Chemosphere 84 (2011) 361–367

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Thermal removal of PCDD/Fs from medical waste incineration fly ash – Effect of temperature and nitrogen flow rate

Hai-long Wu, Sheng-yong Lu *, Jian-hua Yan, Xiao-dong Li, Tong Chen

State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou, Zhejiang Province 310027, China

ARTICLE INFO

Article history:
Received 6 July 2010
Received in revised form 6 January 2011
Accepted 7 February 2011
Available online 6 April 2011

Keywords:
Bag filter
Dechlorination
Destruction
Medical waste incineration

ABSTRACT

The fly ash used in this study was collected from a bag filter in a medical waste rotary kiln incineration system, using lime and activated carbon injection followed by their collection as mixed fly ash. Experiments were conducted on fly ash in a quartz tube, heated in a laboratory-scale horizontal tube furnace, in order to study the effect of temperature and nitrogen flow rate on the removal of PCDD/Fs. Results indicated that in this study PCDD/Fs in the fly ash mostly were removed and desorbed very little into the flue gas under thermal treatment especially when the heating temperature was higher than 350 °C, and dechlorination and destruction reactions took important part in the removal of PCDD/Fs. However, in terms of flow rate, when flow rate was higher than 4 cm s^{-1}, destruction efficiency of PCDD/Fs decreased dramatically and the main contributors were P_5CDF, H_6CDF and H_7CDF desorbed to flue gas, the PCDD/Fs in the fly ash decreased with enhanced flow rate.

1. Introduction

In modern municipal or hazardous solid waste incinerators, the boiler has been well designed, and combustion conditions have been well are controlled. Air pollution control devices (APCDs) are also employed to reduce polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) emissions from the stack. PCDD/Fs emissions from stack have to be well controlled and must be under the Europe limit of 0.1 ng I-TEQ Nm^{-3}. However, PCDD/Fs not only occur from phase transfer from the gas phase to the solid phase (fly ash), but also from the increasing total amount of PCDD/Fs, mainly contributed by the "de novo" reaction of fly ash when passing through the post-combustion zone (Stanmore, 2004; Chen et al., 2008a). Moreover, because of the "memory effect", PCDD/Fs are formed from fly ash continuously even if the incinerator is shutdown when fly ash deposits in duct wall or APCDs is not removed in time (Zimmermann et al., 2001).

It is reported that removing fly ash deposits from the flue duct walls has been shown to reduce the emissions of PCDD/Fs (Wevers and de Fré, 1998). Nevertheless, fly ash accounts for 70% to 90% of the total PCDD/Fs released from an incinerator (Abad et al., 2001), and the problem emerges due to the toxicity of fly ash. In some countries fly ash is considered as hazardous waste, which could not be land-filled directly. Solidification provides a method for fly ash pretreatment before landfill, and result indicates that leachability of PCDD/Fs can be reduced, but the solidification capability depends on characteristic of fly ash (Kim and Lee, 2002; Hsi et al., 2007).

Another promising method is thermal treatment which takes place under inert gas condition at low temperatures. Vogg and Stieglitz (1986) found that under oxidative conditions, a temperature of 400–600 °C was needed to decompose PCDD/Fs; however, PCDD/Fs could be decomposed effectively when under inert gas condition. In the studies followed, identical results were obtained under N_2 or static gas conditions (Hagenmaier et al., 1987; Addink et al., 1995a; Lundin and Marklund, 2005; Cunliffe and Williams, 2007). However, thermal treatment was only a laboratory skill to study fly ash problem, and no researcher has developed a large scale or pilot scale equipment to eliminate PCDD/Fs in fly ash. In China, the definition of toxicity of different fly ashes is not clear, and a large quantity of fly ash from waste incinerators is landfilled either after solidification treatment or directly. In the near future, the management of fly ash will become stricter, and thermal treatment will be a promising method to resolve the fly ash problem.

Medical waste is dangerous and infectious, and needs special treatment even after burning. The characteristics of medical waste are different from municipal solid waste in terms of components such as paper, plastics and textile, and after burning, fly ashes also differ because of the incineration conditions and APCDs, and in most cases are higher in PCDD/Fs, PCBs and other POPs (Oh et al., 1999; Stanmore and Clunies-Ross, 2000). Researchers reported that fly ash from medical waste incinerator has a higher level of PCDD/Fs than that from municipal solid waste incinerators and electrical power plants (Chen et al., 2008b). In recent years, our research has been dedicated to the incineration of medical wastes,

* Corresponding author. Tel.: +86 571 8795 2628; fax: +86 571 8795 2438.
E-mail address: lushy@zju.edu.cn (S.-y. Lu).

0045-6535/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2011.02.015

pollutant control and PCDD/Fs destruction and some achievements have been obtained (Lu et al., 2007; Yan et al., 2009). In this study, thermal treatment was introduced to decompose PCDD/Fs in fly ash collected from a medical waste incinerator, temperature and flow rate parameters were discussed influencing decompose of PCDD/Fs. Finally, guidance for fly ash from medical waste incinerator thermal treatment was obtained to minimize the concentration of PCDD/Fs.

2. Materials and methods

2.1. Fly ash sample

Fly ash was collected from a medical waste rotary kiln incinerator. In this system, medical waste is combusted first in a rotary kiln and the residue passed to a secondary combustor (burnout). After combustion, the flue gas is rapidly quenched by water to keep the temperature between 180 °C and 200 °C, avoiding reformation of PCDD/Fs. The quenching tower is unique for medical waste incineration. Operated with lime injection, acid gas is adsorbed; then PCDD/Fs in the gas phase and solid phase are adsorbed by activated carbon (AC) spray and particles by a bag filter. The mixed lime, AC and fly ash are collected by the bag filter. Finally, the gas from stack satisfies emission control regulations. The fly ash used for the experiments is the mixture taken from the bag filter. The elemental composition and other characteristics of fly ash collected from the bag filter are listed in Table 1.

2.2. Thermal treatment reactor

The experiments were conducted in a laboratory-scale horizontal tube furnace with quartz tube as a reactor. Approximately 0.5 g fly ash was used in each experiment. Before each experiment condition, the tube was flushed with N_2 longer than 10 min, making sure that atmospheric air and remained eluent were expelled. During the experiment, the whole system was inserted with nitrogen gas, and each process lasted for 60 min. During temperature parameter influenced experiment, the gas flow rate was stabilized at 200 mL min^{-1} (2 cm s^{-1}), and temperatures of 300 °C, 350 °C, 400 °C were used; when the flow rate were changed, the temperature was stabilized at 350 °C, and flow rates used were 200 mL min^{-1} (2 cm s^{-1}), 300 min^{-1} (3 cm s^{-1}) and 400 min^{-1} (4 cm s^{-1}). During the experiment, the organic compounds in the flue gas were adsorbed by XAD-2 resin and a toluene scrubbing solution. A blank experiment was used for accuracy. When the experiment ended, the glass trap which contained XAD-2 resin was covered with aluminum foil, and the toluene scrubbing solution was collected in brown bottle, also thermal treated fly ash was collected after cooled. Samples collected were stored in a refrigerator before analysis.

Table 1
Properties of the medical waste incinerator fly ash.

Properties		Properties	
C (wt.%)	8.96	Mg (wt.%)	0.10
H (wt.%)	1.98	Ni (mg kg^{-1})	10.1
O (wt.%)	25.7	Pb (mg kg^{-1})	107
N (wt.%)	0.12	Zn (wt.%)	0.33
S (wt.%)	0.20	Cr (mg kg^{-1})	ND
P (wt.%)	0.03	As (mg kg^{-1})	1.33
Cl (wt.%)	8.70	Hg (mg kg^{-1})	63.0
Cu (wt.%)	0.06	BET surface area (m^2 g^{-1})	65.8
Na (wt.%)	10.4	Micropore area (m^2 g^{-1})	21.4
K (wt.%)	0.36	External surface area (m^2 g^{-1})	44.4
Ca (wt.%)	1.49	Pore volume (cm^3 g^{-1})	0.07
Al (wt.%)	0.08	Micropore volume (cm^3 g^{-1})	0.01
Fe (wt.%)	0.11	Mean pore radius (nm)	4.29
Cd (mg kg^{-1})	12.1	ND: Not detected	

2.3. Analysis

Thermally treated fly ash and gas phase adsorbed samples were transferred to the glass thimble of the Soxhlet extractor and spiked with a mixture of ^{13}C-labeled PCDD/Fs internal standards which were supplied by Wellington Laboratories, Canada. The spiked samples were extracted for 24 h with 250 mL toluene. A rotary evaporator concentrated the extract to 1–2 mL approximately, prior to the cleanup process. After concentration, a labeled cleanup standard was spiked into the extract, which was then cleaned using different methods. The extract should be treated again when using the extract was still colored.

Cleanup of samples were done using conventional manual chromatography columns including a multi-silica gel column, an alumina column and a Florisil column. After cleanup, the extract was concentrated again and transferred to a vial. Then, the remaining solvent in the vial was reduced to about 20 μL in a gentle stream of nitrogen. A ^{13}C-labeled PCDD/Fs recovery standards mixture was spiked prior to HRGC/HRMS analysis.

The analysis was performed by HRGC/HRMS on a 6890 Series gas chromatograph (Agilent, USA) and coupled to a JMS-800D mass spectrometer (JEOL, Japan). A DB-5 ms (60 m × 0.25 mm I.D., 0.25 μm film thickness) capillary column was used for separation of the PCDD/Fs congeners. The GC temperature program and mass spectrometer were operated as described by Chen et al. (2008b). The detailed quantitative determination of PCDD/Fs was according to US EPA method 1613. Tetra- to octachlorinated PCDD/Fs were measured in this study.

The credibility of PCDD/Fs data was assured by adding internal standards mixture, purification standards mixture, and injection standards mixture before Soxhlet extraction, purification and analysis process respectively. Data analysis demonstrated that, the recovery rates of each internal standard were between 66% and 90%, which was accord with the recovery standard of 40% to 130%.

3. Results and discussion

3.1. Temperature influenced removal of PCDD/Fs in fly ash

The original concentration of PCDD/Fs in fly ash from medical waste incinerator is shown in Table 2. The total concentration of PCDD/Fs were 836 000 ng kg^{-1}, this is much higher than that of municipal solid waste incinerator fly ash literatures referred (Chen et al., 2008b; Lundin and Marklund, 2008). The I-TEQ concentration and WHO2005-TEQ concentration were a little different of 19 000 ng I-TEQ kg^{-1} and 19 700 ng WHO2005-TEQ kg^{-1}, respectively, which were due to different TEQ factor of 1, 2, 3, 7, 8-P_5CDD, O_8CDD and O_8CDF, and 2, 3, 4, 7, 8-P_5CDF was the main contributor. Nowadays, 2, 3, 4, 7, 8-P_5CDF becomes the dominant I-TEQ contributor in the emissions from municipal solid waste and hazardous waste incinerators (Fiedler et al., 2000) or in the fly ashes of different sources (Chen et al., 2008b). It is obvious that the PCDDs/PCDFs ratio is much lower than 1 and it might due to improved incineration. Modern municipal solid waste incinerators tend to produce more PCDFs than PCDDs (Ryu et al., 2005), and some old incinerators show PCDDs/PCDFs ratio above 1 (Stieglitz and Vogg, 1987).

After thermal treatment under N_2 atmosphere, PCDD/Fs remained in fly ash was reduced dramatically in terms of tetra- to octachlorinated PCDD/Fs (Table 2), the total concentration of PCDD/Fs decreased from 836 000 ng kg^{-1} to 8430, 2490 and 2350 ng kg^{-1} at the temperature of 300 °C, 350 °C and 400 °C,