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Removal of chloride from electric arc furnace dust

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ABSTRACT

Electric arc furnace (EAF) dust with high chloride content increases the threat of dioxin emissions and the high chloride content reduces the value of recycled zinc oxide produced by EAF dust recycling plants. This study conducts a number of laboratory experiments to determine the technical feasibility of a new dechlorination method. These methods consist of a series of roasting processes and water washing processes. In the roasting process, EAF dust was heated in a tube furnace to evaluate the parameters of atmospheric conditions, roasting temperature, and roasting time. Results indicate that sulfation roasting is more efficient in reducing chloride content than other roasting processes. The water washing process can totally remove water-soluble chloride at a solid to liquid ratio of 1:10. However, the remaining water-insoluble substance is difficult to dechlorinate. For example, lead chloride forms a hydroxyl-halide (PbOHCl) and lead chloride carbonate ($Pb_2CO_3Cl_2$) agglutinative matrix that is hard to wash away.

1. Introduction

Electric arc furnace (EAF) dust is a major byproduct of the EAF steelmaking industry. The EAF process generates about 10–20 kg of dust per metric ton of steel produced [1,2]. Approximately 160,000 tons of EAF dust is generated in Taiwan each year. This dust contains about 30% zinc as zincite and franklinite, 21.30% iron as magnetite, franklinite, and hematite, 7.02% various chlorides, and 3.17% lead as lead oxide and lead chlorides. The minor contents of EAF dust include sodium, potassium, manganese, magnesium, chromium, copper, and cadmium.

In Taiwan, the Waelz Kiln Process is the main process used for recycling EAF dust and recovering valuable zinc oxide. Compared with the EAF dust of other countries, Taiwanese EAF dust has a much higher chloride content (usually about 2%). High-chloride EAF dust causes four major problems at EAF dust recycling plants: (i) a lower value of crude zinc oxide since further dechlorination is required, (ii) the threat of dioxin emissions from pyrometallurgical processes, (iii) the high temperature corrosion of the air ducts of air quality control systems in recycling plants, and (iv) the difficulty of filtering sticky metal chlorides during the crude zinc oxide washing process.

The chloride compounds in EAF dust include sodium chloride (NaCl), potassium chloride (KCl), and lead hydroxyl-halide (PbOHCl) [3,4]. Metallic chlorides that transform into gaseous species in high-temperature reactions act as strong catalysts in de novo synthesis [5,6]. Therefore, chloride may be one of the greatest contributors to dioxin emissions from EAF dust recycling plants. The methods for removing chloride from EAF dust can be classified as pyrometallurgical, hydrometallurgical, and hybrid pyro-hydrometallurgical treatment processes.

Previous studies have presented various methods for decreasing the amount of chloride, including water washing [7–9], thermal treatment [10,11], and electro-dialysis [12]. Highly vaporized chloride can also be removed from EAF dust by reactive roasting. A water washing process usually acts as a pre-treatment step to remove water-soluble chloride prior to recycling EAF dust. However, EAF dust reacts with moisture and carbon dioxide in the atmosphere. This natural weathering process can transform leachable chloride into its insoluble mineral phase in EAF dust. Therefore, this study analyzes this weathering process in a simulation module to better understand phase transformation in a $Pb–Cl–H_2O–CO_2$ system. To minimize the environmental impact of EAF dust treatment and to optimize its economic feasibility, this study also investigates the main difficulties of removing chloride from EAF dust.

2. Methods and materials

2.1. Characterizations

EAF dust sampled from a steelmaking plant in southern Taiwan was characterized chemically and mineralogically. The metallic elements concentrations were determined by an atomic absorption spectrometer (Hitachi Z-8200). In addition, the chloride content

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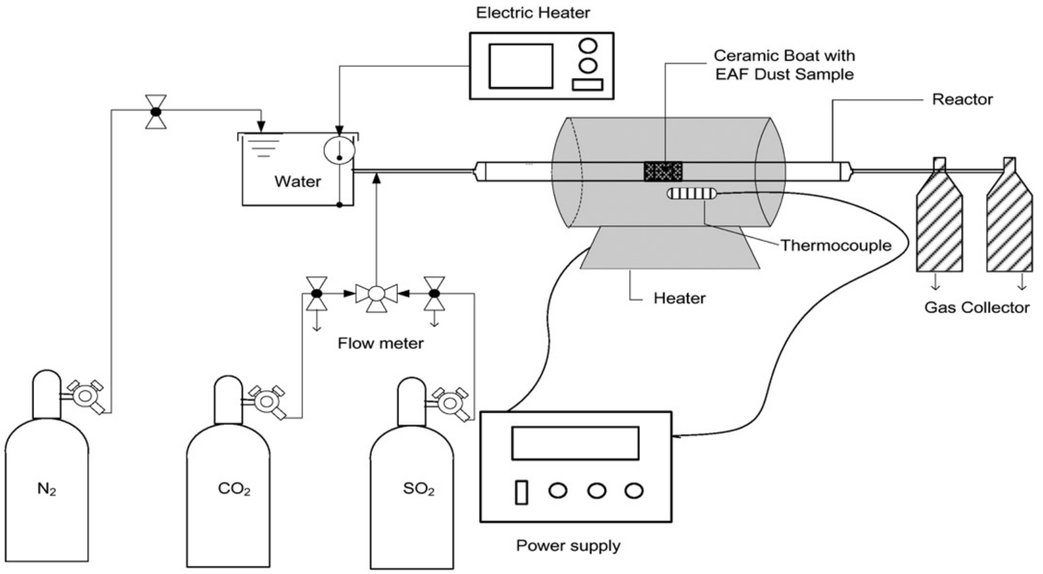

Fig. 1. Schematic diagram of the EAF dust dechlorination apparatus.

was determined by ion exchange chromatography (Dionex DX-120). Particle size distribution was determined by a laser diffraction particle size analyzer (Beckman Coulter LS-230) which provided a size distribution based on the volume of individual particles. The mineral content of the EAF dust was further analyzed by an X-ray diffractometer (BRUKER AXS D8-advance). Scanning electron microscopy with energy-dispersive spectrometry (SEM-EDS) was used to identify crystal phases of metal chlorides. Differential thermal analysis and thermal gravimetric analysis (DTA–TG) was used to determine the thermal behavior of EAF dust.

2.2. Roasting procedure

A tube furnace was used to conduct roasting experiments (Fig. 1). A 5 g sample of EAF dust was placed in a ceramic boat and pushed forward into the central part (i.e. reaction zone) of the tube furnace when the given temperature was reached. The sample was heated to different temperatures (200–600 °C) for different durations (1–5 h) in a quartz tube. During the roasting process, steam was introduced to the reaction zone and mixed with different reaction gases (Air/CO_2/SO_2). Gases were supplied from a gas tank at a flow rate of about 0.5 L/min at room temperature, at one unit atmospheric pressure. At the end of each batch roasting, the residues in the ceramic boat were collected for further analysis. The removal efficiency of all elements and the sample weight losses were measured and calculated according to mass balance.

2.3. Water washing procedure

Water-washing experiments were conducted with distilled water as the extractant at a solid to liquid ratio of 1:10 and at time intervals of 5–60 min. The transformation of the mineral content and leaching behavior of EAF dust were also examined.

2.4. Weathering procedure

Environmental simulations are increasingly used as a method to investigate the reactions between EAF dust and moisture and carbon dioxide, which convert the characteristics of EAF dust. In the weathering experiments in this study, samples were placed in a humidification chamber injected with CO_2 for a certain time period. This experiment illustrates the formation of insoluble chloride mineral interphases.

Table 1
Chemical composition of EAF dust.

Element	Amount (wt.%)
Zn	30.00 ± 2.53
Fe	21.30 ± 1.34
Cl	7.02 ± 0.69
Ca	7.23 ± 0.54
Si	3.32 ± 0.56
Pb	3.17 ± 0.46
Na	2.82 ± 0.32
K	2.68 ± 0.29
Mn	1.55 ± 0.11
Mg	0.53 ± 0.02
Al	0.72 ± 0.02
Cr	0.11 ± 0.01
Cu	0.08 ± 0.01
Cd	0.05 ± 0.01

3. Results and discussion

3.1. Sample characterization

Table 1 shows the chemical composition of EAF dust samples. Fig. 2 shows the particle size distribution of EAF dust as measured by laser diffraction particle size analyzer. Particle sizes exhibited a wide range from 0.14 to 6.76 μm. The majority of the particles were smaller than 0.66 μm (D_{50} value) in diameter.

EAF dust samples were also examined by an X-ray diffractometer. Fig. 3 shows the resulting XRD patterns. The mineralogical phases of zinc were mainly zincite (ZnO) and franklinite ($ZnFe_2O_4$) [3,5,7,13]. The result also revealed that various chloride compounds existed predominantly as potassium chloride (KCl), sodium chloride (NaCl), and lead hydroxyl-halide (PbOHCl) in the EAF dust.

Analysis of SEM-EDS revealed a metal halide rich phase composed of potassium and chloride as shown in Fig. 4. X-ray diffraction analysis also demonstrated that potassium chloride (KCl) exhibited isometric crystal phase.

Fig. 5 presents the DTA/TG results of EAF dust, showing endothermic peaks of phase transformation at 187 °C and 914 °C. The DTA/TG results reported by Li and Tsai [3] indicated that