



# Sulfidation behavior of Zn and ZnS crystal growth kinetics for Zn(OH)<sub>2</sub>–S–NaOH hydrothermal system



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## ABSTRACT

Recently, hydrothermal sulfidation has received much attention for its potential application in the recovery of heavy metals from waste. To achieve a better understanding of the hydrothermal sulfidation process, the sulfidation behavior of Zn and ZnS crystal growth kinetics for the Zn(OH)<sub>2</sub>–S–NaOH hydrothermal system was studied in this article. Based on discussion of the thermodynamics, the behavior of S<sup>0</sup> in the S–H<sub>2</sub>O system and the behavior of Zn(OH)<sub>2</sub>, the reaction steps of hydrothermal sulfidation were proposed. The sulfidation process was then analyzed by a new variant of the shrinking core model in which both the interfacial transfer and the diffusion across the product layer affect the sulfidation efficiency, and its apparent activation energy is 21.4 kJ/mol. The crystalline size data of ZnS are fitted by a standard Ostwald ripening model consistent with crystal growth controlled by the volume diffusion of ions in solution. The deduced activation energy for ZnS crystal growth is 39.8 kJ/mol.

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## 1. Introduction

Inspired by the formation of sulfide ore under geothermal conditions, hydrothermal sulfidation using elemental sulfur as the sulfidizing agent was proposed to dispose of heavy-metal-containing sludge in our previous studies (Chai et al., 2015; Ke et al., 2014; Liang et al., 2012a,b; Xie et al., 2013). In this process, heavy metals contained in waste were initially converted into metal sulfides. Subsequently, the as-generated sulfides could be separated and further enriched by a flotation process, which is a commonly used separation technique in processing metal sulfide ores (Crozier, 1992). It was found that the sulfidation percentages of zinc and lead reached more than 85% and 75%, respectively, after hydrothermal sulfidation. However, the flotation recoveries of ZnS and PbS in the sulfidized sludge were far from satisfactory (Liang et al., 2012b).

It is common knowledge that the flotation behaviors of minerals are closely related to their crystalline structure and surface characteristics. Our previous studies (Ke et al., 2015; Zhang et al., 2012), as well as other studies reported in the literature (Chen et al., 2012, 2015), have shown that the flotation of synthetic sulfides differs greatly from the flotation of natural sulfide ores due to differences in physicochemical properties between synthetic sulfides and natural sulfide ores. Therefore, to achieve the highly efficient flotation recovery of synthetic

sulfides, the most important step is to reduce the differences between synthetic sulfides and natural sulfide ores. To modify the size, shape and structure of synthetic sulfides, further knowledge of the sulfidation reaction and crystal growth is paramount (Lin et al., 2012; Zhuang et al., 2012). During recent years, however, the majority of research on hydrothermal sulfidation has been restricted to the investigation of process optimization (Ke et al., 2014; Liang et al., 2012a,b; Min et al., 2013), resulting in a poor understanding of the sulfidation process and sulfide crystal growth.

Hydroxide is one of the most common components in lime neutralization sludge. To date, lime neutralization is still the most commonly practiced technique for the treatment of heavy-metal-containing acidic wastewater from the Zn/Pb smelting, galvanizing and mineral processing industries (Akcil and Koldas, 2006; Matlock et al., 2002). Thus, large quantities of Zn(OH)<sub>2</sub>-containing neutralization sludge must be disposed of urgently. As repeatedly mentioned in our previous studies (Ke et al., 2015; Liang et al., 2012a,b), hydrothermal sulfidation is especially suitable for the treatment of neutralization sludge because there is no need for pretreatment such as baking and grinding. Therefore, the Zn(OH)<sub>2</sub>–S–NaOH system was chosen as a simulation of the hydrothermal sulfidation of Zn(OH)<sub>2</sub>-containing neutralization sludge. An understanding of the factors that affect the kinetics of sulfidation and ZnS crystal growth for the Zn(OH)<sub>2</sub>–S–NaOH hydrothermal system is fundamental to regulating the crystal growth of ZnS generated during the treatment of actual neutralization sludge. In this work, the sulfidation behavior of Zn for Zn(OH)<sub>2</sub>–S–NaOH hydrothermal system was systematically studied for the first time. In addition, the kinetics of sulfidation and ZnS crystal growth were investigated.

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## 2. Experimental section

### 2.1. Chemicals

Zinc hydroxide ( $\text{Zn}(\text{OH})_2$ ), sulfur powder ( $\text{S}^0$ ), sodium hydroxide ( $\text{NaOH}$ ), glacial acetic acid ( $\text{CH}_3\text{COOH}$ ), ascorbic acid ( $\text{C}_8\text{H}_8\text{O}_6$ ), and saturated bromine water ( $\text{Br}_2$ , >3%) are of analytical grade. All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

### 2.2. Experimental procedure

The primary sulfidation experiments were performed in a floor stand reactor (Parr 4534, USA) with a capacity of 1.9 L.  $\text{Zn}(\text{OH})_2$  (0.3 mol),  $\text{S}^0$  (0.4 mol) and 1 L of 0.24 mol/L  $\text{NaOH}$  were loaded into the floor stand reactor. The reactor was then sealed and heated separately at 180 °C, 210 °C, 240 °C and 260 °C for periods of time ranging from 0 h to 8 h. After reaction, the reactor was cooled naturally to ambient temperature. The precipitates were then isolated via filtration and washed repeatedly with deionized water and ethanol. Finally, the products were dried at 60 °C for 48 h and ground into powder for further measurements.

### 2.3. Analytical methods

#### 2.3.1. Determination of sulfidation efficiency

The sulfidation efficiency of Zn was determined by performing a procedure based on the chemical phase analysis of the sulfide ore (Zhang, 1992), which was repeatedly described in our previous studies (Ke et al., 2014, 2015; Liang et al., 2012a). First,  $0.5000 \pm 0.0005$  g of as-screened sample (sieved with 100 mesh) was placed in a conical flask with 100 mL of 200 g/L  $\text{CH}_3\text{COOH}$ –5 g/L  $\text{C}_8\text{H}_8\text{O}_6$  to extract the unreacted  $\text{Zn}(\text{OH})_2/\text{ZnO}$ . After stirring for 1 h in boiling water, the mixture was filtered through 1  $\mu\text{m}$  filter paper, and the filtrate (1) was collected. The filtered residue was then rinsed repeatedly to remove the residual  $\text{Zn}^{2+}$ . The filter paper was added to the identical conical flask, and 100 mL of  $\text{Br}_2$  solution ( $\text{Br}_2$  > 3%) was added to extract the  $\text{ZnS}$ . After stirring for 45 min, the mixture was filtered, and the filtrate (2) was obtained. The metal-bearing filtrate (1) and filtrate (2) were diluted and analyzed by ICP-AES. The sulfidation efficiency of Zn was calculated according to Eq. (1):

$$\varphi = M_{\text{Zn}(1)} / (M_{\text{Zn}(1)} + M_{\text{Zn}(2)}) \times 100\% \quad (1)$$

where  $\varphi$  is the sulfidation efficiency (%), and  $M_{\text{Zn}(1)}$  (mg) and  $M_{\text{Zn}(2)}$  (mg) denote the amount of Zn in filtrate (1) and filtrate (2), respectively.

#### 2.3.2. Characterization

The initial specimen characterization was performed by X-ray diffraction on a Rigaku D/MAX 2550 VPC diffractometer, operating at 40 kV and 20 mA, with steps of  $0.02^\circ$  at  $10^\circ \text{ min}^{-1}$  in a  $2\theta$  range from  $10^\circ$  to  $80^\circ$ . The average crystallite size of the nano-ZnS crystals was calculated using the Scherrer equation from the full width at half-maximum (fwhm) of the (111) diffraction peaks of ZnS (Hammond, 2009):

$$d = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where  $d$  is the average crystallite size;  $k$  is the Scherrer constant, taken to be 0.89;  $\lambda$  is the wavelength of the X-ray (0.15418 nm);  $\beta$  is the corrected half-width of the diffraction peak; and  $\theta$  is the diffraction-angle.

The microstructure of hydrothermal products was characterized by transmission electron microscopy (TEM, JEM-2100F). All samples were prepared by depositing a drop of ethanol solution containing the sample onto holey carbon-coated copper grids.

The particle size of the sample was analyzed using a laser diffraction particle size analyzer (Micro-plus, Malvern, USA), which includes a wet ultrasonic dispersing module to conduct measurement in suspension.

## 3. Results and discussion

### 3.1. Sulfidation behavior for the $\text{Zn}(\text{OH})_2$ – $\text{S}$ – $\text{NaOH}$ hydrothermal system

#### 3.1.1. Thermodynamics

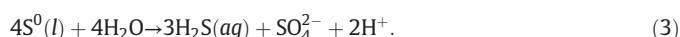
The Eh–pH diagrams for the S– $\text{H}_2\text{O}$  system at 25 °C and 200 °C are presented in Fig. 1. The stability region of  $\text{S}^0$  is observed in acid medium (Munoz et al., 1998) and reduces in area with increasing temperature from 25 °C to 200 °C. The  $\text{S}^0$  zone shown in Fig. 1a is surrounded by the zone of  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{S}$  and  $\text{HS}^-$ , indicating that  $\text{S}^0$  can be oxidized into  $\text{HSO}_4^-$  or  $\text{SO}_4^{2-}$  under oxidation conditions or converted into  $\text{H}_2\text{S}$  or  $\text{HS}^-$  under reduction conditions. However, an interesting point shown in Fig. 1b is that the equilibrium line between  $\text{S}^0$  and  $\text{HS}^-$  disappears at 200 °C, indicating that  $\text{S}^0$  cannot be reduced directly into  $\text{HS}^-$  under these conditions.

The reactions among  $\text{S}^{2-}$ ,  $\text{HS}^-$  and  $\text{H}_2\text{S}$  are listed in Appendix A, and the equilibrium constants are obtained from HSC Chemistry Software Version 6.0 (Outokumpu Research Oy, Finland). Based on the reactions and equilibrium constants shown in Appendix A, the speciation diagram of  $\text{H}_2\text{S}$ ,  $\text{HS}^-$  and  $\text{S}^{2-}$  at 200 °C is plotted in Fig. 2, showing that  $\text{S}^{2-}$  and  $\text{HS}^-$  are dominant in the basic pH region to neutral pH.

In aqueous environments, the hydrolysis or dissolution of  $\text{ZnO}$  or  $\text{Zn}(\text{OH})_2$  forms a series of hydroxy-complexes (Degen and Kosec, 2000; Wang et al., 2011; Zhang and Muhammed, 2001). The reactions of each  $\text{Zn}(\text{II})$  species and their equilibrium constants are shown in Appendix B. The distribution diagram of each  $\text{Zn}(\text{II})$  species is redrawn based on the data in Appendix B and shown in Fig. 3, showing that the distribution of  $\text{Zn}(\text{II})$  species is slightly affected by temperature. The  $\text{Zn}^{2+}$  is relatively significant in the acidic region, whereas the  $\text{Zn}(\text{OH})^+$  and  $\text{Zn}(\text{OH})_2^0$  species are dominant in the neutral pH to mildly basic region. As the pH increases, the dominant species appear to be  $\text{Zn}(\text{OH})_3^-$  and  $\text{Zn}(\text{OH})_4^{2-}$ .

#### 3.1.2. Behavior of $\text{S}^0$ in S– $\text{H}_2\text{O}$ system

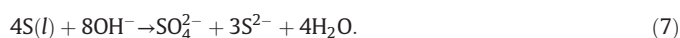
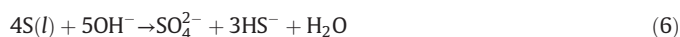
During the course of the current experiments, with increasing temperature, solid  $\text{S}^0$  melts at approximately 119 °C into liquid  $\text{S}^0$ . The pH value is nearly 13.3 (0.24 mol/L  $\text{NaOH}$ ) at the initial time, so  $\text{S}^0$  is quite unstable. The disproportionation of  $\text{S}^0$  occurs according to the following equation (Bottcher et al., 2001; Thamdrup et al., 1993).



As soon as  $\text{H}_2\text{S}$  and  $\text{H}^+$  are produced, they react with  $\text{OH}^-$  to generate  $\text{HS}^-$  and  $\text{S}^{2-}$  (Eqs. (4)–(5)). The disproportionation of  $\text{S}^0$  is thus propelled by removal of  $\text{H}_2\text{S}$  and  $\text{H}^+$  as they are produced (Thamdrup et al., 1993).



Accordingly, the total reactions of  $\text{S}^0$  disproportionation can be written as



As a result,  $\text{S}^{2-}$  is the initial provider of sulfur for the sulfidation reaction in this hydrothermal system. As the reaction proceeds, however, the pH of the solution decreases, and  $\text{HS}^-$  becomes the provider of

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