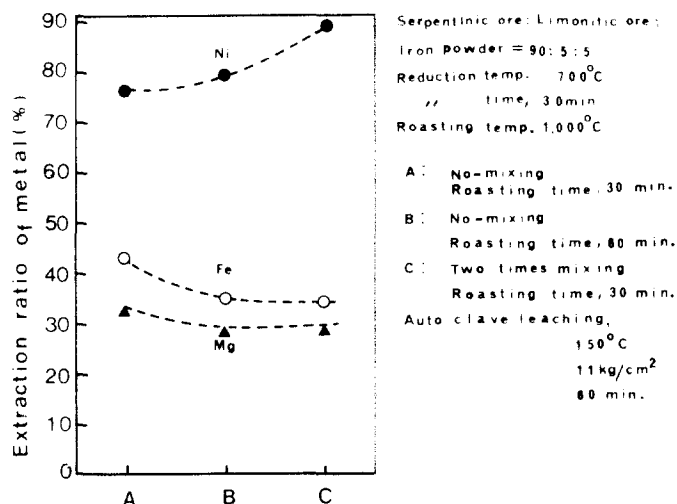
Fig. 5. Influence of the mixing procedure on the metal extraction.

ing times more than 60 min. Otherwise, magnesium extractions were approximately constant.

Notwithstanding low reduction temperatures, the autoclave leaching procedure appeared to improve nickel extraction without a detrimental increase in the iron and magnesium dissolution. However, in spite of this autoclave leaching procedure, iron and magnesium constituents could not be depressed perfectly.

REDUCTION, ROASTING AND OXIDATION OF THE MIXED ORE

We carried out X-ray diffraction research on the leaching residue under ambient pressure with the autoclave. The results showed that pyrolusite and wustite were dissolved by sulfuric acid. On the other hand, enstatite, enstatite (ferroan), quartz, hematite, maghemite, magnetite, kaoline and forsterite remained in an insoluble state.

The autoclave-leaching residue also contained new hydrate minerals such as calcium magnesium hydrate and magnesium metasilicate. Iron and magnesium elements were transformed to magnetite, hematite, maghemite, forsterite (ferroan), enstatite (ferroan) and calcium magnesium hydrate. These transformations were assumed to contribute to an elimination of the detrimental effect of the dissolution of iron and magnesium.

Next, we tried three processes: reduction, roasting and oxidation.

In the oxidation process (carbon dioxide plus steam) gas was used as an oxidation gas in which carbon dioxide gas was injected into water at 85°C and carbon dioxide gas saturated with steam was introduced into the combustion tube. In order to study the effect of the reducibility in the reduction stage,
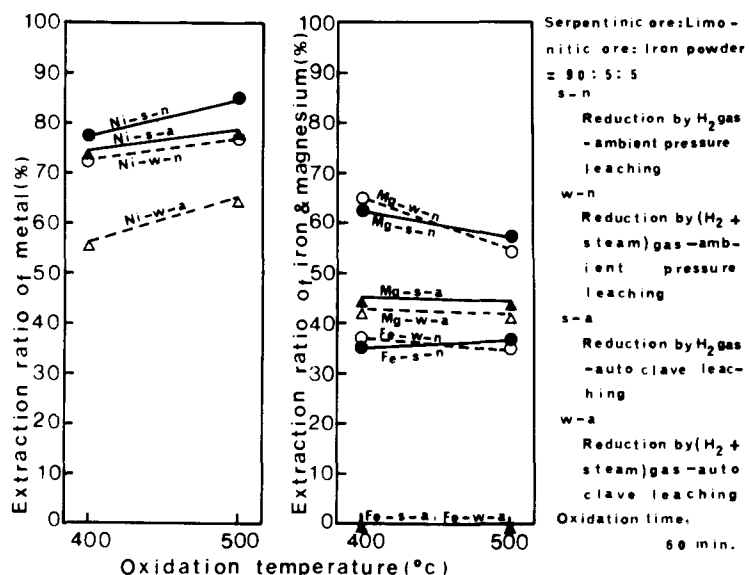
Fig. 6. Influence of oxidation temperature on the extraction ratio of metal under strong and under weak reduction gas.

hydrogen and (hydrogen plus steam) gas were used as the reduction gas. The oxidized ore was finally leached under ambient pressure and high pressure. The experimental results are shown in Fig. 6.

When the strongest hydrogen reduction gas was utilized, the nickel extraction ratios in the ambient pressure and autoclave leaching were not so different. However, when using a weak reduction gas (hydrogen plus steam), those nickel extraction ratios showed a remarkable difference. The iron and magnesium extraction ratios under these leaching procedures also showed a remarkable difference. That is, the solubility of iron and magnesium constituents could be depressed effectively by the autoclave leaching procedure. The dissolution of the iron constituent was perfectly depressed.

In case of the externally added iron powder, the procedure of strong reduction steam roasting, oxidation and autoclave leaching was most effective for preferential nickel extraction, and an oxidation temperature of approximate 500°C was also effective.

Hill and Dufour(5) proposed a reduction–oxidation process in which the iron constituent is changed from metallic iron to wustite and/or magnetite. The wustite and magnetite are insoluble in ammoniacal ammonium carbonate. However, wustite is soluble in diluted sulfuric acid. In the sulfuric-acid leaching process, wustite, which is the excessive iron constituent in roasted ore, has to be transformed to magnetite or maghemite by the oxidation procedure.

After several considerations, we discovered that if the iron constituent in goethite from limonitic ore is transformed to wustite or magnetite by reduc-
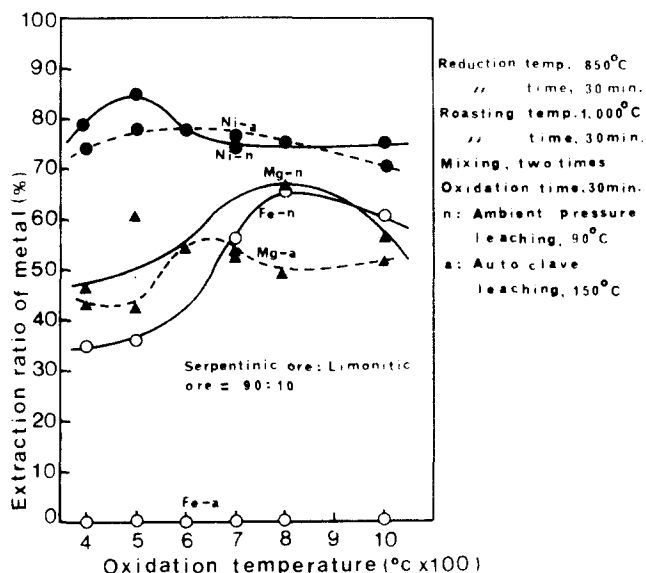
Fig. 7. Influence of oxidation temperature on the extraction ratio of metal under ambient-pressure and high-pressure leaching.

tion, the iron content as the substitutional reagent will be enough and the external iron powder will be unnecessary. From a point of view of the characteristics of laterite deposits, we determined the mixing ratio, and the positive effects were condensed to an optimum oxidation temperature. That is to say, during 60 minutes of oxidation time, the oxidation temperatures were varied about 400°C to 1,000°C, and leachings were carried out under ambient and high pressures. The experimental results are set forth in Fig. 7.

The extraction ratios of iron and magnesium showed a similar tendency at oxidation temperatures more than 600°C, and higher than that of 400°C to 500°C. A large part of iron constituent seemed to be present as wustite, and the magnesium constituent is magnesium oxide in association with iron oxide.

The iron extraction ratios of ambient-pressure leaching and autoclave leaching had remarkable differences. The iron extractions could be depressed perfectly by autoclave leaching. This means that a large part of the iron constituents in the oxidation stage will still remain as wustite, and effective transformation to magnetite and maghemite does not progress.

The X-ray diffraction research on the autoclave-leaching residue revealed the disappearance of wustite, and the appearance of maghemite, hematite, calcium magnesium hydrate and magnesium metasilicate.

In the case of the positive utilization as a substitutional reagent of iron oxide obtained by reduction from goethite, the oxidation procedure after the reduc-
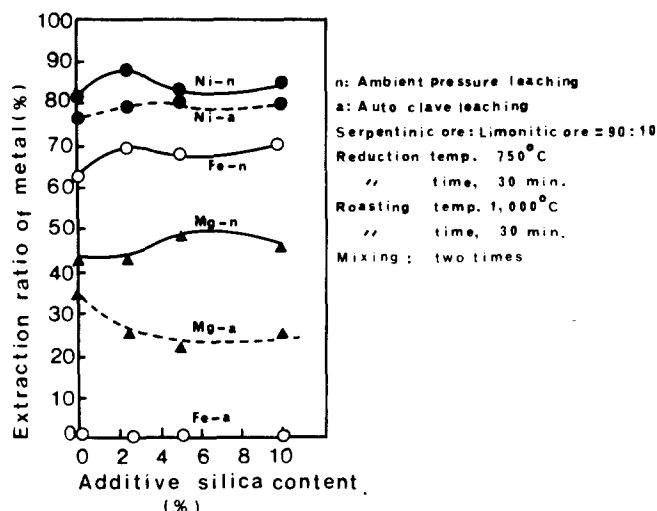
Fig. 8. Relation between respective metal extraction ratios by the ambient pressure and autoclave leaching, and the additive silica content.

tion–roasting process is not the most effective for the depression of iron and magnesium constituents.

In order to eliminate the detrimental effect of wustite remaining in the roasted ore, the best procedure seems to be an application of the autoclave-leaching procedure, and the depression of the magnesium constituent requires another procedure.

INFLUENCE OF THE ADDITIVE SILICA ON THE MIXED ORE

We considered that if quantities of wustite did not remain after the steam-roasting procedure, the wustite would probably be recrystallized to maghemite and hematite by the autoclave-leaching procedure. The oxidation process after the steam-roasting was, therefore, eliminated and the roasted ore was leached directly with the autoclave. We also utilized silica sand as an external additive reagent which would fix the magnesium constituent as magnesium silicate. The experimental results are shown in Fig. 8.

Notwithstanding that silica was added, the iron and magnesium extraction ratios by the ambient pressure leaching were about 70 and 45%, respectively, and these extraction ratios were not so different comparing with the non-addition of silica, and no effect on the depression of iron and magnesium was shown.

Iron and magnesium constituents furthermore will be in the range FeO–MgO–Ni in the equilibrium constitutional diagram (2, 6) under an atmosphere at 1,000°C and (31% H_2 + H_2O) gas (2). A large part of the iron constituent, therefore, may be wustite, and a small part seems to be fayalite, forsterite (ferroan), enstatite (ferroan) and magnetite in the roasting stage.

The magnesium constituent in the roasting stage also seems to be magnesium oxide, forsterite and enstatite. The iron and magnesium extraction ratios by the ambient pressure leaching, therefore, may be high.

However, the iron extraction ratios during autoclave leaching were lower than 0.2%. The nickel extraction ratios were kept up to similar values and were a little bit lower than those in direct leaching under ambient pressure.

In the case of addition of iron metal powder, it was clear that the iron constituent could possibly be depressed as maghemite, hematite, magnetite and etc. by the autoclave leaching.

The addition of a small amount of silica did not have a detrimental effect on nickel extraction and worked as a depressor of magnesium being formed as magnesium metasilicate.

Adding a few percent of limonitic ore was desirable for the substitution of nickel.

The goethite in limonitic ore changed to magnetite, wustite and/or metallic iron by a reduction procedure with hydrogen gas, and the substitutional reaction of nickel by these iron oxides through steam-roasting was performed effectively.

In the hydrometallurgical treatment of serpentinic ore, the addition of a small amount of silica and limonitic ore and reduction-roasting-autoclave leaching are seen to be the best procedure.

SUMMARY

(1) We used ore samples from the Pomalaa mine. These samples were composed of serpentinic and limonitic ores and a mixture of serpentinic and limonitic ores was utilized for hydrometallurgical investigations.

(2) In order to study the characteristics of the ore at high temperatures the mixed ore was calcined with a muffle furnace. Maximum extraction of nickel was obtained at about 900°C which temperature coincided with the initial recrystallization temperature of forsterite from antigorite.

(3) The nickel extraction ratios decreased rapidly at temperatures higher than 900°C.

(4) The iron extraction was depressed effectively and showed a low percentage at 1,100°C. However, the magnesium extraction ratios showed the highest value among these metals, and the depression of magnesium dissolution appeared to be difficult.

(5) However, the depression of the solubility of the iron constituent during the actual experiment after the reduction-roasting procedure was extremely difficult.

(6) When the external iron powder was used as a substitutional reagent many excessive iron oxides remained in the reduction-roasted ore as wustite mainly, an the iron solubility therefore was kept at a high level.

(7) To decrease the solubility of iron, wustite had to be transformed to maghemite, hematite and/or magnetite. We adopted, therefore, the reduction-steam-roasting–oxidation–autoclave leaching procedure by which the solubility of iron could be depressed perfectly.

(8) However, the magnesium constituent couldn't be depressed effectively by the autoclave-leaching method.

(9) In order to utilize the iron oxide as the substitutional reagent, the iron oxide reduced by the reduction procedure from goethite in limonitic ore was considered. That is, the reduction-steam-roasting procedure on the mixed ore was carried out without the addition of external iron powder.

(10) The addition of a small amount of silica was most effective for depressing the solubility of the magnesium constituent, and did not show a detrimental effect on the nickel extraction.

(11) In the hydrometallurgical handling of serpentinic ore, the use of a small amount of external additive silica and limonitic ore followed by reduction-steam-roasting and autoclave leaching appeared to be a good procedure.

(12) By these procedures, nickel, iron and magnesium extractions of 80, 0.2, 23%, respectively, were obtained and the dissolution of the iron was depressed perfectly.

ACKNOWLEDGEMENT

REFERENCES

1 Shirane, Y., Kawahara, M. and Mitune, Y., 1983. Ore–iron magnetic roasting and dilute sulfuric acid leaching of ganierite ore. J. Min. Met. Inst. Japan, 99 (1145): 579–583.
2 Shirane, Y. and Matuzaka, K., 1965. Studies on the treating of laterite. J. Min. Met. Inst.Japan, 925: 469–475.
3 Shirane, Y. and Kuwasaki, N., 1980. Studies on fixation of SO_3 gas into metagarnierite phase with alkaline sulfate evolution and separation of SO_3 gas out of product by means of thermal analysis. J. Min. Met. Inst. Japan, 96(1113): 837–842.
4 Davidson, R.J., 1972. The role of iron oxides in nickel segregation. Panel Discussion on Nickel Segregation, Feb. 1972, pp. 108–127.
5 Hills, R.C. and Dufour, M.F., 1946. Recovery of Nickel and/or Cobalt from Nickelferous Ore. Canadian Patent, 2,400, May 1946.
6 Shirane, Y., Kawahara, M. and Mitsune, Y., 1983. The mechanism of liberation of nickel oxide from garnierite ore by means of the adding iron steam roasting. J. Min. Met. Inst. Japan, 99 (1149): 999–1003.