An Experimental Study on the Melting Solidification of Municipal Solid Waste Incineration Fly Ash

Jing Gao 1, Tao Wang 2, Jie Zhao 3, Xiaoying Hu 1,* and Changqing Dong 1,4

1 National Engineering Laboratory for Biomass Power Generation Equipment, School of New Energy, North China Electric Power University, Beijing 102206, China; jinggao@ncepu.edu.cn (J.G.); dongcq@ncepu.edu.cn (C.D.)
2 Solid Waste Project Department, Beijing Aerospace Petrochemical Technology EC and EP Corporation Limited, Beijing 100010, China; wangt@calt11.cn
3 School of Energy, Power and Mechanical Engineering, North China Electric Power University, Beijing 102206, China; zjwork@ncepu.edu.cn
4 State Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources, North China Electric Power University, Beijing 102206, China
* Correspondence: huxy@ncepu.edu.cn

Abstract: Melting solidification experiments of municipal solid waste incineration (MSWI) fly ash were carried out in a high-temperature tube furnace device. An ash fusion temperature (AFT) test, atomic absorption spectroscopy (AAS), scanning electron microscope (SEM), and X-ray diffraction (XRD) were applied in order to gain insight into the ash fusibility, the transformation during the melting process, and the leaching behavior of heavy metals in slag. The results showed that oxide minerals transformed into gehlenite as temperature increased. When the temperature increased to 1300 °C, 89 °C higher than the flow temperature (FT), all of the crystals transformed into molten slag. When the heating temperatures were higher than the FT, the volatilization of the Pb, Cd, Zn, and Cu decreased, which may have been influenced by the formation of liquid slag. In addition, the formation of liquid slag at a high temperature also improved the stability of heavy metals in heated slag.

Keywords: municipal solid waste incineration; fly ash; melting solidification; minerals; heavy metals

1. Introduction

Municipal solid waste incineration (MSWI) fly ash is classified as hazardous waste [1], because it may contain polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), as well as heavy metals, such as lead, cadmium, chromium, mercury, and zinc. MSWI fly ash management includes separation processes, thermal methods (sintering, melting, and vitrification), and solidification/stabilization technology [2,3]. The melting solidification of fly ash has received attention, because it stabilizes heavy metals and simultaneously removes harmful organics, such as dioxins/furans [4]. Furthermore, the non-volatile heavy metals can be solidified in the dense lattice structure of glassy slag, which reduces the possibility of heavy metal dissolution and, thus, realizes the control of heavy metal [5]. Previous studies in Japan have shown that melting treatment is a promising thermal technology for MSWI fly ash [6].

The content and chemical speciation of heavy metals in MSWI fly ash are closely related to the composition of municipal solid waste. The sources of heavy metals in municipal solid waste are complex, such as Cd, Zn, and Hg in batteries, Cd in pigments and stabilizers in plastics, and Cu, Zn, and Cr in printing inks and paints. Abanades et al. [7] divided heavy metals into three main families, according to their volatility: Cr and Ni, which were mainly found in bottom ash. Pb and Zn are partially volatilized. Hg and Cd highly volatilize during incineration. The volatile heavy metals, except Hg, can adsorb on the surface of fly ash particles during flue gas cooling processes [7,8].
The volatilization of heavy metals from fly ash during the melting process, which can cause secondary pollution, has been widely observed. There are two treatment methods for heavy metals in fly ash: (1) the recovery of heavy metals by promoting the volatilization of heavy metals [9,10] and (2) the solidification of heavy metals in sinter/glass slag by inhibiting the volatilization of heavy metals [11,12]. The migration of heavy metals is influenced by the composition of fly ash, reaction temperature, and atmosphere [13–15]. Chlorides (CaCl₂, KCl, NaCl) in fly ash, especially CaCl₂, can promote the volatilization of heavy metals [16,17]. Most of the chlorides can be recovered by washing [18], thus inhibiting the volatilization of heavy metals during heat treatment [10]. In addition, CaO and SiO₂ in fly ash can influence the migration of heavy metals by affecting the melting process at a high temperature [11,19]. The leaching behavior of heavy metals is an important indicator in environmental monitoring, and it is the basis of distinguishing treatment and disposal methods of MSWI fly ash.

Melting solidification experiments of this fly ash were carried out in a high temperature tube furnace device in order to provide a basis for the treatment method of MSWI fly ash. First, physicochemical properties, including the chemical composition, microstructure, and melting characteristics, of fly ash were investigated. Second, phase analysis and an investigation of the target heavy metal contents (Pb, Cd, Zn, and Cu) in raw fly ash and heated slag were conducted in order to explain the mineral transformation and the migration of heavy metals during the melting treatment process. Last, a characteristic toxicity leaching procedure was applied to evaluate the chemical stability of the heated slag.

2. Method

2.1. Materials and Characterization

The raw fly ash used in the experiment came from the bag filter of a municipal waste incineration plant (circulating fluidized bed boiler) in Shanxi Province. The flue gas desulphurization system consists of CaCO₃ dosing equipment in a furnace and a semi-dry circulating fluidized bed flue gas purification tower. The chemical compositions of fly ash were characterized through X-ray fluorescence spectrometry (ARL ADVANT-XP). The mineral compositions of fly ash were analyzed while using X-ray diffraction (SHIMADZU XRD-6000). The scanning angle (2 Theta) was from 3° to 70° at a scanning speed of 6°/min. The X-ray diffraction (XRD) pattern was analyzed while using the computer software package MDI Jade. A scanning electron microscope (SEM) (HITACHI S-4800) was used to observe the surface morphology of raw fly ash. The melting behavior of raw fly ash was detected using a high-temperature ash fusibility tester. The experiments were conducted according to the procedures that were outlined in the Chinese standard GB/T219-2008 [20]. The ash fusion temperatures (AFTs) were characterized based on the initial deformation temperature (IDT), softening temperature (ST), hemispheric temperature (HT), and flow temperature (FT).

2.2. Experimental Devices and Methods

Figure 1 depicts the fly ash melting system. It is composed of a gas system, a horizontal high-temperature corundum tube furnace, and a gas-cleaning device. The corundum crucible containing 10 g of dried fly ash was placed at the center of the tube when the furnace temperature reached the target temperature (950 °C, 1000 °C, 1050 °C, 1100 °C, 1150 °C, 1200 °C, 1250 °C, and 1300 °C) with a 100 mL/min. air flow rate. After 30 min., the crucible was taken out and cooled. The exhaust gas was purified by activated carbon before being discharged.

2.3. Heavy Metal Concentration

Atomic absorption spectroscopy (AAS) determined the target heavy metals content in the raw fly ash and heated slag after digestion by applying the HCl-HNO₃-HF-HClO₄ method according to the Chinese standard GB17141–1997 [21]. An amount of 0.1 g sample was tested in each experiment and each sample was tested twice.
The surface morphology and specific surface area of fly ash particles affect the surface energy of the particles, which is the driving force of the sintering process. The finer the specific surface area, the higher the surface energy is, and the stronger the surface activity of fly ash particles [24,25]. The particle size of the MSWI fly ash is mainly concentrated in a range of 5–30 μm. The morphologies of fly ash particles under SEM as shown in Figure 2 were varied: (a) the particles were spherical with clastic particles that were attached to the surface. (b) Irregularly shaped polymers formed from the accumulation of particles of

![Figure 1. The fly ash melting system.](image)

### 2.4. Leaching Tests

The leaching behavior of heavy metals from raw fly ash and heated slag was evaluated through a toxicity characteristic leaching procedure according to Chinese standard HJ/T 300–2007 [22]. Firstly, the extraction solution that was used in the experiment was determined. An amount of 96.5 mL of deionized water was added to 5.0 g of raw fly ash, and the mixture was magnetically stirred for 5 min. at a high speed. The pH value was determined to be 10.67. Afterwards, 3.5 mL of 1 mol/L HCl was added to the solution, which was heated at 50 °C for 10 min. and cooled to room temperature. The measured pH value of the solution was 5.78. This and previous measured pH values were greater than 5.0. Therefore, the acetic acid solution with a pH value of 2.64 ± 0.05 was selected as the extract solution. Afterwards, the sample was mixed with an acetic acid solution (pH = 2.64 ± 0.05) at a liquid-to-solid ratio of 20:1, and then flip oscillated for (18 ± 2 h) at a speed of 30 ± 2 r/min. The leaching solution was then extracted through filtration while using a 0.8 μm membrane filter. The concentrations of the target heavy metals were examined using AAS after digestion by applying the HNO₃-HClO₄ method according to the Chinese standard HJ787–2016 [23]. An amount of 2.5 g sample was tested in each experiment and each sample was tested twice.

### 3. Results and Discussion

#### 3.1. Characteristics of the MSWI Fly Ash

XRF and AAS detected the compositions of the raw fly ash. Table 1 shows the main chemical compositions and heavy metal content. The main compositions of fly ash included CaO, SiO₂, Al₂O₃, chloride, and sulfur-containing compounds. The content of Zn, Cu, and Pb were high, while the content of Cd was relatively low.

<table>
<thead>
<tr>
<th>Chemical compositions</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Cl</th>
<th>Fe₂O₃</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt.%)</td>
<td>30.09</td>
<td>17.91</td>
<td>11.9</td>
<td>1.26</td>
<td>2.35</td>
<td>5.45</td>
<td>5.23</td>
<td>4.4</td>
<td>1.97</td>
</tr>
<tr>
<td>Heavy metal</td>
<td>Cd</td>
<td>Pb</td>
<td>Zn</td>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Content (mg/kg)</td>
<td>60.9</td>
<td>677.4</td>
<td>1166.3</td>
<td>1070.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
various shapes, including spherical, flake, and block particles. (c) A bar polymer formed from the accumulation of rod and columnar particles with intergranular porosity. (d) A small number of rod-shaped particles were distributed in the fly ash. (e) There was a small amount regular blocks in the fly ash. The morphological characteristics under the SEM scanning of fly ash are consistent with the results of 60 groups of fly ash found in a study conducted by Guo et al. [26].

(a) Spherical particle.

(b) Irregularly shaped polymer.

(c) Bar polymer.

Figure 2. Cont.
Figure 2. SEM micrographs of fly ash particles: (a) Spherical particle; (b) Irregularly shaped polymer; (c) Bar polymer; (d) Rod-shaped particle; (e) Block.

Table 2 shows the elemental content of fly ash particles with different morphologies that were detected by EDS. Spherical and rod-shaped particles (Zones 1 and 5) were mainly composed of Ca, Si, Al, and O, and small amounts of Cu were attached to the spherical particles. Polymers (Zones 2, 3, and 4) also contained Cl and S, in addition to Ca, Si, Al, and O. The block-shaped particle (Zone 6) was mainly composed of Cl, Na, Ca, and O. Few heavy metals were detected on the surface of the fly ash particles due to their low content. During the melting process, spherical particles, rod-shaped particles, and polymers formed a glass slag matrix, which can immobilize heavy metals.

Table 2. The elemental content of fly ash particles with different morphologies (EDS).

<table>
<thead>
<tr>
<th>Element</th>
<th>Zone 1</th>
<th>Zone 2</th>
<th>Zone 3</th>
<th>Zone 4</th>
<th>Zone 5</th>
<th>Zone 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>41.75</td>
<td>38.67</td>
<td>42.41</td>
<td>37.12</td>
<td>53.33</td>
<td>20.17</td>
</tr>
<tr>
<td>Na</td>
<td>0.39</td>
<td>0.58</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6.45</td>
</tr>
<tr>
<td>Mg</td>
<td>0.23</td>
<td>0.38</td>
<td>0.52</td>
<td>2.25</td>
<td>0.18</td>
<td>0</td>
</tr>
<tr>
<td>Al</td>
<td>8.13</td>
<td>8.79</td>
<td>1.53</td>
<td>2.25</td>
<td>11.42</td>
<td>1.17</td>
</tr>
<tr>
<td>Si</td>
<td>15.55</td>
<td>14.4</td>
<td>2.5</td>
<td>4.33</td>
<td>18.3</td>
<td>1.7</td>
</tr>
<tr>
<td>S</td>
<td>0.79</td>
<td>1.92</td>
<td>1.01</td>
<td>6.1</td>
<td>1.63</td>
<td>0.61</td>
</tr>
<tr>
<td>Cl</td>
<td>0.76</td>
<td>3.94</td>
<td>14.6</td>
<td>9.82</td>
<td>2.28</td>
<td>62.17</td>
</tr>
<tr>
<td>K</td>
<td>2.49</td>
<td>6.33</td>
<td>0.42</td>
<td>1.25</td>
<td>1.21</td>
<td>0.58</td>
</tr>
<tr>
<td>Ca</td>
<td>26.58</td>
<td>22.02</td>
<td>35.49</td>
<td>37.33</td>
<td>11.02</td>
<td>5.76</td>
</tr>
<tr>
<td>Ti</td>
<td>1.45</td>
<td>1.02</td>
<td>0.53</td>
<td>0.85</td>
<td>0</td>
<td>0.23</td>
</tr>
<tr>
<td>Fe</td>
<td>1.45</td>
<td>1.31</td>
<td>0.99</td>
<td>0.94</td>
<td>0.62</td>
<td>1.15</td>
</tr>
<tr>
<td>Cu</td>
<td>0.43</td>
<td>0.65</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3 shows the ash fusion temperatures of MSWI fly ash. From 1167 °C to 1211 °C, liquid slag affected the mass transfer rate of the heavy metals that formed [9]. The melting temperature also affects the energy consumption and equipment investment in the melting treatment process.
The mineral transformation behavior of the fly ash during the melting process is complex. Figure 3 shows the phase characterizations of the raw fly ash and the heated slag at 950 °C, 1250 °C, and 1300 °C in order to obtain the mineral transformation behavior.

![X-ray diffraction (XRD) patterns of raw fly ash and heated slag.](image)

The raw fly ash mainly consists of nine minerals, including gehlenite (Ca$_2$Al$_2$SiO$_7$), quartz (SiO$_2$), anhydrite (CaSO$_4$), halite (NaCl), sylvite (KCl), periclase (MgO), calcite (CaCO$_3$), hematite (Fe$_2$O$_3$), and hydroxylapatite (Ca$_5$(PO$_4$)$_3$(OH)), as shown in Figure 3. In addition, the fly ash contains amorphous substances and the crystallinity determined using Jade software [27] was approximately 79%. When the fly ash was heated at 950 °C, a new, OH-rich mineral phase, grossular (Ca$_3$Al$_2$(SiO$_4$)$_2$(OH)$_4$) was formed. The crystallinity decreased to 67%. At 1250 °C, gehlenite became the main phase in the slag, which was due to the decomposition of CaCO$_3$ and CaSO$_4$ at high temperatures and the reactions with Al$_2$O$_3$ and SiO$_2$. Moreover, there is no NaCl or KCl diffraction peak in the XRD pattern, whereas Na and K were detected in the slag, as shown in Table 4. This may be due to the fact that Na and K were present in other forms. The possible transformation behavior for NaCl or KCl may be: (1) volatilization, (2) the reactions with SiO$_2$/Al$_2$O$_3$/PbO [28–30], and Na and K would enter silicate matrix in the form of oxides. The crystallinity continued to decrease to 52%. When the temperature increased to 1300 °C, all of the crystals transformed into molten slag and formed a glassy slag after quenching.

### Table 4. The main chemical compositions (XRF) of heated slag.

<table>
<thead>
<tr>
<th>Heat Temperature</th>
<th>Chemical Compositions (wt.%)</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>SO$_3$</th>
<th>Cl</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>950 °C</td>
<td></td>
<td>28.29</td>
<td>27.8</td>
<td>19.53</td>
<td>2.63</td>
<td>1.99</td>
<td>1.73</td>
<td>5.75</td>
<td>4.13</td>
<td>3.56</td>
</tr>
<tr>
<td>1250 °C</td>
<td></td>
<td>28.82</td>
<td>34.57</td>
<td>21.41</td>
<td>1.62</td>
<td>0.679</td>
<td>0.503</td>
<td>1.65</td>
<td>3.07</td>
<td>3.54</td>
</tr>
<tr>
<td>1300 °C</td>
<td></td>
<td>28.44</td>
<td>34.35</td>
<td>21.42</td>
<td>1.53</td>
<td>0.62</td>
<td>0.426</td>
<td>1.45</td>
<td>4.1</td>
<td>3.53</td>
</tr>
</tbody>
</table>
3.3. Volatilization of Heavy Metals

The fate of heavy metals during the melting process is expressed through volatilization fraction $R_v$ [9], as shown in the following equation:

$$R_v = \left(1 - \frac{c_d \times m_a}{c_b \times m_b}\right) \times 100\%$$

where $c_d$ is the concentration of heavy metal in the slag after treatment, mg/kg; $m_a$ is the mass of the slag after treatment, g; $c_b$ is the concentration of heavy metal in the sample before treatment, mg/kg; and, $m_b$ is the mass of the sample before treatment, g.

Cd and Pb volatilize more easily than Zn and Cu, as shown in Figure 4. The volatilization fractions of Cd and Pb at 950 °C were 48.5% and 75.7%, respectively, and they increased rapidly to 92.0% and 95.8% at 1050 °C, respectively. As the temperature increased, the volatilization of Cd and Pb slightly increased. When the temperature reached 1200 °C (>HT), the volatilization of Cd and Pb decreased. Cd and Pb are mainly in the form of volatile chlorides and oxides in the MSWI fly ash [31–33], but these were quickly removed. Therefore, it was not easy to react with minerals to form stable compounds at high temperature.

![Figure 4. Effect of temperature on the volatilization of Cd, Pb, Zn, and Cu.](image_url)

The volatilization of Zn did not significantly change from 950 °C to 1100 °C and it stabilized at 43.0–45.1%. There was an increase in this volatilization as temperature increased and, when the temperature reached 1150 °C, it decreased. As temperature increased, Zn could react with SiO$_2$ and Al$_2$O$_3$ and form stable metallic species, such as Zn$_2$SiO$_4$/ZnAl$_2$O$_4$ [16,34], which can also promote the immobilization of Zn. In addition, the production of liquid slag can also promote reactions that can further inhibit Zn volatilization.

The volatilization of Cu increased with the increase of temperature. There was an increase at 1050 °C, which may have been an experimental error. After reaching a maximum of 81.5% at 1250 °C, it began to decline significantly. At a high temperature, under an oxidizing atmosphere, Cu can transform non-volatile CuO and Cu$_2$O [35]. When the temperature is higher than the FT, the liquid slag promotes the immobilization of Cu.

When the temperature is below 1200 °C, the volatilization fraction of heavy metals was Pb > Cd > Zn > Cu. Pb, Cd, and Cu had the same variation trend as the temperature increased, the volatilization increased first, and then decreased after reaching the FT. When compared with Pb, Cd, and Cu, Zn first began to show a downward trend. When the temperatures were higher than the FT, the volatilization of all four heavy metals decreased, which may be due to the following two reasons: first, heavy metals in the fly ash were more likely to enter a vitreous slag matrix as the temperature increased, so the volatilization reduced. Second, the liquid slag filled in the gaps of fly ash particles and led to densification, which increased the volatilization resistance of the heavy metals.
3.4. Leaching Behavior of Heavy Metals

Figure 5 shows the leaching concentrations of Cd, Pb, Zn, and Cu from the fly ash and heated slag. In the raw fly ash, the concentrations of Cd (1.51 mg/L) and Pb (1.49 mg/L) exceeded the limits of the Chinese standard GB16889-2008 (Cd: 0.15 mg/L; Pb: 0.25 mg/L) [36]. Therefore, fly ash cannot be disposed in a landfill without further treatment. When the heating temperatures were below 1200 °C, the leaching concentration of Cd, Pb, Zn, and Cu varied greatly as the temperature increased. When the temperature increased above 1200 °C, the leaching concentration of Cd, Pb, Zn, and Cu decreased significantly. This indicates that the formation of liquid slag at a high temperature improved the stability of the heavy metals in the products and reduced the migration of Cd, Pb, Zn, and Cu. This means that the stability of heavy metals in the glass slag was greater than that in the sintering slag.

Figure 5. Leaching concentrations of Cd, Pb, Zn, and Cu from the fly ash and heated slag.

4. Conclusions

Fly ash contains a large number of particles that can form a glass matrix and a small amount of chloride particles. As the temperature increased, oxide minerals transformed into gehlenite. When the temperature increased to 1300 °C, which was 89 °C higher than the FT, all of the crystals transformed into molten slag, and they formed a glassy slag after quenching. When the heating temperatures were higher than the FT, the volatilization of Pb, Cd, Zn, and Cu decreased, which may have been influenced by the formation of liquid slag. In addition, the formation of liquid slag at a high temperature improved the stability of the heavy metals in the heated slag. After melting solidification, the slag can be disposed of in a landfill according to the Chinese standard GB16889-2008 [36].
**Author Contributions:** Conceptualization, J.G. and X.H.; methodology, T.W.; validation, J.Z.; formal analysis, J.G.; investigation, J.G.; resources, X.H.; data curation, J.Z.; writing—original draft preparation, J.G. and T.W.; supervision, J.Z. and X.H.; Writing—Review & Editing, C.D. All authors have read and agreed to the published version of the manuscript.

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