Reductive clean leaching process of cadmium from hydrometallurgical zinc neutral leaching residue using sulfur dioxide

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A B S T R A C T

Large quantities of cadmium-containing zinc neutral leaching residues (ZNLR) are produced constantly in the electrolytic production of zinc, creating serious cadmium pollution. In order to solve the problem and realize a clean zinc production process, a new reductive cleaning leaching process using sulfur dioxide as reducing agent has been developed, in which the beneficiation of cadmium pollution factor is solved. The cadmium leaching mechanisms were briefly analyzed and the effects of temperature, initial sulfuric acid and partial pressure of sulfur dioxide on the kinetics of cadmium dissolution in the mixed $SO_2+H_2SO_4$ system was investigated. The order of reaction with respect to particle size, initial sulfuric acid concentration and partial pressure of sulfur dioxide at the fixed liquid/solid ratio and stirring speed were determined as -0.98, 1.49 and 0.51, respectively. Diffraction peak of zinc ferrite or cadmium-bearing zinc ferrite disappeared and the main compositions of the reductive leaching residue were lead sulfate ($PbSO_4$), zinc sulfide (ZnS) according to the XRD analysis.

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1. Introduction

Metal smelting activities have been identified as a significant source of toxic metal pollution to atmosphere, water bodies, soils, and crops. Cadmium from zinc smelting industry also has brought great threat to ecosystem and public health. Furthermore, it has a tendency to accumulate in the food chain (Trzcinka-Ochocka et al., 2004; Wu et al., 2008). Generally, cadmium has no independent mineral deposit and often accompanies other nonferrous metal such as zinc and lead. Resultingly, the large tonnages of zinc and lead production represent a significant source of cadmium entering the environment (Safarzadeh et al., 2008, 2009; Turan et al., 2004). Up to now, several serious cadmium pollution events have happened among Xiang river valley in Hunan Province in China; in addition, "Cadmium rice" event also occurred in recent years, which was ascribed to the development of non-ferrous metal metallurgy in Hunan province. Considering the difficult

beneficiation of cadmium in the environmental medium, source control of cadmium release can be a more suitable choice of cadmium pollution prevention (Safarzadeh et al., 2007).

Traditional zinc hydrometallurgical technique includes roasting, leaching and electrowinning procedure. During the roasting procedure, zinc and associated cadmium in zinc concentrate mostly converted into zinc and cadmium oxides. Meanwhile, zinc ferrite ($ZnFe_2O_4$) and cadmium-bearing zinc ferrite ($Cd_xZn_{(1-x)}Fe_2O_4$, $x = 0 - 1$) form inevitably due to general more than 10% iron content in zinc concentrate(Zhang et al., 2010). Zinc and cadmium oxides can be easily dissolved during the neutral leaching stage; zinc and cadmium ferrites remain in the neutral leaching residue for its spinel-type structure (Langová et al., 2009; Zhang et al., 2010). To recover zinc and cadmium absolutely, the structure of the ferrite must be destroyed. However, the present hot sulfuric acid leaching method for treating such spinel-type minerals involves high energy and material consumption (Gharabaghi et al., 2012).

Now, enhancement of reductive leaching of insoluble minerals has attracted some researchers' attention. Leaching of various iron oxide minerals such as magnetite (Fe_3O_4), goethite (a-FeOOH) and hematite (Fe_2O_3) has also been reported in several studies using

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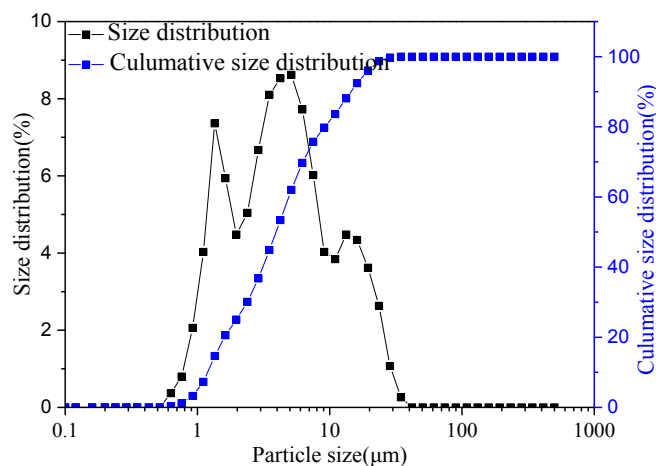 *E-mail address:* mxbcsu@163.com (X. Min).

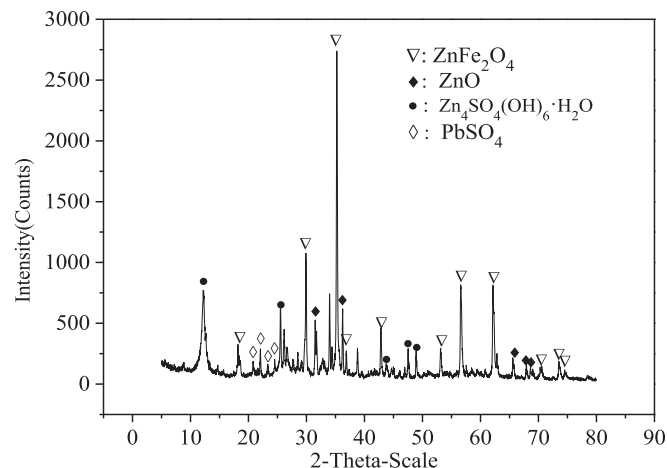Fig. 1. Particle size distribution of zinc neutral leaching residue.

Fig. 2. XRD analysis of the zinc neutral leaching residue.

different mineral acids in the presence and absence of sulfur dioxide (Das and de Lange, 2011; Senanayake, 2003; Senanayake and Das, 2004). Introduction of SO₂ into the leaching system of ZNLR can not only realize its recycling, but also decrease material and energy consumption (Mwema et al., 2002; Senanayake, 2004). Currently, no paper has been published on the recovery of cadmium existing as cadmium-bearing zinc ferrite from zinc smelting slag to the authors' knowledge. Therefore, understanding the reaction mechanisms and kinetics is useful for the optimization of reductive leaching of cadmium from these materials.

The purpose of this work was to evaluate the reductive leaching process of the ZNLR with sulfur dioxide as reducing agent in the sulfuric acid system. The reaction mechanisms were briefly analyzed. The effects of temperature, initial sulfuric acid concentration and partial pressure of sulfur dioxide on cadmium leaching kinetics were investigated and the reductive leaching residue was characterized.

2. Materials and method

2.1. Sample preparation and characterization

ZNLR used in this study was provided by a zinc hydrometallurgical plant in Hunan province, China. The raw residue was crushed, ground and screened to provide materials with particle size of below 100 μm and was characterized by the mineralogical analysis. The particle size distribution analysis with laser scattering particle analyzer (LS-POP(6)) shown in Fig. 1 shows that most of particles are smaller than 30 μm. The chemical composition of the ZNLR shown in Table 1 was carried out using ICP-MS method. The main phases in the raw residue are presented in Fig. 2. The phase analyses of cadmium were completed according to chemical methods suggested by Zhang (1992). The results presented in Tables 1 and 2 show that cadmium content in the raw neutral leaching residue was found to be 0.261%; cadmium ferrite and cadmium-bearing zinc ferrite phase occupied 66.67% of total cadmium.

The X-ray diffraction pattern was recorded using X-ray diffractometer (Bruker D8 Discover) with CuKa radiation (40 kv, 40 mA).

Table 2
Phase composition of cadmium in zinc neutral leaching residue.

Composition	Sulfate	Oxide	Sulfide	Ferrite	Total
Cd content (wt. %)	0.035	0.040	0.012	0.174	0.261
Phase occupation (%)	13.41	15.33	4.60	66.67	100

SEM−EDS analysis was completed using scanning electron microscope (FEI Quanta-200). The X-ray photoelectron spectroscopy (XPS) spectra were obtained with an analyzer (ESCALab250Xi) with an Al KR X-ray source (power: 200 W). The spectra were collected at a fixed retarding ratio mode with band-pass energy of about 20 eV.

2.2. Experimental procedure

30 g ZNLR was added for one time into a 1 L, acid corrosion resistant titanium autoclave equipped with a control device. A plastic bucket, a PID temperature controller, a variable speed stirrer, an internally mounted cooling coil and an electrode cooling tube are equipped inside of the autoclave. The weighted ZNLR and the prepared dilute sulfuric acid with a certain concentration were poured into the plastic bucket in the autoclave; then the autoclave was sealed. When the mixed solution was heated to the given temperature, the sulfur dioxide was injected and the partial pressure of sulfur dioxide was adjusted to the desired value and it was maintained constant during the experiment. When the experiment was finished, the autoclave was water-cooled. The mixed solution was siphoned and then filtered for collecting the filtrate and the remaining residue.

The solution was chemically analyzed to calculate the cadmium leaching rate. The computational formula of leaching efficiency is as follows:

$$\eta = \frac{V_L \times C_L}{G_S \times W_S} \tag{1}$$

where G_S is the mass of the residue used in the experiment, g; W_S is the content of heavy metals, %; V_L is the calibrated volume of

Table 1
Chemical composition of zinc neutral leaching residue.

Components	Zn	Fe	Cd	S	As	Pb	Si	Mn	Ca	Mg
Sample, wt%	36.00	15.60	0.261	10.05	0.383	1.652	1.30	0.739	1.55	0.80