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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.

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 ($Me(OH)_2$) to metal sulfide (MeS) in hydrothermal condition are presented in Eqs. (2) and (3).

$$4S + 6OH^- = 2S^{2-} + S_2O_3{}^{2-} + 3H_2O \quad (1)$$

$$Me(OH)_2 = Me^{2+} + 2OH^- \quad (2)$$

$$Me^{2+} + S^{2-} = MeS \quad (3)$$

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 Cu(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 Charachteristic 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 stablization 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 $CaSO_4 \cdot 2H_2O$, $CaCO_3 \cdot H_2O$, etc. To determined 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, $Zn(OH)_2$, 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.

$$X = \frac{C'_{Me} - C'_{Me_0}}{C_{Me} + C'_{Me} + C''_{Me}} \times 100\% \quad (4)$$

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