Formation, Reduction and Emission Behaviors of CBzs and PCDD/Fs from Cement Plants

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ABSTRACT

The formation, reduction and emission behaviours of chlorobenzenes (CBzs) and polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) were studied in a typical dry cement kiln in China. The operating conditions were scrutinized at various positions by monitoring the concentrations of CO, NO_x, HF and HCl in the flue gas. Furthermore, the concentration, gas/particle partition and congener distribution of CBzs and PCDD/Fs were analyzed at the outlet of cyclone pre-heater, suspension pre-heater, raw mill and stack. The main PCDD/F formation zone was proven to be the first stage of pre-heater and the congener distribution of PCDD/Fs was significantly affected by the recycling ash. Specially, the concentration of CBzs continually increased with the flowing of flue gas. The final emissions of PCDD/Fs and CBzs in the flue gas were 0.016 ng I-TEQ Nm^{-3} and 26 µg Nm^{-3}, respectively. Moreover, the reduction efficiency of I-TEQ via bag filter was up to 81% and 86% for gas and particle phase PCDD/Fs, respectively. Most importantly, the mass balances indicated that raw meal was the dominant input and the rotary kiln incinerating waste was clearly a weighed PCDD/F and CBz sink. Furthermore, HCBzs correlated well with the total I-TEQ during the whole process of cement production.

Keywords: PCDD/Fs; CBzs; Cement kiln; Co-processing RDF; Mass balance.

INTRODUCTION

By the end of 2013, the number of municipal solid waste incineration (MSWI) plants in China increased to 155, with a disposal ability of 164000 ton d^{-1} (National Bureau of Statistics of China, 2014). However, it still could not meet the basic disposal requirement of municipal solid waste (MSW). Thus, co-incineration in cement kilns has been significantly developed and promoted mainly because of its affordable, environmentally sound and sustainable characteristics (Abu-Allaban *et al.*, 2011).

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are major organic pollutants emitted from MSWIs (Olie *et al.*, 1977; Hatanaka *et al.*, 2000; Jin *et al.*, 2009). The main sources for the PCDD/F formation are precursors, which could be also found in the cement kiln. Lots of studies have indicated that the formation and emission of PCDD/Fs from the cement kiln is inevitable (Giannopoulos *et al.*, 2007; Conesa *et al.*, 2008; Karstensen, 2008). For instance, the I-TEQ values were in the range of 0.002–0.017 pg I-TEQ Nm^{-3} from cement kilns in China (Yan *et al.*, 2014). Moreover, the mass concentration of PCDD/Fs varied from 0.280 to 5.32 ng Nm^{-3}, while I-TEQ concentration varied from 0.033 to 0.837 ng TEQ Nm^{-3} in Vietnamese cement plant (Thuong *et al.*, 2014). By using long-term sampling devices, levels of 0.009 ng I-TEQ Nm^{-3} were also detected in the flue gas of cement kilns (Rivera-Austrui *et al.*, 2012). Hence, the emission of PCDD/Fs from the kiln should be paid more attention.

The pre-heater in the kiln may be the main zone for PCDD/F formation, especially for the first stage of cyclone pre-heater (C1) (Iino *et al.*, 1999; Weber and Hagenmaier, 1999; Cunliffe and Williams, 2009). Mass balance of dioxins over a cement kiln has been built by Li *et al.* (2015), suggesting that cement kiln is certainly a sink process of PCDD/Fs (Li *et al.*, 2015). However, the reduction and adsorption behaviors of PCDD/Fs in the flue gas has never been studied. Moreover, the feeding rate of the co-incinerated refuse-derived fuel (RDF) in our previous study is 8 ton h^{-1} and further work should be done when more MSW was co-incinerated.

Chlorobenzenes (CBzs) are generally considered as persistent micropollutants in the environment and they can act as an organic precursors to the PCDD/F molecule (McKay, 2002). The possible formation mechanism of CBzs is concluded in the following: (1) benzene can react with

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chlorine species at a low enough temperature; (2) the resulting radical further reacts with Cl_2 to form CBzs (Gullett *et al.*, 2000). Furthermore, it might also be formed by the reaction of phenyl and Cl radicals (Ryu *et al.*, 2004). Until now, the formation and release of CBzs in the MSWI has been fully studied (Stanmore, 2004). While the knowledge related with formation, reduction and emission behaviors of CBzs for cement kiln is yet very scarce.

The amounts of PCDD/F species formed depend greatly on the gas composition and also associated with the foundation of CBzs. Good correlations are found between CBzs and PCDD/Fs in the MSWI (Lemieux, 2004). For instance, 1,2,4,5-TCBz is the best indicator for PCDD/F among the PCBz congeners (Pandelova *et al.*, 2006). Whereas the relationship between PCDD/Fs and CBzs during the whole process of cement production has never been studied.

This paper describes the formation, reduction and emission behaviors of PCDD/Fs and CBzs in a typical dry cement kiln with 5000 ton d^{-1} clinker capacity. The feeding rate of the co-incinerated RDF was up to 15 ton h^{-1}. The concentrations of SO_2, NH_3, HF and HCl at various sampling positions were monitored. Furthermore, the concentration and congener distribution of PCDD/Fs and CBzs were investigated at the outlet of cyclone pre-heater, suspension pre-heater (SP), raw mill and stack. Gas/particle partition of PCDD/Fs in flue gas was also observed to develop an efficient cleaning system of emission gas. Combined with the measurement of solid samples, mass balances of PCDD/Fs and CBzs were built and their corresponding emission factors were also calculated. The results could be used to fully understand the emission characteristics of PCDD/Fs and CBzs and to guide the further control. Most importantly, the relationship between PCDD/Fs and CBzs during the whole process of cement production was analyzed.

MATERIAL AND METHODS

Cement Kiln

The kiln with clinker capacity of 5000 ton day^{-1} is in a dry process, presenting a state-of-the-art configuration with a pre-heater/precalciner consisting of four stage cyclone type vessels (Li *et al.*, 2015). As shown in Fig. 1, they also feature a SP, raw mill and baghouse filters (BG1). Coal is used as conventional fossil fuel fired into the discharge end of the rotary kiln. The flue gas in the head of kiln is cooled to below 200°C by the ambient air and is then passed through a dust collector (BG2) before discharge. The collected ash from SP and BG1 are usually re-introduced back to the system under controlled conditions to the cement mill feed stream. The mixed raw meal (RM) from the homogenizing storehouse is fed at the top of a vertical tower with four stage cyclone-type heat exchangers. RDF prepared from municipal solid waste (MSW) is transferred into the precalciner and enters at a constant feeding rate to be sufficiently burned. Most of the ash originated from RDF is integrated with hot meal and finally turns into final product. The temperature and pressure at different parts of the kiln are described in the research of Li *et al.* (2012).

Operation Condition

The operation condition during the sampling period is presented in Table 1. The feeding rates were ca. 345 ton h^{-1} for raw meal, 25.2 ton h^{-1} for coal and 15 ton h^{-1} for RDF, respectively. The clinker production was approximately 215 ton h^{-1} together with the flue gas of 700000 Nm^3 h^{-1} for the stack Y1 and 220000 Nm^3 h^{-1} for the stack Y2.

The temperature and content of oxygen at the pre-heater area were 504°C and 2.3% for the second stage of cyclone pre-heater (C2), 330°C and 3.6% for C1 and 211°C and
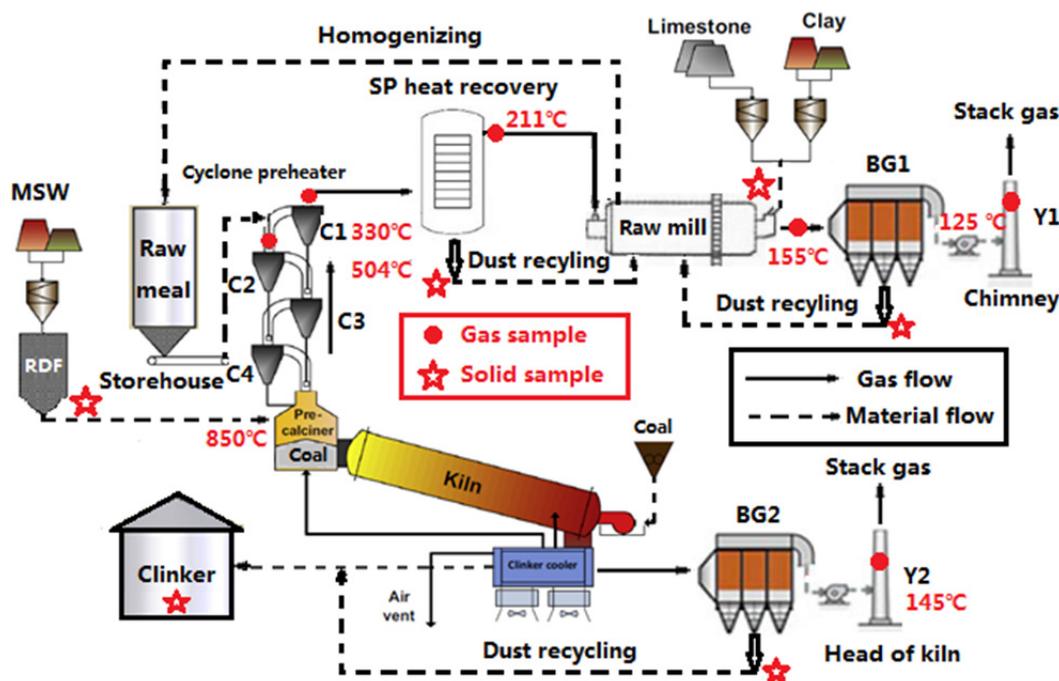

Fig. 1. Diagram of the cement kiln and mass flows of output and input.

Table 1. Operation condition during the sampling period.

Item	Parameter
Raw meal (ton h^{-1})	345
Coal (ton h^{-1})	25.2
RDF as secondary fuel (ton h^{-1})	15
Clinker production (ton h^{-1})	215
Stack gas, Y_1 (Nm^3 h^{-1})	700000
Stack gas, Y_2 (Nm^3 h^{-1})	220000

5.8% for SP, respectively. The concentrations of gaseous compounds were listed in Table 2. The levels of CO and NO were extremely high in C1 because of the primary feeding of raw mill and ash. As to the outlet of raw mill, the temperature and content of oxygen were 155°C and 7.8%, respectively. The temperature of the flue gas emitted from the stack Y1 was 125°C and finally with 8.1% O_2. The levels of NO_x and HF from stack Y1 were higher than the emission standard. On the other hand, the flue gas discharged from the stack Y2 was rich in O_2 and almost no gaseous pollutants presented.

Experimental Set-up

The sampling positions are presented in Fig. 1. The sampling positions of flue gas were located at the outlet of C2, C1, SP, raw mill, stack Y1 and Y2, respectively. Each condition sampled at least two times. Specially, PCDD/Fs and CBzs in gas and particle phase of flue gas were analyzed separately. The solid samples includes raw meal (before mixing with ash), RDF, coal, ash (SP and BG1) and clinker (after mixing with BG2).

In terms of balance calculation, fly ash collected by SP and BG1 were all returned back to the kiln system, so actually just ash from BG_2 was involved in the mixture of clinker. Moreover, the operation period of the cement kiln for calculation was set up to be 8500 h a^{-1}.

As to the correlation analysis, the total amounts of PCDD/Fs and I-TEQ were separately related to each CBz congener. Furthermore, the relationship of PCDD/Fs in gas and particle phase of flue gas was analyzed separately to investigate the possible formation pathway.

Sampling and Analysis

The sampling for PCDD/Fs and CBzs in flue gas and various solid samples was carried out according to USEPA Method 23 and Chinese standard measurement procedure (HJ 77.1–77.4, 2008). Flue gas was collected by an isokinetic sampler (Model KNJ23, KNJ, Korea) and each sampling time was 120–180 min for approximately 2.0–4.0 m^3 in volume

(Alvim Ferraz and Afonso, 2003). In the meanwhile, 0.5 kg ash samples were collected every half an hour during flue gas sampling process. Because of general inhomogeneity, the other solid samples were collected by fully mixed multipoint sampling.

Pre-treatment of CBzs is depicted in detail by Yan *et al.* (2012). GC-ECD (GC 6890N, Agilent, USA) with a DB-5 column (30 m × 0.25 mm × 0.25 μm) is used to analyze CBzs (DBz to HCBz). The temperature program for GC oven was as follows: initial temperature 80°C, held for 4 min; increased at 5 °C min^{-1} to 106°C, held for 0.5 min; increased at 8 °C min^{-1} to 250°C and held for 15 min.

The cleanup procedure of PCDD/F samples is according to the US EPA method 23 (for flue gas) and 1613 (for solid samples), respectively. Identification and quantification of PCDD/Fs are accomplished by HRGS/HRMS on a 6890 Series high-resolution gas chromatograph (Agilent, USA) depending on DB-5ms (60 m × 0.25 mm I.D., 0.25 μm film thickness) capillary column for separation of the PCDD/Fs congeners, and coupled with a JMS-800D high-resolution mass spectrometer (JEOL, Japan) (Chen *et al.*, 2015). The toxic equivalents (TEQ) are calculated using NATO/CCMS factors (McKay, 2002). All the concentrations of flue gas are normalised to dry air, 10% O_2, 1.01 × 10^5 kPa and 237 K.

RESULTS AND DISCUSSION

Formation and Emission of CBzs
Gaseous Samples

The concentration and distribution of CBzs in the flue gas are presented in Table 3. The level of CBzs at the outlet of C2 was 4110 ng Nm^{-3} and it was at the lowest level among all the flue gas samples. The reason could be attributed to the destruction of CBzs by Cu at about 500°C (Fullana *et al.*, 2004). In the meanwhile, the levels of CBzs at the outlet of C1, SP and mill were 8354, 18404 and 22336 ng Nm^{-3}, respectively. Large amount of CBzs was formed in the C1 and SP and could be attributed to the feeding of raw mill and ash in the C1. Incomplete combustion conditions are also an important factor because they can provide main source to form CBzs (Leclerc *et al.*, 2006). In general, the yield of CBzs in the MSWI could increase when the temperature decrease (Fullana *et al.*, 2004). This trend was also found in the cement kiln and the level of CBzs continually increased to 26553 ng Nm^{-3} at the stack Y1. Comparisons showed that the emission of CBzs in the kiln was lower than the value of 55000 ng Nm^{-3} in the MSWI flue gas (Oberg, 2004). While the emission level

Table 2. Temperature and gaseous compounds in different sampling positions, mg Nm^{-3}.

	Temperature, °C	O_2, %	CO	SO_2	NO	NO_2	N_2O	NH_3	HCl	HF
Flue gas at C2 outlet	504	2.3	1.06	0.01	12.58	0.41	0.35	0.04	0.83	0.12
Flue gas at C1 outlet	330	3.6	611.66	0.14	274.70	7.93	41.25	0.02	0.64	0.08
Flue gas at SP outlet	211	5.8	142.40	0.01	46.65	29.96	24.86	0.15	6.92	0.01
Flue gas at mill outlet	155	7.8	295.95	13.23	186.71	10.43	21.16	0.09	7.43	1.11
Stack Y1	125	8.1	340.55	11.51	236.73	10.76	40.45	1.02	4.95	2.11
Stack Y2	145	20.9	1.06	0.01	12.58	0.41	0.35	0.04	0.83	0.12
Emission standard				100.0		300.0		8.0	10.0	1.0

Table 3. Concentration and distribution of CBzs in the flue gas, ng Nm^{-3}.

	C2 outlet		C1 outlet		SP outlet		Mill outlet		Stack Y1		Stack Y2	
	Gas	Solid	Gas	Solid	Gas	Solid	Gas	Solid	Gas	Solid	Gas	Solid
1,3-DCBz & 1,4-DCBz	1725	929	223	3820	4541	1532	1272	6409	4641	4276	346	1458
1,2-DCBz	346	242	100	573	5991	460	7187	247	9429	150	234	204
1,3,5-TCBz	191	109	110	41	692	124	731	295	742	75	81	67
1,2,4-TCBz	111	57	35	48	2426	156	2823	155	3542	63	56	42
1,2,3-TCBz	175	64	1046	2059	1559	95	1584	401	2117	60	63	50
1,2,3,5-TeCBz & 1,2,4,5-TeCBz	32	13	18	2	282	46	433	11	491	15	11	9
1,2,3,4-TeCBz	33	7	46	4	284	11	450	11	562	10	7	6
PeCBz	4	16	95	1	118	19	237	30	335	4	18	7
HCBz	46	10	128	1	57	11	48	13	30	12	13	5
Sum	2662	1448	1805	6549	15950	2454	14764	7572	21887	4666	830	1848
Total	4110		8354		18404		22336		26553		2678	
Gas/Particle	1.84		0.28		6.5		1.95		4.69		0.45	

was higher than the result reported in a hazardous waste incineration (HWI) (Lin *et al.*, 2014). The large difference could be attributed to the adsorption of CBzs and the rather weak chlorination of the catalyst in the cement kiln (Liu *et al.*, 2001). Interestingly, CBzs can also be formed during the cooling process of clinker and discharged through stack Y2 with the value of 2678 ng Nm^{-3}. The level was much lower than that at the stack Y1 but still higher than the result reported in the MSWI flue gas (Takaoka *et al.*, 2003).

As to the congener distribution, DCBz dominated in the flue gas of the whole kiln. Especially for the flue gas at the outlet of C2 and stack Y2, the fractions of DCBz was up to 79% and 84%, respectively. This trend was consistent with the congener distribution of CBzs in the MSWI stack gas (Oberg, 2004). In other studies, TCBz, PeCBz and HxCBz were found to be the leading congeners in the incinerator stack gas (Kaune *et al.*, 1994). The difference might be due to different types of incinerators and fuel, different sampling points and different cleaning devices (Lavric *et al.*, 2005).

The CBzs in the flue gas was more likely to be presented in gas phase due to the low evaporation temperature (Brasseur *et al.*, 2004). However, more CBzs was associated in the particle phase of flue gas at the outlet of C1 due to the feeding of raw meal and ash. The increase of CBzs with the flowing of flue gas could be attributed to two factors. On the one hand, CBzs can be formed from benzene both in the gas phase and on particle surfaces at low temperature (Ryu *et al.*, 2004; Stanmore, 2004;). On the other hand, CBzs in the gas phase will be more difficult to be reduced by the bag filter and active carbon.

Solid Samples

As can be seen from Table 4, the concentrations of CBzs in the raw meal, coal and RDF were ca. 100 ng g^{-1} and slightly higher than that of clinker. The difference could be attributed to the high temperature in the rotary kiln. As to the congener distribution, 1,3-DBz, 1,4-DBz and HCBz were the leading ones and almost no TCBz and PeCBz were detected, showing a similar congener pattern among the raw meal, coal and RDF.

It has been mentioned that CBzs has a tendency to concentrate in fly ash and HCBz is more persistent than other

CBzs (Fujimori *et al.*, 2009). The concentration of CBzs in the SP ash was up to 950 ng kg^{-1} which was similar with that of BG1 ash. As reported, the concentration of CBzs in the MSWI ash is 280 ng g^{-1} (Oberg *et al.*, 2008). The concentration was 2.5 ng g^{-1} for coal ash and 1625–13900 ng g^{-1} for MSWI fly ash (National Bureau of Statistics of China, 2014). Additionally, levels of 870–1900 ng g^{-1} were also detected in the MSWI fly ash (Takaoka *et al.*, 2003). As mentioned above, the concentration of CBzs in the SP and BG1 ash was in the same level with MSWI fly ash. As to the congener distribution, 1,2-DCBz and 1,3,5-TCBz were the dominant congeners for the SP and BG1 ash with the factions of 42% and 64%, respectively. Higher chlorinated CBzs were found to be the leading ones in MSWI fly ash, while almost no TeCBz and PeCBz were presented in the cement kiln ash (Huang *et al.*, 2003). The difference could be attributed to the low content of metal catalyst and chlorine in the cement kilns.

Mass Balance and Emission Factor

Table 5 showed the annual mass balance of CBzs and emission factors over the whole cement production process, according to the operating parameters (Table 1) and data from Table 4. The input of CBzs was from coal, raw meal and RDF, while the output could be merged into three matrixes, namely clinker, stack gas Y1 and Y2, respectively. Mass balance (Table 5) indicated that annual net formation and release of CBzs from the cement kiln was ca. –130 kg year^{-1}, which means cement plants can destroy 12% of CBzs associated in the input material. Organics in raw meal were the main source of organic substance emitted from cement kilns (Dellinger *et al.*, 1993). Therefore, most of the input CBzs content was from raw meal with the proportion up to 88%.

As for the output of CBzs, the total amount was 304 kg year^{-1} and the fractions via clinker, stack gas Y1 and Y2 were 46%, 52% and 2%, respectively. It is consistent that clinker and stack gas Y1 were the major carriers of the organic pollutants (Li *et al.*, 2015). Furthermore, the emission factor was 36 mg ton^{-1} clinker, which was two or three magnitude higher than the emission factor of PCDD/Fs. It is consistent with the trend concluded by Zhang *et al.* (2011)

Table 4. Concentration and distribution of CBzs in the solid samples, ng g^{-1}.

	Raw meal	Coal	RDF	SP ash	BG$_1$ ash	Clinker
1,3-DCBz & 1,4-DCBz	52	60	72	132	172	50
1,2-DCBz	0	0	0	402	49	0
1,3,5-TCBz	0	0	0	47	610	0
1,2,4-TCBz	0	0	0	190	0	0
1,2,3-TCBz	0	0	0	118	0	0
1,2,3,5-TeCBz & 1,2,4,5-TeCBz	8	15	23	27	0	18
1,2,3,4-TeCBz	0	0	0	28	0	0
PeCBz	0	2	4	3	11	1
HCBz	42	30	53	5	113	7
Total	102	107	152	951	955	76

Table 5. Mass balance of CBzs from the cement kiln.

Output/input	CBzs, kg year^{-1}
Input:	
Coal	22
RDF	19
Raw meal	302
Sum$_{in}$	344
Output:	
Stack gas Y1	158
Stack gas Y2	5
Clinker	141
Sum$_{out}$	304
Net emission	–40
Emission factor (mg ton^{-1} clinker)	36

which suggested that the emission factors for HCBz and PeCBz were generally 1 or 2 orders of magnitude higher than the emission factors of PCDD/Fs (Zhang *et al.*, 2011).

Formation, Reduction and Emission of PCDD/Fs
Gaseous Samples

In order to better understand the PCDD/F formation, reduction and emission behaviors in cement kiln, PCDD/Fs in gas and particle phase of the flue gas were separately investigated and presented in Tables 6 and 7. Moreover, 136 species of T4CDD/Fs to O8CDD/Fs was analyzed to find out the possible formation mechanism. As for the PCDD/Fs in gas phase, the level of T4CDD/Fs to O8CDD/Fs at the outlet of C2 was 2369 pg Nm^{-3}. After passing through C1, the value increased to 8469 pg Nm^{-3} and the ratio of PCDFs/PCDDs increased from 5.1 to 9.6. This trend might be attributed to a strong *de novo* synthesis or the precursor formation from CBzs. The possibility that most gas phase PCDD/Fs was generated via *de novo* synthesis has been expounded by a study in MSWI (Chi and Chang, 2005). Moreover, the potential for PCDF formation from reactions of chlorinated benzenes has been largely overlooked. As the temperature below 250°C, adsorption of PCDD/Fs to ash or raw meal significantly affects the gas/particle partitioning of PCDD/F. Therefore, the level of T4CDD/Fs to O8CDD/Fs significantly decreased to 1422 pg Nm^{-3}. With the application of bag filter, the level of T4CDD/Fs to O8CDD/Fs also decreased from 6474 to 2438 pg Nm^{-3} with the evaluating fraction of PCDD/Fs in gas phase. It should be noted that

the level of T4CDD/Fs to O8CDD/Fs at the stack Y2 was up to 1930 pg Nm^{-3}, but no stricter control was needed due to the fact that the PCDD/Fs was originated from the stable cooling process at the head of kiln.

The 2,3,7,8-PCDD/Fs were further analyzed to study the concentration and distribution of toxic PCDD/F congeners. The concentration of 2,3,7,8-PCDD/Fs in gas phase at the outlet of C2 was 1053 pg Nm^{-3} (22 pg I-TEQ Nm^{-3}) and the ratio of PCDD/Fs in gas phase was 40.8%. Moreover, the value at the outlet of C1 was similar with that of C2 and the ratio of PCDD/Fs in gas phase largely decreased to 12.0%, indicating that less of 2,3,7,8-PCDD/Fs could be reformed. While the I-TEQ value was four times higher than that at the outlet of C2 due to the higher fraction of lower chlorinated PCDD/Fs. Moreover, the ratio of PCDD/Fs in gas phase was lower than the results obtained by Li *et al.* (2015), indicating that there are other properties which can affect partitions of PCDD/Fs in flue gas besides saturation vapor pressures of PCDD/Fs (Chi and Chang, 2005). The level of 2,3,7,8-PCDD/Fs decreased to 397 pg Nm^{-3} (12 pg I-TEQ Nm^{-3}) at the outlet of SP owing to the adsorption behavior. After passing through raw mill, the value largely increased to 3552 pg Nm^{-3} (41 pg I-TEQ Nm^{-3}) and the ratio of PCDD/Fs in gas phase also increased to 59.5%. This trend could be attributed to the recycling of ash and it further promoted desorption of PCDD/Fs from particles. The final emission of 2,3,7,8-PCDD/Fs in gas phase from the stack Y1 was 57 pg Nm^{-3} (13 pg I-TEQ Nm^{-3}) and the ratio of PCDD/Fs in gas phase was 61.6%. The reduction efficiency was 94% (81% for I-TEQ) after passing through the bag filter, which was much higher than value reported by Lee *et al.* (2004). For MWI, the removal efficiencies of gas phase PCDD/Fs are 98.5–99.6% (Chi and Chang, 2005). The partition of gas and solid phase PCDD/F could be affected by the type of the air pollutant control devices (APCDs) and the concentration of particulate matter in flue gas (Chi and Chang, 2005). Additionally, the concentration of 2,3,7,8-PCDD/Fs in gas phase at the stack Y2 was 49 pg Nm^{-3} and the level of I-TEQ was higher than that at the stack Y1 owing to the high fraction of 2,3,4,7,8-PeCDF with value of 63%.

As can be seen from Table 7, the level of T4CDD/Fs to O8CDD/Fs in particle phase at the outlet of C2 was 3680 pg Nm^{-3}. After passing through C1, the value increased to 13434 pg Nm^{-3} and the ratio of PCDFs/PCDDs decreased from 6.1 to 4.0, indicating that more PCDDs formed via

Table 6. Level and distribution of PCDD/Fs in gas phase of flue gas.

Property	C2 outlet	C1 outlet	SP outlet	Mill outlet	Stack	Head of kiln	Unit
136-PCDDs	388	801	435	737	616	284	pg Nm^{-3}
136-PCDFs	1981	7668	987	5737	1822	1646	pg Nm^{-3}
136-PCDD/Fs	2369	8469	1422	6474	2438	1930	pg Nm^{-3}
PCDFs/PCDDs	5.10	9.57	2.27	7.78	2.96	5.80	
Ratio of PCDD/Fs in gas phase	39.2	38.7	6.0	32.1	59.6	80.2	%
2,3,7,8-PCDDs	127	114	113	369	48	8	pg Nm^{-3}
2,3,7,8-PCDFs	926	929	284	3183	181	49	pg Nm^{-3}
2,3,7,8-PCDD/Fs	1053	1043	397	3552	229	57	pg Nm^{-3}
PCDFs/PCDDs	7.29	8.15	2.51	8.64	3.75	6.19	
Ratio of PCDD/Fs in gas phase	40.8	12.0	22.7	59.5	66.4	61.6	%
Percentage of tetra and penta-PCDDs	16	26	9	3	4	83	%
Percentage of OCDD	56	48	68	74	58	1	%
Percentage of tetra and penta-PCDFs	8	17	7	2	16	61	%
Percentage of OCDF	59	47	37	66	35	1	%
Weight average level of chlorination	7.24	6.88	7.01	7.52	6.86	5.29	
I-TEQ	22	101	15	68	13	16	pg I-TEQ Nm^{-3}
Ratio of I-TEQ in gas phase	35	23	12	32	81	59	%
PCDFs to I-TEQ	63	62	62	82	84	73	%
2,3,4,7,8-PeCDF to I-TEQ	27	25	25	15	33	63	%

Table 7. Level and distribution of PCDD/Fs in particle phase of flue gas.

Property	C2 outlet	C1 outlet	SP outlet	Mill outlet	Stack	Head of kiln	Unit
136-PCDDs	520	2708	1234	1553	750	146	pg Nm^{-3}
136-PCDFs	3160	10726	21168	12156	905	330	pg Nm^{-3}
136-PCDD/Fs	3680	13434	22402	13709	1655	476	pg Nm^{-3}
PCDFs/PCDDs	6.08	3.96	17.16	7.83	1.21	2.26	
Ratio of PCDD/Fs in particle phase	60.8	61.3	94.0	67.9	40.4	19.8	%
2,3,7,8-PCDDs	244	1566	362	380	12	17	pg Nm^{-3}
2,3,7,8-PCDFs	1282	6077	987	2041	104	19	pg Nm^{-3}
2,3,7,8-PCDD/Fs	1526	7643	1349	2421	116	36	pg Nm^{-3}
PCDFs/PCDDs	5.26	3.88	2.73	5.37	8.68	1.14	
Ratio of PCDD/Fs in particle phase	59.1	88.0	77.3	40.5	66.4	38.4	%
Percentage of tetra and penta-PCDDs	2	1	13	9	1	75	%
Percentage of OCDD	73	59	74	67	1	1	%
Percentage of tetra and penta-PCDFs	2	4	45	22	3	48	%
Percentage of OCDF	65	38	21	45	48	1	%
Weight average level of chlorination	7.54	7.20	6.25	6.89	7.20	5.32	
I-TEQ	40	338	190	147	3	11	pg I-TEQ Nm^{-3}
Ratio of I-TEQ in particle phase	65	77	88	68	19	41	%
PCDFs to I-TEQ	81	87	74	80	91	37	%
2,3,4,7,8-PeCDF to I-TEQ	26	30	51	46	23	30	%

chlorinated precursors (Shibata *et al.*, 2003). The level of T4CDD/Fs to O8CDD/Fs at the outlet of SP further increased to 22402 pg Nm^{-3} owing to the recycling of ash. Surface mediated reactions of chlorinated benzenes can also be a significant source for the formation of PCDD/Fs (Dellinger, 2011). Furthermore, the level of T4CDD/Fs to O8CDD/Fs decreased from 13709 to 1655 pg Nm^{-3} with the decrease of particulate matter concentration. Moreover, the level of T4CDD/Fs to O8CDD/Fs in particle phase at the stack Y2 was 476 pg Nm^{-3} and the ratio of it to the total PCDD/Fs was only 19.8%.

The concentration of 2,3,7,8-PCDD/Fs in particle phase at the outlet of C2 and C1 were 1526 and 7643 pg Nm^{-3} (40

and 338 pg I-TEQ Nm^{-3}), respectively. The level of 2,3,7,8-PCDD/Fs decreased to 1349 pg Nm^{-3} (190 pg I-TEQ Nm^{-3}) at the outlet of SP. Considering the lower weight average level of chlorination at the outlet of SP, dechlorination might occur and further contributed to the congener pattern (Lundin and Marklund, 2008). Although the level of T4CDD/Fs to O8CDD/Fs decreased when the flue gas passed through raw mill, the level of 2,3,7,8-PCDD/Fs in particle phase was on the inverse situation. The difference could be attributed the dechlorination of PCDD/Fs and also with the recycling of ash. The final emission of 2,3,7,8-PCDD/Fs in particle phase was 116 pg Nm^{-3} (3 pg I-TEQ Nm^{-3}) and the total I-TEQ (16 pg I-TEQ Nm^{-3}) was in the range of 0.0054–0.1961

ng I-TEQ Nm^{-3} which was reported by Yan *et al.* (2006) and lower than the value reported by Kao *et al.* (2006). The reduction efficiency of particle phase PCDD/Fs via bag filter was 95% (86% for I-TEQ), which was slightly higher than the PCDD/Fs in gas phase. In addition, the concentration of 2,3,7,8-PCDD/Fs in gas phase at the stack Y2 was 49 pg Nm^{-3} and the level of I-TEQ was higher than that at the stack Y1 owing to the high fraction of 2,3,4,7,8-PeCDF.

Solid Samples

The level and distribution of PCDD/Fs in the solid samples are presented in Table 8. The total concentrations of T4CDD/Fs to O8CDD/Fs in the raw meal, coal and clinker were ca. 100 ng kg^{-1} and it was slightly higher in the RDF. The ratios of PCDFs/PCDDs varied from 0.71 to 4.68, indicating different homologue patterns among them. The concentrations of 2,3,7,8-PCDD/Fs in the raw meal and coal were ca. 20 ng kg^{-1}. The values for RDF and clinker were 30 and 12 ng kg^{-1}, respectively. Accordingly, the ratios of PCDFs/PCDDs also ranged from 0.60 to 3.00. Moreover, raw meal and coal showed different congener distributions from clinker and RDF. Additionally, higher chlorinated PCDFs dominated in the raw meal and the weight average level of chlorination was up to 7.33. In terms of the I-TEQ, the levels were less than 1 ng I-TEQ kg^{-1} in the raw meal and clinker, which was similar with the result reported by Li *et al.* (2015). Comparison showed that the I-TEQ distribution in the raw meal was different from others, with higher contributions of PCDFs (87%) and 2,3,4,7,8-PeCDF (51%) to the I-TEQ value.

The total concentrations of T4CDD/Fs to O8CDD/Fs in the SP and BG1 ash were 302 and 546 pg g^{-1} and the corresponding ratios of PCDFs/PCDDs were 9.07 and 16.06. The significantly high fraction of PCDFs in the SP and BG1 ash indicating that the *de novo* and the precursor mechanisms are significantly involved in the formation of dioxins the fly ash during combustion (Choong Kwet Yive and Tiroumalechetty, 2008). The concentrations of 2,3,7,8-PCDD/Fs in the SP and BG1 ash were 28 and 30 ng kg^{-1}, with

the I-TEQ values of 3.3 and 3.9 ng I-TEQ kg^{-1}, respectively. As to the congener distribution, higher chlorinated PCDD and lower chlorinated PCDFs dominated in the SP and BG1 ash. Moreover, the weight average values of chlorination in the ash were lower than the raw meal, RDF and coal, with values of 6.78 and 6.45, respectively. Dechlorination can occur at low temperatures, so this mechanism also probably contributed to the congener pattern of PCDD/Fs in ash samples (Lundin and Marklund, 2008). Similar with MSWI fly ash, 2,3,4,7,8-PeCDF contributed most to the total I-TEQ value. The contributions of it were 70% and 68.0% for the SP and BG1 ash, respectively.

Mass Balance and Emission Factor

Table 9 showed the annual mass balance of PCDD/Fs and emission factors over the whole cement production process, according to the operating parameters (Table 1) and data from Tables 6, 7 and 8. Some studies also conducted on the mass balance of PCDD/Fs in MSWI and they concluded that MSW incinerators can act as PCDD/F sinks, depending on the PCDD/F concentrations in the waste, on the operating conditions and on the APCDs (Van Caneghem *et al.*, 2010). In this study, mass balance indicated that annual net formation and release of PCDD/Fs from the cement kiln was ca. -42898 mg $year^{-1}$ (-1268 mg I-TEQ $year^{-1}$), which was consistent with the value obtained by Li *et al.* (2015). The results revealed that incineration in the cement kiln was clearly a weighed PCDD/F sink even when large amount of RDF co-incinerated.

The fraction of raw meal to the input of I-TEQ was ca. 77% and the value of clinker to the output was 92%, respectively. The coal and RDF have the similar contribution to the input of I-TEQ with the proportion up to ca. 11%, which was much higher than the percentage reported by Li *et al.* (2015). The difference could be attributed to the higher amount of co-incinerated RDF and the higher concentration of PCDD/Fs. On the other hand, the contributions of stack gas Y1 and Y2 to the output of I-TEQ were 5.4% and 2.8%, respectively. In general, PCDD/Fs emitted from stack flue gases was difficult

Table 8. Level and distribution of PCDD/Fs in solid samples.

Property	Raw meal	RDF	Coal	SP ash	BG1 ash	Clinker	Unit
136-PCDDs	19	101	31	30	32	31	ng kg^{-1}
136-PCDFs	89	72	97	272	514	97	ng kg^{-1}
136-PCDD/Fs	108	172	128	302	546	128	ng kg^{-1}
PCDFs/PCDDs	4.68	0.71	3.13	9.07	16.06	3.13	
2,3,7,8-PCDDs	9	26	15	12	11	3	ng kg^{-1}
2,3,7,8-PCDFs	10	17	9	16	19	9	ng kg^{-1}
2,3,7,8-PCDD/Fs	18	30	24	28	30	12	ng kg^{-1}
PCDFs/PCDDs	1.11	0.65	0.60	1.33	1.73	3.00	
Percentage of tetra and penta-PCDDs	2	2	4	2	3	19	%
Percentage of OCDD	89	54	84	80	86	42	%
Percentage of tetra and penta-PCDFs	14	11	50	38	51	19	%
Percentage of OCDF	40	15	4	24	16	33	%
Weight average level of chlorination	7.33	6.84	6.85	6.78	6.45	6.75	
I-TEQ	0.8	2.9	1.6	3.3	3.9	0.9	ng I-TEQ kg^{-1}
PCDFs to I-TEQ	87	44	61	84	87	63	%
2,3,4,7,8-PeCDF to I-TEQ	51	17	26	70	68	34	%

to be handled and much attention should be paid to it (Chen *et al.*, 2008). Furthermore, the emission factor of the cement kiln was 12.1 mg ton^{-1} clinker (0.99 mg I-TEQ year^{-1}), which was similar with the value obtained by Li *et al.* (2015).

Relationship between PCDD/Fs and CBzs

A good correlation has been found between TeCBz and PeCBz and TeCDF and PeCDF in the MSWI (Pandelova *et al.*, 2006). Moreover, TrCBz was also found to be well related with I-TEQ in the flue gas both under the start-up and normal operation in HWI (Lin *et al.*, 2014). As mentioned above, PCDD/Fs has been suggested to be well related with most of the high chlorinated CBzs and thus they have been regarded as PCDD/F surrogates (Blumenstock *et al.*, 2001; Oh *et al.*, 2007). In this study, the relationships between CBzs and I-TEQ in flue gas were analyzed to verify that CBzs could also be used as PCDD/F surrogate in cement kiln.

The correlation analysis showed that the I-TEQ correlates best with HCBz with the corresponding r^2 value of 0.89 in gas phase of flue gas (Fig. 2). While HCBz correlates slightly, yet positively with I-TEQ ($r^2 = 0.02$) in particle phase of flue gas. On the other hand, the I-TEQ correlates best with

Table 9. Mass balance of PCDD/Fs from the cement kiln.

| Output/input	PCDD/Fs, mg year^{-1}	I-TEQ, mg I-TEQ year^{-1}
Input:		
Coal	5098	343
RDF	5521	370
Raw meal	54838	2346
Sum$_{in}$	65456	3059
Output:		
Stack gas Y1	1409	96
Stack gas Y2	133	50
Clinker	21016	1645
Sum$_{out}$	22558	1791
Net emission	−42898	−1268
Emission factor (μg ton^{-1} clinker)	12.1	-
Emission factor (μg I-TEQ ton^{-1} clinker)	-	0.99
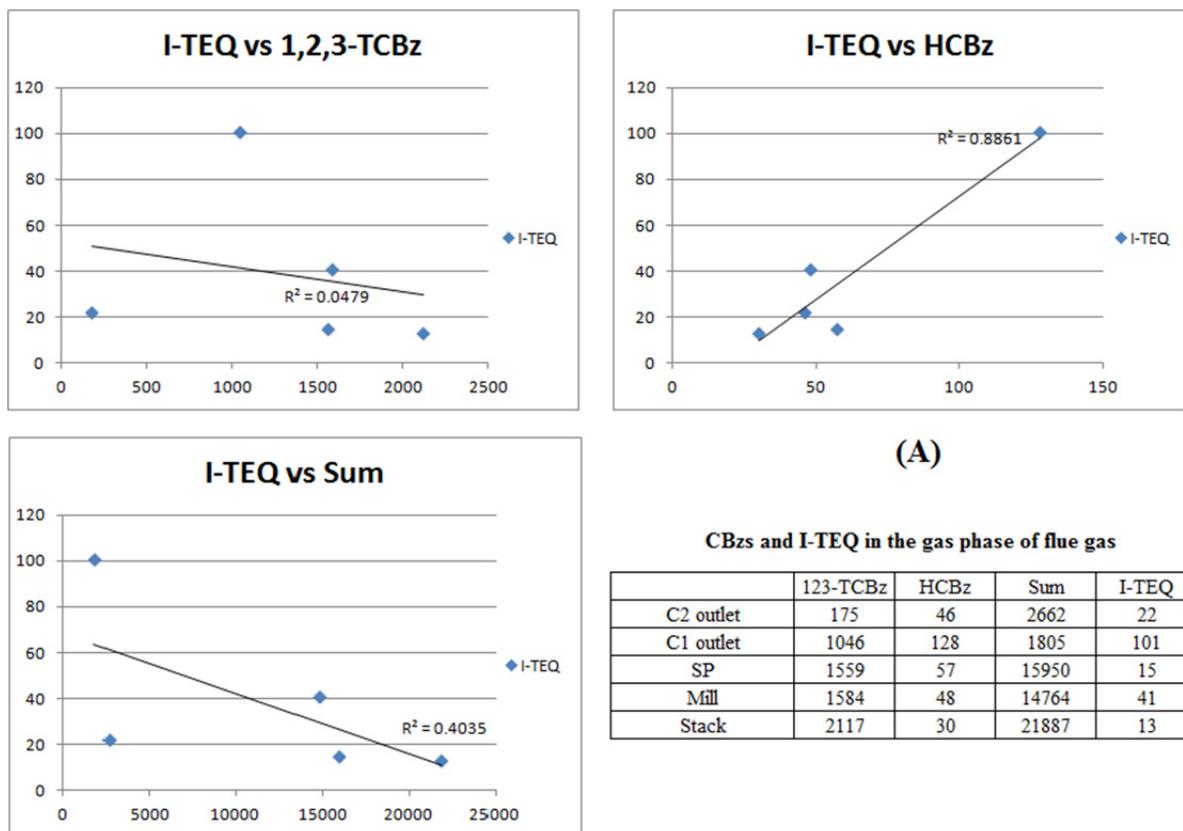
Fig. 2. The relationship between CBzs and I-TEQ in flue gas (A: CBzs and I-TEQ in the gas phase; B: CBzs and I-TEQ in the gas phase; C: Total amount of CBzs and I-TEQ).
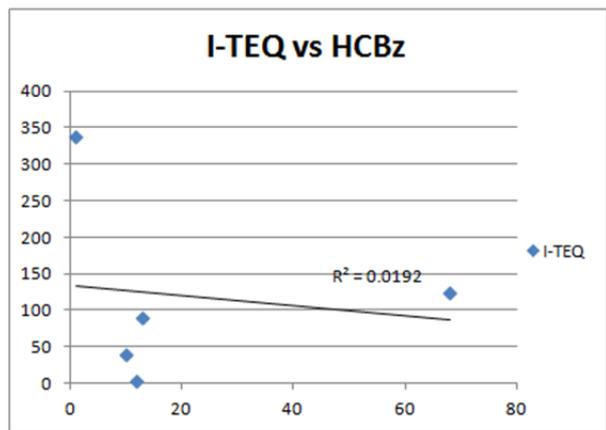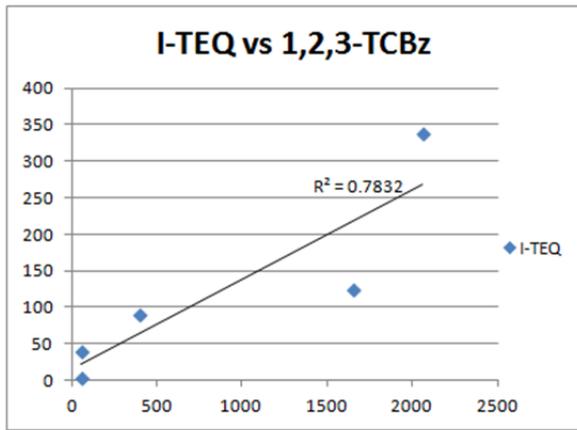
CBzs and I-TEQ in the particle phase of flue gas

	123-TCBz	HCBz	Sum	I-TEQ
C2 outlet	64	10	2662	40
C1 outlet	2059	1	1805	338
SP	1654	68	15950	125
Mill	401	13	14764	89
Stack	60	12	21887	3
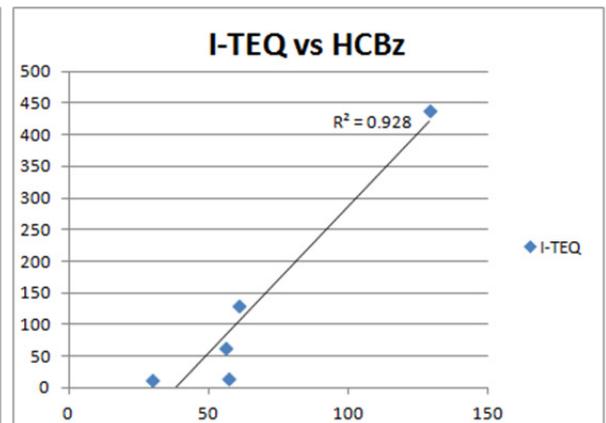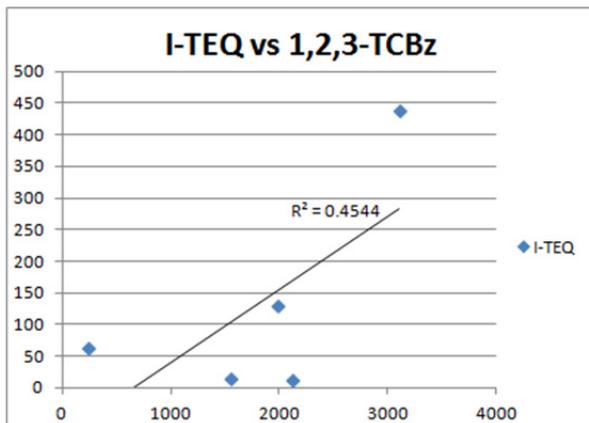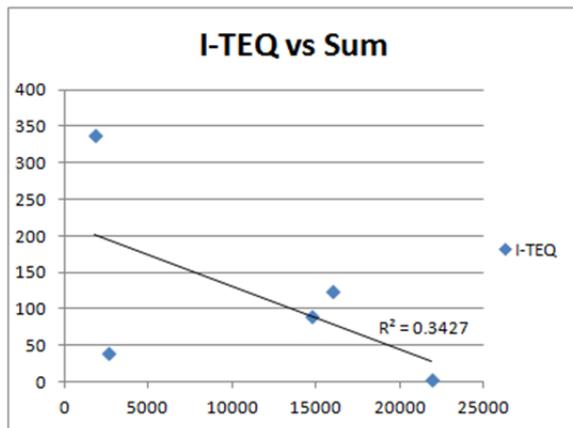
Total amount of CBz and I-TEQ in the flue gas

	123-TCBz	HCBz	Total	I-TEQ
C2 outlet	239	56	4110	62
C1 outlet	3105	129	8354	439
SP	1559	57	15950	15
Mill	1985	61	22336	130
Stack	2117	30	21887	13
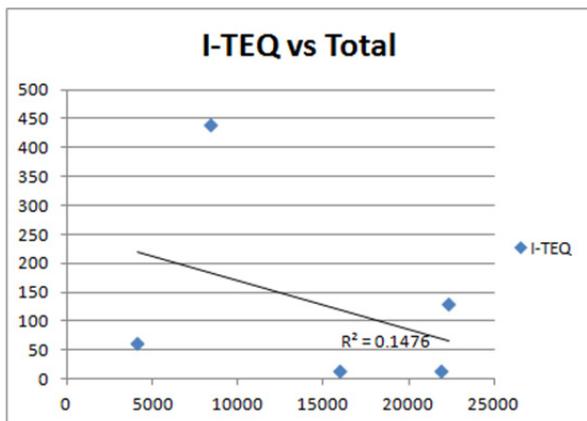
Fig. 2. (*continued*).

1,2,3-TCBz in particle phase of flue gas (r^2 = 0.78), but the corresponding r^2 value was 0.05 in gas phase of flue gas, suggesting different relationships of I-TEQ and CBzs in gas and particle phase of flue gas. The reason could be due to the different formation mechanism of PCDD/Fs via CBzs in gas and particle phase. As to the total amount of I-TEQ, the r^2 value were 0.45 for 1,2,3-TCBz and 0.93 for HCBz, respectively. Therefore, HCBz could be regarded as I-TEQ surrogate during the whole clinker production.

CONCLUSIONS

The formation, reduction and emission behaviors of PCDD/Fs and CBzs were studied in a typical dry cement kiln. Several interesting results were obtained:

1. The concentration of CBzs continually increased with the flowing of flue gas and bag filter has minor reduction effect on it. Hence, the CBz emission was up to 26 μg Nm^{-3}, with much more CBzs presented in gas phase;
2. The PCDD/F emissions of stack gas were 0.016 ng I-TEQ Nm^{-3}. The formation could be attributed to a strong *de novo* synthesis and the precursor formation from CBzs. The recycling of ash and dechlorination probably contributed to the congener pattern of PCDD/Fs;
3. Mass balance indicated that annual net formation and release of CBzs and PCDD/Fs were ca. –1368 mg I-TEQ $year^{-1}$ and –40 kg $year^{-1}$, indicating that the cement kiln incinerating waste was clearly a weighed PCDD/F and CBz sink;
4. Correlation analysis showed that HCBz could be regarded as I-TEQ surrogate during the whole clinker production.

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REFERENCES

Abu-Allaban, M. and Abu-Qudais, H. (2011). Impact assessment of ambient air quality by cement industry: A case study in Jordan. *Aerosol Air Qual. Res.* 11: 802–810.

Alvim Ferraz, M.C. and Afonso, S.A. (2003). Dioxin emission factors for the incineration of different medical waste types. *Arch. Environ. Contam. Toxicol.* 44: 460–466.

Blumenstock, M., Zimmermann, R., Schramm, K.W. and Kettrup, A. (2001). Identification of surrogate compounds for the emission of PCDD/F (I-TEQ value) and evaluation of their on-line real-time detectability in flue gases of waste incineration plants by REMPI-TOFMS mass spectrometry. *Chemosphere* 42: 507–518.

Brasseur, A, Gambin, A, Laudet, A, Marien, J. and Pirard, J.P. (2004). Elaboration of new formulations to remove micropollutants in MSWI flue gas. *Chemosphere* 56: 745–56.

Chen, C.K., Lin, C., Lin, Y.C., Wang, L.C. and Chang-Chien, G.P. (2008). Polychlorinated dibenzo-*p*-dioxins/dibenzofuran mass distribution in both start-up and normal condition in the whole municipal solid waste incinerator. *J. Hazard. Mater.* 160: 37–44.

Chen, T., Zhan, M., Lin, X., Fu, J., Lu, S., Li, X., Buekens, A. and Yan, J. (2011). PCDD/Fs inhibition by sludge decomposition gases: effects of sludge dosage, treatment temperature and oxygen content. *Aerosol Air Qual. Res.* 11: 702–711.

Chi, K.H. and Chang, M.B. (2005). Evaluation of PCDD/F congener partition in vapor/solid phases of waste incinerator flue gases. *Environ. Sci. Technol.* 39: 8023–31.

Choong Kwet Yive, N.S. and Tiroumalechetty, M. (2008). Dioxin levels in fly ash coming from the combustion of bagasse. *J. Hazard. Mater.* 155:179–82.

Conesa, J.A, Gálvez, A., Mateos, F., Martín-Gullón, I. and Font, R. (2008). Organic and inorganic pollutants from cement kiln stack feeding alternative fuels. *J. Hazard. Mater.* 158: 585–92.

Cunliffe, A.M. and Williams, P.T. (2009). De-novo formation of dioxins and furans and the memory effect in waste incineration flue gases. *Waste Manage.* 29:739–48.

Dellinger, B. (2011). Formation of PCDD/Fs from the copper oxide-mediated pyrolysis and oxidation of 1,2-dichlorobenzene. *Environ. Sci. Technol.* 45:1034–1040.

Dellinger, H.B., Pershing, D.W. and Sarofim, A.F. (1993). *Evaluation of the Origin, Emissions, and Control of Organic and Metal Compounds from Cement Kilns Co-fired with Hazardous Wastes: A Report of the Scientific Advisory Board on Cement Kiln Recycling: Executive Summary.* Publisher not Identified.

Fujimori, T., Takaoka, M. and Takeda, N. (2009). Influence of Cu, Fe, Pb, and Zn chlorides and oxides on formation of chlorinated aromatic compounds in MSWI fly ash. *Environ. Sci. Technol.* 43: 8053–9.

Fullana, A., Conesa, J.A., Font, R. and Sidhu, S. (2004). Form1ation and destruction of chlorinated pollutants during sewage sludge incineration. *Environ. Sci. Technol.* 38:2953–2958.

Giannopoulos, D., Kolaitis, D.I., Togkalidou, A., Skevis, G. and Founti, M.A. (2007). Quantification of emissions from the co-incineration of cutting oil emulsions in cement plants - Part II: Trace species. *Fuel* 86: 2491–2501.

Gullett, B.K., Sarofim, A.F., Smith, K.A. and Procaccini, C. (2000). The role of chlorine in dioxin formation. *IChemE* 78: 47–52.

Hatanaka, T., Imagawa, T. and Takeuchi, M. (2000). Formation of PCDD/Fs in artificial solid waste incineration in a laboratory-scale fluidized-bed reactor: influence of contents and forms of chlorine sources in high-temperature combustion. *Environ. Sci. Technol.* 34: 3920–3924.

Huang, Y., Takaoka, M. and Takeda, N. (2003). Chlorobenzenes removal from municipal solid waste incineration fly ash by surfactant-assisted column flotation. *Chemosphere* 52:735–743.

Iino, F., Imagawa, T., Takeuchi, M. and Sadakata, M. (1999). De novo synthesis mechanism of polychlorinated dibenzofurans from polycyclic aromatic hydrocarbons and the characteristic isomers of polychlorinated naphthalenes. *Environ. Sci. Technol.* 33: 1038–1043.

Jin, G.Z., Lee, S.J., Park, H., Lee, J.E., Shin, S.K. and

Chang, Y.S. (2009). Characteristics and emission factors of PCDD/Fs in various industrial wastes in South Korea. *Chemosphere* 75: 1226–1231.

Kao, J.H., Chen, K.S., Chang-Chien, G.P. and Chou, I.C. (2006). Emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from various stationary sources. *Aerosol Air Qual. Res.* 6: 170–179.

Karstensen, K.H. (2008). Formation, release and control of dioxins in cement kilns. *Chemosphere* 70: 543–560.

Kaune, A., Lenoir, D., Nikolai, U. and Kettrup, A. (1994). Estimating concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the stack gas of a hazardous waste incinerator from concentrations of chlorinated benzenes and biphenyls. *Chemosphere* 29: 2083–2096.

Lavric, E.D., Konnov, A.A. and De Ruyck, J. (2005). Surrogate compounds for dioxins in incineration. A review. *Waste Manage.* 25:755–765.

Leclerc, D., Duo, W.L. and Vessey, M. (2006). Effects of combustion and operating conditions on PCDD/PCDF emissions from power boilers burning salt-laden wood waste. *Chemosphere* 63: 676–89.

Lee, W.S., Chang-Chien, G.P., Chen, S.J., Wang, L.C., Lee, W.J. and Wang, Y.H. (2004). Removal of polychlorinated Dibenzo-*p*-dioxins and dibenzofurans in flue gases by venturi scrubber and bag filter. *Aerosol Air Qual. Res.* 4: 27–37.

Lemieux, P.M. (2004). The Use of Surrogate Compounds as Indicators of PCDD/F Concentrations in Combustor Stack Gases. United States Environmental Protection Agency.

Li, Y., Wang, H., Zhang, J., Wang, J. and Zhang, R. (2012). Research on dioxins suppression mechanisms during MSW co-processing in cement kilns. *Procedia Environ. Sci.* 16: 633–640.

Li, Y., Chen, T., Zhang, J., Meng, W., Yan, M., Wang, H. and Li, X. (2015). Mass balance of dioxins over a cement kiln in China. *Waste Manage.* 36: 130–135.

Lin, X., Huang, Q., Chen, T., Li, X., Lu, S., Wu, H., Yan, J., Zhou, M. and Wang, H. (2014). PCDD/F and PCBz emissions during start-up and normal operation of a hazardous waste incinerator in China. *Aerosol Air Qual. Res.* 14: 1142–1151.

Liu, Y., Luo, M., Wei, Z., Xin, Q., Ying, P. and Li, C. (2001). Catalytic oxidation of chlorobenzene on supported manganese oxide catalysts. *Appl. Catal., B* 29: 61–67.

Lundin, L. and Marklund, S. (2008). Distribution of mono to octa-chlorinated PCDD/Fs in fly ash from a municipal solid-waste incinerator. *Environ. Sci. Technol.* 42: 1245–1250.

McKay, G. (2002). Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: Review. *Chem. Eng. J.* 86: 343–368.

National Bureau of Statistics of China (2014). China Statistics Yearbook 2014. China Statistics Press, Beijing, China.

Oberg, T., Bergbäck, B. and Filipsson, M. (2008). Catalytic effects by metal oxides on the formation and degradation of chlorinated aromatic compounds in fly ash. *Chemosphere* 71: 1135–43.

Oh, J.E., Gullett, B., Ryan, S. and Touati, A. (2007). Mechanistic relationships among PCDDs/Fs, PCNs, PAHs, CIPhs, and CIBzs in municipal waste incineration. *Environ. Sci. Technol.* 41: 4705–4710.

Olie, K., Vermeulen, P.L. and Hutzinger, O. (1977). Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in The Netherlands. *Chemosphere* 6: 455–459.

Pandelova, M., Lenoir, D. and Schramm, K.W. (2006). Correlation between PCDD/F, PCB and PCBz in coal/waste combustion. Influence of various inhibitors. *Chemosphere* 62: 1196–205.

Rivera-Austrui, J., Martínez, K., Adrados, M., Abalos, M. and Abad, E. (2012). Analytical approach and occurrence for the determination of mass concentration of PCDD/PCDF and dl-PCB in flue gas emissions using long-term sampling devices. *Sci. Total Environ.* 435–436: 7–13.

Ryu, J.Y., Mulholland, J.A., Dunn, J.E., Iino, F. and Gullett, B.K. (2004). Potential role of chlorination pathways in PCDD/F formation in a municipal waste incinerator. *Environ. Sci. Technol.* 38: 5112–5119.

Shibata, E., Yamamoto, S., Kasai, E. and Nakamura, T. (2003). Formation behavior of PCDD/Fs in PVC pyrolysis with copper oxide. *Chemosphere* 50: 1235–42.

Stanmore, B.R. (2004). The formation of dioxins in combustion systems. *Combust. Flame* 136: 398–427.

Takaoka, M., Liao, P., Takeda, N., Fujiwara, T. and Oshita, K. (2003). The behavior of PCDD/Fs, PCBs, chlorobenzenes and chlorophenols in wet scrubbing system of municipal solid waste incinerator. *Chemosphere* 53: 153–161.

Thuong, N., Nam, V., Hue, N., Son, L., Thuy, N., Tung, H., Tuan, N. Minh, T., Huy, D. and Minh, N. (2014). The emission of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans from steel and cement-kiln plants in Vietnam. *Aerosol Air Qual. Res.* 14: 1189–1198.

Van Caneghem, J., Block, C., Van Brecht, a., Wauters, G. and Vandecasteele, C. (2010). Mass balance for POPs in hazardous and municipal solid waste incinerators. *Chemosphere* 78: 701–708.

Weber, R. and Hagenmaier, H. (1999). Mechanism of the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from chlorophenols in gas phase reactions. *Chemosphere* 38: 529–549.

Yan, D., Peng, Z., Karstensen, K.H., Ding, Q., Wang, K. and Wang, Z. (2014). Destruction of DDT wastes in two preheater/precalciner cement kilns in China. *Sci. Total Environ.* 476–477: 250–257.

Yan, J.H., Chen, T., Li, X.D., Zhang, J., Lu, S.Y., Ni, M.J. and Cen, K.F. (2006). Evaluation of PCDD/Fs emission from fluidized bed incinerators co-firing MSW with coal in China. *J. Hazard. Mater.* 135: 47–51.

Yan, M., Qi, Z.F., Li, X.D., Chen, T., Lu, S.Y., Buekens, A.G., Olie, K. and Yan, J.H. (2012). Chlorobenzene formation from fly ash: Effect of moisture, chlorine gas, cupric chloride, urea, ammonia, and ammonium sulfate. *Environ. Sci. Technol.* 29: 890–896.

Zhang, T., Fiedler, H., Yu, G., Ochoa, G.S., Carroll, W.F., Gullett, B.K., Marklund, S. and Touati, A. (2011).

Emissions of unintentional persistent organic pollutants from open burning of municipal solid waste from developing countries. *Chemosphere* 84: 994–1001.