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Hydrothermal modification to improve the floatability of ZnS crystals

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ABSTRACT

Crystalline structure and surface properties significantly affect the floatability of metal sulphides. In this study, a novel methodology to modify zinc sulphide (ZnS) crystals was proposed to improve the floatability of the crystals. Initially, ZnS crystals, synthesised from zinc hydroxide ($Zn(OH)_2$) and sulphur (S) under hydrothermal conditions, were used to assess the floatability. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were employed to analyse the crystalline structure and surface properties of the sulphides. Conventional flotation tests were performed to evaluate the floatability. The effects of mineraliser (KOH) concentration, precursor ($Zn(OH)_2$) concentration, hydrothermal temperature and holding time on the floatability of the ZnS crystals were investigated. The optimal flotation recovery of ZnS (82.53%) was obtained with a KOH concentration of 5 mol/L, a $Zn(OH)_2$ concentration of 10%, a holding time of 4 h and a hydrothermal temperature of 260 °C. Then, sludge containing fine and amorphous zinc compounds, which was generated during the disposal of metallurgical waste water, was employed to test the recovery of valuable metals using modified hydrothermal sulphidation. The results show that the recovery of Zn in the sludge can reach 66.3% under the optimal conditions.

1. Introduction

The crystalline structure and surface characteristics significantly affect the flotation behaviour of sulphide particles. Many studies in the literature have shown the effects on flotation of properties, including the crystallinity, grain size and particle shape. Hemlund (1961) reported that well-crystallised molybdenite was fast floating, while the amorphous variety was either slow floating or non-floating. The particle size plays a critical role in the probability that particles collide with bubbles, attach to bubbles after collision, and remain attached in the pulp phase (Ross, 1997; Nguyen and Evans, 2004). It has been reported that fine particles typically have slow recovery rates because of decreased particle-bubble collisions and are prone to entrainment. Moreover, very small particles tend to have large specific areas, which can lead to the excessive adsorption of reagents and other effects that are associated with chemically active particles (Feng and Aldrich, 1999). Ahmed (2010) demonstrated that the greater the surface roughness, the stronger the detachment force required to separate the particle from the bubble, and hence, a higher flotation recovery was obtained. Shahbazi and Rezai (2010) found that the flotation recoveries of non-spherical particles are higher than those of spherical particles. Similarly, it has been shown in the literature that elongated particles have high flotation recoveries compared with equivalent round particles because of the stronger adhesion force of the prismatic particles, resulting from the larger contact areas and the longer contact lines (Huh and Mason, 1974; Oliver et al., 1977; Ulusoy et al., 2004).

Based on the material properties, it is known that oxides and hydroxides are less prone to float than are their sulphide counterparts because of the higher solubilities of the oxides and the extensive hydration of the oxide surfaces (Fuerstenau et al., 1987). Therefore, sulphidation treatment has received much attention in the recovery of metals from sludge containing metal oxides or metal hydroxides (Kuchar et al., 2006a, b). Through sulphidation, the heavy metals in the sludge can be converted into metal sulphides that can then be separated by flotation, which is a widely used technique in the mining industries to separate valuable mineral ores from the tailings. However, flotation of the metal sulphide obtained by sulphidation might differ from that of the natural sulphide ore. The most important differences are those in the crystalline structures and surface properties of the formed metal sulphides, which might adversely impact their selective floatability (Rashchi et al., 2005).

There are many methods to improve the flotation behaviour of materials with poor floatability, such as flocculation flotation (Rosa and Rubio, 2005) and carrier flotation (Valderrama and Rubio, 1998). However, researchers mainly concentrate on the process of flotation rather than the properties of the crystal. Because the

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crystalline structures and morphological properties are important to the floatability of particles, transferring the metals in the waste into metal sulphides with a crystalline structure and surface characteristics that favour flotation is beneficial. Recently, the hydrothermal method has provided a promising method for the synthesis of crystals because of its low cost, high efficiency and potential for large-scale production (Byrappa and Adschiri, 2007). Hydrothermal modification has been widely used to prepare crystals with different morphologies, such as shells (Yin et al., 2003), cubes (Lu et al., 2004), spheres (Xu and Xue, 2007) and tubes (Libera and Gogotsi, 2001). In addition, according to the principles of geochemistry and the mineralogy, natural sulphide ores are formed as a result of a hydrothermal reaction (Tivey and Delaney, 1986; Marques et al., 2007). To simulate geothermal conditions in this research, a hydrothermal method was employed to sulphidise the heavy metals in sludge using sulphur as the sulphidiser. In this way, the potentially available heavy metals could be transformed into metal sulphides, which could be floated with a suitable collector.

The synthesis of ZnS by the hydrothermal technique has been well studied (Qian et al., 1995; Wei et al., 2005; Salavati-Niasari et al., 2009); however, to our knowledge, there is little information available in the literature about improving the floatability of ZnS by hydrothermal modification. In our previous work, the extent of zinc sulphidation under optimal hydrothermal conditions was studied systematically and showed that the extent of zinc sulphidation could reach 85% under optimal conditions (Liang et al., 2012). In this paper, an attempt was made to increase the floatability of the synthesised ZnS. The objective of this study was to examine the optimal conditions for the hydrothermal synthesis of ZnS with the ultimate objective of improving the flotation recovery of zinc from sludge.

2. Experimental

2.1. Materials

The chemical reagents used in the experiments, including zinc hydroxide ($Zn(OH)_2$), sulphur (S), potassium hydroxide (KOH), hydrochloric acid (HCl) and sodium hydroxide (NaOH), were of analytical grade. The flotation reagents, such as sodium hexametaphosphate, carboxy methyl cellulose, copper sulphate, butyl xanthate, diethyldithiocarbamate and pine camphor oil, which were obtained from Zhuzhou Mineral Processing Reagent Plant (a reagent producer plant), were of industrial grade.

The sludge sample used in this experiment was obtained from a zinc and lead smelter plant in China. The sludge was generated from the disposal of metallurgical wastewater using precipitation. It contained approximately 13% zinc and a large amount of calcium components, including $CaSO_4{\cdot}2H_2O$ and $CaCO_3$.

2.2. Experimental procedure

2.2.1. Synthesis of ZnS

The hydrothermal reaction was conducted in a Teflon®-lined stainless steel autoclave with a capacity of 1 L, of which 80% was filled. A KOH solution, ranging in concentration from 0 to 10 mol/L, was added slowly while the solution was stirred. The concentration of $Zn(OH)_2$ was controlled from 10% to 30% and S was placed in the autoclave with a Zn/S molar ratio of 1:1.2. Then, the autoclave was sealed and incubated at a temperature ranging from 200 °C to 280 °C for 2–10 h. The contents were cooled to room temperature after the reaction. After filtration through filter paper containing 1 μm pores, the resulting products were collected and washed with deionised water to remove possible left-over ions and then dried at 100 °C for 10 h in the vacuum desiccator.

2.2.2. Sulphidation of zinc-containing sludge

The zinc-containing sludge was obtained from a lead and zinc smelting enterprise in China. The sulphidation was performed in an autoclave with a capacity of 5 L. The reaction was performed at 260 °C for 4 h, with a molar ratio of S^{2-} to Zn^{2+} maintained at 1.2 and a S:L ratio maintained at 1:5. The pH during the sulphidation was approximately 10.0. After heating, the autoclave was allowed to cool to room temperature. Finally, the precipitates were filtered and washed with distilled water several times. After being dried in a vacuum desiccator for 10 h, the resulting powder was collected for flotation and further characterisation.

2.2.3. The flotation of synthesised ZnS

All of the flotation tests were carried out at a pH of 5, adjusted with HCl and NaOH. Butyl xanthate and pine camphor oil were used as the collector and the frother, respectively. The tests were conducted in an XFG laboratory flotation machine, using a 0.25 L glass cell. For each test, 25 g of the sample was added to adequate ion-exchanged water under agitation with a stirrer. After the sequential addition of the pH adjusters, the collector and the frother, the suspension was conditioned for 3, 2 and 1 min, respectively. The flotation time was fixed for 5 min. The floated and non-floated products were filtered and then dried. The floatability was calculated by dividing the total weight of the two products (floated and non-floated) by the floated product weight.

2.2.4. The flotation of sulphidised zinc-containing sludge

The flotation of the sulphidised sludge was performed with a XFG laboratory flotation machine using a 0.5 L glass cell, as shown in the flow sheet in Fig. 1. The sample was conditioned with adjusting agents (sodium hexametaphosphate and carboxy methyl cellulose), an activator (copper sulphate), collectors (butylxanthate and diethyldithiocarbamate) and then a frother (pine camphor oil), with each stage having conditioning periods of 3, 3, 2, and 1 min, respectively. The concentrates were then collected for 5 min. After flotation, the tails and concentrates were filtered, dried, weighed, and analysed for Zn by digestion and atomic absorption spectrophotometric determination.

2.3. Characterisation

The crystallinity and phase of the products were characterised by X-ray diffraction (XRD, D/max2550 VB+ 18 kW). The grain size of ZnS was calculated from Scherrer's equation (Hammond, 1997):

$$d = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

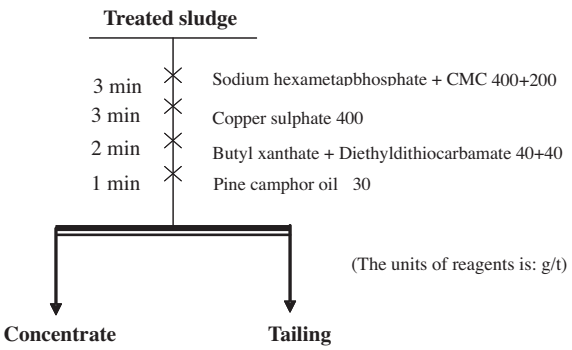

Fig. 1. The process flow sheet of flotation.