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Field pilot study on emissions, formations and distributions of PCDD/Fs from cement kiln co-processing fly ash from municipal solid waste incinerations

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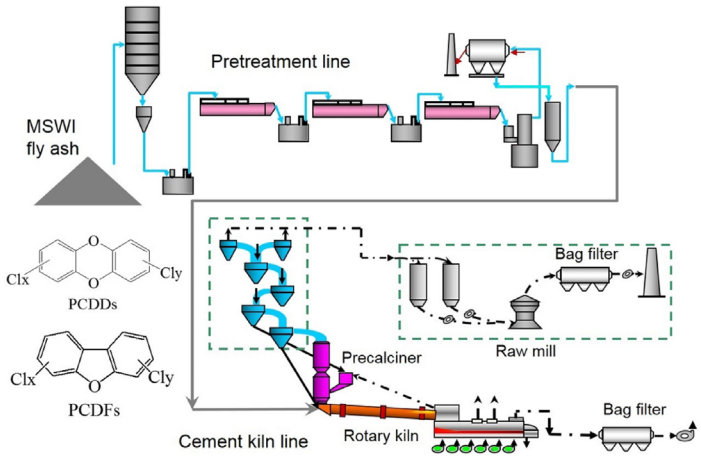
HIGHLIGHTS

- Dioxin distributions in cement kiln co-processing MSWI fly ash was studied.
- Stack emissions of PCDD/Fs were below the European Union limit for cement kilns.
- Tetra- and penta-chlorinated furans are the major homologs formed in cement kilns.
- PCDD/F concentration in particulates was correlated with chloride content.
- Mass balance indicated 94% reduction in PCDD/F TEQ input from the feed materials.

GRAPHICAL ABSTRACT



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ABSTRACT

A pilot study was performed to evaluate formation, distribution and emission of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from cement kilns that co-process fly ash from municipal solid waste incineration (MSWI). Stack gas and particulate samples from multiple stages in the process were collected and analyzed for PCDD/Fs. Stack emissions of PCDD/Fs were below the European Union limit for cement kilns (0.1 ng TEQ m^{-3}). PCDD/F concentrations in particulates from the cyclone preheater outlet, suspension preheater boiler, humidifier tower, and back-end bag filter were much higher than in other samples, which suggests that these areas are the major sites of PCDD/F formation. Comparison of PCDD/F homolog and congener profiles from different stages suggested that tetra- and penta-chlorinated furans were mainly formed during cement kiln co-processing of MSWI fly ash. Three lower chlorinated furan congeners, including 2,3,7,8-tetrachlorodibenzofuran, 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin and 2,3,4,7,8-pentachlorodibenzofuran, were identified as dominant contributors to the toxic

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equivalents (TEQ) of the PCDD/Fs. The concentration of PCDD/Fs in particulates was correlated with chloride content, which is consistent with its positive effect on PCDD/F formation. This could be mitigated by pretreating the feedstock to remove chloride and metals. Mass balance indicated that cement kilns eliminated about 94% of the PCDD/F TEQ input from the feedstock.

1. Introduction

Waste incineration produces polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in stack gas and fly ash, which is of concern as these compounds are toxic, persistent, and can bioaccumulate [1–3]. Filters and activated carbon have been used to reduce emissions of PCDD/Fs into the atmosphere from industrial thermal facilities, including waste incinerators [4–9]. These techniques are very effective, for example, the stack gas concentrations of PCDD/Fs were reduced from 194 ng International Toxic Equivalents (I-TEQ) m^{-3} to below 1.0 ng I-TEQ m^{-3} by injection of activated carbon and addition of a dual baghouse filter system in a kiln using the Waelz process [4]. However, at the same facility, the concentrations of PCDD/Fs in fly ash were still as high (10–100 ng I-TEQ g^{-1}). Similarly, at a municipal solid waste incinerator (MSWI) in Spain, the stack gas emissions of PCDD/Fs were reduced to below 0.01 ng TEQ m^{-3} from 3.26 ng TEQ m^{-3} after installation of a new air pollution control system combined with injection of activated carbon [9]. However, in this case, the PCDD/F concentrations in fly ash samples remained around 0.5 ng TEQ g^{-1} or higher. These case studies show that physical removal and adsorption techniques transfer unintentionally formed persistent organic pollutants into the fly ash phase. Therefore, the treatment of fly ash remains a serious problem for thermal related industries, including waste incineration operations.

Fly ash produced during waste incineration has been classified as hazardous waste in China [10]. It is considered to contain relatively high concentrations of PCDD/Fs because of it contains compounds that catalyze the heterogeneous formation reactions of PCDD/Fs [11,12]. Between 2007 and 2013, the number of MSWIs in China increased from 66 to 166, and the mass of incinerated solid waste increased from 14,351 to 46,337 thousand tons [13]. This increase in solid waste incineration will greatly increase in MSWI fly ash for disposal [13]. On incineration of solid waste, fly ash is produced at a mass fraction of 3–5% of the original waste mass [14–16]. Therefore, it is estimated that the mass of MSWI fly ash produced in China will have increased from 431–718 thousand tons in 2007 to 1390–2317 thousand tons in 2013. Disposal of this hazardous fly ash remains a challenge.

Cement kilns have increasingly been used for destroying hazardous waste because they operate at the high temperatures (normally >1200 °C) that are required for decomposition of organic chemicals [17]. Cement kilns have been used for the disposal of polybrominated diphenyl ether contaminated soils [17]. Formation and emission of PCDD/Fs from a cement kiln processing a solid fuel recovered from municipal solid waste has been studied [18,19]. Dioxins form in cement kilns, and their release and impact on surrounding environment has been demonstrated [20–24]. However, to date, incineration of MSWI fly ash in a cement kiln has not been performed on an industrial scale or in any pilot studies. To the best of our knowledge, the formation and distribution of PCDD/Fs in cement kilns that co-process MSWI fly ash have not been reported. There are hundreds of cement kilns in operation in China, and cement manufacture in China accounts for about 60% of global production. Therefore, application of cement kilns to destruction of MSWI fly ash is an attractive proposition. Research on the formation, emission and distribution of PCDD/Fs in cement kilns that co-combust MSWI fly ash will provide essential knowledge for assessing the suitability of cement kilns for incinerating this material.

In the present study, a pilot study was carried out on a MSWI fly ash pretreatment line and two cement kiln lines to gain insight into the formation, emission and distribution of PCDD/Fs in cement kilns that co-process MSWI fly ash. Stack gas and particulate samples from various stages in the process were collected and analyzed by isotope dilution high resolution gas chromatography combined with high resolution mass spectrometry (HRGC/HRMS). The aims of this study were as follows: (1) to measure emission of PCDD/Fs to the atmosphere during cement manufacturing with co-combustion of MSWI fly ash, which could be used to evaluate the effectiveness of cement kilns for MSWI fly ash destruction; (2) to identify the sites of PCDD/Fs formation in a cement manufacturing line, which could provide specific knowledge for controlling PCDD/F formation from these stages in the process; and (3) to evaluate variations in the distributions and profiles of PCDD/Fs from different stages in the process of cement manufacturing, which might aid understanding of the PCDD/F formation mechanisms in cement kilns that co-process MSWI fly ash.

2. Experimental

2.1. MSWI fly ash pretreatment line, cement kilns, and sample collection

MSWI fly ash was pretreated before co-combustions in the cement kilns in a pilot cement plant. A schematic of the pretreatment line is shown in Fig. 1(A). The capacity of the pretreatment line was about 30 tons per day. The primary aim of pretreatment was to remove compounds, such as chloride and metal ions, contained in the MSWI fly ash that might damage the cement kiln equipment. Removal of these ions would improve the quality of the cement clinker, and also potentially reduce PCDD/F formation in the cement kiln as these ions can act as catalysts for this process. Pretreatment involved washing the fly ash three times with water containing a small quantity of organic surfactant.

Two cement kilns suitable for high-temperature treatment of MSWI fly ash were investigated in the pilot study. The daily outputs for cement kiln lines 1 and 2 were about 2000 and 2500 tons of clinker, respectively. The kilns were both operated at around 1300 °C in a counter-current configuration, in which gases and solids flowed in opposite directions through the kiln to provide efficient heat transfer. Fabric filters were used as air pollution control devices (APCD). A schematic view of the cement kilns is shown in Fig. 1(B). Cement kiln line 1 had been used to co-process MSWI fly ash continuously for about 300 days, at a typical rate of 20 tons of fly ash per day, and produced cement clinker at a mass fraction of about 1% of the original fly ash mass. To evaluate the potential for a memory effect from long-term thermal treatment of MSWI fly ash on PCDD/F formation and distribution, cement kiln line 2 was also used. This cement kiln had not been used for the destruction of MSWI fly ash before this study. Operating parameters (temperature and pressure) for the pretreatment line and cement kiln lines 1 and 2 are provided along with sample labels for samples