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Profiles of polychlorinated biphenyls (PCBs) in cement kilns co-processing solid waste

Rong Jin [a, b], Jiayu Zhan [c], Guorui Liu [a, b, *], Yuyang Zhao [a, b], Minghui Zheng [a, b], Lili Yang [a, b], Mei Wang [a, b]

[a] *State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*
[c] *State Key Laboratory of Solid Waste Reuse for Building Materials, Beijing Building Materials Academy of Sciences Research, Beijing 100041, China*

HIGHLIGHTS

- Variations of PCBs within cement kilns co-processing solid waste were evaluated.
- Kiln end area and cyclone preheater were dominant sites of PCB formation.
- Tetra-to hexa-chlorinated biphenyls were dominant PCB homologues.
- Co-processing of waste in cement kilns did not increase PCB emissions.

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ABSTRACT

Co-incineration of sewage sludge in cement kilns can be used for its disposal. In the present study, samples were collected from three cement production runs where sewage sludge and other wastes (e.g. municipal solid waste, waste acid and wet sewage sludge) were co-processed. The samples were analyzed for polychlorinated biphenyls (PCBs). The dioxin-like (dl)-PCB concentrations in the stack gases from run 1, 2, and 3 were 344.6, 548.7, and 104.3 pg m^{-3}, respectively. The toxic equivalency (TEQs) values for runs 1, 2, and 3 were 5.6, 8.9, and 0.7 pg TEQ Nm^{-3}, respectively. Calculation of net emissions for the three runs indicated that the co-incineration of other waste in addition to sewage sludge in cement kilns would not increase emission of the dl-PCBs. PCB concentrations in samples from the suspension boiler and humidifier tower, kiln-end bag filter, and cyclone preheater were much higher than those in samples from the kiln head area, indicating that these stages will be important for controlling PCB formation. Chlorinated biphenyl (CB)-77, CB-105 and CB-118 were the major dl-PCB congeners, CB-52, CB-101 were the major indicator PCB congeners, and tetra-CB to hexa-CB were the major homologues for the total input or output materials.

1. Introduction

Sewage sludge is a residue that is generated during water treatment. Among the available sewage sludge disposal strategies, thermal processes are considered the most useful for reducing the mass, volume, and organic pollutant content of sewage sludge (Werle and Wilk, 2010). One of thermal processes is co-incineration of sewage sludge in cement kilns, and this method has been studied previously (Conesa et al., 2008; Schuhmacher et al., 2009; Rovira et al., 2011; Aranda Usón et al., 2013; Rivera-Austrui et al., 2014). The benefits of disposing of sewage sludge in cement kilns have been discussed (Werle and Wilk, 2010; Aranda Usón et al., 2013). Due to the toxicity and persistence of persistent organic pollutants (POPs), the formation and emission of unintentionally produced POPs from this thermal process are of increasing public concern. Therefore, studies on the behavior of POPs during cement kiln co-processing of sewage sludge are needed.

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/

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* Corresponding author. State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.
E-mail address: grliu@rcees.ac.cn (G. Liu).

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Fs) and POP precursors, including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated benzenes, are emitted when sewage sludge is co-incinerated in a cement kiln (Harrison et al., 2006; Conesa et al., 2008; Rivera-Austrui et al., 2014). The effects of the PCDD/Fs generated during co-incineration of sewage sludge in cement kilns on the environment and human health have been comprehensively evaluated (Schuhmacher et al., 2009; Rovira et al., 2011). However, previous studies on cement kiln co-processing of waste have mainly focused on PCDD/Fs and PAHs, and few studies have investigated changes in polychlorinated biphenyls (PCBs) in cement kilns, even though these chemicals are harmful to human health and the environment (Ahlborg et al., 1992; Safe, 1993; Giesy and Kannan, 1998; Conesa et al., 2008, 2011; Nomiyama et al., 2014).

In a similar manner to PAHs and polychlorinated benzenes, PCBs will partition onto sewage sludge during wastewater treatment because they are lipophilic (Blanchard et al., 2004; Guo et al., 2009; Ozcan et al., 2013). This means that sewage sludge introduced to a thermal process will contain PCBs and precursors for the formation of PCBs (Weber et al., 2001; Pekárek et al., 2007; Jiang et al., 2015). The existing of PCBs and PAHs in the sewage sludge have been identified by previous studies. For example, Guo et al. reported PCB concentrations ranging from 65.6 to 157 ng g^{-1} dry weight (dw) in sewage sludge samples from eight urban wastewater treatment plants (Guo et al., 2009). Blanchard et al. reported PAH concentrations ranging from 14 to 31 mg kg^{-1} dw, and PCB concentrations ranging from 0.07 to 0.65 mg kg^{-1} dw in sludge from storage chambers (Blanchard et al., 2004). Besides that, the cooling processes after high temperature burning would have the potential to form PCBs (Jansson and Andersson, 2012; Tuan et al., 2012). Unintentional emission from industrial thermal processes is a major source of atmospheric PCBs (Liu et al., 2013). Earlier studies on emission of POPs from industrial thermal processes have shown that PCBs are emitted at the same time as PCDD/Fs and behave in a similar manner (Liu et al., 2009; Hu et al., 2013). Therefore, PCBs could form during co-processing of sewage sludge in cement kilns. Consequently, more studies on PCB formation and distribution within cement kilns during co-processing are needed.

To the best of our knowledge, however, there has been only one study on the emission of PCBs from sewage sludge co-incineration in a cement kiln (Rivera-Austrui et al., 2014). This study mainly focused on the levels of PCBs emitted from the kilns, and did not investigate how PCB formation varied in the different stages of the process. There are several stages in a cement kiln process, and each uses different operating conditions, which would affect PCB formations and degradations (Zhang et al., 2014; Dang et al., 2015; Jiang et al., 2015). Few studies were performed to analyze the variations of PCBs among the different stages of a cement kiln when co-processing sewage sludge. The investigation on the PCB variations from different stages of cement kiln co-processing sewage sludge could provide new knowledge for recognizing the dominant stages of PCB formations during the cement kiln co-processing sewage sludge.

In this study, stack gas and solid samples were collected from different stages of cement kilns during three separate runs of waste co-processing. Dried sewage sludge was the main waste co-processed in all three runs, and was the only waste processed in one of the runs. In the other two runs, other wastes were also processed in addition to the dried sewage sludge, including municipal solid waste (MSW) in one run, and waste acid and wet sewage sludge in the other. The aims of this study were as follows: (1) to clarify how PCBs are distributed at different process stages within cement kilns; (2) to identify the major sites for PCB formation within cement kilns; and (3) to demonstrate the congener and homologue profiles of PCBs from cement kiln co-processing solid waste. The results presented in this study will increase understanding of PCB behavior within kiln systems co-processing solid waste.

2. Materials and methods

2.1. Information on the cement kilns co-processing of solid waste and sample collection

Samples were collected from three waste co-processing runs from two cement kilns, which were operated using the similar protocol. Each cement kiln contained a rotary kiln, a pre-calciner, cyclone preheaters, a humidifier tower, a suspension (SP) boiler, two bag filters (one at the kiln end and one at the kiln head), a cooler, a coal mill, a boiler at the kiln head, and a chimney. For each run, stack gas samples, and solid samples from the kiln-end bag filter (ck-s9), SP boiler and humidifier (ck-s8), C1 preheater (ck-s7), raw meal (ck-s5), coal (ck-s4), clinker (ck-s3), boiler at the kiln head (ck-s2), and bag filter at the kiln head (ck-s1) were collected. In run 3, dried sewage sludge (ck-s6) was also collected. The techniques used in the three runs and the sampling sites are shown in Fig. 1, and were similar to those in a previous study (Jin et al., 2016).

The raw meal used in both Run 1 and Run 2 was from the same silo, and was a mixture of lime stone (87%), sewage sludge (7%), clay (1.5%) and other materials. Raw meal was added to the cyclone preheater, and passed through the pre-calciner, rotary kiln, and cooler. The gaseous products of pyrolysis of the municipal solid waste (MSW) were also imported into the pre-calciner and co-processed in the cement kiln in Run 2. The MSW had a combustible content of about 78% and was combusted in the incinerator at a rate of about 72,000 kg per day. For run 3, sewage sludge was imported separately to the raw meal. Dried sewage sludge (338,000 kg) was imported into the pre-calciner, 10,000 kg of waste acid was imported into the kiln head, and 38,000 kg of wet sewage sludge was added to the bottom of the pre-calciner. The flow rates for the stack gas, the masses of raw meal, masses of coals used, and masses of clinkers produced for the three runs are listed in Table 1. The solid lines represent the flow of solid materials, and the dotted lines represent the gas flows (Fig. 1). The fly ash from the kiln-end bag filter was recycled into the cyclone preheater with the raw meal.

2.2. Analytical method of PCB congeners

The PCBs were analyzed using isotope dilution high-resolution

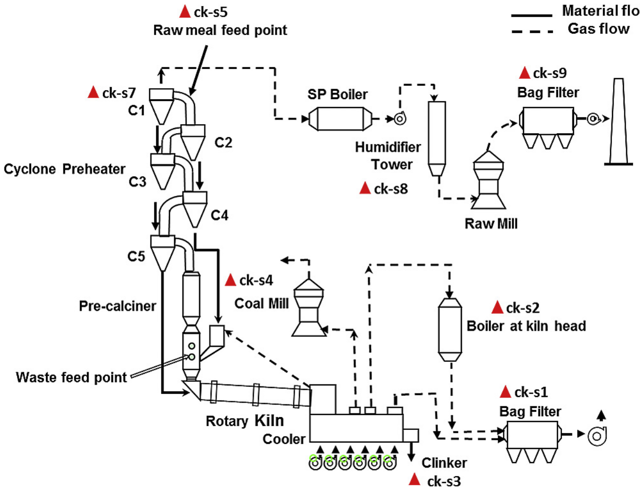

Fig. 1. Diagram of cement kiln production line.