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Metal recovery from sludge through the combination of hydrothermal sulfidation and flotation

Xiaobo Min[a,b,*], Cuiyu Yuan[a], Yanjie Liang[a], Liyuan Chai[a,b], Yong Ke[a]

[a] *School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China*
[b] Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, Changsha, Hunan 410083, China

Abstract

The heavy metal in the waste can react with sulfur and be converted to metal sulfide through the hydrothermal sulfidation. For metal recovery, the synthetic metal sulfide can be enriched through subsequent flotation process. It is a novel way for the recovery of heavy metal from the sludge. In this study, the effects of liquid/solid ratio, mineralizer concentration, precursor concentration and dosage of sulfur on the sulfidation extent and floatation index were investigated. Result shows that with a precursor concentration of 15%, a Zn/S molar ratio of 1:1.2, a liquid/solid ratio of 3:1, the sulfidation extent of zinc in the sludge was greater than 92%, while the flotation recovery of zinc reached up to 45.34%. The toxicity characteristic leaching procedure (TCLP) revealed that stabilization and detoxification of heavy metals occurred during sulfidation.

Keywords: heavy metal containing sludge; hydrothermal sulfidation; flotation recovery; enrichment ratio;

1. Introduction

With the increasingly exhausted natural resource, it is urgent and essential to recover heavy metals from industrial waste.

In China, the nonferrous metal smelting industry produces more than 1.3 billion tons of heavy-metal-containing solid waste every year, most of which are high moisture contained sludge. The increasing sludge not only occupies plenty of land, but also potentially imposes a negative impact to the environment due to the possibility of releasing toxic elements, such as lead (Pb), arsenic (As), cadmium (Cd), etc [1].

* Corresponding author: Tel: +86 731 88830577; Fax: +86 731 88710171
E-mail address: mxb@csu.edu.cn

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However, it is very difficult to realize both the stabilization and recycle of metals involved in the sludge by traditional technology. For instance, roasting consumes large amounts of energy and also brings numerous metal-contained slags which are more difficult to deal with [2]; while leaching generates a great amount of metal-contained wastewater and hazardous residue [3]. Comparing with conventional methods, sulfidation-flotation technology has distinguished advantages. It is well known that the heavy metals in the nature are commonly present as sulfide ores such as galena (PbS), sphalerite (ZnS) or covellite (CuS). They can easily be concentrated by conventional flotation technique. Sulfidation-flotation technology could convert heavy metals to metal sulfides with stable characteristics and good flotability [4]. Therefore, sulfidation treatment has received much attention as a possible way for heavy metal recovery and stabilization [5-7].

The conventional sulfidation with Na_2S has been widely employed to improve the floatabilities of various oxidized minerals [8-9]. In addition, the sulfidation method has been employed for the recovery of heavy metals such as Cu, Pb and Zn from plating sludge and fly ashes [10-11]. Besides that this sulfidation process combined with flotation has been also studied for remediation of soil and sediments polluted with heavy metals such as Cd, Cu and Zn [12]. However, it is difficult to avoid the emission of wastes water and toxic gases when the sulfides are used as sulfidizers [13].

In this research, hydrothermal sulfidation was employed to sulfidize the heavy metals in heavy-metal-containing sludge which is produced in the process of wastewater treatment. Sulfur was used as sulfidizer. In the present work, the effects of hydrothermal sulfidation parameters including liquid/solid ratio, mineralizer concentration, precursor concentration and the reagent dosage of sulfur on the sulfidation extent and floatation recovery of the heavy metal were investigated. The goal of this study was to examine the optimal condition of the hydrothermal sulfidation of heavy-metal-containing sludge with the ultimate objective being to improve the floatation recovery of zinc from sludge.

2. Materials and Methods

2.1. Materials

The sludge samples generated in the disposal process of metallurgical wastewater were air dried ground and sieved with 100-200 mesh (75-150 μm) before they were digested in a mixture of HCl and HNO_3 (v/v 3:1). Then, the solutions were filtrated with 1μm pore sized filter paper and element concentrations in filtrate were analyzed using inductively coupled plasma (ICP-OES, IRIS Intrepid II XSP). The elemental composition of the sludge is obtained and given in Table 1. The phase ratio of each primary element distribution is listed in Table 2.

Table 1 The composition of raw sludge (wt%)

Elements composition									
Zn	Pb	Fe	Ca	S	Cd	Cu	As	Mn	Al
13.80	0.95	4.0	17.4	10.5	0.73	0.10	0.06	1.70	0.52

Table 2 Phase composition of zinc in neutralization sludge (wt%)

Constituent	sulfite	oxide	sulfide	silicate	others
Zn	0.20	84.42	8.89	3.72	2.26

The chemicals used in the experiment, sulfur powder, sodium hexametaphosphate and copper sulfate, were analytical grade reagents supplied by Sinopharm Chemical Reagent Co., Ltd. (China). Butyl xanthate and pine camphor oil were obtained from Zhuzhou Mineral Processing Reagent Plant.

2.2. Experimental Procedure

Hydrothermal sulfidation was carried out in a GCF-1L stainless steel autoclave. Heavy metal containing 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 260 °C furnace for 4 hours, and then water-cooled to room temperature. 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. The flotation tests were conducted in a 0.5 L XFD flotation cell. The flotation flow sheet is shown in Fig. 1. The floatation efficiency was evaluated on the basis of the following parameters:

$$\text{Floatation recovery}(\%) = \frac{\text{Mass forth} \times [\text{Me}]\text{forth}}{\text{Mass total} \times [\text{Me}]\text{total}} \times 100\% \quad [1]$$

$$\text{Enrichment ratio} = \frac{[\text{Me}]\text{forth}}{[\text{Me}]\text{total}} \quad [2]$$

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.

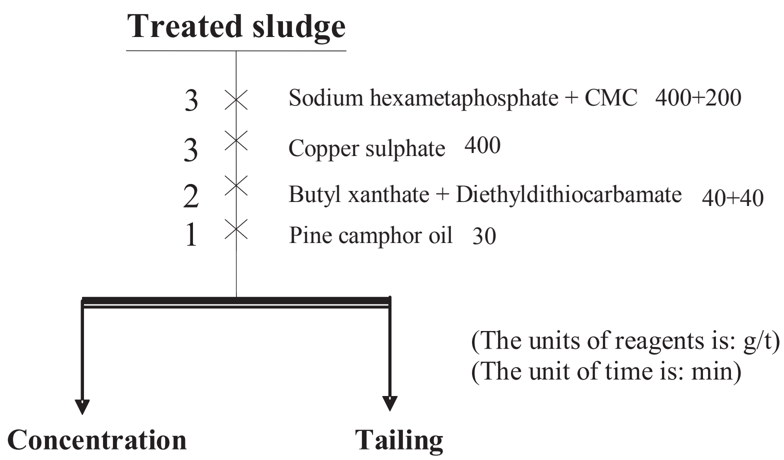

Fig.1. The process flow sheet of flotation

3. Results and discussion

3.1. Effect of liquid/solid ratio

Liquid/solid ratio plays a very important role in the hydrothermal reaction. To investigate the effect of liquid/solid ratio, the sulfidation treatment of sludge was carried out with the liquid/solid ratio range from 2:1 to 6:1 under 260°C for 4h. The results are shown in Fig.2. It can be seen that the sulfidation extent of zinc increased from 91.43% to 94.18% when the liquid/solid ratio increased from 2:1 to 3:1, but there was a slight decrease with the increase of the liquid/solid ratio further. The possible reason may be that too small liquid/solid ratio make the slurry become thicker while too high liquid/solid ratio lead to the fall of effective concentration thus result in the decrease of sulfidation efficiency. Fig.2(b) shows that as the liquid/solid ratio increased, the floatation recovery gradually increased while the enrichment ratio decreased. Therefore the optimum liquid/solid ratio appears to be 3:1 and all further experiments were carried out at this the liquid/solid ratio.

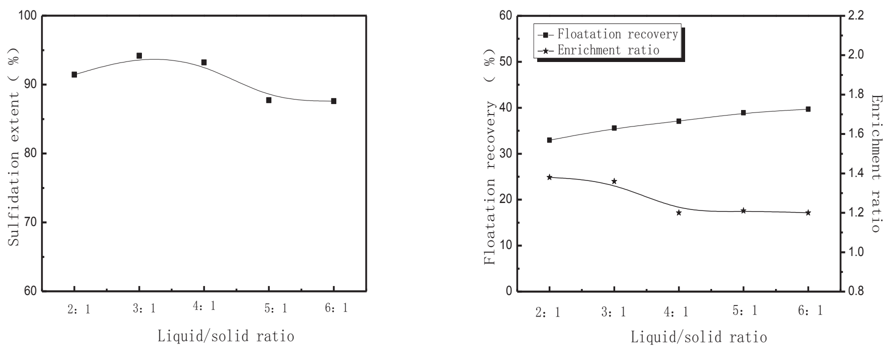

Fig. 2. (a) Effect of liquid/solid ratio on sulfidation extent; (b) Effect of liquid/solid ratio on the floatation recovery and enrichment ratio

3.2. Effect of mineralizer concentration

Mineralizer can provide the OH^- which can promote the hydrothermal reaction. In this study, KOH was used as the mineralizer. To investigate the influence of mineralizer concentration, the hydrothermal treatment of sludge were carried out under 260 °C for 4h with a liquid/solid ratio of 1.2, while keeping the KOH concentration ranging from 0.05 to 0.8 mol/L. From the Fig. 3, we can find that there was a significant decrease in the sulfidation extent of zinc with increase in KOH concentration. The sulfidation extent of zinc decreased from 78.21% to 46.85% when KOH increased from 0.05 mol/L to 0.8 mol/L, while the floatation recovery of zinc maintained low level which is around 35%. Also, the enrichment ratio is decreasing as the KOH increased. The results demonstrated that increasing KOH concentration was harmful to the flotation behavior of sulfidized sludge. It was due to that the increase of OH^- made the slurry thick thus leading to the decrease of sulfidation extent. Worse still, the excessive OH^- made the surface of the products more hydrophilic which had a negative effect on its floatability. So, it is better not to add KOH during the hydrothermal treatment.

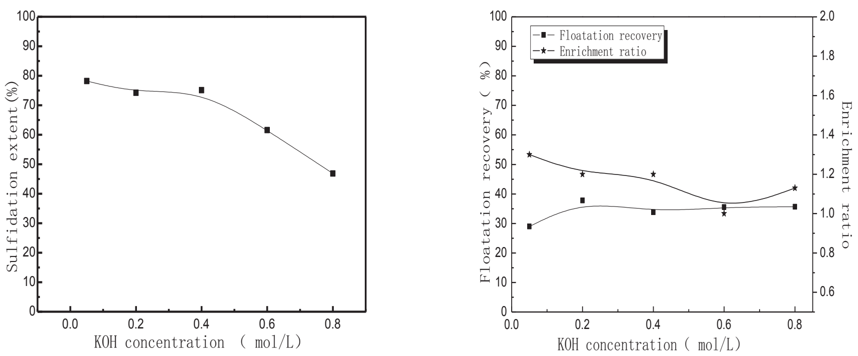

Fig. 3. (a) Effect of KOH concentration on the sulfidation extent; (b) Effect of KOH concentration on the floatation recovery and enrichment ratio

3.3. Effect of precursor concentration

Precursor concentration plays a very important role in hydrothermal reaction. So the effects of the zinc concentration from 13.8% to 30% on the sulfidation extent, flotation recovery and enrichment ratio were studied with the liquid/solid ratio of 2:1 at 260 °C for 4 h. Fig.4(a) revealed that the sulfidation extent of zinc increased from 75.55% to 90.63% as the Zn concentration increased from 13.8% to 30%. Similarly, Fig.4(b) shows that the enrichment ratio rose from 1.31 to 1.55. However, as the precursor above 20%, the flotation recovery decreased gradually. The result indicated that increasing of precursor concentration was helpful to the hydrothermal sulfidation process but had a negative effect on the flotation recovery. Therefore the optimum precursor concentration was chosen as 15% due to it has a highest flotation recovery and a relatively higher enrichment ratio.

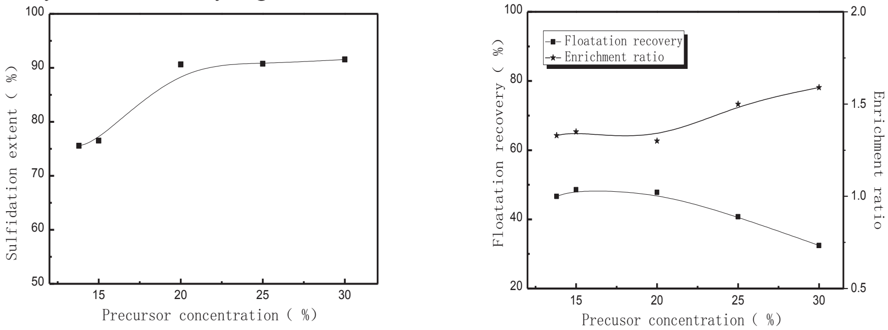

Fig. 4. (a) Effect of precursor concentration on the sulfidation extent; (b) Effect of precursor concentration on the floatation recovery and enrichment ratio

3.4. Effect of reagent dosage of sulfur

The sulfidation treatment of sludge was affected by the dosage of vulcanizing agent. In our present work, a molar ratio of S/Zn from 1:1 to 2:1 was selected and its effects on sulfidation extent, floatation recovery and enrichment ratio were studied. The results are shown in Fig. 5. Fig. 5(a) shows that the sulfidation extent of zinc increased from 63.52% to 99.66% when the molar ratio of Zn/S increased from 1:1 to 2:1. However, from the Fig.5(b), we can find that the flotation behavior of sulfidized sludge is becoming worse as the dosage of sulfur increased. Possible reason may be that with the increase of the content of the sulfur, reactant effective concentration increases, thus leading to enhance of the sulfidation extent; however, it also led to a lower recovery because other impurities element can enter the concentrate since they may be sulfidized as well. Therefore the optimum molar ratio of Zn/S is 1:1.2 and all further experiments were carried out with this dosage.

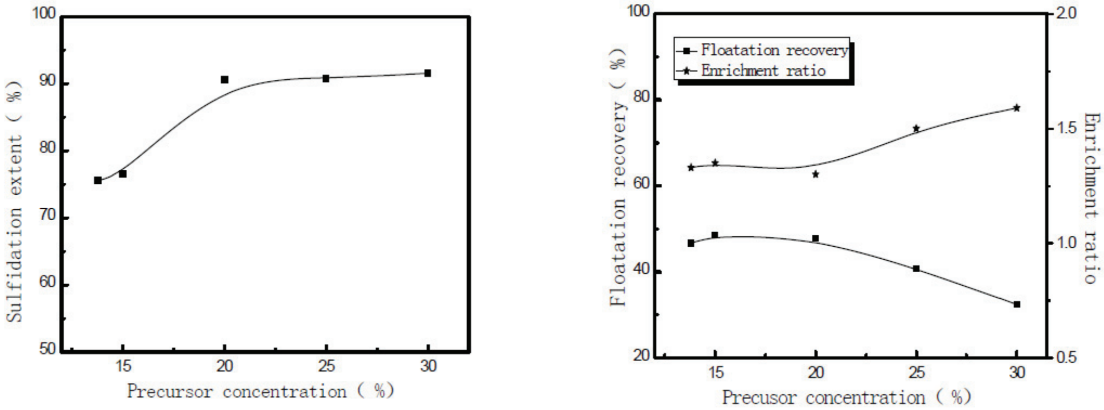

Fig. 5. (a) Effect of reagent dosage of sulfur on sulfidation extent; (b) Effect of reagent dosage of sulfur on the floatation recovery and enrichment ratio

3.5. TCLP test

To evaluate the stability of the floatation tailings, toxicity characteristic leaching procedure (TCLP) was performed according to USEPAMethod1311[14].

The TCLP results shows that the concentrations of Cd and As in leachate of the untreated sludge were 0.370 mg L−1and 0.031mg L−1, respectively. However, after the sulfidation treatment, the concentrations of Cd and As declined to 0.031mg L−1 and 0.006mg L−1, respectively. It revealed that the toxic metal (Cd and As) concentrations in the leachate of the treated sludge were much lower than those of the raw sludge. It was deduced that the stabilization and detoxification of heavy metals occurred during sulfidation process, so it can avoid heavy metal pollution and benefit the disposal of the tailing after flotation.

4. Conclusions

(1) There is a significant effect to the sulfidation extent and floatation index of sludge by liquid/solid ratio, mineralizer concentration, precursor concentration and reagent dosage of sulfur.

(2) The optimum operating process parameters were established as follows: liquid/solid ratio (3/1), precursor concentration (15%) and the molar ratio of Zn/S (1:1.2). Under these experimental conditions, the sulfidation extent of zinc was greater than 92%.

(3) The recovery of Zn from the materials which was treated by sulfidation is 45.34% and the enrichment ratio is 1.6.

(4) The stabilization and detoxification of heavy metals occurred during sulfidation process, so it can avoid heavy metal pollution and benefit the disposal of the tailing after flotation.

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