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Variations and factors that influence the formation of polychlorinated naphthalenes in cement kilns co-processing solid waste

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HIGHLIGHTS

- PCN destruction efficiencies of cement kilns were derived.
- Factors influencing PCN variation and formation were identified.
- Major pathways for PCN formation and decomposition in cement kiln were discussed.
- PCN indicators for sources involved with coal burning were proposed.

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ABSTRACT

Pilot studies of unintentionally produced pollutants should be performed before waste being co-processed in cement kilns. Polychlorinated naphthalene (PCN) formation and emission from cement kilns co-processing sorted municipal solid waste, sewage sludge, and waste acid, however, have not previously been studied. Here, PCNs were analyzed in stack gas samples and solid samples from different stages of three cement production runs. PCN destruction efficiencies were higher when waste was co-processed (93.1% and 88.7% in two tests) than when waste was not co-processed (39.1%), so co-processing waste would not increase PCN outputs. The PCN concentrations were higher in particle samples from the C1 preheater and stages at back end of kiln than in particle samples from other stages, suggesting that cyclone preheater and back end of kiln should be focused for controlling PCN emissions. Besides that, based on the variation of PCN concentrations and corresponding operating conditions in different stages, the temperature, feeding materials, and chlorine content were suggested as the main factors influencing PCN formation. The PCN homologue and congener profiles suggested chlorination and dechlorination were the main PCN formation and decomposition pathways, and congeners CN-23, CN-46, and CN-59 appear to be appropriate indicators of PCNs emitted from coal-burning sources.

1. Introduction

Co-processing waste when producing cement is a waste management technique that offers the benefits of simultaneously destroying waste, producing cement, and recycling energy [1–3]. China has a large cement industry that accounts for about 60% of annual global cement production. Co-processing waste in cement kilns offers economic, technical, and environmental benefits that make it an attractive and promising waste treatment technique. However, the problems such as organic chemical, carbon dioxide, and heavy metal emissions, are already associated with co-processing waste in cement kilns, and more detailed studies need to be performed before the benefits of co-processing waste in cement kilns can be considered to have been comprehensively evaluated [1,4–7].

Unintentionally produced persistent organic pollutants (POPs) are organic chemicals that can form during thermal processes. Estimations of unintentionally produced POPs formed during different thermal processes allowed emissions of unintentionally produced POPs by various industrial plants to be comprehensively recognized and effectively controlled. Polychlorinated naphthalenes (PCNs) are chemicals that have similar structures and toxicities to poly-

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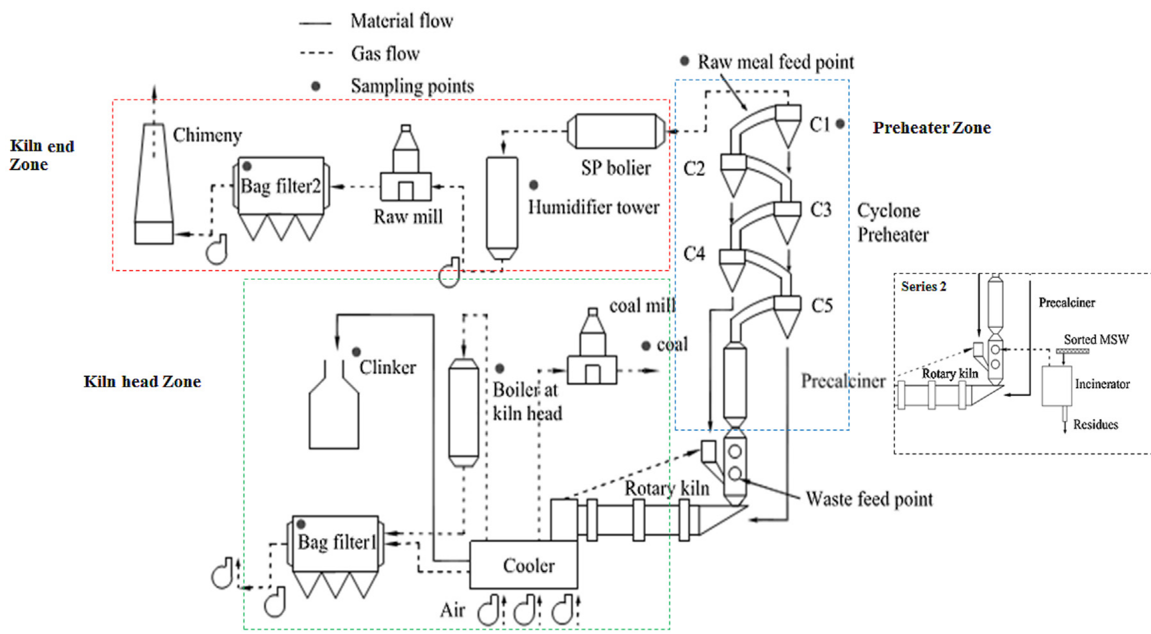

Fig. 1. Diagram of a cement kiln with the sampling points marked.

chlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and have recently been added to Annexes A and C of the Stockholm Convention, indicating the obligation of reducing the unintentional release of PCNs from industrial thermal sources besides forbidding the production and use of PCNs as chemicals for signatories [8]. The unintentional production of PCNs during thermal processes has already been the main source of PCNs in ambient air. Previous studies have reported larger amounts of PCNs than PCDD/Fs were emitted during various thermal processes [9,10]. Therefore, studies of PCN emissions during different thermal processes are of significance necessary. The present study would investigate the formation of PCNs when cement is produced using co-processed waste, and improve our understanding of PCN formation and the factors that influence PCN formation during industrial processes.

The PCDD/Fs are extremely toxic, and various industries are subject to PCDD/F emission standards in many countries. Previous studies of POPs in cement kilns co-processing waste have mainly been focused on PCDD/Fs. PCDD/Fs have been found to be emitted when wastes such as fly ash, meat meal, municipal solid waste (MSW), sewage sludge, and tires are co-processed in cement kilns [1,11–13]. It has been found in previous studies that co-processing waste in cement kilns does not increase PCDD/F emissions, and the concentrations emitted in those studies were always below the European Union limit for cement kilns (0.1 ng toxic equivalents [TEQ] m^{-3}) when the kilns were operated under normal conditions [1,11,14–16]. Mass balances of cement kilns have also shown that co-processing waste in cement kilns is an efficient way for destroying PCDD/Fs [11,15,17]. Co-processing different wastes in cement kilns has been found in previous studies not to markedly affect the congener profiles of the PCDD/Fs emitted, but the results of these studies provided insight into PCDD/F formation pathways and allowed specific PCDD/F sources to be identified and PCDD/F emissions to be apportioned [12,13].

Close correlations have been found between PCN and PCDD/F concentrations in samples from different thermal processes [18]. Thus, the previous literature reports of PCDD/Fs released from cement kiln co-processing wastes hint that the formation and emission of PCNs from similar processes might occur. PCNs have already been found to be emitted from cement kilns with no waste co-processed [19]. However, to the best of our knowledge, no study of PCNs in cement kilns co-processing sorted MSW, or simultaneously co-processing dried sewage sludge, wet sewage sludge and waste acid has been performed. Additionally, no study of the factors that influence the formation of PCNs when waste is co-processed in cement kilns has been carried out. Such studies would provide information that would help in the development of PCN control measures.

In this study, clinker, coal, raw meal samples, sludge, stack gas samples and particle samples from other different stages of the kiln systems in three cement production processes were collected. The samples were analyzed for PCNs by isotope dilution high-resolution gas chromatography and high-resolution mass spectrometry. The aim was to obtain detailed information on the formation of PCNs when cement was produced while co-processing different wastes, to assess variability in the PCNs formed, and to identify factors that influence PCN formation in cement kilns co-pressing waste. The results of this study could improve our understanding of factors that influence PCN formation, and be useful in identifying new PCN sources and developing strategies for controlling PCN emissions from cement kilns co-processing waste.

2. Experimental

2.1. Basic information

Samples were taken during three cement production runs (Series 1, Series 2, and Series 3); information on these is given in Table 1. Series 2 was performed at a plant when sorted MSW was co-processed, and Series 1 was performed at the same plant when no waste co-processed. Non-combustible materials, such as the glass and metals, were also contained in the raw MSW. Thus, the MSW was sorted to remove those non-combustible materials and to improve the heat value before being co-processed by the cement kilns. The sorted MSW contained relatively high proportion of combustible wastes, such as plastics, wood, and papers. The proportion of combustible component was about 78% in the sorted MSW of this study. As shown in Fig. 1 insert, the sorted MSW was incinerated in the incinerator and then the flue gas was added to the bottom of the precalciner. Dried sewage sludge was mixed with raw meals, and co-processed in both Series 1 and Series 2. Series 3 was performed