Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 27(2017) 1180−1187
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Recovery of valuable metals from zinc leaching residue by sulfate roasting and water leaching

Guo-min JIANG[1,3], Bing PENG[1,2], Yan-jie LIANG[1,2], Li-yuan CHAI[1,2], Qing-wei WANG[1,2], Qing-zhu LI[1,2], Ming HU[3]

1. School of Metallurgy and Environment, Central South University, Changsha 410083, China;
2. Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, Changsha 410083, China;
3. Changsha Science Environmental Technology Co., Ltd., Changsha 410000, China

Received 30 June 2016; accepted 11 January 2017

Abstract: Zinc leaching residue (ZLR), produced from traditional zinc hydrometallurgy process, is not only a hazardous waste but also a potential valuable solid. The combination of sulfate roasting and water leaching was employed to recover the valuable metals from ZLR. The ZLR was initially roasted with ferric sulfate at 640 °C for 1 h with ferric sulfate/zinc ferrite mole ratio of 1.2. In this process, the valuable metals were efficiently transformed into water soluble sulfate, while iron remains as ferric oxide. Thereafter, water leaching was conducted to extract the valuable metals sulfate for recovery. The recovery rates of zinc, manganese, copper, cadmium and iron were 92.4%, 93.3%, 99.3%, 91.4% and 1.1%, respectively. A leaching toxicity test for ZLR was performed after water leaching. The results indicated that the final residue was effectively detoxified and all of the heavy metal leaching concentrations were under the allowable limit.

Key words: zinc leaching residue; sulfate roasting; water leaching; valuable metals recovery

---

1 Introduction

In China, a large amount of zinc leaching residue (ZLR) is produced from the traditional zinc hydrometallurgy process. The huge stockpiles of ZLR not only pose an environmental problem, but also result in a great loss of valuable metals, since ZRL contains a high content of heavy metal elements, such as zinc, lead, manganese, cadmium and arsenic [1]. It has been demonstrated that such toxic elements have the potential to be dissolved in rain water, resulting in a negative impact on the environment [2−7]. Therefore, it is urgent to develop a method for ZLR disposal, including the recycling of valuable metals to relieve environmental pollution [8,9]. Zinc and iron, presenting in the form of zinc ferrite, are the major elements in ZLR. Moreover, the cadmium can replace zinc in the crystal lattice of zinc ferrite and form cadmium-bearing zinc ferrite [10]. These compounds are very stable and difficult to dissolve through conventional leaching process. Generally, pyrometallurgical and hydrometallurgical processes are employed to treat such residues. Onsan refinery of Korea Zinc uses top submerged lancing (TSL) technology to recover the valuable metals in such residues. Approximately 82% of Zn, 92% of Pb, 86% of Ag and 61% of Cu in the residue can be recovered in this process [11]. In China, Waelz kilns have been adopted in some factories to fume metal elements by using coal as heat source. Approximately 75% of Zn, 68% of Pb and 80% of Ge in the residue can be recovered [12,13]. However, these processes have some shortcomings due to a high fixed investment and operating costs, as well as a serious air pollution during fuming.

Recently, a series of cleaner recovery technologies have been developed for ZRL recovery. It has been proved that high metal recovery rate can be achieved in these processes, such as high pressure acid leaching, two-staged acid leaching, microwave caustic leaching and highly concentrated alkaline leaching [8,14−22]. However, during these leaching processes, the iron component is easy to be extracted, and it requires a

---

Foundation item: Project (2014FJ1011) supported by Key Project of Science and Technology of Hunan Province, China; Project (201509050) supported by Program for Special Scientific Research Projects of National Public Welfare Industry

Corresponding author: Yan-jie LIANG; Tel: +86-731-88830511; Fax: +86-731-88710171; E-mail: liangyanjie2015@csu.edu.cn

DOI: 10.1016/S1003-6326(17)60138-9

sophisticated process to remove the iron impurities. The traditional purification technologies, such as roasting with Na_2CO_3, reduction roasting magnetization technologies and sulfate roasting have been studied [23−27]. These pyrometallurgy methods can avoid highly sophisticated multi-stepped hydrometallurgical procedures, but these studies have not shown how to recover the cadmium, copper and manganese present in the waste.

This work aims to present a clean and effective approach to recover valuable metal components from ZLR, and avoid the potential risk in environmental pollution. The presented procedure comprises ferric sulfate roasting and water leaching. In the first stage, the valuable heavy metals can be efficiently converted into metal sulfates. Then the metal sulfates can be easily separated from the sludge with water leaching, leaving a detoxified residue. And the sulfate roasting and water leaching processes were optimized.

2 Experimental

2.1 Materials and analysis

Zinc leaching residue used in this work was provided by a zinc hydrometallurgical plant in Hunan Province, China. The samples were dry ground and sieved to yield a particle size below 74 μm before using in the experiment. The chemical composition obtained by X-ray fluorescence spectrometer (XRF) is listed in Table 1. It indicates that Zn and Fe are the major components in the residue. Additionally, the toxic heavy metals such as Pb, As, Cd are also observed in the residue. Based on the XRD analysis (Fig. 1), it is suggested that Zn and Fe mainly exist in the form of $ZnFe_2O_4$. The characteristic peak corresponding to $CaSO_4$ is also identified.

Table 1 Chemical composition of zinc leaching residue by XRF (mass fraction, %)

Fe	Zn	S	Si	Pb	Ca	Mn	Al
22.93	18.43	6.40	4.47	4.35	2.21	1.53	1.15
Cu	As	Cd	Mg	K	Ba	Sr	Sn
1.04	0.52	0.49	0.26	0.24	0.20	0.16	0.16
Cl	Ti	In	P	Ag	Cr	Ni	Mo
0.067	0.057	0.054	0.043	0.037	0.018	0.011	0.010

The chemical composition of the samples was characterized by XRF (Rigaku, ZSX-Ⅱ). The phases of initial and roasted zinc leaching residue were detected by XRD (Rigaku, TTR-Ⅲ). A TG differential scanning calorimetry investigation was carried out using a thermal analyzer (STA449F3A−0488M). The morphological changes during the roasting process were detected by SEM (JEOL Ltd., JSM−6360V). The heavy metal concentrations in the leachate were analyzed with inductively coupled plasma (ICP-OES (Opima 5300DV type).

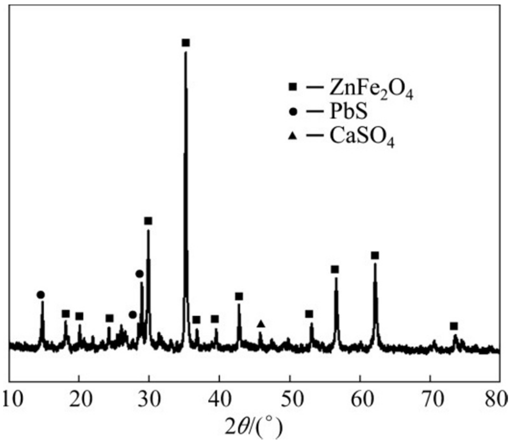

Fig. 1 XRD pattern of zinc leaching residue

2.2 Sulfate roasting

An appropriate amount of ferric sulfate was mixed with 10 g of ZLR ground by mortar and pestle. Then, the mixture was put into a corundum crucible with a cover and roasted in a muffle furnace at a setting temperature. The roasted products were subsequently weighed, ground and analyzed. Zinc ferrite is the major component in the residue, and it is hard to decompose sulfate. Therefore, two parameters, including decomposition rate of zinc ferrite and the proportion of zinc sulfate ($ZnSO_4/Zn_T$), were employed to evaluate the sulfate roasting effects. These parameters were calculated through the following equations:

$$\alpha=\frac{C_0-C_r}{C_0}\times 100\% \tag{1}$$

$$\beta=\frac{C_s}{C_t}\times 100\% \tag{2}$$

where α is the decomposition rate of zinc ferrite, and C_0 and C_r represent the zinc ferrite contents in the initial and roasted residues, respectively. β is the proportion of zinc sulfate, C_s represents the zinc sulfate content in the roasted residue, and C_t is the total zinc content in the roasted residue.

2.3 Water leaching

Water leaching was conducted after sulfate roasting in order to dissolve the formed metals sulfate and detoxify the residue. After water leaching at a controlled temperature, the residue was separated from the liquid phase by filtration and the leachate was analyzed by ICP. The leaching rate of metals was used to evaluate the water leaching effects, determined as follows: