

APPLICATION OF ATTRITION GRINDING IN ACID LEACHING OF NICKEL SULFIDE CONCENTRATE^①

Li Ximing, Chen Jiayong

*Institute of Chemical Metallurgy,
The Chinese Academy of Sciences, Beijing 100080*

Roland Kammel, Franz Pawlek

*Institute of Metallurgy, Technical University of Berlin,
Strasse des 17 Juni 135, 106 23 Berlin, Germany*

ABSTRACT The acid leaching of fine ground nickel sulfide concentrate under atmospheric pressure was studied. The leaching experiments were performed with a pyrrhotite containing nickel sulfide concentrate and ferric ion as oxidant. The effects of attrition grinding, leaching temperature, concentration of sulfuric acid as well as formation of elemental sulfur on the leaching rate were investigated. The experimental results demonstrated that attrition grinding as a technique of mechanical activation can offer significant advantage for hydrometallurgical processing of complex metal sulfide ores and concentrate.

Key words acid leaching nickel cobalt sulfide concentrate

1 INTRODUCTION

The versatile nature of hydrometallurgical processes makes them particularly suitable to the treatment of complex sulfide ores and concentrates. The first commercial operation using hydrometallurgy to the extraction of nickel from sulfide concentrate was carried out by Scherritt Gorden Mine LTD. in 1954^[1]. The concentrate was leached in two stages with strong aqueous ammonia solution at moderate elevated temperature and under oxygen pressure. During the leaching process sulfur in the concentrate was oxidized to a number of oxyacids including sulfate. Since then the Scherritt Gorden Process has been used for treating metallic sulfide concentrate all over the world. However, because of limited market for ammonium sulfate in some areas and difficulties arisen from using elevated pressure treating refractory sulfide ores, the direct acid leaching process under atmospheric pressure has attracted more attention in recent years^[2-11]. Among the various lixivants tested

ferric sulfate and chloride have been commonly used due to the process yield of more environmental benign product—elemental sulfur rather than sulfur dioxide or ammonium sulfate. Although those processes can improve the recovery of nickel, copper *etc.*, the leaching time was often more than 7~8 hours. It is well known that the mechanochemical action—fine and ultra-fine grinding can accelerate the rate of leaching sulfide minerals through increasing its surface area and activating its surface state. The early studies showed that stirred ball milling was a right selection for the purpose of intensifying the leaching process^[10]. This paper is concerned with the sulfuric acid leaching of fine ground nickel sulfide concentrate under atmospheric pressure to demonstrate the advantage of using attrition grinding in hydrometallurgical processing of complex sulfide ores and concentrates.

2 EXPERIMENTAL

2.1 Material

① Received Dec. 3, 1996; accepted Jan. 30, 1997

Nickel sulfide concentrate used in this study was obtained from Kotalahit Mine in Finland. The chemical composition of the concentrate was given in Table 1.

Table 1 Chemical composition of nickel sulfide concentrate tested (mass fraction, %)

Ni	Fe	Cu	Co	Zn
6.3	46.6	0.93	0.23	0.016
S	SiO ₂	MgO	Al ₂ O ₃	CaO
32.4	7.6	2.6	0.91	0.69

The two major minerals in the concentrate are pyrrhotite and pentlandite, and the other minerals were identified as chalcopyrite, pyrite as well as sphalerite. Only chemicals of reagent grade and twice distilled water were used in all experiments.

2.2 Analysis

BET method and laser diffraction method were used for the measurements of specific surface area and grain size of samples respectively. The initial average grain size and value of specific surface area of the concentrate (as received) was *ca.* 40 μm and 1.16 m^2/g , after 80 min fine grinding was < 10 μm and 7.0 m^2/g respectively. The liquid samples were analyzed by atomic absorption spectroscopy (AAS). The solid residue was decomposed by hydrochloric acid at first and then analyzed by AAS. The elemental sulfur in residues was extracted with CS_2 and determined gravimetrically after distillation of CS_2 . The mineral composition of samples was analyzed by XRD.

2.3 Apparatus and experimental procedure

The equipment used for attrition grinding and acid leaching was similar to the previous work^[13]. In the leaching experiments 1 liter solution containing certain amounts of sulfuric acid and ferric sulfate were added into a glass reactor immersed in a water bath in which temperature can be controlled within $\pm 0.1^\circ\text{C}$. Oxygen gas was bubbled at 0.15 NL/min into the solution. When the temperature reached the required value, a charge of 20~60 g concentrate was added

and then the leaching time was recorded. The slurry was agitated with a mechanical stirrer at a constant speed of $800 \pm 10 \text{ r/min}$. During the experiments samples were taken out from the reactor at selected time intervals and analyzed for the metal contents.

3 RESULTS AND DISCUSSION

3.1 Effect of attrition grinding

As is shown in Fig. 1, fine grinding plays an important role on the leaching of complex sulfide concentrate. The leaching rate of fine ground sample was increased remarkably in comparison with the sample as received, *i. e.* the metal extraction was increased 3~4 times. In addition to size reduction the activated surface state which was contributed by the attrition grinding is also an important reason for the significant improvement of leaching rate. These results demonstrate that attritor grinding is effective for the processing of refractory sulfide concentrate.

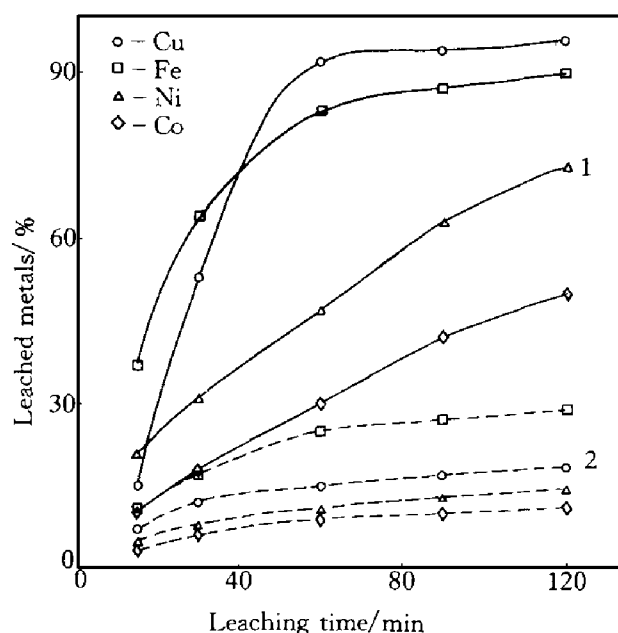


Fig. 1 Effect of fine grinding on the leaching of nickel sulfide concentrate

Conditions: H_2SO_4 0.2 mol/L, Fe^{3+} 0.4 mol/L, 85°C
 1—80 min fine ground sample.
 2—sample as received.

The effect of leaching time on the leaching of fine ground sample is illustrated in Fig. 2.

The recovery of nickel and copper as well as cobalt was increased firstly with the leaching time, but there was no remarkable change after leaching time of 3 hours. That suggests the increase of leaching time further is not necessary.

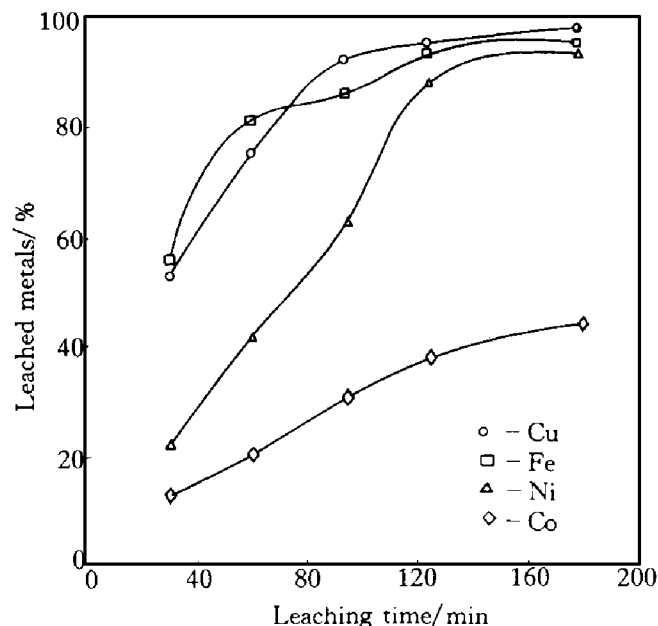


Fig. 2 Effect of leaching time on extraction of nickel sulfide concentrate

Conditions: H_2SO_4 0.2 mol/L, Fe^{3+} 0.4 mol/L, 90 °C.
Fine grinding 80 min in the Attritor.

3.2 Effect of sulfuric acid concentration

The effect of sulfuric acid concentration on the leaching rate is shown in Fig. 3. It has been proved in previous study that the fine ground sample either in the form of solid or slurry has no apparent difference on results of leaching. Hence the concentrate after wet attrition grinding was kept in slurry form in a container, then it was well agitated with a stirrer and was transferred into the reactor. In order to diminish the difference in slurry densities in experiments the leaching results were plotted in the form of recovery of metals *vs* G (G = density of slurry/density of H_2SO_4), within the range of slurry density 15~44 g/L, the recovery of metals did not have remarkable change with the increase of G value. This means that higher concentration of sulfuric acid cannot greatly improve the extraction of valuable metals under the specific condition studied.

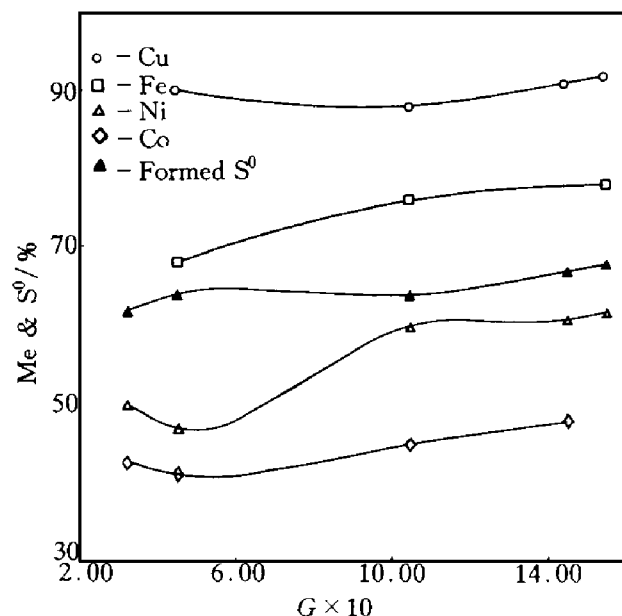


Fig. 3 Effect of sulfuric acid concentration on extraction of metals & formation of S^0

Conditions: H_2SO_4 0.1~1.0 mol/L, Fe^{3+} 0.4 mol/L, slurry density 15~44 g/L, 90 °C
 G = density of slurry/density of H_2SO_4 in leaching solution.

$\text{S}^0\%$ = (recovery of elemental sulfur/sulfur in the nickel sulfide concentrate) \times 100%

3.3 Effect of temperature

The effect of temperature on the leaching rate is illustrated in Fig. 4. It can be seen from Fig. 4 that only the leaching rate of chalcopyrite increased linearly with the increase of temperature, while the others followed a parabola curve. It was observed that the leaching of iron decreased when the leaching temperature was above 80 °C due to hydrolysis and precipitation of ferric ions as goethite (FeOOH), which was confirmed by XRD analysis of leached residues. The relationship between formation of elemental sulfur and temperature is also shown in Fig. 4, the maximal recovery of elemental sulfur was obtained at 80 °C, then after that it decreased with the increase of temperature further.

The sulfuric acid leaching of nickel sulfide concentrate in the presence of ferric ions under atmospheric pressure may be expressed as follows:



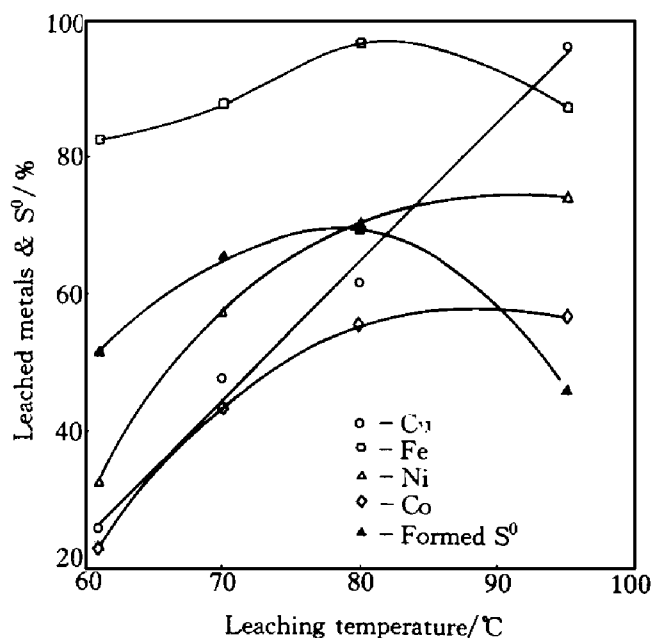
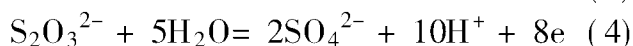
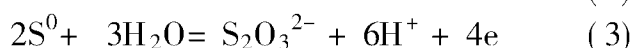


Fig. 4 Effect of temperature on extraction of metals and formation of S^0

Conditions: H_2SO_4 0.2 mol/L, Fe^{3+} 0.4 mol/L, leaching time 120 min, slurry density 20 g/L.



At moderate temperature the sulfur species in the leaching solution after reaction exists in the form of elemental sulfur, but under high temperature the oxidation of elemental sulfur to sulfate can be accelerated, results in the decrease of elemental sulfur recovery.

3.4 Discussion of rate limiting step

Because elemental sulfur is hydrophobic and insoluble in the aqueous solution, it will adhere to the surface of sulfide minerals. With the proceeding of the above mentioned reaction more and more surface of mineral particles was coated by elemental sulfur. The deposition of elemental sulfur provided a diffusion barrier with a moving reaction boundary. Therefore, the diffusion rate of reactants through the surface of mineral particles could be significantly retarded.

The extraction of elemental sulfur *vs* the change of the specific surface area indicated a good linear relationship (see Fig. 5), and that indicated the adhesion of elemental sulfur did block the inner-surface of mineral particles. In

this case the leaching rate can be described by the following kinetic model, which is well known in hydrometallurgy and is suitable for the characterization of leaching kinetics involving with formation of solid product^[12].

$$[1 - 2a/3 - (1 - a)^{2/3}] = kt \quad (5)$$

here a —leached fraction, k —diffusion constant and t —leaching time.

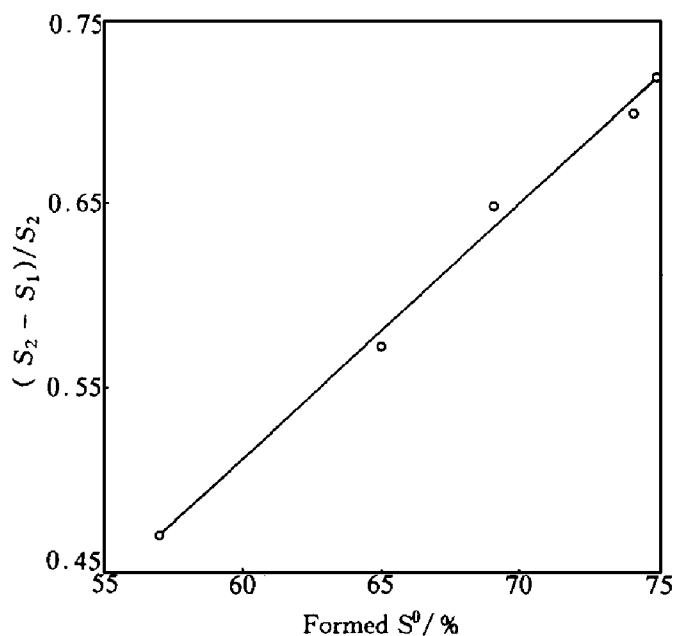


Fig. 5 Relationship between S^0 and change of specific surface area of leached sample

S_1 —specific surface area of leached sample with S^0

S_2 —specific surface area of leached sample without S^0

Provided the solid product of an reaction forms a tightly solid layer on reacting surface, the diffusion of reactants through the product layer may be rate limiting. The plotting of left side of equation (5) *vs* leaching time should show a linear relationship. Fig. 6 indicated that leaching behavior of nickel sulfide concentrate can be described by this model. Based on the data in the above Figs., apparent activation energy of 92 kJ/mol for the leaching of nickel from pentlandite was obtained, this value suggests that in the specific condition the diffusion of reactants through the solid layer and surface reaction are highly possible the rate controlling steps.

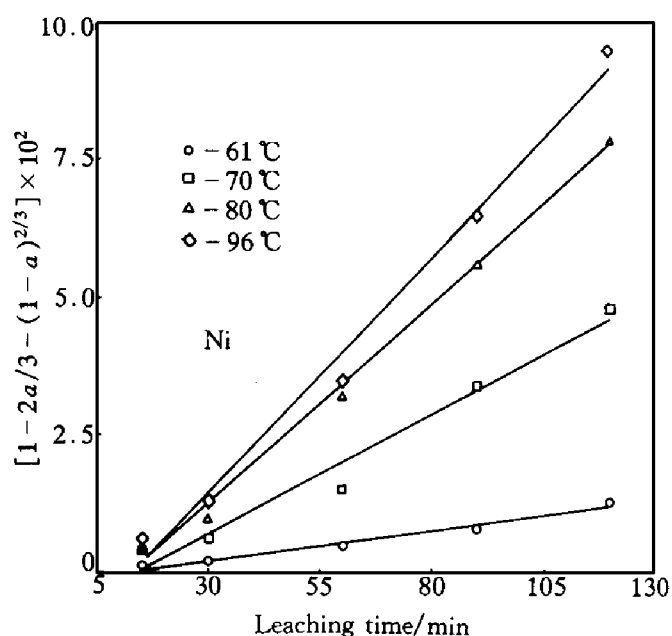


Fig. 6 Influence of temperature on leaching rate of nickel from sulfide concentrate

4 SUMMARY

The leaching rate of nickel sulfide concentrate was remarkably accelerated after 80 min fine grinding in the attritor. The formation of elemental sulfur affected the leaching process, the elevation of temperature was favorable to the extraction of valued metals with the formation of elemental sulfur. The leaching rate of pentlandite can be described by the kinetic model involving with formation of solid product.

The experimental results demonstrate that using attrition grinding as a method for intensification of leaching process could have commercial interest due to its feasibility and flexibility to be connected with any current hydrometallurgical process. Therefore, attrition grinding as a pre-

treatment method should be especially useful for the processing of refractory gold ores and complex sulfide concentrates.

REFERENCES

- 1 Weltman H, Robert Weir D. In: Proceedings of a Chemical Industry Symposium. Manchester in England: University of Manchester Institute of Science and Technology, 1981.
- 2 Dutrizac J E, MacDonald R J C. Miner Sci Eng, 1974, 6: 59– 100.
- 3 Hubli C, Mukherjee T K, Gupta C K. Hydrometallurgy, 1983, 10: 359– 366.
- 4 Thornber M R. J of Applied Electrochemistry, 1983, 13: 253– 267.
- 5 Todd I A, Distin P A. Hydrometallurgy, 1985, 14: 309– 371.
- 6 Daiger K, Gerlach J. Erzmetall, 1983, 36(2): 82– 87.
- 7 Li Ximing, Kammel R, Pawlek F *et al.* In: Zhen Yulian, Xu Jiazhong eds, Proceedings of the first international conference on hydrometallurgy (ICHM '88). Beijing: International Academic Publishers, 1989: 149– 154.
- 8 Mukherjee T K, Hubli R C, Gupta C K. Hydrometallurgy, 1985, 15: 25– 32.
- 9 Balaz P *et al.* Minerals Eng, 1995, 8(11): 1299 – 1308.
- 10 Anderson C G, Harrison K D, Krys L E. In: Proc SEM Annual Meeting. Albuquerque, 1994, Preprint No. 94– 95.
- 11 Gatner C E. Direkte oxidierende Laugung vom im Attritor feinstgemahlenen Kupfer-kieses bei Normaldruck. Germany: Dissertation in TU Berlin, 1986.
- 12 Sohn H Y, Wadsworth M E. Rate process of extractive metallurgy. USA: Plenum, 1979.
- 13 Beckstead L *et al.* In: Yannopoulos J C, Agarwal J C eds, International symposium on copper extraction and refining. 105th AIME Meeting, Las Vegas, Nevada, Feb. 1976 in USA.

(Edited by Yuan Saiqian)