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Sintering of MSWI fly ash by microwave energy

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ABSTRACT

This study presents the sintering of municipal solid waste incineration (MSWI) fly ash assisted by microwave energy. The composition of fly ash was investigated by chemical sequential extraction and modified microwave digestion method. Effects of process time, container materials, aging time and salt contents were also discussed. The major elements of fly ash are Ca, Cl, Na, Si, K, Al, Mg, and Zn, and the metal species, Zn, Cr, Pb, Ca, and Cu, are mainly in the oxide phase. Under microwave processing, the fly ash was sintered into a glass–ceramics and the leaching concentrations of heavy metals were restrained. The stabilization efficiency increased with an increase in processing time in most of the cases. Better stabilization efficiency of fly ash was discovered by using the SiO_2 or Al_2O_3 container than by using the graphite plate/SiC plate. The presence of salt in the fly ash could enhance the sintering and stabilization of fly ash. During the aging time of 0–30 days, negligible Pb in the sintered fly ash was leached out, and the leaching concentration was lower than the criterion.

1. Introduction

Municipal solid waste incineration (MSWI) fly ash is a residue found in waste after incineration. Fly ash in Taiwan amounts to about 160,000 tons/year. MSWI fly ash is regarded as hazardous waste. The components of MSWI fly ash are complex and unfixed [1]. Major contents are soluble salts [2], CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O, K_2O, P_2O_5, TiO_2, MnO, CuO, ZnO, PbO, Cr_2O_3, and SO_3. Minor contents are Zn, Pb, Cr, Cd, Cu, Sn, Ba, Sb, Zr, As, Co, Mo, Rb, Bi, V, Ce, Ga, La, Nd, Nb, and Hg [3]. TCLP leaching of the heavy metals from MSWI fly ash still results in leachate concentrations above the legal limit for land disposal. Hence, it is important to dispose of this troublesome substance thoroughly before it is sent to landfills. The most commonly used treatment method for MSWI fly ash is cement solidification. However, this method increases the volume of ash, which reduces the useful lifetime of landfill sites. This study aims to find a new method to dispose of fly ash and avoid the disadvantage of cement solidification.

Although microwave heating was introduced over 50 years ago, its use in the treatment of MSWI fly ash is relatively new. Microwave energy is a nonionizing electromagnetic radiation with frequencies in the range of 300 MHz to 300 GHz. Compared with other conventional thermal treatment technologies, the microwave technique with its characteristics of polar oscillation and effect of dielectric losses offers the advantage of selective, uniform, and rapid heating. The interaction of dielectric materials with electromagnetic radiation in the microwave range results in energy absorbance as heat [4].

The application of microwave radiation is widely used in many fields, including sintering and joining of ceramics [5–7], synthesis of composites [7], contaminated soil remediation [8], waste treatment [9,10], mineral processing [11], assisted digestion procedures [12], drying or dewatering of materials, polymer curing, and regeneration of activated carbon [10]. Moreover, a growing interest in the stabilization and immobilization of metal ions in soil and sludge through microwave radiation has also been reported. Results indicated that microwave radiation inhibits the leaching of metal ions from soil or sludge and that it makes these solid wastes acceptable for disposal or recycling [13–15].

This project aims to investigate the sintering of MSWI fly ash by microwave radiation. The objective of this study is to: (1) determine the proper procedure for stabilization of MSWI fly ash by microwave energy, (2) discuss the effects of processing time, (3) compare the effects of different crucibles/containers on microwave radiation of MSWI fly ash, and (4) discuss the effect of soluble salts and caustic substances on microwave radiation.

2. Materials and methods

Two specimens of MSWI fly ash from two different incineration plants were tested in this study. The MSWI fly ash was pretreated by drying in an oven at 105 °C (about 24 h), until the mass maintained a constant value within ±1%.

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The composition of the MSWI fly ash was determined by modified microwave digestion method reported in previous studies [15]. Samples of the MSWI fly ash (0.2 g) were mixed with a HNO_3–HCl–HF solution (3 mL). These acidic slurries were processed using the following two-stage microwave program: (1) 650 W for 10 min (final temperature 160 °C) and (2) 800 W for 15 min (final temperature 200 °C). After the microwave-assisted digestion process, the mixtures were cooled to room temperature and filtrated, and the filtrate was adjusted to 100 mL before analysis.

Modified chemical sequential extraction [16] was also conducted to determine the phase of heavy metals in the MSWI fly ash. Portions of fly ash of 2 g were put in PVC tubes and mixed with extracting agents. The extraction procedure was as follows:

(i) *Exchangeable*. The fly ash was extracted at 25 °C with 8 mL of magnesium chloride solution (1 M $MgCl_2$, pH 7.0) and shaken for 1 h (125 rpm).
(ii) *Bound to carbonates*. The residue from (i) was leached at 25 °C with 8 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). It was continuously shaken for 5 h (125 rpm).
(iii) *Bound to Fe–Mn oxides*. The residue from (ii) was extracted with 20 mL of 0.04 M NH_2OH–HCl in 25% (v/v) HOAc. This was performed at 96 ± 3 °C with 6 h shaking (125 rpm).
(iv) *Bound to organic matter*. The residue from (iii) was added to 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3, and the mixture was heated to 85 ± 2 °C for 2 h with shaking (125 rpm). A second 3-mL of 30% H_2O_2 (pH 2 with HNO_3) was then added and the sample was heated again to 85 ± 2 °C for 3 h with intermittent shaking (125 rpm). After cooling, 5 mL of 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added and the sample was diluted to 20 mL and shaken continuously for 30 min.
(v) *Residue*. The residue from (iv) was digested with a 10-mL of 10% HF and 10 mL $HC1O_4$ mixture at 25 °C with 1 h shaking (125 rpm).

Between each successive extraction, separation was effected by centrifuging at 10,000 rpm for 30 min. The resulting solution was filtered though a membrane filter (0.45 μm) and analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES), whereas the residue was washed with 8 mL of deionized water; after centrifugation for 30 min, this second supernatant was discarded.

In the sintering experiments, 20 g samples of fly ash were put in an SiO_2 ceramic crucible, Al_2O_3 ceramic crucible (11 cm diameter), and SiC plate with graphite plate, and the moisture contents were adjusted to 75 wt.% with deionized water. The experiments were conducted with microwave frequency of 2.45 GHz at 600 W. Respective process times were 10, 20, 30, 40, and 50 min. The effects of process time, container type, and aging time were discussed. Moreover, the effect of salt in the fly ash under microwave radiation was also studied. The fly ash was pre-washed by deionized water with liquid to solid ratio (L/S) of 5, 10, 15, and 20 mL/g and followed by the microwave process.

The raw fly ash and treated samples were tested by TCLP and the leaching concentrations were analyzed by ICP-AES. The crystal structure of fly ash samples before and after microwave processes were also determined by X-ray diffraction (XRD) to determine the species variation.

3. Results and discussion

3.1. Chemical composition of MSWI fly ash

Microwave-assisted digestion was performed for analysis of the chemical composition of MSWI fly ash. Table 1 lists the extractable elemental composition measured in samples of the MSWI fly ash from plant A and B. The instrument detection limit (IDL) of the liquid extract was 0.1 mg/L, which translates into a detection limit of 0.05 mg/g for the MSWI fly ash. All the values of metal concentration, mg/kg, are listed in Table 1. The major elements in the MSWI fly ash from plant A, in decreasing sequence, were Ca, Cl, Na, Si, K, Al, Mg, and Zn, while those from plant B (decreasing sequence) were Ca, Cl, Na, Si, K, Al, Zn, and Mg. The amounts of Na, Si, K, and Al in the MSWI fly ash from plant A was higher than those from plant B. However, the amounts of Ca, Cl, Zn, and Pb from plant B was higher than those from plant A. The higher amount of Cl was generated from the composition of refuse in the incineration processes. An amount of HCl was also generated. The higher amount of Ca was generated without HCl/SO_x by the air pollution control device; the device adds excessive limestone to remove acidic gases. Several papers have reported a presence of $CaCl_2$, $CaSO_4$, NaCl, KCl, Al_2O_3, SiO_2, etc. in MSWI fly ash [1,2] determine, which cause the fly ash to be alkaline (pH value >12) because of the residual limestone.

Table 1
Chemical composition of MSWI fly ash

Elements (mg/kg)	Plant A	Plant B
Zn	8,718	10,214
Cr	365	614
Pb	3,270	3,720
Ni	252	1,311
Cd	2,269	614
Ba	1,890	2,094
Co	183	1,137
Mn	671	N.D.
Fe	414	1,889
Mg	8,915	5,975
Ca	232,222	310,204
Cu	1,422	1,173
Ag	469	1,458
Al	16,407	15,617
Ga	111	506
Na	38,633	27,168
K	21,837	19,071
Si	33,236	24,745
Cl	118,365	165,816

D.L. = 0.1 mg/L and N.D. means the concentration of metal ion is below detection limit.

Fig. 1(a) shows the XRD result of MSWI fly ash from plant A. There are amounts of NaCl, KCl, CaClOH, $Ca(OH)_2$, Pb, AlO, SiO_2, PbO_2, and KNO_3 in the MSWI fly ash, which supports the finding that the alkali in MSWI fly ash is caused by CaClOH and $Ca(OH)_2$. In addition, there is a special phenomenon regarding the MSWI fly ash. The present study discovered that the reaction product of Ca and Cl is CaClOH and not $CaCl_2$. The CaClOH seems to deposit the excess limestone in the air pollution control process in plant A. At the same time, the Al species are AlO and not Al_2O_3. The results in Table 1 and Fig. 1(a) support the finding that the major contents of the MSWI fly ash from plant A are NaCl, KCl, CaClOH, $Ca(OH)_2$, AlO, and SiO_2.

Table 2 shows the chemical composition of MSWI fly ash from plant A and B after chemical sequential extraction. The fly ash from the two plants showed similar tendencies, and the chemical phase of compositions (Zn, Cr, Pb, Ca, and Cu) for both plants was mainly oxide bound.

A result of TCLP leaching of MSWI fly ash (liquid to solid ratio L/S = 20) from both plant A and B, showed that the TCLP lead leaching concentrations for both raw and washed fly ash were much higher than the criterion in Taiwan (5.0 mg/L). The concentrations of Zn, Cr, Pb, Ca, and Cu ions from plant A were 14.29, 0.65, 49.10, 0.14, and 0.45 mg/L, respectively, while those from plant B were 6.11, 0.63, 74.58, 0.14, and 0.45 mg/L, respectively. The concentrations of