Hydrometallurgy 169 (2017) 219–228

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Selective leaching of zinc from blast furnace dust with mono-ligand and mixed-ligand complex leaching systems

Duchao Zhang, Xinwang Zhang, Tianzu Yang *, Shuai Rao, Wei Hu, Weifeng Liu, Lin Chen

School of Metallurgy and Environment, Central South University, Changsha 410083, China

ARTICLE INFO

Article history:
Received 30 August 2016
Received in revised form 23 December 2016
Accepted 1 February 2017
Available online 05 February 2017

Keywords:
Blast furnace dust
Iminodiacetic acid
Complex-leaching
Zinc
Iron

ABSTRACT

The nonferrous metals in blast furnace dust, especially zinc, which used to be categorized as hazardous components for blast furnace, are worthy of recovery in this economy. In this paper, a novel processing for extracting zinc from blast furnace dust by using a coordination reaction between the organic ligand and zinc ions was proposed. When blast furnace dust was leached in a 0.2 M iminodiacetic acid (Ida) solution at 20 °C for 2 h with a liquid-to-solid ratio of 10 mL/g, the leaching rates of zinc and iron were 62.78% and 6.07%, respectively. To accomplish the maximum separation of zinc from iron during the leaching process, a mixed-ligand complex leaching system consisting of Ida as the primary ligand and ammonium as the secondary ligand was developed. The optimal conditions for the leaching process with a mixed-ligand complex leaching system were investigated. We found that 65.58% of zinc was extracted by the solution with Ida:NH_4Cl:$NH_3 \cdot H_2O$ at 0.2:2:2 M and a 20:1 liquid-to-solid ratio at 40 °C for 2 h.

1. Introduction

Blast furnace dust is a byproduct of the ironmaking process and consists of Fe, C, Si, some valuable metals, and so on. To recycle large amounts of iron, blast furnace dust used to be sent directly back into the blast furnace system as sintering raw material. However, in the closed circulation process of recycling blast furnace dust, the gradual accumulation of volatile metals (Zn, Pb, etc.) will decrease the utilization coefficient of the blast furnace and reduce blast furnace service life (Mansfeldt and Dohrmann, 2004; Yang et al., 2009). Therefore, it is necessary and valuable to separate the volatile metals from blast furnace dust.

Blast furnace dust can be treated with pyrometallurgical and hydrometallurgical processes to recover metallic zinc. The Waelz process is viewed as the leading and most representative pyrometallurgical method (Busè et al., 2014; Schneeberger and Antrekowitsch, 2011). In the Waelz process, with coke as the reducing agent and fuel, ZnO and $ZnFe_2O_4$ are reduced to gaseous metallic zinc and the gaseous metallic zinc is then further oxidized and collected in the form of a zinc oxide phase. Although the pyrometallurgical process can yield a high zinc recovery, it still has various shortcomings, including high energy consumption, large capital investments and the production of harmful greenhouse gases.

Various leaching agents are used in the hydrometallurgical processes for zinc extraction from blast furnace dust (Das et al., 2007; Huang et al., 2007; Soria-Aguilar et al., 2008). Zeydabadi et al. (1997) examined blast furnace flue dust with H_2SO_4 as the leaching agent. The preliminary results of the investigation revealed that approximately 80% zinc was extracted by a 1 M solution of H_2SO_4 with a residence time of 10 min and a solid-to-liquid ratio of 1/10 at room temperature. Steer and Griffiths (2013) studied a leaching process for dust using organic carboxylic acids to determine whether they were capable of extracting high levels of zinc and low levels of iron. The results showed that high levels of zinc and low levels of iron were extracted by a solution of 1 M prop-2-enoic acid. Furthermore, the use of a non-aqueous solvent with prop-2-enoic acid was found to reduce the level of iron extraction from 8.5% to 0.1%, without a detrimental effect on zinc extraction. A hydrometallurgical process whereby the sludge was leached under both acid (HCl) and oxidizing conditions was investigated by Herck et al. (2000). More than 90% of zinc leaching efficiency and 40% of the iron leaching efficiency were obtained under the conditions of a pH below 1.5 and a redox potential above 650 mV. An acidic leaching process can obtain a high zinc leaching rate, but undesired metals (i.e., iron, copper, etc.) are also extracted into the waiting solution, and in addition, the acidic solution is corrosive to the metallurgical instruments, leading to a higher cost of recovery.

Ma Aiyuan et al. (2006) researched an ammonia leaching system (ammonia/ammonium) for zinc recovery from blast furnace dust, producing an extraction efficiency for zinc of up to 86.48% with a total ammonia concentration of 5.0 mol/L and an ammonia/ammonium ratio of 1:1. With alkaline leaching, sodium hydroxide was preferred as the leaching agent. The results showed that an alkaline solution could extract over 70% zinc from the dust and avoid iron and copper being

---

* Corresponding author.
E-mail address: tianzuyang@csu.edu.cn (T. Yang).

http://dx.doi.org/10.1016/j.hydromet.2017.02.003
0304-386X/

leached into the lixivium (Jha et al., 2001). Sodium hydroxide is selective for zinc dissolution but further development is required for metal recovery from the sodium zincate solution by electrolysis. In addition, the physical methods were applied for the direct removal of zinc or to assist chemical processing to extract zinc from blast furnace dust (Kiventerä et al., 2016; Ma, 2008; Vereš et al., 2011b; Vereš et al., 2011a). Vereš et al. (2011b) treated the blast furnace sludge with microwave-assisted leaching for the selective removal of zinc, and at microwave heating at a power level of 160 W, the zinc recoveries were 10–20% higher than the recoveries observed with conventional leaching.

For electric arc furnace dust (EAFD), which contains compounds similar to blast furnace dust, zinc is separated from iron in the form of gaseous chlorides by the method of chloridizing volatilization (Pickles, 2009). Aimed at solving the shortcomings of the pyrometallurgical and hydrometallurgical processes, a hybrid process using thermal reduction followed by leaching for EAFD was investigated (Chairaksa-Fujimoto et al., 2016). During this process, dust was roasted with calcium oxide to turn the insoluble and structurally stable zinc ferrite into calcium ferrite. Simultaneously, zinc was separated from zinc ferrite and oxidized to zinc oxide throughout the duration of the transition process. Then, dust treated by calcium oxide was leached by an acidic or alkaline solution to extract zinc into lixivium.

Recent reports have studied several organic ligands as leaching agents for extracting zinc from different zinc-bearing materials, for example, iminodiacetic acid for complex-leaching smithsonite (Yang et al., 2010) and nitrilotriacetic acid for complex-leaching low grade zinc oxide (Yang et al., 2016). Those studies indicated that the formation of stable zinc complexes can improve zinc extraction.

Based on the coordination ability of the ligands with zinc ions and iron ions, this paper selected iminodiacetic acid as the ligand to form chelate complexes ($[Zn(Ida)_i]^{2-2i}$). A novel moderate mono-ligand complex leaching system with an iminodiacetic solutions to leach the blast furnace dust was proposed. Furthermore, because the mixed-ligand complex has a greater stability constant than the mono-ligand complex (Rao et al., 2015), ammonium chloride and ammonia were added to the system to generate mixed-ligand complexes ($[Zn(Ida)(NH_3)_i]$) of zinc, with Ida as the primary ligand and ammonium as the secondary ligand, to explore the efficiency of complex-leaching for blast furnace dust. The factors influencing zinc extraction in two complex-leaching systems, including the ligand concentration, temperature, liquid-to-solid ratio, time, and pH were studied in detail.

2. Experimental

2.1. Samples characterization and assays

The blast furnace dust used in this paper was supplied by a steel plant in Yunnan, China. The following values of the chemical analysis for the main elements were obtained. As shown in Table 1, the main elements of the sample are Fe, O, C, Zn, Al, among others.

The mineralogical composition of the samples was determined by X-ray diffraction (XRD) using a Rigaku, SmartLab Automatic Powder Diffractometer with a graphite monochromator and Cu $K\alpha$ radiation. Powder samples were measured in the range of 10–90° 2θ at a scanning rate of 10°/min.

The XRD pattern is shown in Fig. 1, and the blast furnace dust sample consists of zincite (ZnO), franklinite ($ZnFe_2O_4$) or magnetite (Fe_3O_4), hematite (Fe_2O_3), wustite (FeO), zinc silicate (Zn_2SiO_4) and quartz (SiO_2). The presence of franklinite in the sample is difficult to prove by XRD because this material is isostructural with magnetite.

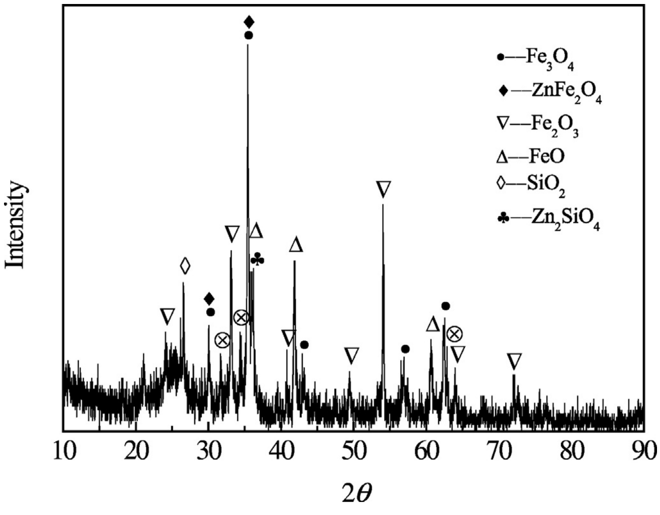

Fig. 1. XRD pattern of the blast furnace dust sample.

Using chemical analysis, the percentage of zinc present as different phases (i.e., zinc oxide, zinc silicate, zinc sulfide and zinc ferrite) was measured (Zhang, 1992). The results, consistent with the XRD pattern, are shown in Table 2. The zinc oxide is the major phase, with a percentage close to 50%, and zinc silicate makes up 15.38% of the zinc. The second-largest phase is zinc ferrite, which accounts for more than 28%. In addition, a small amount of zinc sulfide is found in blast furnace dust by chemical analysis.

The morphology, granularity and surface composition of the raw material were detected by Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM, JEOL, Ltd., JSM-6360LV). As shown in Fig. 2, the particles of the blast furnace dust have various shapes and sizes. The partial tiny bright particles visible with SEM, which are supposed to be mixtures of metal oxides, i.e., Fe_3O_4, ZnO, and so on, are attached to larger, dark particles, which are believed to be coke, according to the EDS analysis.

The acidity was measured using a pH meter (Mettler Toledo, FE20).

2.2. Experimental procedure

Leaching experiments were performed in a beaker immersed in a water bath with a thermostat that was equipped with a mechanical stirrer and a thermometer. After leaching, the waiting solution and residue were obtained by vacuum filtration. Then, the leaching residue was dried and weighted. The content of zinc and iron in the residue was determined using the methods of EDTA titration and dichromate titration respectively. The calculation of the formula for the zinc or iron extraction is given as follows:

$$\text{Extraction}(\%) = \left(1\text{-}\frac{w_r}{w_T}\right) \times 100\%$$

where w_r is the weight of zinc or iron in the leaching residue and w_T is the total weight of the zinc and iron in the material being tested.

The effects of the concentration of the leaching agent, temperature, leaching time, liquid-to-solid ratio, and pH value of the solution on the

Table 1
Composition of the blast furnace dust sample.

Component	Zn	Fe	O	Si	Al	Ca	Pb	C
Wt%	5.10	38.49	20.39	4.66	2.57	2.25	0.94	21.90

Table 2
Percentages of different phases containing zinc.

Phases	Zinc oxide	Zinc silicate	Zinc sulfide	Zinc ferrite
Percentage (%)	49.76	15.38	6.74	28.12