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Short communication

Extraction of molybdenum and nickel from Ni-Mo ore by acid leaching combined with chlorate oxidation and phosphate complexation

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ABSTRACT

The extraction of molybdenum and nickel from Ni-Mo ore was attempted using oxidation complexation acid leaching. The effects of leaching temperature, leaching time, concentration of sodium chlorate and hydrochloric acid as well as sodium dihydrogen phosphate on the leaching of nickel and molybdenum were investigated. The addition of phosphate anion can react with molybdenum and form Standberg type phosphomolybdic heteropoly acid, which can improve the leaching of molybdenum. 98.5% of molybdenum and 95.0% of nickel can be leached at a leaching temperature of 90 °C for a leaching time of 3 h with hydrochloric acid concentration of 2.4 mol/L, sodium chlorate concentration of 1.88 mol/L and sodium dihydrogen phosphate concentration of 1.8 mol/L.

1. Introduction

In China, Ni-Mo ore is an important source of molybdenum and nickel, which contains 0.17–7.03% Ni and 0.35–8.17% Mo (Wang et al., 2012; Bao et al., 2001). Several mineral processes have been tested for treating the Ni-Mo ore, such as flotation separation and gravity separation combined with flotation (Sun et al., 2012; Li et al., 2013; Hu et al., 2013). However, the recovery of molybdenum and nickel for each process was poor. The utilization of Ni-Mo ore is still directly carried out by metallurgical processes.

Over the past 40 years, the processes of oxidizing roasting-melting reduction and oxidizing roasting-sodium carbonate roasting-water leaching have been widely employed to treat Ni-Mo ore (Li, 2010). The first process can extract both molybdenum and nickel, however, it has two main disadvantages: low recovery of molybdenum (< 80%) and nickel (< 70%) as well as high impurity Ni-Mo-Fe alloy product (Shi et al., 2011). The other process can only extract molybdenum, and it also has the disadvantage of low recovery of molybdenum (< 70%). In recent years, several other metallurgical processes have been proposed to extract molybdenum from Ni-Mo ore, such as direct leaching with NaOH and NaClO (Li et al., 2007), oxygen pressure NaOH leaching (Wang et al., 2015), roasting followed by NaOH and Na_2CO_3 leaching (Wang et al., 2009), leaching molybdenum by air oxidation in alkali solution (Zhao et al., 2010) and sodium hypochlorite leaching under mechanical activation (Liu et al., 2011). These processes all can effectively extract molybdenum, but nickel remains in the leach residue.

To extract both molybdenum and nickel from Ni-Mo ore, a technology named as oxidation roasting, sulphation roasting and water leaching technology (Wang and Wang, 2010) was proposed. The Mo and Ni leaching of this technology are both high in all cases, but the roasting process has severe impacts on the environment. In Ni-Mo ore, molybdenum and nickel both mainly occur in the form of sulfide. A toxic gas of SO_2 is produced in roasting process. Much attention has thus been recently paid to the direct acid leaching process as it can effectively lead to a more environmentally friendly technology. Oxygen pressure acid leaching (Wang et al., 2013), two-stage oxygen pressure acid leaching (Liu et al., 2014) and HCl with $NaClO_3$ leaching (Xiao et al., 2010) were developed for the extraction of molybdenum and nickel from Ni-Mo ore. The Ni leaching of the above technologies is all more than 92%, however, the leaching of molybdenum is all below 80%.

In this study, a novel process for the extraction of molybdenum and nickel from Ni-Mo ore was introduced. In this process, molybdenum and nickel is leached by hydrochloric acid combined with chlorate oxidation and phosphate complexation. The process was characterized by high extraction of molybdenum and nickel.

2. Materials and methods

2.1. Materials and analysis

The Ni-Mo ore used in this study was obtained from Xiangxi district,

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Table 1
XRF elemental analysis of the Ni-Mo ore (mass fraction%).

Mo	Ni	O	Mg	Al	Si	P	S	Ca	Fe	As	Others
4.98	2.48	36.39	1.35	3.61	11.5	2.44	14.97	7.68	7.89	1.46	5.25

Hunan province in China. The sample was crushed and ground to 170 mesh (100% through 170 mesh) before leaching. The X-ray fluorescence (XRF) analysis result of the Ni-Mo ore is listed in Table 1. All the reagents used in this study were of analytical grade.

The X-ray diffraction (XRD) patterns of the Ni-Mo ore and the leach residue were recorded by a Rigaku D/MAX 2200 Diffractometer with Cu Ka radiation at 35 kV and 20 mA using a scan speed of 8° min^{-1} in 2θ ranges from 10° to 80°. The content of Mo in both raw Ni-Mo ore and leach residue was determined by the thiocyanate spectrometric method. It was in accord with the national standard method of China (GB/T 14352.2-93). The content of nickel was determined by inductively coupled plasma (ICP) emission spectroscopy with a PS-6 PLASMA SPECTROVAC, BAIRD (USA). The Raman spectra were recorded using a Renishaw inVia Raman microscope with laser wavelength of 532 nm.

2.2. Experimental procedure

The leaching procedure was performed in a round-bottom 1000 mL Pyrex reaction flask equipped with an agitator, thermometer and reflux condenser while heated through a thermostatically controlled water bath. A measured amount of distilled water, calculated amounts of hydrochloric acid (12 mol/L) and sodium dihydrogen phosphate were added to the flask as the leaching solution, and then it was heated to a specific temperature. The stirring speed and liquid to solid ratio are kept constant at 500 rpm and 4 mL/g, respectively. The liquid to solid ratio refers to the ratio of the total volume of water and hydrochloric acid to Ni-Mo ore quantity. When the leaching solution reached the expected temperature, the mixture of 150 g ground Ni-Mo ore and calculated sodium chlorate was added to the flask, and the reaction time was initiated. At the end of each test, the mixture consisting of the leach solution and the leach residue was vacuum-filtered, and the leach residue was successively washed with 150 mL water. The washed leach residues were dried, weighed and analyzed for molybdenum and nickel content.

3. Results and discussion

3.1. Effect of leaching temperature

The effect of temperature on the leaching of molybdenum and nickel was studied at a fixed leaching time of 3 h with concentrations of sodium chlorate, hydrochloric acid and sodium dihydrogen phosphate of 1.88 mol/L, 2.4 mol/L and 1.8 mol/L respectively, and the results are shown in Fig. 1.

As can be seen, there is a rapid increase both in the leaching of molybdenum and nickel with the leaching temperature from 20 °C to 90 °C. It is obvious that the leaching temperature has a significant effect on the leaching of molybdenum and nickel. The higher the leaching temperature is, the greater the leaching of molybdenum has. However, in view of the volatility of hydrochloric acid, the leaching temperature of 90 °C was chosen for subsequent experiments.

3.2. Effect of leaching time

The effect of time on the leaching of molybdenum and nickel was studied by varying the leaching time from 1 h to 5 h at 90 °C with the concentration of sodium chlorate, hydrochloric acid and sodium dihydrogen phosphate of 1.88 mol/L, 2.4 mol/L and 1.8 mol/L, respectively, and the results are shown in Fig. 2(a). According to the results illustrated in Fig. 2(a), the leaching of Mo and Ni increased quickly to 98.2% and 94.8%, respectively, with the leaching time of 3 h. Further prolonging leaching time resulted in insignificant increase in the leaching of Mo and Ni. Considering that the higher the temperature is, the more corrosive of hydrochloric acid will be. The tests of leaching at 65 °C were also finished, and the results are shown in Fig. 2(b). It can be seen from Fig. 2(b) that there is also a rapid increase both in the leaching of molybdenum and nickel with the leaching time from 1 h to 5 h. Further prolonging leaching time gives only a slight increase in the leaching of molybdenum and nickel. It is obvious by comparison between Fig. 2(a) and (b) that the leaching rates of Mo and Ni at 65 °C are both lower than those at 90 °C. Even if the leaching time is 9 h at 65 °C, the leaching rates of molybdenum and nickel were also only 95.4% and 91.1%, respectively. And therefore, for subsequent experiments the leaching time was kept to 3 h and the leaching temperature was also kept as 90 °C.

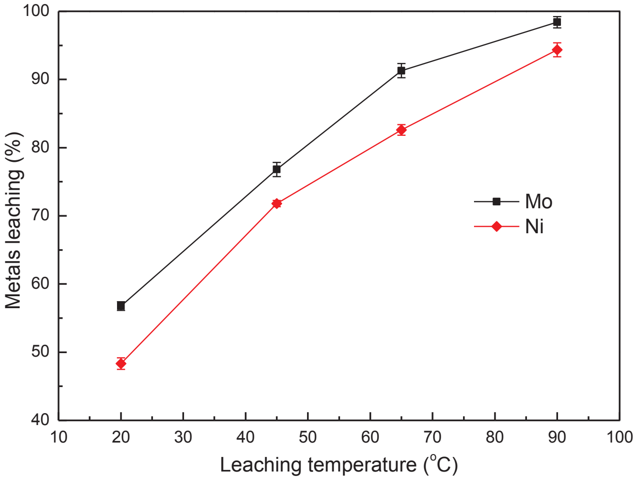

Fig. 1. Effect of temperature on the leaching of Mo and Ni.

3.3. Effect of sodium chlorate concentration

The effect of sodium chlorate concentration was conducted under the following conditions: leaching temperature 90 °C, leaching time 3 h, and the concentration of hydrochloric acid and sodium dihydrogen phosphate of 2.4 mol/L and 1.8 mol/L, respectively. As shown in Fig. 3, the leaching of molybdenum and nickel increased from 60.9% to 98.7% and 36.1% to 94.9% respectively with an increase in sodium chlorate concentration from 0.47 mol/L to 1.88 mol/L. A further increase in the sodium chlorate concentration does not significantly affect the leaching of molybdenum and nickel. Therefore, the sodium chlorate concentration of 1.88 mol/L was chosen for subsequent experiments.

In Ni-Mo ore, the molybdenum mainly occurs in the form of MoS_2 which occupies 55–65% of total molybdenum and the rest mainly exists in the form of molybdite (MoO_3) (Chen et al., 2006). Nickel mainly occurs as NiS_2, Ni_3S_4 and NiS (Pan et al., 2005). When sodium chlorate was used as the oxidizing agent, the sulfide of molybdenum and nickel can be oxidized (Cao et al., 2009; Zeng et al., 2013; Zhong and Mei, 1986; Ye, 1981):

$$MoS_2 + 3ClO_3^- + 3H_2O = H_2MoO_4 + 2SO_4^{2-} + 3Cl^- + 4H^+ \quad (1)$$

$$\Delta_r G_m^\theta \text{ (kJ/mol)} = -1379.93$$