



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 (Pb₂CO₃Cl₂) agglutinative matrix that is hard to wash away.

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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–H₂O–CO₂ 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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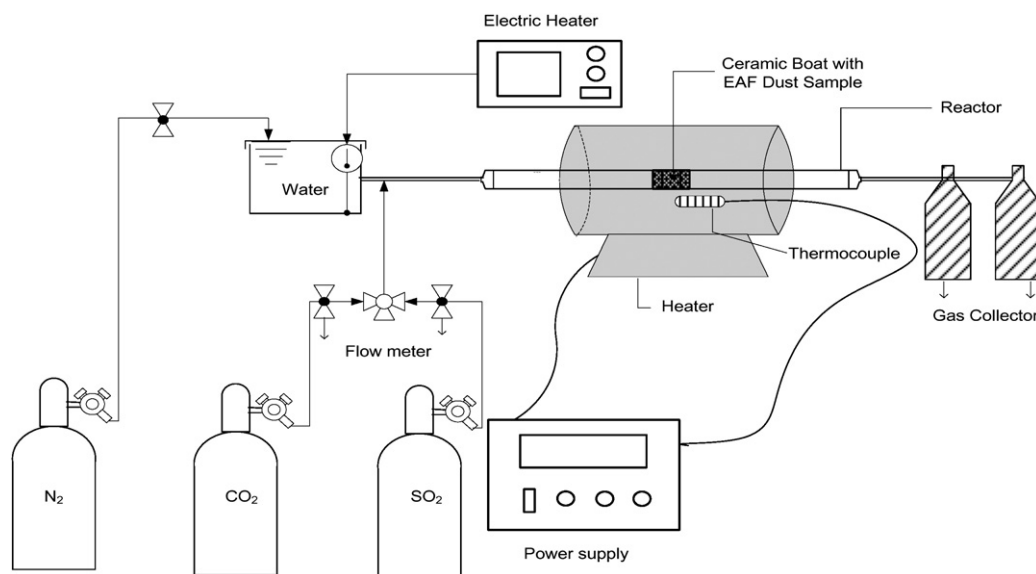


Fig. 1. Schematic diagram of the EAF dust dechlorination apparatus.

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/CO₂/SO₂). 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 CO₂ for a certain time period.

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

This experiment illustrates the formation of insoluble chloride mineral interphases.

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 (ZnFe₂O₄) [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

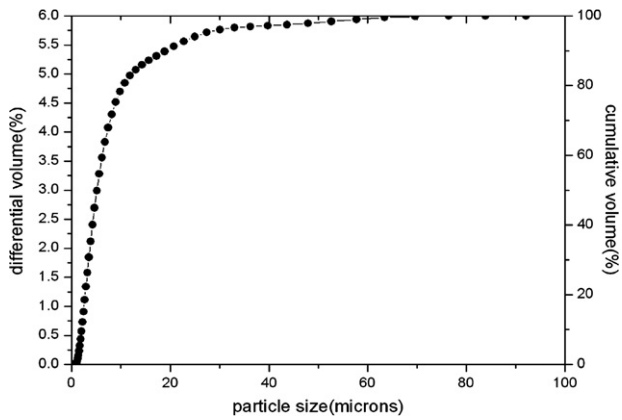


Fig. 2. Particle size distribution of initial EAF dust.

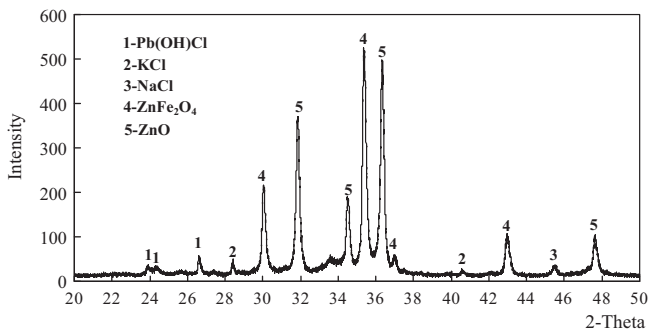


Fig. 3. X-ray diffraction spectrum of initial EAF dust.

the endothermic peak at 187°C represents the dehydration of metal hydroxide chloride. In the current study, the most significant weight loss occurred when the temperature exceeded 900°C.

3.2. Roasting results

Chloride can normally be removed from EAF dust by high temperature roasting. However, high temperature roasting wastes a large quantity of recyclable metal and decreases the commercial value of the zinc oxide product. Therefore, this study employed reactive roasting methods at mean temperature (<600°C) to simultaneously reduce recyclable metal losses and solve chloride problems. In all roasting experiments, recyclable metals such as lead and zinc were preserved with small amounts of weight loss where the lead content was less than 10% and zinc content was below 12% at 600°C.

Fig. 6 shows the dechlorination curves of EAF dust by roasting with air/sulfation/carbonation at temperatures of 200°C, 300°C, 400°C, and 600°C. The chloride content of roasted dusts decreased with increasing temperature and roasting time was observed at the individual atmospheres. The air-roasting method was the least effective at chloride removal. Sulfation roasting at 600°C achieved the highest chloride removal efficiency and had the lowest chloride content in roasted dust. In this case, the overall chloride level in the roasted dust was reduced from 70,200 mg/kg to 12,100 mg/kg, corresponding to 83% removal efficiency. Under the same conditions, carbonation roasting reduced the total chloride content in EAF dust from 70,200 mg/kg to 13,230 mg/kg, corresponding to 81% removal efficiency.

Roasting temperature could be raised higher than 600°C to remove remaining chloride from EAF dust. However, this would result in a large quantity of recyclable metal loss, i.e. zinc and lead. Potassium chloride (KCl) and sodium chloride (NaCl) may be easier to be removed by water washing. The roasted EAF dust may also be subjected to the washing process to remove all other chlorides.

3.3. Effects of water washing on chloride and heavy metal behavior

Fig. 7 shows the washing kinetic curves of chloride at ambient temperature for various washing times. The rate of dechlorination in the washing step was rapid in the first 5 min and most of the

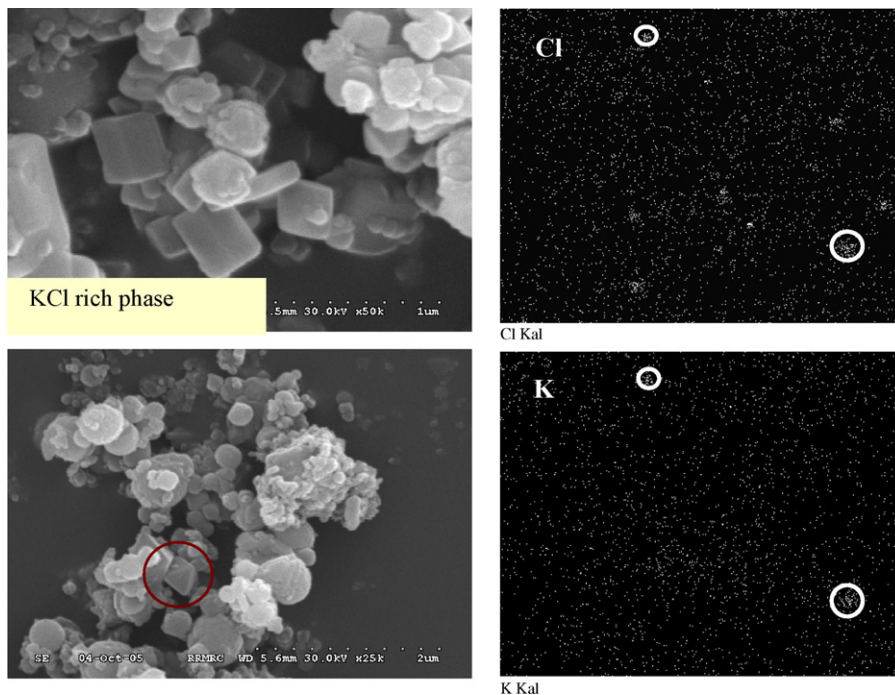


Fig. 4. SEM-EDS image of KCl-rich phase in EAF dust.

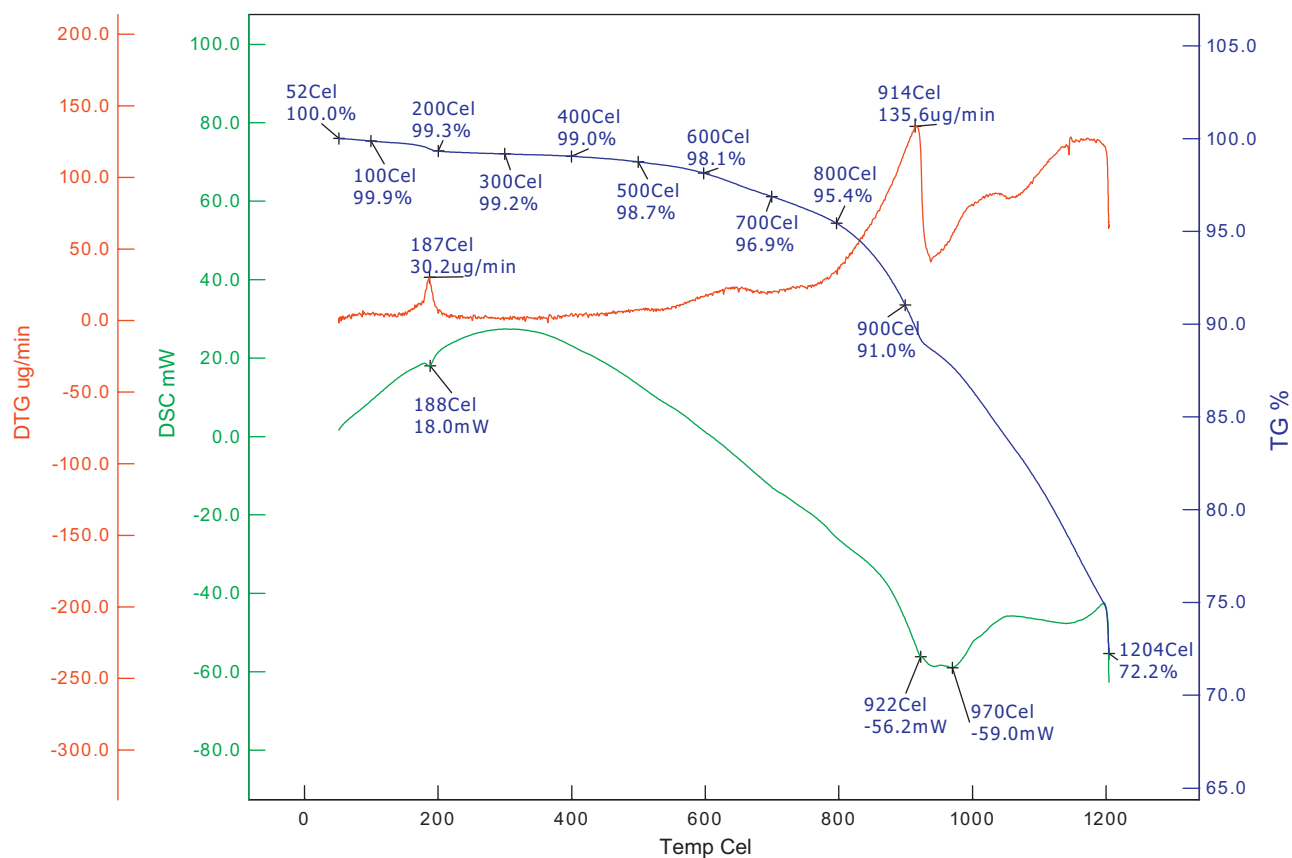


Fig. 5. TG/DTA plot of EAF dust.

removal was complete after 40 min. The total chloride level in the dust was reduced from 70,200 mg/kg to 17,500 mg/kg, corresponding to a 75% removing efficiency. Temperature had a significant effect on soluble chloride removal. The water washing test at 80 °C rapidly released chloride as compared to the ambient temperature test. The overall chloride removal efficiency was 88%.

The dechlorination efficiency in this study was much less than that of previous studies, which was typically >99% [7]. The washing step proposed by Bruckard et al.; successfully removes chloride when the EAF dust sample only consists of water-soluble chloride. However, the formation of water-insoluble compounds observed in this research has a significant effect on chloride removal. The result was proved by mineralogical analysis (Fig. 8). After the water washing step, the water-soluble species of sodium chloride (NaCl) and potassium chloride (KCl) were completely removed. However, water-insoluble matrixes were formed with lead hydroxyl-halide (PbOHCl, $k_{sp}: 10^{-13.377}$) and lead chloride carbonate (Pb₂CO₃Cl₂), making hydrometallurgical treatment more difficult and inefficient.

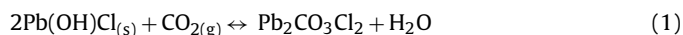
The coherence phenomena of water-insoluble substances may make it difficult to remove chloride from EAF dust. Li and Tsai [3] reported a similar coherence phenomena indicating that agglutinative substances such as zinc hydroxide chloride (ZnCl₂·4Zn(OH)₂·H₂O) might adhere to ferrite particles in EAF dust.

The solubility of metal is pH dependent. Fig. 9 shows the relationship of pH level, metal leaching rate, and leaching time. After several days, the level of pH decreased along the leaching time because of the increase of CO₂ dissolving. In the range of pH 9–11.8, the solubility of zinc and iron in the leachate was close to zero. The solubility of lead showed a pH dependent relationship. When leaching time was over 4 days and pH level was down to 9.5, the solubility of lead decreased to zero.

3.4. Effects of weathering upon lead-hydroxyl carbonate formation

The mineral composition of EAF dust can be dissolved or converted to new mineral interphases by a variety of natural weathering processes and environmental conditions [14]. Fig. 10 presents the XRD patterns of initial EAF dust and weathered dusts obtained after CO₂ aging at different times. After weathering for 1 day, the lead hydroxyl-halide (Pb(OH)Cl) phase appeared totally. We presumed that the hydrolysis of lead chloride and lead oxide by moisture was responsible for the formation of lead hydroxyl-halide (Pb(OH)Cl).

Note that the formation sequence of lead hydroxyl-halide phases in a weathering system is related to some important reactions. The hydrolysis and carbonization reactions were similar to Edward's description [15], which stated that the formation of main lead-hydroxyl carbonate compounds is as follows:



If sufficient carbon dioxide and moisture exist in EAF dust, they can dramatically alter the chemistry of lead compound formation. Thus, relationships (1) and (2) are held. Meanwhile, lead chloride carbonate (Pb₂CO₃Cl₂) and hydrocerussite (Pb₃(CO₃)₂(OH)₂) phases can be present. This result was obtained and proved through mineralogical analysis (Fig. 10). Lead chloride carbonate (Pb₂CO₃Cl₂) and hydrocerussite (Pb₃(CO₃)₂(OH)₂) phases can also be present under weathering circumstances.

Due to the low extraction (<0.8 ppm) of lead found in solution after water washing and because the carbon content did not show a

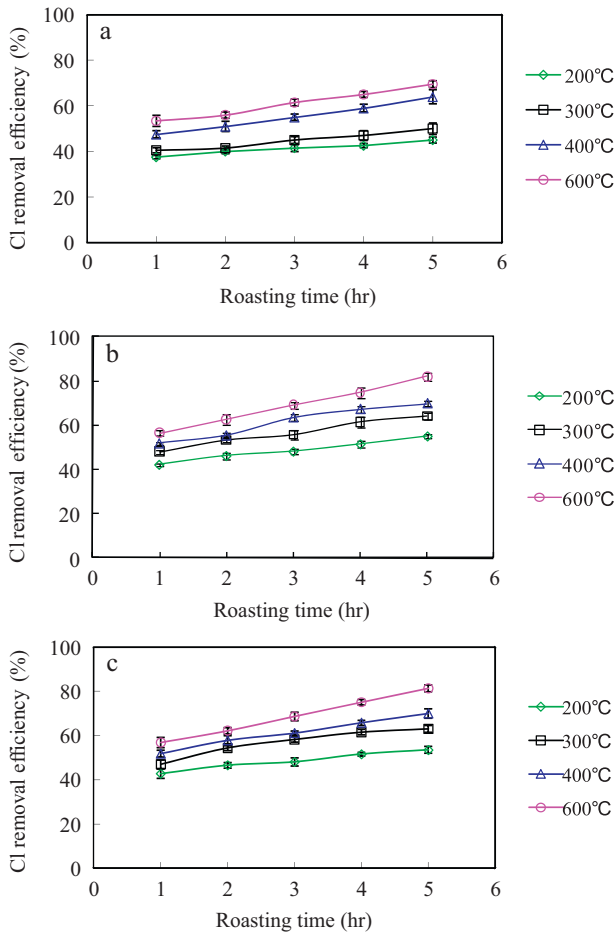


Fig. 6. The dechlorination curves of EAF dust in (a) air roasting, (b) sulfation roasting, and (c) carbonation roasting at different temperatures.

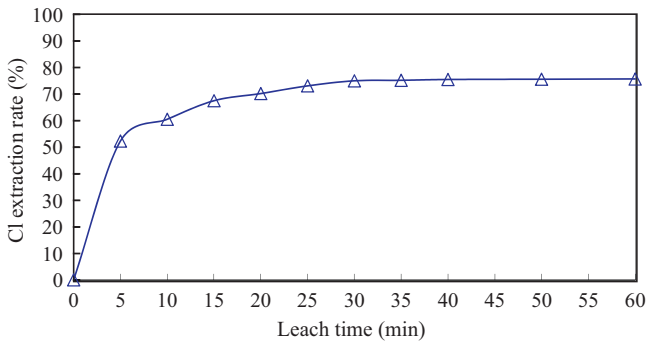


Fig. 7. Washing kinetic curves of chloride depending on various flushing time at ambient temperature.

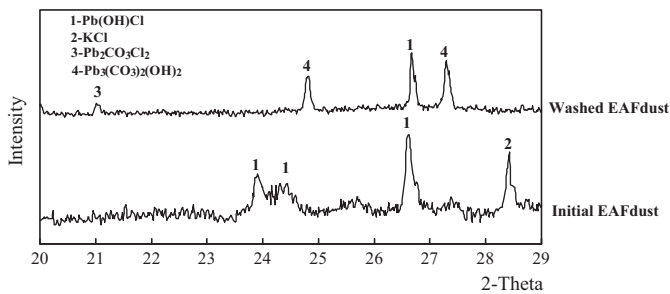


Fig. 8. XRD patterns of EAF dust before and after water washing.

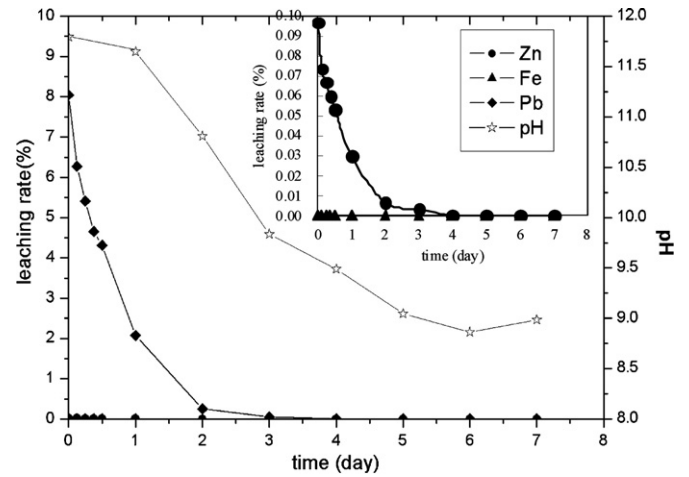


Fig. 9. Concentration of leached heavy metals with various pH values and washing time.

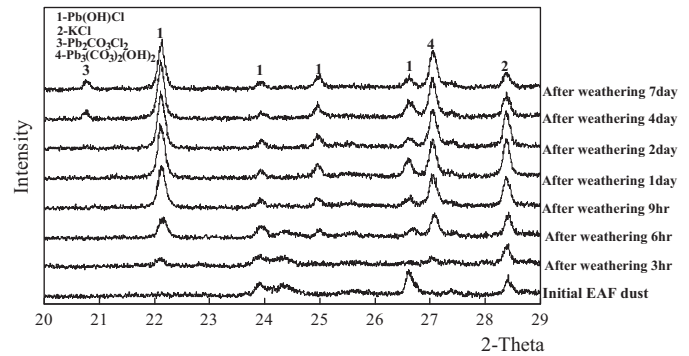


Fig. 10. XRD patterns of EAF dust before and after weathering.

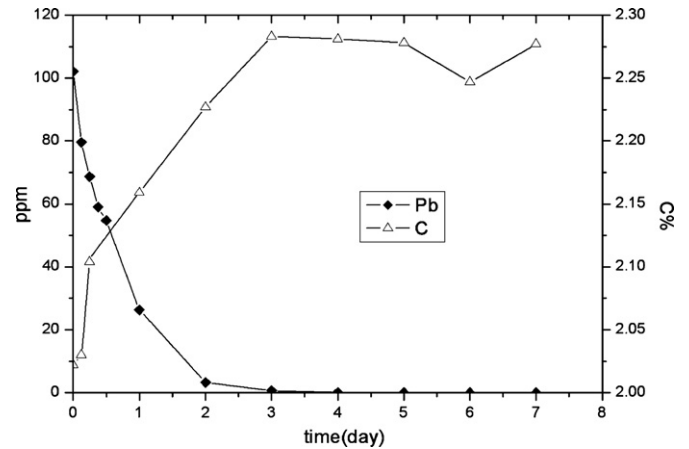


Fig. 11. Effect of weathering time on the extraction of lead and carbon content from dust.

further increase, we concluded that $(Pb_3(CO_3)_2(OH)_2)$ and $(PbCO_3)$ were at equilibrium after weathering for 4 days (Fig. 11).

4. Conclusions

Chloride species in EAF dust exist predominantly as potassium chloride (KCl), sodium chloride (NaCl), and lead hydroxyl-halide ($PbOHCl$), causing treatment problems at EAF dust recycling plants. Therefore, this study tests different methods of removing chloride content from EAF dust. Sulfation roasting achieved a higher level of

dechlorination than carbonation and air roasting. The metal halides remaining in roasted dust consist of potassium chloride (KCl) and sodium chloride (NaCl). Such soluble chlorides are easily removed through subsequent washing processes.

The water washing process can reduce the total chloride content from 70,200 mg/kg to 17,500 mg/kg within 40 min at ambient temperature. Though wet processing techniques can easily remove water-soluble species from EAF dust, environmental weathering results in the formation of a water-insoluble matrix in EAF dust. This study shows that water-insoluble matrixes of lead hydroxyl-halide (PbOHCl) and lead chloride carbonate (Pb₂CO₃Cl₂) form in weathered EAF dust. Therefore, the coherence phenomena of water-insoluble substances affect the removing efficiency of chloride from EAF dust. This is the main challenge of removing chloride by the water-washing process.

Variations of pH levels also have a considerable effect on the solubility of heavy metals. The solubility of lead was higher than zinc and iron under alkaline conditions at pH 9.0–11.8. We concluded that the basic value of pH improve the immobility of heavy metals. As a result, the solubility of zinc and iron was quite low in the leachate.

Water washing is good for removing all kind of metal chloride, such as potassium chloride, sodium chloride, lead chloride and zinc chloride in fresh EAF dust. However, it becomes difficult to remove zinc hydroxide chloride, lead hydroxide chloride and lead chloride carbonates when EAF dust was weathered. It is recommended that introduce fresh EAF dust direct to washing process after collected. Otherwise, using roasting with carbon dioxide at 600 °C, follow by water washing, to avoid adhesive lead and zinc hydroxide chloride to be formed and improve the removal of chloride from EAF dust.

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