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Effect of grinding with sulfur on surface properties and floatability of three nonferrous metal oxides

Zhao LI, Min CHEN, Peng-wu HUANG, Qi-wu ZHANG, Shao-xian SONG

School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, China

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Abstract: Co-grinding three nonferrous metal oxides (CuO, PbO and ZnO) with element sulphur under mild conditions and flotation of the ground samples were conducted to investigate the surface properties and floatability of the oxides. Phase transition, morphological features, electrochemical properties and surface chemical compositions of ground samples were studied. The results show that the floatability of CuO is improved after grinding with sulfur, by the formation of surface layer with properties similar to CuS due to the Cu—S bonding. The floatability of PbO is deteriorated after mechanochemical processing due to surface carbonation and the formation of PbS and $PbSO_4$ by disproportionation reaction with sulfur. ZnO shows no evident response to mechanochemical sulfidation.

Key words: grinding; nonferrous metal oxides; flotation; sulfur; recycling

1 Introduction

Nonferrous metals, such as copper, lead and zinc, are mainly extracted from natural sulfide ores which are the primary nonferrous sources and steadily becoming depleted [1,2]. Meanwhile, it is reported that one third outputs of the nonferrous metals in Japan have been discharged in various types of waste. The utilization of low-grade oxidized type of ores and recycling of these metals from high metal-contained wastes, in which metals also exist commonly in an oxidized type rather than sulfide type, are of urgent demand, from the point of environmental resources preservation and sustainable development [3−9].

One common method for processing nonferrous metal minerals is flotation, and the flotation of oxidized minerals is more difficult than that of the corresponding sulfide minerals [10−12], due to the hydrophilicity surface and electrostatic repulsion between negatively charged surfaces of bubble and solids. Many methods have been reported to deal with nonferrous metal oxides, such as alkaline leaching [13,14] and sulfidation roasting [15,16], but without enough satisfactory results. An improved flotation recovery of nonferrous oxides can be obtained by adding Na_2S solution into the pulp to modify the mineral surface with a layer of properties similar to that of natural sulfides from the adsorption of sulfide ions [17,18]. However, it is not easy to control the dosage of Na_2S solution to obtain high recovery, which may be easily worsened by either an inadequate or excess initial Na_2S concentration, not to say the environmental burden of treating the wastewater with sulfide ions.

Mechanochemical process has been widely used in many fields, such as syntheses of functional materials [19−22], hydrometallurgical process [23−25] and bio-pharmaceuticals [26,27]. Basic researches have been conducted on the transformation of oxides into sulfides by co-grinding with sulfur and reducing agents such as iron or aluminum powders [28−31], allowing the use of cheap sample of element sulfur to replace sulfides as sulfidizing agent. The use of element sulfur may also help to avoid the need to treat the wastewater with sulfide ions. Mechanochemical process may offer a relatively easy pathway for processing the oxides; however, the heavy agglomeration from the mechanochemical operation did not permit an easy application of the current flotation technique on the mechanochemically synthesized sulfides to obtain satisfied recovery. Changes are required to regulate the grinding operation without the formation of heavy

Corresponding author: Qi-wu ZHANG; Tel: +86-17771490085; E-mail: zhangqw@whut.edu.cn
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agglomeration to match flotation operation to raise the floatability of the samples.

As part of basic researches to develop new process to exploit oxidized type of minerals as well as related solid wastes, pretreatment by co-grinding nonferrous metal oxides with element sulfur under relatively mild conditions without triggering obvious solid state reaction and heavy agglomeration is proposed as a key operation to improve the floatability of the oxide samples under typical flotation conditions. In this work, the obtained fundamental results are reported regarding the changes in the floatability of CuO, PbO and ZnO before and after co-grinding with sulfur. Quartz SiO_2 has been applied as a reference sample. Changes in physico-chemical properties of these oxides after grinding have been investigated to understand the reasons for the changes in floatability.

2 Experimental

2.1 Materials

All the chemical reagents were of analytical grade from Sinopharm Chemical Reagent Co., Ltd., China and used as received. Copper oxide (CuO), lead oxide (PbO), zinc oxide (ZnO), quartz (SiO_2) and sulfur (S) were used in the mechanochemical sulfidization. Element sulfur was used as the sulfidizer. Conventional flotation agents, butyl xanthate and pine camphor oil were used in flotation test, as collector and froth agent, respectively.

2.2 Procedure and apparatus

Metal oxides were mixed with sulfur at a mass ratio of 20:1, without any other additive. A planetary ball mill (QM−3SP4, Nanjing, China) was used for grinding of the mixtures. 5.25 g starting compounds were put into a stainless steel pot (500 cm^3 inner volume) with 140 g stainless steel balls (7 balls with 17 mm in diameter) and subjected to grinding in air at different rotational speeds for 20 min. All grinding operation was conducted under ambient atmosphere, as a simulation to the actual industry situation.

A conventional rougher flotation operation was conducted to investigate the changes in floatability of the as-prepared samples. 5.25 g as-ground samples were employed in flotation experiment. Flotation tests were performed with a laboratory scale flotation machine (XFGC2 5−35 g, Jilin, China) under a constant pulp content of 10.5% with laboratory deionized water at room temperature. After the pulp was agitated for 5 min, collector in a concentration of 0.2 g/L was added and conditioned for another 5 min. Then, the foaming agent in a concentration of 0.05 g/L was added and conditioned for further 2 min. The froth was scraped by hand every 10 s and continued for totally 3 min, according to a plateau level of conventional rougher flotation procedure. The flotation efficiency was evaluated on the basis of the recovery of metal oxides.

2.3 Characterizations

The crystallographic compositions of the ground products were characterized with X-ray diffractometer (XRD, RIGAKU, D/MAX-RB, Japan). The morphological change and the superficial chemical composition of the samples after ball milling were observed with a scanning microscope (SEM-EDS, JEOL Ltd, JSM−5610LV, Japan). A Fourier transformation infrared spectrometer (FTIR, Thermo Nicolet, Nexus, USA) was used to analyze the ground samples with a conventional KBr method. A Raman spectrometer (Raman, RENISHAW, INVIA, UK) was used to analyze the property change of the ground sample. Power−compensation differential scanning analysis (DSC, Perkin Elmer, Pyris, USA) was carried out under N_2 atmosphere heating from room temperature to 700 °C at 10 °C/min to assess the adsorption of moisture and carbon dioxide on the sample surface. Laser particle size analysis (Mastersizer 2000, Malvern, UK) was used to investigate the size distributions of ground samples. Before operating, 0.01 g of sample was dipped in 100 mL deionized water and then dispersed for 5 min using an ultrasonic disperser. The adjustment of pH value was based on the addition of NaOH solution and diluted hydrochloric acid. A Zeta-potential measurement (Zetasizer Nano, Malvern, UK) was performed to investigate the surface electrochemical properties of samples before and after grinding.

3 Results and discussion

3.1 Phase transition of three oxides during grinding with sulfur

Figure 1 shows the XRD patterns of three oxide samples ground at 500 r/min for 20 min, respectively. In CuO and ZnO cases, all the peaks for the ground mixtures are the same as those of the initial materials except for their heights. This implies that such a mild grinding cannot cause the formation of metal sulfide. The clear peaks of sulfur in ZnO pattern testify the uneven dispersion and feeble binding of sulfur on ZnO surface after grinding. Differently, the broad and weak peaks of sulfur in CuO case indicate the more uniform dispersion of sulfur on the surface of CuO.

Compared with above two cases, the XRD peaks of PbO are obviously of weak intensity and broad shape, indicating that its crystallinity has changed in some sense. Simultaneously, there is no initial sulfur but slight PbS in the pattern of PbO, confirming a kind reaction with PbO, represented as Eq. (1):