



A cleaner process for valuable metals recovery from hydrometallurgical zinc residue

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ABSTRACT

Most of hydrometallurgical zinc residues were stored in slag dump and unprocessed worldwide. Heavy metal and acid contained in these residues can be dissolved in rain water and then transfer to soil and groundwater system whereas threatening the health of aquatic systems and ecosystem. In this work, an innovative slag cleaning technique (reducing-matting smelting-thermal decomposition reduction) was proposed to harmlessly co-treat jarosite residue and lead silver residue, which can avoid environmental pollution and at the same time, effectively recover the valuable metal. Thermodynamic analysis and experimental results indicated that reducing atmosphere was a significant smelting parameter for recovery of valuable metal. Sulfur contained in various residues can be fixed in the form of solid sulfide (ferrous matte) without generation and emission of $\text{SO}_2(\text{g})$. Moreover, the matte product is a good collector for silver collection. In addition, various smelting parameters were investigated in detail to detect and obtain the smelting optimum condition: 12% coke addition, $\text{FeO}/\text{SiO}_2 = 1.6$, $\text{CaO}/\text{SiO}_2 = 0.4$, smelting temperature 1300°C and smelting time 2.5 h. Under these smelting condition, the recovery of Cu, Zn, Pb and Ag can reach 98.82%, 98.84%, 90.35% and 97.17%. The feasibility and reliability of this innovative process were confirmed. The main phases in the slag are $\text{CaFe}\cdot 2\text{SiO}_2$, $\text{NaCaAlSi}_2\text{O}_7$ and silicate. It can be used in cement production so that the secondary pollution of slag can be avoided. Copper matte is comprised of FeS , $\text{Cu}_{10}(\text{Pb}, \text{Fe})\text{S}_6$, Cu_5FeS_6 and Fe_9S_{11} . Ag is inlaid in copper mattes in the form of silver particles.

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1. Introduction

At present, 80%–85% of worldwide annual zinc was produced from traditional zinc hydrometallurgical process. However, this process produces a lot of leaching residues (Chen et al., 2009), especially, Jarosite residue which is huge quantity, lower stability and poor storage (Swarnkar et al., 1996). Typically, these kind of residues always contain various heavy metals, such as Zn, Cu, Pb, Ag and In as well as some undesirable toxic metals like As, Cd, Sb (Han et al., 2014). If these heavy metal were left untreated for a long time, it will be dissolved in rain water and then transfer to soil and groundwater system threatening the health of aquatic systems and ecosystem (Akasaka et al., 2011). As a result, this residue not only takes massive land, but also wastes valuable resource.

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Recently, more interest lies in non-hazardous fixed treatment and recovering valuable metals from jarosite residue (Li et al., 2016). High temperature sintering method was main technology of non-hazardous fixed treatment (Chen and Dutrizac, 2001). Pappu et al. (2006) mixed jarosite residue and clay with a ratio of 1:1 then mix with 15% pulverized coal and react 1.5 h at 960°C to sintering. Sintering block which had good mechanical properties can be used as the building material, but valuable metals were not effectively recycled and could lead to the risk of secondary environmental pollution. The representative of pyrogenic process is rotary kiln volatilization method (Barna et al., 2004). Jarosite residue and pulverized coal were mixed evenly in appropriate, and then put into the rotary kiln, heating at 1000°C – 1200°C . Under this condition, more than 90% zinc could be volatilized into the flue gas and recovered, but other difficulty volatile substances were not effectively recycled (Zou et al., 2016). Rus En et al. (2008) developed a process of acid leaching and brine leaching to reclaim Zn and Pb. This approach, 71.9% Zn and 98.9% Pb can be recovered. Ju et al. (2011) developed a process of roasting- NH_4Cl leaching-alkali

leaching-Zn cementation process to extract Pb, Ag, Cu and Cd. More than 93% Pb, Ag, Cu and Cd could be extracted from the residue.

Erdem and Özverdi (2011) presents a non-hazardous fixed treatment route, the main step of this process is that mix ordinary cement, fly ash, lime by a certain proportion. PbSO_4 contained in the residue was transferred into $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$ and PbCO_3 , which could stably exist in nature. Zhang et al. (2016) developed leaching-flotation process to recycle Pb, Ag and Zn from lead silver residue. However, it was difficult to control flotation parameters and remain the stabilization in this process, such as Zn^{2+} concentration of pulp and pH under different residues' property. Chen et al. (2018) present a process to recover valuable metals, in which lead silver residue was leached in sulfuric acid, then continually leached in sulfuric acid and sodium chloride mixture. The leaching rates of Zn, Pb and Ag were 92.15%, 94.88% and 93.24%.

Rotary kiln volatilization method was a typical pyrogenic process for the treatment of lead silver residue in China, in which dry lead silver residue and 40%–45% coke powder was mixed and roasted (Wei et al., 2014). Zinc would volatilize at a high temperature and finally, was recovered in the form of ZnO powder (Zou et al., 2016). Moreover, the combination of roasting and leaching process is also usually used to dispose lead silver residue, such as sulfation roasting-washing (Li-Ting, 2010), sulfation roasting-washing-chlorination leaching (Raghavan et al., 1998), washing dezincification-oxidation roasting-cyanidation immersion silver-chlorinated immersion lead (Turan et al., 2004). Zijin Mining Co., Ltd. use "washing dezincification-oxidation roasting-cyanidation immersion silver-chlorinated immersion lead" process to deal with lead silver residue, leaching rate of Ag and Pb can reach 95.28% and 90.49%.

In this work, reducing-matting smelting and thermal reduction-decomposition process were proposed to co-treat jarosite residue and lead silver residue. The recovery efficiency of Cu, Zn, Pb and Ag were investigated in detail from thermodynamic and experimental perspective. Optimum smelting conditions were achieved. Moreover, the phase composition of smelting products was characterized by XRD (XRD, Rigaku 3014, Cu-K α -radiation, $\lambda = 1.54 \text{ \AA}$) and SEM-EDS (SEM, LEO 1450, Germany. EDS, Oxford, INCA Wave 8570, UK) technology.

2. Materials and methods

2.1. Materials

Jarosite residue was taken from Baiyin Nonferrous Metals Group, one of the biggest smelters of copper, zinc, and lead in China. Lead silver residue was obtained from Yunnan Chihong Zn & Ge Co. After drying water at 80 °C for 48 h, the materials were ground to powder. Chemical compositions of residues were analyzed by ICP-AES (Perkin Elmer, Optima 3000 ICP-AES, Norwalk, USA). Coke was provided by Xiangtan Iron and Steel Co., LTD of Hunan province, China. The chemical compositions of materials were shown in Table 1.

To better enriching and recovering the valuable metals, a proper amount of CuO was added to produce more copper matte, which

Table 1
Chemical compositions of lead silver residue, jarosite residue and coke (wt%).

Materials	Pb	Zn	Cu	S	Fe	Ag	Ca	Si
Lead silver residue	1.97	7.04	0.28	12.2	20.7	0.015	1.71	3.94
Jarosite residue	3.24	7.19	0.24	10.9	19.8	0.0017	1.79	3.97
Reductant	Industrial analysis			Chemical composition of the ash				
	FC_d	V_d	A_d	Fe_{total}	MgO	SiO_2	CaO	Al_2O_3
	81.27	3.30	15.43	25.23	0.53	41.23	6.60	25.24

acts as valuable metal trapping agent. In actual production, it could be replaced by waste slag rich in Cu. Each experiment according to the quality of lead silver residue, jarosite residue and copper oxide were 100 g, 100 g and 12.6 g mixed ingredients, got mixed material evenly, its main components are shown in Table 2.

Fig. 1 illustrated XRD patterns of lead silver residue and jarosite residue. It was observed that lead silver residue mainly comprised Fe_2O_3 , (Fe,Zn)S, $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$, SiO_2 , ZnSO_4 and PbSO_4 . Zinc in lead silver residue mainly exists in the form of $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$, (Fe,Zn)S and ZnSO_4 . Lead in lead silver residue mainly exists in the form of PbSO_4 . Jarosite residue mainly contained Fe_2O_3 , $(\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6)$, $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$, ZnSO_4 , PbSO_4 , Cu_2S and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. Zinc in jarosite residue mainly exists in the form of zinc ferrite and zinc sulfate, main mineral phase of lead is lead sulfate.

Fig. 2 shown the SEM-EDS results of lead silver residue. Combining the phase results of XRD, the main composition of bright white mineral spot A is PbSO_4 and wrapped with a small amount of $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$, where a small amount of Cu was lost in the form of oxides. It could be seen from the figure that bright white minerals are less content in residue. The main components of the dark black mineral spot B was $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$, FeS, Fe_2O_3 complex.

SEM-EDS analysis results of jarosite is presented in Fig. 3. Dark gray mineral spot C represents $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, in which wrapped with a little amount of $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$, where a small amount of Cu was lost in the form of oxides. It contained 4.07% and 4.97% of Cu and Zn. Cu is mainly lost in the form of Cu_2S , Zn is mainly lost in the form of ZnO and ZnSO_4 in the jarosite residue. The main composition of bright white mineral spot D is PbSO_4 , which a little amount of Cu was lost in it. Bright white minerals are less content in residue.

2.2. Methods

Serial of experiments were conducted in high-temperature box resistance furnace (6 kW) which illustrated in Fig. 4. As an experimental procedure, 100 g dried lead silver residue and 100 g jarosite residue were mixed with the given amount of coke and additives, then put into a 400 ml corundum crucible (84 mm o. d., 77 mm i. d., 55 mm b.d and 105 mm high) and, loaded into the furnace. Smelting temperature of furnace was raised to the desired value and hold for preset time. The product was taken out and rapid cooling at room temperature after smelting. The recovery rate of valuable metals can be calculated according to formula (1) and (2)

$$R_{\text{Zn/Pb}} = \left(1 - \frac{m_{\text{slag}} + m_{\text{matte}}}{m_{\text{Total}}} \right) \times 100\% \quad (1)$$

$$R_{\text{Cu/Ag}} = \frac{m_{\text{matte}}}{m_{\text{total}}} \times 100\% \quad (2)$$

where $R_{\text{Zn/Pb}}$ (%) is the Zn/Pb recovery, m_{slag} (g) is the valuable metals content in cleaned slag, m_{matte} (g) is the valuable metals content in matte, m_{total} (g) is the valuable metals content in raw material, and $R_{\text{Cu/Ag}}$ (%) is the Cu/Ag recovery.

Table 2
Element contents of mixture.

Element	Cu	Pb	Zn	Ag	Fe	Si	Ca
Lead silver/g	0.28	1.97	7.04	0.015	20.7	3.94	1.71
Jarosite/g	0.24	3.24	7.19	0.0017	19.8	3.97	1.79
Copper oxide/g	10.08	–	–	–	–	–	–
Mixture/%	5	2.45	6.7	0.008	19.05	3.7	1.65

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