

Experimental Investigation on Melting Treatment of Municipal Solid Waste Incinerator Fly Ash

Xuetao Wang¹, Baosheng Jin¹, Zhaoping Zhong¹, Xiaojian Dang¹

¹Key Laboratory of Clean Coal Power Generation and Combustion Technology
of Ministry of Education, China

Institute for Thermal Power Engineering, Southeast University, Nanjing 210096, China

Abstract: Melting process was used to convert hazardous heavy metals fly ash from municipal solid waste incinerator into useful products. Some parameters such as chemical composition, microstructure morphology, mineralogy, leaching characteristic, of slag melted from fly ash were investigated at 1100 to 1400 °C temperature (for 90 min). Good melting effects are achieved when the temperature at 1300 °C. It showed that the molten sample became full smooth, much hard in surface structure, while the section of the molten sample had lustrous or no apparent aperture. The raw fly ash had completely melted. Compared with the changes of chemical composition and melting effect by X-Ray diffractometry, for the raw ash and molten slag. The results indicated that the main crystalline phases of raw fly ash were halite, sylvite, quartz, calcite, anhydrite, larnite and mayenite. Samples with a high ratio have a crystalline matrix consisting of CaS, gehlenite, Ca-Al-silicates mellite, anorthite and an interstitial glassy phase. The leaching test on melted slags samples showed that the fly ashes were successfully detoxified to meet of the limits toxicity characteristic leaching procedure (TCLP) in China and United States. After melting, the volatile heavy metals, like Cd and Pb were found in the gas collected, where Zn, Cr, and Ni were fixed into the melted slag. The concentration of heavy metal Zn, Cr, Pb, Cu, and Cd decreased distinctly. Thus, melting process is efficient for heavy metals stabilization in fly ash from municipal solid waste incinerator.

Keywords: municipal solid waste, fly ash, melting, heavy metals, morphology, leachability

1. INTRODUCTION

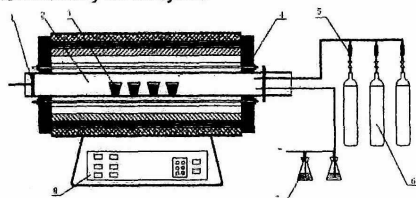
Incineration is a technique widely used for the treatment of municipal solid waste (MSW) in many industrialized countries. The amount of fly ash from MSWI is steadily increasing year by year with the expansion of MSWI in China, so it is becoming more important to detoxify fly ash. Recently, the fly ash melting process is often used to reduce the volume of waste and to prevent hazardous heavy metals from leaching into the soil at landfill sites, to secure the final disposal sites [1]. Jakob et al. [2] studied the evaporation of Zn, Pb, Cd and Cu in an ESP ash in various atmospheres at temperatures between 670 °C and 1300 °C, and found that the evaporation was most effective at temperatures just below the melting range of the ash 1000-1100 °C. Fray [3] reported that Zn, Pb and Cd could be separated from arc furnace dust, which was mainly iron oxide, when the dust was heated with chlorine in air.

In this study, the chemical compositions, microstructure morphology, mineralogy, leaching characteristic, of slag melted from fly ash were investigated at 1100 to 1400 °C temperature for 90 min. Based on the results of investigation, some significant factors for melting process of fly ashes were suggested as conclusions.

2. MATERIALS AND METHODS

2.1 Fly ashes samples

The fly ashes used in this study came from a MSW incineration plant in Shanghai, China. Fly ash was collected from a stoker-type French incinerator, which handled 1000 ton/day MSW. The feed MSW is combusted in the grates of the primary combustion chamber is about 950 °C; the flue gases produced are re-combusted in the second combustion chamber at 1100 °C. The flue gases are cooled through heat exchangers, semi-dry scrubbers and electrostatic precipitators. The fly ash used for experiments were taken from a MSW incinerator using Ca(OH)₂ in a semidry scrubbing process for flue gas control. Fly ash samples collected from the bag filters were dried at 105 °C for 24 h, then samples were passed through a 100 mesh sieve and mixed well by a tumbling mixer in the laboratory for analyses.



1-baffle; 2-tube of Al₂O₃; 3-crucible; 4-stick of quartz-molybdenum; 5-flowmeter; 6-atmosphere; 7-absorber; 8-control unit of temperature

Figure 1: Scheme of fly ash from MSWI melting apparatus

2.2 Heating apparatus and analytical instruments

A quartz tube furnace; Model CTF 16/75/610, with a programmed temperature controller, Model 902 P; a quartz tube, 100 cm long and 6 cm i.d. to contain the sample boat and to confine the heating space; a gas absorber containing 5% HNO₃ to absorb the volatile metal chloride; air supply from a cylinder; graphite crucibles, 15 mL size; inductively coupled plasma spectrometer, POEMS-II, scanning electron microscope, JSM-5610LV.

2.3 Chemical analysis

A tube furnace was used for the fly ash melting treatment. The furnace has flexible operating parameters, such as temperatures, melting time and atmospheres. Sample ash of about 3.0 g was put in graphite crucible and then introduced into the furnace. The samples in the crucibles were rapidly heated up by radiation in the tube furnace. The heating rate to the hold temperature, which was set in the range between 1100 °C and 1400 °C, was 200 °C/min. The samples were heated to the desired temperature then held constant for proper melting time.

Solid samples, including incinerator fly ash and slag, were all pulverized to the size that passed through a Teflon 100 mesh sieve to ensure uniform digest efficiency. Samples were weighed precisely and digested in vessels hermetically at 180 °C for 5 h with an acid mix, which was composed respectively of 1, 5 and 10 mL of hydrofluoric acid. The digests were diluted to exactly 25 mL, filtrated by a 0.8 µm mixed cellulose ester filter and analyzed. The toxicity characteristic leaching procedure (TCLP) was carried out to assess the mobility of hazardous metal species in incinerator fly ash and melted slag. The extracts of TCLP were digested and diluted to a fixed volume following the detail procedure given in Method 1311 and then analyzed^[4]. The targeted heavy metals contents were determined with flame atomic absorption spectroscopy after the digestion process. Heavy metals species in solid sample digests and TCLP extracts were analyzed with an inductively coupled plasma-atomic emission spectrometry (ICP-AES). Arsenic and mercury were analyzed by atomic absorption.

3. RESULTS AND DISCUSSION

3.1 Chemical composition of fly ash

Fly ash from a stoker-type French incinerator at 950 °C was used as a sample. The chemical compositions of fly ash are analyzed by X-ray fluorescence (XRF) and given in Table 1. The amounts of several major elements are calculate regarding as their oxides. Fly ash is rich in CaO, SiO₂, Al₂O₃, Na₂O, and Fe₂O₃, which may act as glass-forming, melting and matrix-modifier oxides during the process. This fly ash contains a lot of zinc, lead, cadmium, Cr and copper, because the source of municipal solid waste contains many kinds of metallic materials. Heavy metals Cd, As, Hg, and Pb are higher volatile, resulting in the enrichment in the fly ashes. They can be leached into soil and water bodlied if the fly ash is disposed of in a landfill. The fabric filter captures the

fly ashes, containing condensed volatile elements, which cause the enrichment of volatile elements. Meanwhile, some minerals (such as lime, the Ca-containing compound) are added into the flue gas scrubber to remove the acid gases of the flue gases, for instance, HCl and SO₂. That is the reason the concentration of the corresponding elements (such as Ca, Cl and S) in the fly ashes increases significantly^[5].

The compositions of Cr, Cu, Zn, and Pb in fly ash were 468.40 µg g⁻¹, 831.80 µg g⁻¹, 4981.00 µg g⁻¹, 2048.00 µg g⁻¹, respectively. The Pb and Zn contents were extremely high in comparison to those in the incinerator ash, implying that recovering by acid or alkaline leaching deserves consideration^[6]. Both metals can also be reconcentrated to higher levels by the fly ash into the furnace for more economical recovery^[7].

Table 1: Compositions analysis of MSW incineration fly ash

Major species	Content /wt%	Heavy metals	Content/ µg·g ⁻¹
SiO ₂	28.91	Zn	4981.00
CaO	24.85	Cu	831.80
Al ₂ O ₃	13.34	Cr	468.40
Fe ₂ O ₃	6.26	Pb	2048.00
MgO	2.38	Ni	78.54
Na ₂ O	10.68	Cd	5.04
K ₂ O	9.42	As	38.35
P ₂ O ₅	1.52	Hg	21.67

3.2 SEM analysis

SEM micrograph of fly ash before melting treatment is shown in Figure 2. The particles size is very little above 100 µm in fly ash samples. The crystalline phases exist in untreated fly ash. The structure of samples is loose and complex.

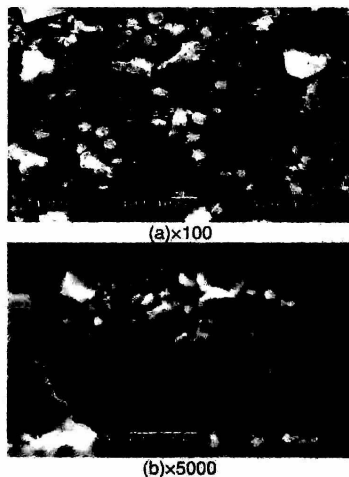


Figure 2: SEM micrograph of fly ash before melting treatment

SEM micrographs of fracture surfaces of milled incinerator ash samples sintered at 1100, 1200, 1300, and 1400 °C for 90 min are shown in Figure 3 (a)-(d). The marked crystallizes were found in SEM micrograph of slag at 1100°C in Figure 3 (a). Therefore, samples were occurred to sintering action and formed brittle agglomeration because the melting temperature was less than the melting point of the fly ash. The matrixes of melted slag were loose due to the MgCO_3 and CaCO_3 decomposing incompletely existing in fly ash. Studies on other organic containing wastes have reported weight losses up to 550°C resulting from the release of occluded gases, primarily CO_2 [9]. A significant weight loss accounting for 8.2 % of original sample weight occurs between 500 and 900°C. Samples heated to 650 and 750°C and this confirmed decomposition of calcite (CaCO_3) to lime (CaO) with consequent loss of CO_2 [9]. The sections of melted slag samples are coarse and a little lustre. It suggests that the samples occurs partly melting action at 1200°C. There are marked crystals by SEM, but the sizes of crystalline granules are less than that of samples at 1100°C. These indicate that the crystals have already transformed. A further weight loss of 2.1 % between approximately 1100 and 1200°C thought to be due to evolution of gaseous SO_2 from decomposition of alkali metal sulphates [10]. The surfaces of samples showed plenty of pores with different particles size. Samples melted at 1200°C appeared to be poorly melted with a granular fracture surface due to high porosities. The fracture surfaces of the samples melted at 1200°C showed a dense, well-melted microstructure, although occasional elongated cavities were clearly evident. The fracture surfaces of the samples melted between 1100°C and 1200°C were very different with reduced densities and sample expansion clearly associated with the formation of large isolated approximately spherical closed pores. The development of this foamed internal structure is believed to be due to evolution of SO_2 from decomposition of alkaline metal sulphates, together with melting of a significant amount of the glassy material Present in the ash [11]. The particles size of crystals became small at 1300°C, the outside surfaces of samples were up to complete melting, but a little non-melted material existed in the internal sections of melted slag. The samples achieved completely melting at 1400°C, it showed that the molten sample became full smooth, much hard in surface structure, while the section of the molten sample had lustrous or no apparent aperture. The raw fly ash had completely melted.



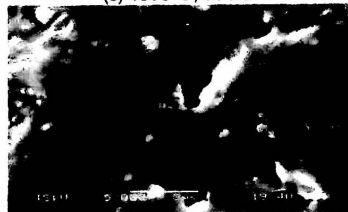
(a) 1100 °C, 90 min



(b) 1200 °C, 90 min



(c) 1300 °C, 90 min



(d) 1400 °C, 90 min

Figure 3: SEM micrograph of fly ash after melting treatment at different temperature

3.3 Mineralogy of raw fly ash and melted slag

Toxicity of MSW incineration solid residues is dependent not only on the polluting elements concentration, but also on the speciation of the pollutant elements and nature of the host phases. Therefore, it is necessary to knowledge the mineralogy of melted slags. The fly ash from MSWI is composed of inorganic compounds, including alkali metal oxides, non-metal oxides, hydroxides, chlorides and sulphate. Inorganic compounds like metallic element, especially in fly ash, are redistributed after the melting treatment according to the boiling temperature. It is considered that metals with high boiling Points like Si, Al and Ca, are converted into slag and substances with low boiling points like Cd and Pb are converted into fly ash or melting furnace exhaust gas. XRD analyses of the before and after samples are shown in Figure 4. The mineralogy of fly ash and slags are very complex. The complex mineralogy of fly ash results from processes, including vaporization, melting, crystallization, vitrification, condensation and precipitation, which occur during combustion and treatment of the flue gas. The major crystalline phases identified in raw ash were NaCl, KCl, SiO_2 , CaCO_3 , CaSO_4 , Ca_2SiO_4 , and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$. Samples with a high ratio have a crystalline matrix consisting of CaS, gehlenite, Ca-Al-

silicates melilite, anorthite and an interstitial glassy phase at 1400 °C. Secondly, it exist CaSiO_3 , Ca_2SiO_4 , $\text{CaMgSi}_2\text{O}_6$. The crystalline phases of melted slag were more complex than those of raw fly ashes. The main reason is that the silicates and metals oxides take place occur complex melting actions in high temperature.

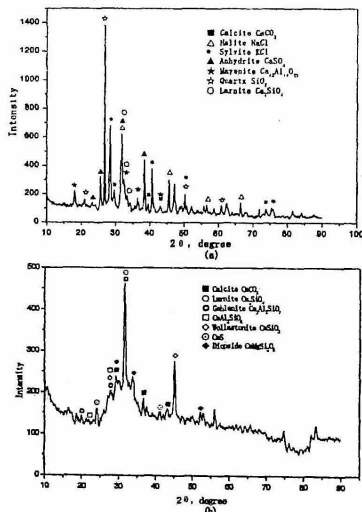


Figure 4: XRD results of fly ash before and after melting treatment

3.4 TCLP of melted samples

The leaching behaviour depends on one or several matrix phases, whose decomposition rates control the accessibility of heavy metals containing phases, and the heavy metal containing phase itself.

Results of the fly ash from MSWI by TCLP are shown in Table 2. The leaching ratios of melted samples at several runs were very low. Because the leachable heavy metals in form of salts (such as chlorides and sulphate) happen to vapour during melting process. Thus, the leaching ratios of heavy metals were decreased. Relatively, it is difficult for the heavy metals to vapour during melting process at above 1300°C because the heavy metals oxides, in melted slags have higher melting and boiling points. It showed that melting treatment could strikingly decrease leachable ratios of heavy metals in melted samples. The leaching ratios of Cr, Ni, Cd and Pb were apparently lowered, particularly that of Cd. Therefore, it is inferred that the melting process enhances the three metals' fixation. It seems that Cr, Ni, Pb and Cd may replace parent ions (Al^{3+} and Ca^{2+}) enclosed in the framework of silicates to have low leachability [12]. Interestingly, their leaching ratios seem to be independent of the slag structure (more crystalline or amorphous glassy matrix). A few of heavy metals and their compounds such as, Pb, Cd,

As and Hg would vapour with chlorides and be captured in gas phase during melting process, due to having lower melting and boiling points. The leaching test on melted slags samples showed that the fly ashes were successfully detoxified to meet of the limits toxicity characteristic leaching procedure (TCLP) in China and United States. After melting, the volatile heavy metals, like Hg, Cd and Pb were found in the gas collected, where Zn, Cr, and Ni were fixed into the melted slag. The concentration of heavy metal Zn, Cr, Pb, Cu, and Cd decreased distinctly. Thus, melting process is efficient for heavy metals stabilization in fly ash from municipal solid waste incinerator. The melted residues have a potential to be used as secondly raw material.

Table 2: Results of the fly ash from MSWI by TCLP /mg. L⁻¹

T/°C	1100	1200	1300	1400	U.S. limits	China limits
Cr	0.7520	0.6835	0.5688	0.5294	5.0	1.5
Ni	0.1684	0.1567	0.1474	0.1243	-	10
Pb	0.0646	0.0578	0.0382	0.0354	5.0	3.0
Cu	0.9683	0.9713	0.9421	0.9270	-	50
Zn	1.4753	1.449	1.2770	1.2210	-	50
Cd	0.4911	0.3421	0.2932	0.2443	1.0	0.3
As	0.0485	0.0462	0.0457	0.0418	5.0	1.5
Hg	0.0024	0.0023	0.0008	0.0005	0.2	0.05

4. CONCLUSION

(1) Fly ash is rich in CaO , SiO_2 , Al_2O_3 , Na_2O , and Fe_2O_3 , as well as alkali metal oxides, hydroxides, chlorides and sulphate. This fly ash contains a lot of Zn, Pb, Cd, Cr and Cu.

(2) Good melting effects are achieved when the temperature at 1300°C. It showed that the molten sample became full smooth, much hard in surface structure, while the section of the molten sample had lustrous or no apparent aperture. The raw fly ash had completely melted. The crystalline particles sizes in melted slag became small with the melting temperature improvement.

(3) The major crystalline phases identified in raw ash were NaCl, KCl, SiO_2 , CaCO_3 , CaSO_4 , Ca_2SiO_4 , and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, as well as a great quantity of hazardous heavy metals. Therefore, the fly ash must be melting treatment. Samples with a high ratio have a crystalline matrix consisting of CaS, gehlenite, Ca-Al-silicates melilite, anorthite and an interstitial glassy phase at 1400°C. Secondly, it exist CaSiO_3 , Ca_2SiO_4 , $\text{CaMgSi}_2\text{O}_6$. The crystalline phases of melted slag were more complex than those of raw fly ashes. The main reason is that the silicates and metals oxides take place occur complex melting actions in high temperature.

(4) The volatile heavy metals in melted residues, like Hg, Cd and Pb were found in the gas collected, where Zn, Cr, and Ni were fixed into the melted slag. The concentration of heavy metal Zn, Cr, Pb, Cu, and Cd decreased distinctly. Thus, melting process is efficient for heavy metals stabilization in fly ash from municipal solid waste incinerator.

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