A CASE STUDY OF POLYCHLORINATED DIBENZO (P) DIOXIN AND FURAN (PCDD/F) EMISSION FROM A CEMENT KILN IN VIETNAM

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Introduction

Vietnam has joined Stockholm convention on persistent organic pollutants (POPs) in 2004 and the annex C of the convention pointed out that elimination of the release of unintentionally produced POPs such as polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) are urgently concern. There were 17 different industrial source categories defined in the Convention, which have comparatively high formation and releases of dioxins and furans into the environment. In those, the cement kiln produced industry co-processing hazards wastes was mentioned as the high formation and release of these toxic chemical to environment.

There are four main procedures for manufacture of cement, include wet process, semi-wet process, dry process and semi-dry process. Nowadays, most of processing of clinker which was used in Vietnam is dry process. In the dry process, the raw materials were ground and dried to fine and fed to pre-heater process. CKA is a cement kiln manufacturer with co-processing of alternative raw materials, fed to the pre-heater. According to new search of Foundation for Industrial and Scientific Research (SINTEF, Norway)[1,2], this process does not influence or change PCDD/PCDF emission. The SINTEF reported also that many cement kiln factories in developing countries met the requirement of 0.1 ng TEQ/Nm^3 for PCDD/PCDF effluents

In Vietnam, the levels and patterns of these emissions from cement kiln industry were limited. This study investigates concentration and pattern of PCDD/F from a modern cement kiln factory (named as CKA) which is co-processing hazard wastes in cement kiln under normal operating condition. Total of four samples, including two stack-gas samples and two residue samples provided data on PCDD/F congener concentration. The average PCDD/F concentration of stack gas samples was 0.232 ng/Nm^3 and the WHO toxic equivalent quantity (TEQ) was 0.0345 ng TEQ/Nm^3. This study indicated that the PCDD/F concentration in the stack-gas samples collected in the cement kiln CKA was much lower than the international guidelines for emission of PCDD/F for cement kiln facility (most regulation was 0.1 ng TEQ/Nm^3).

This is the first study measuring PCDD/PCDF in a modern cement kiln with co-processing of textiles wastes and the emission characteristics of PCDD/PCDF in this factory in Vietnam were evaluated. These results can be compared with PCDD/PCDF data from toolkit software provided by UNEP and SINTEF.

Material and method

Sampling collection

A rotary kiln cement factory in the South of Vietnam has been chosen to investigate for baseline of PCDD/F concentration. Several of samples were taken from this cement kiln factory, including raw meal, fuel, fly ash, by-pass dust, clinker and stack-gas. The flue gas samples were taken from main stack of cement kiln following Figure 1. The details of other sampling points have been showed in Figure 1.

The stack gas sampling was conducted following the isokinetic sampling procedure of US EPA Method 23 -[7]. The sampling train equipment in this study was comparable to that specified by US EPA-modified method 5. Before sampling, XAD-2 resin was spiked with PCDD/F surrogate standards, including $^{37}Cl_4$-2,3,7,8-TCDD, $^{13}C1_2$-1,2,3,4,7,8-HxCDD, $^{13}C1_2$-2,3,4,7,8-PeCDF, $^{13}C1_2$-1,2,3,4,7,8-HxCDF, and $^{13}C1_2$-1,2,3,4,7,8,9-HpCDF. Particulate matter was collected on a quartz fiber filter (Pall Corporation, USA) in a glass holder. Following the filter, the gas stream passed through a condenser and resin contenting XAD-2 material to trap PCDD/PCDF in gas phase of flue gas. After that ,three impinges were connected in a series, including two impinges contenting

100ml of water and one impinges contenting 100 g of silica gel. Each stack-gas sampling was conducted in the condition of normal operation of this cement kiln factory and samples were collected in 4 hours. To ensure free contamination of the collected samples, travel blank and filed blank samples were also taken during this field sampling campaign.

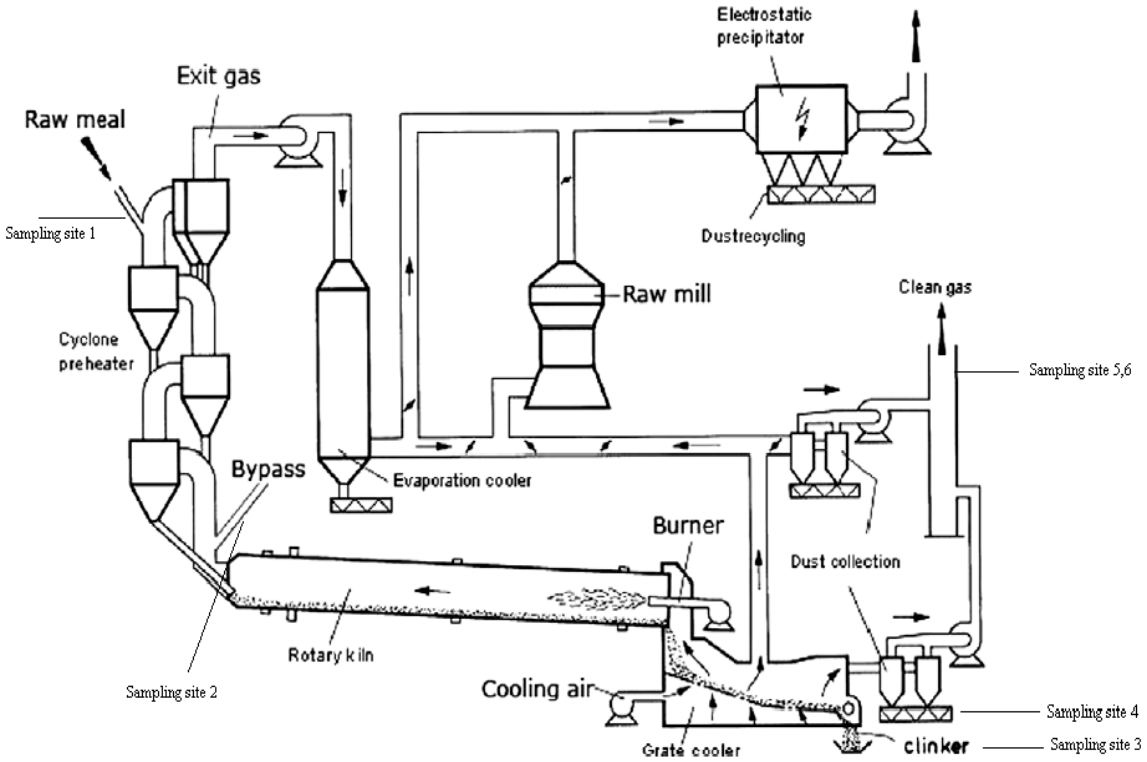

Figure 1: Sampling sites at CKA cement kiln

Sample analysis

Stack-gas samples including both of gas phase and particle phase had been combined and Soxhlet extracted by 200 ml of toluene in 24 hours. The solid matrix samples including electrostatic precipitator (EP) dust, bypass dust, raw meal and clinker were air-dried and crushed to less than 1 mm before extract. For analysis, 10 g of solid matrix sample was Soxhlet extraction by 200 ml of toluene in 24 hours. The extracts were concentrated to 1 ml and treated by concentrated sulfuric acid (98 %) to colorless. Sample was clean-up by two stages of multi-layer silica gel column and carbon column. Both silica gel and carbon columns were purchased from Supelco. Finally, ^{13}C-labeled injection standards were added to concentrated samples under N_2 gas stream before injection to HRGC/HRMS instrument.

Analysis procedure for 17 toxic - PCDD/F congeners has been carried out on the high resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS) based on US EPA method 23 with slight modifications. The samples were analyzed by isotope dilution on a Micromass Autospec Ultima system (Waters, UK) with GC Agilent 7890A and DB-5MS (60m x 250µm i.d x 0.25 µm film thickness) capillary column. The oven temperature program was as follows: 140^{o}C to 220^{o}C at 5^{o}C/min, 220^{o}C for 16 minutes, 220 ^{o}C to 235at 5 ^{o}C/min, 220-235°C at 5 °C/minute, 235°C for 7 minutes and 235-330°C, at 5 °C/minute. The injector and interface temperatures were 270^{o}C, 290^{o}C, respectively. The mass spectrometer was operated with a resolution greater than 10,000 under positive EI conditions, and data were obtained in the voltage selected ion -recording (Voltage SIR) mode.

Result and conclusion

PCDD/PCDF concentration

The obtained results on PCDD/F concentration in various samples from CKA cement are given in Table 1. Stack gas samples contained TEQ concentration of 0.0124-0.0566 ng/Nm^3, which are comparable to PCDD/F emission from cement kiln in other countries. The UNEP toolkit for dioxin emission has recommended that the modern cement needs to meet an emission limit of 0.1 ng TEQ/Nm^3 to the air[6]. Recently, Vietnam Ministry of Natural Resources and Environment promulgated the national technical regulation on co-processing of hazard wastes in cement kiln, which maximum concentration of PCDD/F was 0.6 ng TEQ/Nm^3 (namely as QCVN 41:2001). Thus, the result showing in this study was much lower than Vietnam and international guideline for PCDD/F emission for cement kiln. In addition, PCDD/F concentration of stack gas samples were also compared with other measurements from industrial countries, such as EU countries (mean: 0.016 ng TEQ/Nm^3)[9], Japan (<0.094 ng TEQ/Nm^3)[8], Australia (0.001-0.007 ng TEQ/Nm^3)[10] and developing countries such as Thailand (0.0105 ng TEQ/Nm^3)[1] and Sri Lanka (0.018 ng TEQ/Nm^3)[1]. Overall, the concentration of PCDD/F from CKA cement was below the emission factor of UNEP toolkit and Vietnam emission limit values. The emission factor for PCDD/PCDF of CKA cement was not calculated and comparable with the emission factor from UNEP toolkit[6], which needs more PCDD/F data.

Bypass dust has collected at sampling site 2 (Figure 1) containing TEQ concentration of 2.4 ng TEQ/kg, and most congener was below or closes the detection limit. Low emission in bypass dust has been reported in some other studies in UK kiln (0.001-30.0 ng TEQ/kg)[5]. Beside, dust samples collected at electrostatic precipitator had concentration of 19.5 ng TEQ/kg; this was also in range of concentration measured by UK cement kiln.

Table 1: Comparison of PCDD/F concentration in various samples from CKA cement and other countries

Country	PCDD/Fs value	Unit	Sample matrix	Number of sample	Year of reference	Reference
EU countries	0.001-0.163	ng TEQ/Nm^3	Stack gas	110	2003	The European Cement Association
	0.016	ng TEQ/Nm^3	Stack gas	243	2006	
UK	0.001-30.0	ng TEQ/kg	Residue	ND	1997	Dyke et al
Japane	< 0.094	ng TEQ/Nm^3	Stack gas	54	2000	Japan ministry of environment
	<0.126	ng TEQ/Nm^3	Stack gas	51	2001	
Australia	0.001–0.07	ng TEQ/Nm^3	Stack gas	15	2002	Australia EPA
Thailand	0.655	ng TEQ/kg	Residue	2	2008	Kare K
	0.0105	ng TEQ/Nm^3	Stack gas	2	2008	Kare K
Sri Lanka	0.018	ng TEQ/Nm^3	Stack gas	ND	2010	Kare K
Vietnam	0.012-0.057	ng TEQ/Nm^3	Stack gas	2	2011	This study
	2.4-19.5	ng TEQ/kg	Residue	2	2011	

PCDD/F congener profile

Figure 2 showed PCDD and PCDF congeners profile at the CKA cement kiln factory. Overall, the PCDD/PCDF profile of CKA cement kiln showed that PCDF congeners contributed proportion higher in concentration than PCDD congener, Moreover, four PCDD/F congeners, namely 2,3,7,8-TCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,7,8-HpCDD and OCDD were showed at the highest concentration. The 2,3,7,8-TCDF and OCDD were the most frequently the congeners found at cement facilities that both use or not use hazardous wastes. The results in this study were comparable with those reported by Karstensen and Michael Ames[2,3,4] . Further studies are needed to provide more databases on PCDD/F emission from industrial facilities in Vietnam.

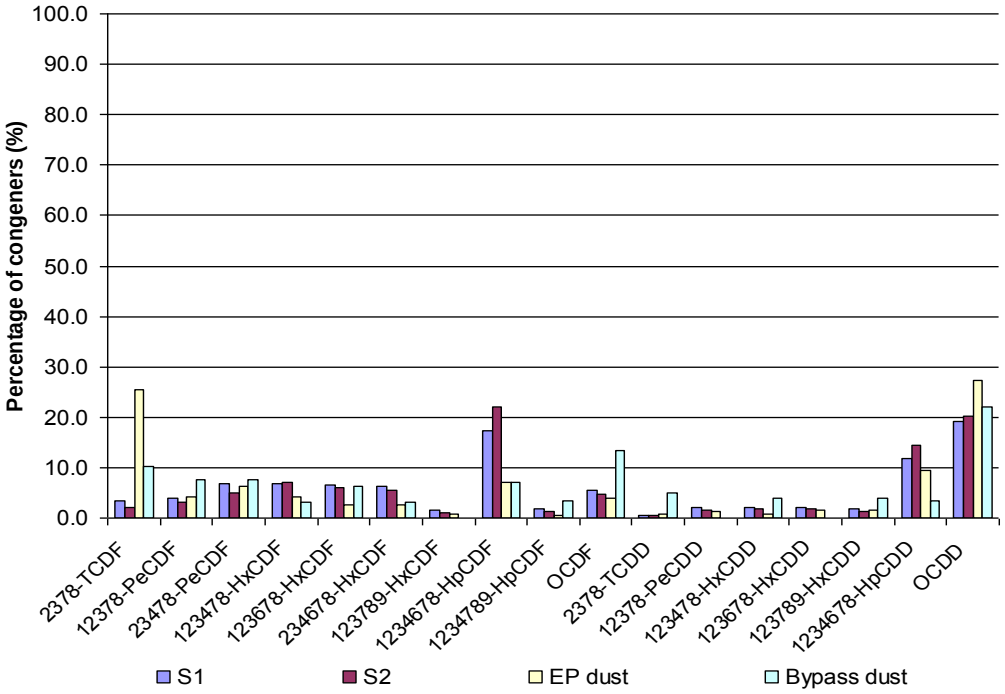

Figure 2: PCDD/F congeners profile in difference matrix samples

Acknowledgements

This study was supported by grants from Dioxin Laboratory Project funded by Bill and Melinda Gates Foundation and the Atlantic Philanthropies Foundation, and the Project "Introduction of BAT and BEP methodology to demonstrate reduction or elimination of unintentionally produced persistent organic pollutants (UP-POPs) releases from industry in Vietnam" (GF/VIE/08/005) funded by the Global Environment Facility (GEF) through the United Nation Industrial Development Organization (UNIDO).

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