

Hydrothermal sulfidation and floatation treatment of heavy-metal-containing sludge for recovery and stabilization

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ABSTRACT

This study focuses on the application of hydrothermal sulfidation and floatation to treat the heavy-metal-containing sludge for recovery and stabilization. After the hydrothermal sulfidation, the sulfidation percentage of zinc and lead reach up to 85.0% and 75.4%, respectively. 33.3% of Zn, 58.9% of Pb and 68.8% of Cu can be recovered from the sludge by floatation. The lower recovery of ZnS attributes to its surface and structural characteristics. To compare these characteristics, three types of synthetic metal sulfide (ZnS, PbS and CuS) were prepared and examined with XRD, SEM and TEM. The poor floatability of the finely dispersed, round shape of ZnS can be improved by crystal modification in hydrothermal condition. With increasing the temperature and reaction time, the grain size of the ZnS increased from 7.95 nm to 44.28 nm and the recovery of Zn increased to from 33.3% to 72.8%. The TCLP results indicate that all the leached heavy metal concentrations of floatation tailings are under the allowable limit. No obvious increase of heavy metal concentration was observed in continuous leaching procedure. The presence of alkaline compounds after hydrothermal sulfidation might act as mineralogical scavengers of dissolved heavy metal released by sulfide oxidation to avoid the heavy metal pollution.

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1. Introduction

Tons of heavy metal containing wastes are generated every year by industries such as nonferrous smelting, mining and electroplating. The huge quantities of these wastes can potentially impose a negative impact to the environment due to the possibility of releasing toxic elements, such as lead (Pb), cadmium (Cd), arsenic (As), etc. [1]. Therefore, the stabilization of the toxic elements becomes very urgent and essential. On the other hand, since the waste usually contains plenty of valuable metals, it should be considered as a secondary resource of metals that can be recycled, rather than an end waste, in order to relieve the global metal supply [1–3]. However, current methods used for heavy metal recovery from this waste are difficult to avoid secondary pollution. For example, the widely-used direct extraction technique often leads to a large quantity of wastewater and residue containing unstable state heavy metals [4,5]; while roasting method requires too much time and energy and generates a great deal of heavy-metal-containing slag, resulting in various problems during elimination [6].

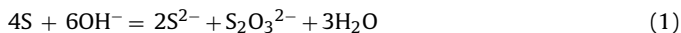
Recently, sulfidation has received much attention as a potential effective process for heavy metal recovery [7–9]. The heavy

metals contained in the waste are initially converted into metal sulfides with good floatability. It can be thereafter separated from the sludge by floatation and the tailings' chemical property turns stable. Conventional sulfidation with Na_2S has been widely employed to improve the floatability of some mineral oxide ores [4,10] and heavy metal pollution control [7,8,11]. Nevertheless, the use of sulfide as a sulfidizing agent is accompanied by the generation of secondary wastes and the emission of toxic gases, such as H_2S . Hence, sulfur has been suggested as a substitute for sulfidizer. Wang et al. [12] reported that nonferrous metal oxides can be converted into sulfides through mechanical ball milling. Roasting with sulfur is another method for heavy metal sulfidation. It was found that the sulfidation of Pb and Zn oxides reached 98% and 95%, respectively, under optimal conditions [13]. However, floatation of the formed metal sulfide (MeS) might differ from natural sulfide ore floatation [11]. One of the most important differences is the fact that the formed MeS has different crystalline structures and surface properties and it might make adverse impacts on their selective floatability [14].

According to the mineralogy and the geochemistry, the natural sulfide ores are generated through hydrothermal reaction [15]. As a simulation of geothermal conditions, in this research, hydrothermal sulfidation was employed to sulfidize the heavy metals in heavy-metal-containing sludge using sulfur as raw materials. The sulfidation reaction is accomplished by S^{2-} generated by the disproportionation reaction of sulfur as shown in Eq. (1). The reactions

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of metal hydroxide ($\text{Me}(\text{OH})_2$) to metal sulfide (MeS) in hydrothermal condition are presented in Eqs. (2) and (3).



Generally, hydrothermal sulfidation can achieve much higher conversion rates because the metals are transformed into metal ions and are easily dissolved in solution under hydrothermal conditions [16]. In addition, hydrothermal sulfidation offers distinct advantages over conventional methods, especially for the sulfidation of heavy metal containing sludge with very high moisture content. First, the reaction occurs efficiently without any pretreatment such as baking or grinding. Second, sulfur is a low-cost material and causes only slight secondary pollution as compared with other sulfidizers such as Na_2S . Moreover, hydrothermal sulfidation offers a possible way to modify the metal sulfide surface and structural properties in order to improve their floatability. Many metal sulfides have been successfully synthesized with some particular structures in hydrothermal condition, like quantum dots, nanorods, nanowires, hollow spheres, nanosheets, and so on [17,18]. Besides, Viñals et al. [19] found that after hydrothermal treatment of sphalerite with $\text{Cu}(\text{II})$ ions, a compact layer of copper sulfide surrounded the sphalerite and its selective floatation was improved. Despite the above-mentioned advantages, the hydrothermal sulfidation approach is mainly employed for the synthesis of specific sulfide materials [20] and as a pretreatment for natural ores [21]. Only a little work has been reported on the management of heavy-metal-containing sludge by recycling via hydrothermal sulfidation.

Additionally, the stabilization test should be performed to evaluate of the environmental activities of heavy metals in high-sulfide floatation tailings. Most works use the TCLP (Toxicity Characteristic Leaching Procedure) to evaluate the stabilization effect. The TCLP test has come to unfavorable criticism because of its limitation on simulating different disposal conditions of the waste [22]. Exposure of waterlogged tailings to air, especially the high-sulfide tailings, can result in oxidation reactions, acid-drainage and metal leaching, probably creating severe environmental problems [23]. Therefore, the high-sulfide tailings were subjected to a 24-day continuous leaching experiment to evaluate the stabilization of the heavy metals.

This study focuses on the application of hydrothermal sulfidation converting certain heavy metal remained in the sludge into metal sulfide (MeS) to obtain the recovery of such metal by subsequent floatation as well as the environmental benefits from such treatment. Neutralization sludge, which is generated after the disposal of heavy metal containing wastewater by lime milk precipitation, was employed as the treated object in the present study. The extents of Zn and Pb sulfidation were used as an indicator to discover the optimal reaction conditions. After the sulfidation treatment, floatation and stabilization tests were carried out to examine the recovery and stabilization effect. The goal of this study was to find a novel way for heavy-metal-bearing sludge disposal that could not only enhance metal recovery but also maintain the stabilization of heavy metals in the tailings.

2. Experiment

2.1. Materials

The sludge sample was obtained in Zhuzhou Smelter Group, which is one of the largest zinc and lead smelter plants in China. The sludge used in this experiment was generated after the disposal

process of metallurgical wastewater by lime milk precipitation, with an annual generation capacity of about 50 000 tons. There is a large amount of calcic component in raw neutralization, such as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaCO}_3 \cdot \text{H}_2\text{O}$, etc. To determine the heavy metals content in the sludge, the samples were air dried, ground and sieved with 100–200 mesh (75–150 μm) before being digested using a mixture of concentrated HCl and HNO_3 (3:1, v/v). Then, the solutions were filtrated with 1 μm pore sized filter paper and element concentrations in filtrate were analyzed with inductively coupled plasma (ICP-AES, IRIS Intrepid II XSP). The elemental composition and main heavy metal (Zn and Pb) phase composition of raw sludge are given in Table 1. The phase composition of Zn and Pb was tested by chemical phase analysis as described by Zhang [24].

2.2. Experimental apparatus and operational procedure

The hydrothermal sulfidation reaction was carried out in high-pressure reactor, in which the raw sludge and sulfur were mixed in an appropriate mass ratio, then the mixture was loaded into a 1000 mL capacity stainless steel autoclave, and 700 mL of water was added. The autoclave filled with the reactant solution was sealed and placed into a 180–240 °C furnace from 0 to 8 h, and then cooled to room temperature under tap water. After the reactions, the resulting products were filtered with a 1- μm pore sized filter paper. The precipitate was collected and washed with deionized water to remove ions possibly remained in the final product, and finally it was dried at 80 °C overnight in a vacuum oven.

2.3. Analyses

2.3.1. Sulfidation percentage

The sulfidation percentages of Zn and Pb were tested in triplicate based on the chemical phase analysis of the sulfide ore [24]. Take Zn sulfidation percentage for example, the test procedure was described as follow. Initially, 0.5000 ± 0.0005 g of screened sample (sieved with 200 mesh) was placed in a conical flask with 100 mL of a mixed solution of 100 g L^{-1} of CH_3COOH and 5 g L^{-1} of ascorbic acid that was employed to extract the un-reacted Zn compounds, like ZnO , $\text{Zn}(\text{OH})_2$, and ZnSO_4 . After stirring for 1 h in boiling water, the mixture was filtered through 1 μm filter paper, and the filtrate (1) was collected and stored in a plastic container. The filtered residue (1) was then rinsed for 30 min with deionized water. The filter papers were placed into the same conical flask and 100 mL of 30 g L^{-1} of Br_2 solution was added as an extracting solution for ZnS. After stirring for 45 min, the mixture was filtered. The filtrate (2) and residue (2) were obtained. After rinsing and drying, the residue (2) was digested by a mixture of concentrated acid (HF (1 mL), HClO_4 (3 mL), HNO_3 (5 mL) and HCl (15 mL)) at 180 °C for 2 h. The digested solution was collected to determine the Zn content. The concentrations of heavy metals in solutions were analyzed by ICP-AES. The schemes of Zn and Pb sulfidation percentage test procedures are list in Table 2.

The sulfidation percentage was determined according to Eq. (4), where X is the sulfidation percentage (%), C'_{Me_0} is the initial MeS amount in raw sludge, and C_{Me} , C'_{Me} , and C''_{Me} stand for the metal concentrations of filtrate (1), filtrate (2) and digestion solution, respectively.

$$X = \frac{C'_{\text{Me}} - C'_{\text{Me}_0}}{C_{\text{Me}} + C'_{\text{Me}} + C''_{\text{Me}}} \times 100\% \quad (4)$$

2.3.2. Floatation test

In order to investigate the floatability of the treated sludge, the mixed floatation of these sulfidized materials was carried out by a conventional floatation process, consisting of traditional roughing, re-concentrating and scavenging. Floatation tests were made with

Table 1
The elemental composition and main heavy metal (Zn and Pb) phase composition of raw sludge.

Elements composition (wt%)										
Zn	Pb	Fe	Ca	S	Cd	Cu	As	Na	Mn	Al
19.9	0.95	1.20	8.00	3.7	0.73	0.10	0.06	0.17	1.70	0.52
Phase composition of zinc and lead										
Constituent		Sulfite	Oxide	Sulfide	Silicate	Others				
Zn		0.20%	84.42%	8.89%	3.72%	2.26%				
Pb		0.05%	83.51%	4.33%	2.80%	9.31%				

laboratory scale floatation machines (XFD-0.5 L). The pulp density was 20% and the pulp temperature was adjusted to 60 °C. Subsequently, 0.04% (w/w) of dispersant (sodium hexametaphosphate) and 0.04% (w/w) of depressant (carboxymethyl cellulose) were added to the pulp, followed by conditioning for 3 min. After conditioning, 0.04% (w/w) of copper sulfate (CuSO₄·5H₂O) was added as the activator, followed by conditioning for 3 min. Then, 0.008% (w/w) of diethyl dithiocarbamate and 0.008% (w/w) of butyl xanthate were added as the collectors, followed by conditioning for 2 min. Finally, 0.002% (w/w) of pine oil was added to the slurry as further. Roughing floatation was started by opening the air supply of the floatation apparatus for a period of 10 min and the froth layer was removed manually. After re-concentrating and scavenging, the obtained froth and rest fractions were scavenging dried and weighed, followed by microwave digestion and ICP-AES analysis to determine the heavy metal content. The floatation efficiency was evaluated on the basis of the following parameters.

$$\text{metal recovery (\%)} = 100\% \times \frac{\text{Mass}_{\text{forth}} \times [\text{Me}]_{\text{forth}}}{\text{Mass}_{\text{total}} \times [\text{Me}]_{\text{total}}} \quad (5)$$

$$\text{concentrating factor} = \frac{[\text{Me}]_{\text{forth}}}{[\text{Me}]_{\text{total}}} \quad (6)$$

Mass_{forth} (g) and Mass_{total} (g) are the weight of froth fraction and total mass respectively, and [Me]_{forth}, [Me]_{total} stand for the heavy metal contents of froth fraction and treated sludge, respectively.

To investigate the selective floatability and the surface characteristics of synthetic sulfide, analytical grade of metal hydroxide (Cu(OH)₂, Pb(OH)₂, Zn(OH)₂) and sulfur were employed as raw materials to synthesize the single sulfides through hydrothermal sulfidation, including CuS, PbS and ZnS. A certain amount of CaCO₃ (80% of the total mass) was added as the substitute of calcic component in raw neutralization sludge. The crystallographic compositions of the sulfidation resultant were characterized by X-ray diffraction (XRD, D/max 2550 VB+ 18 kW). Scanning electron microscopy (SEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, JEM-2100F) were used to observe the morphology of the synthetic sulfide.

2.3.3. Stabilization test

2.3.3.1. TCLP test. To evaluate the stability of the floatation tailings, toxicity characteristic leaching procedure (TCLP) was performed

according to USEPA Method 1311 [25]. The concentrations of heavy metals in leachate were analyzed by ICP-AES.

2.3.3.2. Continuous leaching test. A continuous leaching scenario was simulated in the laboratory by passing leaching liquor through the floatation tailings. The influent with pH adjusting to 3.2, was stirred continuously and delivered in an up-flow manner using a peristaltic pump (0.6 mL min⁻¹) over a period of approximate 24 days. The total liquid-to-solid ratio (L/S) was 20 L kg⁻¹. At different points of time, the leachate was collected and the heavy metal concentrations were measured by ICP-AES.

3. Results and discussion

3.1. The factors influencing sulfidation percentage of heavy metals

3.1.1. Effect of reaction temperature

Temperature plays a vital role in hydrothermal sulfidation (Fig. 1(a)). The sulfidation percentage of Zn increased from 60.5% to 89.8%, and Pb increased from 58.4% to 77.1% when the temperature varied from 160 °C to 240 °C. The sulfidation percentage of Pb was lower than Zn. That might be ascribed to the formation of PbSO₄, a stable and insoluble Pb compound, which can be generated during hydrothermal sulfidation as expressed by Eq. (7).



As shown in Fig. 1(a), higher temperature greatly affected hydrothermal sulfidation because the hydrothermal conditions probably increased the diffusive coefficient of metal ions and decreased the attachment of MeS to the reaction interface due to the increasing solubility of MeS [16]. The optimal temperature was determined to be higher than 180 °C, and all the subsequent experiments were carried out at 200 °C.

3.1.2. Effect of reaction time

The effect of the reaction time (0.5–8 h) on the extent of Zn and Pb sulfidation was studied at 200 °C with a pulp density of 200 g L⁻¹. As shown in Fig. 1(b), the sulfidation percentage of Zn was 48.7% within 1 h and 87.0% after 2 h. It also showed that the sulfidation percentage of Pb rapidly increased and reached 74.5% within 2 h, implying that the hydrothermal sulfidation reaction of

Table 2
Schemes of Zn and Pb sulfidation percentage test procedure.

	Stage	Fraction	Reagents/0.500 g sample	Shaking time and temperature
Zn	Filtrate (1)	ZnSO ₄ , Zn(OH) ₂ , ZnO	0.1 L 100 g L ⁻¹ CH ₃ COOH and 5 g L ⁻¹ ascorbic acid mixed solution	1 h at 96 ± 3 °C
	Filtrate (2)	ZnS	0.1 L of 30 g L ⁻¹ Br ₂ solution;	45 min at room temperature
	Digestion solution	Zn in other phases	5 mL HNO ₃ , 15 mL HCl, 3 mL HClO ₄ , 1 mL HF	2 h at 180 ± 5 °C
Pb	Filtrate (1)	PbSO ₄ , Pb(OH) ₂ , PbO	0.1 L 100 g L ⁻¹ NH ₄ COOH and 4 g L ⁻¹ ascorbic acid mixed solution	15 min at room temperature
	Filtrate (2)	PbS	0.05 L of 30 g L ⁻¹ Br ₂ and 250 g L ⁻¹ NaCl mixed solution	45 min at room temperature
	Digestion solution	Pb in other phases	5 mL HNO ₃ , 15 mL HCl, 3 mL HClO ₄ , 1 mL HF	2 h at 180 ± 5 °C

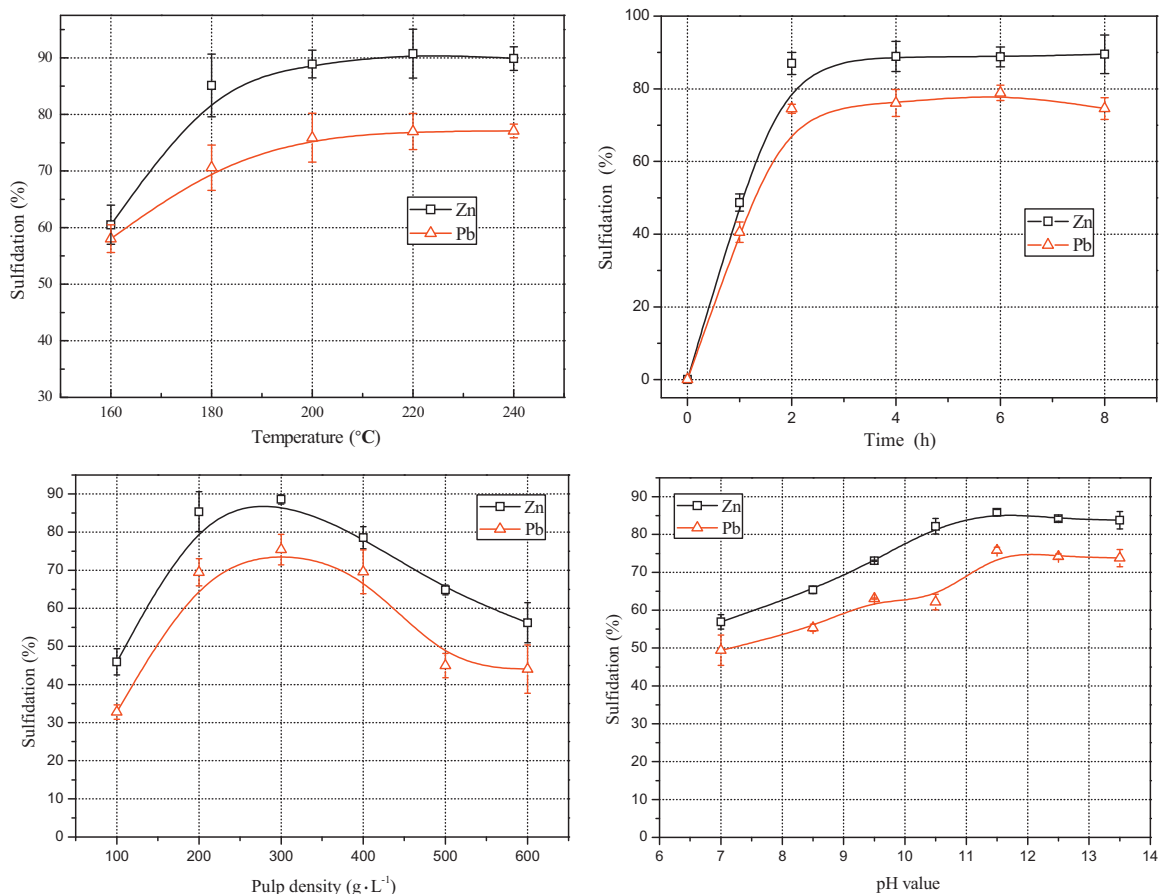


Fig. 1. The factors influencing sulfidation percentage of Zn and Pb. (a) Effect of temperature (2 h, pulp density 200 g L^{-1} , pH 10.3). (b) Effect of reaction time (200°C , pulp density 200 g L^{-1} , pH 10.3). (c) Effect of pulp density (200°C , 2 h, pH 10.3). (d) Effect of the pH value (200°C , 2 h, pulp density 300 g L^{-1}).

metals already completed after 2 h. Considering the long reaction time will consume energy, the optimal time span for hydrothermal sulfidation was 2 h.

3.1.3. Effect of pulp density

The effect of pulp density on the extent of Zn and Pb sulfidation at 200°C and a reaction time of 2 h is shown in Fig. 1(c). The sulfidation percentage of Zn increased from 46.0% to 88.6% when the pulp density increased from 100 g L^{-1} to 300 g L^{-1} and then decreased to 56.0% when the density increased to 600 g L^{-1} . The sulfidation percentage of Pb also decreased from 75.4% to 44.0% when the pulp density increased from 300 g L^{-1} to 600 g L^{-1} . The results indicated that higher or lower pulp densities decreased the extent of sulfidation percentage. It appears that a low density does not result in the maximum reaction rate between the metal and sulfur ions in the thick pulp. However, the sulfur ion concentration was reduced when the density was too low [21]. A satisfactory sulfidation percentage was achieved when the pulp density is $200\text{--}300 \text{ g L}^{-1}$. In fact, a 300 g L^{-1} may be more efficient in promoting the disposal capacity of a reactor with a certain volume.

3.1.4. Effect of pH

To investigate the effect of initial pH on the sulfidation percentage, HCl and NaOH were employed to adjust the initial pH value from 7 to 13.5. As illustrated in Fig. 1(d), pH obviously influenced on the sulfidation percentage. The sulfidation percentage of Zn and Pb rose from 56.9% and 49.1% to 85.0% and 75.4% when the initial pH

varied from 7 to 13.5, respectively. It can be explained that alkaline condition was suitable for the disproportionation reaction of sulfur, as shown in Eq. (1). Besides that, the $\text{Me}(\text{HS})_3^-$ predominated in alkaline solutions and the precipitation of MeS did not occur in sulfide-rich hydrothermal solutions until the temperature was decreased [16,26]. It will improve the combination of the metal ion with the sulfide ion. The initial pH value of the reaction should be adjusted to higher than 10.0. In this research, the pH value of the neutralization sludge was about 10.3, so there is no need to adjust its pH. However, for some acid sludge, such as leaching residue, a certain amount of lime milk should be added to increase the pH value.

The optimum operating process parameters of hydrothermal sulfidation were determined to be a reaction time of 2 h, a temperature of 200°C , a pulp density of 300 g L^{-1} and pH value higher than 10. Employing these experimental conditions yielded zinc sulfidation percentage of 85.0% and lead sulfidation percentage of 75.4%.

3.2. Flotation treatment and metal recovery

Employing the optimal experimental conditions of hydrothermal sulfidation can result in a high heavy metal sulfidation percentage. However, flotation of these heavy metal sulfides differs from natural sulfide ore flotation. One of the most important reasons is the fact that the synthetic sulfides possess different surface and structural characteristics, so the floatabilities of various synthetic sulfides should be investigated.

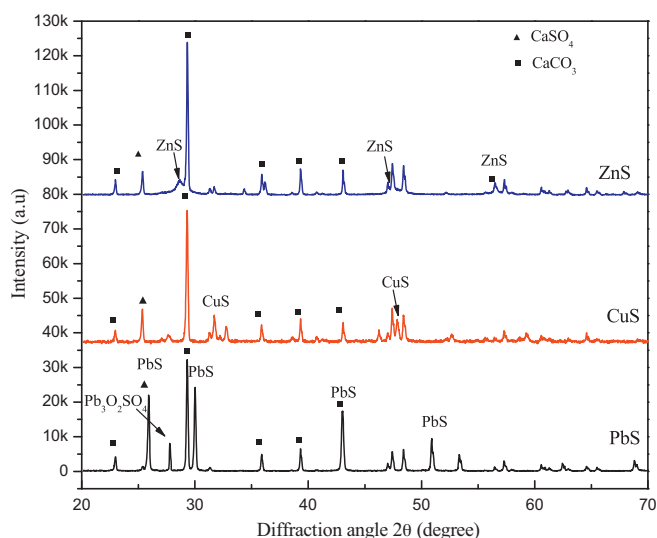


Fig. 2. XRD patterns of simulated sludge after hydrothermal sulfidation (2 h, 200 °C).

3.2.1. Flotation treatment of the synthetic sulfides

The flotation treatment of the sulfidized neutralization sludge was carried out by a conventional flotation process. Compared with untreated sludge, hydrothermal sulfidation resulted in an increase of concentrating factor, as well as an increase of the metal recovery for all the investigated heavy metals (Table 3). 33.3% of Zn, 58.9% of Pb and 68.8% of Cu can be recovered from the sludge through flotation. And the concentrating factor increased from about 1.02 to 1.67 for Zn, 1.05 to 2.44 for Pb and 1.10 to 2.50 for Cu. However, both of the recovery and concentrating factor for Zn, which was related to its selectivity floatability, were much lower than those of Pb and Cu. Therefore, we can conclude that the presently observed low selective flotation behaviour of ZnS might due to its surface or structural properties.

3.2.2. Characterization of the synthetic sulfide

To investigate the selective floatability and the surface characteristics of synthetic sulfides, three kinds of simulative-treated-sludge were obtained with hydrothermal sulfidation reaction of analytical grade metal hydroxide and sulfur as described in Section 2.1. The flotation treatment of these samples was carried out by the conventional flotation process. The flotation results are shown in Table 3. Similarly, the formed ZnS possessed a poor selectivity floatability than that of PbS and CuS. The concentrating factor of CuS and PbS was 3.29 and 3.44, respectively, and the recovery of CuS and PbS was 91.0% and 72.8% respectively. However, only 28.3% of ZnS were recovered through flotation with a low concentrating factor of 1.73.

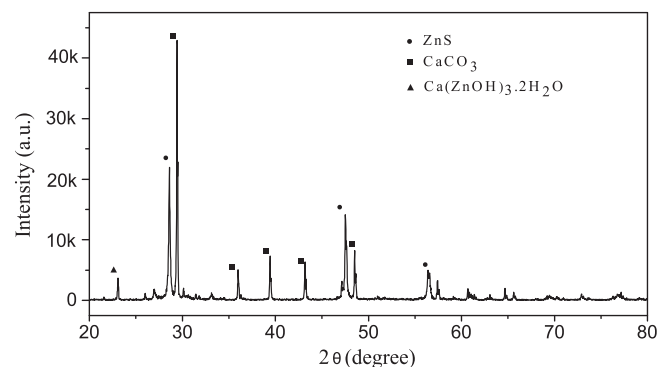


Fig. 4. The XRD patterns of the ZnS after crystal modification (4 h, 260 °C).

Compared with PbS and CuS, the formed ZnS showed very broad diffraction peaks in the XRD patterns (Fig. 2), which was the characteristics of nanosized materials [27]. The grain sizes of these sulfide were calculated by the Scherer formula [28].

$$D = \frac{0.9\lambda}{B \cos\theta} \times 100\% \quad (8)$$

where D is the mean particle size, λ is the wavelength of the X ray radiation, B is the full width at half maximum (FWHM) of the characteristic peak, and θ is the diffraction angle. The result showed that the mean grain size of ZnS is only 7.95 nm, while the sizes of PbS and CuS were 49.76 nm and 38.57 nm, respectively. Therefore, the formed ZnS grain was much smaller than PbS and CuS grain. For the fine particles of sulfide, the particle diameters/air bubble diameter ratio is less favorable for collision, resulting in lower flotation specificity, which is in agreement with the result reported by Cauwenberg et al. [29].

The surface properties of sulfides could clearly be observed at higher magnifications (Fig. 3). The CuS and PbS crystal grains were angular shape with smooth surface. The ZnS particle was composed by 5-nm-round grain. It has been comprehensively shown that particles with angular shape favors flotation more efficiently than round particles, and this effect is evident over a wide size range [30]. The enhanced flotation performance of the angular particles was attributed to particle topographical features better thinning and rupturing wetting-films surrounding bubbles [31]. The synthetic sulfide with a larger and angular shape and smooth surface might be beneficial for its selective recovery through flotation.

3.2.3. Modification of ZnS crystal

In order to achieve a high recovery of ZnS, its crystal structure should be modified. In our previous study, we found the hydrothermal conditions made a significant influence on the crystal structure of synthetic ZnS. In particular, a higher reaction temperature and longer reaction time helped to increasing the grain size of ZnS, improving its flotation performance. When

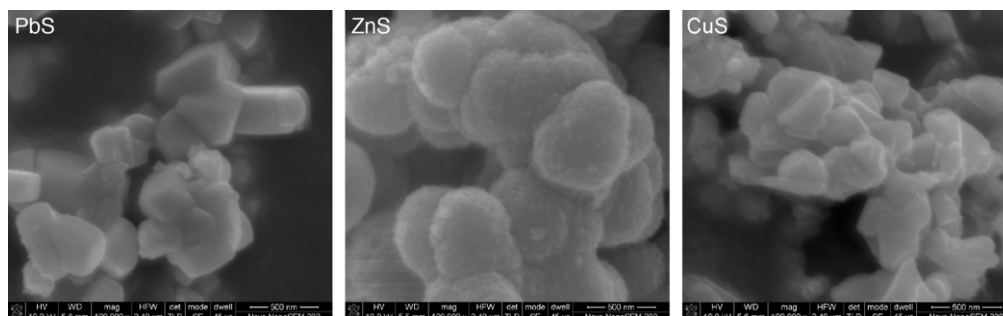


Fig. 3. The SEM of synthetic sulfides formed in hydrothermal sulfidation (2 h, 200 °C, pulp density 200 g L⁻¹).

Table 3
Flotation result of hydrothermal sulfidation treated sludge.

	Metal	Head grade (wt%)	Concentrate grade (wt%)	Recovery	Concentrating factor
Untreated sludge	Zn	19.90	20.30	17.3%	1.02
	Pb	0.95	1.00	20.5%	1.05
	Cu	0.10	0.11	22.3%	1.10
Treated sludge	Pb	0.90	2.20	58.9%	2.44
	Cu	0.11	0.28	68.8%	2.50
	Zn	23.23	31.80	33.3%	1.36
	Zn _(M)	21.47	33.67	72.8%	1.57
Treated simulated sludge	Pb	14.85	51.07	72.8%	3.44
	Cu	15.02	49.43	91.0%	3.29
	Zn	10.72	18.54	28.3%	1.73
	Zn _(M)	10.31	24.00	63.9%	2.33

Zn_(M): The Zn flotation result after crystal modification.

the reaction temperature increased from 200 °C to 280 °C with reaction time of 2 h, the mean grain size of ZnS increased from 24.86 nm to 102.33 nm based on the XRD patterns (figures were not shown). Moreover, when the reaction time increased from 2 h to 10 h under 260 °C, the mean grain size of ZnS increased from 72.68 nm to 96.16 nm. The optimal hydrothermal condition for the modification of ZnS crystal was determined to be a reaction time of 4 h and a temperature of 260 °C (Fig. 4).

Under the optimal modification condition, the ZnS crystal was improved as we expected. The average diameter of synthetic ZnS without modification approximates 20 nm (Fig. 5(a) and (b)). These crystals were rounded, with irregular modular appearance (Fig. 5(a)). The surface of these crystals was rough, showing little or no defined structural arrangement according to HR-TEM images (Fig. 5(b)). These apparent properties will result in a terrible inclusion by gangue. However, well-defined crystals of ZnS after the crystal modification were found (Fig. 5(c)).

These crystals size of zinc sulfide increased to 100–300 nm, and the regular arrangement in electron diffraction patterns demonstrated its crystalline structure (inset in Fig. 5(c)). The surface of these crystals was smooth (Fig. 5(d)) which decreased the gangue inclusion.

The flotation treatment of the ZnS after crystal modification was carried out in stimulated and raw sludge. The results showed that, in the stimulated sludge, the recovery of Zn increased from 28.3% to 63.9% with the increasing of the concentrating factor of Zn from 1.73 to 2.33, respectively. In terms of raw sludge, the recovery of Zn increased from 33.3% to 72.8% with an increase of concentrating factor of Zn from 1.36 to 1.57, respectively. Therefore, the modification of ZnS crystal effectively improved the selective recovery rate of Zn. The obtained results are encouraging for further research in this field. Up to 70% of Zn could be recovered from the neutralization sludge after flotation.

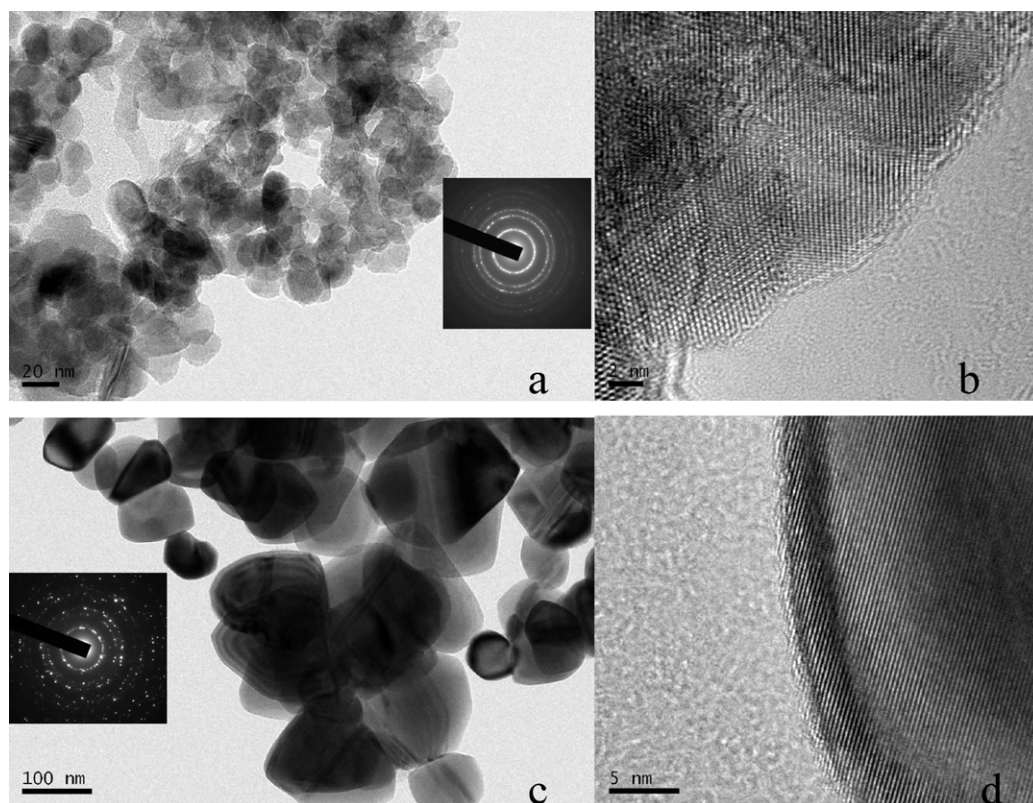


Fig. 5. TEM and HR-TEM images of ZnS crystal. (a) TEM and (b) HR-TEM images of ZnS before crystal modification. (c) TEM and (d) HR-TEM images of ZnS after crystal modification. Inset in (a) and (c) is the selected area electron diffraction pattern.

Table 4
Heavy metal leaching concentration of tailings after sulfidation-flotation.

Elements	Threshold	Heavy metal leaching concentration	
		Raw sludge (mg L ⁻¹)	Tailings (mg L ⁻¹)
Zn	^a	1.996	0.138
Pb	≤5	0.487	0.420
Cd	≤1	0.370	0.031
Be	^a	–	–
Cu	^a	0.166	0.002
Ag	≤5	–	–
Hg	≤0.2	0.010	–
Cr	≤5	–	–
Se	≤1	–	–
As	≤5	0.031	0.006

(-) Not detected.

^a Not specified by the USEPA.

3.3. Stabilization test

Although most of the heavy metal could be separated from the sludge after hydrothermal sulfidation and floatation treatment, a certain amount of heavy metal might remain in the tailings. Therefore, a series of stabilization tests should be performed to evaluate the stabilization of the remained heavy metals in tailings.

3.3.1. TCLP test

As seen in Table 4, the heavy metal concentration in leachate for the treated sludge was under the allowable limit of set by USEPA [32]. And it should be pointed out that, more stabilized effect for some toxic metals will be achieved during hydrothermal sulfidation. For example, the concentrations of Cd and As in leachate of the untreated sludge were 0.370 mg L⁻¹ and 0.031 mg L⁻¹, respectively. However, after the sulfidation treatment, the concentrations of Cd and As declined to 0.031 mg L⁻¹ and 0.006 mg L⁻¹, respectively. The result reveals that stabilization of heavy metals occurred during the

sulfidation process, so it will benefit the disposal of the tailing after floatation.

3.3.2. Continuous leaching test of the floatation tailings

The formed metal sulfide might be remobilized after exposure to the air. Tony et al. [33] suggested that oxidation and dissolution were the principle release mechanisms affecting the long-term stability of metals immobilized by sulfidation. Thus, a continuous leaching process (over a period of approximately 24 days) was conducted to simulate the in situ leaching of acid-rain (pH 3.2) through the floatation tailings with virtually no physical disturbance in a subsurface environment.

The results show a rapidly decrease in Zn, Cd and Pb concentrations in the leachate within 96 h (Table 5). The higher concentrations in the initial leaching stage (0–48 h) may be attributed to the release of the metals that were not fully sulfidized and incorporated into solid-phase sulfide phases. However, at 96 h, the heavy metals leaching process reached the steady point. It should be pointed out that the Pb concentration in leachate is higher than Zn and Cd. For example, after 576 h leaching, the Pb concentration in leachate was 0.27 mg L⁻¹, while the concentrations of Zn and Cd were 0.03 mg L⁻¹ and 0.05 mg L⁻¹ respectively. It might be due to the formation of PbSO₄ in hydrothermal sulfidation, whose solubility is higher than that of PbS. Thus the Pb concentration is a little higher than that of other metals. However, no obvious increase of heavy metal concentration was observed during the continuous leaching procedure. Possible explanations might be that the continuous leaching procedure was conducted to simulate the in situ leaching of acid-rain through the floatation tailings with no physical disturbance in a subsurface environment. So the oxidation of MeS only takes place in the surface of the tailings. Moreover, the presence of alkaline compounds such as CaCO₃, Ca(OH)₂ and CaSO₄ in the residue will act as mineralogical scavengers of dissolved heavy metal released by sulfide oxidation to avoid the heavy metal pollution [34]. The results revealed that, after

Table 5
Time course of leached concentration and amount of heavy metals from tailings in continuous leaching process.

Heavy metal content in tailing (w%)							
Zn	Cd	Pb					
8.30	0.27	0.39					
Heavy metal concentration (C _{Me} , mg L ⁻¹) and amount (A _{Me} , wt%) in leachate							
No.	Time (h)	C _{Zn}	A _{Zn}	C _{Cd}	A _{Cd}	C _{Pb}	A _{Pb}
1	24	0.92	0.001	0.28	0.009	0.21	0.004
2	48	1.33	0.002	0.29	0.018	0.22	0.009
3	72	0.58	0.003	0.13	0.022	0.18	0.013
4	96	0.06	0.003	0.08	0.024	0.12	0.016
5	120	0.16	0.003	0.11	0.028	0.25	0.021
6	144	0.13	0.003	0.11	0.031	0.32	0.028
7	168	0.14	0.003	0.07	0.033	0.35	0.035
8	192	0.07	0.003	0.06	0.035	0.48	0.046
9	216	0.19	0.004	0.06	0.037	0.39	0.054
10	240	0.01	0.004	0.05	0.039	0.53	0.065
11	264	0.04	0.004	0.05	0.040	0.45	0.075
12	288	0.02	0.004	0.04	0.041	0.54	0.086
13	312	0.06	0.004	0.04	0.043	0.37	0.094
14	336	0.01	0.004	0.04	0.044	0.52	0.105
15	360	0.01	0.004	0.04	0.045	0.45	0.115
16	384	0.02	0.004	0.05	0.047	0.56	0.127
17	432	0.01	0.004	0.06	0.049	0.49	0.137
18	456	0.05	0.004	0.06	0.050	0.44	0.147
19	480	0.02	0.004	0.06	0.052	0.43	0.156
20	504	–	0.004	0.06	0.054	0.34	0.163
21	528	–	0.004	0.06	0.056	0.27	0.169
22	552	0.02	0.004	0.06	0.058	0.26	0.175
23	576	0.03	0.004	0.05	0.059	0.27	0.180

(-) Not detected.

hydrothermal sulfidation and floatation treatment, the heavy metal remaining in the tailings was in a stable state.

4. Conclusions

The heavy metals in heavy-metal-containing sludge can be easily converted to metal sulfides through hydrothermal sulfidation reaction. Under the optimum experimental conditions, the sulfidation percentage of zinc and lead is 85% and 75.4% respectively. Floatation test indicates that 33.3% of Zn, 58.9% of Pb and 68.8% of Cu can be recovered from the sludge. The lower recovery of ZnS might attribute to its crystal grains which are finely dispersed, and round shape with rough surface. Hydrothermal sulfidation offers a possible way to modify the surface and structural characteristics of metal sulfide to improve their floatability. With increasing the reaction temperature and extending the reaction time, the ZnS grain size increased from 7.95 nm to 44.28 nm with angular shape and smooth surface, and the recovery of Zn can increase from 33.3% to 72.8%. Stabilization test results revealed that, after sulfidation and floatation treatment, the heavy metal remaining in the tailings was in a stable state. The application of the hydrothermal sulfidation has a wide prospect on the management of heavy-metal-containing waste.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.03.025.

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