

# A novel method to enhance polychlorinated dibenzo-*p*-dioxins and dibenzofurans removal by adding bio-solution in EAF dust treatment plant

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## Abstract

In order to understand the effect of different amounts of powder-activated carbon (PAC) injection and bio-solution (NOE-7F) addition on the removal efficiencies of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in a fly ash treatment plant with Waelz rotary kiln process, the PCDD/F concentrations in the stack flue gasses were measured and discussed.

In the amount of 20, 40 and 50 kg/h PAC injection, the removal efficiencies of PCDD/Fs in the stack flue gas were 86, 96 and 97%, respectively. While adding more amounts of PAC did enhance the removal efficiencies, the reduction fractions of low chlorinated PCDD/F congeners were much higher than those of highly chlorinated PCDD/F congeners. Particularly, a lower amount of PAC injection (20 kg/h), not only cannot remove highly chlorinated PCDD/Fs, but also the carbon surface of the PAC can act as a precursor for the formation promotion of highly chlorinated PCDD/F congeners.

The addition of NOE-7F in the raw materials had the dechlorination effect on the PCDD/F removal and mainly inhibited highly chlorinated PCDD/F formation. The combination of both PAC injection and NOE-7F addition has a high potential for practical application.

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## 1. Introduction

In 1977, the polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) were discovered in both flue gas and fly ash of municipal solid waste incinerators [1]. The PCDD/Fs exhibit a hydrophobic nature and resistance towards metabolism. Hence, these chemicals persist in the environment

and bioaccumulate in fatty tissues of animals and humans [2]. In numerous countries, the public is seriously concerned about the PCDD/F problems from incineration and industrial thermal processes [3]. For example, the electric arc furnace (EAF) plays an important role in industrial manufacturing via recycling of waste iron products and emits a great amount of PCDD/Fs to the atmosphere.

In Taiwan, the EAF process produced 170,000 metric tonnes of dust per year [4]. Due to the high contents of both heavy metals and PCDD/Fs, the EAF dust was categorized as hazardous wastes. The Waelz rotary kiln process (abbreviation as Waelz process) is an appropriate method for treating EAF dust and recovering zinc oxide as well. However, the zinc recovery

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from EAF dust by using the Waelz process had been proven as a highly potential source of PCDD/F emission in both France and Germany [5,6].

There are three mechanisms for PCDD/F emission from incinerators: (1) high-temperature gas phase formation (300–600 °C) [7]. (2) PCDD/Fs are formed from precursors such as chlorophenols, polychlorinated diphenyl ethers and chlorobenzenes [8,9], for example, the chlorophenols was a good surrogate of toxicity equivalence (TEQ) related PCDD/Fs in different incineration processes [10]. (3) PCDD/Fs are produced by de novo synthesis that is in the low-temperature post-combustion zone (200–400 °C) through residue carbon or metal catalyst in the fly ash reaction [7,11].

In order to reduce the PCDD/F emissions from stack flue gas, some technological methods have been used. In a hazardous waste incinerator, the removal rate of 57% on total PCDD/F and 58% on the international toxicity equivalence (I-TEQ) basis by using the injection of powder-activated carbon (PAC) was recorded [12]. The PAC injection was followed by various types of air pollution control devices (APCDs) to enhance the removal of PCDD/Fs, e.g., municipal waste incinerators, and approach the range of 92–99% [13–16]. However, the PAC injection only has adsorption function on PCDD/Fs not to decompose them. In addition, in order to conform to the PCDD/F emission standard, the amount of PAC injection was usually overdosed and therefore was a costly treatment process.

Other research adopted chemical inhibitors to control PCDD/F emissions. For example, triethanolamine and monoethanolamine were mixed with fly ash in the sintering process, respectively, and the fraction of PCDD/F inhibition was increased from 17 to 90% [17]. The reduction fractions of total PCDD/Fs were 64, 75 and 90% with 0.1, 0.5 and 1.0% urea added, respectively. The urea inhibitor could affect PCDD/F formation at a stage when the chlorophenols are not yet to be formed [18]. The effect of urea for the reduction of PCDD/F concentration by a maximum of 74% and it was observed to be greatest with greatest number of chlorine atoms [19]. In municipal waste incineration, the urea species could be reacted with catalysts (e.g., Cu). Moreover, the urea can be rapidly decomposed under appropriate flue gas conditions, indicating that the decomposition product of urea can be also be responsible for the reduction of PCDD/F production during incineration [20].

The sulphur and nitrogen compounds, such as  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  were added in the fuel as an inhibitor for the PCDD/F reduction in the flue gas. The  $(\text{NH}_4)_2\text{SO}_4$  present at 3% of the fuel, could reduce the PCDD/F emissions by 90% [21]. Different amount of elemental sulphur was applied to the fly ash in waste incineration processes and the PCDD/F emission was reduced by 54% [22]. Sulphur showed a very strong inhibitor of PCDD formation; it could convert into  $\text{SO}_2$  and reduces  $\text{Cl}_2$  to HCl [23].

Polycyclic aromatic hydrocarbons (PAHs) are the major precursors of PCDD/F formation. In a previous study, a bio-solution (NOE-7F) was used to produce emulsified diesel to reduce emissions from diesel engines and to save energy. The energy saving, reduction of particulate matter and total-PAH emissions by using

E13 (13 wt% NOE-7F + 83 wt% premium diesel fuel), E16 and E19, respectively, were 3.38, 37, 34.9%; 5.87, 38.6, 49.3%; 4.75, 31.1 and 47.3%, compared with premium diesel fuel. The NOE-7F had a catalytic effect which elevated the combustion efficiency and decreased pollutant emissions during the combustion process [24].

In this study, different amounts of PAC injection were applied and the PCDD/F concentrations in the stack flue gasses were measured, respectively, to investigate the removal efficiencies of PCDD/Fs under each situation. In addition, the NOE-7F combined with a certain amount of PAC injection was applied and the effect of PCDD/F inhibition by using NOE-7F was reported. In addition, the difference of removal mechanisms for PCDD/Fs by using PAC and NOE-7F, respectively, were proposed and discussed.

## 2. Experimental

### 2.1. EAF dust treatment plant

In this study, the EAF dust treatment plant was established to recover zinc oxide via the Waelz process. The EAF dust treatment capacity was approximately 700,00 metric tonnes per year and the input materials included EAF dust (9.5 metric tonnes/h), coke (1.71 metric tonnes/h), and sand (1.71 metric tonnes/h) [25]. The ignition is by a burner that is fed with diesel oil and consecutive ambient air. The Waelz process is conducted in a high-temperature rotary-kiln that is 40 m long and has a 3.6 m outer diameter. It is equipped with various air pollution control devices, such as a dust settling chamber (DSC), a venturi tower, cyclones, and bag filters (Fig. 1). The height of stack was 35 m and the flow rate of flue gas was approximately 52,200  $\text{N m}^3/\text{h}$ .

### 2.2. The properties of powder-activated carbon

The specifications of powder-activated carbon (PAC) are as follows. The bulk density was 0.55  $\text{g}/\text{cm}^3$ , the specific surface was 300  $\text{m}^2/\text{g}$ , the fraction of grain size smaller than 32  $\mu\text{m}$  was 63%, the fraction of grain size between 32 and 63  $\mu\text{m}$  was 30%, the fraction of grain size larger than 63  $\mu\text{m}$  was 7%, the moisture was 0.5 wt%, the ash was 10 wt%, the volatility was 3.0 wt%, and the fixed carbon was 68.5 wt%. The PAC injector was located between the cyclone and bag filters.

### 2.3. The addition of bio-solution (NOE-7F)

The bio-solution was named as natural organic enzyme-7F (NOE-7F). The process of producing NOE-7F is as follows. First, molasses, rice wine, acetic acid, water and an anti-oxidant enzyme were mixed together. Second, the mixture was domesticated by adding both lactic acid bacteria and yeast. Finally, the mixture was put through a separation and purification process. Due to the EAF fly ashes were collected from different companies, the pellet process was designed to make the raw materials size uniformly. In this study, 180 L of water and 20 L of NOE-7F were added in one metric ton of the raw materials

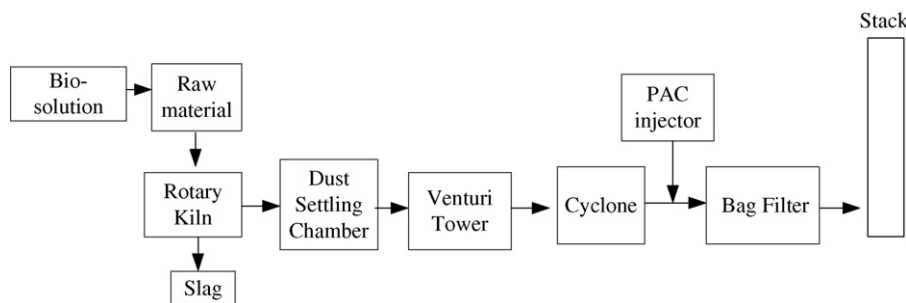


Fig. 1. The flowchart of EAF dust treatment plant.

and well mixed with the raw material during the pellet process. In this experimental condition, the amount of PAC injection was 40 kg/h.

#### 2.4. Sampling

A total of 13 samples were collected from the flue gas in the EAF dust treatment plant in applying different amounts of PAC injection and NOE-7F, respectively. Each stack gas sampling lasted for 2–3 h. The sampling procedures followed those of the US EPA Modified Method 23 [26]. Three samples were collected during the period without applying PAC or NOE-7F. In the amount of 20, 40 and 50 kg/h of PAC injection, the numbers of sampling and analyses were all two. Four samples were collected and analyzed during the period while applying both PAC (40 kg/h) and NOE-7F (2%).

#### 2.5. Analysis

Prior to sampling, XAD-2 resin was spiked with PCDD/F surrogate standards prelabeled with isotopes. The analyses of stack flue gas samples were performed according to the US EPA Modified Method 23 [26]. Essentially, samples were extracted with toluene for 24 h and then followed by a series of sample cleanup procedures. The extracts were transferred to a vial, and finally further concentrated by a N<sub>2</sub> stream.

Two high-resolution gas chromatographs/high-resolution mass spectrometers (HRGC/HRMS) were used for PCDD/F analysis. The HRGC (Hewlett-Packard 6970 Series gas, CA) was equipped with a DB-5 fused silica capillary column ( $L=60$  m,  $id=0.25$  mm, film thickness =  $0.25$   $\mu$ m) (J&W Scientific, CA) with a splitless injection, while the HRMS (Micromass Autospec Ultima, Manchester, UK) had a positive electron

Table 1  
PCDD/F concentrations in the stack flue gases without injecting the powder-activated carbon (PAC) or bio-solution (NOE-7F)

PCDD/Fs	Sample A (ng/N m <sup>3</sup> )	Sample B (ng/N m <sup>3</sup> )	Sample C (ng/N m <sup>3</sup> )	Mean (ng/N m <sup>3</sup> )	R.S.D. (%)
2,3,7,8-TeCDD	20.3	1.98	1.51	7.92	135
1,2,3,7,8-PeCDD	92.1	9.52	7.32	36.3	133
1,2,3,4,7,8-HxCDD	86.5	11.7	10.7	36.3	120
1,2,3,6,7,8-HxCDD	152	16.1	16.7	61.6	127
1,2,3,7,8,9-HxCDD	153	15.9	16.7	61.8	128
1,2,3,4,6,7,8-HpCDD	215	50.0	75.8	114	78
OCDD	239	63.5	145	149	59
Total PCDDs	957	169	274	467	92
2,3,7,8-TeCDF	159	42.0	33.5	78.2	90
1,2,3,7,8-PeCDF	274	86.7	68.7	143	79
2,3,4,7,8-PeCDF	213	97.0	72.4	128	59
1,2,3,4,7,8-HxCDF	305	136	86.0	176	65
1,2,3,6,7,8-HxCDF	284	157	102	181	52
1,2,3,7,8,9-HxCDF	96.0	30.3	23.7	50.0	80
2,3,4,6,7,8-HxCDF	244	103	77.0	141	64
1,2,3,4,6,7,8-HpCDF	449	295	240	328	33
1,2,3,4,7,8,9-HpCDF	92.4	34.4	59.0	61.9	47
OCDF	184	50.5	137	124	55
Total PCDFs	2300	1031	900	1410	55
Total PCDD/Fs	3257	1200	1173	1877	64
PCDFs/PCDDs ratio	2.40	6.10	3.28	3.02	–
Total PCDDs (ng I-TEQ/N m <sup>3</sup> )	108	11.7	10.5	43.3	129
Total PCDFs (ng I-TEQ/N m <sup>3</sup> )	235	103	75.0	138	62
Total PCDD/Fs (ng I-TEQ/N m <sup>3</sup> )	342	115	85.5	181	78
PCDFs/PCDDs I-TEQ ratio	2.18	8.80	7.14	3.19	–

Table 2  
The PCDD/F concentrations in the stack flue gases after different amount of PAC injection

PAC injection	20 kg/h		40 kg/h		50 kg/h	
	A-20 (ng/N m <sup>3</sup> )	B-20 (ng/N m <sup>3</sup> )	A-40 (ng/N m <sup>3</sup> )	B-40 (ng/N m <sup>3</sup> )	A-50 (ng/N m <sup>3</sup> )	B-50 (ng/N m <sup>3</sup> )
2,3,7,8-TeCDD	0.338	0.390	0.103	0.203	0.0641	0.0990
1,2,3,7,8-PeCDD	2.78	3.30	0.812	1.20	0.493	0.869
1,2,3,4,7,8-HxCDD	3.82	4.43	1.20	1.08	0.703	0.783
1,2,3,6,7,8-HxCDD	11.0	12.9	3.41	2.19	1.83	1.59
1,2,3,7,8,9-HxCDD	8.38	9.69	2.64	1.95	1.67	1.41
1,2,3,4,6,7,8-HpCDD	104	121	38.5	9.44	25.4	6.84
OCDD	248	263	114	104	64.4	70.9
Total PCDDs	378	414	160	120	94.6	82.5
2,3,7,8-TeCDF	4.35	5.11	1.59	3.52	1.00	2.55
1,2,3,7,8-PeCDF	10.5	12.4	3.41	4.49	2.02	3.25
2,3,4,7,8-PeCDF	14.4	17.5	4.94	5.46	2.63	3.95
1,2,3,4,7,8-HxCDF	21.9	25.3	6.71	6.95	3.95	5.04
1,2,3,6,7,8-HxCDF	24.1	28.4	7.48	6.84	4.42	4.96
1,2,3,7,8,9-HxCDF	24.9	31.3	8.18	7.45	4.81	3.55
2,3,4,6,7,8-HxCDF	9.42	11.7	3.02	5.78	1.78	4.19
1,2,3,4,6,7,8-HpCDF	100	123	34.7	16.7	23.6	12.1
1,2,3,4,7,8,9-HpCDF	27.3	33.8	10.3	8.63	7.59	1.83
OCDF	174	189	80.4	69.4	67.2	79.9
Total PCDFs	411	478	161	135	119	121
Total PCDD/Fs	790	892	321	255	214	204
PCDFs/PCDDs ratio	1.08	1.15	1.00	1.13	1.26	1.46
Total PCDDs (ng I-TEQ/N m <sup>3</sup> )	5.34	6.21	1.73	1.52	1.05	1.05
Total PCDFs (ng I-TEQ/N m <sup>3</sup> )	17.7	21.3	5.87	6.33	3.39	4.39
Total PCDD/Fs (ng I-TEQ/N m <sup>3</sup> )	23.0	27.5	7.60	7.85	4.44	5.43
PCDFs/PCDDs I-TEQ ratio	3.31	6.43	3.39	4.16	3.23	4.18

impact (EI+) source. The analyzer mode of the selected ion monitoring was used with the resolving power at 10,000. The electron energy and source temperature were specified at 35 eV and 250 °C, respectively. The oven temperature program was set according to the following: initially at 150 °C (held for 1 min), then increased by 30 °C/min to 220 °C (held for 12 min), and finally increased by 1.5 °C/min to 310 °C (held for 20 min). Helium was used as the carrier gas.

### 3. Results and discussion

#### 3.1. PCDD/F concentrations in the stack flue gases without applying PAC or NOE-7F

Without applying PAC or NOE-7F, the mean concentration of total PCDD/Fs and mean total-PCDD/F I-TEQ in the stack flue gases were 1877 ng/N m<sup>3</sup> ( $n=3$ , R.S.D. = 64%) and 181 ng I-TEQ/N m<sup>3</sup> ( $n=3$ , R.S.D. = 78%), respectively (Table 1). Their PCDFs/PCDDs ratio and PCDFs/PCDDs I-TEQ ratio were 3.02 and 3.19, respectively, which indicated the significance of the de novo mechanism for the PCDD/F formation [27]. Fig. 2a shows that the major PCDD/F congeners in the stack flue gas were 1,2,3,4,6,7,8-HpCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,4,7,8-HxCDF and OCDD. However, the mean total-PCDD/F I-TEQ concentration in the stack flue gases was greater than 100 ng I-TEQ/m<sup>3</sup> in France [5]. Additionally, Germany has set strict standards for stack flue gas from EAF dust treatment plants (zinc recov-

ery) below 0.1 ng I-TEQ/N m<sup>3</sup> to control PCDD/F emissions [5].

#### 3.2. PCDD/F concentrations in the stack flue gases with the PAC injection

When the amount of PAC injection was 20 kg/h, the mean concentration of total PCDD/Fs and mean total-PCDD/Fs I-TEQ were reduced to 841 ng/N m<sup>3</sup> ( $n=2$ , RPD = 8.60%) and 25.3 ng I-TEQ/N m<sup>3</sup> ( $n=2$ , RPD = 12.7%), respectively (Table 2). This means that by the injection of PAC in the amount of 20 kg/h, the mean reduction fraction of total PCDD/Fs and total-PCDD/Fs I-TEQ were 55.2 and 86.1%, respectively (Table 3). Their PCDFs/PCDDs ratio decreased to 1.12 which indicated a greater amount of PCDF mass was absorbed by the PAC than that of PCDDs. Other research also reported that the removal efficiencies of PCDFs were higher than PCDDs by PAC injection [13,15]. Fig. 2b shows that when the amount of PAC injection was 20 kg/h, the major PCDD/F congeners in the stack flue gas were OCDD, OCDF, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF. When the reduction fractions of seventeen PCDD/F congeners were compared, the reduction fractions of low chlorinated congeners were much higher than those of highly chlorinated congeners. For example, the reduction fractions of 2,3,7,8-TeCDD and 2,3,7,8-TeCDF were 95.4 and 94.0%, respectively, those of 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF were 0.881 and 66.0%, respectively, but the OCDD and

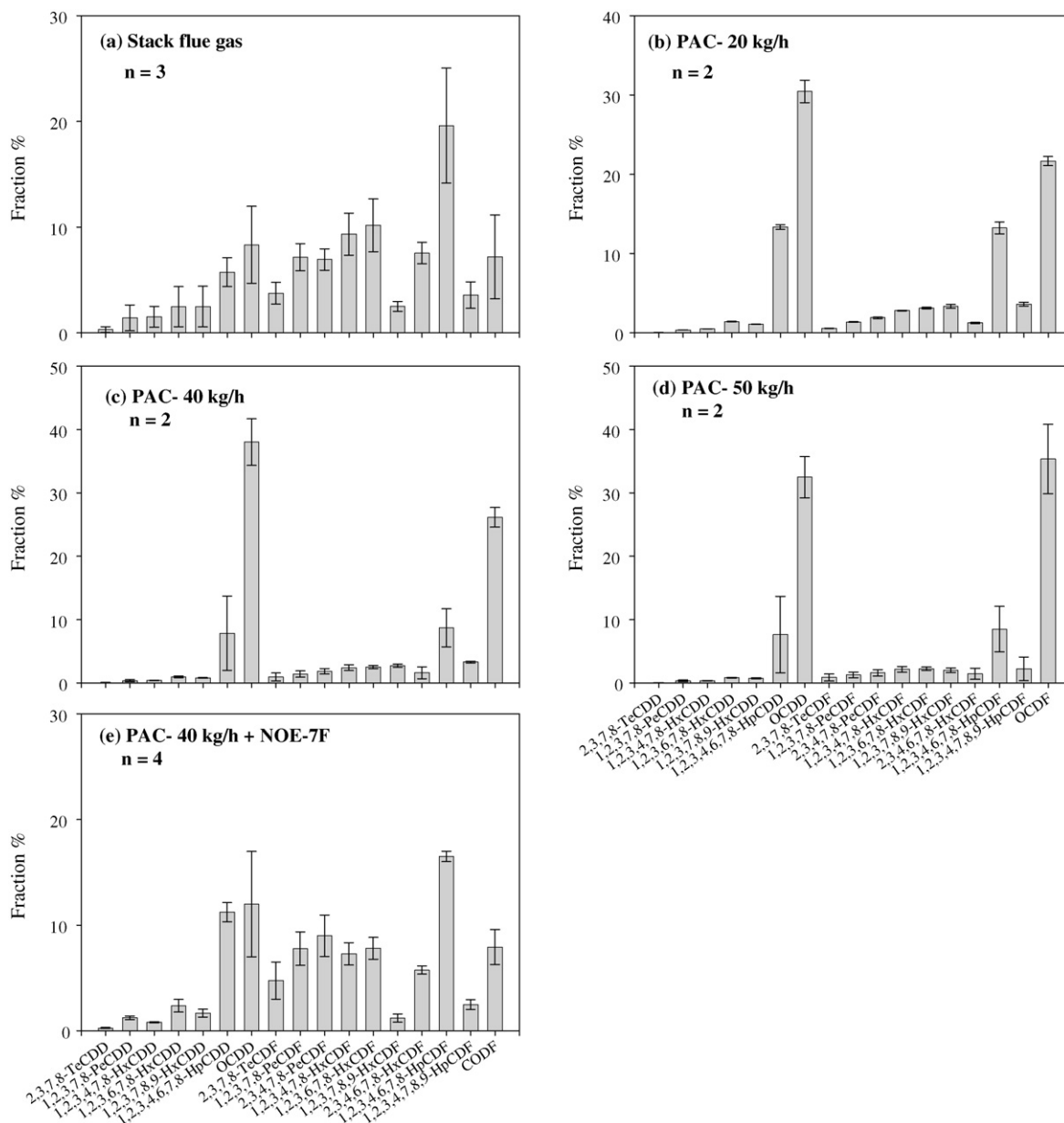


Fig. 2. Congener profiles of 17 2,3,7,8-PCDD/Fs. (a) Stack flue gas without PAC or NOE-7F; (b) with 20 kg/h of PAC injection; (c) with 40 kg/h of PAC injection; (d) with 50 kg/h of PAC injection; (e) with both 40 kg/h of PAC injection and NOE-7F addition.

OCDF were  $-71.2$  and  $-46.4\%$ , respectively (Fig. 3a). The above results also indicated that a lower amount of PAC injection in the front of the bag filter not only cannot remove highly chlorinated PCDD/Fs like OCDD or OCDF, but also the carbon surface of PAC can act as a precursor for the formation of highly chlorinated PCDD/F congeners.

When the PAC injection was 40 kg/h, in the stack flue gas, the concentrations of total PCDD/Fs and total-PCDD/Fs I-TEQ were reduced to  $288 \text{ ng/N m}^3$  ( $n=2$ , RPD = 17.2%) and  $7.73 \text{ ng I-TEQ/N m}^3$  ( $n=2$ , RPD = 19.8%), respectively (Table 2). This means that by the injection of PAC in the amount of 40 kg/h, the mean reduction fraction of total PCDD/Fs and total-PCDD/Fs I-TEQ were 84.6 and 95.7%, respectively (Table 3). Their PCDFs/PCDDs ratio decreased to 1.07. Fig. 2c shows the major PCDD/F congeners were OCDD, OCDF, 1,2,3,4,6,7,8-

HpCDD and 1,2,3,4,6,7,8-HpCDF. When the reduction fractions of seventeen PCDD/F congeners were compared, the reduction fractions of low chlorinated congeners were also much higher than those of highly chlorinated congeners. For example, the reduction fractions of 2,3,7,8-TeCDD and 2,3,7,8-TeCDF were 98.1 and 96.7%, respectively, those of 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF were 78.9 and 92.2%, respectively, but those of OCDD and OCDF were only 26.9 and 39.6%, respectively (Fig. 3b).

When the amount of PAC injection was increased to 50 kg/h, the concentrations of total PCDD/Fs and total-PCDD/F I-TEQ was decreased to  $209 \text{ ng/N m}^3$  ( $n=2$ , RPD = 3.3%) and  $4.94 \text{ ng I-TEQ/N m}^3$  ( $n=2$ , RPD = 14.3%), respectively (Table 2). This means that by the injection of PAC and in the amount of 50 kg/h, the mean reduction fractions of total PCDD/Fs and total-



Table 3  
Reduction fraction (%) of PCDD/F emissions in the stack flue gas with PAC or/and NOE-7F

PCDD/Fs <sup>a</sup>	PAC injection			NOE-7F	PAC (40 kg/h) + NOE-7F
	20 kg/h	40 kg/h	50 kg/h		
2,3,7,8-TeCDD	95.4	98.1	99.0	63.7	99.3
1,2,3,7,8-PeCDD	91.6	97.2	98.1	72.6	99.2
1,2,3,4,7,8-HxCDD	88.6	96.9	98.0	84.4	99.5
1,2,3,6,7,8-HxCDD	80.6	95.5	97.2	82.2	99.2
1,2,3,7,8,9-HxCDD	85.4	96.3	97.5	84.7	99.4
1,2,3,4,6,7,8-HpCDD	0.881	78.9	85.8	89.6	97.8
OCDD	-71.2	26.9	54.6	97.4	98.1
Total PCDDs	15.1	69.9	81.0	95.2	98.6
2,3,7,8-TeCDF	94.0	96.7	97.7	61.8	98.8
1,2,3,7,8-PeCDF	92.0	97.2	98.2	58.4	98.8
2,3,4,7,8-PeCDF	87.5	95.9	97.4	63.5	98.5
1,2,3,4,7,8-HxCDF	86.6	96.1	97.4	77.3	99.1
1,2,3,6,7,8-HxCDF	85.5	96.0	97.4	76.7	99.1
1,2,3,7,8,9-HxCDF	43.8	84.4	91.6	96.5	99.4
2,3,4,6,7,8-HxCDF	92.5	96.9	97.9	71.7	99.1
1,2,3,4,6,7,8-HpCDF	66.0	92.2	94.6	85.9	98.9
1,2,3,4,7,8,9-HpCDF	50.6	84.7	92.4	94.1	99.1
OCDF	-46.4	39.6	40.7	97.6	98.6
Total PCDFs	68.5	89.5	91.5	89.7	98.9
Total PCDD/Fs	55.2	84.6	88.9	92.4	98.8
Total PCDDs I-TEQ	86.7	96.2	97.6	80.1	99.3
Total PCDFs I-TEQ	85.9	95.6	97.2	73.0	98.8
Total PCDD/Fs I-TEQ	86.1	95.7	97.3	74.5	98.9

<sup>a</sup> All values are in percentage.

PCDD/Fs I-TEQ were 88.9 and 97.3%, respectively (Table 3). Fig. 2d shows the major PCDD/F congeners were OCDD, OCDF, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,6,7,8-HpCDD. The reduction fractions of low chlorinated congeners were also much higher than those of highly chlorinated congeners. For example, the reduction fractions of 2,3,7,8-TeCDD and 2,3,7,8-TeCDF were 99.0 and 97.7%, respectively, those of 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF were 85.8 and 94.6%, respectively, but those of OCDD and OCDF were only 54.6 and 40.7%, respectively (Fig. 3b).

The removal efficiencies of gas-phase PCDD/Fs were higher than particle-bound PCDD/Fs for PAC injection, because the low chlorinated PCDD/F congener with higher vapour pressure have more mass fraction in the gaseous phase, but the highly PCDD/F congeners are primarily associated with particulates [12]. Therefore, by using PAC injection in the front of the bag filter, the removal mechanism of PCDD/Fs in stack flue gas is mostly due to gas phase adsorption. In the stack flue gas, a very minor part of particulates was via the mechanism of inertia impaction hitting the PAC and finally being removed by the bag filter. This point can explain that in a higher amount of PAC injection like 40 or 50 kg/h, the removal efficiencies of PCDD/Fs is low but still exists.

PAC injection in the amount of 20, 40 and 50 kg/h, the adsorption of total PCDD/F mass on the PAC were 4.17, 3.31 and 2.84 mg/kg, respectively, while for those of total PCDD/F I-TEQ were 0.63, 0.36 and 0.30 mg I-TEQ/kg, respectively (Table 4). The above results show that an increased amount

Table 4  
Mean PCDD/F mass was adsorbed on PAC (mg/kg) in different amount of PAC injection

PAC injection	20 kg/h	40 kg/h	50 kg/h
PCDD/Fs (mg/kg)			
2,3,7,8-TeCDD	0.03	0.02	0.01
1,2,3,7,8-PeCDD	0.13	0.07	0.06
1,2,3,4,7,8-HxCDD	0.13	0.07	0.06
1,2,3,6,7,8-HxCDD	0.20	0.12	0.10
1,2,3,7,8,9-HxCDD	0.21	0.12	0.10
1,2,3,4,6,7,8-HpCDD	0.01	0.19	0.17
OCDD	-0.43	0.08	0.14
Total PCDDs	0.29	0.68	0.64
2,3,7,8-TeCDF	0.30	0.16	0.13
1,2,3,7,8-PeCDF	0.53	0.29	0.24
2,3,4,7,8-PeCDF	0.45	0.26	0.21
1,2,3,4,7,8-HxCDF	0.61	0.35	0.29
1,2,3,6,7,8-HxCDF	0.62	0.36	0.30
1,2,3,7,8,9-HxCDF	0.09	0.09	0.08
2,3,4,6,7,8-HxCDF	0.53	0.28	0.23
1,2,3,4,6,7,8-HpCDF	0.87	0.63	0.53
1,2,3,4,7,8,9-HpCDF	0.13	0.11	0.10
OCDF	-0.23	0.10	0.09
Total PCDFs	3.89	2.63	2.19
Total PCDD/Fs	4.17	3.31	2.84
Total PCDDs (mg I-TEQ/kg)	0.15	0.09	0.07
Total PCDFs (mg I-TEQ/kg)	0.48	0.28	0.23
Total PCDD/Fs (mg I-TEQ/kg)	0.63	0.36	0.30

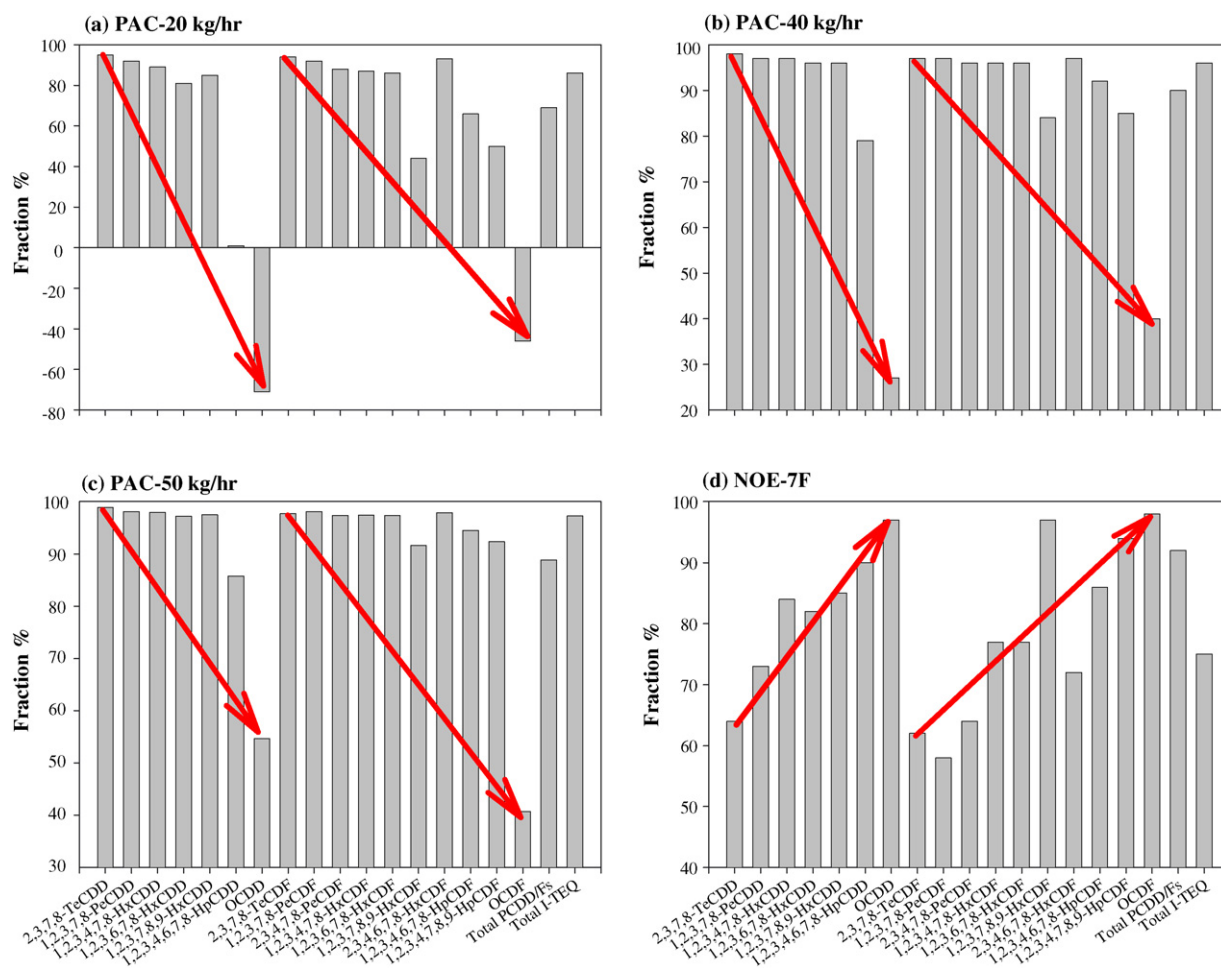


Fig. 3. Reduction fraction of 17 2,3,7,8-PCDD/Fs: (a) with 20 kg/h of PAC injection; (b) with 40 kg/h of PAC injection; (c) with 50 kg/h of PAC injection; (d) NOE-7F addition.

of PAC injection did not increase the adsorption of PCDD/F mass proportionally. Previous research also indicated that the increased quantity of activated carbon has a limited effect on the overall PCDD/F removal efficiency [28].

### 3.3. PCDD/F concentrations in the stack flue gases with both PAC injection and NOE-7F addition

By applying both PAC injection (40 kg/h) and NOE-7F addition (20 L/per metric tonne raw material), in the stack flue gas, the mean concentrations of total PCDD/F and total-PCDD/F I-TEQ were reduced to  $21.9 \text{ ng/N m}^3$  ( $n=4$ , R.S.D. = 27.9%) and  $1.97 \text{ ng I-TEQ/N m}^3$  ( $n=4$ , R.S.D. = 17.9%), respectively (Table 5). This means that by applying both PAC injection (40 kg/h) and NOE-7F addition in the stack flue gas, the mean reduction fractions of total PCDD/Fs and total-PCDD/Fs I-TEQ were 98.8 and 98.9%, respectively (Table 3). The PCDFs/PCDDs ratio was increased to 2.28, which indicated an increase amount of PCDDs removal. Fig. 2e shows, in the above condition, the major PCDD/F congeners were 1,2,3,4,6,7,8,HpCDF, OCDD, 1,2,3,4,6,7,8,HpCDD and 2,3,4,7,8-PeCDF.

By the addition of NOE-7F, in the stack flue gas, the reduction fractions of total PCDD/F and total-PCDD/F I-TEQ were 92.4 and 74.5%, respectively (Table 3). The removal efficiencies of highly chlorinated congeners were higher than those of low chlorinated congeners; for example, the OCDD and OCDF were 97.4 and 97.6%, respectively, while those of 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF were 89.6 and 85.9%, respectively and the 2,3,7,8-TeCDD and 2,3,7,8-TeCDF were 63.7 and 61.8%, respectively (Fig. 3d). The above results revealed that the addition of NOE-7F in the raw materials had a dechlorination effect for the PCDD/F decomposition. PAC injection was responsible for the removal of low chlorinated PCDD/F congeners, while the NOE-7F mainly inhibited highly chlorinated PCDD/F formation. The combination of both PAC injection and NOE-7F addition has a high potential for practical application. Compared with the results of emulsified diesel by using NOE-7F, it had a catalytic effect which elevated the combustion efficiency and decreased pollutant emissions during the combustion process [24]. Other inhibitors, the urea species could be reacted with catalysts (e.g., Cu) and they can be rapidly decomposed under appropriate flue gas conditions. The greatest decomposition fraction

Table 5  
The PCDD/F concentrations in the stack flue gases after both PAC injection (40 kg/h) and NOE-7F addition

PCDD/Fs	A (ng/N m <sup>3</sup> )	B (ng/N m <sup>3</sup> )	C (ng/N m <sup>3</sup> )	D (ng/N m <sup>3</sup> )	Mean (ng/N m <sup>3</sup> )	R.S.D. (%)
2,3,7,8-TeCDD	0.0749	0.0446	0.0446	0.0578	0.0555	26
1,2,3,7,8-PeCDD	0.442	0.273	0.174	0.214	0.276	43
1,2,3,4,7,8-HxCDD	0.256	0.191	0.113	0.151	0.178	34
1,2,3,6,7,8-HxCDD	0.550	0.426	0.441	0.574	0.498	15
1,2,3,7,8,9-HxCDD	0.386	0.316	0.306	0.395	0.351	13
1,2,3,4,6,7,8-HpCDD	3.72	2.55	1.61	2.10	2.50	36
OCDD	5.07	3.51	1.14	1.57	2.82	64
Total PCDDs	10.5	7.31	3.84	5.07	6.68	44
2,3,7,8-TeCDF	1.06	0.669	1.00	1.18	0.977	22
1,2,3,7,8-PeCDF	2.02	1.39	1.45	1.72	1.65	18
2,3,4,7,8-PeCDF	2.23	1.61	1.64	2.11	1.90	17
1,2,3,4,7,8-HxCDF	1.82	1.51	1.24	1.63	1.55	16
1,2,3,6,7,8-HxCDF	2.00	1.61	1.33	1.72	1.67	17
1,2,3,7,8,9-HxCDF	0.408	0.380	0.135	0.178	0.275	50
2,3,4,6,7,8-HxCDF	1.55	1.32	0.883	1.22	1.24	22
1,2,3,4,6,7,8-HpCDF	4.87	3.90	2.45	3.25	3.62	28
1,2,3,4,7,8,9-HpCDF	0.762	0.697	0.299	0.464	0.556	38
OCDF	2.57	2.23	0.932	1.40	1.78	42
Total PCDFs	19.3	15.3	11.4	14.9	15.2	21
Total PCDD/Fs	29.8	22.6	15.2	19.9	21.9	28
PCDFs/PCDDs ratio	1.84	2.09	2.97	2.94	2.28	–
Total PCDDs (ng I-TEQ/N m <sup>3</sup> )	0.457	0.304	0.235	0.299	0.324	29
Total PCDFs (ng I-TEQ/N m <sup>3</sup> )	1.96	1.47	1.38	1.77	1.65	16
Total PCDD/Fs (ng I-TEQ/N m <sup>3</sup> )	2.42	1.77	1.62	2.07	1.97	18
PCDFs/PCDDs I-TEQ ratio	4.29	4.83	5.87	5.92	5.09	–

was obtained for the most highly (octa-) chlorinated isomers [19,20].

#### 4. Conclusions

In the amount of 20, 40 and 50 kg/h PAC injection, the removal efficiencies of PCDD/Fs in the stack flue gas were 86, 96 and 97%, respectively. By adding an increased amount of PAC, the removal efficiencies were enhanced while the reduction fractions of low chlorinated PCDD/F congeners were much higher than those of highly chlorinated PCDD/F congeners.

Particularly, at 20 kg/h of PAC injection, the removal fractions of OCDD and OCDF were –71.2 and –46.4%, respectively. The above results indicate that a lower amount of PAC injection in the front of the bag filter, not only cannot remove highly chlorinated PCDD/Fs like OCDD or OCDF, but also the carbon surface of PAC can act as a precursor for the formation promotion of highly chlorinated PCDD/F congeners.

In addition, increased amounts of PAC injection did not increase the adsorption of PCDD/F mass proportionally. The mean total-PCDD/Fs I-TEQ absorbed by the PAC were 0.63, 0.36 and 0.30 mg I-TEQ/kg in the amount of 20, 40 and 50 kg/h injection, respectively.

The addition of NOE-7F in the raw materials had a dechlorination effect on the PCDD/F removal and mainly inhibited highly chlorinated PCDD/F formation. The combination of both PAC injection and NOE-7F addition has a high potential for practical application.

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