Minerals Engineering 127 (2018) 265–276

Contents lists available at ScienceDirect

Minerals Engineering

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

Improved removal of zinc from blast furnace sludge by particle size separation and microwave heating

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ARTICLE INFO

Keywords:
Blast furnace sludge
Dielectric properties
Zinc removal
Microwave heating

ABSTRACT

Several hydrometallurgical and pyrometallurgical processes, or a combination of both, have been developed for the removal of zinc from blast furnace sludge (BFS). In the present work, the properties of BFS were utilized to effectively remove zinc by microwave heating. A combined process entailing particle size separation followed by microwave processing was proposed.

The dielectric properties of BFS are exceptional owing to its high content of carbon and iron oxides, which are classified as excellent microwave absorbers. Analysis of the effects of temperature on the dielectric properties of BFS showed that its dielectric constant (ε') and loss factor (ε'') increased in the temperature range 400–800 °C due to carbon gasification (CO/CO_2 gas). This indicated that microwave heating of BFS was most effective in the temperature range 400–800 °C, beyond which heating decelerated due to the removal of carbon from the sample.

Based on elemental distribution, BFS can be divided into two parts: one with zinc content of about 0.108 wt.% (coarse fraction with particle size greater than 63 µm), and the other with higher zinc content, of about 1.02 wt.% (fine fraction with particle size less than 63 µm). The microwave tests indicated that zinc content in the fine fraction of the BFS decreased from 1.02 wt.% to < 0.13 wt.% (86.24% zinc removal rate) upon microwave processing for 10 min at 800 °C. This level of zinc content is acceptable for the material to be recycled i.e., reused in the blast furnace.

1. Introduction

Blast furnace sludge (BFS) is a byproduct of pig iron production and is generated during the purification of the flue gases emitted by the blast furnace (Machado et al., 2006; Mansfeldt and Dohrmann, 2004). It is a mixture of oxides comprising mainly iron oxides and coke fines alongside silicon, calcium, magnesium, and minor metals such as zinc and lead (Omran et al., 2017a; Trung et al., 2011). The factory SSAB Europe Oy at Raahe, Finland, produces liquid steel through the blast furnace-basic oxygen furnace (BOF) production route. The amount of BFS and BOF sludge generated at the site are approximately 35000 t a^{-1} and 40000 t a^{-1}, respectively (Wang et al., 2015). The direct reuse of BFS in the blast furnace is hindered by the presence of zinc, which evaporates and condenses on the furnace walls, causing operational difficulties (Kretzschmar et al., 2012; Van Herck et al., 2000).

Hydrometallurgical leaching of zinc from BFS has been carried out using both acidic and alkaline solutions such as sulfuric acid (Vereš et al., 2012), hydrochloric acid (Van Herck et al., 2000), and a mixture of prop-2-enoic acid and methylbenzene (Steer and Griffiths, 2013). The main challenge in hydrometallurgical leaching is that zinc exists in BFS mainly as zinc ferrite, which is quite stable and insoluble in most acidic and alkaline solutions (Elgersma et al., 1992); the unwanted dissolution of iron presents yet another obstacle. Van Herck et al. (2000) studied the leaching of BFS under both acidic (HCl) and oxidizing conditions, and concluded that franklinite does not dissolve in either acidic or oxidizing conditions. Cantarino et al. (2012) investigated the removal of zinc from BOF sludge by a hybrid process based on thermal treatment followed by leaching of the sludge. The zinc removal efficiency obtained after the decomposition of franklinite by thermal treatment and leaching with NaOH, was greater than 90%. Zhang et al. (2017) extracted zinc from blast furnace dust using a coordination reaction between the organic ligand and zinc ions.

The Waelz process is the leading pyrometallurgical method for recovery of zinc (Busè et al., 2014). This process is based on the carbothermic reduction of ZnO and $ZnFe_2O_4$, and volatilization of metallic zinc. Although the pyrometallurgical process can yield a high rate of zinc recovery, it entails economic and environmental drawbacks due to

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https://doi.org/10.1016/j.mineng.2018.08.002
Received 26 March 2018; Received in revised form 11 July 2018; Accepted 1 August 2018
0892-6875/

its high energy requirement and the need for dust collection and gas cleaning systems (Trung et al., 2011; Jha et al., 2001). On the other hand, researchers (Drobíková et al., 2016; Singh et al., 2011; Esezobor and Balogun, 2006) have studied the possibility of BFS utilization by forming self-reducing briquettes and in the pelletization of iron ore. Drobíková et al. (2016) prepared BFS briquettes using starch as a binder; BFS can be used as a self-reducing material due to its high iron and carbon content. The primary obstacles to recycling BFS are its high moisture content and the presence of contaminants such as zinc (Esezobor and Balogun, 2006).

The use of microwaves, a form of electromagnetic radiation, as a heat source in material processing applications has become increasingly frequent over the past three decades (Omran et al., 2015a, 2015b; Al-harahsheh et al., 2014; Nishioka et al., 2002). Compared to conventional methods, microwave processing offers several advantages such as selective heating, rapid heating, and volumetric heating (Omran et al., 2015c; Haque, 1999). The dielectric properties of materials define how well they absorb microwaves and whether they can be heated under microwave irradiation (Al-harahsheh et al., 2014; Lovas et al., 2010). Materials with high loss factors are easily heated by microwave energy (Omran et al., 2014). A few studies have been published on the microwave processing of BFS. Vereš et al. (2012) studied the removal of zinc from BFS by leaching in acidic solutions using microwave energy as the heat source. The authors concluded that the microwave-assisted leaching of BFS resulted in very rapid dissolution of the zinc-bearing phase. Omran and Fabritius (2017) studied the reduction of iron oxides in BFS by microwave heating; they concluded that microwave heating can be used effectively to process BFS.

Aiming to avoid the disadvantages of pyrometallurgical and hydrometallurgical processes, this study investigated the properties of BFS and their implications in zinc removal. A combined process using particle size separation followed by microwave processing was proposed. In this study, the effect of temperature on the dielectric constant (ε') and loss factor (ε'') of the BFS at frequencies of 1064 MHz and 2423 MHz was measured. The distribution, concentration, and mode of occurrence of iron, zinc, and carbon in the different size fractions of the BFS were examined. The effect of temperature on the rate of zinc removal from BFS by microwave heating was studied.

2. Material and experimental

2.1. Material

A sample of BFS from SSAB Europe Oy, Raahe, Finland, was used in this study. Subsamples used for the analysis were dried at 75 °C. The results for the mineralogical and chemical analyses of the BFS are shown in Fig. 1 and Table 1, respectively. The main crystalline phases of the BFS were hematite (Fe_2O_3), calcite ($CaCO_3$), and quartz (SiO_2). Fig. 2A and 2B show that hematite was present as aggregates of particles of irregular shape. Coke was present as elongated crystals of larger-sized particles. Carbonate and silicate materials were detected as massive aggregates (Fig. 2C). The chemical composition of the BFS revealed that iron and carbon were the dominant elements. The BFS contained 38.95 wt.% iron, 24.90 wt.% carbon, 7.07 wt.% SiO_2, 6.60 wt.% CaO, 2.21 wt.% Al_2O_3, and 1.57 wt.% MgO (Table 1). The concentration of zinc and alkaline elements such as sodium and potassium was less than 0.56 wt.%. The zinc content of the sample was low compared to that of BFS samples previously studied (Vereš et al., 2012; Mansfeldt and Dohrmann, 2004), yet unacceptably high for the purpose of recycling. The concentration of zinc was 0.56 wt.%. The moisture content of the sludge was about 32.5%. The pH of the BFS was 8.1, indicating that the sludge was alkaline. The alkalinity of the BFS was due to its high content of calcium oxide (Mansfeldt and Dohrmann, 2004).

2.2. Analysis methods

2.2.1. Chemical analysis

The chemical composition of the BFS was determined using a Bruker AXS S4 Pioneer X-ray fluorescence (XRF) spectrometer. The XRF spectrometer was equipped with an Rh-tube with a maximum power of 4 kW. The zinc content of the experimental residues was measured using atomic absorption spectroscopy (ASS). A Perkin Elmer AAnalyst 400 flame atomic absorption spectrometer with S10 autosampler was used. Zinc was inserted into HNO_3 acid at 100x dilution and autoclaved at 121 °C for around 20 min. A single-element lumina hollow cathode lamp (HCL) was used to detect elemental zinc. The carbon and sulfur content were determined using a LECO carbon analyzer. The pH value of the sample was measured after leaching 10 g of the sludge with 25 mL of doubly deionized water. The moisture content was calculated after drying a constant weight of the sludge overnight at 115 °C in a stainless steel oven.

2.2.2. XRD analysis

The mineralogical composition was measured using X-ray diffraction (XRD). The measurements were taken using a Rigaku diffractometer (D/Max 2200, Rigaku, Japan) with CuKa radiation and a nickel filter operated at a voltage of 35 kV and anode current of 20 mA. The measurement range is from 4° to 90° 2 θ using a step size of 0.02° 2 θ and step time of 1 s.

2.2.3. Particle analysis

The micromorphology of the BFS was studied and microanalyses of its particles were conducted using a field emission scanning electron microscope (FE-SEM) attached to an energy-dispersive X-ray spectroscopy (EDS) unit for chemical analysis. The SEM (XL30ESEM-TMP, Philips, Holland) was operated at 20 kV in low vacuum. The particle diameters were determined by a laser diffraction and scattering method using a Beckman Coulter LS 13 320 analyzer.

2.2.4. Thermal analysis

The thermal behavior of the BFS was studied using thermogravimetry-differential scanning calorimetry (TG-DSC) and mass spectrometry (MS). The tests were performed using a Netzsch STA 409 PC Luxx simultaneous thermal analyzer under air and nitrogen atmosphere. Approximately 30.84 mg of the sample was placed in a platinum crucible on a pan of the microbalance and subjected to a heating rate of 20 °C min^{-1}. The temperature range was 20–1300 °C.

2.3. Experimental procedure

2.3.1. Microwave experimental set-up

A single-mode microwave tube furnace was used in the experiments. The power source of the microwave furnace was a magnetron with a frequency of 2.45 GHz and power of 1.1 kW. The diagram of the microwave experimental set-up is shown in Fig. 3.

A thermocouple was used to measure the temperature. The thermocouple provides feedback to the control panel, which controls the power supply to the magnetron, thus regulating the temperature of the sample during microwave heating. The experiments were carried out at 750 °C, 800 °C, and 850 °C. The samples were placed in a microwave-transparent alumina crucible. Nitrogen was pumped into the microwave cavity at a rate of 0.2 L min^{-1} to provide an inert atmosphere until the end of the experiment. The off-gas vapors from the experiments were extracted by a pump.

The residue in the crucible after each experiment was cooled to room temperature in the microwave oven. It was then investigated through chemical analysis to determine the rate of zinc removal. The zinc removal rate (R) was calculated according to the following equation (Falciglia et al., 2017):