



# Leaching kinetics of calcification roasting calcinate from multimetallic sulfide copper concentrate containing high content of lead and iron



Yalong Liao\*, Juan Zhou, Feirong Huang, Yiyang Wang

State Key Laboratory of Complex Nonferrous Metal Resources Cleaning Utilization, Kunming University of Science and Technology, Yunnan, Kunming 650093, China  
Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Yunnan, Kunming 650093, China

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## ABSTRACT

The multimetallic sulfide copper ore containing large amounts of lead and iron was roasted in air atmosphere in the presence of calcium oxide, and the calcinate obtained was leached in sulfuric acid solution to extract copper. Characterization of the raw materials, calcinates and leach residues was conducted by using XRD and SEM/EDS analysis. The calcification mechanism of the complex ore was studied. The effects of temperature, stirring speed, liquid/solid ratio and sulfuric acid concentration on the kinetics and mechanism of copper dissolution from the calcinate were also investigated. Results of experiments show that sulfur retention efficiency in the calcinate achieves 97.77%, and that increasing both reaction temperature and acid concentration are capable of resulting in the increase of dissolution rate of copper. Leaching kinetics follows the un-reacted shrinking core model with a rate controlling step by diffusion through the solid product layer and the corresponding apparent activation energy is calculated as 19.21 kJ/mol, and consequently the rate of the dissolution of copper on aspect of  $H_2SO_4$  concentration, liquid/solid ratio, and stirring speed can be expressed as  $1 + 2(1 - x) - 3(1 - x)^{2/3} = 6.44 \times 10^{-4} \times C_A^{1.72} \times (L/S)^{1.25} \times \omega^{0.94} \exp(-2310/T)t$ .

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## 1. Introduction

With the exploitation and consumption of mineral resources, there are lots of complex sulfide copper concentrates associated and inter-grown with chalcopyrite, sphalerite, and galena in mineral industry of copper. Being that most of coppers in the ores are generally very finely disseminated and existed usually within a pyritic matrix [1,2], pyrometallurgical methodology involving smelting, converting and electro-refining does not favor recovery of valuable metals from the complex sulfide ores for technical and economy reason. On the one hand a great amount of  $SO_2$  and lead fume are generated when the concentrates are used as a raw material of smelting copper, which may contribute to serious environmental problems if not be carefully controlled. On the other hand loss of lead in the form of copper dross is induced while it is used as material for smelting lead. Therefore the traditional pyrometallurgical process is not suitable for reclaiming valuable metals from complex sulfide copper concentrates rather than the method of hydrometallurgy.

A lot of studies on the hydrometallurgy routes or alternative processes for disposing sulfide copper ores were reported. Direct acid leaching processes such as ferric salt leaching, pressure oxidative leaching [3,4], and bioleaching [5–7] were performed. An alternative process by roasting prior to direct leaching was also employed for improving dissolution efficiency of valuable metals. The roasting pretreatment processes were mainly conducted by oxidization and sulphation [8,9]. However, neither direct acid leaching nor the alternative methods seems to be suitable for complex sulfide copper concentrate contains high lead content in terms of copper extraction. Especially, lower melting point of the ore, mainly resulting from lead, induces absence of sulfur removal during the calcination, and subsequent treatment processes are found to be very difficult, even by pressure oxidative leaching process, due to the generation of sulfates and covellinisation of minerals [10]. Fortunately, compared to conventional pyrometallurgical and hydrometallurgical processes, an alternative method which was in combination with activation roasting and oxidative sulfuric acidity pressure leaching was employed to dispose a bulk concentrates associated with  $CuFeS_2$ - $PbS$ - $ZnS$  or  $CuFeS_2$ - $FeS_2$  for metals' recovery [11,12]. Besides the roasting of pellets of copper concentrates with lime as a reagent to absorb the sulfur dioxide and prevent the emission of sulfur dioxide was investigated [13]. Furthermore, calcification roasting was performed in disposing

\* Corresponding author at: No. 253 Xuefu Road Kunming, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093 China.

E-mail address: [liaoysy@163.com](mailto:liaoysy@163.com) (Y. Liao).

manganese ore and extracting of Ni and Mo from carbonaceous shale etc [14,15]. However, the calcification roasting methodology of complex multimetallic sulfide copper concentrates containing large amounts of lead and iron has not been reported in any document, especially the leaching kinetics of the roasting products obtained by roasting calcified the complex ore in sulfuric acid solution has not been well documented.

Based on the advantage of being capable of eliminating sulfur dioxide emission and the property of improving the melting point of raw material while sulfide ores was roasted in the presence of calcium oxide, therefore, the method using calcification roasting and then by acid leaching was employed to extract copper from complex sulfide copper concentrate containing high amounts of lead and iron in this work. The dissolution kinetics of calcification roasting calcinate in sulfuric acid was examined according to the heterogeneous reaction models. Key parameters such as temperature, concentration of  $H_2SO_4$ , stirring speed and solid/liquid ratio were selected to investigate influences on the dissolution rate of the calcinate in the sulfuric acid solution, and the dissolution kinetics was also examined based on the shrinking core model.

## 2. Experimental and methods

### 2.1. Materials

The sulfide copper concentrate used in this study was friendly supported by a copper smelter in Yunnan Province of China. The analytical result conducted by inductively coupled plasma-atomic emission spectrometry (ICP-AES) indicates that the sulfide copper concentrate consists of 7.70% Cu, 28.20% Pb, 20.52% Fe, and 23.72% S. Which confirms it belongs to complex and multimetallic sulfide copper concentrate containing large amounts of lead and iron. Calcium oxide and sulfuric acid were analyzed grade and purchased from Sinopharm chemical reagent Co., Ltd. The sulfide copper ore and the calcium oxide were ground to the required particle size  $-75 \mu m$  before using.

### 2.2. Calcification roasting

Typically, each 100 g of the sulfide copper concentrate was mixed thoroughly with 50 g CaO, then pelletized to a particle size of  $10.0 \pm 1.0 \text{ mm}$  by spraying some water as cohesive material. The pellets prepared were dried in an oven at  $120 \text{ }^\circ\text{C}$  for 2 h to remove the moisture and consequently roasted in a pipe furnace at  $820 \text{ }^\circ\text{C}$  for 1 h in air atmosphere.

### 2.3. Leaching with sulfuric acid

The product of calcification roasting was leached in a 500 mL spherical glass reactor equipped with a mechanical stirrer having a digital controller unit and a thermostat used for controlling the reaction temperature with an accuracy of  $\pm 0.5 \text{ }^\circ\text{C}$ . Also, the reactor was provided a reflux cooler for preventing mass loss resulting from evaporation. A certain amount of specified concentration sulfuric acid was first input the reactor. When it was heated up to the required temperature, 80 g roasting calcinate was added into the reactor with constant stirring. The rate of leaching was determined by testing the sample withdrawn ( $<5 \text{ mL}$ ) at a certain interval of 20 min.

### 2.4. Analyzing and characterizing method

The chemical element analysis of the raw materials, the calcinate and the leaching residue was conducted by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The

copper content of filtrate was determined by iodometry method [16]. The extraction efficiency of Cu denoted as sign of  $\eta$  was calculated as follows:

$$\eta = \frac{CV}{m\omega} \times 100\% \quad (1)$$

where  $C$ ,  $V$ ,  $m$  and  $\omega$  are the concentration of copper in the filtrate (g/L), filtrate volume (L), the weight of roasting calcinate (g) and the mass fraction of copper in the sample, respectively. All given results in the study were the averages of three repetitions experiments.

Mineral compositions of the complex multimetallic sulfide copper concentrate, the calcification roasting calcinate and the leaching residue were characterized by X-ray diffraction (XRD) on a Rigaku model D/Max-3B diffractometer using  $\text{Cu K}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation and scanning electron microscopy (SEM, Hitachi model S3400 N) equipped with an energy-dispersive X-ray spectrometer (EDS, model EDAX - TSL) and operated at a voltage of 30 kV.

## 3. Results and discussion

### 3.1. Calcification roasting mechanism

The X-ray diffraction analysis of the concentrate shown in Fig. 1 confirms that the ore consists of the  $\text{CuFeS}_2$ ,  $\text{PbS}$ ,  $\text{FeS}$ , and  $\text{FeS}_2$ , and that the raw materials used in this study belongs to a complex sulfide copper concentrate associated and intergrown with chalcopyrite, sphalerite, and galena, which are generally very finely disseminated, usually within a pyritic matrix. Especially owing to the high content of lead and iron, it becomes very difficult to dispose. After being calcined with calcium oxide, most sulfur were fixed by the additive (CaO) in the form of  $\text{CaSO}_4$ ,  $\text{CuFeS}_2$  was decomposed and oxidized into  $\text{CuO}$  and  $\text{Fe}_3\text{O}_4$ , and  $\text{PbS}$  was transformed into  $\text{PbO}$  (Fig. 1). According to analyzing result performed by ICP-AES that the content of sulfur in the calcinate was

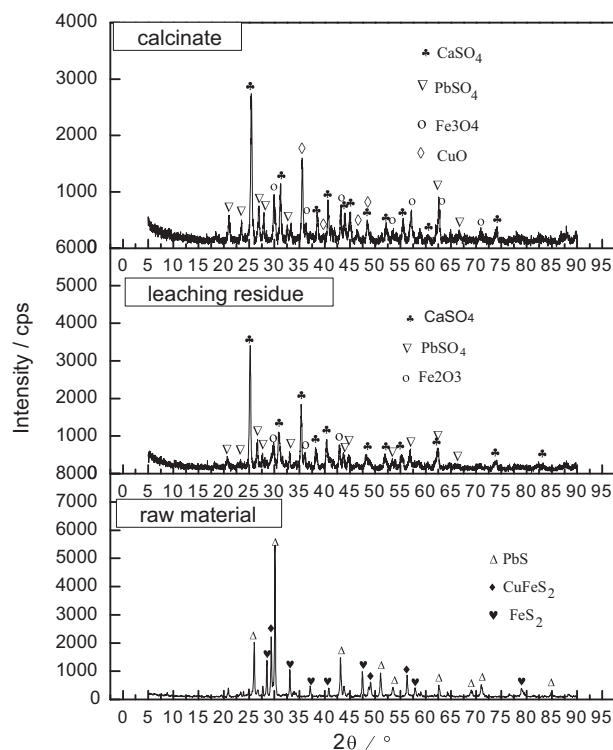


Fig. 1. X-ray diffraction patterns of raw material, calcinate and leaching residue.

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