Effects of sodium salts on the sulfidation of lead smelting slag

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ABSTRACT

The effects of sodium salts on the sulfidation behavior, phase transformation, ZnS particle growth, and zinc floatability of lead smelting slag (LSS) were investigated by roasting experiments and flotation tests. The roasting results indicated that sodium salt additives could enhance the reactivity of zinc sulfidation and the percentage of liquid phase and thus promoted the sulfidation of LSS and the growth of ZnS particles. However, with the increase in temperature, the positive effects were reduced because the reactivity of the sulfidation and the percentage of liquid phase were not the determining factors at high temperatures. The effect of Na_2CO_3 was stronger than Na_2SO_4, while Na_2SO_4 was stronger than NaCl on the sulfidation of zinc and the growth of ZnS particles. The addition of Na_2CO_3 or Na_2SO_4 favored the conversion of marmatite to wurtzite, which could be evaporated at temperatures above 1000 °C. Flotation test results revealed that sodium salt additives had different influences on the zinc grade and recovery at different temperatures. Na_2CO_3 was the best additive in roasting for increase in zinc grade, due to the formation of metallic iron rather than iron sulfides.

1. Introduction

Lead has been widely applied in many fields, such as lead-acid batteries, protection from X-ray and radioactive radiation. It is primarily produced from sulfide ores through beneficiation and pyrometallurgical processes, in which millions tons of lead smelting slag (LSS) are generated annually in the world (Lima and Bernardez, 2011). The slag contains various heavy metals, such as Zn, Pb, Cd, As, and Cr, which are rarely in sulfides but occur as in oxides and oxidized compounds that are generally more soluble in the environment than their sulfide counterparts, and is thus considered as a kind of hazardous wastes (Shen and Forssberg, 2003; Yin et al., 2016). The stockpiling of LSS not only wastes a considerable amount of secondary resources containing valuable metals but also causes a potential environmental threat. Hence, it is imperative to develop an economical and eco-friendly approach to recycling the valuable metals from LSS for meeting the sustainable development requirement of nonferrous industry (Han et al., 2015a). For the past decades, various pyrometallurgical, hydrometallurgical and combined routes have been developed to recover valuable metals from LSS, but the fuming process is still the most common current method commercially (Buse et al., 2014; Kurama and Goktepe, 2003; Li et al., 2015; Shirinbayan et al.,

2014; Yin et al., 2014). It is well known that the high-temperature process requires a complicated dust collection system and is relatively energy intensive and high risk to workers' health due to the volatilization of heavy metals, such as As, Cd, and Pb (Han et al., 2015b). Therefore, this technology is being gradually eliminated with the development of society.

Sulfidation has recently received much attention as a possible generic technology for the recovery of valuable metals from wastes or low-grade oxide ores (Ke et al., 2014; Kobayashi et al., 2000, 2002). In this process, metal oxides and/or oxidized compounds are converted into sulfides, which have a good floatability and are relatively insoluble in aqueous solutions. As a result, metals can be recovered by flotation and the pollution of heavy metals can be reduced. At present, many sulfidation methods have been proposed to convert various oxidized materials, mainly including conventional sulfidation with Na_2S (Kuchar et al., 2006, 2007; Walcarius et al., 2006; Wu et al., 2015), mechanochemical sulfidation (Wang et al., 2003; Yuan et al., 2012), hydrothermal sulfidation (Chai et al., 2015; Li et al., 2013a; Liang et al., 2012; Peng et al., 2016), and sulfidation roasting (Li et al., 2014; Zheng et al., 2015, 2014a), among which sulfidation roasting is more conducive to the formation and growth of sulfide crystals and thus shows better results for the recovery of nonferrous metals by flotation. Li et al. (2010) investigated the recovery of lead and zinc from low-grade Pb-Zn oxide ore by sulfidation roasting and flotation process. The results indicated that the sulfidation degree of lead and zinc

reached 98% and 95%, respectively, and 79.5% Pb and 88.2% Zn were recovered while the flotation concentrate contained 10.2% Pb and 38.9% Zn. Wang et al. (2014) studied the sulfidation roasting and flotation of cervantite (Sb_2O_4). A flotation concentrate grading 21.04% Sb with a recovery of 77.15% was achieved. Zheng et al. (2014b, 2016) employed sulfidation roasting and flotation process to recycle valuable metals from lead smelter slag and zinc leaching residue. The experimental results of zinc leaching residue showed that a flotation concentrate with 39.13% Zn, 6.93% Pb and 973.54 g/t Ag was obtained, and the recovery rates of Zn, Pb and Ag were 48.38%, 68.23% and 77.41%, respectively. For lead smelter slag, it was found that Na_2CO_3 additive could promote the sulfidation and recovery of zinc, but a satisfactory flotation result was always not achieved. This is attributed to the fact that the zinc contained in the slag are mainly in the form of amorphous silicates and ferrites, resulting in the generated ZnS crystals with low crystallinity and fine grains (Min et al., 2016). Hence, it is more difficult to recover valuable metals from the slag than from low-grade oxide ores or leaching residues using sulfidation roasting followed by flotation, because crystallization and particle growth processes are necessary to produce metal sulfides with good floatability.

Based on previous studies, Han et al. (2016d, 2016e) proposed a high-temperature selective sulfidation process to initially convert the zinc and iron in LSS to sulfides with good floatability and non-sulfides, respectively. The results demonstrated that the selective transformation of LSS could be achieved and zinc sulfides with coarse grains and good crystallinity were obtained after the sulfidation roasting with sulfur or pyrite in the presence of sodium salts above 1000 °C. It was found that the formation of a liquid phase during the roasting was the key to the growth of ZnS particles, because of liquid bridge connections accelerated the aggregation of fine grains. Sulfurizing agent dosage and carbon dosage are significant factors on the sulfidation of LSS. If the carbon is added too much, the residual carbon will absorb reagents in subsequent flotation process, which is bad for the recovery of valuable metals. If the sulfurizing agent dosage is beyond its optimum value, some iron sulfides will remain in the roasted LSS, causing the difficulty in the separation of zinc and iron by flotation. Both Zheng and Han's studies revealed that sodium salt additives could enhance the sulfidation of zinc in LSS and the floatability of synthetic ZnS. They considered that sodium salt additives could increase the activity of sulfidation reactions and thus decrease the melting point of the reaction mixture. However, a systematic study on the effects of sodium salts was never reported. An opportunity exists to clarify the mechanism of sodium salts in promoting the sulfidation of LSS and the growth of ZnS particles for a better understanding of this technology.

In the present study, the effects of Na_2CO_3, Na_2SO_4 and NaCl additives on the sulfidation behavior of zinc, phase transformation of LSS, particle growth behavior and floatability of ZnS crystals were investigated by inductively coupled plasma (ICP), X-ray powder diffraction (XRD), optical microscope coupled with scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), and conventional flotation, respectively. Correspondingly, thermodynamic analysis was studied using thermogravimetry–differential scanning calorimeter (TG-DSC), HSC Chemistry 5.0, and FactSage 7.0 to interpret some phenomenon observed in the experiments.

2. Experimental

2.1. Materials and analysis

The LSS used in this study was a water-quenched slag supplied by a lead smelter in Henan province, China. The chemical composition and zinc phase composition of the LSS are given in Tables 1 and 2, respectively. It is seen from Table 1 that the LSS contains high Zn, Fe, Si, and Ca, minor Pb, Na, Mg, Al, and Mn, and other trace elements. As presented in Table 2, the zinc is mainly in the form of silicate and ferrite. The XRD pattern, SEM image and corresponding EDS spectra of LSS sample are shown in Fig. 1. The results indicate that the slag mainly exists as amorphous glass structures, in which some wustite (FeO), hardystonite ($Ca_2ZnSi_2O_7$) and zinc ferrite ($ZnFe_2O_4$) phases with a certain degree of crystallinity are detected. It was found that the zinc is dispersed into all phases in the slag, which requires an aggregation process of ZnS grains during the sulfidation to form coarse particles with good floatability.

A pyrite with 47% Fe and 47.9% S and a carbon powder containing 53% C were used as the sulfidizing agent and reductant, respectively. Sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4) and sodium chloride (NaCl) of analytical grade were used as the additives of sulfidation roasting. Sodium hydroxide (NaOH) as a pH regulator, copper sulfate ($CuSO_4$) as an activator, sodium isobutyl xanthate (SIBX) as a collector, sodium hexametaphosphate (SH) as a dispersant, sodium silicate (SS) as a depressor and pine oil as a frother were used in the flotation process. All of these agents for flotation were analytical grade except butyl xanthate which was industrial grade.

2.2. Experimental setup and procedure

A schematic diagram of the roasting furnace used is shown in Fig. 2. Before the experiments, the samples including LSS, pyrite, and carbon powder were ground and sieved to −74 μm and were air dried and stored for sulfidation roasting tests. Typically, 120 g LSS was thoroughly mixed with scheduled amount of pyrite and carbon powders and different sodium salt additives (12 g Na_2CO_3,

Table 1
Chemical composition of the lead smelting slag (wt.%).

Zn	Fe	Pb	Cu	Mn	Ti	Sn	Co	Si	Ca
18.79	23.48	1.00	0.084	0.863	0.150	0.118	0.016	9.20	7.20
Na	Mg	Al	K	Cr	Rb	As	S	P	Cl
3.47	1.01	2.11	0.714	0.086	0.003	0.027	0.531	0.126	0.035

Table 2
Zinc phase composition of the lead smelting slag.

Phases	Metal	Oxide	Sulfide	Silicate	Ferrite	Total
Zn content (wt.%)	0.03	0.13	0.24	12.68	6.05	19.13
Proportion (%)	0.16	0.68	1.25	66.28	31.63	100.00