



Sodium sulfate activation mechanism on co-sulfating roasting to nickel-copper sulfide concentrate in metal extractions, microtopography and kinetics

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ARTICLE INFO

Keywords:

Copper-nickel sulfide concentrate
Ammonium sulfate
Sodium sulfate
Activating mechanism
Kinetics
Mineral phase transformation

ABSTRACT

Due to the complexity of occurrence of valuable metals and high content of alkali gangue in nickel-copper sulfide concentrate, traditional pyrometallurgical processing is not suitable. In this work, a two-stage co-sulfating roasting process was used to selectively extract valuable metals from Chinese nickel-copper sulfide concentrate. A mixture of $(\text{NH}_4)_2\text{SO}_4$ and Na_2SO_4 was selected as the co-sulfating agents. The effect of the dosage of $(\text{NH}_4)_2\text{SO}_4$ and Na_2SO_4 , first stage roasting temperature, roasting time and second roasting temperature on metal's extractions were investigated. XRD, SEM, DTA-TG, and DSC-TG were used to reveal the mechanism of action of Na_2SO_4 and the mineral phase transformations in the two-stage sulfating roasting process. The results show that nearly all of Ni and Co, Cu, and 1.12% of Fe were extracted at the mass ratio of ammonium sulfate to ore of 3.5, first roasting at 500 °C for 2 h, dosage of sodium sulfate of 4 g (10 g ore), followed by second roasting at 680 °C for 2 h, then water leaching at 95 °C for 2 h. $\text{Na}_2\text{S}_2\text{O}_7$ generated from Na_2SO_4 in the roasting process, shrinks the particle size of the ore, decrease the surface area of the roasted product, significantly promotes extent of the sulfating of metals, in particular for Ni. Thermal analysis kinetics indicates that Na_2SO_4 significantly reduces the apparent activation energy of the sulfating roasting process. The metal bearing mineral phases were transformed into sulfates or sodium double or ternary sulfates in the first roasting process, then the sodium double sulfates of $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ were decomposed.

1. Introduction

Jinchuan Group Ltd. is a large mining group engaged in mining, concentrating, metallurgy, ranking the fourth nickel and the second cobalt manufacturing enterprise in the world and the third copper producer in China. It also has the largest sulfide nickel ore reserves in China (Chai and Naldrett, 1992a). With depletion of rich sulfide nickel ore, the large amount of low grade copper-nickel sulfide ore has become the main nickel resource for Jinchuan. However, this nickel ore has a high content of MgO (20 wt%) present in the main gangue minerals of chlorite, antigonite, lizardite, spinel, talc, and tremolite, and a part of the nickel exists as crystalline substitution in iron lattice or silicates (Chai and Naldrett, 1992b; Li et al., 2004; Song et al., 2012; Song et al., 2009). Due to the natural hydrophobicity of some gangue, especially

talc and lizardite, the concentrate of copper-nickel sulfide ore often contains relatively high levels of Mg bearing silicates (Cao et al., 2015; de São José et al., 2016; Fornasiero and Ralston, 2005; Huang et al., 2007; Pietrobon et al., 1997), which reduces the grade of nickel and copper but may also cause smelting problems as well as the low recovery of value metals (Peach et al., 1990; Toscano and Utigard, 2003; Warner et al., 2007).

The pyrometallurgical process used to treat copper-nickel sulfide concentrate containing high concentrations of MgO is uneconomical because of high energy requirements and the low recovery of valuable metals. In the past decade, studies on processing sulfide nickel concentrate using hydrometallurgical methods included bioleaching, high pressure sulfuric acid leaching, atmospheric acid leaching, ammonium leaching, ferric chloride leaching, organic acids leaching (de Lemos

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<https://doi.org/10.1016/j.mineng.2018.04.013>

Received 20 November 2017; Received in revised form 8 April 2018; Accepted 15 April 2018

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et al., 2012; Dew et al., 1999; Hernández et al., 2007; Li et al., 2009; Maurice and Hawk, 1999; Norris, 2017; Tromans, 2000; Watling, 2013). Unfortunately, in the bioleaching of nickel sulfide ore, high Mg inhibits ferrous ion oxidation, which leads poor leaching efficiency of nickel or copper, many days of acid pre-leaching and longer leaching times (Li and Ke, 2001; Ojumu et al., 2007; Yang et al., 2011; Zhen et al., 2009). Pressure leaching requires high-level equipment and high maintenance costs. Other leaching processes suffer from low recovery of valuable metals and less selectivity. Therefore, pre-activation of nickel sulfide concentrate, such as sulfating roasting or chlorinating roasting, has extensive applicability to treatment of multi-metal ore, and is a potential way in which to process copper-nickel sulfide concentrate (Imideev et al., 2014; Xu et al., 2017; Yu et al., 2014).

Ammonium sulfate roasting-water leaching is a promising and clean method due to the elimination of SO₂, low cost, high metal extraction and high selectivity for complex nickel ore. The process involves roasting the mixture of (NH₄)₂SO₄ and ore in a relatively low temperature range of 200–600 °C and then leaching in hot water. In this roasting process, the metal oxides and metal sulfides can be transformed into soluble metal sulfates or ammonium salts which are dissolved in hot water during the leaching process (Hamamci and Ziyadanoğullari, 1991; Liu et al., 2012a; Sukla et al., 1986; Yu et al., 2014).

Sodium sulfate is an efficient additive in both the sulfating process and for grade enrichment. Much research has been carried out to reveal the effect of sodium sulfate in the sulfating roasting process (Battle et al., 2015; Jiang et al., 2013; Li et al., 2012; Li et al., 2015; Prasad and Pandey, 1998; Sui et al., 2016). However, the role of sodium sulfate in the kinetics has not been reported. TAK (thermal analysis kinetics) has been widely used for solid reactions, crystallization, phase transition and solid phase decomposition. Considering the superior activation during ammonium sulfate roasting to treat nickel-copper concentrate and its potential application as a modification agent, this study analyzes the kinetics of each stage without and with addition of sodium sulfate to determine the activation kinetics for each system.

Furthermore, controllable phase transformation of metal bearing phases can be achieved by controlling the roasting conditions, and the selective separation of metals is obtained because of the different thermal stability of metal sulfates.

In this study, co-sulfating roasting-water leaching was used to process copper-nickel sulfide concentrate. We focused on the phase transformation behavior and mechanism in ammonium sulfate roasting, and the activation mechanism of the addition of sodium sulfate, by using XRD, SEM and DSC-TG analysis. The effects of different variables, such as the (NH₄)₂SO₄ dosage, Na₂SO₄ dosage, roasting temperature and roasting time on the metals' transformation were investigated; furthermore, the roasting temperature in second stage was also optimized.

2. Experimental and materials

2.1. Product analysis

The concentration of Ni and Cu in the final leach liquor were measured using a double beam UV–vis spectrophotometer (TU-1901, Beijing Puxi Co., Ltd.), the concentration of Fe was determined using a titration method (Knop, 2002), the concentration of Co and Mg were analyzed using a Shimadzu AA-6880 series Atomic Absorption Spectrophotometer (AAS). X-ray diffraction equipment SmartLab using Cu-Kα radiation was used to identify components of raw ore, roasting products and residues from 5° to 90°, at a scan speed of 4°/min. SEM and EDS analysis of the raw ore and roasted products were conducted using a ZEISS Sigma 500 Scanning Electron Microscope and Energy Dispersive Spectrometer. The reaction kinetics of different systems were studied using a METTLER TGA/DSC1/1600HT instrument operated in a steady air atmosphere (50 ml/min) using a corundum crucible. An empty corundum crucible and pure indium were used as the reference

Table 1

Chemical composition of copper-nickel sulfide concentrate.

Elements	Ni	S	Cu	MgO	Fe	SiO ₂	Co	other
(wt%)	5.7	21.5	4.5	8.1	21.9	10.0	0.1	1.3

and standard for calorimeter calibration, respectively. After the samples were blended well, the temperature was raised at heating rates of 5, 10, 15 and 20 K/min from room temperature to 800 °C.

2.2. Materials

The copper-nickel sulfide concentrate used in this study originates from low-grade copper-nickel ore flotation from Jinchuan Group, China. The chemical composition of the concentrate is shown in Table 1.

The main minerals in the concentrate, as determined by X-ray diffraction (see Fig. S1 in Supplementary Materials), were chalcopyrite (CuFeS₂), pentlandite (Fe,Ni)₉S₈, talc (Mg₃Si₄O₁₀(OH)₂), lizardite (Mg₃Si₂O₅(OH)₄), pyrite (FeS₂) and magnesioferrite (MgFe₂O₄).

Fig. 1(a and b) shows an SEM image of the copper-nickel sulfide concentrate. It can be seen that the ore particles have variable size and angularity and relatively smooth surfaces. Furthermore, phases of some curly or platy silicates are separate from other mineral phases or attached to the smooth surface of particles (as shown in Fig. S2, mapping in Supplementary Materials).

Chemical phase analysis (the method, see section 2 in Supplementary Materials) was used to further confirm the phase distribution of nickel and copper (Table 2). A little nickel exists in the form of nickel sulfate. The nickel existing in nickel oxide and nickel sulfide is 22.4% and 45.6%, respectively. And nearly 1/3 of the nickel is present as isomorphic substitution in the form of silicates or spinel, which is hard to roasting process. 95.1% of copper is hosted in copper-nickel sulfide concentrate as copper sulfide which consist of 89.1% of primary 6.0% of secondary copper sulfide, but about 5% of copper is hosted in copper oxide.

2.3. Methods and procedure

The copper-nickel sulfide concentrate was dried at 80 °C for 12 h, and then divided into 10 g aliquots to mix with solid ammonium sulfate (and sodium sulfate) at a particular mass ratio in each experiment.

The mixture was placed into a corundum crucible and put into a horizontal crucible furnace, connected with an intelligent temperature control instrument (accuracy ± 5 °C), with an inert synthetic air gas (80% N₂, 20% O₂) and absorbing tail gas instruments. After each roasting process, the roasted product was leached with hot deionized water in a water bath. The resultant liquor was filtered through a vacuum filtration system and the remaining solids were washed with deionized water several times. The filtrate was analyzed to determine the percentage of each metal leached. The flow sheet is shown in Fig. 2.

3. Results and discussion

3.1. Roasting process

3.1.1. Effect of mass ratio of ammonium sulfate to ore

The effect of mass ratio of ammonium sulfate to copper-nickel sulfide concentrate on the extractions of metals was studied at the roasting temperature of 400 °C, roasting time of 2 h, the roasting products were then leached at 95 °C for 2 h. The results are presented in Fig. 3.

It can be seen from Fig. 3 that the extraction of nickel, copper, magnesium and cobalt increase with the mass ratio of ammonium sulfate to copper-nickel sulfide concentrate. Altogether, copper was easiest to convert into copper sulfate by the addition of ammonium

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