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RESEARCH ARTICLE

Suppression of dioxins by S-N inhibitors in pilot-scale experiments

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Abstract S-N inhibitors like thiourea and sewage sludge decomposition gases (SDG) are relatively novel dioxins suppressants and their efficiencies are proven in numerous lab-scale experiments. In this study, the suppression effects of both thiourea and SDG on the formation of dioxins are systematically tested in a pilot-scale system, situated at the bypass of a hazardous waste incinerator (HWI). Moreover, a flue gas recirculation system is used to get high dioxin suppression efficiencies. Operating experience shows that this system is capable of stable operation and to keep gaseous suppressant compounds at a high and desirable molar ratio (S + N)/Cl level in the flue gas. The suppression efficiencies of dioxins are investigated in flue gas both without and with addition of S-N inhibitors. A dioxin reduction of more than 80 % is already achieved when the (S + N)/Cl molar ratio is increased to ca. 2.20. When this (S + N)/Cl molar ratio has augmented to 4.18 by applying suppressant recirculation, the residual PCDD/Fs concentration in the flue gas shrank from 1.22 to 0.08 ng I-TEQ/Nm^3. Furthermore, the congener distribution of dioxins is analysed to find some possible explanation or suppression mechanism. In addition, a correlation analysis between (S + N)/Cl molar ratios and PCDD/Fs is also conducted to investigate the chief functional compounds for dioxin suppression.

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Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs, "dioxins") are unintentionally formed and released from combustion and numerous other thermal processes. Studies have shown that hazardous waste incineration (HWI) is potentially a major source of airborne emissions. Gao et al. (2009) and Lee et al. (2003a, b) estimated the total PCDD/Fs concentration in stack gas samples from HWI, finding that the mean PCDD/F emission is generally higher than the European Union directive emission limit, 0.1 ng I-TEQ/Nm^3 (Directive 2000). Therefore, stack gas emissions from hazardous waste incinerators (HWIs) are a serious concern and need appropriate control tools to deal with it.

As the previous research, the formation of PCDD/Fs occurs mainly via heterogeneous reactions at temperatures between 250 and 450 °C in post-combustion regions (Addink et al. 1991; Fangmark et al. 1995; Li et al. 2005; Cunliffe and Williams 2007a, 2009), contributing largely to the dioxin emission (Ballschmiter et al. 1988; Addink et al. 1995; Tuppurainen et al. 1998; McKay 2002). Therefore, it is better to suppress the formation of dioxins in post-combustion regions.

Addition of S-compounds, such as S, Na_2S, $Na_2S_2O_3$, CS_2, FeS_2, SO_3 and SO_2, can achieve strong inhibition on dioxin formation (Pandelova et al. 2005; Chang et al. 2006; Yan et al. 2006; Chen et al. 2008a; Jin et al. 2008; Wu et al. 2012). In fact, dioxins could be suppressed when coal with high sulphur is used as fuel (Griffin 1986). Lot of work has been done on the dioxin emissions when waste is incinerated with coal, showing good suppression effects by sulphur compounds (Gullett et al. 1992; Gullett et al. 1998; Gullett et al. 2000a;

Chen et al. 2008a). Besides S-containing compounds, some N-compounds (e.g. urea and NH_3) are also regarded as effective inhibitors (Tuppurainen et al. 1999; Ruokojârvi et al. 2001; Ruokojârvi et al. 2004; Cunliffe and Williams 2009). Poisoning the catalyst metal has been proven to be the main suppression mechanism for S- and N-compounds (Ruokojârvi et al. 2001; Ryan et al. 2006). In detail, S- or N-compounds could poison some metal chloride into sulphate or metal complexes (Ryan et al. 2006; Shao et al. 2010a; Wu et al. 2012; Tuppurainen et al. 1999; Luna et al. 2000). Moreover, SO_2 can also react with Cl_2 to form HCl, and the chlorine available for dioxins formation will reduce (Griffin 1986; Gullett et al. 1992). The S- or N-compounds have showed dioxin suppression effects in real-scale experiments, with a reduction efficiency of more than 50 % (Chang et al. 2006; Wu et al. 2012). Therefore, increasing the concentration of S- or N-compounds, namely the value of S/Cl or N/Cl molar ratio, might further increase suppression efficiency.

In recent years, both S- and N-compounds have been observed to strongly suppress the PCDD/Fs formation route via de novo synthesis (Chen et al. 2014). More specifically, high PCDD/Fs inhibition efficiencies of up to 96 % could be achieved by adding 1 wt. % amidosulfonicacid; thiourea and sludge decomposition gases (SDG) could reduce more than 95 % of PCDD/Fs when the (S + N)/Cl molar ratio declines to only 0.47 (Chen et al. 2014; Fu et al. 2015). However, the suppression of dioxins formation by S-N inhibitors has never been explored in a pilot-scale experimental system.

In this study, a 500 Nm^3/h capacity pilot-scale system with flue gas recirculation and thermal treatment of filtered ash, designed for the bypass of an actual hazardous waste incinerator (HWI) is used to observe and quantify the suppression effects of S-N inhibitors (Lin et al. 2015). At first, the stability of the pilot-scale system will be checked, by monitoring the concentrations of SO_2, NH_3 and HCl in flue gas. The corresponding (S + N)/Cl molar ratios will be calculated and analysed. Then the suppression efficiencies of dioxins are also investigated in flue gas without and with addition of thiourea and SDG, respectively. Furthermore, the enhancement of the dioxin suppression effects by recirculating gaseous S-N inhibitors is also studied. In addition, the characteristics of PCDD/Fs and the correlation between (S + N)/Cl molar ratios and PCDD/Fs are further analysed to find some possible suppression mechanism and investigate the main functional gaseous compounds for dioxin suppression.

Materials and methods

The pilot-scale experimental system (PES) in the HWI

The pilot-scale experimental system is carried out in a 50-tonne/day hazardous waste rotary kiln incinerator (Wu et al. 2012; Lin et al. 2014). Emissions of dioxins and others pollutants are controlled by means of the following sequence of operations: quenching tower, acid neutralising tower, activated carbon dosing, baghouse filter, and alkaline scrubber (Fig. 1.). The amounts of activated carbon and lime sprayed into the flue gas are adjusted to 10 and 120 kg/h, respectively. The volumetric flow of flue gas during the experimental stage is about 20,000 Nm^3/h and the linear flow velocity is about 7.5 m/s (Table 1).

The PES is mainly composed of a baghouse filter system, a thermal treatment and a flue gas recycling system (Lin et al. 2015). As shown in Fig. 2, the baghouse filter (BF) captures both the fly ash and AC, and then discharges the mixture into the thermal treatment system (inlet A). The filter ash, including fly ash and AC, is then treated at 400 °C under a stream of inert N_2 in the thermal treatment unit (TTU), a sealed system excluding any air entries. The gaseous compounds captured by the AC are again desorbed in this TTU. The flue gas recycling system returns the desorbed gaseous phase inhibitors into the flue gas, aspired by a negative pressure to inhibit the formation of PCDD/Fs. During dioxin suppression tests, S-N inhibitors could be added into the TTU to increase the concentration of gaseous phase inhibitors in flue gas.

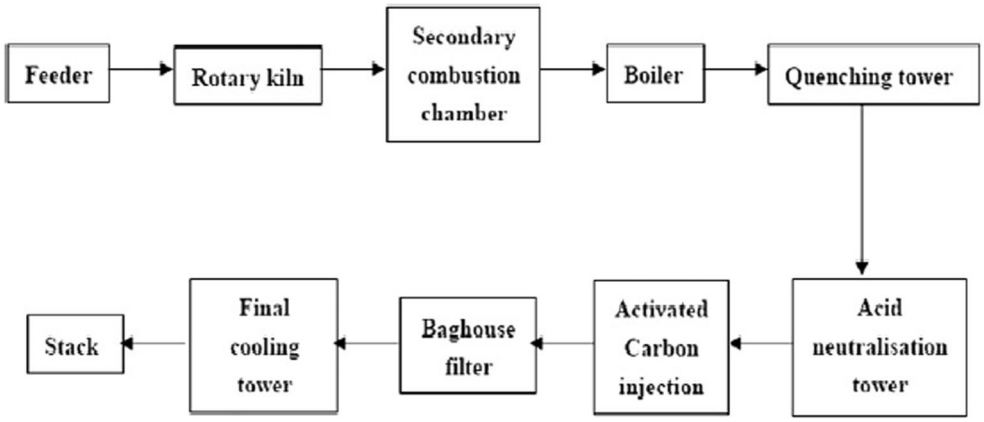

Fig. 1 Systemic diagram of the hazardous waste incinerator

Table 1 Parameters of incineration and air pollutant control system

Item	Value	Item	Value
Temperature in rotary kiln	850–1050 °C	Temperature of flue gas at the outlet of the baghouse filter	170–180°C
Average heat value of waste	12.9 MJ/kg	Temperature of flue gas in the inlet of the quenching tower	170–180°C
Temperature in secondary combustion chamber	1100–1200 °C	Temperature of flue gas in the outlet of the quenching tower	70–75°C
Retention time in secondary combustion chamber	>2 s	Amount of flue gas in the outlet of the quenching tower	2.8×10^4 Nm^3/h
Temperature of flue gas in the inlet of the boiler	1100–1250 °C	Flow rate of stack gas	7.5 m/s
Temperature of flue gas in the outlet of the boiler	500–550°C	Lime input	120 kg/h
Temperature of flue gas in the intlet of quenching tower	500–550°C	Activated carbon concentration	150–200 mg/Nm^3
Temperature of flue gas in the outlet of quenching tower	180–200°C	Flow of hazardous waste	50 t/d
Retention time in quenching tower	<1 s	Destruction and removal efficiency	>99.9 %
Temperature of flue gas in the inlet of baghouse filter	180–200 °C	Clinker ignition loss	<2.5 %

Table 2 shows the design parameters of the PES. The thermal treatment system is composed of three horizontal tubular furnaces and a horizontal screw conveyer. During the experiment, about 500 Nm^3/h of flue gas (450 °C) is introduced from the boiler by an induced fan with a constant rotation rate. The flue gas cools to about 200 °C to simulate the de novo synthesis of dioxins in the bypass flue gas. The retention time of bypass flue gas in the PES is about 35 s. Then AC is injected into the flue gas (at 185 °C) to adsorb PCDD/Fs and SO_2 and then it is filtered out by the baghouse filter. The inlet and outlet temperature of the BF system is 170 °C and 150 °C, respectively. Gaseous compounds could be desorbed at 400 °C and recycled into the system (inlet D), where the temperature of the flue gas is about 400 °C.

After thermal treatment, the filtered ash will be discharged from exit B of the TTU. The gas velocity and pressure of the system is 0.35 m/s and −1.0 kPa, respectively. The type of AC is HC 767, produced by Zhejiang Hangmu Timber Industrial Co., Ltd. The particle size of AC is primarily distributed between 10 and 100 μm. The average pore radius and BET surface area is 3.164 nm and 1292 m^2/g, respectively.

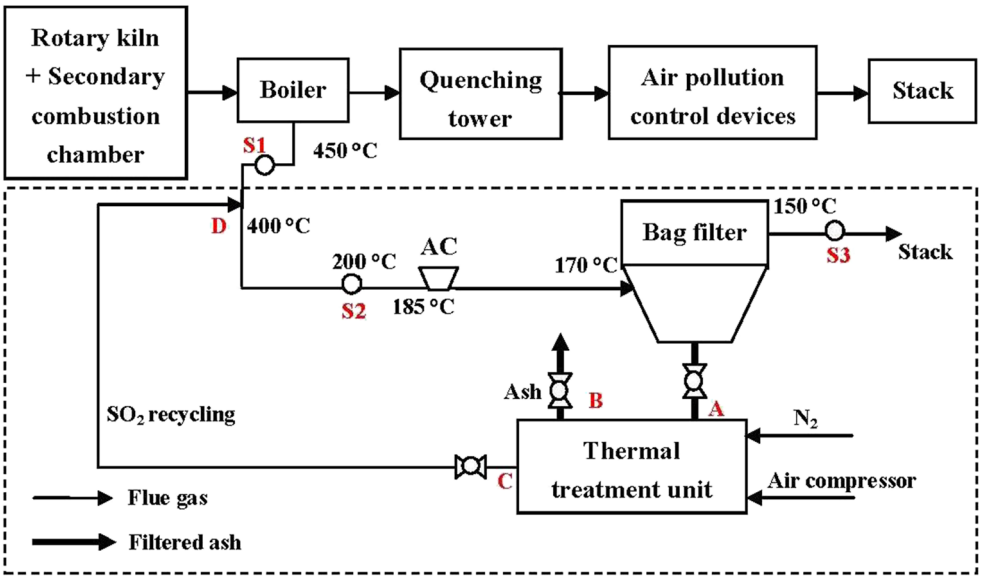

Fig. 2 Pilot-scale experimental system for S-N inhibitors suppression tests

Table 2 Design parameters of the pilot-scale experimental system

Items	Parameter
Baghouse filter system	
Material of filter	Teflon laminated glass fibre
Area of a single bag filter (m^2)	0.34
Thickness of filter (m)	2.4×10^{-3}
Number of filters	24
Area of filtration (m^2)	8.16
Pressure drop (mm H_2O)	180
Cleaning intervals (min)	30
Thermal treatment system	
Horizontal tube furnace	KTL1600
Heating temperature (°C)	100 ~ 1600
Furnace size (mm)	650 × 450 × 670
Horizontal screw conveyer	LS 150 × 1.5 × 50-M2
Rotor diameter (mm)	150
Length (m)	1.5
Rotating speed (m/s)	50
Volume flow of air compressor (m^3/min)	0.17
Others	
Gas velocity (m/s)	0.35
Pressure (kPa)	−1.0
Volume of flue gas (Nm^3/h)	500
Inlet temperature (°C)	170
Outlet Temperature (°C)	150

Experimental setup

The experiments are conducted to study the reduction efficiency of dust and dioxins by baghouse filter and activated carbon in the pilot-scale experimental system (Tests 1 and 2). As shown in Table 3, thiourea and sludge are added into the TTU with a flow rate of 0.25 and 2.5 kg/h to suppress the formation of dioxins in bypass flue gas (Tests 3 and 4). The characteristics of dried sludge used are described in detail in our previous studies (Chen et al. 2014). In Tests 5 and 6, the recycling system is put into use to increase the concentrations of gaseous phase inhibitors to realise a high suppression efficiency of PCDD/Fs formation. The thermal treatment of filtered ash is conducted in the TTU at 400 °C under an inert gas flow of 1 L/min.

Table 3 Experimental design conditions

Tests	System	Note
1	Baghouse filter (BF) + activated carbon (AC)	AC:300 mg/Nm^3
2	BF + AC + thermal treatment unit (TTU)	Desorption temperature:400 °C; N_2: 1 L/min
3	BF + AC + thiourea	Thiourea:0.25 kg/h
4	BF + AC + TTU + thiourea	Thiourea:0.25 kg/h
5	BF + AC + thiourea	Sludge:2.5 kg/h
6	BF + AC + TTU + thiourea	Sludge:2.5 kg/h

Three sampling points (S1, S2 and S3) are setup (Fig. 2.). S1 is set to detect the original PCDD/Fs and gaseous compounds concentration in the flue gas from the waste incinerator. S2 is set to the PCDD/F concentration by de novo synthesis within the 450–200 °C window from S1 to S2 before baghouse filter system, as well as to detect the concentration of gaseous compounds in the recirculating system. S3 is set to detect the emission concentration of PCDD/Fs and gaseous phase inhibitors after the recirculating system. The temperature of S1, S2 and S3 is 450, 200 and 130 °C, respectively. All tests are conducted in duplicate. We conducted each experiment when the system became stable, and the sampling time lasted for 2 h for each run.

Sampling and analysis

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, NO_x and CO.

Dioxin samples in the flue gas are collected by an isokinetic sampler (Model KNJ23, KNJ, Korea) according to US EPA method 23a (Chen et al. 2008a, b). The filtered ash from the exit of the thermal treatment unit is also sampled for dioxin analysis.

The cleanup procedure of PCDD/F samples are according to the US EPA method 23 (for flue gas 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. Target compounds are the 17 toxic 2,3,7,8-substituted 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. Details of cleanup procedure and analysis method of PCDD/Fs could be found in our previous study (Chen et al. 2008a, b; Yan et al. 2012a). The toxic equivalents (TEQ) are calculated using NATO/CCMS factors (Bhavsar et al. 2008). All the concentrations are normalised to dry air, 11 % O_2, 1.01×10^5 kPa and 237 K.

Results and discussion

(S + N)/Cl molar ratios in the flue gas

The (S + N)/Cl molar ratios in flue gas are based mainly on the concentrations of SO_2, NH_3 and HCl, as shown in Fig. 3. In Test 1, the (S + N)/Cl molar ratio is only 0.76.

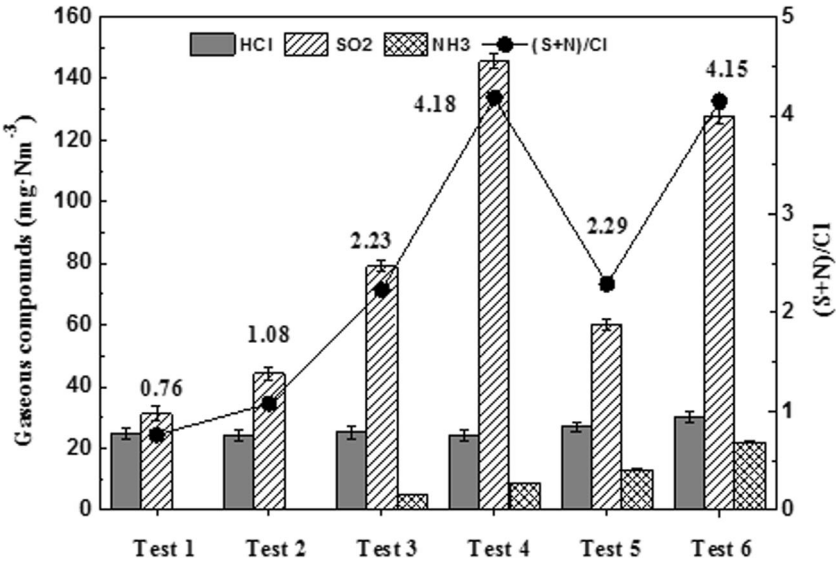

Fig. 3 Gaseous compounds and molar ratio of (S + N)/Cl in different tests

Specifically, the clean gas concentration of SO_2, NH_3 and HCl is 31.3, 0.4 and 24.7 mg/Nm^3, similar with those in our previous study (Lin et al. 2015). After the thermal treatment of bag filter fly ash, the SO_2 adsorbed on activated carbon returns to PES, resulting in an incremental rise of SO_2 to 44.4 mg/Nm^3. However, largely the concentrations of NH_3 and HCl do not increase, indicating that they were not adsorbed effectively by activated carbon (Lee et al. 2003a, b; Zhu et al. 2005). As a consequence, the (S + N)/Cl molar ratio went up to 1.08. With addition of thiourea, the concentrations of SO_2 and NH_3 significantly increase, to 79.2 and 5.1 mg/Nm^3, respectively. Moreover, the concentration of HCl little changes during stable operation of HWI. Therefore, the (S + N)/Cl molar ratio could rise to 2.23. After recirculating the gaseous phase inhibitors, the concentration of SO_2 and NH_3 further increased to 145.6 and 8.6 mg/Nm^3, respectively. Finally, the (S + N)/Cl molar ratio continually added up to 4.18.

Continuing to add SDG into PES (Test 5), the concentration of SO_2 in the flue gas increased from 31.3 to 60.3 mg/Nm^3, and so as to NH_3 which also increased from 0.4 to 16.2 mg/Nm^3. Normally protein in sludge could be hydrolysed fast to emit NH_3, whereas thiourea needs certain amount of oxygen to decompose NH_3. However, the content of oxygen in the outlet of the boiler is in the range of 6 to 9 %. Thus, dry sludge is supposed to decompose more NH_3 than thiourea (Deng et al. 2009; Yan et al. 2012a; Chen et al. 2014). Because more HCl would be also formed by thermal treatment of dry sludge, the (S + N)/Cl molar ratio only had the same level with that in Test 3. By circulation, the (S + N)/Cl molar ratio could be up to 4.15 with the SO_2 concentration of 128.1 mg/Nm^3 and also with the NH_3 concentration of 23.2 mg/Nm^3. Interestingly, the increment of (S + N)/Cl molar ratio for thiourea and SDG seemed to rely on the increasing amount of SO_2 and NH_3, respectively.

The concentrations of gaseous pollutants in the bypass stack gas are listed in Table 4. With the adsorption effect of activated carbon, the emission of SO_2 and NH_3 are well below the national emission standards. Due to the incomplete combustion of dry sludge, the concentration of CO increased to more than 50 mg/Nm^3 in Tests 5 and 6, while still below the national standards of 80 mg/Nm^3. Therefore, the PES did not have further negative effects on the pollutant emissions. However, if more S-N inhibitors are added, desulphurization tower should be introduced into the PES to reduce the emission of SO_2 and NH_3.

Table 4 Concentrations of some gaseous compounds at the sampling position S3

Gaseous compounds (mg/Nm^3)	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	National emission standard
SO_2	11.3	17.4	28.2	43.6	25.2	40.6	300
NH_3	0.4	0.4	3.4	4.4	10.4	13.4	–
HCl	7.6	7.4	5.2	8.1	7.2	10.1	70
NO_x	20.79	27.30	21.4	34.4	75.1	94.6	500
CO	10.3	12.1	10.9	11.9	50.9	54.9	80

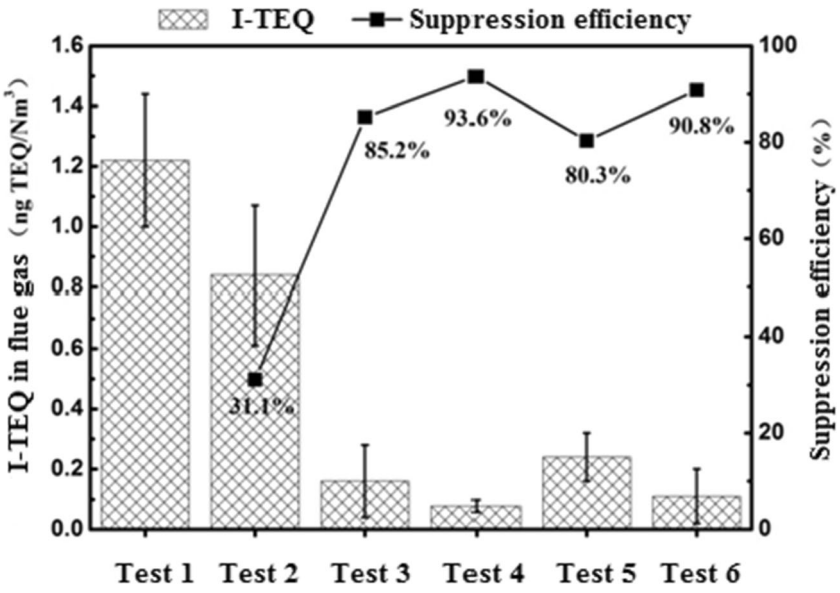

Fig. 4 The residual values and suppression efficiencies of I-TEQ in flue gas

PCDD/Fs suppression by S-N inhibitors

By using the recirculating system, the concentration of PCDD/Fs in the flue gas which has passed through the baghouse filter system with AC injection decreased from 1.22 to 0.84 ng TEQ/Nm^3, with a reduction efficiency of 31.1 % (Fig. 4). The result confirmed that dioxin formation would be suppressed when the (S + N)/Cl molar ratio is higher than 1. With addition of thiourea, the concentration of PCDD/Fs in flue gas further decreased to 0.16 ng TEQ/Nm^3 and the suppression efficiency is up to 85.2 %, suggesting that SO_2 and NH_3 are effective dioxin suppressants. The results also revealed that the suppression efficiencies of dioxins in flue gas correlate well with the (S + N)/Cl molar ratios (Anthony et al. 2001; Chang et al. 2006; Wu et al. 2012). After flue gas circulation, the concentration of PCDD/Fs is below the new national standards of 0.1 ng TEQ/Nm^3, with a value of 0.08 ng TEQ/Nm^3. With addition of SDG, the concentration of PCDD/Fs in the flue gas decreased from 1.22 to 0.24 ng TEQ/Nm^3, with a reduction efficiency of 80.3 %. Although the (S + N)/Cl molar ratios for SDG suppression tests are slightly higher than that for thiourea, the suppression efficiencies are lower than the later ones. The reason could be attributed to the different suppression mechanism by SO_2 and NH_3. In previous studies, SO_2 has been proven to have a better suppression effect on dioxin formation than NH_3 when they are at the same level (Hajizadeh et al. 2012; Chen et al. 2015). The result confirmed that a relatively high SO_2 and NH_3 concentration

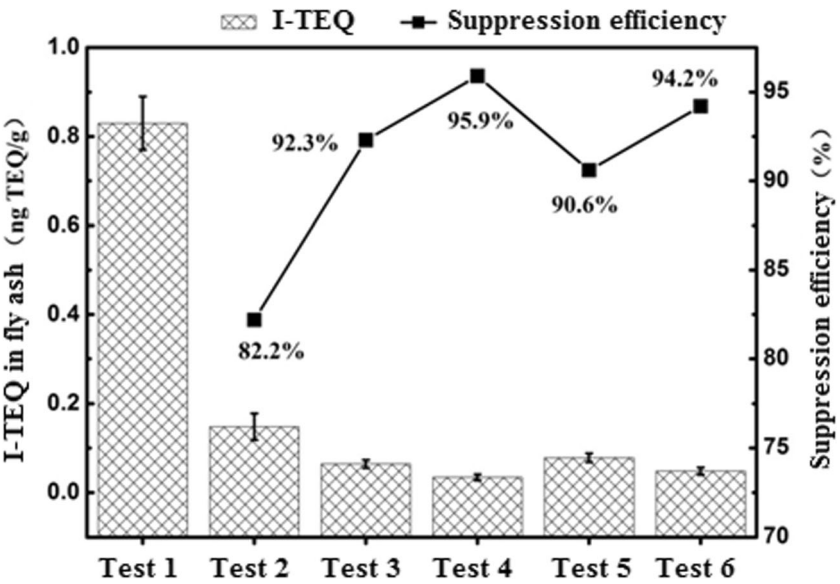

Fig. 5 The values and suppression efficiencies of I-TEQ in fly ash

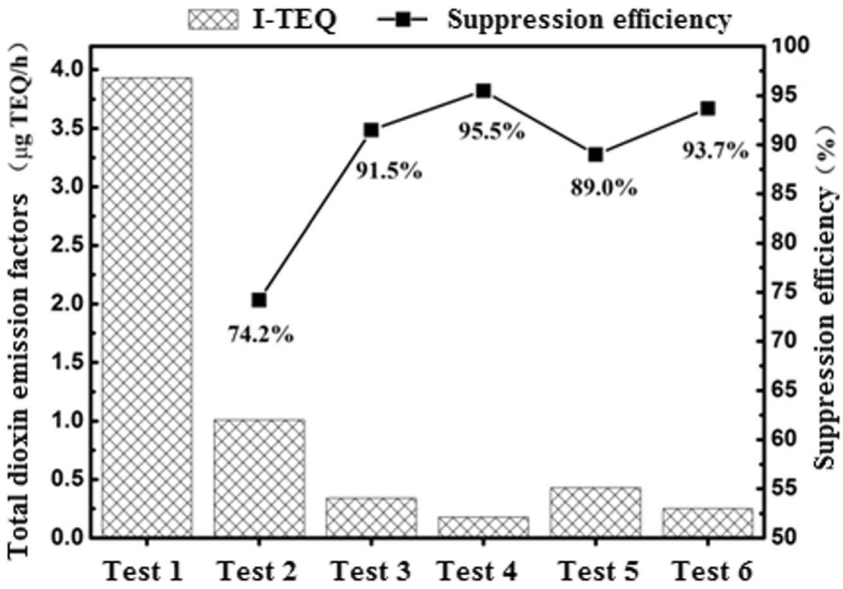

Fig. 6 Emission factors and suppression efficiencies of PCDD/Fs

in the flue gas could react with HCl to reduce the chloride availability (Gullett et al. 2000b; Xie et al. 2000; Wikström and Marklund 2001; Yan et al. 2012b) or poison the metal catalyst in the fly ash to reduce the possible formation of dioxins (Ryan et al. 2006; Shao et al. 2010b).

The concentrations of PCDD/Fs in fly ash under different experimental conditions are presented in Fig. 5. By thermal treatment, the concentration of PCDD/Fs in the fly ash decreased from 0.83 to 0.15 ng TEQ/g, with a reduction efficiency of 82.2 %. The degradation and dechlorination effects possibly contributed to the reduction of PCDD/Fs (Weber et al. 2002; Lundin and Marklund 2007; Gao et al. 2008; Song et al. 2008; Wu et al. 2011). Moreover, the degradation efficiency could be affected by temperature, atmosphere, velocity of flue gas and the characteristics of fly ash (Weber et al. 2002; Cunliffe and Williams 2007b; Song et al. 2008; Wu et al. 2011). With addition of thiourea, the concentration of PCDD/Fs in the fly ash decreased to 0.06 ng TEQ/g, indicating that PCDD/Fs could be effectively suppressed even without the application of thermal treatment. By recirculating the gaseous phase inhibitors, the concentration of PCDD/Fs in the fly ash further decreased to 0.03 ng TEQ/g, with a reduction efficiency of 95.9 %. As to the SDG, the concentration of PCDD/Fs could decrease to 0.05 ng TEQ/g when combined with the recycling system. Accordingly, the PCDD/Fs levels of fly ash emitted from PES are well below the Chinese landfill acceptance criteria for waste (3.0 ng I-TEQ/g), showing that PES is an effective system

Table 5 Characteristics of PCDD/Fs in different tests

Item	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Units
PCDD/Fs in flue gas							
PCDDs	1.07	0.74	0.21	0.24	0.34	0.12	ng/Nm^3
PCDFs	3.96	2.65	0.72	0.46	1.27	0.43	ng/Nm^3
PCDD/Fs	5.03	3.39	0.93	0.70	1.61	0.55	ng/Nm^3
PCDDs/PCDFs	0.27	0.28	0.30	0.52	0.27	0.28	Mass ratio
Cl-PCDDs	7.04	7.20	7.16	7.71	7.49	6.98	Weight average level
Cl-PCDFs	6.11	6.42	6.58	7.09	6.33	6.54	of chlorination degree
PCDD/Fs in fly ash							
PCDDs	1.22	1.60	0.43	0.51	0.33	0.50	ng/g
PCDFs	7.75	4.35	0.75	0.17	0.91	0.16	ng/g
PCDD/Fs	8.97	5.95	1.18	0.68	1.24	0.66	ng/g
PCDDs/PCDFs	0.16	0.37	0.58	2.99	0.36	3.17	Mass ratio
Cl-PCDDs	7.18	7.83	7.44	7.59	7.40	7.31	Weight average level
Cl-PCDFs	5.90	6.69	6.84	6.65	6.49	6.54	of chlorination degree

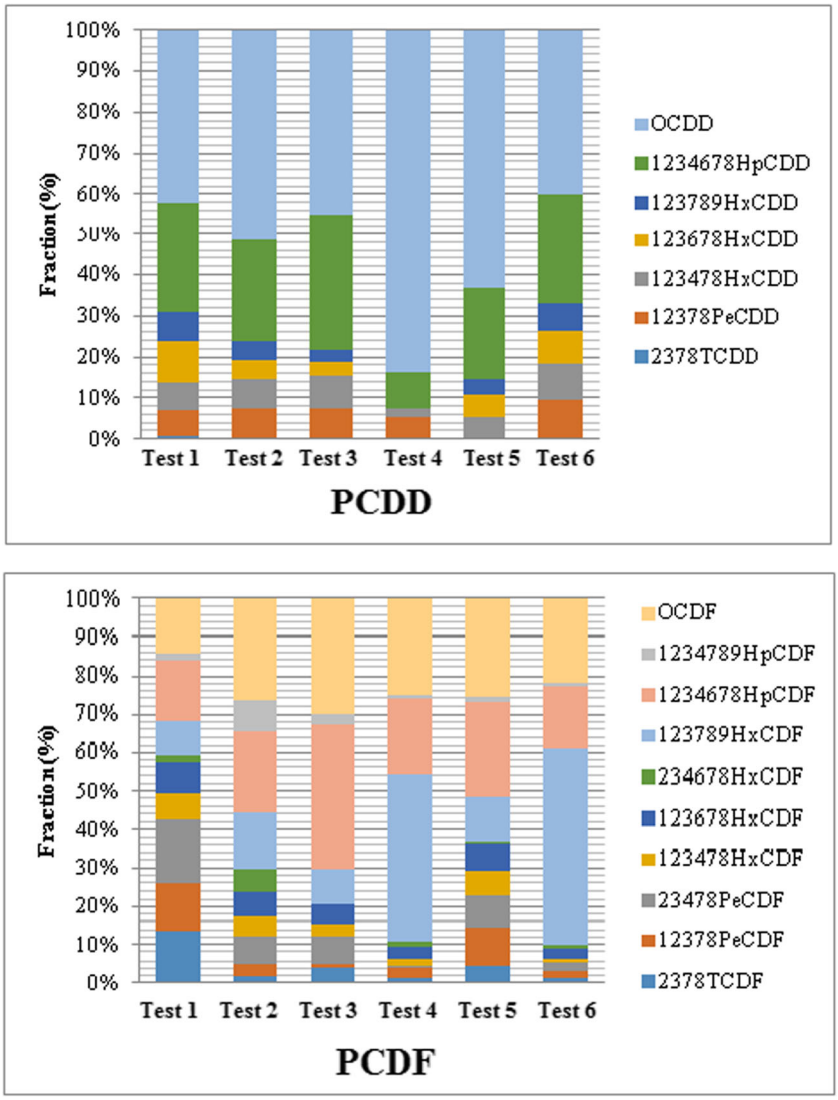

Fig. 7 Distribution of 2,3,7,8-PCDD/Fs in flue gas

to control the emissions of PCDD/Fs and other chlorinated organic chemicals.

In order to evaluate the emission characteristics of dioxins in different tests, the concept of emission factor is introduced, and its formula is presented below:@@@

F emission factor (average value every 4 h)
C_f concentration of total PCDD/Fs in flue gas after baghouse filter treatment
V_f volume of flue gas
C_a concentration of total PCDD/Fs in fly ash collected by baghouse filter
V_a amount of fly ash emitted per hour.

In this study, the volume of flue gas is 500 Nm^3/h and the flow rate of fly ash emitted is 4.0 kg/h. As shown in Fig. 1, the emission factor is 3.93 μg TEQ/h for the blank experiment (Test 1). As shown in Fig. 6, the emission factor decreased to 1.01 μg TEQ/h with a reduction of 74.2 % after accumulating the gaseous phase inhibitors by the recycling system (Test 2). With addition of thiourea (Test 3), the emission factor decreased to 0.34 μg TEQ/h with a reduction of 91.5 %. Hence, the suppression efficiency could reach 95.5 % after the gaseous phase inhibitors recycling (Test 4). With addition of SDG (Test 5), the emission factor decreased to 0.43 μg TEQ/h with a reduction of 89.0 %, which is slightly lower than that of thiourea. A better suppression effect is also detected with the application of the recycling system for SDG, showing a reduction efficiency of 93.7 % (Test 6). Therefore, the dioxin suppression efficiencies could be up to 90 %, and the value could further increase to 95 % after recycling. It means that the reduction amount of dioxins could be 784 g TEQ/year for a 50-tonne/day waste incinerator if it operates 7000 h/year.

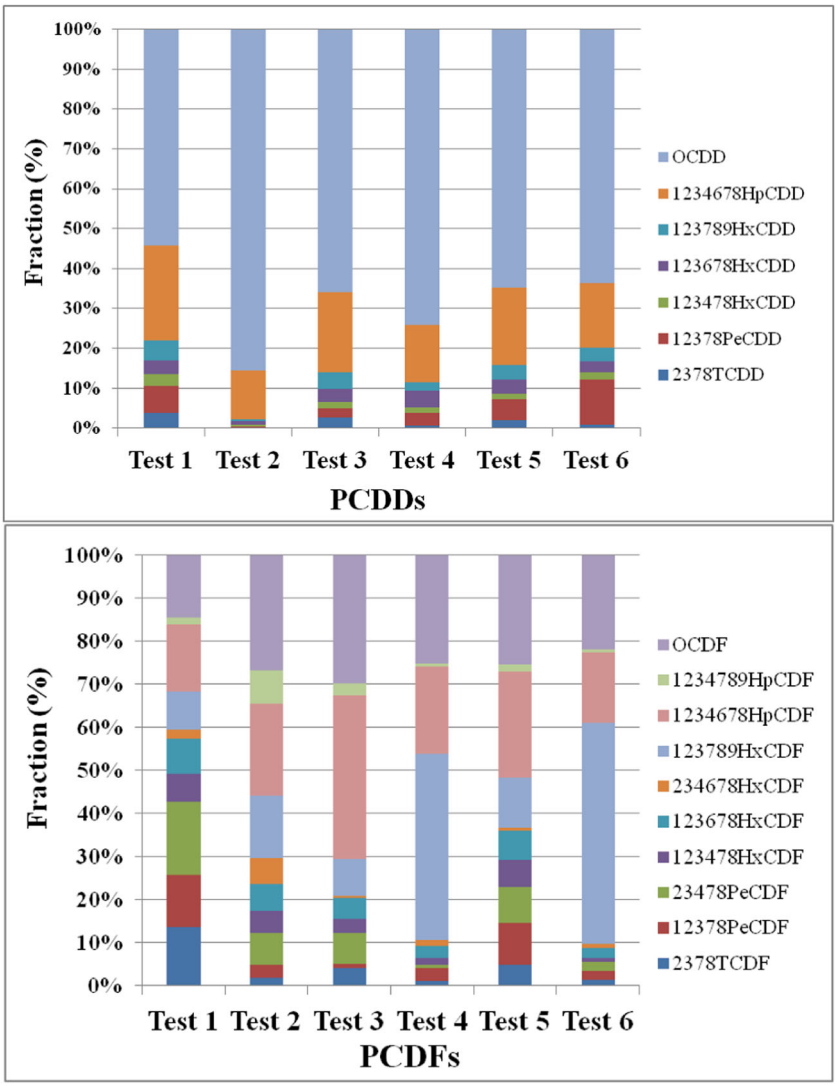

Fig. 8 Distribution of 2,3,7,8-PCDD/Fs in fly ash

Characteristics of PCDD/Fs

The profile of PCDD/Fs is shown in Table 5 for different experimental conditions. In Test 1, the ratios of PCDDs/PCDFs are lower than 1 in both of the flue gas and the filtered ash. This ratio agrees with our previous suppression experiments (Wu et al. 2011; Lin et al. 2014; Lin et al. 2014), suggesting that the low-temperature heterogeneous catalytic formation of PCDD/Fs is the main pathway in the post-combustion regions (Stieglitz et al. 1989; Altwicker et al. 1990; Addink and Olie 1995; Huang and Buekens 1995; Cunliffe and Williams 2009). The ratios of PCDDs/PCDFs in Test 2 did not change so much that the reason could be attributed to the still low levels of gaseous phase inhibitors in flue gas, even with the recycling system. After adding thiourea, the ratio of PCDDs/PCDFs in the flue gas increased, especially in Test 4 where the value increased from 0.27 to 0.52, indicating that S-N inhibitors have a better suppression effect on PCDFs than PCDDs (Chang et al. 2006; Ryan et al. 2006; Aurell and Marklund 2009). However, in Tests 5 and 6, the ratios of PCDDs/PCDFs almost remained the same, and the difference with that of thiourea might be attributed to the composition of S-N inhibitors and also to the different inhibitory effect of SO_2 and NH_3. Considering the desorption effect, the ratios of PCDDs/PCDFs significantly varied, especially for Tests 4 and 6 (Cunliffe and Williams 2007b). Possibly the PCDFs associated to fly ash are desorbed and destructed in a easier way than PCDDs (Lundin and Marklund 2007). Addink et al. (1995) also obtained similar results and they supposed that PCDDs are more stable than PCDFs.

The rising chlorination degree of PCDDs and PCDFs in flue gas and fly ash indicate that S-N inhibitors exert a better suppression effect on low chlorinated PCDD/Fs (Wikström

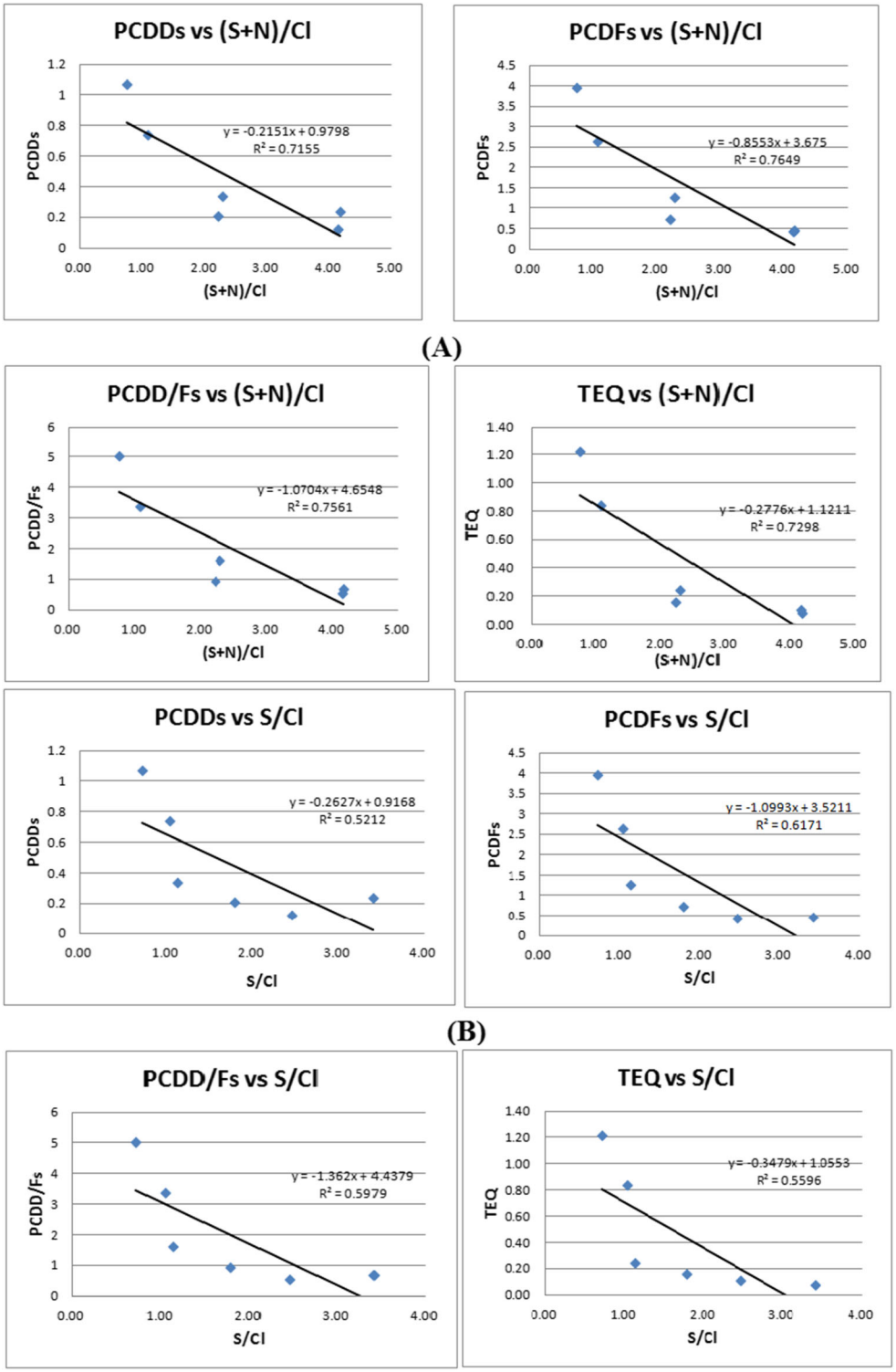

Fig. 9 The relationship between (S + N)/Cl molar ratio and PCDD/Fs in flue gas (*A*: (S + N)/Cl; *B*: S/Cl; *C*: N/Cl)

et al. 1999; Nakahata and Mulholland 2000). This phenomenon could also be attributed to the high vapour pressure for low chlorinated PCDD/Fs, and they could be desorbed more easily than high-chlorinated ones (Chang et al. 2002; Chi et al. 2006; Wu et al. 2011).

The congener distributions of 2,3,7,8-PCDD/Fs are presented in Figs. 7 and 8. The leading PCDD congeners in flue gas and fly ash are both 1,2,3,4,6,7,8-HpCDD and OCDD for Test 1, and the percentage of them is ca. 70 %; the PCDF congeners are relatively homogeneous. After

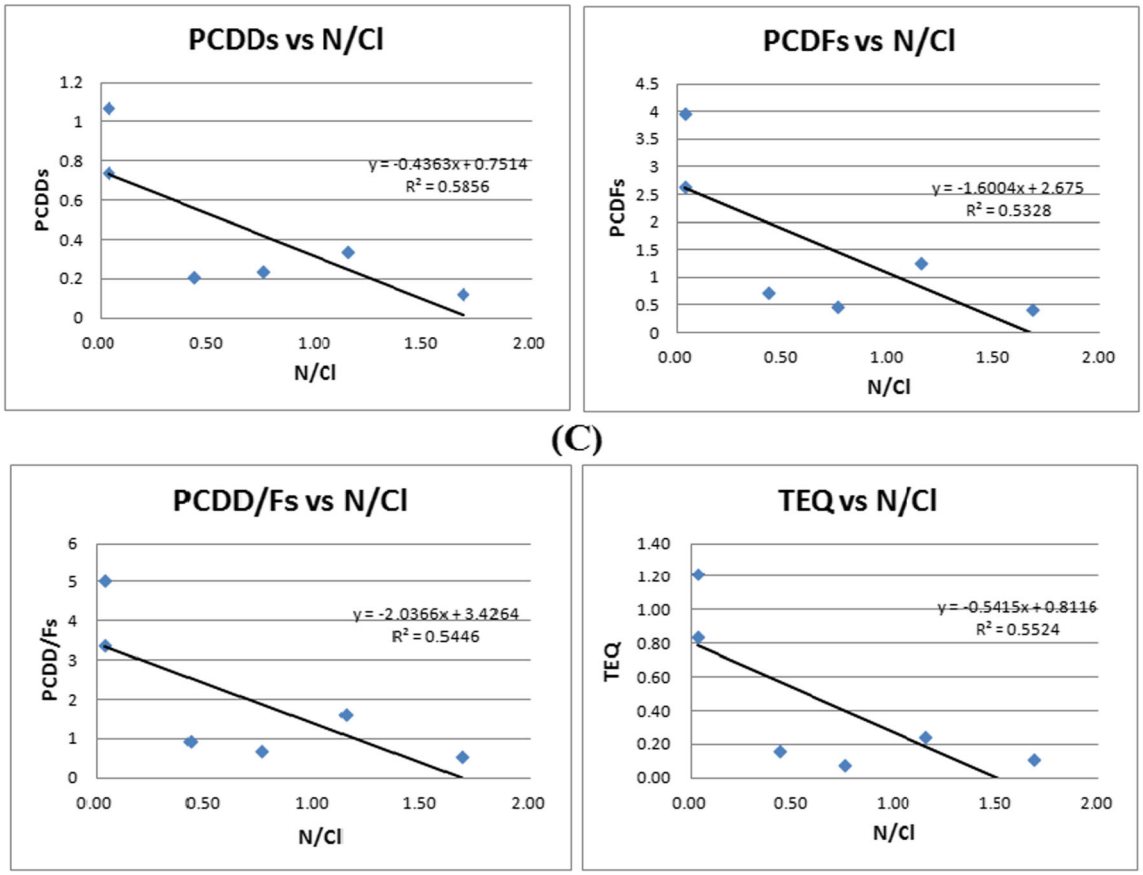

Fig. 9 (continued)

adding the S-N inhibitors and recirculating them in the system, the behaviour of congener profiles trended to be low chlorinated PCDD/Fs, especially for Test 4. Comparison with other tests, the fraction of OCDD decreased in the flue gas of Test 5. The reason could be attributed to the suppression effects of N-compounds (Ruokojârvi et al. 1998, 2004).

Correlation between (S + N)/Cl molar ratios and PCDD/Fs

In order to establish the optimum operating modes and investigate the role of both nitrogen and sulphur compounds in the suppression of PCDD/Fs formation, the relationship between the (S + N)/Cl molar ratio and PCDD/Fs in flue gas and fly ash are analysed. As shown in Fig. 9a, the (S + N)/Cl molar ratio correlates relatively well with PCDDs, PCDFs, PCDD/Fs and TEQ in flue gas ($r^2 = 0.72$, 0.76, 0.76 and 0.73, respectively). As expected, PCDFs has a better relationship with the (S + N)/Cl molar ratio than PCDDs, indicating that S-N inhibitors have more stable suppression effects on PCDFs in flue gas. In terms of the S/Cl molar ratio, it does not correlate well with PCDDs, PCDFs, PCDD/Fs and TEQ, and their corresponding r^2 values are 0.52, 0.62, 0.60 and 0.56, respectively. For N/Cl, it correlates badly with PCDDs, PCDFs, PCDD/Fs and TEQ, which is similar with the results of S/Cl molar ratio (r^2 values between 0.53 and 0.59). Considering the best relationship between (S + N)/Cl molar ratio with PCDDs, PCDFs, PCDD/Fs and TEQ, S-compounds and N-compounds could have synergistic reaction on dioxin suppressions, which may be the reason for the better suppression effects for S-N inhibitors than S- or N-inhibitors.

The relationship between the (S + N)/Cl molar ratio and PCDD/Fs in fly ash is presented in Fig. 10. Similar with PCDD/Fs in flue gas, the (S + N)/Cl molar ratio correlates relatively well with PCDFs, PCDD/Fs and TEQ in fly ash ($r^2 = 0.70$, 0.70 and 0.70, respectively). Whereas PCDDs correlates slightly, yet positively with the (S + N)/Cl molar ratio, suggesting that S-N inhibitors could not suppress the formation of PCDDs effectively. The same r^2 values for PCDFs and TEQ indicates that PCDFs contribute most to TEQ, which is accordance with the congener distribution of PCDD/Fs. As to the S/Cl molar ratio, it correlates slightly with PCDFs, PCDD/Fs and TEQ. However, for PCDDs, the corresponding r^2 value is only 0.29. The PCDD-values in flue

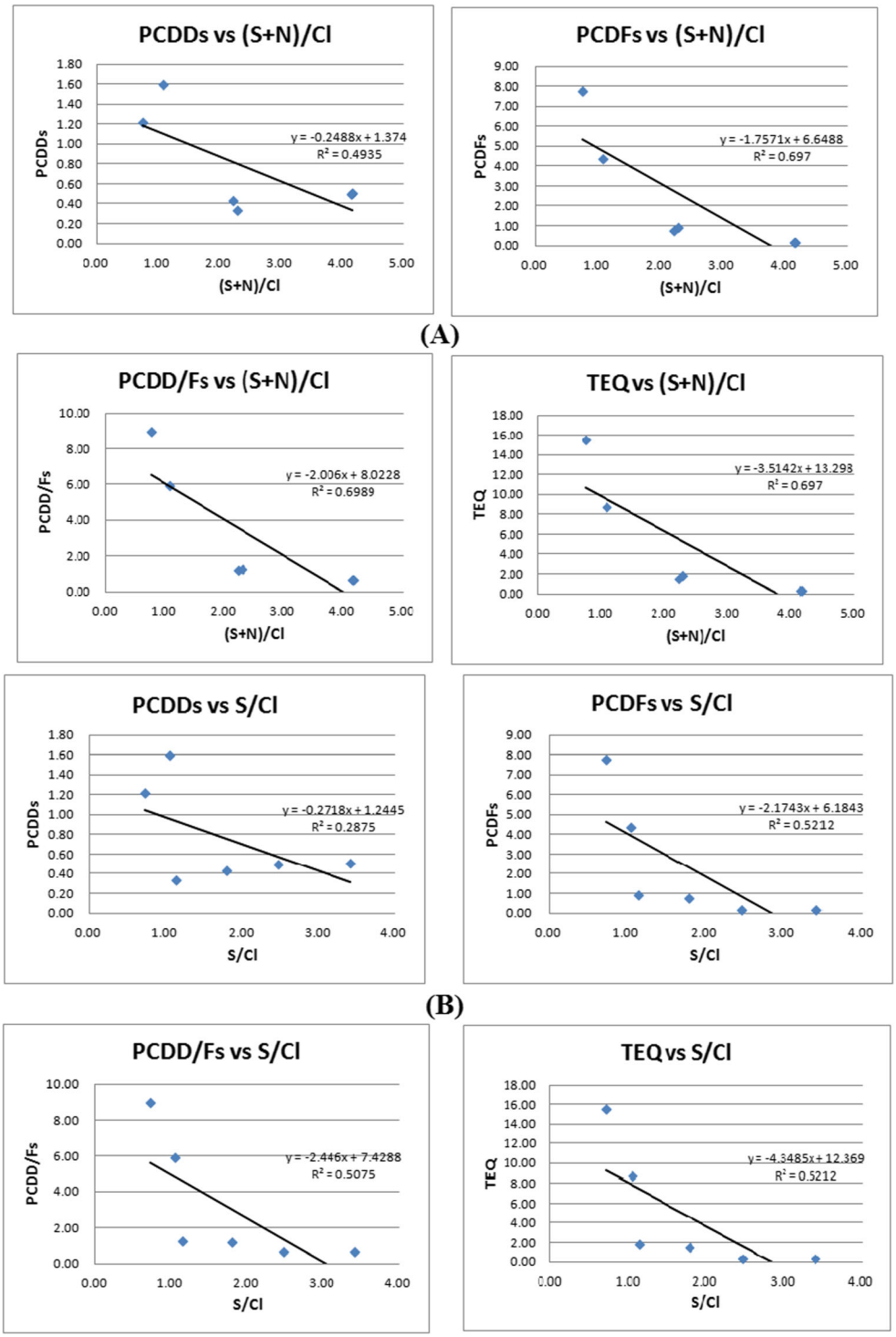

Fig. 10 The relationship between (S + N)/Cl molar ratio and PCDD/Fs in fly ash (*A*: (S + N)/Cl; *B*: S/Cl; *C*: N/Cl)

gas and fly ash refer to different suppression mechanism, while N-compounds are the dominant functional groups for PCDDs in fly ash. Considering the negative correlation between the S/Cl molar ratio and PCDDs it could not follow that the S/Cl molar ratio has no relationship with PCDDs in fly ash, since the desorption effect of PCDD/Fs in fly ash also occurs.

Conclusions

High suppression efficiencies of dioxins are achieved in this pilot-scale system by recirculating and accumulating the gaseous compounds emanating from decomposing S-N inhibitors. This system maintains high concentrations of suppressants in the flue gas so that it reduces PCDD/

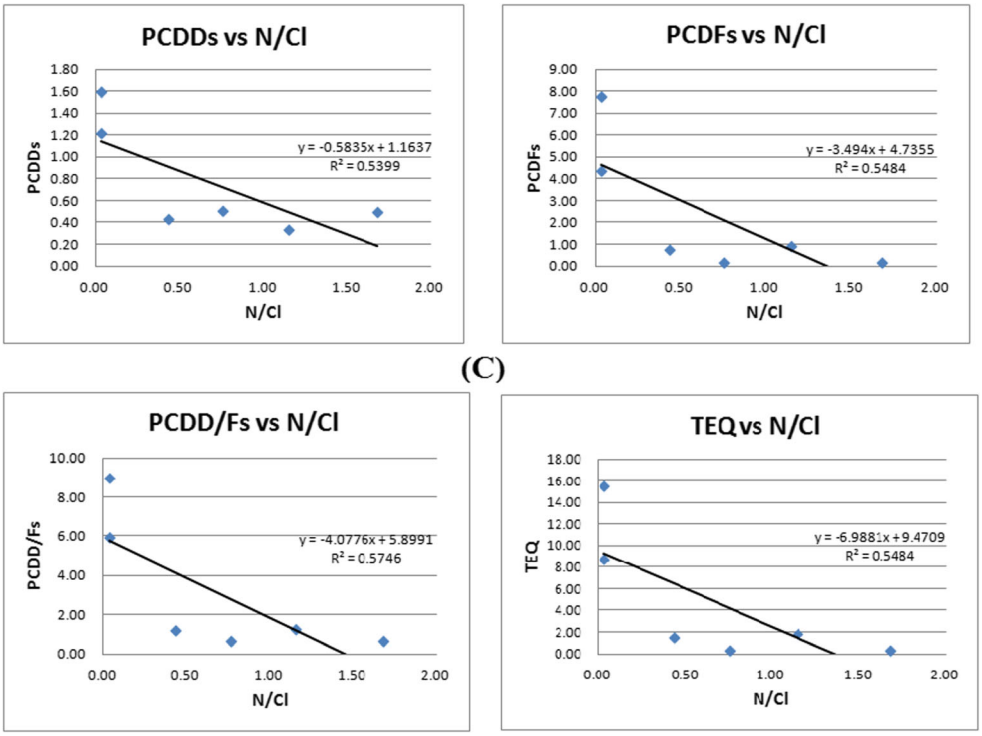

Fig. 10 (continued)

Fs effectively. With addition of thiourea, the value of (S + N)/Cl in flue gas almost doubled, from 2.23 to 4.18. As for the addition of SDG, the value (S + N)/Cl also amplified, from 2.29 to 4.15. However, these concentrations of SO_2, NH_3 and NO_x etc. all still remain below the national emission standard. By comparison and analysis, thiourea and SDG strongly suppress the formation of PCDD/Fs, even without the use of flue gas circulation, with I-TEQ reductions in flue gas of 85.2 and 80.3 %. Meanwhile, even higher suppression efficiencies could be obtained for dioxins in fly ash, with I-TEQ reductions of more than 92 %. After recirculating the flue gas, the suppression efficiencies of dioxins in flue gas could rise even to 93.6 and 90.8 % for thiourea and SDG, respectively. In terms of the congener distribution of dioxins, the fraction of high-chlorinated PCDD/Fs increased during the suppression tests, indicating that the dechlorination of higher chlorinated PCDD/Fs weakened. Most importantly, correlation analysis suggested that for S-N inhibitors the S-compounds play a more important role in dioxin suppression than N-compounds, and that the suppression mechanism might be different for dioxins in flue gas from that in fly ash.

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