Metal Behavior during Vitrification of Municipal Solid Waste Incinerator Fly Ash

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ABSTRACT

This study described the mass distribution of metals and the crystalline characteristics of slag during the vitrification of incinerator fly ash. The fly ash, mainly composed of Ca (180,000 mg/kg), Si (25,500 mg/kg), Pb (19900 mg/kg), and Zn (14,400 mg/kg), was vitrified with cullet at a basicity of 0.921 in an electric heating furnace. After vitrification, metals with low boiling points (Cd, Pb, and Zn) vaporized into flue gas as particulate phase. High levels of Pb (315,000 mg/kg) and Zn (226,000 mg/kg) made the particulate phase worth reclaiming. No ingot formed due to lack of ingot forming metals, and thus metals with high boiling points mainly stayed in the slag. After being identified by X-ray diffractometer (XRD) analysis, the major crystalline phases of the slag were found to be Ca2SiO4 and CaSiO3, which coincided with the results of scanning electron microscopy (SEM). The results of the toxicity characteristics leaching procedure (TCLP) suggest that recycling the slag could be taken into consideration. The overall results indicate that vitrification is a promising technology that is able to transform incinerator fly ash into stable slag, reduce secondary environmental pollution, and transform valuable metals (Pb and Zn) in a recoverable form.

Keywords: Basicity; Heavy metal; Municipal solid waste; Stabilization; Slag.

INTRODUCTION

Due to the rapid growth of economic development, a large amount of municipal solid wastes (MSW) are generated in human activities. Confronting the increasing amount of MSW amount, the most common strategy is the combination of incineration and landfill. According to 2011 Taiwan Environmental Protection Administration (TEPA) report for the collection and transportation for MSW, there were 7,750,000 tons of MSW generated in Taiwan last year. Among the MSW, 45.5% (3,520,000 tons, including bulk waste recycling and reuse, food waste recycling, and resource recycling) were recycled, 52.1% (4,040,000 tons) were incinerated, and the residual fraction were disposed by landfill or other method (TEPA, 2011). For the incineration process, the flue gas was controlled stringently by regulated emission standard for decades (TEPA, 2006a), but the disposal of the ashes was relatively ignored.

During the MSW incineration process, 1,210,000 tons of ashes (fly ash + bottom ash) were generated last year (TEPA, 2011). Among the ashes, the bottom ash (about 80% of the ashes) was recycled as road pavement and building materials; meanwhile, the fly ash was solidified with cement and landfilled. A recent research shows that ashes brought out more than 90% of polychlorinated dibenzo-p-dioxins dibenzofurans (PCDD/Fs, as I-TEQ), polybrominated diphenyl ethers (PBDEs, as TEQs), and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) from an incinerator (Lin et al., 2010; Wang et al., 2010a; Chiu et al., 2011). The level of persistent organic pollutants in the fly ash collected from baghouse filters was much higher than that in other ashes (Wang et al., 2010b). Neither recycling nor cement can destroy the organic toxicity, and thus, the recycling or solidification/landfill may cause secondary pollution.

Vitrification is widely used the treatment of hazardous materials, including fly ash, spent catalyst, radioactive waste, spent batteries, and electroplating sludge (Hrma et al., 2005; Li et al., 2007; Wei et al., 2007; Kuo et al., 2009; Yang et al., 2009). There are three major advantages of this technology. First, it can immobilize heavy metals and transform the hazardous metals into stabilized slag (Zhao et al., 2010). Second, it can destruct organic toxics such as
PCDD/Fs, PBDE or PAHs (Kuo et al., 2003; Lin et al., 2011; Lin et al., 2012). Third, it can gather useful metals in the products as recoverable forms (Chou et al., 2011). This study attempted to investigate the vitrification of fly ash with the addition of cullet. Input materials (fly ash and cullet) and output materials (slag and flue gas) were sampled and analyzed. Also, the mass distribution of metals during the vitrification process was elucidated and the characteristics of output materials were investigated.

**METHODS**

**Raw Materials Preparation and Vitrification System**

The fly ash was sampled from the baghouse filters of a municipal solid waste incinerator located in southern Taiwan. The specimen was dried at 105°C for 24 hrs to remove water content. Cullet, acting as an additive, was pulverized. The specimen was premixed with a mass ratio of cullet: fly ash = 3:10 before vitrification. Fig. 1 shows the flow chart of the involved vitrification system which was a modified version used in a previous study (Kuo et al., 2009). The premixed powdery specimens were weighed, held in graphite crucibles, and then heated in a vitrification furnace (Dengyng DFH-30) with a heat source of electricity (220 V, AC). The involved furnace is equipped with eight SiC heating rods and has inner space (25 cm × 25 cm × 20 cm) which is coated with refractory materials. The specimens were heated from 25 to 1000°C at a heating rate of 6 °C/min, from 1000 to 1450°C with a heating rate of 4 °C/min, isothermal held at 1450°C for 0.5 hr, and cooled to room temperature without any convection.

**Gas Phase Sampling**

During the vitrification process, the flue gas was pumped from the top outlet using a pump (1AM, Gast) with a flow rate of ~3 L/min. The flue gas then passed through a water-cooling circulation device to reduce the temperature to about 50–60°C. For calculating the total sampled gas volume, the mean flow rate was determined by averaging the flow rates before and after sampling. The following units are a filter and a gas-phase sampling modules which sample particulate phase and gas phase metals in the flue gas, respectively. The total air sampling volume was 10.1 L which was enough for subsequent analysis.

During the cooling process, some particulate matter adhered to the inner wall of the stainless steel tubes (between the furnace and water-cooling circulation device) and the water circulation tubes (in the water cooling circulation device). To dissolve the metals in the particulate matter, the tube walls were rinsed using an acid solution of 0.1 N HNO₃. The rinsed solution was filtrated and analyzed to measure the metal mass. Passing through the water cooling circulation device, a glassfiber filter was used to trap the finer particulate matter. The filter was conditioned and weighed before and after vitrification to determine the particulate matter mass. After sampling, the filter was digested, filtration and analyzed to determine the metal mass. The summation of the metal mass collected from the filter and the inner wall of the stainless steel tubes and the water circulation tubes was regarded as particulate-phase metals.

Following the filter is the gas-phase metal sampling module which is composed of five serially connecting impingers (in Fig. 2). The impingers were vacant (No. 1 and 4), filled with an acid mixture of 5% HNO₃ + 10% H₂O₂ (No. 2 and 3), and filled with silica gel (No. 5). The experimental procedure of the standard method for gas-phase sampling is described in NIEA A302.72C (NIEA, 2006). The metal concentrations of the solutions were then analyzed using ICP-AES to calculate the gas-phase metal mass.

**Digestion Procedure**

The solid specimens, namely fly ash, cullet, slag, and particulate matter, were all digested in triplicate for following analysis. The digestion procedure was modified from the standard method given in the United State Environmental Protection Agency (USEPA) Method Study 37-SW-846 Method 3050b to improve the digestion efficiency (USEPA, 1996). Specimens were pulverized to the size smaller than 148 μm to ensure consistent digestion. Each aliquot (0.3 g) was added with an acid solution composed of 1 mL HF (hydro fluoride, 37%) + 2 mL HCl (hydro chloride, 32%) + 3 mL HNO₃ (nitric acid, 65%), held in a capped Teflon vessel, and heated using a microwave digester (MARS Xpress, CEM). The heating program was: being heated from 30°C to 200°C with a heating rate of 10 °C/min, kept isothermally for 20 min, and cooled down to room temperature with ventilation. The digests were added with deionized water to 50 mL, filtrated by a mixed cellulose ester filter, and then analyzed using ICP-AES.

![Fig. 1. Process of vitrification system.](image-url)
Toxicity Characteristics Leaching Procedure
For evaluating the heavy metal mobility of the slag, toxicity characteristics leaching procedure (TCLP) was conducted in this study. The procedures for leaching, specimen shaking, dilution, and digestion followed the standard method given in the Method 1311 (USEPA 1992). The TCLP digests were then analyzed by ICP-OES (inductively coupled plasma optical emission spectrometry).

Instrumental Analysis
After pretreatment of specimens, ICP-OES was used to analyze the impinger solutions, solid specimen digests and TCLP extracts. The concentrations of Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Si, and Zn in the solutions were measured in triplicate for each sample to acquire an average value and its relative standard deviation (RSD = standard deviation/average × 100%).

Analysis of Surface and Crystalline Characteristics
Ground solid fly ash and slag (particle size smaller than 74 μm) were adhered to a metallic plate and coated with a film of Au using an ion coating sputter. The surface characteristics of solid specimens were examined using Field Emission Scanning Electron Microscopy (FE-SEM, JEOL JSM-7000). Scanning electron beams were generated by Schottky type field emission electron gun and accelerated with a voltage of 10 kV.

The crystalline phases (CPs) of solid specimens were determined using an X-ray diffractometer (XRD, Geigerflex 3063) with Ni-filtered Cu-Kα radiation. The solid specimens were powdered to a particle size smaller than 74 μm. The powdered specimens were mixed with high-purity silica powder with a Si/specimen mass ratio of 0.1 to serve as an internal standard, and then scanned by XRD in the 2θ range of 10–60° at an angular speed 4°/min. The internal standard served as an indicator for the semi-quantitative measurement of the amount of CP (Cullity and Stock, 2001). The amount of CP was approximately proportional to the summation of the area under the CP peaks, and thus, each CP was semi-quantitatively measured by comparing the total area under the CP peaks with that under Si peaks. The semi-quantitative XRD analysis, described in detail in a previous study, was used to measure the crystalline characteristics of slag (Chen et al., 2000). The amorphous volume fraction (AVF) of the specimens was then calculated using the following equation:

\[ AVF = 1 - \sum_{i=1}^{n} CP_i \]  

CP: the volume fraction of the i\textsuperscript{th} crystalline phase

RESULTS AND DISCUSSION

Composition and Mass Contribution of Input Materials
Table 1 shows the composition of input materials. The main metal composition of the fly ash was Ca (180,000 mg/kg), Si (25,500 mg/kg), Pb (19,900 mg/kg) and Zn (14,400 mg/kg). In the air pollution control processes of a incineration plant, a Ca(OH)\textsubscript{2} slurry (an acid neutralizer) is commonly injected into semidry scrubbers to remove acid gaseous pollutants. (Ca(OH)\textsubscript{2} may also be used to reduce the formation of PCDD/Fs (Wang et al., 2012).) This injection of Ca(OH)\textsubscript{2} slurry into semidry scrubbers usually produces basic fly ash (pH > 10) with high level of Ca (~150,000 mg/kg or even higher) (Jung et al., 2005). In this study, the pure fly ash had a high basicity of 4.61 and was unsuitable to be directly vitrified without addition of SiO\textsubscript{2} (Li et al., 2003). Therefore, cullet was added to decrease the basicity and served as a glass former during vitrification. The major component of cullet was Si (341,000 mg/kg) with other crust additives, such as Al (6,500 mg/kg) and Ca (3,510 mg/kg).

After the addition of cullet, the basicity of the specimens (mass ratio of (CaO+MgO)/(SiO\textsubscript{2}+Al\textsubscript{2}O\textsubscript{3}) before vitrification) was adjusted to 0.929 which was suitable for vitrification.

Table 2 shows the metal mass contribution of materials. For crust metals, Ca (99.4%), Fe (93.8%), and Mg (97.4%) were mainly from the fly ash; while Si (80.1%) was mostly contributed by the cullet. The donations of Al by the fly ash and the cullet were roughly equal. All of the anthropogenic metals came from the fly ash. Overall speaking, the cullet mainly contributed Si, acting as a glass former, to encapsulate anthropogenic metals contained in the fly ash. Ca, mainly from the fly ash, acted as a glass modifier to improve the encapsulation of the glass matrix (Kingery et al., 1976).

Composition of Output Materials
Table 3 shows the composition of output materials. The slag was majorly composed of Ca (397,000 mg/kg) and Si (232,000 mg/kg). Next to them were Fe (17,000 mg/kg), Al (10,700 mg/kg) and Mg (8,500 mg/kg). The level of Cr (223 mg/kg), Cu (771 mg/kg), and Mn (415 mg/kg) were relatively lower in one order or more. Other anthropogenic
metals, including Cd (0.134 mg/kg), Co (9.67 mg/kg), Ni (98.6 mg/kg), Pb (13.0 mg/kg), and Zn (67.5 mg/kg), were in trace amounts. The particulate phase in the flue gas had high level of Pb (315,000 mg/kg) and Zn (226,000 mg/kg). In a practical application, the particulate phase can be collected by air pollution control devices (APCDs) that commonly comprise of cyclones and baghouse filters as secondary fly ash. The high concentration of valuable metals makes the secondary fly ash worthy to be reclaimed. A previous study reported that a series of APCDs which includes baghouse filter with a good design can easily achieve > 99% (Gabites et al., 2008). Previous studies reported that vitrification might greatly reduce (> 95%) persistent toxics (e.g., PCDD/Fs and PBDEs (polybrominated diphenyl ethers)) to meet the requirements regulated by the stack flue gas emission standards of Taiwan (Lin et al., 2011; Lin et al., 2012). Therefore, it is expected that secondary pollution may be avoided in the vitrification process when suitable APCDs are used and properly operated.

Metals with high BP, including Al (99.8%), Ca (100.0%), Co (64.6%), Cr (69.4%), Cu (94.2%), Fe (89.5%), Mg (99.8%), Mn (90.2%), Ni (74.2%), and Si (99.9%), predominately existed in the slag. Among them, Cr, Cu, and Ni are regarded as hazardous substance and encapsulation deserves concerned. In a vitrification process, BP and density governed the distribution of metals. Metals with high BP and high density go into ingot; meanwhile those with high BP but low density stay in slag (Kuo et al., 2011). There was no ingot generated in this study process which is different from that vitrified other raw materials, such as spent batteries or electroplating sludge (Kuo et al., 2009; Kuo, 2012). The fly ash was mainly composed of Ca, Pb, and Zn. According to mass distribution results, Pb and Zn mainly went to the flue gas and Ca stayed in the slag as glassy matrix. Therefore, the movement of metals with high BP and high density toward ingot was not found in this experiment. This can be explained that the levels of ingot forming metals, which are usually Co, Cr, Cu, Fe, Mn, and Ni according to previous studies (Kuo et al., 2011), were too low (< 1,000 mg/kg) and thus, there are insufficient amounts to form the ingot.

**TCLP Results and Crystalline Characteristics of Slag**
Table 4. Metal mass distribution of output materials.

<table>
<thead>
<tr>
<th>Metal species</th>
<th>Slag (%)</th>
<th>Flue gas (particulate phase, gas phase)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>99.8</td>
<td>0.1 (0.1, 0.0)</td>
<td>100</td>
</tr>
<tr>
<td>Ca</td>
<td>100.0</td>
<td>0.0 (0.0, 0.0)</td>
<td>100</td>
</tr>
<tr>
<td>Cd</td>
<td>0.2</td>
<td>99.8 (99.8, 0.0)</td>
<td>100</td>
</tr>
<tr>
<td>Co</td>
<td>64.6</td>
<td>35.3 (35.3, 0.0)</td>
<td>100</td>
</tr>
<tr>
<td>Cr</td>
<td>69.4</td>
<td>30.6 (30.5, 0.1)</td>
<td>100</td>
</tr>
<tr>
<td>Cu</td>
<td>94.2</td>
<td>5.7 (5.6, 0.1)</td>
<td>100</td>
</tr>
<tr>
<td>Fe</td>
<td>89.5</td>
<td>10.5 (10.4, 0.1)</td>
<td>100</td>
</tr>
<tr>
<td>Mg</td>
<td>99.8</td>
<td>0.2 (0.2, 0.0)</td>
<td>100</td>
</tr>
<tr>
<td>Mn</td>
<td>90.2</td>
<td>9.8 (9.8, 0.0)</td>
<td>100</td>
</tr>
<tr>
<td>Ni</td>
<td>74.2</td>
<td>25.8 (25.0, 0.8)</td>
<td>100</td>
</tr>
<tr>
<td>Pb</td>
<td>99.6</td>
<td>0.4 (99.5, 0.1)</td>
<td>100</td>
</tr>
<tr>
<td>Sn</td>
<td>99.9</td>
<td>0.1 (0.1, 0.0)</td>
<td>100</td>
</tr>
<tr>
<td>Zn</td>
<td>5.8</td>
<td>94.2 (94.0, 0.2)</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 5 shows the TCLP results of the slag. The leaching concentrations for anthropogenic metals were all much below the Taiwan regulated standards. The metal ions in TCLP solution were mainly Ca (601 mg/L), Mg (17.8 mg/L), and Si (55.1 mg/L) which were non-toxic to environment. The TCLP result suggested that the slag was not a hazardous material (TEPA, 2006) and the leaching of metals would not cause secondary pollution. Fig. 3 shows the XRD patterns of the fly ash and the slag. The predominant CP of the fly ash was CaCO3. In the APCDs of an incinerator, lime slurry with excess equivalent amount was used in a semidry scrubber to remove acid gas pollutants. The unreacted lime would react with CO2, coming from the flue gas, to form CaCO3 with a crystalline volume fraction of 19.0%. The reaction for the CaCO3 formation is shown as the following equation.

\[
\text{Ca(OH)}_2 + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} (\text{g})
\]

After vitrification, the CPs of the specimen were transformed into Ca2SiO4 (larnite, nesosilicates) and CaSiO3 (wollastonite, inosilicates) with the amounts of 15.9 and 12.1%, respectively. These two CPs which are igneous rock
species are often found in a thermal melting environment with a mass ratio of CaO/SiO₂ \( \approx 1 \) (Ball et al., 1993; Dana, 2002). The AVF of the slag was 64.6\%, indicating that the structure was amorphous with significant amounts of CPs.

Fig. 4 shows the SEM images of the solid specimens. In Fig. 4(a), the fly ash shows a powdery, porous and uneven structure. After vitrification, the structure transformed into amorphous, flat and sharp edged surface with some needle-like crystals. The shape of the crystals embed on the glassy matrix surface coincided with that of CaSiO₃ and Ca₂SiO₄. The amorphous structure with obvious amount of crystals indicated that the XRD analysis was supported by the observation of SEM.

CONCLUSIONS

This study shows that vitrification can successfully stabilize fly ash. The addition of the cullet adjusted the basicity of the specimen to 0.921 which was suitable for vitrification. The cullet, acting as a glass former, provided Si to form glassy matrix to heavy metals. During vitrification, metals with low BP, including Cd, Pb and Zn, vaporized into flue gas as particulate phase. The high level of Pb (315,000 mg/kg) and Zn (226,000 mg/kg) suggested the reclamation of particulate phase being taken into consideration. Metals with high BP mostly stayed in the slag. No ingot was formed in this study due to the lack of ingot forming metals. The TCLP results showed that the leaching concentration of heavy metals was extremely low, indicating that the slag was chemically stable after vitrification. The XRD analysis identified that the major CP of the slag was CaSiO₃ and Ca₂SiO₄ which were supported by the observation of SEM. The results suggested that vitrification was a promising technology to stabilize fly ash and collect Pb and Zn as a recoverable form. Secondary environmental pollution can be avoided when suitable APCDs are used and properly operated.

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