Adsorption of Dioxins on the Entering Raw Meal

Ming-Xiu Zhan[1], Jian-Ying Fu[2], Tong Chen[1*], Ye-Qing Li[3], Xiao-Dong Li[1], Jian-Hua Yan[1], Alfons Buekens[1]

[1] *State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, China*
[2] *China United Engineering Co., Ltd, Hangzhou, China*
[3] *Huaxin Environment Engineering Co., Ltd, Wuhan, China*

ABSTRACT

Cement kilns still emit considerable amounts of dioxins, more precisely polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) whether these kilns co-incinerate waste, or not. The emission level depends on the quality of meals (composition of mixed and ground limestone and shale or clay) on the one hand, the co-firing of waste on the other. Waste can be fired at the lower, discharge end of the rotary kiln, or be introduced to mid-kiln, at the kiln entrance, in the calcination section, or even further downstream along the path of the combustion gases. The temperature/time history of these combustion gases and of the meal are decisive factors in the formation, collection and destruction of dioxins. Still, very little is known on the extent and location of such phenomena along the path of meal, in countercurrent to that of combustion gases. In this study, the adsorption effects of the entering meal on the flows of dioxins were fully investigated in a 4500 ton day^{-1} clinker production line. The meal was characterised by its Ultimate Analysis, its specific surface and by XRD- and EDS-analysis, indicating that CaO, CaCO$_3$ and SiO$_2$ were the main compositions of it. In laboratory experiments, it was observed that the entering raw meal could indeed adsorb 2,3,7,8-substituted PCDD/Fs from combustion gas thus cleaning the raw gas even before its treatment by dust collection. The results revealed that meal could adsorb 2,3,7,8-PCDD/Fs from RDF incineration flue gas, with an efficiency up to 84.8% in wt. units and 71.0% in I-TEQ units.

Keywords: PCDD/Fs; Cement kiln; Raw mill; Co-incinerated RDF; Adsorption.

INTRODUCTION

Co-disposal of solid waste in cement manufacturing not only provides fuel and raw materials to the cement plant, but also solves an external problem, i.e., eliminating waste, even its residue. Compared to MSW incineration, 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 (Yamada *et al.*, 2004; Li *et al.*, 2012) leading to high destruction efficiency of any hazardous waste entering the kiln together with the fuel at the side of clinker discharge. The clinker incorporates the incineration residue, which – after considerable dilution - is eventually sold as cement. Moreover, the high specific surface area presented by alkaline raw material (lime) and clay has proved to provide intensive adsorption towards dioxins (Choy *et al.*, 2004) and other semi-volatile compounds (e.g., PAHs). Still, these advantages do not fully apply to the firing of waste

introduced after the cement kiln, i.e., at the level of the cyclonic preheaters and the decarbonatation of limestone, which requires a temperature of only 800°C. Moreover, both pollutant emission standards and clinker quality should be respected (Abu-Allaban *et al.*, 2011; Thuong *et al.*, 2014).

European cement industries annually dispose of about 6.1 million ton of waste, which corresponds to a thermal substitution rate of 17% (van Loo, 2008). At the end of 2013, the amount of municipal solid waste (MSW) co-incinerated in cement kilns in China has increased to 4700 ton day^{-1}. However, fuel replacement by co-incinerated MSW was only 1.2%, still far away from most levels in developed countries (CICounsulting, 2014). During co-disposal, some persistent organic pollutants (POPs), such as polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), will be generated, similarly as the traditional MSW incineration process (Huang and Buekens, 1995; Chen, 2004; Kao *et al.*, 2006; Chen *et al.*, 2014). Therefore, the key to spreading the co-disposal of solid waste in cement kilns in China is to characterise, control and reduce the generation of PCDD/Fs.

Fig. 1 schematically shows a dry process cement kiln. Raw meal is composed of limestone and clay or shale in precisely controlled ratios. This feed is gradually preheated in a tower

---

* Corresponding author.
 Tel.: +86-571-87953385; Fax: +86-571-87952438
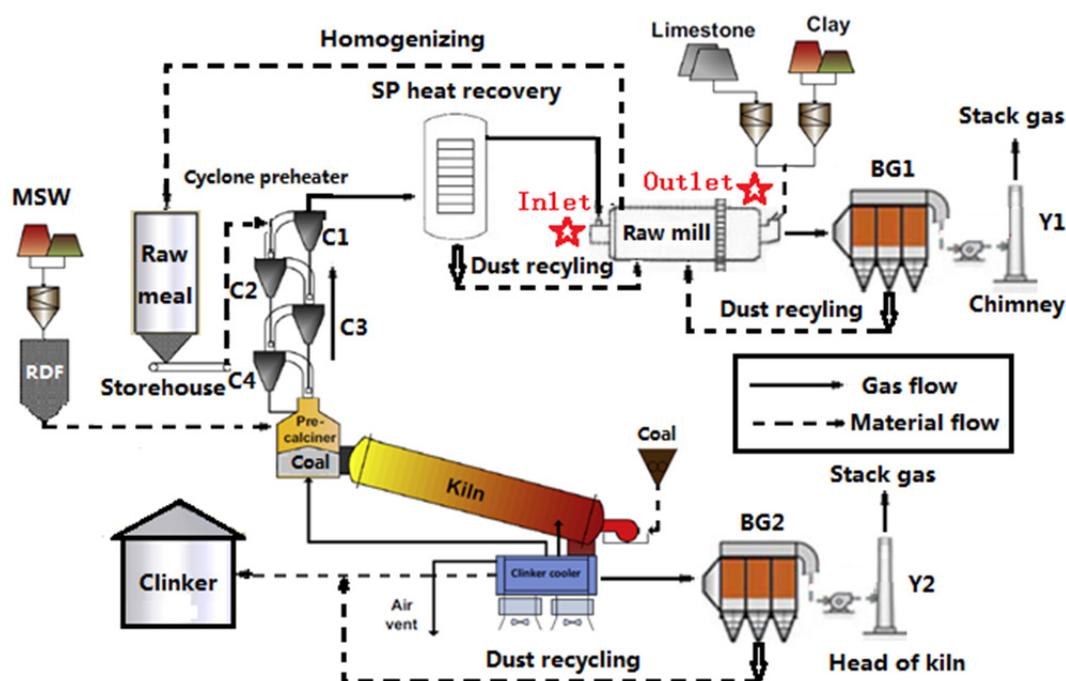 *E-mail address:* chentong@zju.edu.cn

Fig. 1. Diagram of the cement kiln.

composed of a battery of four cyclonic heat exchangers: hot gas swirls and suspends the meal in direct contact and leaves the cyclone through an axial pipe at the top. The meal is heated directly in contact with the combustion gases, yet then separates from the gas and leaves the cyclone at the bottom. Typical operating temperatures of the four cyclones are, from top to bottom: ca. 330, 520, 650 and 800°C. The last preheater before entering the rotary kiln is the precalciner, operating at ca. 850°C. Here the limestone partly converts into quicklime (CaO). In the rotary kiln, clinker chemistry converts CaO and clay minerals into the ternary compounds constituting the cement clinker.

RDF is produced from raw waste by a combination of coarse and fine shredding, magnetic separation, eddy current metal separation, screening, and air classification. RDF can be fired in suspension at the discharge end of the kiln. It can also be introduced to mid kiln, or at the feed end. Today most modern cement kilns practicing co-disposal of waste can meet the emission level of 0.1 ng I-TEQ m^{-3}, when well managed and operated (Karstensen, 2008). Several recent studies examined the use of industrial waste, municipal solid waste and hazardous waste as supplemental fuels, and found that most emissions of PCDD/Fs are lower than this limit value (Zabaniotou and Theofilou, 2008; Rivera-Austrui *et al.*, 2014). For instance, when waste tyres and sewage sludge were used to feed the kiln, the dioxin emissions with flue gas varied in a range of 0.0019–0.0221 ng I-TEQ Nm^{-3} (Conesa *et al.*, 2008). Zemba *et al.* (2011) conducted 150 tests using various special fuels, including hazardous waste, refuse derived fuel (RDF), and cokes and found that the type of waste had only minor influence on dioxin emissions, all remaining below 0.1 ng I-TEQ Nm^{-3}. Yan *et al.* (2014) reported that DDT waste is effectively destroyed by feeding to the precalciner in a dry process cement kiln, and the

emissions of PCDD/Fs in the flue gas varied in a range of 0.0019–0.0171 ng I-TEQ Nm^{-3} (Yan *et al.*, 2014).

In cement plant, the flow of raw materials and of flue gas are moving in the opposite direction (i.e., in counter-current), creating ample area and time for them to contact directly, exchanging heat and semi-volatiles at the same time. Therefore, raw meal is preheated, an important feature for energy-saving, and adsorbs a certain amount of PCDD/Fs formed by combustion of waste, as well as carbon present in the raw materials. Thus, the mass balance of dioxins should be established, taking into account the transfer of dioxins from hot flue gas to the cold meal, as well as the occurrence of de novo or precursor formation.

Moreover, the adsorption of dioxins may be affected by the specific surface and particle size of raw meal. In municipal solid waste incineration (MSWI) the effect has been investigated for fly ash, bottom ash and activated carbon (Chi *et al.*, 2006). Hence, the highly alkaline environment in cement kilns could suppress chlorination of organic compounds in raw meal (Liu *et al.*, 2005; Wang *et al.*, 2012) and avoid the synthesis of dioxins during flue gas cooling. Gálvez *et al.* (2007) studied the interaction of flue gas from the combustion of sewage sludge and cement meal in a laboratory furnace, and found that it decreases pollutant emissions. Thus, it is important and meaningful to further research the reduction of dioxins by contacting with raw materials in cement kilns.

Cement production in China now represents 60% of the world amount. Meanwhile, pollutants emitted from cement plants also influence and threat the environment and public health (Li *et al.*, 2015). In order to better understand the formation and distribution of dioxins in cement industry, the concentration of dioxins in raw materials was investigated in a 4500 ton day^{-1} clinker production line, both when RDF

was co-incinerated, or not. Moreover, raw material flow was subdivided into three fractions of different particle size by PM_{10} impactor (Dekati, Finland), to study the corresponding adsorption effects as a function of diameter and particle size. In addition, the concentration of dioxins was evaluated at the entrance and outlet, in an attempt to establish balances and to confirm the reduction effect on dioxins by their adsorption on raw materials. Finally, laboratory experiments were conducted in a small tubular reactor to verify the findings derived from measuring dioxins in the cyclonic heat exchanger section of full-scale cement manufacturing.

MATERIALS AND METHODS

Cement Kiln Experiments

RDF Feeding Concept – Fly Ash and Dust Recirculation

A measurement program was undertaken in duplicate at a continuously operating cement kiln (dry process, clinker capacity of 4500 ton day^{-1}) in Hubei province, without and with RDF added. The kiln shows a state-of-the-art configuration, with a pre-heater/pre-calciner comprising a vertical tower with four cyclone heat exchanger vessels (cf. Fig. 1). It also features a waste heat recovery system, a suspension pre-heater (SP), waste heat boiler and baghouse filters (BG).

Coal was used as conventional fossil fuel fired into the discharge end of the rotary kiln, and the raw meal was introduced at the top of a vertical tower with four stage cyclone-type heat exchangers. RDF prepared from municipal solid waste (MSW) was mixed with the raw meal and entered at a constant feeding rate of RDF of 8–12 t h^{-1}. Meanwhile, dust and fly ash separated by the bag house filter were re-introduced back into the system, after mixing with the raw material in a conditioning tower.

Sampling Method

Sampling for PCDD/Fs in flue gas and raw material was carried out according to USEPA Method 23 and the Chinese standard measurement procedure (HJ 77.1–77.4, 2008). The sampling positions A and B were located at the inlet and the outlet of the raw mill, respectively. During the test, the flue gas was isokinetically sampled at both positions A and B, and each sampling time was 120–180 min for collecting a volume of gas of ca. 2.0–4.0 m^3; at the same time the oxygen concentration of flue gas was continuously recorded. Meanwhile, before and after the raw mill solid samples were simultaneously collected every half hour until 2 kg was reached. Since such samples show a general inhomogeneous appearance, they were collected by fully mixed multipoint sampling.

Extraction and Cleanup

Prior to the extraction process each sample was spiked with 1 ng of $^{13}C_{12}$-labeled Internal Standards described in USEPA method 23. Soxhlet extraction by toluene was applied to XAD-2 and the filter for 24 h. The toluene extract was transferred to n-hexane and rotary-concentrated, prior to the cleanup process. The concentrated extracts were cleaned sequentially by means of a multi-layer silica gel and carbon column. Sequentially the extracts were concentrated to 20 μL with nitrogen and then spiked with 1 ng of $^{13}C_{12}$-labeled Recovery Standards prior to analysis.

Instrumental Analysis

Identification and quantification of PCDD/Fs are accomplished by a 6890 Series high-resolution gas chromatograph (HRGS, 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 (HRMS, JEOL, Japan). The recovery of the label standards is seen as indicator for evaluating potential losses of the entire pretreatment process, while $^{13}C_{12}$-labeled Surrogate Standards and Internal Standards should range from 70–130%, 40–120% respectively. Toxic equivalents (I-TEQ) were calculated using the NATO/CCMS factors (NATO/CCMS, 1988).

Lab-Scale Experiments

The RDF and raw materials required were collected from the cement kiln during the experiments with RDF added. The RDF contained 42.3 wt.% moisture, 0.30 wt.% chlorine and 151.8 mg copper kg^{-1}, respectively. Its calorific value was 6615 kJ kg^{-1}. The chlorine content of raw materials was 1.90 mg g^{-1}.

The raw material adsorption experiments were conducted in the test reactor system shown schematically in Fig. 2. The apparatus comprises a tubular reactor, externally heated by a furnace consisting of three sections a, b, and c (0.5 m each section) and featuring an independent heater and temperature controller to maintain the set temperature in each section.

The simulated flue gas (300 mL min^{-1}; 15% O_2 in N_2) contacted the reaction materials at 900°C in section a; the set points for section b and c were 500 and 350°C, respectively; the reaction time for each test was 30 min; the total residence time involved was 130 s. During the experiments, the real temperature in each section fluctuated within ca. 10°C, with temperature simultaneously compared with a S-type thermocouple reading to keep the target temperature.

The cleanup of PCDD/Fs samples was conducted according to USEPA 1613 method (U.S EPA, 1994). The detailed cleanup procedure and PCDD/Fs analysis can be found in previous papers (Wu *et al.*, 2012; Yan *et al.*, 2012). Target compounds were the 17 toxic 2,3,7,8-substituted PCDD/Fs congeners.

RESULTS AND DISCUSSION

Effects of RDF Addition on Concentration of Dioxins in Raw Material

The percentage of CaO in raw meal could even reach 42.5 wt.%, so alkaline environment will be easily built in raw material (Cong *et al.*, 2015), which could be better for raw material to adsorb dioxins (Choy *et al.*, 2004). Moreover, CaO addition was proven efficiently to inhibit the formation of PCDD/Fs during the thermal treatment at a low temperature (Wang *et al.*, 2012). By ultimate analysis, we found that the contents of volatile and fixed carbon in raw material were 14.98 and 18.74 wt.%, respectively. For F and Cl,
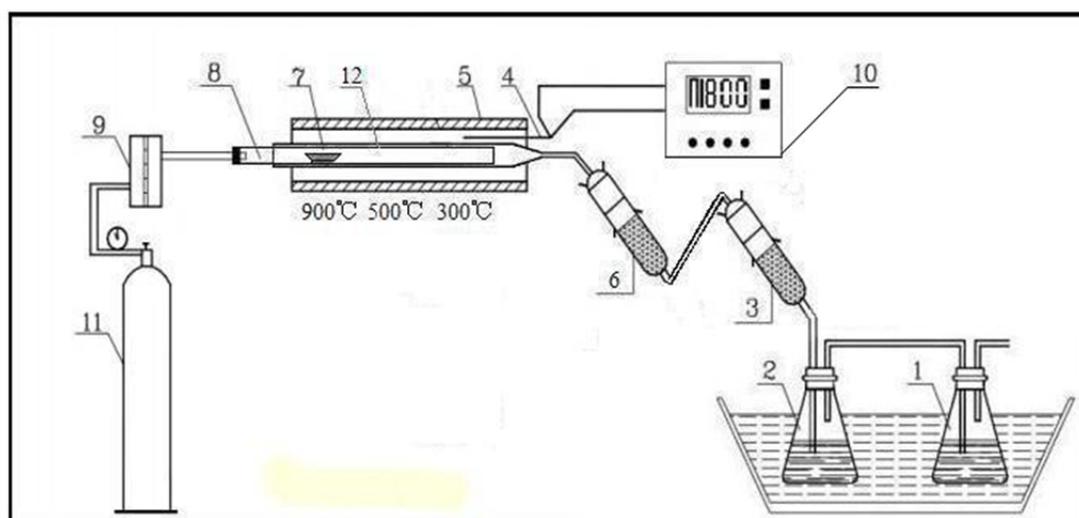
1, 2: Toluene in ice bath, 3: XAD-II resin, 4: Thermocouple, 5: Tubular furnace, 6: Raw meal, 7: Reaction material,
8: External quartz tube, 9: Mass flow meter, 10: Temperature controller, 11: Gas cylinder, 12: Internal quartz tube.

Fig. 2. Experimental system for dioxins desorption experiments.

both of them were below 0.4 mg g^{-1}, which is much lower than MSW fly ash (Yılmaz, 2015). Furthermore, the results of XRD and EDS analysis are presented in Fig. 3, and corresponding element analysis by EDS is listed in Table 1. The normalization is carried out by the weight of all the elements. CaO, CaCO$_3$ and SiO$_2$ are the main compositions of raw material in this study, which is consistent with the results of Cong *et al.* (2015) reported.

The homogeneous raw material prepared in the conditioning tower was fed into the raw mill, with a concentration of 2,3,7,8-PCDD/Fs of 1.80 ng g^{-1} (or 0.022 ng I-TEQ g^{-1}).

In test A no RDF was co-incinerated; the raw material merely flowed out of the raw mill and its concentration of 2,3,7,8-PCDD/Fs increased to 2.96 ng g^{-1} (or 0.041 ng I-TEQ g^{-1}). The temperature of raw material is ca. 150°C, not high enough for *de novo* synthesis, indicating that the meal might have adsorbed PCDD/Fs from flue gas.

The distribution of dioxins in meal flowing in and out of the raw mill is presented in Table 2. The leading PCDD/Fs congeners were OCDD (20.5%), OCDF (49.7%) and 1,2,3,4,6,7,8-HpCDF (18.4%). After passing through the raw mill, the congener distribution of PCDD/Fs in the feed did not show any marked difference.

In test B (RDF co-incineration), the concentration of PCDD/Fs in the meal flowing out of the raw mill increased to 4.0 ng g^{-1} (or 0.066 ng I-TEQ g^{-1}), a rise markedly higher than in test A. RDF co-disposal had, however, only a minor effect on the congener distribution.

Dioxin Distribution in Different Particle Sizes
The particle distribution of meal is presented in Fig. 4. Its average particle size is 12.4 μm, and the d$_{50}$ and d$_{90}$ values are 8.4 and 27.2 μm, respectively. The meal sampled at the inlet of the raw mill was separated into three size fractions, i.e., PM < 2.5 μm, PM 2.5–10 μm and PM >10 μm.
Table 3 shows the details for characteristics of PCDD/Fs

in three size fractions of meal. After sieving and analysis, the mass percentage for particles < 2.5 μm, particles 2.5–10 μm and particles > 10 μm were 15.1%, 47.8% and 39.1%, respectively. The total concentrations of 2,3,7,8-substituted PCDD/Fs were 0.695, 0.074 and 0.059 ng g^{-1} in particles < 2.5 μm, particles 2.5–10 μm and particles > 10 μm. Smaller particles have higher specific surface area, thus offering more adsorption sites (Lu *et al.*, 2012). Also for MSWI fly ash, small particles usually show higher dioxin content, than large particles (Chang and Chung, 1998). For MSWI bottom ash, the peak in the PCDD/F content was found for < 210 μm (Chen *et al.*, 2006). Moreover, more PCDD/Fs was also presented in fine particles in ambient air in a suburban area (Zhang *et al.*, 2015).

As shown in Fig. 5(a), higher chlorinated congeners appear preferably in particles < 2.5 μm, which is similar with MSWI fly ash (Stanmore, 2004). In details, the fractions of OCDD and 1,2,3,4,6,7,8-HpCDF were 14.8% and 13.9% in particles < 2.5 μm, whereas 9.7% and 3.3% for them in particles > 10 μm, respectively. The I-TEQ values in particles < 2.5 μm, particles 2.5–10 μm and particles > 10 μm were 0.022, 0.041 and 0.066 ng I-TEQ g^{-1}, respectively. The contribution of PCDFs to I-TEQ value was 80.46% in particles < 2.5 μm, while only 48.34% and 47.89% in particles 2.5–10 μm and particles > 10 μm (Fig. 5(b)). The I-TEQ values were dominated by the low chlorinated ones, including TeCDD/Fs and PeCDD/Fs, and the contributions of them were 74.86%, 86.47% and 78.45% for different particles.

Dioxin Concentration in Inlet and Outlet Gas
Sampling Condition
The particle concentrations in inlet and outlet of the raw mill were 68.2 and 23.7 g Nm^{-3}, respectively. The large difference could be attributed to the possible adsorption effect by the entering raw meal. The temperature at positions A and B were 176 and 103°C, showing the depth of energy saving. Normally, the oxygen content of gas was low when

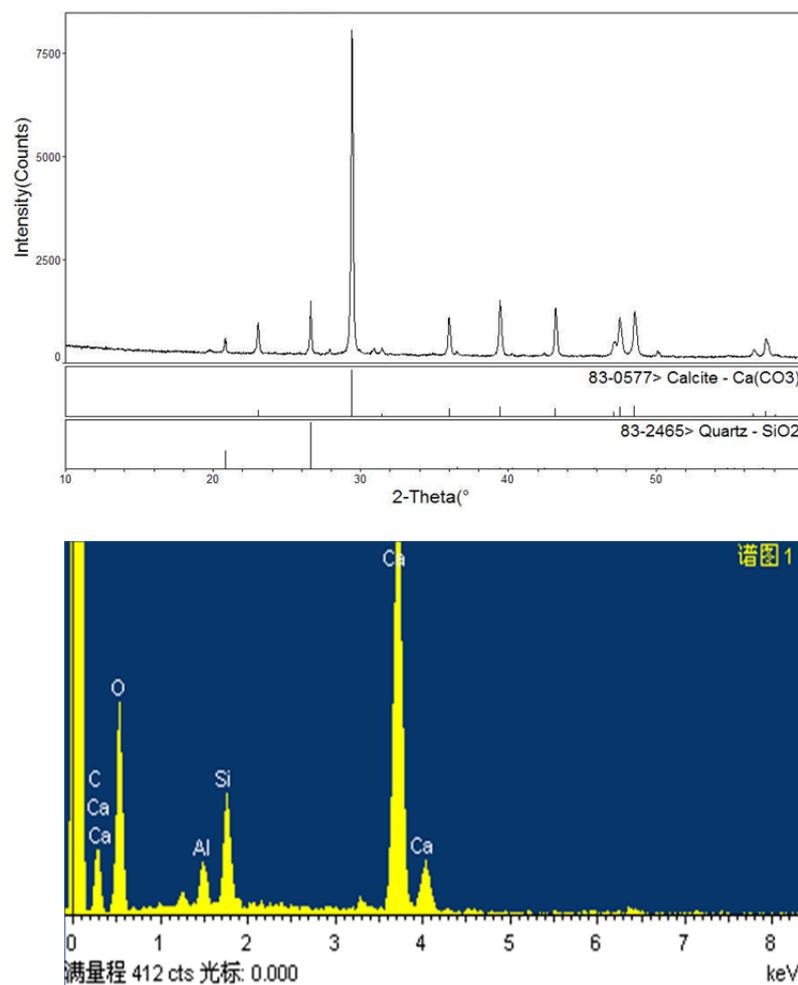**Fig. 3.** XRD and EDS analysis.

Table 1. EDS analysis (wt.%).

Element	Weight	Atom
C	16.76	25.34
O	52.44	59.52
Al	1.74	1.17
Si	4.16	2.69
Ca	24.91	11.28

it flowed out of C1 cyclone preheater, and then it flowed into the raw mill directly. So the oxygen content of flue gas at position A was 7.1%. Meanwhile, because of the leakage of air in raw mill, the value increased to 12.9% at position B.

The concentration of common gaseous pollutants at position A and B are listed in Table 4. The content of CO_2 decreased largely from 21.48 vol.% to 12.61 vol.% because of the leakages at the entrance of the raw mill, and large amount of air flowed into the kiln system. The result for CO was accordant with the value that reported by Karstensen *et al.* (2006), while the corresponding sampling positions were separately at raw mill and chimney (Karstensen *et al.*, 2006). Occasionally, CO can arise from any organic content in the raw material. Comparison between position A and B showed that injection of raw material at raw mill

will not increase the emission of CO. As for NO_x, the total concentration of it amounted to 213.0 mg m^{-3} and was less than the emission limit value (320 mg m^{-3}). The high level during the test was due to high heat input through the main flame. 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).

Dioxin Distribution at Position A and B

The average concentration of total PCDD/Fs at position A was 17.99 ± 12.3 ng Nm^{-3} (0.62 ± 0.31 ng I-TEQ Nm^{-3}), and the reason for large variation between samples could be attributed to the different amount of PCDD/Fs at solid phase (Table 5). For position A, the largest amount of PCDD/Fs reported to the solid phase and only 2.3 wt.% remained at flue gas, which was similar with the distribution of PCDD/Fs in the exhaust gases from automobiles (Karstensen *et al.*, 2006). This figure rose to 4.7 wt.%, when expressed in I-TEQ. The average concentration of total PCDD/Fs at position B was 1.90 ± 0.9 ng Nm^{-3} (0.12 ± 0.06 ng I-TEQ Nm^{-3}), with a reduction efficiency of 89.5% when compared with that at position A. The fraction of PCDD/Fs at solid phase to all the weight of PCDD/Fs was 67.1%, and decreased to 55.0% when expressed in I-TEQ (Fig. 6). Moreover, lower

Table 2. Distribution of dioxins in raw material at different positions and conditions.

| ng g^{-1}	Inlet raw material	Outlet raw material Without RDF	Outlet raw material With RDF
2,3,7,8-TCDD	0.0004	0.0004	0.0021
1,2,3,7,8-PeCDD	0.0013	0.0015	0.0027
1,2,3,4,7,8-HxCDD	0.0010	0.0012	0.0033
1,2,3,6,7,8-HxCDD	0.0006	0.0035	0.0018
1,2,3,7,8,9-HxCDD	0.0017	0.0024	0.0027
1,2,3,4,6,7,8-HpCDD	0.0321	0.0629	0.0728
OCDD	0.3689	0.5950	0.7472
2,3,7,8-TCDF	0.0048	0.0053	0.0102
1,2,3,7,8-PeCDF	0.0040	0.0090	0.0228
2,3,4,7,8-PeCDF	0.0094	0.0177	0.0299
1,2,3,4,7,8-HxCDF	0.0378	0.0862	0.1514
1,2,3,6,7,8-HxCDF	0.0249	0.0497	0.0771
2,3,4,6,7,8-HxCDF	0.0140	0.0234	0.0380
1,2,3,7,8,9-HxCDF	0.0231	0.0460	0.0601
1,2,3,4,6,7,8-HpCDF	0.3320	0.5459	0.7657
1,2,3,4,7,8,9-HpCDF	0.0491	0.0852	0.1271
OCDF	0.8947	1.4203	1.8865
ΣPCDD/Fs	1.8000	2.9557	4.0014
Σ(I-TEQ)	0.0222	0.0412	0.0663
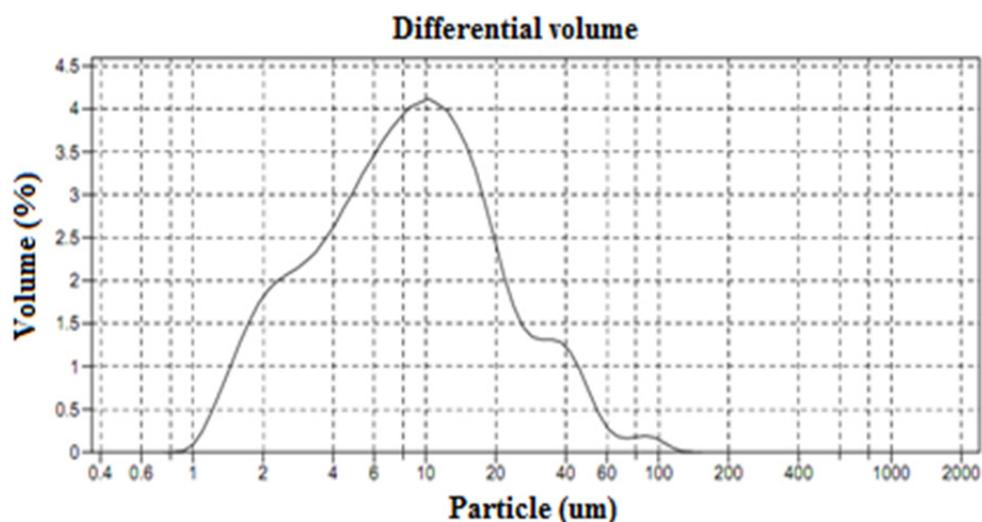
Fig. 4. Particle distribution of meal.

Table 3. Comparison of three size fractions of meal.

Property	PM < 2.5 μm	2.5 μm < PM < 10 μm	PM > 10 μm	Unit
Amount	15.1	47.8	39.1	wt.%
2,3,7,8-PCDD/Fs	695	74	59	pg g^{-1}
I-TEQ	22	41	66	pg I-TEQ g^{-1}
of which PCDF	80.5	48.3	47.9	%

chlorinated PCDD/Fs favored in gas phase, which was different with that of the MSWI flue gas reported by Chi *et al.* (2005). The difference could be attributed to the significant amount of particulate PCDD/Fs at the inlet and outlet of raw mill.

The ratio of 2,3,7,8-PCDFs to 2,3,7,8-PCDDs were 6.94 and 6.78 at position A and B, respectively. As can be seen in Fig. 7, the leading PCDD congeners were 1,2,3,4,6,7,8-HpCDD and OCDD; the dominant PCDF congener was 1,2,3,4,6,7,8-HpCDF for flue gas at position A and B, which was similar with PCDD/Fs distribution of raw material. When flue gas passed through raw mill, the fraction of 2,3,7,8-TCDF, 1,2,3,4,6,7,8-HpCDF and OCDF decreased from 8.11%, 20.95% and 14.42% to 3.84%, 15.51% and
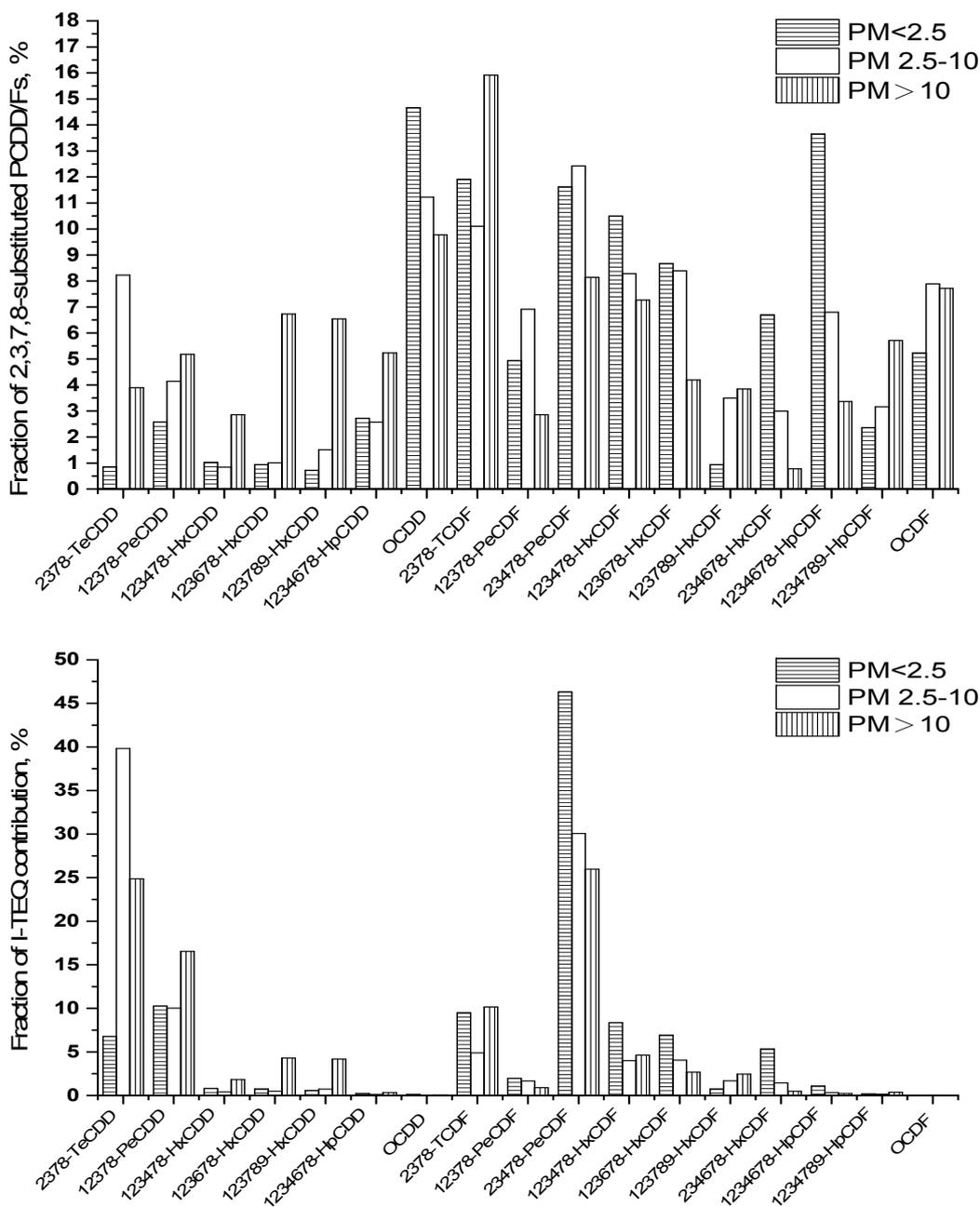
Fig. 5. Fractions of dioxin concentration and I-TEQ contribution in different particle size.

4.54%, respectively. While for lower chlorinated PCDF, most of them slightly increased by 4%.

A correlation analysis of PCDD/Fs congener distribution was conducted with the aim to identify the adsorption effect of PCDD/Fs in the flue gas by raw material. The corresponding r^2 value was 0.98 for gaseous PCDD/Fs between samples collected at position A and B, and the value for particulate PCDD/Fs was 0.99. The positive correlation indicated that physical adsorption may be the main function to reduce the concentration of PCDD/Fs existed in flue gas.

As for I-TEQ, 2,3,4,7,8-PeCDF contributed most to the total I-TEQ value at position B. However, for outlet flue gas, 2,3,7,8-TCDF made the highest contribution to the I-TEQ value. In addition, the contribution of 2,3,7,8-TCDF decreased

from 23.5% to 6.1% when flue gas passed through raw mill. Whereas, the value increased from 15.4% to 35.4% for 2,3,4,7,8-PeCDF at the same time.

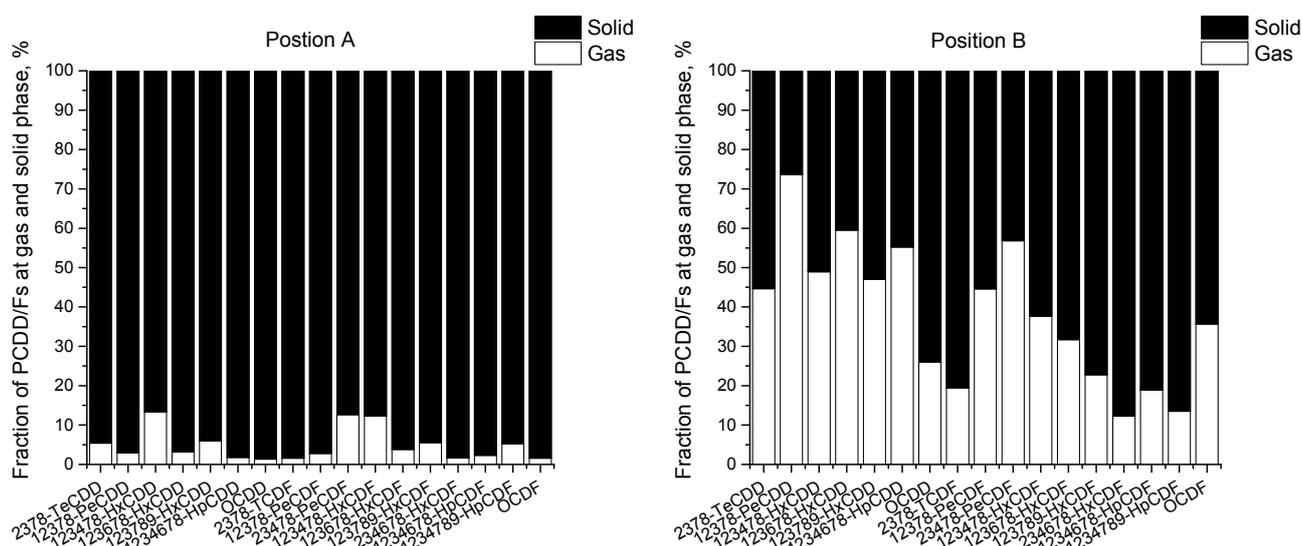### Lab Experiments to Verify the Adsorption Effects of Raw Material

A Gasmet analyser was used to estimate the evolution of the concentration of common gaseous pollutants during experiments. The raw material may also adsorb common gaseous pollutants, specifically HCl. For experiment without the adding of raw material, the average concentration of HCl was 12.7 mg m^{-3}. With the adding of 15 g raw materia, the average concentration of HCl decreased down to 1.60 mg m^{-3}. The reduction of 91.9% is attributed to the alkaline

Table 4. Gaseous compounds in inlet and outlet flue gas of raw mill during test B.

	units	inlet-Position A 10:14–10:19	outlet-Position B 11:07–11:15	National standard of flue gas GB 30485-2013 and GB4915-2013
H_2O	vol-%	0.24	0.21	-
CO_2	vol-%	21.48	12.61	-
CO	mg m^{-3}	84.31	71.6	-
SO_2	mg m^{-3}	ND.	ND.	100
NO	mg m^{-3}	268.95	199.65	-
NO_2	mg m^{-3}	8.14	13.3	320
N_2O	mg m^{-3}	1.89	ND.	-
NH_3	mg m^{-3}	ND	ND.	8
HCl	mg m^{-3}	ND.	ND.	10
HF	mg m^{-3}	0.56	1.06	1
CH_4	mg m^{-3}	0.38	0.27	-
HCN	mg m^{-3}	2.56	0.42	-
O_2	%	7.05	12.91	-

Table 5. Concentration of dioxins in the flue gases at the position A and B during the test B.

Samples	Concentration ng Nm^{-3}	Total	Average	I-TEQ ng I-TEQ Nm^{-3}	Total	Average
Position A-1	Gas 0.338 Solid 29.931	30.269	17.99	Gas 0.027 Solid 0.900	0.927	0.622
Position A-2	Gas 0.491 Solid 5.221	5.712		Gas 0.032 Solid 0.285	0.317	
Position B-1	Gas 0.950 Solid 1.815	2.765	1.896	Gas 0.081 Solid 0.099	0.18	0.12
Position B-2	Gas 0.297 Solid 0.732	1.028		Gas 0.027 Solid 0.033	0.06	

Fig. 6. Fractions of 2,3,7,8-substituted PCDD/Fs at position A and B.

nature of the raw material. The national emission standard of HCl in China for cement kilns was set up at 10 mg m^{-3}, much lower than the MSW incineration emission standard (MEP, 2014). Still, it must be granted that part of the HCl captured by the meal will be released again when the temperature increased.

The experiment without the adding of raw material was conducted to evaluate the amount and distribution of PCDD/Fs resulting from RDF combustion, whereas the experiment with the adding of raw material was to verify the adsorption effect of PCDD/Fs on raw meal. The concentration of 2,3,7,8-substituted PCDD/Fs was originally 3.63 ng g^{-1} RDF (or 0.23 ng I-TEQ g^{-1}); then their average concentration decreased to 0.55 ng g^{-1} RDF (or 0.07 ng I-TEQ g^{-1}) with
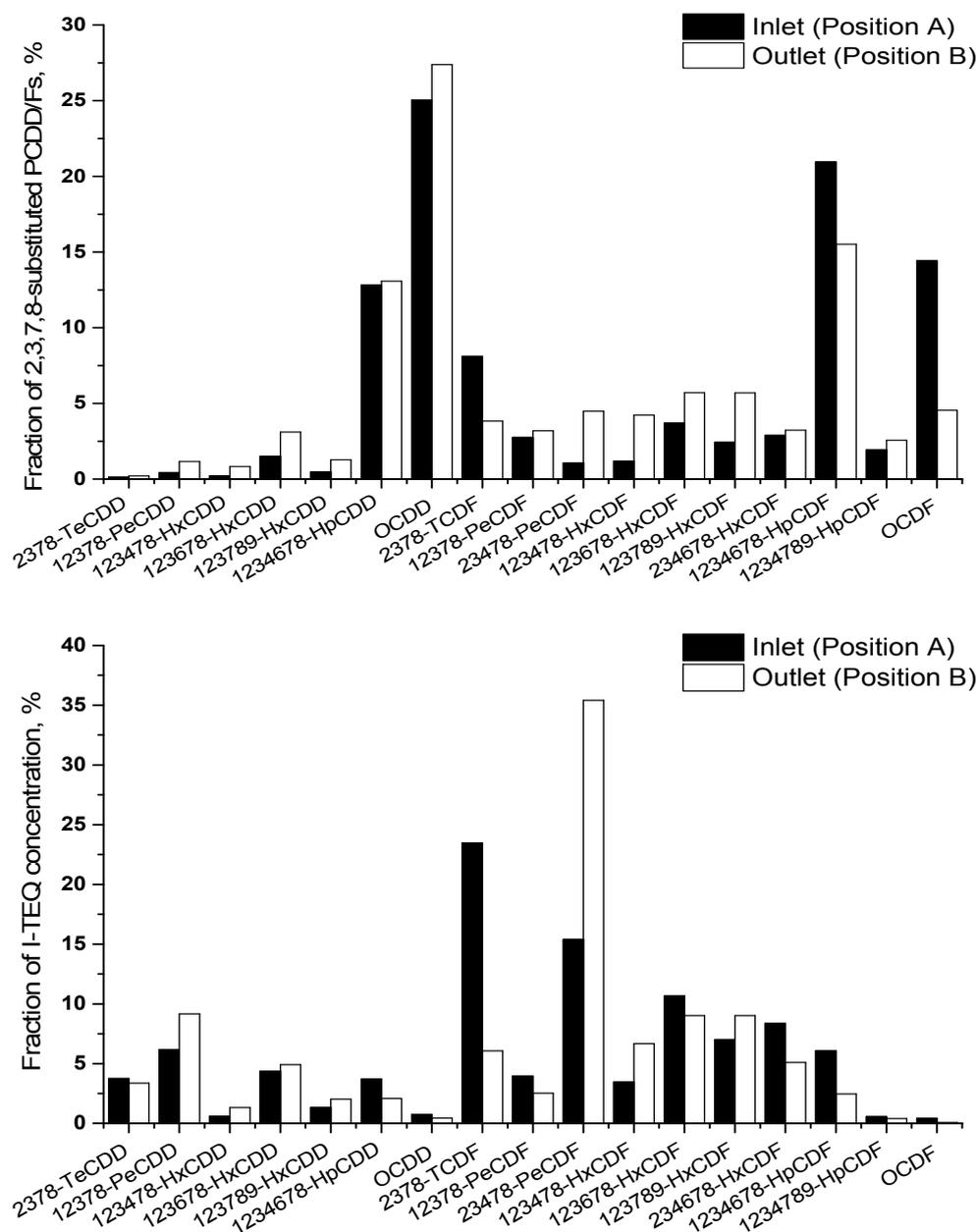
Fig. 7. Fractions of dioxin concentration and I-TEQ contribution in flue gas at position A and B.

the adding of raw material, showing strong adsorption on PCDD/Fs.

As shown in Fig. 8, during experiment C the leading PCDD congeners were 1,2,3,4,6,7,8-HpCDD and OCDD and the dominant PCDF congener was 1,2,3,4,6,7,8-HpCDF. the distribution of PCDD/Fs for experiment D was similar.

The ratio of 2,3,7,8-PCDFs to 2,3,7,8-PCDDs for experiment C and D were 5.8 and 3.7, indicating a preferred formation and also a better reduction of PCDFs over PCDDs (Huang and Buekens, 1995). Considered in more detail, the reduction efficiency ranged from 40.3 to 93.2% for each congener, except for 2,3,7,8-TCDF, which increased by 24.3%. Higher chlorinated congeners seem to be better adsorbed by meal, and thus the reduction efficiencies slightly increased with the chlorinated level increasing, which is

generally different from the desorption effect of active carbon (Atkinson *et al.*, 2015).

CONCLUSIONS

The adsorption effect of incoming raw meal on dioxins separation was studied, both in a typical dry cement kiln and in a laboratory reactor. Several interesting results were obtained:

1. Cement kiln. Without RDF co-incineration, the concentration of PCDD/Fs in the meal flowing out of the raw mill is 0.041 ng I-TEQ g^{-1} and about one time higher than that of meal which flows into raw mill; during RDF co-incineration, the concentration of PCDD/Fs in outflowing meal increases slightly, to 0.067 ng I-TEQ g^{-1};
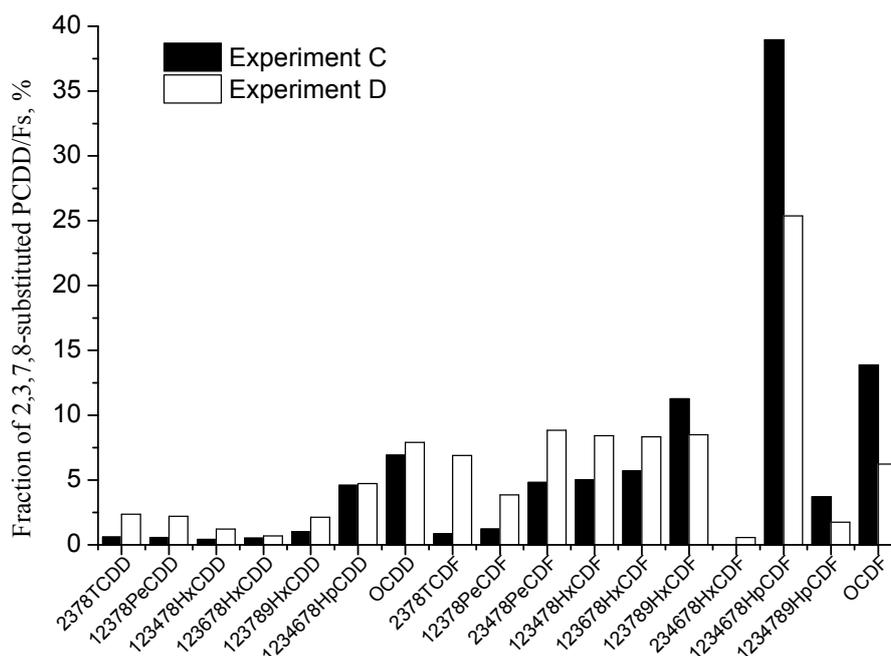
Fig. 8. Fractions of dioxin concentration before and after the adding of raw meal.

2. The level of PCDD/Fs in outflowing meal escalates for smaller particle size. The concentration for particle size < 2.5 μm amounts to 0.087 ng I-TEQ g^{-1} and lower chlorinated (tetra and penta-) congeners contribute most to its I-TEQ value;

3. Raw mill. The concentration of 2,3,7,8-PCDD/Fs in the gas at the inlet of the raw mill is 18 ng Nm^{-3} (0.62 ng I-TEQ Nm^{-3}) with a gas phase fraction of 2.3%. In the outlet gas, the 2,3,7,8-PCDD/Fs concentration reduces to 1.90 ng Nm^{-3} (0.12 ng I-TEQ Nm^{-3}), while their fraction in the gas phase rise to 32.9%. These results reveal that the incoming meal effectively adsorbs 2,3,7,8-PCDD/Fs with an efficiency up to 89.5%;

4. Laboratory test. In a laboratory test, meal could adsorb 2,3,7,8-PCDD/Fs from RDF incineration flue gas, with an efficiency up to 84.8% in wt. units and 71.0% in I-TEQ units.

These results revealed that meal significantly reduces the emission of dioxin and that this technique of cleaning flue gas from cement kilns by adsorption on meal is really practical and feasible.

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.

Atkinson, J.D., Hung, P.C., Zhang, Z., Chang, M.B., Yan, Z. and Rood, M.J. (2015). Adsorption and destruction of PCDD/Fs using surface-functionalised activated carbons. *Chemosphere* 118: 136–142.

Chang, M. and Chung, Y. (1998). Dioxin contents in fly ashes of MSW incineration in Taiwan. *Chemosphere* 36: 1959–1968.

Chen, C. (2004). The emission inventory of PCDD/PCDF in Taiwan. *Chemosphere* 54: 1413–1420.

Chen, C., Lin, C., Wang, L. and Chang-Chien, G. (2006). The size distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the bottom ash of municipal solid waste incinerators. *Chemosphere* 65: 514–520.

Chen, T., Guo, Y., Li, X., Lu, S. and Yan, J. (2014). Emissions behavior and distribution of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) from cement kilns in China. *Environ. Sci. Pollut. Res.* 21: 4245–4253.

Chi, K.H., Chang, M.B., Chang-Chien, G.P. and Lin, C. (2005). Characteristics of PCDD/F congener distributions in gas/particulate phases and emissions from two municipal solid waste incinerators in Taiwan. *Sci. Total Environ.* 347: 148–162.

Chi, K.H., Chang, S.H., Huang, C.H., Huang, H.C. and Chang, M.B. (2006). Partitioning and removal of dioxin-like congeners in flue gases treated with activated carbon adsorption. *Chemosphere* 64: 1489–1498.

Choy, K.K.H., Ko, D.C.K., Cheung, W.H., Fung, J.S.C., Hui, D.C.W., Porter, J.F. and Mckay, G. (2004). Municipal solid waste utilization for integrated cement processing with waste minimization: A pilot scale proposal. *Process Saf. Environ. Prot.* 82: 200–207.

CICounsulting (2014). Percentage of Co-disposal MSW in Cement Kiln is only 1.2%, http://www.ocn.com.cn/chanj ing/201412/shuini885091021.shtml (in Chinese).

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: 585–592.

Cong, J., Yan, D., Li, L., Cui, J., Jiang, X., Yu, H. and Wang, Q. (2015). Volatilization of heavy metals (As, Pb, Cd) during co-disposal in cement kilns. *Environ. Eng. Sci.* 32:425–435.

Gálvez, A., Conesa, J.A., Martín-Gullón, I. and Font, R. (2007). Interaction between pollutants produced in sewage sludge combustion and cement raw material. *Chemosphere* 69: 387–394.

Huang, H. and Buekens, A. (1995). On the mechanisms of dioxin formation in combustion processes. *Chemosphere* 31: 4099–4117.

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., Kinh, N.K., Thang, L.B., Viet, P.H., Tuan, N.D., Toi, D.T., Hung, N.H., Quan, T.M., Hanh, L.D. and Thang, D.H. (2006). Environmentally sound destruction of obsolete pesticides in developing countries using cement kilns. *Environ. Sci. Policy* 9:577–586.

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

Li, Y., Wang, H., Zhang, J., Wang, J. and Zhang, R. (2012). Research on dioxins suppression mechanisms during MSW co-disposal 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.

Liu, W., Zheng, M., Zhang, B., Qian, Y., Ma, X. and Liu, W. (2005). Inhibition of PCDD/Fs formation from dioxin precursors by calcium oxide. *Chemosphere* 60:785–790.

Lu, S.Y., Du, Y., Yan, J.H., Li, X.D., Ni, M.J. and Cen, K.F. (2012). Dioxins and their fingerprint in size-classified fly ash fractions from municipal solid waste incinerators in China—Mechanical grate and fluidized bed units. *J. Air Waste Manage. Assoc.* 6: 717–724.

MEP (2014). Standard for Pollution Control on the Municipal Solid Waste Incineration (GB 18485-2014).

Rivera-Austrui, J., Martinez, K., Marco-Almagro, L., Abalos, M. and Abad, E. (2014). Long-term sampling of dioxin-like substances from a clinker kiln stack using alternative fuels. *Sci. Total Environ.* 485–486:528–533.

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

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 Loo, W. (2008). Dioxin/furan formation and release in the cement industry. *Environ. Toxicol. Pharmacol.* 25: 128–130.

van Oss, H.G. and Padovani, A.C. (2003). Cement manufacture and the environment Part II: Environmental challenges and opportunities. *J. Ind. Ecol.* 7: 93–126.

Wang, Y., Wang, L., Hsieh, L., Li, H., Jiang, H., Lin, Y. and Tsai, C. (2012). Effect of temperature and CaO addition on the removal of polychlorinated dibenzo-p-dioxins and dibenzofurans in fly ash from a medical waste incinerator. *Aerosol Air Qual. Res.* 12: 191–199.

Wu, H., Lu, S., Li, X., Jiang, X., Yan, J., Zhou, M. and Wang, H. (2012). Inhibition of PCDD/F by adding sulphur compounds to the feed of a hazardous waste incinerator. *Chemosphere* 86: 361–367.

Yamada, M., Waki, I., Sakairi, M., Sakamoto, M. and Imai, T. (2004). Real-time-monitored decrease of trichlorophenol as a dioxin surrogate in flue gas using iron oxide catalyst. *Chemosphere* 54: 1475–1480.

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, M., Li, X., Yang, J., Chen, T., Lu, S., Buekens, A.G., Olie, K. and Yan, J. (2012). Sludge as dioxins suppressant in hospital waste incineration. *Waste Manage.* 32: 1453–1458.

Zabaniotou, A. and Theofilou, C. (2008). Green energy at cement kiln in Cyprus—Use of sewage sludge as a conventional fuel substitute. *Renewable Sustainable Energy Rev.* 12: 531–541.

Zemba, S., Ames, M., Green, L., Botelho, M.J., Gossman, D., Linkov, I., Palma-Oliveira, J. (2011). Emissions of metals and polychlorinated dibenzo(p)dioxins and furans (PCDD/Fs) from Portland cement manufacturing plants: Inter-kiln variability and dependence on fuel-types. *Sci. Total Environ.* 409: 4198–4205.

Zhang, X., Zhu, Q., Dong, S., Zhang, H., Wang, X., Wang, M., Gao, L. and Zheng, M. (2015). Particle size distribution of PCDD/Fs and PBDD/Fs in ambient air in a suburban area in Beijing, China. *Aerosol Air Qual. Res.* 15: 1933–1943.