Journal of Hazardous Materials 330 (2017) 135–141

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Research paper

Evaluation of dioxins and dioxin-like compounds from a cement plant using carbide slag from chlor-alkali industry as the major raw material

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HIGHLIGHTS

- POP profiles from a cement kiln using carbide slag as raw material were studied.
- PCN emissions were higher than those of PCDD/Fs and PCBs.
- Mass balance showed that TEQs of all POPs were reduced by this kiln system.
- PCN emissions from the investigated system should be emphasized.

ARTICLE INFO

Article history:
Received 18 November 2016
Received in revised form 8 February 2017
Accepted 12 February 2017

Keywords:
Cement
Dioxin
Polychlorinated biphenyl
Polychlorinated naphthalene
Carbide slag

ABSTRACT

Carbide slag produced from chlor-alkali industry contains high amounts of calcium compounds and can potentially be used as raw material for cement production; however, it contains large amounts of chlorine so it is essential to evaluate the emissions of chlorinated organic pollutants, including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polychlorinated naphthalenes (PCNs). A field study of the emission profiles of these pollutants in a cement plant using such slag was performed. The average concentrations of PCDD/Fs, PCBs, and PCNs in stack gases collected at the kiln back end were 6.31, 1.07, and 31.89 pg TEQ m^{-3}, respectively. PCDFs dominated over PCDDs in particulate samples. Di- to pentachlorinated biphenyls were dominant homologs in the particulate samples. MonoCBs were the dominant homolog in stack gases from the kiln back end, and homolog concentrations decreased with increasing chlorine numbers. Mono- and diCNs accounted for 48–98% of PCNs. The estimated toxic equivalents of stack gas emissions of PCNs, classified as new persistent organic pollutants under Stockholm Convention, were unexpectedly higher than those of PCDD/Fs and PCBs. A mass balance indicated that all of the toxic equivalents were reduced by this cement kiln system. The highest 2,3,7,8-PCDD/F output is with clinker.

1. Introduction

In 2014, the amount of industrial solid waste produced in China was 3.3 billion tonnes, which was significantly more than the 2004 value of 1.2 billion tonnes [1,2]. Significant reutilization of solid wastes as resources and sustainable development of traditional industries are important to enable environmental protection and human health. Chlor-alkali production is widely recognized as a polluting industry [3,4]: large amounts of carbide slag are produced in the generation of acetylene from the reaction of carbide (CaC_2) with water. In 2013, the annual amount of carbide slag produced in China was about 20.1 million tonnes, as a consequence of the rapid development of acetylene-involved polyvinyl chloride (PVC) production. A long-term problem for this industry is that the carbide slag occupies valuable land and can lead to pollution of soils and waters [5]. Carbide slag requires emerging disposal strategies that consider its large mass and volume: resource utilization of such solid wastes is the best approach. The calcium oxide content of

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http://dx.doi.org/10.1016/j.jhazmat.2017.02.018
0304-3894/

carbide slags is about 60%, and the major component of the raw materials used for clinker production is also calcium-containing minerals [6]. It has been shown to be possible to use carbide slag as the dominant component in cement production, which could save limestone resources [5]. The potential of cement kilns to use these solid wastes as raw materials is large; however, before using these wastes for cement production, it is key to understand and resolve possibly elevated formation and emissions of toxic and bioaccumulative chlorinated organic pollutants.

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like compounds, including polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs), are unintentionally produced chlorinated persistent organic pollutants (POPs). In 2015, PCNs were listed as new POPs in the Stockholm Convention [7]. POPs have adverse effects, including carcinogenicity, endocrine disruption, and bioaccumulation [8–13]. Furthermore, their persistence in the environment or biota, as well as their long-range transport on global scale [14], have led to their control and elimination proving to be an intractable problem for researchers worldwide [15,16]. Research into unintentionally produced POPs is important: unintentional sources of PCDD/Fs, PCB, and PCNs could include waste incineration [17,18], secondary non-ferrous metallurgy [19–21], steeling-making [22–24] and other sources, such as cement kilns [25–27]. According to 2012 data, 58% of global cement was produced in China [28]. An increasing number of cement kilns are used to co-process solid wastes in China, and the release of POPs from cement kilns has been the subject of recent focus [29,30]. Research into POP emissions from cement kilns co-processing municipal solid wastes [31,32], sewage sludge [33,34], municipal solid waste incinerator fly ash [35], pesticides [36], contaminated soils [37], and other solid wastes is reported, but there is no available knowledge about unintentional POP emissions from cement kilns reusing high-volume solid wastes as major components of the raw materials for clinker production.

As a typical industrial process using materials involving chlorine, the chlor-alkali industry is an important source of formation and emission of unintentional POPs [38–43]. Formation and emissions of POPs in cement kilns using solid waste from this industry should therefore be investigated to determine feasibility of its intensive practical industrial application. The key concern is the levels and profiles of unintentional POP formation and release from cement plants using carbide slag that contains a high chlorine content as a raw material for clinker production. Previous co-processing studies have mainly investigated industrial wastes, including chromium slag and electroplating sludge, that might cause heavy metal pollution; solid wastes with high chlorine contents have not yet received sufficient attention [44]. To best of our knowledge, the emissions and profiles of unintentional POPs in stack gas and particulate samples in cement kilns using carbide slag as the major raw material component for clinker production have never been studied.

In this work, a field study on the emissions and profiles of PCDD/Fs, PCBs, and PCNs in a cement kiln using such slag was performed. Particulate and stack gas samples from multiple process stages of the kiln were collected and analyzed. The primary aims of this study were: (1) to evaluate the concentrations and emission factors of PCDD/Fs, PCBs, and PCNs in stack gas emissions from a cement plant using carbide slag as a major component of the raw material for clinker production; (2) to clarify the levels and profiles of PCDD/Fs, PCBs, and PCNs in particulate samples from different process stages of the cement plant. The study could provide essential knowledge to develop possible strategies and techniques to control POP releases during utilization of the slag as a resource. The results are important in promoting sustainable development of the cement and chlor-alkali industries.

2. Experimental

2.1. Cement kiln description and sample collection

The investigated cement kiln was a rotary kiln with two-stage cyclone preheaters for the raw feed (Fig. 1). A by-pass system was designed to remove chloride salts through a branched duct from the back of the kiln to ensure low chloride ion levels in the clinker and simultaneously improve conditions for reducing POP formation. The main constituent of the carbide slag was calcium hydroxide. The slag constituted 76% of the total raw material used for

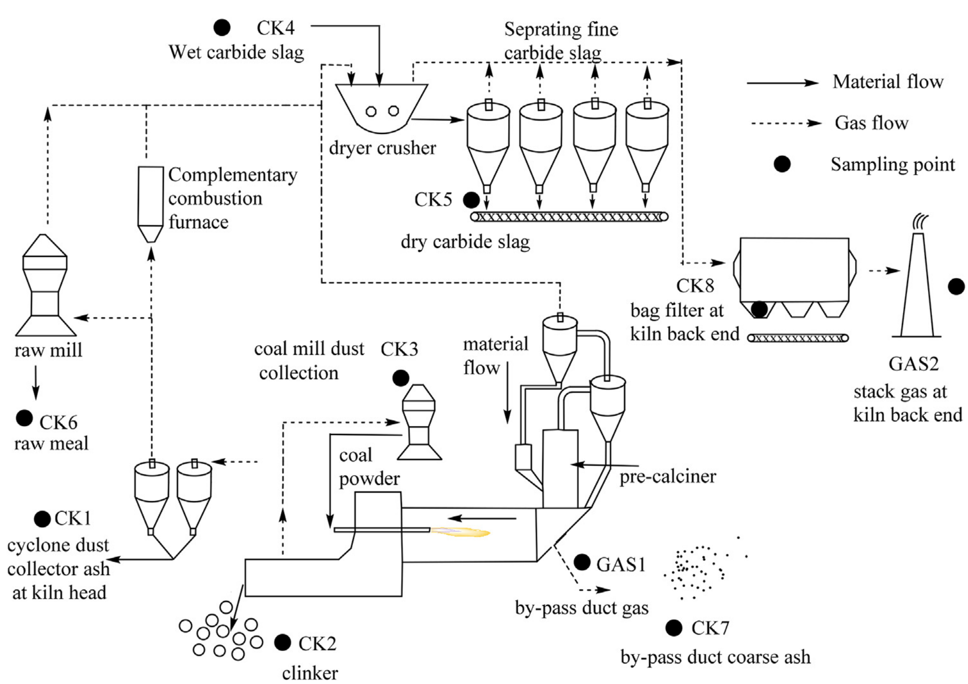

Fig. 1. Sampling points for particulates and gases in a cement kiln using carbide slag as the major raw material component.