

Selective extraction of molybdenum from copper concentrate by air oxidation in alkaline solution



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ABSTRACT

Alkaline leaching of copper concentrate bearing molybdenite was investigated. Thermodynamic analysis of Mo-S-H₂O and Cu-Fe-S-H₂O indicates that alkaline leaching of copper concentrate is feasible for selective extraction of molybdenum. The oxidation mechanisms of sulfide ores in the copper concentrate were discussed based on the analysis results of X-ray diffraction (XRD) and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM-EDS) of copper concentrate before and after leaching. The effects of leaching factors including sodium hydroxide concentration, temperature, leaching time and liquid to solid (L/S) ratio on the leaching rate were studied. The results show that molybdenite was oxidized and then dissolved selectively. The optimum parameters were as follows: temperature 80 °C, L/S ratio 6/1 mL/g, sodium hydroxide concentration 2 mol/L, air with ventilation volume 0.6 m³/h and leaching time 8 h. About 97.5% of Mo was selectively extracted and only 1.84% of Cu was dissolved into the solution under the conditions.

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1. Introduction

In China, there are numerous copper deposits associated with molybdenite. Currently, molybdenite is mainly separated from copper concentrate by a flotation process (Guo et al., 2016; Liao, 2016; Song et al., 2016). In the traditional froth flotation dressing, most of the molybdenite floats along with the copper sulfides, forming Cu-Mo concentrates. This stream would ultimately be turned into a copper concentrate after differential flotation. To obtain the high grade copper concentrate, it is necessary for Mo to be removed. Therefore the whole flotation process would be inevitably long and complicated (Huang et al., 2015). In most cases, sulfide copper ore and molybdenite are usually intergrown closely and it is especially difficult to remove molybdenite from the copper concentrate which was only processed by froth flotation.

Other methods used to separate molybdenum from polymetallic ores have been reported in other literatures. These methods contain oxygen pressure leaching (Wang et al., 2013a, 2013b), acid leaching (Liu et al., 2016; Zhang et al., 2015), alkaline leaching (Wang et al., 2015; Liu et al., 2011; Zhao et al., 2009), electro-oxidation leaching (Cao et al., 2015;

Cao et al., 2010) and bioleaching (Abdollahi et al., 2015; Abdollahi et al., 2013).

Wang et al. (2013a) studied an oxygen pressure leaching of nickel and molybdenum from a nickel-molybdenum ore. The extraction rates of nickel and molybdenum were 97% and 76% respectively under those optimum conditions: without sulfuric acid, leaching time of 5 h, leaching temperature of 150 °C, liquid-to-solid ratio of 2.0 mL/g, oxygen partial pressure of 1.2 MPa and stirring speed of 500 r/min. Liu et al. (2016) reported that the extraction of Mo from metalliferous black shale in acid solution using persulfate as oxidant. The effects of leaching factors including leaching temperature and time, initial concentration of sodium persulfate and sulfuric acid, stirring speed, and particle size on the leaching rate were studied.

Wang et al. (2015) performed the selective extraction of Mo from a Ni-Mo ore using pressure alkaline leaching. The results showed that 95.7% of Mo and 1.3% of Ni were extracted, respectively, under the optimum conditions. Direct oxidative leaching of molybdenite from copper concentrate by caustic-hypochlorite solution (Liu et al., 2011) is an environment-friendly method with high molybdenum recovery. However the operation is still inconvenient because of an over-swelling phenomenon and high cost of NaClO. Herein, Zhao et al. (2009) proposed an environment-friendly and low cost technology for selective leaching of Mo from Ni-Mo ore using air instead of NaClO as oxidant.

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Table 1
Main chemical composition of the copper concentrate (mass ratio %).

Component	Cu	Mo	S	Fe	Ca	Zn	SiO ₂	Pb
% (w/w)	12.41	1.82	17.8	15.11	4.38	0.21	28.73	0.04

Therefore the purpose in this work is to study and develop a relatively novel hydrometallurgical process to selectively extract molybdenum from copper concentrate bearing molybdenite using air as oxidant of low-cost.

2. Materials and experiments

2.1. Materials and characterization

The copper concentrate used in the experiments was collected from Yunnan province in China. It was dried firstly for 12 h at 100 °C in an oven to remove moisture, and then sieved to obtain particles with less than 75 μm. The leaching solution of metal ions was determined by using an Atomic Absorption Spectrophotometer (AAS, WFX-130B, Rayleigh, China). The elemental analysis of copper concentrate and leach residues were obtained by digestion and Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES, PS-6, Baird, USA). The

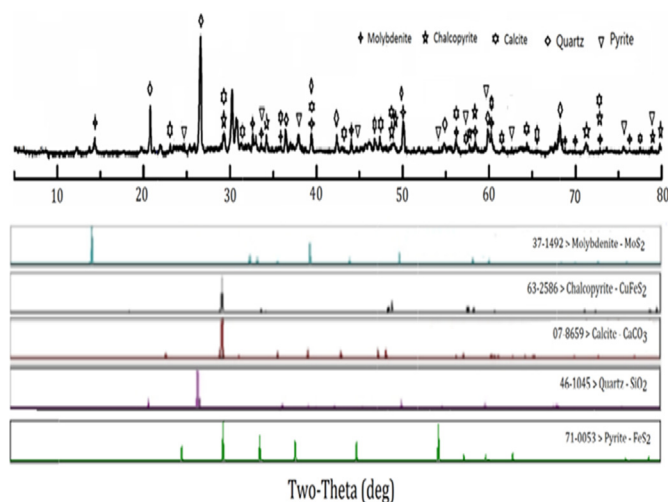


Fig. 1. XRD patterns of the copper concentrate.

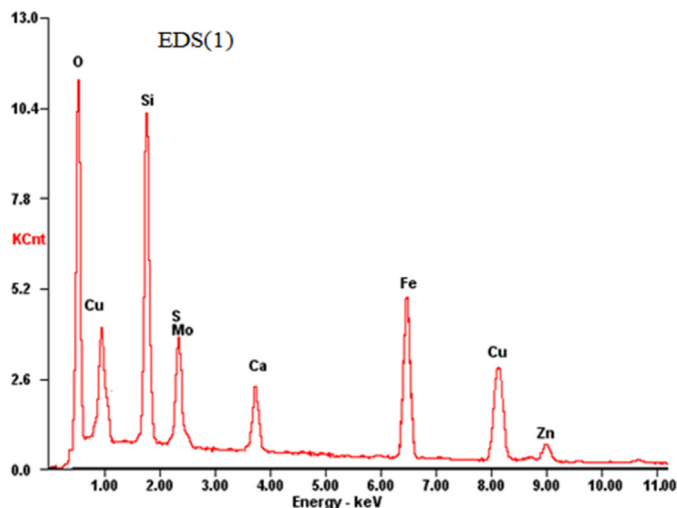


Fig. 2. SEM-EDS analysis of the copper concentrate.

mineralogical phase was identified with X-ray diffraction (XRD, D/max 3B, Rigaku, Japan). The morphology and micro-area element analysis were examined with scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS, MLA 250, FEI, Australia). Sodium hydroxide used in this work was analytical grade and was manufactured by Shanghai Chemical Plant. Ultra-pure water and air supplied by an air compressor were used in all experiments.

2.2. Experimental procedure

The leaching experiments were performed under atmospheric pressure in a 2 L stainless steel cylinder reactor. It was heated by a thermostatically controlled disc type electric heater and was fitted with a diaphragm pump to agitate well the slurry instead of the stirred equipment.

Leaching agent of 1000 mL sodium hydroxide solution as the required mole ratio was added into the reactor. When the temperature was up to the set value, a certain amount of copper concentrate was added into the reactor, at the same time the oxidant air with ventilation volume 0.6 m³/h was pumped by an air compressor. After the leaching treatment, the slurry was withdrawn from the reactor and vacuum filtered. The volume of the filtered pregnant solution was measured by a measuring cylinder and 10 mL of liquor sample was collected to analyze molybdenum and copper by AAS. The filtered cake was washed for three times with 600 mL distilled water and then was dried at 100 °C for 12 h. The dried cake was analyzed by XRD and SEM-EDS.

3. Results and discussion

3.1. Analysis and characterization of the copper concentrate

The main chemical composition of the copper concentrate is listed in Table 1. Mineralogical phase analysis of the copper concentrate is shown in Fig. 1. It is indicated that the sample mainly consists of chalcopyrite (CuFeS₂), molybdenite (MoS₂), pyrite (FeS₂), calcite (CaCO₃) and quartz (SiO₂). The SEM-EDS analysis of the concentrate is given in Fig. 2, the SEM image demonstrates that the concentrate particles are compact with rough surface and the EDS elemental analysis of micro-area is in agreement with the results of chemical and XRD analysis.

3.2. Chemistry of solution and theory of Cu and Mo phase

The leaching of copper concentrate bearing molybdenite was dealt with the oxidation and the dissolution of Cu and Mo, mainly presents in the form of sulfides in the raw material. The leaching behavior of Cu

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