Abstract

Characteristics of heavy metals during heat-treatment municipal solid waste incinerator (MSWI) fly ash were investigated in this paper. The experiment was performed using a pilot-scale oil furnace in the range 800-1350°C. In this work we investigated the effect of temperature on solidification efficiency, evaporation of heavy metals and on composition change, X-ray diffractometer (XRD), the leach toxicity of molten slag. The results showed that the main contents, solidification efficiency and evaporation of heavy metals had a tremendous change between 1150-1260°C. With temperature increasing, the percentage of CaO, SiO2 and Al2O3 increased, and SO3, K2O, Na2O and Cl decreased. Especially in 1260°C, the four compositions decreased sharply from 43.72% to 0.71%. Finally, the leaching concentrations of all heavy metals in molten slag were far lower than the standard values of TCLP.

1. Introduction

In recent years, municipal solid waste incineration (MSWI) has become a popular method to treat MSW in many countries, such as Japan and several European countries, for the method has the merits of volume reduction up to 90% [1,2] and recovery of much of the energy bound in the waste. By 2010, there are about 104 MSWI incineration plants with a total yearly treatment capacity of 31.0 million tons in China.

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Keyword: heavy metals; MSWI fly ash; pilot-scale
Nevertheless, MSWI generates a large amount of fly ash up to the proportion of 3–5 wt% of the original amount of waste. Due to the presence of leachable heavy metals, high concentrations of soluble salts and residual amounts of hazardous organics (e.g. dioxins) [2], this waste is classified as hazardous in many countries and must be treated prior to disposal [3,4]. These hazardous substances in fly ash can pollute groundwater and soils. Some of them are difficult to degrade, they accumulate and are harmful to organisms when expose to organisms. Thus, fly ash must be detoxified or decontaminated prior to disposal or reuse.

As a method of fly ash treatment, the melting and solidification has been widely and deeply studied because the process can fix the heavy metal and other toxic materials in the melting residues and so not to pollute the environment.

Jakob [5] studied the effect of temperature on the evaporation of heavy metals, Young jun [6] studied the characteristic of melting residues and the leachability of heavy metals, Chan and Stucki [7,8] investigated the effect of various parameters (such as temperature, time, and the kinds of chloride), on the evaporation of heavy metals, and Ryo Yosiie [9] studied the factors that influenced the volatilization of heavy metals in melting process.

In this paper, the migration characteristics of heavy metals during the vitrification of MSWI fly ash were investigated. The experiment was performed in a high-temperature melting furnace in the range 800–1350°C.

2. Experimental

2.1. Materials

The fly ash from a MSW incineration plant in a South City was used as the materials. The particle sizes are about 90-200μm in the untreated fly ash, real density is 2800kg/m3, and percentage of moisture is 0.9%. Main chemical compositions of fly ash are Ca, Si, Al, Cl, S and K, which exist with the oxidation. The elementary compositions of the samples are given in Table 1.

| Chemical compositions of fly ash (m/m %) |
| CaO | SiO₂ | Cl | SO₃ | Al₂O₃ | K₂O | Na₂O | P₂O₅ | Fe₂O₃ |
| 32.77 | 10.59 | 20.59 | 10.74 | 3.23 | 8.58 | 3.81 | 1.53 | 3.28 |

2.2. Analysis methods

The fly ash was mixed completely, desiccated for 24h at 105°C till get constant weight, and then preserved. The experiment was performed in a high-temperature furnace between 800 -1350°C. The sample of 40g fly ash was cased into ten corundum crucibles of 200mL and put them into the furnace in turn.

When temperature reached the needed point, made the furnace temperature in hypothesis temperature constant 30min, then took out the crucible, rapidly poured the melting residues into the water. The experiment used the air atmosphere, gas flow 5L/min.

The melting residues were analyzed by X-ray Fluorescence (XRF, PW-2402); Phase analysis was analyzed by X-ray Diffraction (XRD, PW-1700); Toxicity characteristic leaching procedure (TCLP) tests were commonly used to characterize the potential toxicity of heavy metals.
3. Result and discussion

3.1. The effect of temperature on the components of the melting residues

The results showed that the fly ash didn’t melt in the range 800 -1100°C, and the fly ash was yellow or yellow brown, soft with tinny holes on it, it was named as ‘furnace ash’. With temperature increasing, fly ash was becoming darker and hardness. When the temperature reached 1200°C, the fly ash on the surface of crucible began to melt, yet the fly ash at the bottom didn’t. When it was 1260°C, both upper and lower layers of ash began to melt, but the fluidness was not good, when it cooled down, compact, dark black and surface-glazed residues could form. When the temperature was 1350°C, the fluidness of fly ash was very good. The characteristic of fly ash was shown in Table 2.

Table 2. The melting state of MSW fly ash

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1200</th>
<th>1260</th>
<th>1350</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>State</td>
<td>Surface melted</td>
<td>Melted with bad fluidness</td>
<td>Melted with good fluidness</td>
</tr>
</tbody>
</table>

Figure 1 showed, the percentage of CaO, SiO2 and Al2O3 increased with the increase of temperature, especially the SiO2. When it was 900°C, the percentage of SiO2 was 12%; when it came to 1260°C, the percentage increased to 36.5%. Compared with SiO2, CaO and Al2O3 increased less than 10%. During the whole process, CaO concentration was the highest and stable (40%), for Al2O3, the highest concentration was 12%. The percentage of SO3, K2O, Na2O and Cl decreased with the increase of the temperature. When it was 1260°C, these four elements decreased sharply from 43.72% to 0.71%, when it was 1350°C, these four elements nearly disappeared. The decomposition of K2O, Na2O and Cl happened through the whole process, yet the decomposition of SO3 only occurred from 1150°C to 1260°C.

![Fig.1 Changes of the main compositional contents during vitrification process](image_url)
The phase analysis was carried out on the untreated fly ash and melting residues to study the migration characteristics of all the substances. Figure 2 showed the XRD analysis for the fly ash under different temperatures. It showed that the crystal phase of untreated fly ash mainly was made up by NaCl, KCl and CaCl₂·Ca (OH)₂·H₂O, some high concentration substances such as SiO₂, Al₂O₃ and S stayed as uncrystal state. When the temperature rose to 1100°C, CaSO₄ and Ca₂Al(AlSi)O₇ became prominent. Then the temperature came to 1150°C, the signal of Ca₂Al(AlSi)O₇ became highest yet the CaSO₄ decreased, which showed that CaSO₄ began to decompose under such temperature, thus the concentration of S in the fume increased. For NaCl and KCl, they have been vaporized completely; when the temperature rose to 1350°C. All the substances phases were destroyed and became uncrystal.

![XRD patterns of the fly ash](image)

It could be estimated from figure 1 and figure 2 that sodium salts and potassium salts exist as chloride and then evaporate, the increase of CaO, Al₂O₃ and SiO₂ was mainly due to the evaporation of other substances. The main reactions are as followed:

- \( \text{CaCl}_2\text{Ca (OH)}_2\text{H}_2\text{O} \rightarrow \text{CaO + CaCl}_2 + 2\text{H}_2\text{O} \) (900°C–1100°C)
- \( \text{M} + \text{CaCl}_2 \rightarrow \text{MCl}_2 + \text{CaO} \)
- \( \text{CaO + SO}_3 \rightarrow \text{CaSO}_4 \) (900°C–1100°C)
3.2. The effect of temperature on the efficiency of evaporation

Evaporation rate not only indicates the intensity for the reaction of the components during the vitrification, but also could regards as the parameters to justify the effect of vitrification. The efficiency of evaporation (EVP) can be defined as followed:

\[ EVP = \frac{\text{mass of fly ash} - \text{mass of melting residues}}{\text{mass of fly ash}} \times 100\% \]

In the range 800-1150°C, the evaporation rate of fly ash became smooth (figure 3), and only rose 9%; when temperature rose to 1150-1260°C, the evaporation rate increased 36.8% sharply. At this range, the fly ash began to melt and turned fluid gradually. Then, with the temperature increased, evaporation rate became smooth. From figure 1, 2 and 3, we could see that the evaporation was mainly due to the degradation of chloride substances with low point (such as CaCl₂, KCl and NaCl) and the evaporation of low boiling point metals. During the range of 1150-1260°C, the chloride substances nearly decomposed completely because of the intense reaction between the components of the fly ash, element S participated the reaction with the form of CaSO₄ and then was decomposed to go to the fume, and caused the increase of evaporation rate of fly ash. It is known that the more the concentration of Cl and S in the fly ash, the more the evaporation rate.

Fig.3 Influence of melting temperatures on evaporation of fly ash


3.3. The effect of vitrification temperature on the solidification efficiency

During the vitrification of fly ash, most of high boiling point heavy metals were fixed in the compact crystal lattice of the melting residues, and so the leaching concentration of the metals decreased sharply. For the low boiling point metals, they were evaporated as gas and increased the load for the treatment and caused further-pollution. In order to understand the characteristic of the vitrification for heavy metals and carry on the analysis of the concentration of heavy metals, the solidification efficiency \( K \) was introduced as followed:

\[
K = \frac{\text{concentration of heavy metals in the melting residues} \times \text{mass of melting residues}}{\text{concentration of heavy metals in fly ash} \times \text{mass of fly ash}}
\]

Figure 4 showed that the solidification efficiency of the heavy metals in the melting residues decreased with temperature increasing. The elements Pb, Cd and Zn were easily-evaporated metals and they existed as the form of oxidation and chloride substance on the surface of the fly ash. Therefore, with temperature increasing, the solidification efficiency decreased because these heavy metals were easily released. The solidification efficiency of Cd was the lowest; the efficiency was 4% in 800°C. However, it nearly evaporated completely in 1000°C. Cr belongs to the difficult-evaporated metals and mainly existed inside the melting residues in 1150°C, and now the evaporation began to take place. The solidification efficiency of Cr changed little when the temperature was less than 1000°C, and its solidification efficiency could reach 100%. When the temperature came to 1200°C, the solidification efficiency decreased to 75%; the binding efficiencies of Pb and Cu at 800°C were 78.5% and 100% respectively. When it was 1260°C, the binding efficiencies decreased sharply to 2.3% and 8.6%. The elements Cu, Pb and Cd evaporated with the form of chloride substance [10]. For Cr and Zn, they formed the compounds like \( \text{Zn}_2\text{SiO}_4 \) and \( \text{ZnAl}_2\text{O}_4 \) and restrained the evaporation.
3.4. The result of TCLP for the melting residues

Toxicity characteristic leaching procedure was used to test the melting residues for different temperature after the residues were minced to 450µm in diameter.

Table3. Results of toxicity characteristic leaching procedure of melting residue

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pb</th>
<th>Cu</th>
<th>Zn</th>
<th>Cr</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1150</td>
<td>0.09</td>
<td>1.01</td>
<td>29.8</td>
<td>0.29</td>
<td>0.01</td>
</tr>
<tr>
<td>1260</td>
<td>0.02</td>
<td>1.35</td>
<td>3.87</td>
<td>3.01</td>
<td>ND</td>
</tr>
<tr>
<td>1350</td>
<td>0.05</td>
<td>0.09</td>
<td>2.12</td>
<td>0.1</td>
<td>ND</td>
</tr>
<tr>
<td>Fly ash</td>
<td>14.48</td>
<td>14.72</td>
<td>41.8</td>
<td>0.19</td>
<td>1.98</td>
</tr>
<tr>
<td>Limit value</td>
<td>5</td>
<td>—</td>
<td>—</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

*——ND （No detect）

Figure 3 showed every metal leaching concentration of the melting residues didn’t exceed the limit value, thus they didn’t belong to harmful wastes. Since the melting residues were minced to 450µm, the metals inside the residues exposed, thus the leaching concentration was much higher than the actual value. But in reality, the ash couldn’t reach such small volume, then the concentration could regard as the highest since they were under extreme condition.

4. Conclusion

The results showed that the solidification efficiency for low boiling point metal elements such as Pb, Cd and Zn decreased prominently with temperature going up. But for Cr, Its solidification efficiency was 95%. The effect of temperature on the components of the melting residues was great. With temperature increasing, the concentration of CaO, SiO₂ and Al₂O₃ increased rapidly, yet the concentration of SO₃, K₂O, Na₂O and Cl decreased sharply. The leaching concentrations of all heavy metals in molten slag were far lower than the standard values of TCLP.

Acknowledgements

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Reference


