

Selective leaching of nickel from low-sulfur Ni-Cu matte at atmospheric pressure

FU Yan(符岩)¹, LI Bin-chuan(李斌川)¹, FAN Chuan-lin(范川林)¹,
ZHAI Xiu-jing(翟秀静)¹, ZHANG Xi-jun(张希军)¹, LI Dong-he(李东和)²

1. School of Materials and Metallurgy, Northeastern University, Shenyang 110004, China;

2. Liaoning Provincial College of Communications, Shenyang 110122, China

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Abstract: A process of the selective leaching of nickel from low-sulfur Ni-Cu matte at atmospheric pressure was described. This matte was obtained from high grade Ni-Cu matte by magnetic separation, which mainly contained Ni-Cu alloy and a small quantity of sulfides. Firstly, the acid-oxygen ($\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-O}_2$) leaching of the matte was conducted at atmospheric pressure. When the solution pH value reached 1.0–2.0, the oxygen flow was ceased. Then, the aqueous copper was rejected by cementation reaction with Ni in the alloy. The mineralogical characteristics of the matte in the process were analyzed by X-ray diffractometry, optical microscopy and scanning electron microscopy. And the effects of variations in temperature, particle size distribution, oxygen flow rate, pulp density, initial acid concentration and initial concentration of copper ion were investigated.

Key words: Ni-Cu matte; selective leaching; Ni-Cu alloy; cementation

1 Introduction

Although nickel-copper mattes have been conventionally treated by pyrometallurgical method, hydrometallurgical processes gain much attention for reducing the environmental impact of industrial activities and recovering valuable metals from feeds in recent years[1]. Numerous studies on the leaching of Ni-Cu matte have been reported for many years. The leaching behaviors of nickel-copper matte at atmospheric pressure had been studied[2–5]. The studies on high pressure leaching of nickel-copper matte were also conducted [6–8]. In addition, the studies on the operations and improvements of the existing Ni-Cu matte refining processes have been conducted[9–12]. For an atmospheric leaching process, aqueous copper rejection is mainly performed by two methods. Aqueous copper is precipitated as basic cupric sulphate $\text{Cu}_3(\text{OH})_4\text{SO}_4$ (antlerite) by raising solution pH value to 5.0[4–5], or alternatively, the rejection of aqueous copper is conducted by cementation with addition of reactive nickel or nickel sulphide powder after the liquid–solid separation of leaching pulp[6].

Compared with Ni-Cu matte, low-sulfur Ni-Cu

matte contains a large number of Ni alloys. And this shows the potential of aqueous copper rejection by cementation with unreacted Ni alloys. To determine the feasibility of this process, the selective leaching of nickel from low-sulfur Ni-Cu matte at atmospheric pressure was presented. Firstly, the acid-oxygen ($\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-O}_2$) leaching of the matte was conducted at atmospheric pressure. When the solution pH reached 1.0–2.0, the oxygen flow was ceased. Then, the aqueous copper was rejected by cementation reaction with unreacted Ni in the alloy. The mineralogical characteristics of the matte in the process were analyzed. And the effects of variations in temperature, particle size distribution, oxygen flow rate, pulp density, initial acid concentration and initial concentration of copper ion were investigated.

2 Experimental

The raw material, low-sulfur Ni-Cu matte, was obtained from high grade Ni-Cu matte by magnetic separation. From the X-ray diffraction analysis, the main phases present in the matte were nickel alloy, heazlewoodite (Ni_3S_2) and chalcocite (Cu_2S) (Fig.1). Chemical analysis of the matte indicated the following elemental contents: Ni 48.1%, Cu 21.1%, Co 1.08%, Fe

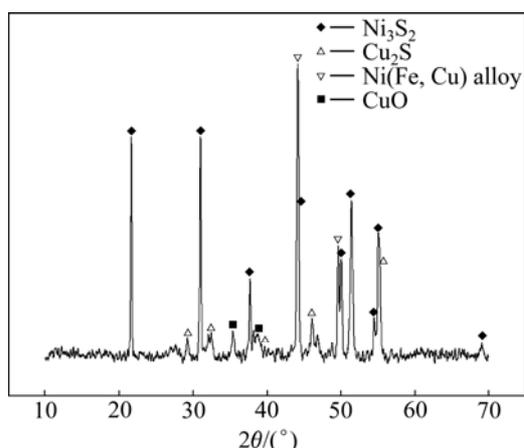


Fig.1 X-ray diffraction pattern of low-sulfur Ni-Cu matte

5.56%, S 12.5% (mass fraction) and precious metals: Ag 131 g/t, Au 32 g/t, Pt 112 g/t and Pd 74 g/t.

Before the conduction of leaching tests, the grinding characteristic of low-sulfur Ni-Cu matte was obtained from grinding tests which were performed in a laboratory stainless steel mill. 800.00 g matte sample was fed into the mill with 3.0 L tap water and ground for pre-set time. The size analyses of the feed and the individual fractions were obtained by screen separation.

Leaching tests were performed in a 1.5 L glass vessel which was placed in a water bath with temperature control. The cover of the vessel was fitted with baffles, a thermometer, a pH probe and a variable speed stirrer. Gas was supplied by an oxygen bomb and a nitrogen bomb with adjustable flow meters. And oxygen partial pressure was controlled by adjusting the flow rate ratio of oxygen to nitrogen. As a typical experimental procedure, 0.8 L solution with predetermined concentrations of copper sulfate and sulfuric acid was added to the leaching vessel and heated to the desired temperature. Then, gas was injected into the pulp with required flow rate and oxygen partial pressure. The stirrer was set at the speed of 500 r/min after 80.00 g matte sample was added. The pH value of the solution was monitored by a digital pH meter during the leaching processes. When the solution pH value reached 1.0–2.0 (a typical value of 1.0), the oxygen flow was ceased. Then, the aqueous copper rejection by cementation was conducted for 3.0 h at the same temperature.

During the leaching process, samples were taken using a pipette at predetermined time. All samples were immediately filtered and the solids were washed with distilled water before drying at (80 ± 5) for at least 5.0 h. The characterization of the solid samples was done by X-ray diffractometry, optical microscopy and scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS). At the end of tests, the solution samples were analyzed using inductively coupled plasma

(ICP). Then, the fraction of nickel extraction was calculated. And the concentration of aqueous copper was appointed to be another index of the selective leaching process.

3 Results and discussion

3.1 Grinding characteristic of low-sulfur Ni-Cu matte

Due to the ductility of the metals in the nickel alloy, the grinding characteristic of the low-sulfur Ni-Cu matte is quite different from Ni-Cu matte. The results of grinding tests are shown in Fig.2. From the curves of cumulative mass fraction versus grain size, the particle size of the matte decreases with the increasing of grinding time. When the grinding time is more than 90 min, however, the particle size distribution of the matte sample is almost independent of grinding time. And the particle size fractions of $< 74 \mu\text{m}$ is only about 62%. Such a particle size distribution shows an obvious difference from the Ni-Cu matte in previous work[5]. The matte milled for 240 min (see Fig.2) was used as typical raw material in the following tests.

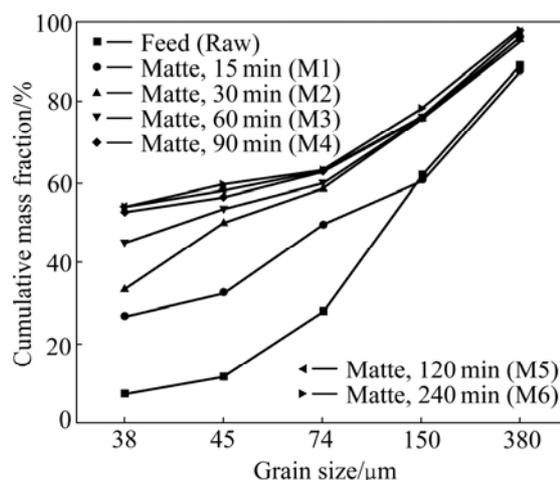


Fig.2 Particle size distribution of matte with various grinding time

3.2 Mineralogical characteristics of low-sulfur Ni-Cu matte

To determine mineralogical characteristics of the matte during leaching process, solid samples were obtained at 10 min, 60 min, solution pH 1.0 and the end of the test, respectively. From the X-ray diffraction analysis of these samples, the Ni alloy is dissolved and pure copper is presented in the leaching process (Fig.3). Based on the literature data in previous works[2–5] and this study, the following chemical reactions were chosen to describe the selective leaching process of the low-sulfur matte at atmospheric pressure.

In the acid-oxygen leaching stage, the dissolving of nickel alloy and a small quantity of sulfides are conducted.

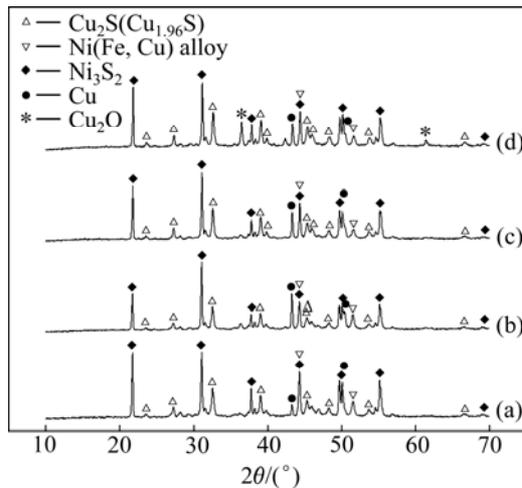
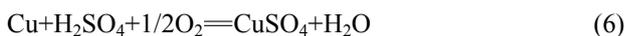


Fig.3 X-ray diffraction patterns of solid samples during leaching process with oxygen partial pressure of 80 kPa (Conditions: initial acid concentration 50 g/L, initial copper ion concentration 15 g/L, temperature 90 and gas flow rate per litre slurry 1.0 L/min: (a) 10 min; (b) 60 min; (c) Solution pH 1.0; (d) Leaching end

The main reactions are



and at the later of this stage, copper is dissolved by the following reaction:



When the gas flow is ceased, the cementation between aqueous copper and nickel alloy in the matte is the main reaction, as shown in Eqs.(2) and (3).

The characteristics of the solid sample were also analyzed by optical microscopy and scanning electron microscopy. From the results, a pure copper product layer is obviously found on the surface of the matte particles (Figs.4 and 5). This agrees with the phase change during the leaching process, which is obtained from X-ray diffraction analysis.

3.3 Effect of temperature

During the acid-oxygen leaching process, the pH value of solution increases with leaching time (Fig.6). Under the applied process conditions, it would spend about 200 min for raising the pH value of solution to 2.0. To determine the effect of temperature, tests were carried out in the temperature range of 80–90 . From the results shown in Fig.7, temperature plays an important role in the process of copper rejection. Higher temperature

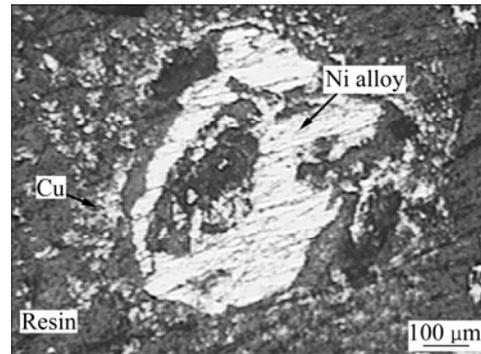


Fig.4 Optical microscopy photograph of solid sample at end of leaching

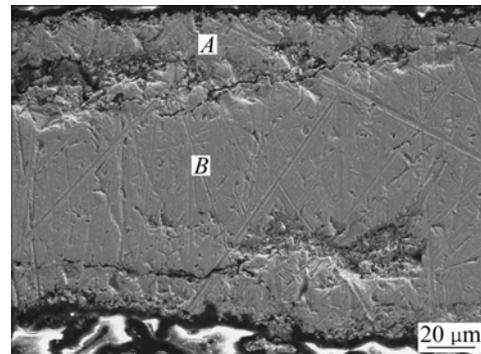


Fig.5 Scanning electron microscopy photograph of solid sample at end of leaching (A: Pure copper; B: Ni alloys, according to EDS results)

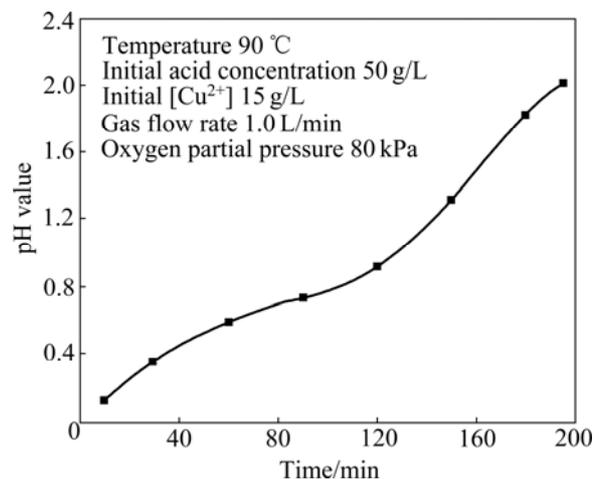


Fig.6 Plot of solution pH value vs time at acid-oxygen leaching stage

is of benefit to cementation reaction. The similar result for the leaching of Ni-Cu matte was found in the previous work[1]. Therefore, higher temperature for selective leaching of nickel from the matte is preferred.

3.4 Effect of particle size distribution

During the mill test, three matte samples were

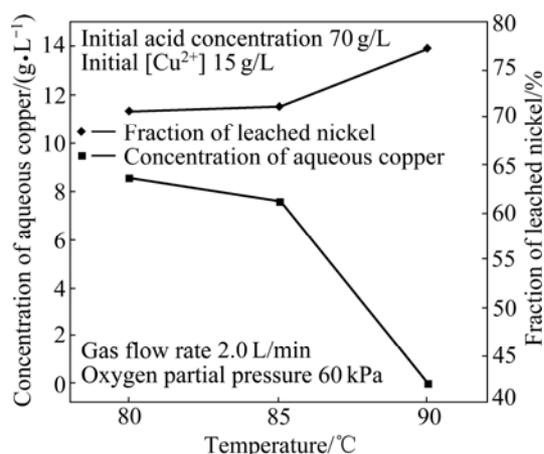


Fig.7 Effect of temperature on selective leaching process

selected for leaching tests, which include the Raw, M1 and M6 (see Fig.2). The results are shown in Fig.8. It is found that smaller particle size is good for copper rejection. The fine particles supply larger reaction area for cementation and promote the copper rejection process. With the leaching proceeding, a diffusion layer (mainly metal copper) forms. The leaching process can also be promoted by thinner diffusion layer supplied by fine particles. For a well selective leaching process, the particle size of the matte should be reduced as small as possible by grinding.

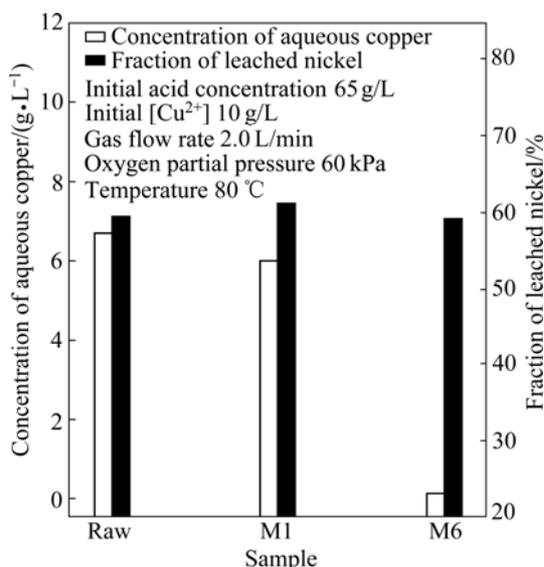


Fig.8 Effect of particle size distribution on selective leaching process

3.5 Effects of oxygen partial pressure and gas flow rate

To determine the effect of effective oxygen partial pressure, tests were conducted in various oxygen partial pressures and gas flow rates. The results are concluded in Figs.9 and 10. From these curves, it can be found that the

oxygen partial pressure in the range of 60–80 kPa and gas flow rate have little or no effect on the selective leaching process. Oxygen supply is only influences the acid-oxygen leaching of the matte. As oxygen partial pressure or/and gas flow rate increases, the effective oxygen partial pressure of leaching system increases. Then, more dissolved oxygen can accelerate the acid-oxygen leaching process.

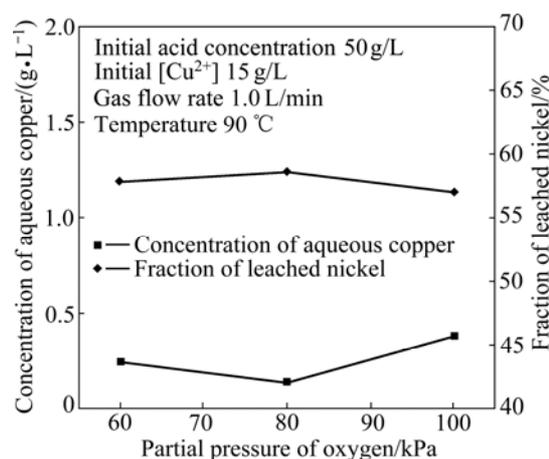


Fig.9 Effect of oxygen partial pressure on selective leaching process

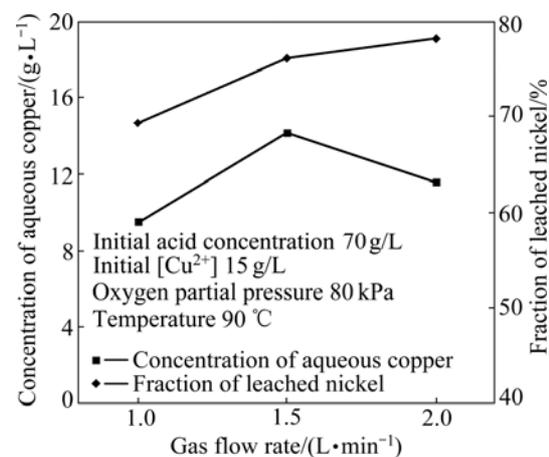


Fig.10 Effect of gas flow rate on selective leaching process

3.6 Effect of pulp density

To examine the effect of pulp density, tests were carried out in the range of 7.69%–11.11% (mass fraction of solid in pulp). With the pulp density decreasing, both the fraction of leached nickel and concentration of aqueous copper at the end of leaching process decrease (Fig.11). Lower pulp density indicates that the concentration of dissolved oxygen decreases. But the reaction area increases with a more amount of the matte sample in the pulp. As a whole, the lower pulp density is of benefit to copper rejection but not to increasing the fraction of leached nickel. For an industry practice, it should take economic factor into consideration.

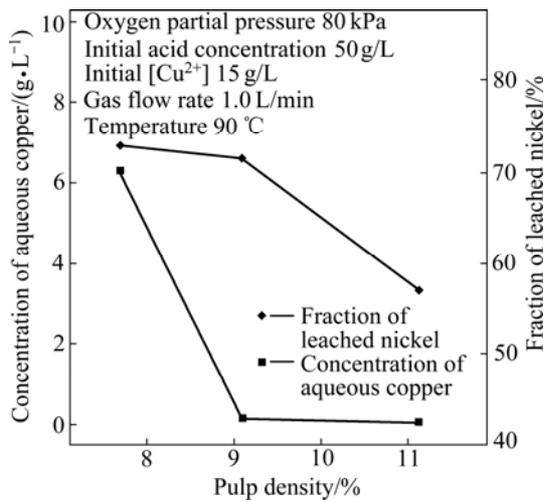


Fig.11 Effect of pulp density on selective leaching process

3.7 Effect of initial acid concentration

Tests with different initial acid concentrations were performed at temperature of 80 °C. When the solution pH value reaches 1.0, the tests with lower initial acid concentrations will have a lower nickel extraction and a larger nickel alloy surface area for cementation. The results of tests with different initial acid concentrations (Fig.12) agree with the statement described above. Under the applied conditions, when the initial acid concentration is 60 g/L, the end concentration of aqueous copper of 0.12 g/L and fraction of Ni leached of 65.7% are obtained.

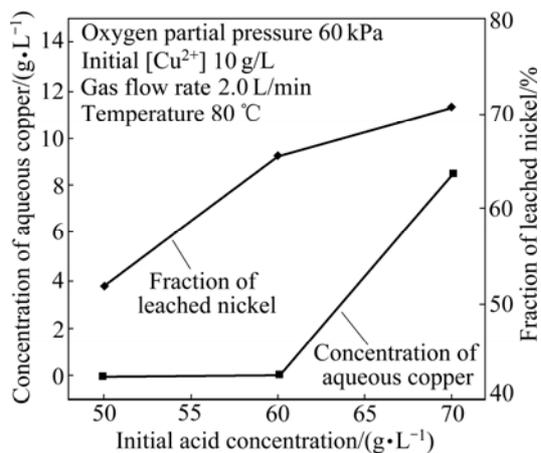


Fig.12 Effect of initial acid concentration on selective leaching process

3.8 Effect of initial concentration of copper ion

To investigate the effect of the initial concentration of copper ion, leaching tests were conducted for the initial concentration of copper ion of 5–15 g/L. The results are shown in Fig.13. The tendency of the results is similar to that in the tests for determining the effect of initial acid concentration. In addition, the decrease of the

time for raising solution pH value to 1.0 is found with the increase of initial concentration of copper ion. A small amount of copper ion acts as catalyst for the leaching of Ni-Cu matte, and it has been determined in previous work[13]. From the dramatic decrease of the time to pH=1.0 (Fig.14), it can be also presumed that the concentration of copper ion has a low value during the acid-oxygen leaching process with a lower initial concentration of copper ion under the applied processing conditions.

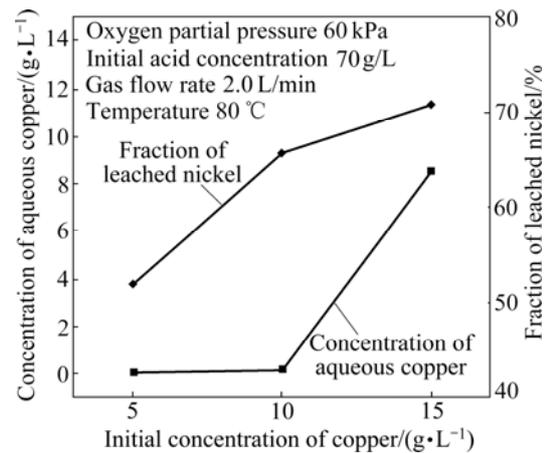


Fig.13 Effect of initial concentration of copper ion on selective leaching process

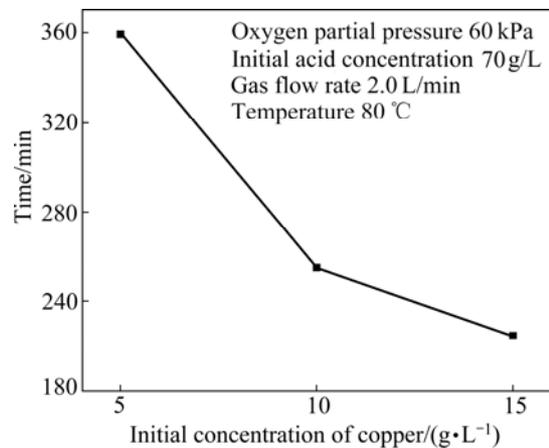


Fig.14 Effect of initial concentration of copper ion on time of acid-oxygen leaching stage

4 Conclusions

1) During the acid-oxygen (CuSO₄-H₂SO₄-O₂) leaching of the matte, when the solution pH value reaches 1.0–2.0, the oxygen flow is ceased, and then the aqueous copper can be rejected by cementation reaction with Ni in the alloy.

2) Under the applied test conditions, the selective leaching process is influenced by process parameters, such as temperature, particle size distribution, oxygen flow rate, pulp density, initial acid concentration and

initial concentration of copper ion. The end concentration of aqueous copper of 0.12 g/L and the fraction of Ni leached of 65.7% are obtained under optimized conditions.

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