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Detoxifying PCDD/Fs and heavy metals in fly ash from medical waste incinerators with a DC double arc plasma torch

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Abstract
Medical waste incinerator (MWI) fly ash is regarded as a highly toxic waste because it contains high concentrations of heavy metals and dioxins, including polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Therefore fly ash from MWI must be appropriately treated before being discharged into the environment. A melting process based on a direct current thermal plasma torch has been developed to convert MWI fly ash into harmless slag. The leaching characteristics of heavy metals in fly ash and vitrified slag were investigated using the toxicity characteristic leaching procedure, while the content of PCDD/Fs in the fly ashes and slags was measured using method 1613 of the US EPA. The experimental results show that the decomposition rate of PCDD/Fs is over 99% in toxic equivalent quantity value and the leaching of heavy metals in the slag significantly decreases after the plasma melting process. The produced slag has a compact and homogeneous microstructure with density of up to 2.8 g/cm³.

Key words: medical waste incinerator; fly ash; plasma torch; PCDD/Fs; heavy metal
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Introduction
The Chinese government has paid great attention to the management of medical waste, since the nationwide outbreak of severe acute respiratory syndrome in 2003. Medical waste must be appropriately treated before it can be discharged into the environment. Incineration is one of the most promising and competitive technologies for the disposal of medical wastes, because it is capable of high-efficiency sterilization and detoxification owing to its high temperature. This technology can not only effectively treat various medical wastes, such as infectious waste, pathological materials, pharmaceuticals and chemical waste, but also significantly reduce the mass and volume of medical waste. Presently, incineration has been proved to be the most promising technology for medical waste treatment in many developed countries (Shaaban, 2007; Alvim-Ferraz and Afonso, 2005).

Now incineration has become the most widely adopted technology for treating medical waste in China. However, during incineration of wastes, many highly dangerous and toxic burning ashes, especially fly ash enriched with plentiful heavy metals and dioxins or furans, are emitted (Sukandar et al., 2006; Zhao et al., 2008, 2010). With the rising awareness of environmental protection and environmental quality, a technology for disposal of fly ash from medical waste incinerators (MWI) is urgently required. MWI fly ash is not allowed to be used directly for landfill with other solid wastes, because it contains ample chlorine and organics which will be leached out in the landfill site. Special attention must be paid to the fact that MWI fly ash has a higher concentration of dioxin than that in municipal solid incinerator (MSW) fly ash, by about 2–3 orders of magnitude (Martha et al., 2009; Yan et al., 2007). Persistent organic pollutants, such as polychlorinated dibenzo-p-dioxins (PCDDs)/polychlorinated dibenzofurans (PCDFs), are highly hypertoxic and pose high risk for the environment and human health (Aristizábal et al., 2008; Chen et al., 2008; Cobo et al., 2009). Therefore, MWI fly ash must be properly treated to decompose PCDD/Fs. However, the chemical properties of PCDD/Fs are too refractory to be decomposed by general methods of disposing fly ash, such as chemical stabilization and solidification. In the past decade, melting technology has gained more and more attention because such a high temperature process can easily decompose organic pollutants and effectively immobilize leachable heavy metals in the melted slag. Moreover, melting has been widely used for
the treatment of MSW fly ashes (Wang et al., 2008, 2009; Yang et al., 2007).

Among several melting methods, plasma melting technology has attracted increasing interest for hazardous waste treatment. Compared with a fuel melting furnace, a thermal plasma system has the advantages of high temperature and high energy density, which allows fast heat transfer at the reactor boundaries and correspondingly shorter treatment time (Tu et al., 2010). In the past decade, thermal plasma technology has been extensively used for the treatment of various hazardous wastes (Pan et al., 2008a; Tu et al., 2008b; Wang et al., 2009; Katou et al., 2001; Liu et al., 2011; Chen et al., 2011; Károly et al., 2007; Bonizzoni and Vassallo, 2002; Gomez et al., 2009).

In this study, a direct current (DC) thermal plasma system has been developed for the vitrification of MWI fly ashes. The density and micro-structure of the original ash and melted slag were investigated to evaluate the performance of the plasma melting process. The effect of the treatment on the destruction of PCDD/Fs and the immobilization of heavy metals was also examined.

1 Experimental

1.1 Experimental system

The plasma torch used in the experiments consists of four major parts: cathode, first anode, second anode and linked part, as shown in Fig. 1a. Compared with conventional thermal plasma torches, this torch has a special design with two nozzle-shaped copper anodes set at different axial distances from the cathode tip (Pan et al., 2008b; Tu et al., 2007a, 2007c, 2008a). This configuration can not only extend the jet length but also enhance the arc stability (Tu et al., 2007b). In this study, the working gas of the plasma torch was argon and its flow rate was varied from 12 to 14 L/min. The double arc plasma torch was operated in direct current mode with typically 20–30 V/100 A for the first arc and 50–60 V/100 A for the second arc. The temperature of the argon plasma jet near the torch exit is about 11,000 K, and the heat flux of the plasma jet is around 65 kW/m² at 14 cm downstream from the plasma torch exit (Pan et al., 2008b; Yan et al., 2008; Tu et al., 2008b, 2008c, 2008d).

A fly ash melting system based on thermal plasma technology has been developed in our lab (Fig. 1b). A crucible filled with MWI fly ash was vitrified by atmospheric pressure thermal plasma jet. The crucible had a capacity of 30–50 g of fly ash, which could be completely vitrified within about 15 min. The off-gas generated from the plasma melting process was introduced into an absorption vessel for the post-measurement of PCDD/Fs.

1.2 Fly ash

Two types of fly ashes named FA1 and FA2 from medical waste incinerators were used in this study. FA1 was sampled from a medium-scale incinerator with handling capacity of 10 tons/day in Zhejiang Province, equipped with a simplified stoker furnace. Air pollution cleaning devices installed in this incinerator are comprised of a wet scrubber and a cyclone separator, and FA1 was obtained from the cyclone, in which no activated carbon was sprayed into the flue gas. FA2 was sampled from the bag filter of a rotary kiln fluidized bed multi-stage pyrolysis-incineration system with activated carbon spraying into the flue gas.

The physical and chemical properties of these two samples were quite different since they were collected from two different medical waste incinerators. The ash content (incombustible inorganics) of FA1 was 81.85%, much higher than that of FA2, which was only 34.45%. The detailed composition of FA1 and FA2 is listed in Table 1 (dry base).

| Table 1 | suggests that the major elements in FA1 were oxygen, calcium and chlorine, while oxygen, carbon and silicon were the major elements of FA2. Both fly ashes contained high concentrations of heavy metals, especially zinc and lead.

1.3 Analytical methods

In this study, the chemical composition of the fly ash was determined by X-ray Energy Dispersion Spectroscopy (GENENIS 4000, EDAX Inc., USA). Heavy metals were extracted by an acid mixture of HNO₃, HClO₄ and HF.
Table 1  Chemical composition of fly ashes (FA1, FA2)

| Element | FA1 (wt.%) | FA2 (wt.%) |
|---------|------------|------------|
| C       | 13.5       | 25.4       |
| O       | 23.9       | 35.5       |
| Na      | 1.75       | 0.95       |
| Mg      | 3.01       | 1.03       |
| Al      | 4.28       | 8.95       |
| Si      | 6.17       | 14.4       |
| Cl      | 17.2       | 1.28       |
| K       | 1.50       | 1.56       |
| Ca      | 21.7       | 8.55       |
| Cd (mg/kg) | 88.0   | 31.9 |
| Ni (mg/kg) | 82.4  | 21.2 |
| Pb (mg/kg) | 1444 | 1174 |
| Cr (mg/kg) | 153   | 32.1 |
| Cu (mg/kg) | 243   | 157 |
| Zn (mg/kg) | 8720 | 4614 |

method 1311). Acetic acid solution (pH 2.88 ± 0.05) was used as the leaching liquid. The liquid-to-solid ratio was 20:1 and agitation time was 18 hr with rotary tumbler at (30 ± 2) r/min. After extraction, the leachates were examined by AAS.

Scanning electron microscopy (SEM) was used to get a better understanding of the microstructure changes after the plasma melting process. Archimedes method was utilized to measure the density of the samples.

2 Results and discussion

2.1 PCDD/Fs distribution in fly ash

The concentrations of 17 toxic PCDD/F homologues in FA1 and FA2 are illustrated in Fig. 2. The concentration of PCDFs was much higher than that of PCDDs in both FA1 and FA2, and the ratio of PCDFs/PCDDs was 5.1 for FA1 and 2.92 for FA2. For FA1, 2,3,7,8-TCDF, 1,2,3,4,6,7,8-HpCPF and 2,3,4,7,8-PeDF were the dominant compounds, but for FA2 hepta-PCDD and OCDD as well as penta-, hexa- and hepta-PCDFs were the major compounds, as shown in Fig. 2a.

However, the distribution of the international toxic equivalent quantity (I-TEQ) of PCDD/Fs was significantly different as shown in Fig. 2b. For both fly ash samples, the I-TEQ concentration of 2,3,4,7,8-PeCDF was much higher than that of other congeners. The total TEQ values of FA1 and FA2 were 15.62 and 25.50 ng/g, respectively, which are much higher than that of fly ashes from municipal solid waste incinerators (Wang et al., 2010; Shi et al., 2008), and both TEQ values have far exceeded the criteria for soil in China (1 ng/g).

2.2 Decomposition of dioxin after melting

During the plasma melting of ashes, the emission of PCDD/Fs in the off-gas was absorbed by XAD-2 resin. The produced slags were obtained after the plasma melting process, Slag1 was from FA1 and Slag2 from FA2 respec-
Table 2

| PCDD/Fs homologue | Slag1 | Slag2 | Off-gas1 | Off-gas2 |
|-------------------|-------|-------|----------|----------|
| 2,3,7,8-TCDD      | ND    | ND    | ND       | 1.266    |
| 1,2,3,7,8,PeCDD    | ND    | ND    | ND       | ND       |
| 1,2,3,4,7,8-HxCDD  | 0.606 | 1.523 | 0.185    | 0.207    |
| 1,2,3,6,7,8-HxCDD  | 0.705 | 2.255 | 0.387    | 0.932    |
| 1,2,3,7,8,9-HxCDD  | 0.939 | 4.759 | 0.244    | 0.507    |
| 1,2,3,4,6,7,8-HpCDD| 0.576 | 2.437 | 0.339    | 0.667    |
| OCDD              | 0.155 | 0.355 | 0.085    | 0.116    |
| 2,3,7,8-TCDF      | 1.792 | 1.547 | 2.420    | 0.537    |
| 1,2,3,7,8,PeCDF    | 1.275 | 1.598 | 0.261    | 0.783    |
| 1,2,3,4,7,8-PeCDF  | 19.19 | 206.5 | 11.09    | 11.31    |
| 1,2,3,7,8-HxCDF    | 5.220 | 59.21 | 2.804    | 3.105    |
| 1,2,3,6,7,8-HxCDF  | 4.867 | 26.87 | 1.806    | 3.598    |
| 2,3,4,6,7,8-HxCDF  | 1.475 | 10.98 | 1.360    | 2.469    |
| 1,2,3,7,8,9-HxCDF  | 3.865 | 30.05 | 2.724    | 4.303    |
| 1,2,3,4,6,7,8-HpCDF| 2.397 | 12.954| 0.990    | 1.496    |
| OCDF              | 0.166 | 1.641 | 0.063    | 0.120    |
| Total I-TEQ       | 43.47 | 366.7 | 24.91    | 31.52    |

The total I-TEQ concentration of PCDD/Fs in Slag1 was 43.47 pg/g, and 366.7 pg/g in Slag2. It is apparent that the former value is much lower than the latter. The reason was that FA2 was burned rather than was vitrified by plasma jet because of its high content of combustible matter such as activated carbon, which also led to much less time for the disposal of FA2.

However, compared to the original ashes, the degradation efficiency of PCDD/Fs with respect to the I-TEQ concentration reached 99.72% for Slag1 and 98.57% for Slag2 respectively. The I-TEQ concentration of PCDD/Fs in off-gas1 was similar to off-gas2, under the same operating conditions, in both a wind-tight and oxygen-poor chamber.

2.3 TCLP characteristic of heavy metals

Since FA2 was burned and gasified when heated in the melting furnace, the residue was too small to examine its heavy metal leaching behavior with the method of TCLP. Thereby, the TCLP experiment was carried out only for FA1 and Slag1 and the results are shown in Fig. 3. As can be seen, the leaching content of heavy metals in the slag was much lower compared with the original ash, indicating that slag could effectively retain heavy metals to prevent them from dissolving out.

2.4 Microstructure characterization of ash and slag

SEM micrographs of FA1 and Slag1 are shown in Fig. 4. The SEM image of FA1 demonstrates that the particles have irregular shape and diverse size and the interspace between particles can be clearly observed. However, the particle structure of Slag1 was homogeneous and compact,
with a few crystals of 20–400 nm in size embedded in a glassy matrix.

2.5 Volume reduction
The density of FA1 and Slag1 was 0.62 and 2.82 g/cm³, respectively. The volume reduction of the fly ash reached 78% after plasma melting.

3 Conclusions
Fly ashes from medical waste incinerators contained abundant hazardous materials, such as heavy metals and dioxins. Specifically, the I-TEQ concentration of PCDD/Fs in FA1 and FA2 was as high as 15.62, 25.50 ng/g respectively, which far exceeded the regulatory levels. After the melting process, the major components of PCDD/Fs in the original ash were decomposed, with high destruction rate of 99.72% for FA1 and 98.57% for FA2. After the plasma melting process, the leaching of heavy metals in slag significantly decreased compared to the raw fly ash. The microstructure of the slag was uniform and dense, and the volume reduction was near 78%. In conclusion, these experimental results demonstrate that the thermal plasma torch is an alternative and promising technology for disposal of MWI fly ash.

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