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Mass balance of dioxins over a cement kiln in China

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ABSTRACT

The cement production process may be a potential source of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs, "dioxins"), due to the widespread distribution of dioxins and potential precursors in raw materials and to conditions favorable to de novo formation in the heat exchangers. The emission, gas/particle distribution, and mass balance of PCDD/Fs were investigated at a typical state-of-the-art Chinese cement kiln. Input and output inventories were established for three campaigns, including two in normal operation and one while co-processing refuse derived fuel (RDF). Sample analysis from stack gas, cement kiln dust, raw meal, fly dust and clinker for the analysis of PCDD/Fs were reported in this study. Dioxins were also analyzed at various positions in the pre-heater, presenting an adsorption–desorption circulation process of PCDD/Fs. The over-all dioxin mass balance was negative, indicating that this cement kiln is not a source but a sink process of dioxins.

1. Introduction

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs, "dioxins") can be unintentionally formed and released from combustion and other thermal processes. In order to Stockholm Convention on Persistent Organic Pollutants, more stringent regulations and emission limit standards related to dioxins were enacted and enforced in China. Lot of work has been conducted in dioxin formation, emission and control technology, since the first detection of dioxins was reported in municipal solid waste incinerator in 1977 (Olie et al., 1977; Abad et al., 2002; Pandelova et al., 2006; Duan et al., 2011; Zhang et al., 2012). As the previous research, there are two main mechanisms of the formation of PCDD/Fs as follows: (a) PCDD/Fs formation by heterogeneous catalysis condensation reaction of direct precursors on the surface of dust at 250–400 °C; (b) PCDD/Fs formation through an oxidative breakdown of macromolecular carbon structures namely de novo synthesis from simple hydrocarbons and chlorine. As one of main sources of PCDD/Fs listed in the Annex of the Stockholm Convention, cement kiln also need further scrutiny.

Compare to the investigation on dioxin issues related to municipal solid waste incinerator, quite few were done in the formation and emission of dioxins from cement (Dyke et al., 1997; Quass et al., 2004; Karstensen, 2008; Ames et al., 2012). The co-processing of solid wastes (municipal solid waste and hazardous waste) in cement kilns is still a controversial issue. Karstensen (2008) made a review at Formation, release and control of dioxins in cement kilns. Mass balance study is useful to understand the dioxins formation and to guide the further control. PCDD/Fs in the output is not only formed during the cement process, but also might be from the original input samples. PCDD/Fs was detected in the raw material feed for cement (Liske et al., 1996). PCDD/Fs level in cement kiln dust (CKD) were in the range of 0.001–30 ng I-TEQ/kg for UK kilns (Dyke et al., 1997), 1.0–40.0 ng I-TEQ/kg for German kilns and 0.03 ng I-TEQ/kg of average PCDD/Fs concentration for Switzerland kilns (UNEP, 2005). The emission factors can be used to evaluate emission inventories for different industries. Different emission factors in cement were reported, for instance, 0.15 μg I-TEQ/ton for European (Quass et al., 2004), 0.014 μg I-TEQ/ton Spanish (Fabrellas et al., 2002, 2004) and 0.025–1.2 μg I-TEQ/ton UK cement (Eduljee and Dyke, 1996; Eduljee, 1998).

Cement production in China account for 60% of the world amount, meanwhile, the pollutants emitted from cement plants potentially influence and threaten the environment and public health. In order to better understand the dioxins emission and distribution in cement, mass balance of dioxins over a cement kiln in China was investigated in this study.

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2. Material and method

2.1. Sampling method

A measurement program was undertaken in three sampling campaigns (R_A, R_B and R_C) at a continuously operating pre-heater and pre-calciner cement kiln in Hubei province, China. The kiln with clinker capacity of 5000 ton/day was in a dry process, presenting a state-of-the-art configuration with a pre-heater/pre-calciner consisting of a vertical tower containing four stage cyclone-type vessels. It had waste heat recovery system, a suspension pre-heater (SP) waste heat boiler and bag filters (BG).

Raw meal was input at the top of a tower with four stage cyclone-type vessels, and the feeding rate was 395 ton/h for R_A, 387 ton/h for R_B and 379 ton/h for R_C, respectively. Meanwhile, CKD was usually re-introduced back to the system, feeding with raw material. Coal was the conventional fuel feeding into kiln with 31.4 ton/h to 31.7 ton/h, and RDF was input as alternative fuel through the bottom of pre-calciner during R_C measurement. Each item of output and input was clearly distinguished and presented in Fig. 1. Operating parameters during sampling were recorded as shown in Table 1.

The sampling for PCDD/Fs in stack gas, CKD, clinker, raw meal and coal samples were carried out according to USEPA Method 23 and Chinese standard measurement procedure (HJ 77.1–77.4, 2008). In addition, flue gas and dust samples from the cyclone-type vessels of pre-heater/pre-calciner were also collected to access PCDD/Fs distribution between gaseous and particle phase. The flue gas was isokinetically sampled and each sampling time was 120–180 min for approximately 2.0–4.0 m^3 in volume; the oxygen concentration of flue gas was recorded. Meanwhile, dust samples were simultaneously collected every half hour during flue gas sampling process until 2 kg. Because of general inhomogeneity, the other solid samples were collected by fully mixed multipoint sampling.

2.2. Extraction and cleanup

Each sample prior to the extraction process was spiked with 1 ng of $^{13}C_{12}$-labeled Internal Standards described in USEPA Method 23. Analyte was extracted from XAD-2 and the filter by Soxhlet extraction using toluene for 24 h. The toluene extracts were transferred to n-hexane and rotary-concentrated prior to the cleanup process. The concentrated extracts were cleaned up sequentially by means of a multi-layer silica gel and carbon column. Sequentially the extracts were concentrated to 20 µl with nitrogen and then spiked with 1 ng of $^{13}C_{12}$-labeled Recovery Standards prior to analysis.

Table 1
Operation condition during three sampling campaigns.

	R_A	R_B	R_C
Raw meal (ton/h)	395	387	379
Coal (ton/h)	31.4	31.7	31.6
RDF as secondary fuel (ton/h)	–	–	8
Clinker production (ton/h)	247	241	238
CKD from [a]BG_2 (ton/h)	47.1	49.2	52.3
Rate of re-introduced (%)	90	90	90
CKD from SP boiler (ton/h)	4.64	4.72	4.81
Rate of re-introduced (%)	0	50	0
Stack gas, Y_1 (km^3/h)	705	741	714
Temperature, Y_1 (°C)	90–250	90–250	90–250
Stack gas, Y_2 (km^3/h)	847	881	909
Temperature, Y_2 (°C)	130–250	130–250	130–250

[a] BG_2: all of fly dust collected by BG_1 was re-feed to the kiln system, so actually just dust form BG_2 involved in the balance calculation.

2.3. Instrumental analysis

Identification and quantification of PCDD/Fs are accomplished by HRGS/HRMS on a 6890 Series high-resolution gas chromatograph (Agilent, USA) depending on DB-5 ms (60 m × 0.25 mm I.D., 0.25 µm film thickness) capillary column for separation of the PCDD/Fs congeners, and coupled with a JMS-800D high-resolution mass spectrometer (JEOL, Japan). The recovery of the label standards is seen as indicator for evaluating potential losses of the entire pretreatment process, while $^{13}C_{12}$-labeled Surrogate Standards and Internal Standards should range from 70–130%, 40–120% respectively. Toxic equivalents (I-TEQ) were calculated using NATO/CCMS factors (NATO/CCMS, 1988).

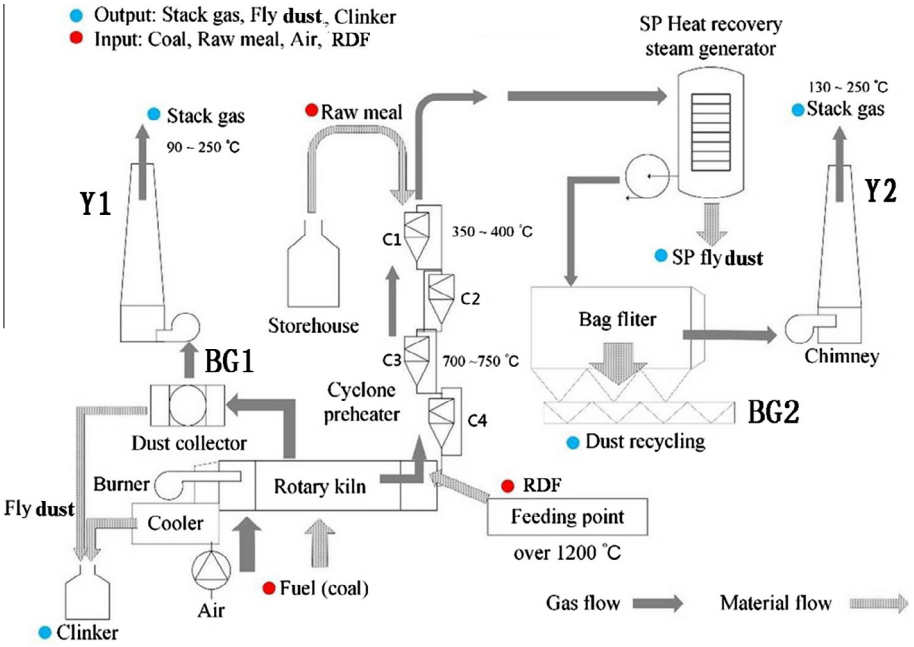

Fig. 1. Diagram of the cement kiln and mass flows of output and input (Chen et al., 2014).