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# Hydrothermal sulfidation of zinc-containing neutralization sludge for zinc recovery and stabilization

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ABSTRACT

The conventional lime-neutralization process generates a huge volume of neutralization sludge (NS). The disposal of NS is difficult because it contains large amounts of heavy metals, moisture and complex components. The present study describes the application of hydrothermal sulfidation (HS) toward the conversion of certain heavy metals (mainly zinc) in NS to metal sulfide (MeS) for subsequent metal recovery through flotation. The effects of temperature, time, sulfur concentration and liquid-to-solid ratios were investigated under laboratory conditions. The extent of zinc sulfidation was up to 85% under optimal conditions. Flotation tests indicated that the ZnS produced could be separated from the NS, increasing the recovered Zn concentration from 19.9% to 38.8%. The toxicity characteristic leaching procedure (TCLP) revealed that stabilization and detoxification of heavy metals occurred during sulfidation. The formation of metal sulfide by HS enhanced the stabilization effect. Moreover, flotation technology provided a means to enhance metal recovery from the NS.



## 1. Introduction

Tons of wastewater containing heavy metals are generated every year by industries such as electroplating, mining and nonferrous smelting (Weber, 1999). Lime milk neutralization is a widely practiced technique to remove heavy metals from such waters. The advantages of this technique include a high removal rate, low cost, a well-developed technique and a simple and convenient operation (John et al., 1972; Muga and Mihelcic, 2008). However, neutralization sludge (NS) is produced in excessively large quantities. NS is characterized by high moisture content and complex components, and landfilling is considered to be the most appropriate choice for its disposal. Heavy metals can easily be trapped in the water cycle due to the increasing chances of acid rain (Liu et al., 2005), which is a potential threat to the environment. On the other hand, NS is actually a secondary metal resource because it usually contains reasonable amounts of valuable metals that could be recycled to augment the global metal supply.

Recently, sulfidation has received attention as a possible means of heavy metal recovery. For recovery, the heavy metals contained in the NS are initially converted into metal sulfides with good floatability and stable chemical properties. Therefore, sulfidation is an ideal option for the management of NS and can not only recover metals but also protect the environment.

Conventional sulfidation with $Na_2S$ has been widely employed to improve the floatability of some mineral oxide ores (Rashchi et al., 2005; Newell and Bradshaw, 2007). In addition, this method was applied toward heavy metal pollution control. Kuchar et al. (2006, 2007) used $Na_2S$ to recover Zn, Pb and Cu from fly ash and plating sludge. Vanthuyne and Maes (2002) also reported that heavy metals could effectively be removed from contaminated soils by a combination of $Na_2S$ addition and flotation.

Nevertheless, the use of sulfide as a sulfidizing agent is accompanied by the emission of secondary wastes and the release of toxic gases. Hence, sulfur has been suggested as a substitute for sulfide. Wang et al. (2003) reported that nonferrous metal oxides can be converted into sulfides through mechanical ball milling. The sulfidation of CuO, ZnO and PbO was realized in a mechanical–chemical process by grinding with sulfur and iron powders at room temperature, giving iron oxide as the only byproduct. Roasting with sulfur is another method for heavy metal sulfidation (Li et al., 2010). It was found that the extent of sulfidation of Pb and Zn oxides reached 98% and 95%, respectively, under optimal conditions.

This study examines the use of hydrothermal sulfidation (HS) to synthesize ZnS using NS and sulfur as raw materials. During HS, the sulfidation reaction is accomplished by $S^{2-}$ generated by the disproportionation reaction of sulfur as shown in Eq. (1). The HS reactions of zinc are presented in Eqs. (2) and (3).

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

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

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$$Zn^{2+} + S^{2-} = ZnS \quad (3)$$

Generally, HS can achieve much higher conversion rates because the metals are transformed into metal ions and are easily dissolved in solution under hydrothermal conditions. In addition, metal sulfide precipitation does not occur until the temperature decreases, making the reaction of the metal ion with the sulfide ion possible to form hydrosulfide/sulfide complexes, as expressed by the following equation (Tagirov et al., 2007):

$$Zn^{2+} + 2HS^{-} = ZnS(HS)^{-} + H^{+} \quad (4)$$

HS offers distinct advantages over other methods for the sulfidation of NS with very high moisture content. The reaction occurs efficiently without any pretreatment such as baking or grinding. In addition, sulfur is a low-cost material and causes only slight secondary pollution compared with other sulfidizers such as $Na_2S$. The hot water remaining from HS may also favor flotation. Despite the above-mentioned advantages, the HS approach is mainly employed for the synthesis of specific sulfide materials (Chen et al., 1996; Zhang et al., 2003) and as a pretreatment for oxide ore (Li et al., 2008); however, little work has been reported on the management of heavy-metal-containing sludge by recycling via hydrothermal sulfidation. In this study, the extent of zinc sulfidation was used as an indicator of the conversion ratio of heavy metal in NS to discover the optimal reaction conditions for HS. The goal of the HS treatment was to transfer the potentially available heavy metals into a unique metal sulfide chemical phase that could not only enhance metal recovery from NS through flotation technology but also achieve a perfect stabilization effect.

## 2. Experimental

### 2.1. Materials

NS samples were generated during the disposal of metallurgical waste water. The samples were air dried, ground and sieved with 100–200 mesh (75–150 μm) before digestion in a mixture of HCl and $HNO_3$ (v/v 3:1). Later, the solutions were filtered through 1-μm filter paper, and elemental concentrations in the filtrate were analyzed with inductively coupled plasma (ICP, IRIS Intrepid II XSP). The elemental composition of the sludge is given in Table 1. The phase ratio distribution of the primary elements is listed in Table 2; the XRD pattern of the sludge is presented in Fig. 1 and indicates that the sludge mainly contained $CaSO_4{\cdot}2H_2O$ and $CaCO_3{\cdot}H_2O$.

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 setup

A schematic diagram of the experimental set up is shown in Fig. 2. The HS reaction was carried out in a high-pressure reactor, in which NS and sulfur were mixed in an appropriate mass ratio. The mixture was then 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 in a furnace at 150–250 °C for 30 min–8 h. The contents were cooled to room temperature after the reaction. The resulting products were filtered using 1 μm pore sized filter paper. The precipitate was collected and washed with deionized water to remove possible left-over ions from the final product and then dried at 80 °C overnight in a vacuum oven. To evaluate the stability of the product, a toxicity characteristic leaching procedure (TCLP) was performed according to United States Environmental Protection Agency (USEPA) Method 1311 (USEPA, 1992). A flotation test was performed using a conventional rougher flotation process to investigate the floatability of the treated sludge (Fig. 2).

**Table 1**
The composition of raw sludge (wt.%).

| Elements composition | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 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 |

**Table 2**
Phase composition of zinc in NS.

| Constituent | Sulfite | Oxide | Sulfide | Silicate | Others |
|---|---|---|---|---|---|
| Zn | 0.20% | 84.42% | 8.89% | 3.72% | 2.26% |

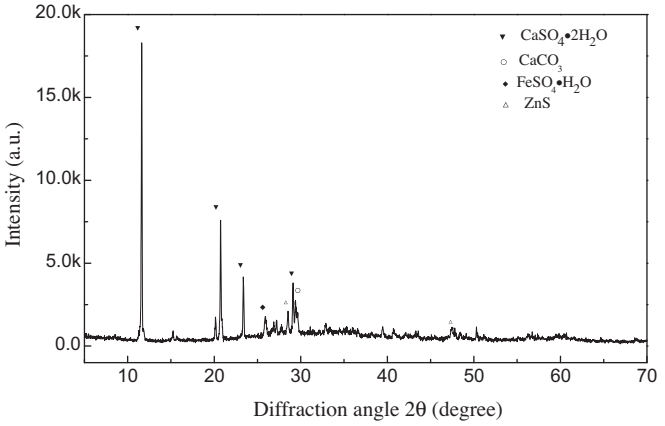


**Fig. 1.** The XRD pattern of NS.

### 2.3. Analytical procedures

The crystallographic composition of the sulfidation products was characterized by X-ray diffraction (XRD, D/max2550 VB + 18 KW). TCLP leachate was analyzed by ICP.

The ZnS conversion was judged according to subsequent flows (Fig. 3), based on the chemical phase analysis of the sulfide ore (Zhang, 1992). Initially, 0.500 ± 0.0005 g of screened sample was placed in a conical flask with 100 ml of a solution of 100 g/L of $CH_3COOH$ and 5 g/L of ascorbic acid that was employed to extract the un-reacted Zn compounds, 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, the filter papers were charged into the same conical flask and 100 ml of 3% $Br_2$ solution was added as an extracting solution for ZnS. After stirring for 45 min, the mixture was filtered, and the filtrate (2) and residue (2) were obtained. After rinsing and drying, the residue (2) was digested by a mixture of concentrated hydrofluoric acid, perchloric acid and nitric acid at 200 °C; the digested solution was collected to determine the Zn content in other phases.

The extent of sulfidation was determined from Eq. (5), where X is the extent of sulfidation (%), $C'_{Zn_0}$ is the initial ZnS amount in original compounds or sludge, and $C_{Zn}$, $C'_{Zn}$, and $C''_{Zn}$ denote the Zn concentrations of the filtrate (1), the filtrate (2) and the digestion solution, respectively.