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Removal of chloride from MSWI fly ash

Wei-Sheng Chen[a], Fang-Chih Chang[b,*], Yun-Hwei Shen[c], Min-Shing Tsai[c], Chun-Han Ko[d,**]

[a] Sustainable Environment Research Center, National Cheng Kung University, No. 500, Sec. 3, An-Ming Rd., Tainan 709, Taiwan
[b] Department of Environmental Engineering, National Cheng Kung University, No. 1, University Rd., Tainan 701, Taiwan
[c] Department of Resources Engineering, National Cheng Kung University, No. 1, University Rd., Tainan 701, Taiwan
[d] School of Forestry and Resource Conservation, National Taiwan University, Taipei 10617, Taiwan

HIGHLIGHTS

- 14% improvement in chloride removal can be achieved by aeration process.
- 16% improvement in chloride removal can be achieved by carbonation process.
- Aeration and carbonation had a major influence on fly ash pH.
- Mineralogy change prove that the chloride removal mechanism and efficiency.

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ABSTRACT

The high levels of alkali chloride and soluble metal salts present in MSWI fly ash is worth noting for their impact on the environment. In addition, the recycling or reuse of fly ash has become an issue because of limited landfill space. The chloride content in fly ash limits its application as basis for construction materials. Water-soluble chlorides such as potassium chloride (KCl), sodium chloride (NaCl), and calcium chloride hydrate ($CaCl_2{\cdot}2H_2O$) in fly ash are easily washed away. However, calcium chloride hydroxide (Ca(OH)Cl) might not be easy to leach away at room temperature. The roasting and washing-flushing processes were applied to remove chloride content in this study. Additionally, air and CO_2 were introduced into the washing process to neutralize the hazardous nature of chlorides. In comparison with the water flushing process, the roasting process is more efficient in reducing the process of solid–liquid separation and drying for the reuse of Cl-removed fly ash particles. In several roasting experiments, the removal of chloride content from fly ash at 1050 °C for 3 h showed the best results (83% chloride removal efficiency). At a solid to liquid ratio of 1:10 the water-flushing process can almost totally remove water-soluble chloride (97% chloride removal efficiency). Analyses of mineralogical change also prove the efficiency of the fly ash roasting and washing mechanisms for chloride removal.

1. Introduction

The increasing amount of municipal solid waste is a global environmental problem. Incineration is a general management option [1,2]. Currently, there are 22 municipal solid waste incinerators (MSWI) in Taiwan with a total processing capacity of 7.89 million tons per year [3]. In 2010, 1.29 million tons of municipal incinerator residues were produced. Bottom ash and fly ash constituted up to 77 and 23%, respectively, of the total ash. The MSWI fly ash is usually a mixture of ash, lime and carbon and is sent to landfills for final disposal. In recent years, the recycling and reuse of MSWI fly ash has become a main issue because of the limited availability of landfill space.

MSWI fly ash is generally categorized as hazardous waste due to high levels of heavy metals, dioxins, alkali chlorides, and soluble metal salts [2,4,5]. The alkali chlorides mainly include sodium chloride, potassium chloride, and calcium chloride. The amounts of chloride compounds in fly ash in Taiwan are generally higher than 8%; this may lead to critical problems if untreated MSWI fly ash were to be recycled as construction materials [6]. Therefore, MSWI fly ash needs to be treated before recycling. The major treatment or recycling technologies currently under development or in use are washing-immobilization, stabilization/solidification and thermal treatment [7–9]. The main usage of fly ash after treatment is for the production of construction materials. The high levels of metal chlorides are harmful not only during

* Corresponding author. Tel.: +886 6 2383620; fax: +886 6 2373476.
** Corresponding author. .
E-mail addresses: d90541003@ntu.edu.tw (F.-C. Chang), chunhank@ntu.edu.tw (C.-H. Ko).

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the recycling process but also during the application of products from the raw materials. Therefore, the elimination of chloride from MSWI fly ash is important prior to recycling or reuse.

In Taiwan, MSW is characterized by a high plastic and food residue content, which in turn leads to the high chlorine content. The high levels of chlorine result in the formation of HCl in fly ash. During the incineration process, the flue gas is treated by semi-dry lime and activated carbon for the removal of acid gas and pollutants to meet emission criteria. A number of researchers studied thermal treatment, such as sintering and vitrification, in recent years. However, the removal of chloride from MSWI fly ash is still a question in the application of recycled materials. Thus, the roasting and washing processes for chloride removal and mineralogical change are investigated in this study. The results of this study can also be used to facilitate the recycling and reuse of MSWI fly ash as basis for construction materials.

2. Methods and materials

2.1. Characterizations

MSWI fly ash sampled from an incinerator in southern Taiwan was characterized chemically and mineralogically. The metallic element concentrations were determined by ICP-OES (Varian Vista-Mpx). In addition, the chloride content was determined by ion exchange chromatography (Dionex DX-120). The mineral content of the fly ash 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, PerkinElmer-Pyris Diamond) was used to determine the thermal behavior of fly ash in a temperature range of 25–1100 °C at a heating rate of 10 °C/min.

2.2. Roasting procedure

A tube furnace was used to conduct roasting experiments [10]. A 10 g sample of fly ash 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 in a quartz tube to 600 °C, 800 °C, 950 °C, and 1050 °C for 7 h, 4 h, 2 h, and 1 h (the stable state of equilibrium), respectively. During the roasting process, steam was introduced to the reaction zone and mixed with the reaction gas (air). Gas was supplied from an air tank at a flow rate of about 0.5 L/min at room temperature and at one unit atmospheric pressure. At the end of each batch roasting, the residues in the ceramic boat were collected for further analysis. The collected residues were examined by X-ray diffractometer (Bruker AXS-D8A) in order to identify any crystalline phase present in the residues and to observe the mineralogical change at different temperatures. Then, the residues were washed with ion-free water to extract the chlorine. The aqueous samples were analyzed by using ion chromatography (Dionex DX-120). The removal efficiency of all elements and the sample weight loss were measured and calculated according to mass balance.

2.3. Water-flushing procedure

Samples of fly ash were taken for the washing step at a given solid to liquid ratio (100 g/L) and stirred in an agitation apparatus for 1.5 h at room temperature (25 °C) and higher dissolution temperature (90 °C). Ash washing allows the extraction of chloride and soluble salts. The accelerated carbonation washing procedure was also tested by introducing two kinds of reactive gases (CO_2/air) separately into the washing reactor at ambient temperature. After finishing the washing procedure, the solution was filtered and the solid residue was dried and weighed. The pH value was recorded after each washing test. The solid residues were examined by X-ray diffractometer (Bruker AXS-D8A) in order to identify any crystalline phase present in the residues and to observe the mineralogical change at different leaching conditions. The solution samples were analyzed by using ion chromatography (Dionex DX-120). The chloride removal efficiency and weight loss of all samples were calculated according to the differences between residues and initial fly ash.

Table 1
Chemical composition of initial fly ash.

Element	Amount ($\times 10^4$ mg/kg)
O	47.50 ± 1.81
Ca	15.00 ± 1.64
Si	10.30 ± 1.19
Cl	8.60 ± 1.03
Al	4.60 ± 0.13
Na	4.22 ± 0.24
K	4.00 ± 0.30
Mg	1.60 ± 0.11
S	1.2 ± 0.03
Fe	1.10 ± 0.04
Zn	0.89 ± 0.03
Pb	0.16 ± 0.01
Cu	0.11 ± 0.01
Cr	0.05 ± 0.00
Cd	0.03 ± 0.00

3. Results and discussion

3.1. Sample characterization

Due to the treatment of flu gas from municipal solid waste incinerators, its residues (MSWI fly ash) are actually a mixture of fly ash, lime and carbon. Table 1 shows the chemical composition of a fly ash sample. The fly ash contained about 15.0×10^4 mg/kg calcium, 10.3×10^4 mg/kg silicon, 8.6×10^4 mg/kg chloride, 4.6×10^4 mg/kg aluminum, 4.2×10^4 mg/kg sodium, and 4.0×10^4 mg/kg potassium as major components. The minor elements in the fly ash were magnesium, iron, zinc, lead, copper, chromium, and cadmium. The calcium and silicon mostly come from lime and solid waste ash. MSWI fly ash is highly alkaline because of the presence of lime, which presents a problem for its recycling or reuse. The high level of chloride is from chlorine content in the solid waste, especially from plastic waste and food waste.

Fig. 1 shows the thermogravimetry and differential thermal analysis (DTA/TG) curve that served for kinetics data determination. The dehydration temperature of fly ash was under 200 °C. The combustion of organics occurred between 300 and 450 °C, as is characterized by a positive ΔT peak. At 600–700 °C, calcium carbonate was transformed to calcium oxide; the exothermic reaction was coupled with a 6% weight loss. Above 950 °C, the potassium chloride and sodium chloride were vaporized with a 10% weight loss.

Fig. 2 shows the XRD pattern of the initial fly ash sample. Calcium-bearing compounds were rich in MSWI fly ash. A major calcium crystalline phase (including calcium oxide, calcium hydroxide, and calcium carbonate) and chloride compound (including KCl, NaCl, $CaCl_2{\cdot}2H_2O$, and Ca(OH)Cl) were identified. The XRD pattern shows that $Ca(OH)_2$, $CaCl_2{\cdot}2H_2O$, and Ca(OH)Cl were present in the sample. Most of the studies reported in literature [11–13] assume that $CaCl_2{\cdot}2H_2O$ and Ca(OH)Cl are both chlorinated products of the reaction between $Ca(OH)_2$ and HCl, according to the following equation:

$$Ca(OH)_2 + HCl \rightarrow Ca(OH)Cl + H_2O \quad (1)$$