The role of $CaCO_3$ in the extraction of valuable metals from low-nickel matte by calcified roasting—acid leaching process

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Abstract. The extraction of valuable metals from low-nickel matte via a calcified roasting-acid leaching process was investigated. The influences of process parameters on the extraction of metals were studied, including the roasting temperature, roasting time and the addition of $CaCO_3$. Under the optimum condition, 92.4% of Ni, 97.1% of Cu, 95.1% of Fe, and 91.2% of Co were recovered. In addition, the removal of iron via goethite precipitation process was studied. The results show that 99.8% of Fe could be removed by goethite process. The reaction mechanism of calcified roasting of low-nickel matte was also studied by XRD and XRF analysis. It was shown that the formation of ferrite can be effectively inhibited by $CaCO_3$ addition, leading to enhancement of the metal recovery.

1. Introduction

Nickel (Ni) is the twenty fourth most common elements in the earth's crust; it naturally occurs as sulfides or laterites (oxides), in which almost 60% of the nickel production is via processing sulfide ores, while only 30% of the nickel reserves exist in sulfide deposits [1-2]. As a strategic metal, Ni is widely used in stainless steel, alloys, batteries, and catalysts [3]. With the increasing discrepancy between the growing industrial demand and the continuous diminution of nickel sulfide ores, alternative methods applicable to complex sulfide ores have become an important research topic.

Conventionally, the floating-smelting-converting process, which is of high efficiency and low cost, is used to treat sulfide ores [4]. This process includes the following steps. Firstly, Nickel sulfide minerals are amenable to concentration by milling and flotation, with rejection of a high proportion of ore rock and pyrrhotite prior to smelting. Secondly, the nickel sulfide concentrate is smelted in a flash furnace or electric furnace, separating gangue and resulting in low-nickel matte. During this process, Ni, Cu, and Co are enriched and the loss of valuable metals is rare. Thirdly, the low-nickel matte is treated by converter blowing to decrease the contents of Fe and S, resulting in high-nickel matte which is further enriched in Ni, Cu, and Co. However, in this process, part of valuable metals, especially a large amount of cobalt, might be over oxidized and translated into slag. Finally, for refining high-nickel matte, different refining processes such as floatation-magnetic separation, selective leaching and layered melting processing have been used to eventually obtain Ni, Cu, and Co metals or compounds [5]. Thus, to reduce the loss of metals during the converter blowing process and shorten the traditional complex treating process, we selected low-nickel matte as the subject of our study to elucidate the metals extraction process and mechanism.

Recovery of Ni, Cu, and Co from the low-nickel matte has been studied by several researchers via a hydrometallurgical process, such as atmospheric pressure acid leaching, ammonia leaching, oxygen

pressure acid leaching and oxidative leaching [6,7]. Among these processes only the oxygen pressure acid leaching method could achieve a high recovery of metals, while it still encounters some problems, such as high requirement for specialized facilities and complex operation.

The combined of pyrometallurgy and hydrometallurgy process, which is of less energy consumption and less pollution, has strong adaptability to raw materials and gradually becomes a hotspot of metallurgy research [8]. Among the alternative processes, calcified roasting followed by acid leaching is an important technique in the recovery of many nonferrous metals from minerals or concentrates. Calcified roasting is generally used for vanadium extraction from vanadium ore, which has been replaced sodium roasting that may cause corrosion of equipment and environment pollution [9-12]. The treatment of sulfide ores via calcified roasting was firstly reported in the extraction of copper from flotation copper concentrates, which can achieve a high recovery of Cu and is friendly to the environment [13-15]. Researchers in the Central South University used the calcification roasting, sulphation roasting and water leaching process to treat the carbonaceous shale containing Ni and Mo and studied the recovery rate of metals from the ore. The results show that via this process the leaching rate of Ni and Mo can reach a high level and the experiments confirm that $CaCO_3$ can decompose $NiFe_2O_4$ and iron silicates during roasting [16-18].

In this study, we investigated the feasibility of calcified roasting of low-nickel matte and the application of the subsequent iron-removing method through a goethite process. The effects of the roasting temperature, the addition of $CaCO_3$ and the roasting time on the extraction behavior of metals were studied. In addition, the role of $CaCO_3$ in the roasting process and the reaction mechanisms were analyzed and discussed.

2. Experimental

2.1. Materials
The low-nickel matte sample used in this study was from Jinchuan Co., Ltd in Gansu Province, China. In this study, the low-nickel matte was ground into particles smaller than 75 μm. The composition of the sample was analyzed by X-ray fluorescence (XRF) and the result is shown in Table 1. It is shown that the concentrations of nickel, copper and iron in the low-nickel matte is higher, while the cobalt content is very low, only 0.5 wt%. Fig. 1 presents the X-ray diffraction (XRD) pattern of material, of which the main phases are pentlandite $((Ni,Fe)_9S_8)$, chalcocite (Cu_2S), magnetite (Fe_3O_4), trevorite (Ni_3Fe), and quartet pyrite (FeS). The diffraction line of silicon (SiO_2) was not detected by XRD, due to its low content.

All chemical reagents used in this study were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China. The acid used for this study is H_2SO_4 (98 wt%) diluted with deionized water to 2 mol/L.

Table 1. Chemical Composition Of The Low-Nickel Matte (Wt%).

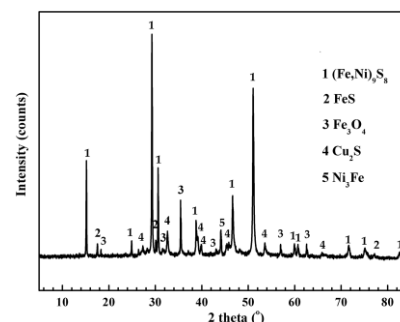| Fe	Ni	Cu	Co	S	Si	O
29.90	27.24	16.21	0.50	20.91	0.18	4.94

Figure 1. XRD pattern of the low-nickel matte.

2.2. Methods

2.2.1.   Calcified roasting and acid leaching: In this experiment, 10 g of low-nickel matte was mixed thoroughly with a certain amount of $CaCO_3$, and the mixture was transferred into a 100 mL crucible. The crucible was then placed into a vertical furnace containing a quartz reaction tube, held for a required time after the furnace had been preheated to the designated temperature. After cooling to room temperature, the roasted sample was removed from the crucible, and then leached in 2 mol/L dilute H_2SO_4 at 90 $^{\circ}$C with a liquid-to-solid ratio of 25:1 ml/g for 60 min to extract valuable metals. The experimental procedure is illustrated in Fig. 2. The leaching solution was then filtered and transferred to a 1000 mL volumetric flask. The extractions of Ni, Cu, Fe and Co (η) were calculated according to the following equation:

$$\eta = \frac{CV}{1000m\omega}$$

where C is the content of metals from the leach liquor, mg/L; V is the volume of the leach liquor, L; m is the mass of the low-nickel matte used in the experiments, g; and ω is the percent content of a certain metal in the low-nickel matte. Parallel experiments were conducted thrice, and the average extractions were obtained to ensure the reproducibility of the results.

Removal of irons from the leaching liquor was carried out in a 2 L water-heated reaction kettle. The leaching liquor was first diluted to a concentration of irons less than 1 g/L, and then added to the reaction kettle at 85 °C and stirred at 80 r/min. The pH value of the solution were adjusted using $NH_3 \cdot H_2O$ by adding slowly to maintain the appropriate pH values as shown in Fig. 2. The experiment duration was 60 min.
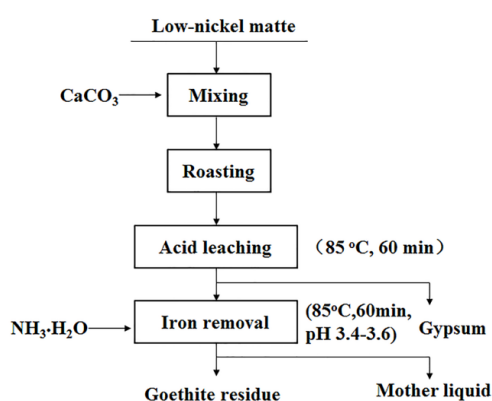

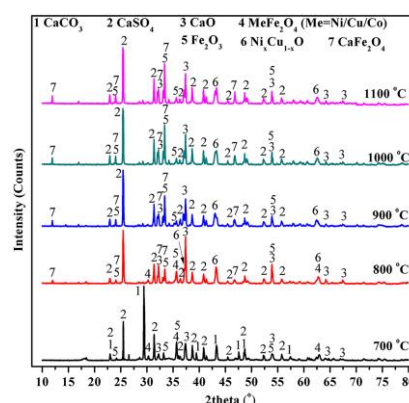**Figure 2.** The flow diagram of the calcified roasting—acid leaching process.

Figure 3. XRD patterns of products after roasting at different temperature

2.2.2.   Characterization: The chemical compositions of the samples were determined by X-ray Fluorescence (XRF, XRF-1800, Shimadzu, Kyoto, Japan). The contents of nickel, copper, cobalt and iron in the leach liquor were determined by ICP-OES (Perkin-Elmer 7300DV, USA). The pH values of the leach liquor were measured using a pH meter (pH, Shanghai INESA, PHS-3C). The phases of the low-nickel matte and roasted products were characterized by X-ray diffraction analysis (Bruker AXS, D8 Advance, Cu radiation, 40kV/40mA).
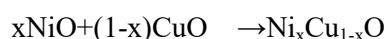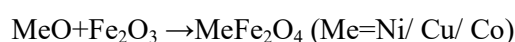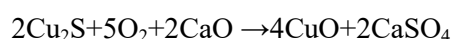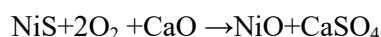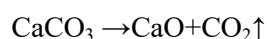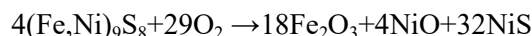
3. Results And Discussion

3.1.   Phase changes during calcified roasting
To identify the reaction process of calcified roasting, a series of roasting experiments were carried out between 700 ~ 1100 $^{\circ}$C for 2 h with the addition of $CaCO_3$. The experimental results are presented in Fig. 3. The main products roasting at 700 $^{\circ}$C are $CaCO_3$, $CaSO_4$, CaO, $MeFe_2O_4$ (Me=Ni/Cu/Co), and

Fe_2O_3. As the temperature increased to 800 ^{o}C, $CaCO_3$ is completely converted to CaO, indicating that the decomposition temperature of $CaCO_3$ is 700 ~ 800 ^{o}C. Compared to 700 ^{o}C, an obvious difference is that the peak intensity of $MeFe_2O_4$ decreased and the peaks of $CaFe_2O_4$ and $Ni_xCu_{1-x}O$ started to appear. When the temperature reached 900 ^{o}C, the peaks of $MeFe_2O_4$ disappeared and the main phases are $CaSO_4$, CaO, Fe_2O_3, $Ni_xCu_{1-x}O$ and $CaFe_2O_4$. As the temperature continues to increase, the main phases have no change.

Possible chemical reactions during the roasting process are as follows [19,20]:

$$4(Fe,Ni)_9S_8+29O_2 \rightarrow 18Fe_2O_3+4NiO+32NiS$$

$$CaCO_3 \rightarrow CaO+CO_2\uparrow$$

$$NiS+2O_2 +CaO \rightarrow NiO+CaSO_4$$

$$2Cu_2S+5O_2+2CaO \rightarrow 4CuO+2CaSO_4$$

$$MeO+Fe_2O_3 \rightarrow MeFe_2O_4 \ (Me=Ni/ \ Cu/ \ Co)$$

$$MeFe_2O_4+CaO \rightarrow CaO•Fe_2O_3+MeO \ (Me=Ni/ \ Cu/ \ Co)$$

$$xNiO+(1-x)CuO \rightarrow Ni_xCu_{1-x}O$$

3.2.   Effect of roasting temperature

A series of calcified roasting experiments were carried out between 700 and 1100 °C with the addition of $CaCO_3$ and with the reaction time kept constant. The extraction of metals was determined by the methods described in section Ⅱ. The effect of roasting temperature on the extraction of metals is shown in Fig. 4. A significant improvement was observed in the extraction of nickel, copper, iron, and cobalt as the temperature was increased to 1100 °C; further raising the roasting temperature will increase energy consumption, thus for subsequent tests the roasting temperature was kept to 1100 ^{o}C.
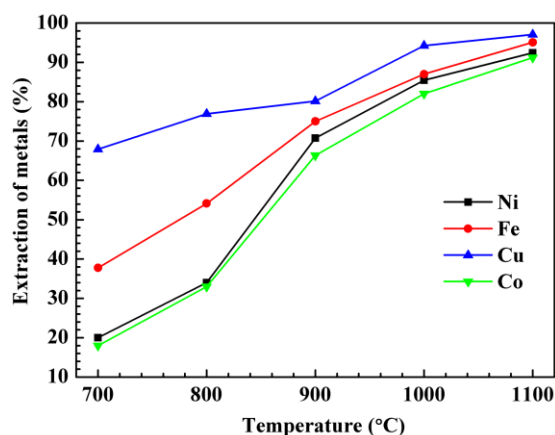

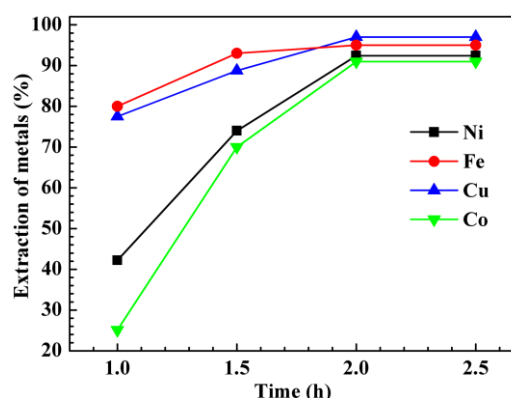**Figure 4.** Effect of roasting temperature on the extraction of metals

Figure 5. Effect of roasting time on the extraction of metals

3.3.   Effect of roasting time

The effect of roasting time on the extraction of valuable metals was investigated. Fig. 5 presents the extraction of metals as a function of roasting time at 1100 ^{o}C with addition of $CaCO_3$ (1:1.8 in mass ratio of low-nickel matte and $CaCO_3$). It is shown that the extraction of the metals increased rapidly as the roasting time increased to 2 h, which maintained almost constant as the roasting time continued to increase. It is indicated that after 2 h, the reactions have been basically completed. Hence, 2 h was taken as the optimum roasting time for the rest of the experiments.
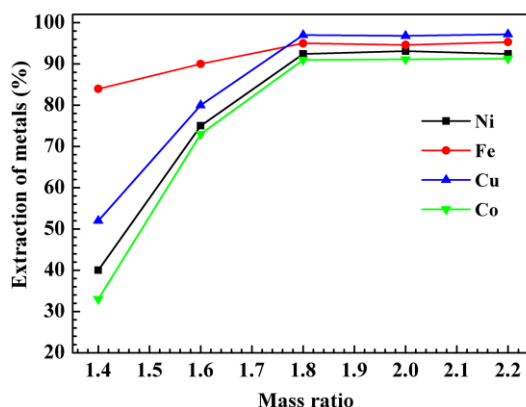
Figure 6. Effect of $CaCO_3$ addition on the extraction of metals

3.4. Effect of $CaCO_3$ addition

To save the material costs and enhance the extraction of metals, an appropriate amount of $CaCO_3$ should be added. Fig. 6 shows the relationship between the metals extraction and the amount of $CaCO_3$ added at 1100 ^{o}C for 2 h. The extraction of these metals increased with the increased amount of $CaCO_3$ addition when the mass ratio of $CaCO_3$ to low-nickel matte is lower than 1:1.8, which maintained almost constant as the continued addition of $CaCO_3$. Therefore, the optimum mass ratio of low-nickel matte to $CaCO_3$ should be 1:1.8.

3.5. Iron Removal Process

As the experimental results shown above, under the optimum conditions (i.e, 1:1.8 mass ratio of the low-nickel matte to $CaCO_3$, 2 h, 1100 ^{o}C), about 95.1% of Fe was transferred into the leach liquor. And so, an iron-removal step (goethite process) is adopted to separate iron from the solution. The essential feature of the goethite process is to keep low concentrations of ferric iron (<1 g/L) in the reactor during precipitation. This requirement can be met by either reducing all ferric ions to the ferrous state (V.M. method) or by adding the concentrated pressure leaching solution into a large precipitation vessel at the same rate as goethite precipitation (E.Z. method) [21,22]. Considering the main iron ions in leach liquor are trivalent and the concentration is not high, here we chose the E.Z. method. The reaction equation can be written as

$$Fe^{3+}+2H_2O=FeOOH+3H^+$$
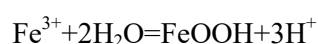
   The precipitation process will generate acid, which decreases the removal rate of iron. A neutralizing agent is added at a fixed rate to adjust the pH within the range of 3.4–3.6. The experiment duration was 60 min.

   The results after the iron-removal process are shown in Table 2. It indicates that 99.8% of Fe can be removed via the goethite process. Although about 2.4% of Ni, 0.9% of Cu and 2.6% of Co may be lost, due to the adsorption and co-precipitation with iron particles in the goethite process, a high recovery of these metals can still be achieved in the final mother liquor.

Table 2. The Extraction Of Metals After Leaching Process, The Metal Losses During The Iron-Removal Process And The Total Recovery Of The Metals.

Metals	Ni	Cu	Co	Fe
Metals extraction/%	92.4	97.1	91.2	95.1
Metal losses /%	2.4	0.9	2.6	99.8
Total recovery /%	90.1	96.2	88.8	

4. Conclusion

The extraction of valuable metals (Ni, Cu and Co) from low-nickel matte can be performed in a three-step procedure consisting of calcified roasting, acid leaching and an iron-removal process. The results showed that the formation of ferrite can be effectively inhibited by $CaCO_3$ when calcified roasting low-nickel matte at 1100 ^{o}C. The main reaction products after roasting were confirmed as calcium ferrite ($CaFe_2O_4$) for Fe and oxides for Ni, Cu and Co. All of them can be easily dissolved by sulphuric acid. Under the optimum experimental conditions (the weight ratio of low-nickel matte to $CaCO_3$ reached 1:1.8; calcified roasting at 1100 ^{o}C for 2 h; leaching for 60 min at 85 ^{o}C with 2 mol/L dilute H_2SO_4), the maximum extraction of Ni, Cu, Fe and Co achieved 92.4%, 97.1%, 95.1% and 91.2%, respectively. And iron was effectively precipitated in the form of goethite using a goethite process with temperature and pH carefully controlled. Though, a small amount of Ni, Cu and Co (2.4% of Ni, 0.9% of Cu and 2.6% of Co) may be lost, ~99.8% of Fe could be effectively removed from the leach liquor after the iron-removal step.

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