Waste Management 56 (2016) 229–237

Contents lists available at ScienceDirect

Waste Management

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

Recycling ash into the first stage of cyclone pre-heater of cement kiln

Ming-Xiu Zhan [a], Jian-Ying Fu [b], Jouni Havukainen [c], Tong Chen [a,*], Xiao-Dong Li [a], Jian-Hua Yan [a], Alfons Buekens [a]

[a] State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, China
[b] China United Engineering Corporation, Hangzhou 310052, China
[c] Lappeenranta University of Technology, Laboratory of Environmental Engineering, P.O. Box 20, FI-53851 Lappeenranta, Finland

ARTICLE INFO

Article history:
Received 31 January 2016
Revised 10 April 2016
Accepted 18 June 2016
Available online 4 July 2016

Keywords:
PCDD/Fs
Cement kiln
Soxhlet fly ash
Formation
De novo synthesis
Influencing factor

ABSTRACT

Fly ash collected from the bag filter could be recycled into the first stage of the cyclone pre-heater of the cement kiln, resulting in the possible enrichment of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). In this study, soxhlet fly ash (SFA) and raw meal (RM) were selected as the basis for the PCDD/F formation experiments. The levels of 2,3,7,8-PCDD/Fs formed on the SFA and RM were observed to be 2550 pg/g (157 pg I-TEQ/g) and 1142 pg/g (55 pg I-TEQ/g), respectively. While less 2,3,7,8-PCDD/Fs was detected when SFA was mixed with RM, suggesting that recycling cement kiln ash would not largely increase the concentration of PCDD/Fs in flue gas. Furthermore, the possible influencing factors on the PCDD/F formation were also investigated. The formation of 2,3,7,8-PCDD/Fs was up to 10,871 pg/g (380 pg I-TEQ/g) with the adding of $CuCl_2$, which was much higher than the results of CuO and activated carbon. Most importantly, the homologue, congener and gas/particle distribution of PCDD/Fs indicated that *de novo* synthesis was the dominant PCDD/F formation pathway for SFA. Lastly, principal component analysis (PCA) was also conducted to identify the relationship between the compositions of reactant and the properties of PCDD/Fs produced.

1. Introduction

After polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) were discovered in the emissions of municipal solid waste incineration (MSWI) (Olie et al., 1997), PCDD/Fs are also known to be able to form in most of the other combustion systems (Anthony et al., 2001). A variety of studies have shown that the formation of PCDD/Fs in cement kilns is inevitable (Ames et al., 2012; Chen, 2004; Zemba et al., 2011). Fly ash has been observed to be the main PCDD/F source of MSWI system and this trend was also found in cement kilns (C.K. Chen et al., 2008; Li et al., 2015). In general, MSWI ash is well treated in high temperature and then transported to landfill. However, the fly ash produced from the cement kiln could be recycled into the first stage of the cyclone pre-heater with the raw meal (RM), although it is a potentially hazardous waste.

Chlorine compounds and metal catalysts are minor additional constituents contained in the cement kiln ash (Lanzerstorfer and Feichtinger, 2016). They will re-enter into the kiln system with the recycled ash and partially accumulate at the first stage of cyclone pre-heater. Moreover, the temperatures at the inlet and the outlet of the first stage of the cyclone pre-heater are 500 °C and 300 °C, which unfortunately coincides with the expected range of the *de novo* synthesis (Li et al., 2012). It has been found that PCDD/Fs can be formed by the *de novo* synthesis mechanism in or after the preheater if chlorine and metal catalysts are available in sufficient quantities in the temperature range of 200–450 °C (Pirard and Pauw, 2001). Therefore, such accumulations of chlorine and catalytic metals may cause deposit formation of dioxins at the first stage of the cyclone pre-heater because of recycling ash. Furthermore, 94% of dioxins in the fly ash could be released into the flue gas when the temperature increases to 350 °C (Altwicker et al., 1994). Thus, higher concentration of dioxins will be observed in the flue gas when the cement kiln ash is recycled, which could further increase the final emission level of dioxins (Li et al., 2015).

There are two principal pathways to explain the emissions of dioxins into the environment from combustion processes: (1) the organic precursors adsorb onto the surface of the fly ash in the post-combustion zone, and following a complex series of reactions which are catalyzed by metals (mainly copper) in the fly ash, leading to the formation of PCDD/Fs (McKay, 2002); (2) chlorine and catalytic metal which are incorporated into fly ash could lead to

* Corresponding author at: Laboratory of Clean Energy Utilization, Zhejiang University, 310027 Hangzhou, Zhejiang, China.
E-mail address: chentong@zju.edu.cn (T. Chen).

http://dx.doi.org/10.1016/j.wasman.2016.06.024
0956-053X/

the *de novo* synthesis of PCDD/Fs (Conesa et al., 2002; Pirard and Pauw, 2001; Wikström et al., 2003). Considering the above, the fly ash plays an important role in PCDD/F formation. Furthermore, chlorine, catalytic metal and carbon are the dominant influencing factors to the PCDD/F formation (Stanmore, 2004). Among them, CuO has been studied in the chlorination/oxidation reaction on MSWI fly ash, showing that the yield of PCDD/Fs was lower than those observed in the experiments with ash only (Fullana et al., 2004); $CuCl_2$ is a well-known chlorination catalyst and is able to oxidize active carbon at relatively low temperatures (Luijk et al., 1994); the rate of release of PCDD/Fs from the MSWI fly ash is also proportional to the rate of carbon consumption (Stanmore, 2004). Moreover, these components could also affect the release characteristics of dioxins from the fly ash. Up to date, inadequate amount of information has been published about whether PCDD/Fs could be formed due to utilization of the cement kiln ash and which influencing factor contributed most to this formation.

In order to fully understand the dioxin formation behavior of the recycling fly ash, the amount of PCDD/Fs formed on the soxhlet fly ash (SFA) was estimated in laboratory scale. Moreover, the formation behavior of PCDD/Fs on the RM was also observed and the RM was further mixed with the SFA to investigate the mutual effect of them. Most importantly, the possible influencing factors (e.g. catalytic metal, chlorine and carbon source) on the PCDD/F formation were also studied. Lastly, principal component analysis (PCA) was conducted to identify the relationship between the compositions of the reactant and the properties of PCDD/Fs produced.

2. Materials and methods

2.1. Experimental materials

The original fly ash and the RM were collected from a cement kiln with a clinker capacity of 5000 t/day. The cement kiln utilizes the dry process and presents a state-of-the-art configuration with a preheater/precalciner containing four stage cyclone type vessels (Li et al., 2015). The collected ash from the bag filter is recycled into the first stage of cyclone pre-heater with the RM. The refuse derived fuel (RDF) prepared from municipal solid waste (MSW) is fed into the precalciner and enters at a constant feeding rate of 15 ton/h.

The cement kiln ash is soxhlet extracted for 48 h in toluene and after the drying of the resulting sample is referred to as SFA (SFA). Scanning Electron Microscope (SEM) analysis (Fig. 1) reveals that large amount of particles exists on the surface of SFA and RM. X-ray Photoelectron Spectroscopy (XPS) analysis shows that CaO, $CaCO_3$ and SiO_2 are the main components of the RM, which is consistent with the results reported by Cong et al. (2015). The share of Cu in the SFA and RM are 0.0034 and 0.0030 wt% and the share of Cl are 0.032 and 0.053 wt%, respectively. Moreover, the results of Energy Dispersive Spectrometer (EDS) analysis are presented in Table 1.

2.2. Experimental set-up

The formation experiments on the SFA and the RM were performed using the apparatus described in Fig. 2. It comprises of a tubular furnace consisting of three separately heated sections a, b, and c (0.5 m each section) and featuring independent heaters and temperature controllers, with the temperature simultaneously compared with a S-type thermocouple reading to ensure that the target temperature has been met (Chen et al., 2014). The reactants were positioned in a quartz boat at section b when the aim temperature was stable. The external and internal diameter of the quartz reactor tube was 45 and 30 mm. The simulated flue gas (1 L/min; 6% O_2 in N_2) flows over the reactants and carries the gaseous PCDD/Fs to the collection zone (including XAD-II resin and Toluene) with the retention time of 34 s (see Fig. 3).

2.3. Experimental design

The experimental conditions are presented in Table 2. Considering the operation parameters at the first stage of the cyclone preheater, the temperatures for section a, b and c were all set to 350 °C and the content of oxygen was controlled at 6%. Each test was conducted for 30 min to ensure the complete reaction.

In the test group A the formation behavior of SFA, RM and their mixture were tested to simulate heterogeneous formation of PCDD/Fs at the first stage of cyclone pre-heater. First, the PCDD/Fs formation from 8 g SFA was established during the test A-1. Then, similar test was conducted on 8 g RM in the test A-2. Considering the weight ratio of the fly ash and the RM at the first stage of the cyclone pre-heater, 7 g RM was mixed with 1 g SFA in the test A-3. Above results could be used to investigate the effects of recycling fly ash on PCDD/F formation during the process of cement production.

Test group B was conducted to learn the possible influencing factors on PCDD/F formation and experiments A-1 could be regarded as blank one. First, the PCDD/Fs formation from 8 g mixture of CuO and SFA with 3 wt% of Cu was tested in the test B-1, to investigate the role of copper in chlorination/oxidation phenomena. Then, the similar test was conducted on 8 g mixture of $CuCl_2$ and SFA with 3 wt% of Cu and also with 3.3 wt% of Cl in the test B-2. Lastly, 3 wt% of activated carbon was mixed with SFA to investigate the influence of carbon source on the PCDD/F formation.

Since the PCDD/Fs largely remained on the model fly ash, both the fly ash and the gas phase were analyzed together in the further

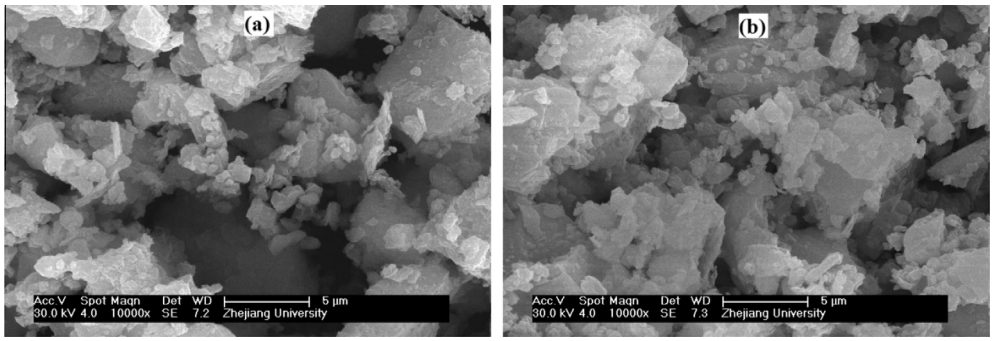

Fig. 1. SEM analysis of RM (a) and SFA (b).