RESEARCH ARTICLE

Emission and distribution of PCDD/Fs and CBzs from two co-processing RDF cement plants in China

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Abstract An analysis of the emission and distribution characteristics of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and chlorobenzenes (CBzs) from two cement kilns (CK1 and CK2) is done. Six measurements in CK1 showed an increase of PCDD/F emission from 76 to 97 pg I-TEQ/Nm^3 after feeding 10 ton/h RDF (refuse derived fuel). For CK2, the effect of increasing the RDF substitution rates from 0 to 21 t/h on the emission of PCDD/Fs was investigated. The correlation analysis indicated that replacing parts of the conventional fuel with RDF could not increase the emission of PCDD/Fs. Furthermore, the gas/particle partitions of PCDD/Fs and CBzs in stack gas were investigated, indicating that PCDD/Fs and CBzs were more associated in gas phase, especially for the lower chlorinated ones. Moreover, the bag filter fly ash was characterized by its particle distribution, XRD- and EDS-analysis. Additionally, the level of PCDD/Fs in outflowing fly ash escalates for smaller particle size. In order to evaluate the environmental effect on inhabitants, the levels of PCDD/Fs were also determined in samples of ambient air collected in the vicinity of CK2 (~200 m).

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Introduction

In 2013, the generation of municipal solid waste (MSW) has increased to 172 million ton in China, which caused huge risk on the proper and responsible treatment of waste (NBSC 2014). On the one hand, cement kilns have shown to constitute an affordable, environmentally sound, and sustainable treatment option for MSW (Conesa et al. 2008; Li et al. 2014). On the other hand, cement factory is widely spread in China, as the cement production account for 60 % of total all over the world (Li et al. 2015). Furthermore, a major change has been considered necessary since the Chinese government called for an increasing incineration disposal ability to 35 % in recent years. Therefore, co-processing MSW in cement kilns has been rapidly developed and prompted in China.

The cement manufacturing process will produce large amounts of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) except for approximately 5 % of global CO_2 (Huntzinger and Eatmon 2009). As reported, the cement kilns produced significant portion (>10 %) of dioxins into the environment, making it one the most controversial chemicals found in the environment (Chen 2004).

Numerous tests in developed countries have demonstrated that there is almost no difference of PCDD/F emission when waste materials are used to replace the conventional fuels (Karstensen et al. 2006). In that case, co-processing is strongly recommended and well implemented in developed countries. Currently, an average of 11 % fuel substitution for cement production in US and 28 % substitution in Europe is achieved (Galvez-Martos and Schoenberger 2014). For instance, the

substitution rates in Germany and the Netherlands are 61 and 83 %, respectively. However, the replacement ratio of fuel by MSW was still rather low in China. The fierce opposition from the public, the complicated composition of waste with low heating value, and the outdated pre-treatment technology in China contribute significantly to this situation. Therefore, more measurements should be done to investigate the emission levels of PCDD/Fs from the co-processing cement plants, and further to accelerate the application of this technology in China.

Co-disposal of MSW in a cement kiln has many advantages, e.g., high treatment temperature (>1500 °C), long retention time (ca. 20 s), and high turbulence to reduce PCDD/F emission (Li et al. 2012; Lohman and Seigneur 2001). More than 2000 PCDD/Fs cement kiln measurements have been evaluated, indicating that most modern cement kilns co-processing waste today can meet the emission standard (Karstensen 2008). By using long-term sampling devices, levels of 0.009 ng I-TEQ/Nm^3 were detected in cement plants (Rivera-Austrui et al. 2012). Heidelberg cement (Haegermann 2004) made a comparison between kilns using a high substitution rate of alternative fuels and kilns using fossil fuel only. Nine plants with a substitution rate of minimum 40 % showed an average value of 0.007 ng I-TEQ/m^3 while the average of eight kilns using fossil fuel was 0.016 ng I-TEQ/m^3. Furthermore, the reported data obtained from Spanish cement kiln plants concluded that the addition of used tires or meat meals had no effect on PCDD/F emission levels (Abad et al. 2004).

Although MSW has been utilized as alternative fuel for energy recovery in cement kilns for the last 30 years, it is still at the beginning stage in developing countries (Rahman et al. 2013; Karstensen 2007). For instance, the I-TEQ values were in the range of 9.3–90.8 pg I-TEQ/Nm^3 from cement kilns in China (Chen et al. 2014), whilst the I-TEQ values could be up to 837 pg TEQ/Nm^3 for some Vietnam cement kilns (Thuong et al. 2014). Yan et al. (2014) also studied the emission characteristics of PCDD/Fs from two co-processing DDT cement kilns, finding that the I-TEQ values varied from 1.9 to 17.1 pg I-TEQ/Nm^3. However, the effect of substitution rate of RDF (refuse derived fuel) on PCDD/F emission has never been systematically explored and so as the emission characteristics of chlorobenzenes (CBzs).

Similar with municipal solid waste incineration (MSWI) fly ash, cement plant will produce large amount of dust which is a potential hazardous waste, in part because of the caustic nature and its potential to be a skin, eye, and respiratory irritant. Moreover, traces of PCDD/Fs can be also found in cement kiln dust and are estimated to be 0–48 ng I-TEQ/kg (Jin et al. 2009). While the concentrations of PCDD/Fs and CBzs in suspension pre-heater (SP) ash and bag filter fly ash have never been separately investigated.

As reported, the concentration of PCDD/Fs in air samples could be viable to assess the health risk from cement kiln. Air samples around one cement kiln were collected and analyzed, showing that the concentration of PCDD/Fs is rather low with an average value of 0.006 pg WHO-TEQ/Nm^3 (Rovira et al. 2010). Moreover, almost no change of PCDD/F concentration was found in air samples around the cement plant after alternative fuel as a secondary fuel (Rovira et al. 2014).

This paper describes the emission and distribution characteristics of PCDD/Fs and CBzs over two cement kilns which were named CK1 and CK2. The PCDD/F concentrations in stack gas were estimated when the thermal substitution ratios of fuel increased from 0 to 17.4 %. Moreover, the PCDD/F and CBz concentrations in SP ash and bag filter fly ash were also analyzed. Specially, the bag filter fly ash was subdivided into three fractions of different particle size to study the corresponding PCDD/F concentration as a function of diameter and particle size. In order to understand the atmospheric fate and transport of dioxins from the cement kiln, levels of PCDD/Fs were determined in samples of ambient air around the cement kiln.

Material and methods

Facility description

The clinker capacities of CK1 and CK2 are 4800 and 5000 t/day, respectively. Both of them show a state-of-the-art configuration, with a pre-heater/pre-calciner comprising a vertical tower with cyclone heat exchanger vessels (Li et al. 2015). As shown in Fig. 1, they also features a waste heat recovery system, a suspension pre-heater (SP), waste heat boiler, and baghouse filters (BG), which is in accordance with the best available techniques suggested by European IPPC Bureau (2013). A selective non-catalytic reduction (SNCR) system is also installed at the inlet of the pre-calciner to reduce the emission of NO$_x$. Furthermore, large amounts of dust and fly ash collected by the baghouse filter are recycled into the kiln system. RDF prepared from municipal solid waste (MSW) is fed into the pre-calciner and entered at a constant feeding rate. Coal is used as conventional fuel fired into the discharge end of the rotary kiln. The raw material from the homogenizing silo was introduced at the top of the cyclone-type heat exchangers.

Material description

In this study, the feeding rates of raw meal were 345 and 380 t/h for CK1 and CK2 when only coal was used as fuel. The ultimate analysis, calorie value, and F and Cl content of raw meal and coal are listed in Table 1. As stated, the recommended content of Cl in fuels for the cement industry should below

Fig. 1 Diagram of the cement kilns
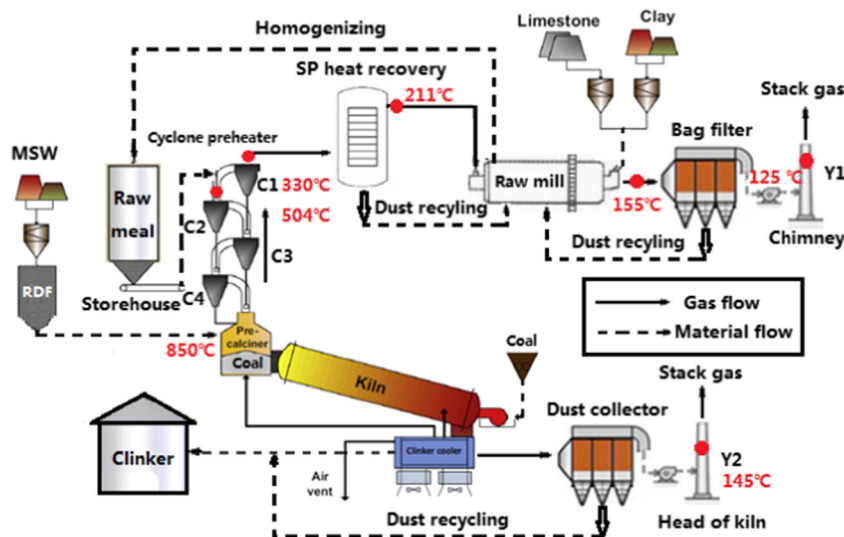
0.2 %, while the value was up to 0.26 % for the coal in CK1 (Tunesi 2011).

There are notable different chlorine, sulfur, and water contents among MSW according to different sources. Their different physical and chemical properties can cause difficulties in the kiln combustion process if MSW is unsorted (Gao et al. 2014). Therefore, MSW is made into RDF for better combustion condition. Moreover, the contents of Cu and Cl are 152 mg/kg and 0.30 wt.% for RDF in CK1 and 149 mg/kg and 0.14 wt.% for RDF in CK2, respectively.

Experimental set-up

In this study, a total of 26 samples were collected from CK1 and CK2 under typically stationary operating conditions, including 21 stack gas samples, 3 fly ash samples, and 2 ambient air samples.

As showed in Table 2, tests 1 and 2 were conducted in CK1 to investigate the change of PCDD/F emission when RDF was co-incinerated. The bag filter fly ash collected from CK1 was further to be subdivided into three fractions of different particle size (PM < 2.5 μm, PM 2.5–10 μm, and PM > 10 μm, respectively) by PM10 impactor (Dekati, Finland).

Tests 3 to 7 were set up to study the effects of RDF substitution ratios on PCDD/F emission. Additionally, the gas/

particle distribution of PCDD/Fs and CBzs in stack gas was also analyzed in tests 3 and 6. As for the ambient air samples, the sampling point was situated at the downwind situation and 200 m away from the CK2.

Sample collection

A Gasmet detector (FTIR DX-400, Finland) is used to monitor the gaseous compounds in the flue gas, such as SO_2, NH_3, HCl, and CO. Additionally, the chemical and physical characteristics of fly ash were determined by SEM-EDS (SIRISON, FEI).

PCDD/F and CBz samples in the flue gas are collected by an isokinetic sampler (Model KNJ23, KNJ, Korea) according to US EPA method 23 (US EPA 1995). The stack gas was isokinetically sampled, and each sampling time was 120–180 min for approximately 2.0–4.0 m^3 in volume; each condition was sampled at least three times; the oxygen concentration was also recorded. The filtered ash from the exit of the thermal treatment unit is also sampled for dioxin analysis. Ambient air samples were collected according to US EPA Method TO-9A (US EPA 1999) using SIBATA HV-1000F sampler, which was equipped with a glass fiber filter (GFF, 20.3 × 25.4 cm, GB100R, 0.6-μm nominal rating) followed by a glass cartridge containing two polyurethane foam (PUF, 5.0 × 9.0 cm) plugs (Xu et al. 2009).

Table 1 Ultimate analysis, calorie value, and F and Cl content of raw meal and coal

	F and Cl		Ultimate analysis (dry basis, %)				Calorie
	F, mg/g	Cl, mg/g mg/g	Mad	Aad	Vad	FCad	Qnet, J/g
Raw meal (CK1)	0.542	1.896	–	–	–	–	–
Coal (CK1)	0.206	2.587	–	–	–	–	–
Raw meal (CK2)	0.192	0.320	0.65	65.93	19.31	15.14	–
Coal (CK2)	0.198	1.030	1.76	17.85	27.96	52.43	23,177

Mad moisture, *Aad* ash, *Vad* volatile, *Fcad*, fixed carbon

Table 2 Experimental design conditions

Tests	Cement kiln	Amount of RDF (t/h)	Substitution rate (%)	Detection
1	CK1	0	0	PCDD/Fs
2	CK1	10	8.3	Gaseous compounds and PCDD/Fs
3	CK2	0	0	PCDD/Fs
4	CK2	6.5	5.4	PCDD/Fs
5	CK2	8	6.6	PCDD/Fs
6	CK2	15	12.4	Gaseous compounds, PCDD/Fs, and CBzs
7	CK2	21	17.4	PCDD/Fs

Sample analysis

Pre-treatment of CBz 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. The temperature program for GC oven was as follows: initial temperature 80 °C, held for 4 min; increased at 5 °C/min to 106 °C, held for 0.5 min; increased at 8 °C/min 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 ambient air samples) and 1613 (for fly ash samples), respectively. The PCDD/Fs are identified and quantified by HRGC/HRMS, using a 6890 Series gas chromatograph (Agilent, USA) coupled to a JMS-800D mass spectrometer (JEOL, Japan). A DB-5 ms (60 m × 0.25 mm I.D., 0.25-μm film thickness) capillary column is used for separating the PCDD/Fs congeners. The mean recoveries of standards for PCDD/Fs range from 55 to 125 %, which are all within the acceptable 25 to 150 % range. The toxic equivalents (TEQ) are calculated using NATO/CCMS factors (Bhavsar et al. 2008). All the concentrations are normalized to dry air, 10 % O_2, 1.01×10^5 kPa, and 237 K.

Results and discussion

Stack gas emission of PCDD/Fs

Experimental condition

The temperatures of stack gas in CK1 and CK2 were 109 and 110 °C, respectively. The velocity of stack gas was ca 7.0 m/s, and the flow volume could be up to 700,000 m^3/h. Moreover, the oxygen contents of stack gas were 9.8 and 8.1 % for CK1 and CK2, respectively.

The concentrations of common gaseous pollutants in the flue gas are listed in Table 3. Due to high content of $CaCO_3$ in the raw material, the emission level of CO_2 was up to ca. 15 %. Comparison between tests 1 and 2 showed that the replacement of coal by RDF will not increase the emission of CO. Some researchers stated that CO_2 emission and other air emissions such as NO_x, SO_2, and dust can be reduced by increasing the usage of alternative fuel (Rahman et al. 2013). This is true for SO_2 with a decrease from 61 to 1 mg/m^3. However, the concentration of NO significantly increased from 163 to 312 mg/Nm^3. The reason could be contributed to the complex composition of RDF. The result also confirmed that more than 90 % of the NO_x emissions from cement kilns were NO, and the rest was NO_2 (van Oss and Padovani 2003). Moreover, the national emission standard for NO_x is 320 mg/Nm^3, and the SNCR system will be put into use automatically when the emission level exceeds the limitation. In terms of HCl and HF, the concentrations of them were much higher than the emission limit value. The reason was due to the high contents of fluorine (0.542 mg/g) and chlorine (2.587 mg/g) in the raw material and coal, respectively.

Emission level of PCDD/Fs in CK1

In this study, RDF was used as alternative fuel in CK1, and the feeding rate was 10 t/h. The average concentration of PCDD/F emission was 1.189 ± 0.605 ng/m^3 (0.076 ± 0.040 ng I-TEQ/m^3) during normal operation (no RDF added) and slightly increased to 1.208 ± 0.734 ng/m^3 (0.097 ± 0.045 ng I-TEQ/m^3) when RDF was fed into the system. The emission was relatively high, and the air pollution control system (APCS) needed stricter operation. Furthermore, the emission factor increased from 279 to 352 ng I-TEQ/t clinker when the coal

Table 3 Gaseous compounds of stack gas when RDF co-incinerated, mg/Nm^3

|	CO_2, %	CO	SO_2	NO	NO_2	N_2O	NH_3	HCl	HF
CK1 (tests 1)	14.7	265.04	61.3	163.0	7.5	0.3	0.4	13.8	11.2
CK1 (tests 2)	15.8	97.0	1.2	311.6	3.8	0.1	0.8	5.9	3.9
Standard (GB30485-2013)			100	320 (NO_x)			8	10	1

was partially replaced by RDF, and it was much higher than that of Spanish cement plant (Fabrellas et al. 2002, 2004).

As shown in Fig. 2, the leading congeners were 1,2,3,4,6,7, 8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF, and OCDF before and after the partial replacement of coal. Moreover, the value of chlorination remained the same and so as to the ratio of PCDDs/PCDFs, indicating that usage of RDF to replace parts of the fossil fuel does not seem to affect the PCDD/F distribution. The distribution of I-TEQ contribution was also presented in Fig. 2. The major contribution to total I-TEQ came from 2,3,4,7,8-PeCDF owing to its TEF of 0.5. The contribution increased from 31.1 to 50.4 % with the adding of RDF.

Emission level of PCDD/Fs in CK2

The level of dioxin emission was 0.041 ng I-TEQ/m^3 without the adding of RDF. While the value decreased to 0.018 ng I-TEQ/m^3 when 6.5 t/h RDF was fed into the kiln, indicating that the replacement of coal has almost no effect on the PCDD/F emission. Moreover, the emission levels were more likely to be affected by the stability of incineration system and the characteristics of fuel (Aurell and Marklund 2009). It showed that the concentrations of PCDD/Fs varied from 0.006 to 0.073 ng I-TEQ/m^3 when the disposal amount of RDF further increased to 8, 15, and 21 t/h. The difference of

Fig. 2 Fractions of dioxin concentration (**a**) and I-TEQ contribution (**b**) in stack gas of CK1
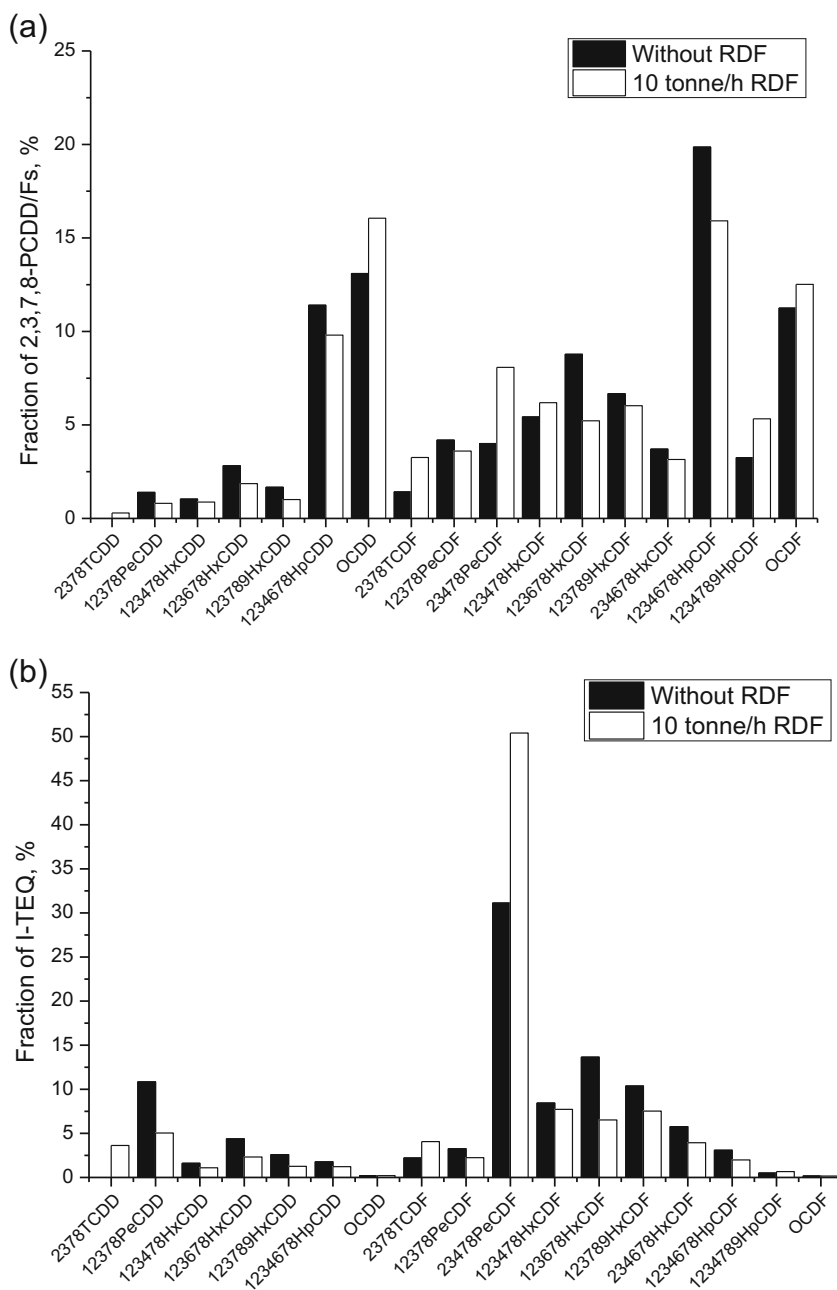
PCDD/F emission could be attributed to both of the performance of the APCS and the operational condition of the kiln.

As regard to the 17 toxic PCDD/Fs, the fraction of PCDDs was much lower than that of PCDFs in all the experiments, with value of more than 70 % for PCDFs. As shown in Table 4, the percentages of the lower chlorinated PCDDs were much lower than that of OCDD. Moreover, the value of chlorination was in the range of 6.09–6.62 and has no possible relationship with the co-processing amount of RDF. Similar with CK1, the major contribution to total I-TEQ also came from 2,3,4,7,8-PeCDF, and the contribution was more than 40 % except for the test 6.

In order to investigate the contribution of RDF to the total PCDD/F emission, the relationship between the amount of RDF co-incinerated and the emission value of PCDD/Fs in flue gas is analyzed. The results show that PCDDs, PCDFs, PCDD/Fs, and TEQ do not correlate well with the disposal amount of RDF, and their corresponding r^2 values are 0.28, 0.20, 0.21, and 0.25, respectively. Therefore, the substitution rate of alternative fuels seems to have minor effect on the emission of PCDD/Fs, which is accordance with the results obtained by other researchers (Karstensen 2008; Rovira et al. 2014; van Loo 2008).

Gas/particle distribution of PCDD/Fs and CBzs in stack gas

As shown in Fig. 3, the fractions of PCDD/Fs in gas phase was 97.0 % when only coal as fuel. While the fraction decreased to 66.3 % when the co-processing amount of RDF was 15 t/h in CK2. The difference could be attributed to the different characteristics of ash produced from RDF and raw meal, resulting in higher fraction of PCDD/Fs in gas phase. In terms of the congener distribution, lower chlorinated PCDD/Fs were more adhered to gas phase even for co-processing tests.

The total concentration of CBzs in the stack gas from CK2 was 26.9 μg/Nm³, which was three orders of magnitude higher than the PCDD/F concentration. This trend was in line with the behavior of stack gas from waste incinerators (Zimmermann et al. 1996). The gas/particle partition of CBzs was also together analyzed in CK2, showing that 82.4 % of CBzs were presented in gas phase. The reason for this distribution could be attributed to the lower vapor pressures of CBzs. Moreover, almost no PeCBzs and HCBzs were detected, which is different with the stack gas from waste incinerators (Kaune et al. 1994).

Fly ash emission of PCDD/Fs and CBz

Concentrations of PCDD/Fs and CBzs

The concentrations of PCDD/Fs in the SP and bag filter fly ash were 28 and 30 pg/g with the I-TEQ values of 3.3 and 3.9 pg I-TEQ/g, respectively. It should be noted that the value was two or three orders of magnitude lower than the fly ash produced from MSWI (Chen et al. 2008; Pan et al. 2013). The big difference could be attributed to the composition of fly ash. Combination of EDS- and XRD-analysis showed that CaO, CaCO₃, and SiO₂ were the primary components of fly ash produced from cement kiln. The fractions of PCDDs and PCDFs were 43 and 57 % in the SP fly ash, respectively. Compared with MSWI fly ash, the content of Cu in bag filter fly ash discharged from CK2 is rather low with a value of 0.03 wt.%. As to the congener distribution, the leading ones were OCDD and OCDF in the SP fly ash accounting

Table 4 Results regarding the stack gas emission of PCDD and PCDF in CK2

Property	Co-processing amount of RDF (t/h)					Unit
	0	6.5	8	15	21	
Thermal substitution ratio	0	5.4	6.6	12.4	17.4	%
2,3,7,8-PCDDs	110	58	202	20	38	pg/Nm³
2,3,7,8-PCDFs	307	185	670	54	133	pg/Nm³
PCDFs/PCDDs	2.80	3.19	3.33	2.66	3.52	
Percentage of 2,3,7,8-PCDFs	89	80	88	73	78	%
2,3,7,8-PCDD/Fs	417	243	872	74	171	pg/Nm³
Percentage of tetra- and penta-PCDDs	ND	2	ND	2	2	%
Percentage of OCDD	12	10	6	9	11	%
Percentage of tetra- and penta-PCDFs	19	10	11	9	12	%
Percentage of OCDF	ND	17	4	10	20	%
Weight average level of chlorination	6.09	6.56	6.24	6.49	6.62	
I-TEQ	41	18	73	6	13	pg I-TEQ/Nm³
2,3,4,7,8-PeCDF to I-TEQ	44	49	42	22	40	%

Fig. 3 Gas/particle distribution of 2,3,7,8-PCDD/F congener before (**a**) and after (**b**) fuel replacement

PCDD/Fs in different particle sizes of bag filter fly ash
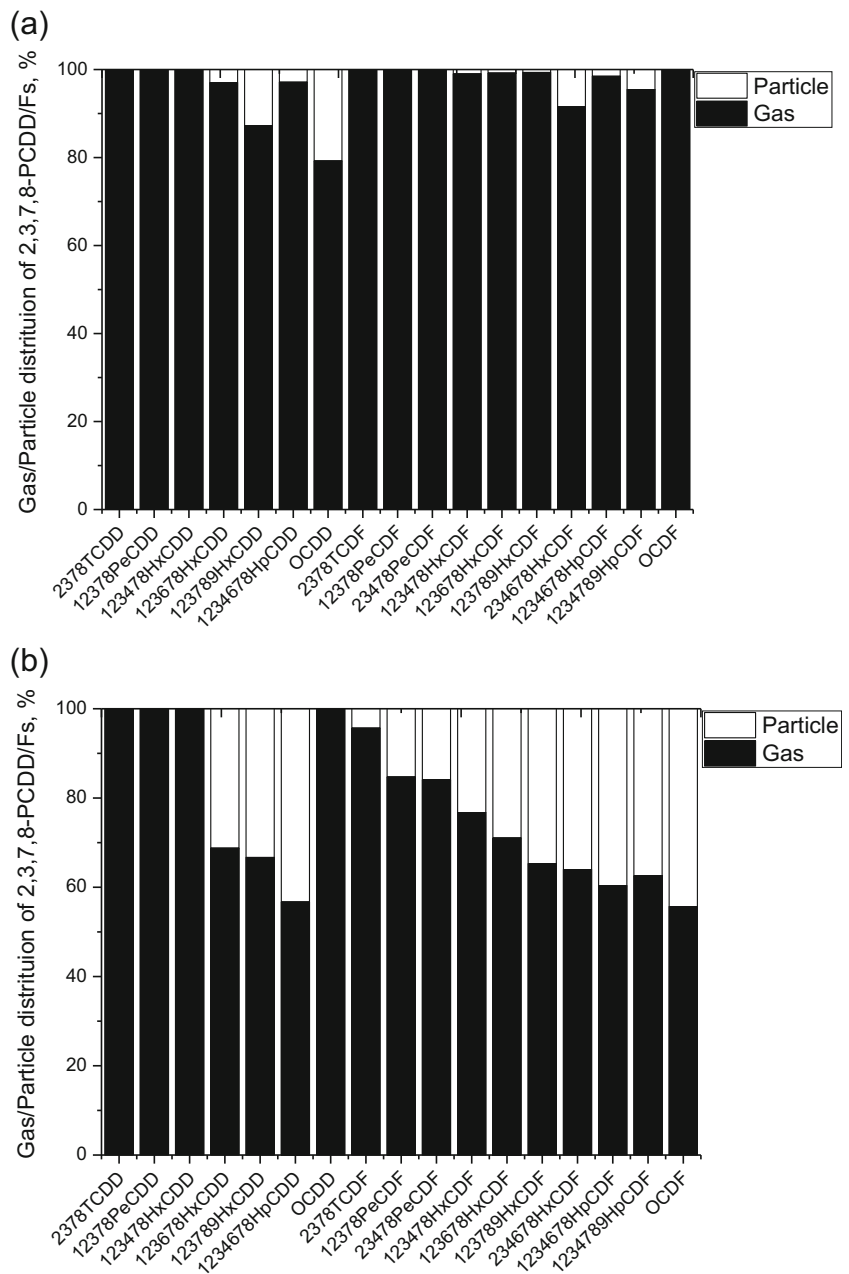
for 34 and 13.8 %. Similar with the SP fly ash, higher chlorinated congers were dominated in the bag filter fly ash with a fraction value of 31 % for OCDD.

Similar with MSWI fly ash, 2,3,4,7,8-PeCDF contributed most to the total I-TEQ value. The contribution of it was 69.6 and 68.0 % for the SP and bag filter fly ash, respectively. Therefore, the contribution of PCDFs could be up to 87 and 84 %, which was much higher than that of MSWI fly ash.

The total concentration of CBzs in the SP and bag filter fly ash was 951 and 954 pg/g, respectively. Similar with stack gas, DCBzs and TCBzs were the leading congeners in both of the SP and bag filter fly ash, and the total fractions of them were 93 and 86 %, respectively.

The average particle size, d_{50}, and d_{90} values of fly ash are 9.7, 7.4, and 19.2 μm, respectively. The fly ash collected from bag filter was separated into the three size fractions by PM10 impactor, i.e., PM < 2.5 μm, PM 2.5–10 μm, and PM > 10 μm. The fractions of fly ash in PM < 2.5 μm, PM 2.5–10 μm, and PM > 10 μm are 15, 53, and 32 wt.%, respectively.

As showed in Table 5, the PCDD/F concentrations for fly ash in PM < 2.5 μm, PM 2.5–10 μm, and PM > 10 μm amount to 562, 319, and 158 pg/g, respectively. The level of PCDD/Fs in fly ash escalates for smaller particle size, which is similar with MSWI fly ash and bottom ash (Chang and Chung 1998;

Table 5 Results regarding the fly ash emission of PCDD and PCDF in various size fractions

Property	PM < 2.5 μm	2.5 μm < PM < 10 μm	PM > 10 μm	Unit
2,3,7,8-PCDDs	153	83	47	pg/g
2,3,7,8-PCDFs	409	236	111	pg/g
2,3,7,8-PCDD/Fs	562	319	158	pg/g
PCDFs/PCDDs	2.67	2.86	2.34	
Percentage of 2,3,7,8-PCDFs	73	74	70	%
Percentage of tetra- and penta-PCDDs	7	10	5	%
Percentage of OCDD	8	9	11	%
Percentage of tetra- and penta-PCDFs	18	28	16	%
Percentage of OCDF	8	6	8	%
Weight average level of chlorination	6.05	5.72	6.05	
I-TEQ	82	52	24	pg I-TEQ/g
2,3,4,7,8-PeCDF to I-TEQ	39	24	41	%

Chen et al. 2006; Stanmore 2004). The reason for this distribution can be attributed to the relative high specific surface area for smaller particles.

PCDFs contribute most to the concentration of 2,3,7,8-PCDD/Fs in fly ash with percentage of more than 70 %. Thus, the ratios of PCDFs to PCDDs are all expected to above 2.0. Furthermore, lower chlorinated (tetra- and penta-) PCDF congeners contribute most to the concentration of 2,3,7,8-PCDD/Fs. The highest fraction of low chlorinated PCDF congeners results in the lowest weight average level of chlorination for fly ash in PM 2.5–10 μm. As for I-TEQ, it also increases with the decreasing of particle size. The I-TEQ values for fly ash in PM < 2.5 μm, PM 2.5–10 μm, and PM > 10 μm are 82, 52, and 24 pg I-TEQ/g, respectively. Similar with MSWI fly ash, 2,3,4,7,8-PeCDF contributes most to the value of I-TEQ, especially for the fly ash in PM > 10 μm.

Table 6 PCDD/Fs in ambient air around the CK2, pg/Nm^3, or pg I-TEQ/Nm^3

	#1		#2		Average	
	PCDD/Fs	I-TEQ	PCDD/Fs	I-TEQ	PCDD/Fs	I-TEQ
2,3,7,8-TCDD	0.022	0.022	0.016	0.016	0.019	0.019
1,2,3,7,8-PeCDD	0.088	0.044	0.048	0.024	0.068	0.034
1,2,3,4,7,8-HxCDD	0.053	0.005	0.050	0.005	0.052	0.005
1,2,3,6,7,8-HxCDD	0.224	0.022	0.143	0.014	0.184	0.018
1,2,3,7,8,9-HxCDD	0.127	0.013	0.104	0.010	0.116	0.012
1,2,3,4,6,7,8-HpCDD	1.200	0.012	0.766	0.008	0.983	0.010
OCDD	2.231	0.002	1.512	0.002	1.871	0.002
2,3,7,8-TCDF	0.229	0.023	0.207	0.021	0.218	0.022
1,2,3,7,8-PeCDF	0.463	0.023	0.353	0.018	0.408	0.020
2,3,4,7,8-PeCDF	0.419	0.210	0.421	0.211	0.420	0.210
1,2,3,4,7,8-HxCDF	0.859	0.086	0.850	0.085	0.854	0.085
1,2,3,6,7,8-HxCDF	0.580	0.058	0.444	0.044	0.512	0.051
1,2,3,7,8,9-HxCDF	0.534	0.053	0.489	0.049	0.512	0.051
2,3,4,6,7,8-HxCDF	0.091	0.009	0.086	0.009	0.088	0.009
1,2,3,4,6,7,8-HpCDF	3.323	0.033	2.300	0.023	2.812	0.028
1,2,3,4,7,8,9-HpCDF	0.382	0.004	0.391	0.004	0.387	0.004
OCDF	4.372	0.004	3.260	0.003	3.816	0.004
∑PCDDsP	3.946	0.121	2.640	0.079	3.293	0.100
∑PCDFs	11.250	0.503	8.801	0.466	10.026	0.485
PCDFs/PCDDs (TEQ)	2.851	4.170	3.334	5.889	3.045	4.851
Total concentration	15.196	0.624	11.441	0.545	13.319	0.585

Concentration of PCDD/Fs in atmosphere air

The concentration of PCDD/Fs (I-TEQ value) in the atmosphere air around the CK2 was 13.32 ± 1.87 pg/Nm^3 (0.59 ± 0.04 pg I-TEQ/Nm^3), which was slightly lower than the air quality limitation of PCDD/Fs (0.6 pg I-TEQ/Nm^3). The air samples around a co-processing MSWI were also analyzed by Rovira et al. (2010), and the average concentration of PCDD/Fs was 0.007 pg I-TEQ/Nm^3 (Rovira et al. 2010).

The congener distribution of PCDD/Fs was listed in Table 6. The samples had much greater PCDF level than PCDD. This trend was in agreement with the atmosphere samples collected within the residential area at 700 m away from the MSWI (Lee et al. 2007). The values of chlorination were 7.40 and 6.95 for PCDDs and PCDFs, which is similar with the air samples near a MSWI in eastern China (Xu et al. 2009). The leading congeners were 1,2,3,4,6,7,8-HpCDF and OCDF. The fractions of them were up to 21 and 29 %, respectively. Moreover, 2,3,4,7,8-PeCDF was the most important I-TEQ contributor accounting for ca. 36 %, which was equal to the ambient air samples collected from residential area (Lee et al. 2007). The similar situation was also found in the atmosphere where 2,3,4,7,8-PeCDF contributed 30–53 % to the total I-TEQ value (Khumsaeng et al. 2013).

Conclusions

The emission and distribution behaviors of PCDD/Fs and CBzs were studied in two typical dry cement kilns. Several interesting results were obtained:

1. The PCDD/F emission from the CK1 was 0.076 ng I-TEQ/m^3 and increased by 25.97 % with RDF co-processing. Furthermore, the operational conditions and APCS performance have more significant effect than RDF substitution rate on PCDD/F emission;
2. The fractions of PCDD/Fs in gas phase was 97.0 %, and it decreased to 66.3 % when the co-processing amount of RDF was 15 t/h;
3. The I-TEQ values of the SP and bag filter fly ash were 3.3 and 3.9 pg I-TEQ/g, respectively. The level of PCDD/Fs in fly ash escalates for smaller particle size;
4. The TEQ value in the atmosphere air around the CK2 was 0.59 ± 0.04 pg I-TEQ/Nm^3, which was slightly lower than the air quality limitation of PCDD/Fs.

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