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Effects of Sulfation Roasting and Sodium Sulfate Addition on Dissolution of Nickel and Cobalt from Laterite

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In this study, lateritic nickel ore from Manisa-Çaldağ, Turkey was subjected to sulfation roasting. Experimental parameters were as follows, acid concentration (10–90 wt.%), roasting temperature (200–900 °C) and time (15–90 min). Effect of sodium sulfate addition (1–9 wt.%) on dissolutions of nickel and cobalt was also investigated. It was concluded that iron dissolution has increased with increased acid concentration. Dissolutions of nickel and cobalt increased with increasing roasting temperature and time below the decomposition temperature of related metal sulfates. It was concluded that addition of sodium sulfate in roasting stage has no significant effect on dissolutions of related metals.

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1. Introduction

Ferrous and non-ferrous alloying industries, petrochemical works, aerospace applications, nickel based catalysts and battery production, military applications, coinage and coating practices are some of the nickel usage areas, which had lead to a growing demand for this metal [1]. Materials, comprising iron and cobalt have been subjected to studies of magnetic properties [2] and giant magnetoresistance [3]. Cobalt also finds application in biomedical alloys [4] and hardfacing materials [5].

Nickel oxides (laterites), which constitute the largest reserves, 73% of world's nickel resources, and nickel sulphides are the two types of ores used in industrial practice for nickel production [6]. However the depletion of sulphide ores and growing demand for nickel have lead to production of nickel from the laterites [7].

Three metallurgical extraction processes are currently being applied; pyrometallurgical, hydrometallurgical and the Caron process [1]. Because of high-cost equipment and maintenance price of high pressure acid leaching system [8], energy intensive characteristic of pyrometallurgy, usage of acidic solutions and consequently occurring environmental problems, the roasting process becomes advantageous.

Sulfation-roasting process is an alternative process of dissolving nickel and cobalt from lateritic ores, due to its ease of operation. Sulfation-roasting process consists of mixing of ore with water and sulphuric acid, roasting at a desired temperature and for the desired time, and of water leaching [9]. By roasting, it is possible to turn metal oxides to chloric or sulfuric forms, that enable leaching with water instead of acid. Thus, in this study, roasting parameters were investigated for Ni and Co extraction.

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2. Materials and methods

Lateritic nickel ore, provided from Manisa-Çaldağ region in Turkey, was crushed and sieved under 75 μm for standardization of the particle size. Chemical composition was determined by X-ray fluorescence (XRF) with Bruker AXS S8 Tiger. Preparation of mixture was done in silica crucible by adding 40 wt.% of water, as moisturizing agent, before sulfuric acid addition. This slurry was dried in oven at 50 °C for 24 h and roasted in muffle furnace with 10 °C/min at desired temperature (200–900 °C) and soaking time (15–90 min). Roasted mixture was leached at 80 °C for 30 min with 200 ml of water under atmospheric conditions in 500 ml glass flasks, that were placed on a temperature controlled and magnetically stirred hot plate. Liquid-to-solid ratio was kept constant at 20 (wt/wt). String speed was kept constant at 450 rpm.

In this study, firstly the effect of acid ratio (10–90 wt.%) at 700 °C for 30 min was studied. After determination of acid concentration, roasting temperature (200–900 °C) for 30 min and soaking time (15–90 min) were studied, respectively. Effect of sodium sulfate addition (between 1–9 wt.%) was also studied.

Nickel, cobalt and iron concentrations of the pregnant leach solutions were determined by atomic absorption with Thermoscientific Ice 3300 model AAS. Some of the roasted samples were characterized using Rigaku Ultima X-ray diffractometer.

3. Results and discussion

Lateritic nickel ore contains 31.59% Fe, 12.86% Si, 1.47% Ni and 0.12% Co, by weight. In the literature, it is concluded that water addition in the interval of 10% to 40% has similar effect on the leach efficiency [9]. While adding acid to the moisturized ore, an increase of temperature occurs because of the exothermic reaction. Xu et al. stated that temperature can raise to 140 °C [10].

Effect of acid concentration on nickel, cobalt and iron dissolutions is given in Fig. 1a. Nickel concentration increases below 30 wt.% of H_2SO_4 and decreases slowly above this ratio. Cobalt concentration has shown a rapid decrease above 50 wt.% of H_2SO_4.

On the contrary to the nickel and cobalt dissolutions, iron dissolution has shown a linear increase for all acid ratios. Maximum dissolutions of nickel, cobalt and iron were determined as 68.8%, 51.1% and 28%, respectively.

Acid concentration was chosen to be 30 wt.% of H_2SO_4, because of low iron, high nickel and cobalt dissolutions. In literature [9], similar results were obtained and it was concluded that acid ratio should be kept between 30–50% for high nickel and cobalt and low iron extraction.

Effect of roasting temperature on dissolutions is given in Fig. 1b. Increase in roasting temperature causes a decrease in iron dissolution and an increase in nickel and cobalt dissolutions. Maximum dissolutions of nickel and cobalt were obtained at 700 °C as 68.8% and 44.2%, respectively.

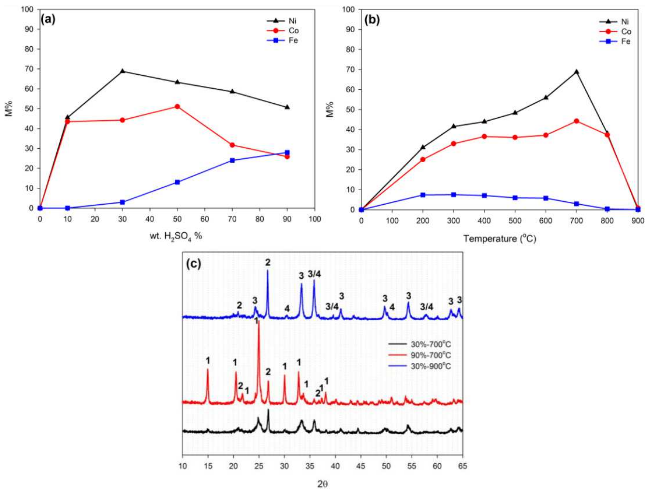

Fig. 1. Effects of (a) acid concentration and (b) roasting temperature on extraction of Fe, Ni and Co. (c) XRD analyses of roasted samples (1: $Fe_2(SO_4)_3$, 2: SiO_2, 3: Fe_2O_3, 4: Fe_3O_4).

Iron dissolution was about 7% at low temperatures and then decreased with increasing temperature. Mechanism of sulfation is based on SO_2 and/or SO_3 gasses that occur by thermal decomposition of less stable metal sulfates, which form during mixing of moisturized ore with H_2SO_4. Studies show that decomposition of nickel and cobalt sulfate does not occur until 760 °C, but decomposition of iron sulfate takes place before those of nickel and cobalt sulfates [11].

Results of XRD analysis of roasted samples are given in Fig. 1c. As seen from this figure, increased acid concentration promotes formation of iron sulfate. At 900 °C all metal sulfates are decomposed and turned to metal oxides.

As a result of previous experiments, ratio of acid and water to laterite in the slurry and the roasting temperature were kept constant at 30 wt.% H_2SO_4, 40 wt.% water and 700 °C, respectively, for studies of the effect of roasting time and Na_2SO_4 addition. Effects of roasting time and Na_2SO_4 addition are given in Fig. 2a and 2b, respectively. For 90 min of roasting, extractions of 71.3% Ni, 47.6% Co and 1.1% Fe and for 60 min 69.42% Ni, 46.00% Co and 1.38% Fe were achieved.

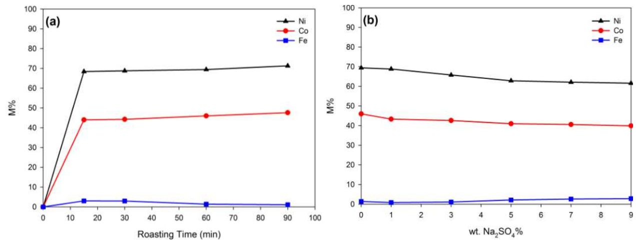

Fig. 2. Effect of (a) roasting time and (b) Na_2SO_4 addition on the extraction of Fe, Ni and Co.

For 90 min of roasting at 600 °C the effects of dissolution were 61.4% Ni, 42.5% Co and 5.1% Fe. Decrease in iron dissolution occurred due to prolonged roasting time or higher temperature. Thus, for Na_2SO_4 studies, roasting time was kept constant at 60 min. In this study, Na_2SO_4 addition did not show any effect on dissolutions of Ni, Co and Fe as stated in the literature [9].

4. Conclusions

Effects of acid ratio, roasting temperature, roasting time and addition of Na_2SO_4 on dissolutions of Ni, Co and Fe from laterite were investigated. The experimental results show that increased acid ratio, roasting temperature and time have caused an increment in Ni, Co and Fe dissolutions, to a certain point. Above acid ratio of 30 wt.% of H_2SO_4, Ni dissolution was decreased because of decomposition of its sulfate. The roasting temperature should be selected by taking into account the temperature at which the iron sulphate decomposes and nickel and cobalt sulphates remain. Roasting time must be longer at lower roasting temperatures but it must be shorter at higher roasting temperatures.

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