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Green and efficient utilization of waste ferric-oxide desulfurizer to clean waste copper slag by the smelting reduction-sulfurizing process

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ABSTRACT

This research proposed an efficient, innovative and environmentally friendly technology named smelting reduction-sulfurizing process, which uses one waste (waste ferric-oxide desulfurizer) to treat another (waste copper slag). In the new process, the waste ferric-oxide desulfurizer was employed not only as a sulfurizing agent to sulfurize and collect the copper lost in copper slag, but also as a reductant to reduce the magnetite to "FeO" and thus improve slag fluidity. It was revealed that 90.81% Cu was recovered and enriched in copper matte under the smelting conditions. The matte contained 15.87% copper, 20.25% S and 49.56% Fe, which can be returned to the copper smelting process as a feeding. Meanwhile, the removal rate of hazardous elements, such as Ni, Pb, Zn, As, Sb, Bi and Hg, from the initial copper slag by the new process was also determined, and the elimination rate of those elements was all over 90%.The leaching toxicity was used to further evaluate the environmental impact of the cleaned slag, indicating that the concentrations of toxic element ions in the leachate are all much lower than the thresholds, which confirmed that the cleaned slag with trace toxic elements is safe and harmless.

1. Introduction

Copper is one of important base metals required for various applications in modern industries, and nearly 80% of copper in the word is produced by pyro-metallurgical process (Potysz et al., 2015; Gbor et al., 2000). Approximately 30 million tons of smelting slag is estimated to be produced and dumped around the word annually (Shen and Forssberg,2003; Heo et al., 2013). Typically, the slag contains not only valuable metals such as Cu, Co, Ni, Pb, Zn, but also many undesirable hazardous metals like As, Sb, Bi, Hg (Shibayama et al., 2010). Unfortunately, of these, more than 80% is dumped directly in many countries without treatment, which not only wastes the limited resources extravagantly but also occupies precious land and even poses potentially damages to the ecological environment (Gorai et al., 2003; Chen et al., 2016).

In recent years, extensive researches have been carried out to clean the copper slag. Basically, they can be classified into two main categories, namely hydrometallurgical process and pyro-metallurgical process (Krishna et al., 2015; Al-Jabri et al., 2002). Hydrometallurgical processes are effective methods to extract metals from copper slags including flotation, leaching, roasting followed by leaching and bioleaching (Subrata et al., 2015; Li et al., 2008; Sandeep et al., 2015). But it is very difficult to treat the waste water generated from that, and its production efficiency is limited. However, pyro-metallurgy, as a widely used technology in today's production of base and precious metals, is mainly used for slag treatment (Huiting and Forssberg, 2003; Hughes, 2000; Jung et al., 2016; Tang et al., 2015; Zhou et al., 2015). Moreover, if the pyro-metallurgical process is employed to clean the slag, the slag may be treated at its molten stage once it is discarded from the furnace before it cools down (Dirk et al., 2008; Guo et al., 2016a, b; Guo et al., 2018). Thus, processing in the molten condition to recover the valuables is more energy efficient. Maweja et al. had attempt to clean the copper smelting slag from a water-jacket furnace by direct reduction (Maweja et al., 2009). But more coal were used to obtain the higher metals recovery, resulting in unacceptably high iron content in matte phase. Mikhail and Matusewicz reported that pyrite concentrate, as a collector phase, was employed to improve cleaning of copper slag (Mikhail and Webster, 1992; Matusewicz and Mounsey, 1998) in sulfurizing process. Indeed, it is an effective way to clean slag to produce low grade matte. However, the excessive addition of pyrite concentrate inevitably causes higher

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cost. Moreover, the iron content in the matte produced in this process is too high, leading to a difficulty in further converting process. Li et al. reported the gypsum was used as a sulfurizing agent to sulfurize and recover copper and cobalt from copper-cobalt smelting slag (Li et al., 2017; Jeong et al., 2016), however, the removal of toxic elements was neglected. Therefore, this investigation is set to develop an eco-friendly and cost-effective process for selective extraction of valuable metals from copper slag and maximized removal of toxic elements simultaneously.

Besides, we have noticed that waste ferric-oxide desulfurizer(WDS), as a kind of solid residue, is generated from coal-derived gas industry with high temperature H_2S removal process (Ren et al., 2010). With the rapid development of the coal-derived gas industry, iron oxides desulfurizer has been attracted more attention due to their low cost and high desulfurization performance (Liu et al., 2013). Concomitantly, the more and more waste ferric-oxide desulfurizer is produced, which is under considerable pressure of green treatment and effective utilization. Unfortunately, it has been rarely reported to process waste ferric-oxide desulfurizer with high efficiency and environment protection so far. Hao et al. reported that WDS can be applied in sulfuric acid production area due to its high sulfur content (Hao and Wang, 1992). Qian reported that WDS could be recycled and prepared to iron oxide red, which is an excellent pigment and has fine qualities such as covering power, coloring power, heat resistance, resistance to solvent, acid fastness, innocuity and anti-rust (Qian, 2010). The WDS Generally, it primarily contains iron sulfide (FeS, Fe_2S_3), sulfur (S_2), calcium carbonate($CaCO_3$), calcium sulfate($CaSO_4$), carbon (C) and etc (Hao and Wang, 1992). Thus, it bears the potential to be used as a sulfurizing agent, flux, or reductant that may play important roles in cleaning process of smelting slag replacing the traditional sulfurizing agent, such as pyrite and calcium flux.

In this study, a novel method named smelting reduction-sulfurizing process was proposed to recover copper and eliminate other hazardous metals simultaneously from copper slag. In this new slag cleaning process, the waste ferric-oxide desulfurizer was employed as a sulfurizing agent to sulfurize and capture the metals into matte phase from the slag at molten stage. Then the separation between matte and secondary slag took place in the crucible by density difference at high temperature, with the heavier matte dropping to the bottom of the crucible. The matte phase carrying valuable metals and hazardous elements would be further processed for refinement. And the cleaned slag containing less toxic elements has the potential to be utilized as an eco-friendly, clean functional material, which can avoid land occupancy and minimize environmental risks.

2. Experimental

2.1. Materials

2.1.1. Copper slag

Copper slag used in this study was collected from Tongling Nonferrous Metals Group Holding Co., Ltd, Anhui, China. Chemical compositions of copper slag are shown in Table 1. It can be seen from that the copper slag contains 2.71 wt.% Cu, 0.48 wt.% Ni, and some toxic elements, including Pb, Zn and As, are also observed in it. Phase compositions of the copper slag were determined by X-ray diffraction (XRD)analyses and the result are shown in Fig. 1. It indicates that the used slag is mainly composed of magnetite and fayalite. The distribution of copper in associated minerals in smelting slag were carried out based on solubility difference of various phases in solvent and results are shown in Table 2. As can be seen from that 50.55% of copper is present in the form of copper sulfide, 24.35% of copper exists in metallic copper and the proportion of copper in oxide form entrapped in slag is as high as 25.09%.

2.1.2. WDS

The chemical composition of the WDS from Baosteel Group Corporation is shown in Table 3. WDS mainly comprises 32.33 wt.% S, 17.91 wt.% CaO and 7.89 wt.% Fe, which was used in this work as a replacement of sulfurizing agent and flux. In addition, it also contains 5.82% C, which might be suitable to substitute some of the reductant.

The XRD patterns shown in Fig. 2 confirms that the WDS consists of crystalline gypsum, pyrite, sulfur with calcite and some unidentified minor phases. In smelting reduction-sulfurizing process, sulfur, existing in $CaSO_4$, FeS_2 and S_2, would transfer into and fix in the metal sulfides through contacting and reacting with metal oxides. Meanwhile, $CaCO_3$, as a kind of fluxes, can decrease the viscosity of the molten slag by breaking its silica bonds, which can accelerate the settling of matte particles and minimize the metal losses with mechanical entrapment of matte (Guo et al., 2016a, b).

2.1.3. Reductant

Blind coal, which was crushed and screened to a size of −1.0 mm, served as the reductant. Its ash chemical composition, proximate analysis and ash fusibility analysis were determined by GB/T212−2008 and GB/T219-2008, and results are shown in Tables 4 and 5, respectively.

2.2. Experimental methods

2.2.1. Smelting reduction-sulfurizing process

All samples were dried, ground and sieved to yield a particle size below 1.0 mm prior to the smelting process. In the smelting reduction-sulfuring step, for each test, 200 g ground slag and a

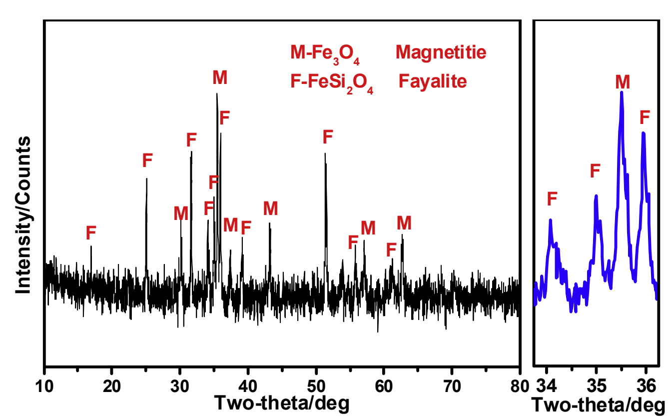

Fig. 1. XRD patterns of the copper slag.

Table 1
Chemical analysis of copper smelting slag (Wt.%).

Element	Fe_{total}	Ni	Cu	Pb	Zn	As	SiO_2	Al_2O_3	CaO	MgO	Cr	S	P	LOI
Copper slag	39.56	0.48	2.71	0.68	1.93	0.043	26.61	3.71	2.50	1.05	0.04	0.83	0.01	0.98