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Investigation of MSWI fly ash melting characteristic by DSC–DTA

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Abstract

The melting process of MSWI (Municipal Solid Waste Incineration) fly ash has been studied by high-temperature DSC–DTA experiments. The experiments were performed at a temperature range of 20–1450 °C, and the considerable variables included atmosphere (O_2 and N_2), heating rates (5 °C/min, 10 °C/min, 20 °C/min) and CaO addition. Three main transitions were observed during the melting process of fly ash: dehydration, polymorphic transition and fusion, occurring in the temperature range of 100–200 °C, 480–670 °C and 1101–1244 °C, respectively. The apparent heat capacity and heat requirement for melting of MSWI fly ash were obtained by DSC (Differential Scanning Calorimeter). A thermodynamic modeling to predict the heat requirements for melting process has been presented, and it agrees well with the experimental data. Finally, a zero-order kinetic model of fly ash melting transition was established. The apparent activation energy of MSWI fly ash melting transition was obtained.

1. Introduction

In recent years, high efficient incineration technology has become increasingly important in MSW treatment, which meets ecological or environmental requirements. Nevertheless the problem of incineration residue treatment remains. Because slag ash and fly ash, which are usually landfilled without additional treatment, contain high concentrations of heavy metals and dioxins, their latent threat to environment cannot be ignored (Yang and Tsai, 1998; Van der Sloot et al., 1997). Studies by Sakai and Hiraoka (2000) indicate that there are much more volatile heavy metals (e.g., Hg, Pb, Cd) and toxic organic substances in fly ash than in bottom ash. The leaching characteristic of these hazardous materials leads to secondary pollution on groundwater after landfilling. Therefore MSWI fly ash was classified as hazardous waste requiring additional processing in most countries worldwide. Much effort has been devoted to seek the most convenient and secure way of treating fly ash from MSW incinerators.

In response to these problems, the melting process has been newly developed since 1990s. It is considered to be a prospective technology for stabilizing MSWI fly ash since it has the advantage of being innocuous. The melting operation works by heating ash up to fusion temperature. In such a process the organic pollutants decompose and the inorganic substances are transformed to more steady glassy molten slag, which can be used in the glass- and ceramic industry according to different demands since the heavy metals are prevented from leaching out. Furthermore, the melting process can densify the ash and greatly reduce the volume required for handling; the volume of the slag can be reduced by 70%. If the utilization of molten slag is taken into account, the bulk-reduction for landfilling can reach 95%. More recently, melting technology has been developing in many industrialized countries. Takaoka et al. (1997) investigated the behavior of heavy metals during ash melting in both a lab-scale and in pilot-scale experiments. Yasui et al. (1998) studied the influence of atmosphere gases on the fly ash melting in a plasma furnace. Tettamanti et al. (1998) carried out a thermal analysis on MSWI fly ash below 600 °C using DSC; in their paper the characteristics of carbon residue and evaporation of moisture

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Nomenclature

A	pre-exponential factor
C_p	heat capacity
E	apparent activation energy
K	basicity of fly ash
k_0	reaction rate constant
H	endothermic heat
H_t	total endothermic heat
n	reaction order
R	universal gas constant
S	total area surrounded by DSC curve and baseline
S'	area surrounded by DSC curve and baseline at time τ
S''	area surrounded by DSC curve and baseline from time$\tau$and finish
T	temperature
T_0	initial temperature
T_f	ultimate temperature
x_i	the ratio of ith composition of fly ash
α	conversion degree
β	heating rate
ΔH	enthalpy variation
ΔH_i	enthalpy variation of ith composition
τ	time

were discussed in detail. There have been intensive studies focused on the chemical recycling and melting technology of MSWI fly ash (Wenger and Farouk, 1999; Wei et al., 1998), however, very little research has been carried out on the melting kinetics and heat requirement for MSWI fly ash melting.

In China, more than 4,000,000 tons of waste was incinerated in 2005, and approximately 300,000 tons of fly ash were produced. Yet due to the financial limitations, as well as lack of availability of equipment for testing, it is not applicable for China to permit scientific institutes and factories to build expensive experimental equipment for melting to pursue a suitable method to deal with fly ash. The kinetics of melting play a vital role in the design and operation of fly ash melting facilities. Studies on the kinetics of melting are essential for developing new fly ash treatment techniques. The ceramic and metallurgical industries may also benefit from this investigation. The heat requirement for melting significantly determines the operation costs. The concrete research work investigates the heat requirement and kinetics of the melting reaction, and it identifies the factors that influence MSWI fly ash melting, using high-temperature DTA–DSC.

2. Thermal analysis experiment

2.1. DSC and DTA

The melting process of MSWI fly ash is usually conducted at high temperatures (generally above 1300 °C), which makes it difficult to measure the melting thermodynamics and kinetics. Moreover, the melting of MSWI fly ash differs greatly from ordinary chemical reactions in which the variation of mass or concentration of reactants or products can be easily measured. As far as DTA (differential temperature analysis) and DSC are concerned, the results produced by the two methods are qualitatively similar. It should be noted that more accurate and reliable quantitative information is obtained from DSC; however, DSC could not be used at temperatures higher than 800 °C in the past. Only with the recent appearance of high-temperature DSC, has the precise investigation of the solid phase transition, such as melting of MSWI ash, become possible.

2.2. Sample preparation

The samples used in the experiments were collected from two sources: sample A from a fixed-bed MSW incinerator in South China, while sample B from an incineration plant in Rouen, France. The composition of the samples was analyzed by using 'Finder 1000 X-ray Energy Spectrum Analyzer', as shown in Table 1 and Fig. 1. To eliminate the impact of carbon residue, the two samples were calcined for about 2 h in a muffle oven at 600 °C. Then the samples were ground to a size of 0.25 mm in order to minimize the influence of heat transfer within the sample. In addition, the effect of CaO content on the melting characteristic was also studied by adding various amounts of CaO into the samples.

Table 1
Composition of experimental fly ashes in weight percentage (%)

Sample A		Sample B	
Item	Content	Item	Content
SiO_2	10.3	SiO_2	1.67
CaO	47.09	CaO	76.75
Fe_2O_3	7.06	Fe_2O_3	0.56
Al_2O_3	2.36	Al_2O_3	1.06
K_2O	9.50	KCl	2.22
P_2O_5	3.43	P_2O_5	0.71
CuO	3.63	$CuCl_2$	9.63
TiO_2	5.80	TiO_2	0
$ZnCl_2$	10.85	$ZnCl_2$	7.40