



# Inhibition of PCDD/Fs in a full-scale hazardous waste incinerator by the quench tower coupled with inhibitors injection<sup>\*</sup>

Fengyu He, Yaqi Peng<sup>\*</sup>, Fei Wang, Yuhang Dong, Ken Chen, Shengyong Lu

*Institute for Thermal Power Engineering, Zhejiang University, Hangzhou, 310027, China*

## ARTICLE INFO

### Keywords:

Formation mechanism  
Hazardous waste incineration  
Inhibition  
PCDD/Fs  
Quench tower

## ABSTRACT

The control of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) from the flue gas in hazardous waste incinerators (HWIs) is an intractable problem. To figure out the formation mechanism of PCDD/Fs and reduce the emission, a field study was carried out in a full-scale HWI.  $\text{Ca}(\text{OH})_2$  &  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  or  $\text{CH}_4\text{N}_2\text{S}$  &  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  were injected into the quench tower, and the detailed inhibition effect on PCDD/Fs formation by the inhibitors coupled with quench tower was studied. Gas and ash samples were collected to analyze PCDD/Fs. XPS, EDS characterization and Principal component analysis were adopted to further analyze the de novo and precursors synthesis. The PCDD/Fs emissions reduced from 0.135 ng I-TEQ/ $\text{Nm}^3$  to 0.062 or 0.025 ng I-TEQ/ $\text{Nm}^3$  after the injection of  $\text{Ca}(\text{OH})_2$  &  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  or  $\text{CH}_4\text{N}_2\text{S}$  &  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ , respectively. The quench tower was found mainly hindering de novo synthesis by reducing reaction time. CP-route was the dominant formation pathway of PCDD/Fs in quench tower ash.  $\text{Ca}(\text{OH})_2$  &  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  effectively inhibit precursors synthesis and reduce proportions of organic chlorine from 4.11% to 2.86%.  $\text{CH}_4\text{N}_2\text{S}$  &  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  show good control effects on both de novo and precursors synthesis by reducing chlorine content and inhibiting metal-catalysts. Sulfur-containing inhibitors can cooperate well with the quench tower to inhibit PCDD/Fs formation and will be effective to reduce dioxins formation in high chlorine flue gas. The results pave the way for further industrial application of inhibition to reduce PCDD/Fs emissions in the HWIs flue gas.

## 1. Introduction

The rapid development of China has resulted in a dramatic rise in the production of hazardous waste. 80.74 million tons of hazardous waste were disposed in 2020 in China (Yearbook, 2021). Incineration technology has been widely applied to dispose hazardous waste. However, the incineration process will also result in the generation of various pollutants, especially polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs). PCDD/Fs are highly concerned due to the long biological half-life and extreme toxicity, and exposure to PCDD/Fs may cause headache, infertility and cancer (Bo et al., 2022). The main formation mechanisms of PCDD/Fs can be divided into: (1) de novo synthesis, (Kuzuhara and Kasai, 2003; Xu et al., 2018; Zhang and Buekens, 2016); (2) precursors synthesis, (Lomnicki and Dellinger, 2003; Sidhu et al., 1995). And the chlorination of DD/DF can also participate in the formation of PCDD/Fs (Tuppurainen et al., 2003).

Unlike municipal solid wastes with basic material components (fabrics, plastics, paper, kitchen residues, metal, glass), hazardous

wastes are identified due to their harm to the environment. Thus the phase, elemental composition and incineration characteristics of various hazardous wastes could be completely different in China, especially heavy metals and chlorine contents (Wang et al., 2019). The incineration of hazardous waste with high chlorine content can lead to great pressures on PCDD/Fs emission control. To meet the challenge of PCDD/Fs emissions in HWIs, quench tower is required (China, 2005), in which water was injected for rapid cooling from 500 °C to 200 °C within 1 s to reduce the reaction time for PCDD/Fs formation. Air pollution control devices such as quench tower and activated carbon injection coupled with baghouse filter are installed to reduce the emission of dioxins (Ma et al., 2011).

However, PCDD/Fs emissions of HWIs could still exceed the standard, which is 0.5 ng I-TEQ/ $\text{Nm}^3$  in China and 0.1 ng I-TEQ/ $\text{Nm}^3$  in Europe (China, 2020). Wang et al. studied the PCDD/Fs emission levels of 12 HWIs and found that the PCDD/Fs emission in stack gas was as high as 0.902 ng I-TEQ/ $\text{Nm}^3$  due to the high chlorine content in hazardous waste, and only PCDD/Fs emissions of 4 HWIs were lower than 0.1 ng I-TEQ/ $\text{Nm}^3$  (Wang et al., 2014). Gao et al. focused on the

<sup>\*</sup> This paper has been recommended for acceptance by Dr SU SHIUNG LAM.

<sup>\*</sup> Corresponding author.

E-mail address: [pengyaqi@zju.edu.cn](mailto:pengyaqi@zju.edu.cn) (Y. Peng).

### Nomenclature

PCDD/Fs	Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans
HWIs	Hazardous waste incinerators
MSWIs	Municipal solid waste incinerators
APCDs	Air pollution control devices
SEM	Scanning electron microscopy
EDS	Energy dispersive spectroscopy
XPS	X-ray photoelectron spectroscopy
QT	Quench tower
I-TEQ	International toxic equivalents
DD	Dibenzo-p-dioxins
DF	Dibenzofurans
CP	Chlorophenol
PCA	Principal component analysis
CR	Correlation coefficient
TCDD/Fs	Tetrachlorinated dibenzo-p-dioxins and dibenzofurans
PeCDD/Fs	Pentachlorinated dibenzo-p-dioxins and dibenzofurans
HxCDD/Fs	Hexachlorinated dibenzo-p-dioxins and dibenzofurans
HpCDD/Fs	Heptachlorinated dibenzo-p-dioxins and dibenzofurans
OCDD/Fs	Octachlorinated dibenzo-p-dioxins and dibenzofurans

PCDD/Fs emissions of 14 HWIs and also found a large variation (from 0.08 to 31.6 ng I-TEQ/Nm<sup>3</sup>) (Gao et al., 2009). Moreover, PCDD/Fs emissions in HWIs during startup and shutdown were significantly higher than normal conditions (Li et al., 2017). Existing investigations show that HWIs in China struggled to control PCDD/Fs emissions, and most of them failed to achieve the strict standards of Europe (0.1 ng I-TEQ/Nm<sup>3</sup>). All of these call for more measures to effectively control PCDD/Fs emissions in HWIs.

Chemical inhibition technology is an effective method to reduce PCDD/Fs formation, which has been widely studied in laboratory and adopted in municipal solid waste incinerators (MSWIs) (Moreno et al., 2019; Ren et al., 2021a; Xing et al., 2019). Some former studies adopted inhibitors in field MSWIs, and the inhibition efficiencies were about 40%–70% (Chen et al., 2019; Ren et al., 2021a). Three categories of inhibitors have been developed so far: sulfur-containing compounds (Chen et al., 2019; Shao et al., 2010), nitrogen-containing compounds (Ren et al., 2021b; Wang et al., 2020) and hydroxides/oxides of alkali metals (Qian et al., 2005; Zhang et al., 2020). Sulfur- and nitrogen-containing inhibitors can hinder PCDD/Fs formations by inhibiting catalyst metal and chlorination, and oxides/hydroxides of alkali metals show good inhibition effects on chlorine source (Ma et al., 2018). Phosphorus-containing compounds are considered as inhibitors due to the reactions with heavy metals to form complexes (Lu et al., 2021; Ma et al., 2019). While inhibition effects and mechanisms of inhibitors in HWIs can be different from that in MSWIs due to differences in incineration materials and operating conditions, flue gas composition, temperature distribution and flue humidity.

Previous studies on HWIs only reported and analyzed PCDD/Fs emission in the stack gas and fly ash, ignoring the formation and migration mechanism. Specially, effects of quench tower on PCDD/Fs formation need to be further figured out. In addition, most of these inhibition studies focus on laboratory experiments, and the full-scale inhibition experiment focusing on the incineration of hazardous waste is lacking (Isabel et al., 2019; Soler et al., 2018). In this study, two chemical inhibitors were chosen to cooperate with quench tower for further PCDD/Fs inhibition in HWIs, and the inhibition mechanism was studied. Rather than simply clarify formation mechanisms by stack gas

samples, this study analyzed two main mechanisms (de novo and precursors synthesis) in full-scale HWIs. This study figured out the inhibition of PCDD/Fs by the quench tower coupled with inhibitors injection for low PCDD/Fs emission in HWIs, which is helpful for industrial application of further emission control of PCDD/Fs in HWIs.

## 2. Materials and methods

### 2.1. HWI systems and characteristics of hazardous waste

This study was carried out in a full-scale HWI with a capacity of 80 t/d located in Shandong Province, China. The systemic diagram and sampling sites of the HWI are shown in Fig. 1. The hazardous waste in the waste pool and hazardous waste in SMP (Shredding, Mixing and Pumping) system were fed into the rotary kiln with an average rate of 50 t/d and 30 t/d, respectively. The HWI system was operated under the principle of “3T+E”: high combustion Temperature, long residence Time, high Reynolds number of Turbulence and Excess oxygen (McKay, 2002). After the secondary combustion chamber, flue gas was cooled from 1100 °C to 500 °C in cooling tower. In the quench tower, weakly alkaline wet deacidification wastewater was directly injected into flue gas, leading to the rapid cooling of flue gas from 500 °C to 200 °C. Then dry deacidification, activated carbon injection coupled with baghouse filtration (ACI+BF) and wet deacidification scrubber are applied before the emission of stack gas. The discharging rates of fly ash and quench tower ash are 6000 kg/d and 200 kg/d respectively. The characteristics of hazardous waste are shown in Table S1. It can be seen that there is a high content of chlorine (up to 10 wt%) in hazardous waste raw materials, which provides a probability for large-scale synthesis of PCDD/Fs in flue gas at low temperature. Operation conditions and emissions of conventional pollutants (including oxygen) are shown in Fig. S1 and Fig. S2. And the concentrations of metals in ash are shown in Table S4.

### 2.2. Experimental design

Carbon source, chlorine source, metal catalyst, temperature and reaction time are the main factors of PCDD/Fs formation, while the quench tower can only hinder PCDD/Fs formation by reducing reaction time (Stanmore, 2004). To further inhibit dioxin emission, the inhibitors were adopted and injected into the flue gas to cooperate with the quench tower. As shown in Fig. 1, four sampling points were adopted for this field study: flue gas at quench tower outlet, quench tower ash, bag filter fly ash and stack gas. In blank test A, four points were sampled without inhibitors injection. In test B and test C, mixtures of Ca(OH)<sub>2</sub>/(NH<sub>4</sub>)<sub>2</sub>H<sub>2</sub>PO<sub>4</sub> and CH<sub>4</sub>N<sub>2</sub>S/(NH<sub>4</sub>)<sub>2</sub>H<sub>2</sub>PO<sub>4</sub> were adopted as inhibitors respectively. Inhibitors with a rate of 15 kg/h (weight ratio of 0.45% of 80 t/d hazardous waste materials) were added. About 4 m<sup>3</sup> of wastewater was sprayed into the quench tower every hour. The details about inhibition conditions are shown in Fig. S3. And the experimental operation conditions are shown in Table S2.

### 2.3. Sampling, analyzing and QA/QC

To collect PCDD/Fs samples in the flue gas and stack gas, the isokinetic samplers (model KNJ23, KNJ, Korea) were adopted following EPA Method 23a (Agency, 2017).

Before the sampling process, PCDD/Fs surrogate standards were added to the XAD-2 resin. For pretreatment, dioxins were firstly Soxhlet extracted with toluene for 24h. Prior to extraction, samples were spiked with <sup>13</sup>C labeled compound solution of PCDD/Fs. The extracts were then purified with a series of clean-up procedures to remove the heavy metals and other impurities. The solutions were concentrated by a purified nitrogen flow to 30 μl and spiked with <sup>13</sup>C recovery standard solutions. The sampling and pretreatment processes were described in detail in **supplement information**, and in our previous research (Chen et al., 2008). The purified samples were analyzed by high-resolution gas

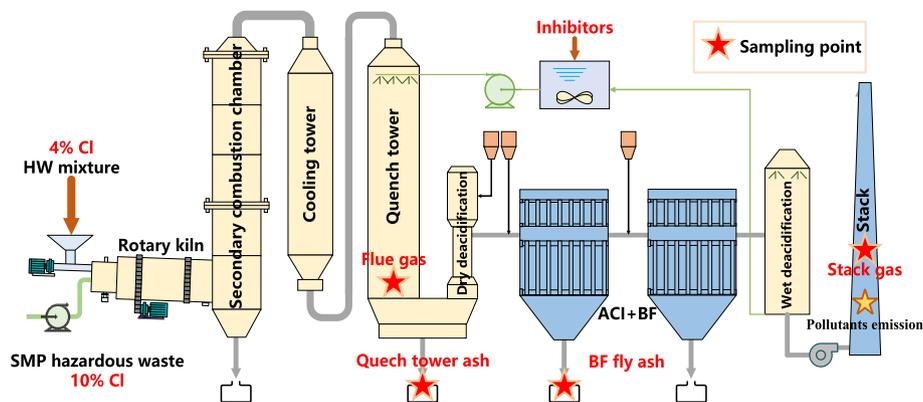


Fig. 1. Systemic diagram and sampling sites of the HWI.

chromatography coupled with high-resolution mass spectrometry (HRGC/HRMS) (JMS-800D, JEOL, Japan).

In the quality assurance and quality control (QA/QC) testing, the recoveries of all PCDD/Fs standards in gas samples and ash samples range from 47.6% to 125.9%, which were in accordance with the required recovery standard of 25%–130%. The stability of hazardous waste feeding and operation conditions was verified in Fig. S1, Fig. S2 and Table S4. Between each group of experiments, a half-hour interval was reserved for the buffer time of the next experiment. Inhibitors were added into the tank, as shown in Fig. S3. To ensure that there is no interference between different test groups, the liquid tank was emptied every 4 h, and filled up before the next experiment group. Three parallel samples were collected in each test and the average as the final result. The detailed description was shown in **supplement information**.

#### 2.4. Statistical analysis

In this study, 136 tetra- to octa-PCDD/Fs congeners were separated and analyzed. The mass concentrations were converted to values under the standard condition of 1 atm and 0 °C and corrected referring to an 11% oxygen content, according to:

$$C = \frac{21 - 11}{21 - O_A} \times C_A$$

$C$ , the PCDD/F mass concentration under the standard condition ( $\text{ng}/\text{Nm}^3$ );  $O_A$ , the action oxygen content (%);  $C_A$ , the actual PCDD/F mass concentration in the flue gas ( $\text{ng}/\text{m}^3$ ).

For the 17 toxic 2,3,7,8-substituted congeners, international toxic equivalents (I-TEQ) were obtained according to the toxic equivalency factors (VandenBerg et al., 1998), and the total TEQ of the 17 toxic PCDD/F congeners was calculated:

$$C_{TEQ} = \sum C_i \times TEQ_i$$

$C_i$ , the concentration of each PCDD/Fs congener;  $TEQ_i$ , the TEQ values of each PCDD/Fs congener;  $C_{TEQ}$ , the overall TEQ values of each sample.

The inhibition efficiency of inhibitors and chlorination degree were calculated as follows:

$$\text{Inhibition efficiency} = \frac{C_N - C_I}{C_N}$$

$C_N$ , the concentration of PCDD/Fs congeners in normal conditions;  $C_I$ , the concentration of PCDD/Fs congeners in inhibition conditions.

$$\text{Chlorination degree} = \frac{\sum C_i \times n_i}{C}$$

$C_i$ , the concentration of each PCDD/Fs congener;  $n_i$ , the number of substituted chlorines in each PCDD/Fs congener;  $C$ , the overall concen-

tration of PCDD/Fs congeners.

In order to further analyze the formation and inhibition pathways in this HWI, principal component analysis (PCA) and correlation analysis were applied using SPSS 24 software based on the congeners distributions.

Moreover, to better study the characteristics of ash and analyze the de novo synthesis comprehensively, scanning electron microscopy (SEM, Sigma300, ZEISS, Germany), energy dispersive spectroscopy (EDS, Sigma300, ZEISS, Germany) and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, America) were adopted to analyze element distribution, surface morphology, surface element content, and surface element chemical states of ash, respectively.

### 3. Results and discussion

#### 3.1. PCDD/Fs concentrations under different conditions

The PCDD/Fs concentrations from three sampling points (flue gas, stack gas, fly ash) under different conditions are shown in Fig. 2. In test A without inhibition, the PCDD/Fs concentration in stack gas was  $6.64 \text{ ng}/\text{Nm}^3$  ( $0.135 \text{ ng I-TEQ}/\text{Nm}^3$ ). The emission levels in test A achieved the emission standard in China ( $0.5 \text{ ng I-TEQ}/\text{Nm}^3$ ) (China, 2020), but exceeded the EU emission standard ( $0.1 \text{ ng I-TEQ}/\text{Nm}^3$ ). The total concentration of PCDD/Fs at the quench tower outlet was  $8.83 \text{ ng}/\text{Nm}^3$  ( $0.173 \text{ ng I-TEQ}/\text{Nm}^3$ ), and the PCDD/Fs concentration in fly ash was  $3.86 \text{ ng}/\text{g}$  ( $0.074 \text{ ng I-TEQ}/\text{g}$ ). For test B, the PCDD/Fs concentration in stack gas decreased to  $4.84 \text{ ng}/\text{Nm}^3$  ( $0.062 \text{ ng I-TEQ}/\text{Nm}^3$ ). While the PCDD/Fs concentration at the quench tower outlet was  $13.2 \text{ ng}/\text{Nm}^3$  ( $0.248 \text{ ng I-TEQ}/\text{Nm}^3$ ), and the PCDD/Fs concentration in fly ash was  $8.03 \text{ ng}/\text{g}$  ( $0.168 \text{ ng I-TEQ}/\text{g}$ ). The increase of PCDD/Fs concentration in quench tower outlet in test B was resulted from the increase of PCDFs due to the bad control effect on oxidation process despite the good control on chlorine source, which will be discussed later and shown in Fig. 5 and Fig. 7. Oxidation process could result in the release of CO, CO<sub>2</sub> and few PCDD/Fs at the same time. A laboratory research also found that the alkali metal oxide/hydroxide could promote carbon gasification (Wang et al., 2022).

Inhibitor C showed a better effect and markedly reduced the emission of PCDD/Fs. Compared with normal condition, the PCDD/Fs concentration in stack gas has been reduced to  $2.69 \text{ ng}/\text{Nm}^3$  ( $0.025 \text{ ng I-TEQ}/\text{Nm}^3$ ) with an inhibition efficiency of 59.4% (81.7% for I-TEQ) in test C. The PCDD/Fs concentrations in flue gas and fly ash decreased to  $1.91 \text{ ng}/\text{Nm}^3$  ( $0.049 \text{ ng I-TEQ}/\text{Nm}^3$ ) and  $2.24 \text{ ng}/\text{g}$  ( $0.025 \text{ ng I-TEQ}/\text{g}$ ) respectively. Sulfur-containing inhibitors show a good potential on cooperating with quench tower to control PCDD/Fs emission during hazardous waste incineration.

The previous study on 12 HWIs has found that the emissions of PCDD/Fs in HWIs ranged from  $0.031 \text{ ng I-TEQ}/\text{Nm}^3$  to  $0.902 \text{ ng I-TEQ}/\text{Nm}^3$  (Wang et al., 2014). And the emission levels of the three

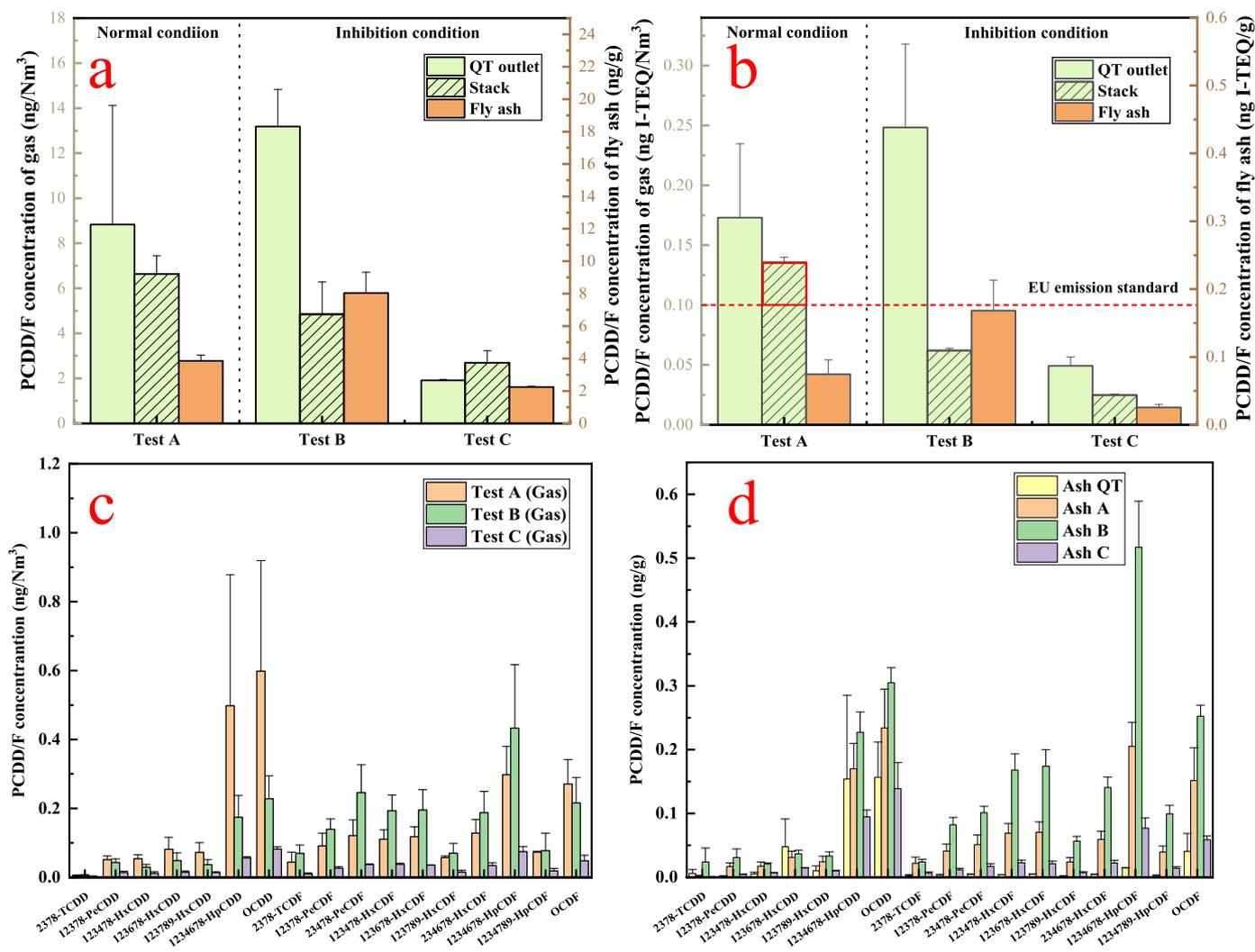


Fig. 2. (a) Total PCDD/Fs concentrations under different conditions (b) PCDD/Fs concentrations (I-TEQ) (c) Concentration of toxic PCDD/Fs congeners in flue gas (d) Concentration of toxic PCDD/Fs congeners in fly ash and quench tower ash.

experimental groups in this work were within the scope. The concentrations of 17 toxic PCDD/Fs congeners in flue gas and ash were shown in Fig. 2c and d. PCDD/Fs in quench tower ash was dominated by high chlorinated PCDDs. Similarly, the injection of inhibitor C caused an obvious decrease of toxic PCDD/Fs congeners, and inhibitor B had a good inhibition effect on PCDD congeners in flue gas. The percentage distributions of all PCDF and PCDD congeners in flue gas and ash are shown in Fig. S4 and Fig. S5, which will be discussed in section 3.3.2.

### 3.2. PCDD/Fs congener distribution and chlorination degree in flue gas and ash

In the post-combustion zone PCDD/Fs are mainly formed in low-temperature (500–200 °C) through heterogeneous reactions, which can be divided into: (1) de novo synthesis, PCDD/Fs formed by simultaneous chlorination and oxidation from carbonaceous matrix, (2) precursors synthesis, PCDD/Fs formed from structurally similar compounds, through catalytic coupling of precursor molecules or radicals (Babushok and Tsang, 2003; Gullett et al., 1994; Stanmore, 2004). Importantly, PCDDs is mainly formed by precursors synthesis such as CP-route, and de novo synthesis from carbon matrix prefers to form PCDFs (Huang and Buekens, 1995; Stanmore, 2004; Weber and Hagenmaier, 1999). Thus, the PCDD/PCDF ratio is generally lower than 1 when de novo synthesis dominates, while the ratio is higher than 1 if precursors synthesis is the major formation pathway (Tuppurainen

et al., 1998; Zhang et al., 2012).

The previous studies found the proportional advantage of PCDF over PCDD in stack gas in HWIs, and regarded de novo synthesis as the main formation mechanism (Wang et al., 2019; Wang et al., 2014). While the distribution of PCDD/Fs congeners could remarkably change after a series of air pollution control devices. As shown in Fig. 3, most PCDD/PCDF ratios in fly ash were lower than 1, indicating that de novo synthesis was the main formation mechanism in HWI systems. While in test A the PCDD/PCDF ratios of flue gas at quench tower outlet and quench tower ash were 1.04 and 4.58. The proportional advantage of PCDD over PCDF in both flue gas and quench tower ash indicates that the precursors synthesis is the main formation pathway in quench tower section. Similar result of PCDD/PCDF ratios in flue gas at quench tower outlet has been observed in another study on HWI system (Wang et al., 2019).

In many MSWIs, de novo synthesis was considered to be main formation mechanism because of the higher proportions of PCDFs over PCDDs in flue gas or stack gas (Guo et al., 2020). The ratio differences between MSWIs and HWI could be resulted from the effect of quench tower and abundance of chlorine. In previous studies, the reaction rate of de novo synthesis is considered in the order of seconds, and the rate of de novo synthesis is much lower compared with that of precursor synthesis (Altwickler and Milligan, 1993; Milligan and Altwickler, 1995; Stanmore, 2004). Thus the quench tower would mainly suppress the de novo mechanism because of the reduction of reaction time (within 1 s) in

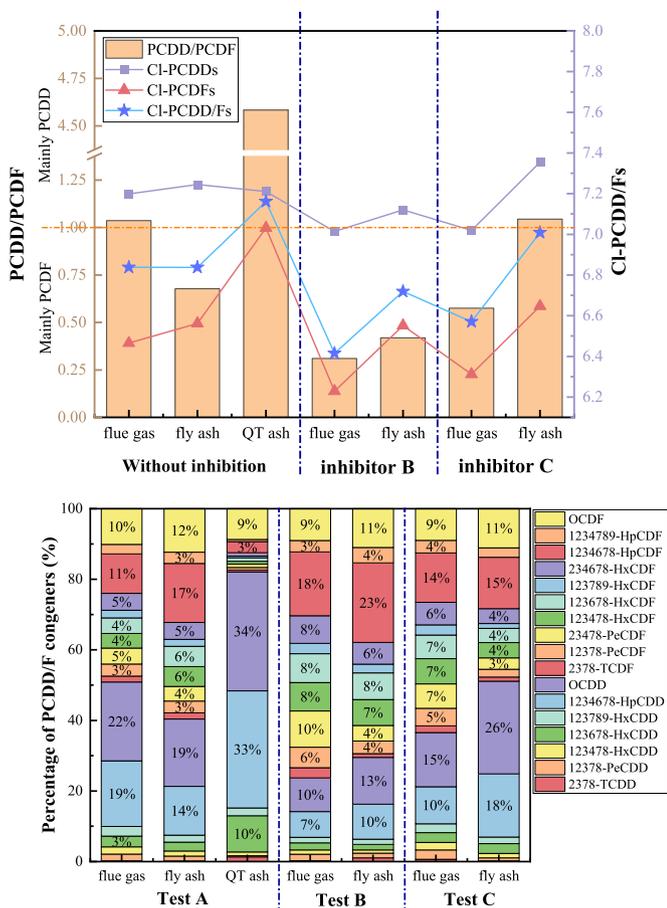


Fig. 3. Distribution and chlorination degree of toxic PCDD/Fs.

the section of 500–200 °C. There would be a huge potential for PCDF formation by de novo synthesis if the quench tower does not work well. While the precursors synthesis was not greatly affected by the quench tower because by precursors synthesis PCDD/Fs can be formed rapidly (Pulido et al., 2016). In test B, the ratios of PCDD/PCDF in flue gas and fly ash decrease to 0.31 and 0.42 compared with test A. For test C, inhibitor C better inhibits PCDD than PCDF in flue gas and better inhibits PCDF in fly ash. Detailed discussion for inhibition efficiency is displayed in section 3.3.1.

The chlorination degree of PCDD/Fs is an important factor to study the influence of chlorine source in PCDD/Fs formation. As shown in Fig. 3, inhibitor B and inhibitor C effectively reduced the chlorination degree of PCDD/Fs in flue gas from 6.84 to 6.41 and to 6.57, respectively. Compared with inhibitor C, inhibitor B shows a better effect on the reduction of chlorination degree of fly ash, which could be attributed to the alkali metal hydroxide in inhibitor B (Ma et al., 2018). It is worth mentioning that the chlorination degree of PCDD/Fs in quench tower ash was the highest among all samples, reaching 7.15. Due to the better adsorption of higher chlorinated PCDD/Fs with lower vapor pressure, the chlorination degree values in fly ash are higher than the values in quench tower flue gas (Ryan et al., 2005). And the chlorination degrees of PCDDs were higher than those of PCDFs. Compared with the studies on full scale MSWI systems, the chlorination degree of PCDD/Fs in the HWI is higher, which indicates the abundance of chlorine source (Chen et al., 2019; Ma et al., 2021).

2,3,7,8- substituted congeners are the most concerned toxic PCDD/Fs among all the congeners, and Fig. 3 shows the percentage distribution of toxic PCDD/Fs congeners. For flue gas and fly ash, the major toxic PCDD/Fs congeners are 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF and OCDF. In test B, the proportion of low chlorinated PCDD/

Fs increases obviously for flue gas and fly ash. For quench tower ash, more than 80% of PCDD/Fs was high chlorinated except 2,3,7,8-TCDD. The dominance of OCDD congener indicated the excessive chlorination conditions in HWIs due to the high chlorine content in hazardous waste.

### 3.3. Formation and inhibition mechanisms of PCDD/Fs in HWI

#### 3.3.1. Inhibition efficiency in flue gas and fly ash

Fig. 4 shows the inhibition efficiency of PCDD/Fs in flue gas and fly ash. Two inhibitors showed distinct inhibition effect due to the difference of inhibition mechanism. For inhibitor B, the inhibition efficiencies in flue gas increased with the increase of chlorination degree. The variety of inhibition efficiencies indicates the good control on chlorine source by Ca(OH)<sub>2</sub>, which is consistent with the former study (Gullett et al., 1994). The injection of inhibitor B caused the decrease of PCDD and total toxic PCDD/Fs in flue gas by 58.3% and 10.4%, and finally reduced the PCDD/Fs emission at stack. But the PCDF in flue gas and PCDD/Fs in fly ash increased.

The increase of PCDD/Fs in fly ash in test B could be attributed to two reasons: (1) memory effect in APCDs cause the increase of PCDD/Fs concentration, then activated carbon adsorbs PCDD/Fs into bag filter fly ash (Zimmermann et al., 2001); (2) the injection of inhibitor B weakens the effect of quench tower due to the exothermic reaction with the chlorine source, resulting in the abundance of PCDF by de novo synthesis. The discussion about de novo synthesis and PCDF is displayed in section 3.3.3. A field study on HWIs also found an obvious increase of PCDD/Fs concentration in quench tower outlet mainly due to the abundance of PCDF (Wang et al., 2019).

Inhibitor C showed a better and more stable inhibition effect compared with inhibitor B. The PCDD/Fs inhibition effect in flue gas samples (80.0%) is better than that in fly ash samples (59.3%). This phenomenon was consistent with an S-, P-, and N-containing inhibition study on MSWIs (Guo et al., 2020). The differences in inhibition effects were induced by that the inhibitors reacted more readily with chlorine in flue gas than catalytic metals in fly ash. In addition, the migration of PCDD/Fs, which tends to adsorb on the surface of the fly ash, impaired the inhibition efficiency.

Catalyst metal plays an important role in deacon reaction, de novo synthesis and precursors synthesis (Olie et al., 1998). The overall good inhibition efficiencies for PCDDs and PCDFs indicated that inhibitor C can poison catalyst metal. The sulfur-containing substances could play the key role. Laboratory studies show that sulfur can convert copper chloride (CuCl<sub>2</sub>) into copper sulfate (CuSO<sub>4</sub>) with weak catalytic activity, thus inhibiting de novo synthesis and precursors synthesis (Fujimori et al., 2016; Raghunathan and Gullett, 1996).

#### 3.3.2. Precursors synthesis and chlorination process

Fig. 5 shows the formation mechanisms of precursor synthesis. One of the representative mechanisms of precursors synthesis is CP-route synthesis, and PCDD/Fs can be formed by condensation of rearrangement of three kinds of CPs (2,4,6-, 2,3,4,6- and 2,3,4,5,6- Chlorophenol) (Ballschmitter et al., 1988). Phenoxy radicals are important intermediates in CP-route pathway (Yang et al., 2017). These CPs can directly form 1,3,6,8-, 1,3,7,9-TCDD and 2,4,6,8-, 1,2,3,8-TCDF, which are considered to be the representatives of CP-route (Wiater et al., 2000; Yang et al., 2017). 1,2,4,7,9-, 1,2,3,6,8-, 1,2,3,7,9-PeCDD and 1,2,3,4,6,8-HxCDD are also considered as the CP-route representatives due to their highly correlation with 1,3,6,8-, 1,3,7,9-TCDD (Tuppurainen et al., 2003; Zhang et al., 2017). The relative importance of CP-route representatives compared with their own homologues and total PCDD/Fs was shown in Table 1. For quench tower ash, the CP-route representatives were dominant in their own homologue groups at PCDD side, and the overall proportion of CP-route congeners in the total PCDD/Fs concentration reached 76.5%. Combined with the former discussion of PCDD/PCDF ratios, these results indicated that the main formation

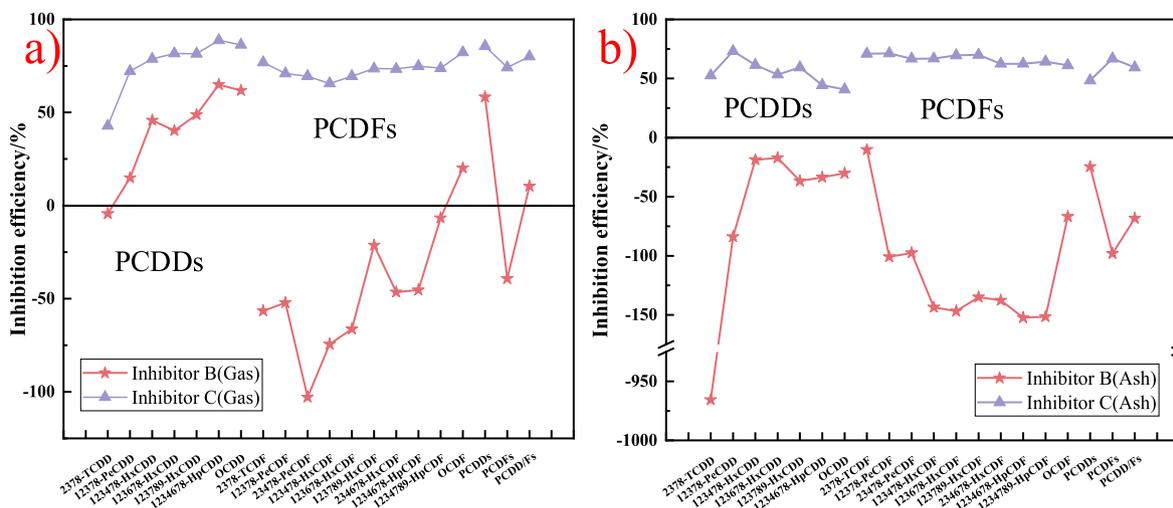


Fig. 4. (a)Inhibition efficiency of toxic PCDD/Fs congeners in flue gas of quench tower outlet (b) Inhibition efficiency of toxic PCDD/Fs congeners in fly ash.

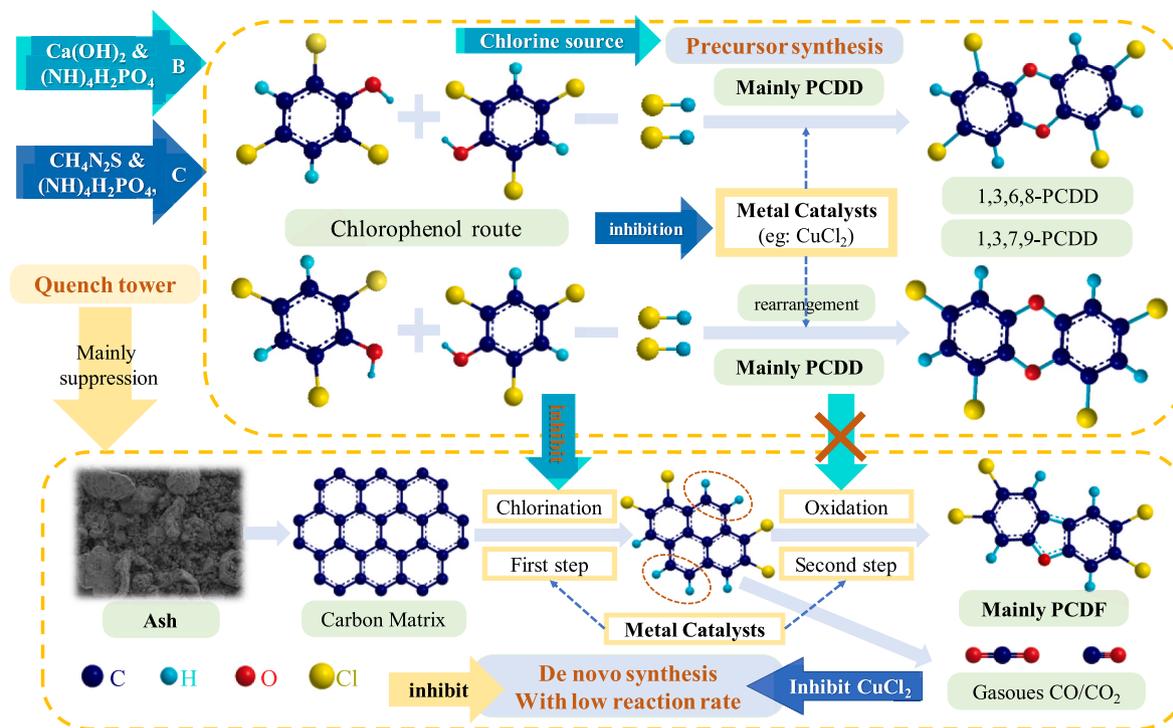


Fig. 5. Formation mechanisms and inhibition effect of inhibitors and quench tower.

mechanism in quench tower section was precursors synthesis, especially CP-route pathway. Compared with test A, the proportion of CP-route representatives decreased from 22.94% to 25.20%–13.73% and 16.21% respectively in test B. This indicated that inhibitor B has a better inhibition effect on CP-route synthesis. For test C, the proportion of CP-route representatives slightly decrease in flue gas, and increase in fly ash.

The PCDD/Fs congeners were also analyzed by PCA and correlation coefficients based on the distributions in both inhibition and normal conditions. Table S5 shows the correlation coefficients (CR) between 1,3,7,9-TCDD (1,3,6,8-TCDD) and the other PCDDs congeners based on the distribution data. Six CP-route representatives (1,3,6,8-, 1,3,7,9-TCDD, 1,2,4,7,9-, 1,2,3,6,8-, 1,2,3,7,9-PeCDD and 1,2,3,4,6,8-HxCDD) mentioned above appear CRs higher than 0.92 with 1,3,7,9-TCDD, which clearly indicates the pathways of CP-route. Results of CRs

obtained in this HWI are consistent with the studies in laboratory and MSWIs (Wang, P.Y. et al., 2020; Zhang et al., 2017). Interestingly, 1,2,3,4,7-PeCDD and 1,2,3,6,7,9-HxCDD also show a correlation with two TCDDs, which may be originated from the further reactions of 1,3,7,9-TCDD. This phenomenon was also observed in the PCA results.

Fig. 6 shows the PCA loading plot of all PCDD/Fs congeners and individual groups. Two factors explained 82.2% of the total variance for total PCDD/Fs congeners (96.6% for TCDDs, 88.5% for PeCDDs, 85.6% for HxCDD and 93.2% for PCDFs). In Fig. 6a, The CP-route representatives (red-marked) were closely distributed in the lower left quadrant due to high correlations. Consistent with the previous research, separations of CP-route congeners from other congeners were observed in Fig. 6b and c (Zhan et al., 2019; Zhang et al., 2017). And part of PCDDs congeners clustered in group B. Most PCDFs congeners were distributed in group C, which indicates the differences between de novo synthesis

**Table 1**  
Relative importance of CP-route congeners and 2,3,7,8-substituted congeners.

Congeners	Test A		Test B		Test C		Quench tower
	Gas	Ash	Gas	Ash	Gas	Ash	Ash
<b>CP-route congeners</b>							
<b>Proportion in their own homologues (%)</b>							
1,3,6,8-TCDD	45.2	58.4	42.7	20.6	46.7	63.0	60.9
1,3,7,9-TCDD	23.8	21.0	24.4	10.6	25.5	23.8	35.7
1,2,4,7,9-PeCDD	32.5	30.8	33.9	31.0	33.9	28.9	18.9
1,2,3,6,8-PeCDD	26.2	30.1	23.7	28.3	26.3	33.6	47.8
1,2,3,7,9-PeCDD	19.3	20.8	16.5	20.8	18.5	24.7	28.6
1,2,3,4,6,8-HxCDD	62.5	65.9	52.2	65.9	57.0	74.8	80.6
2,4,6,8-TCDF	3.77	3.82	4.35	2.48	3.49	5.84	5.95
1,2,3,8-TCDF	17.3	10.6	10.4	9.85	12.4	13.2	21.6
<b>Proportion of CP-route congeners in the total concentration of PCDD/Fs (%)</b>							
PCDD/F	22.94	25.20	13.73	16.21	21.05	40.39	76.5
<b>2,3,7,8-substituted PCDD/Fs congeners</b>							
<b>Proportion of 2,3,7,8-substituted PCDD/Fs in PCDD or PCDF (%)</b>							
PCDD	15.4	12.0	4.97	8.29	10.0	12.1	9.37
PCDF	17.6	21.6	19.3	23.6	21.0	13.5	0.90
<b>Proportion of 2,3,7,8-substituted PCDD/Fs in the total concentration of PCDD/Fs (%)</b>							
PCDD/F	33.0	33.6	24.3	31.9	31.0	25.6	10.3

and CP-route synthesis, and different formation pathways between PCDFs and PCDDs (Altarawneh et al., 2009).

The previous study figured out that the chlorination of DF/DD was strongly favored at lateral sites, and the congeners substituted by chlorine at 2,3,7,8 positions are the main products (Ryu et al., 2003). And a preferred substituted sequence (2 → 8 → 3 → 7 → 1 → 4 → 6 → 9) was found in the chlorination process of DD/DF (Luijk et al., 1992). Zhao et al. also found a sequence (1 → 4 → 6 → 9) with lower Gibbs free energy for chlorination of 2,3,7,8-PCDFs (Zhao et al., 2017). Table 1 summarized the proportion of 2,3,7,8-substituted PCDD/Fs in the total PCDD/Fs congeners. For quench tower ash, the low proportion (10.3%) indicated that the chlorination of DD/DF does not greatly influence PCDD/Fs formation in quench tower ash. And both the injection of inhibitor B or inhibitor C slightly decreased the proportion.

### 3.3.3. De novo synthesis and characteristics of ash

Ash is an important medium for PCDD/Fs formation, especially for de novo synthesis (Chen et al., 2014). The study on the characteristics of ash can help to further research de novo synthesis and inhibition mechanism in HWI. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were adopted to analyze element distribution, surface morphology, surface element content, and surface element chemical states of ash, respectively.

SEM showed that the particle size of quench tower ash is markedly larger than that of bag filter fly ash, and the particle size of fly ash increased after the injection of inhibitors (Fig. S6). Similar results of fly ash were found in the inhibitors injection field studies on MSWIs (Guo et al., 2020). The surface element content of chlorine in quench tower ash was highest among these samples (23.53%) by EDS. And the surface chlorine content in fly ash decreased from 19.93 wt% to 18.09 wt% and to 13.76 wt% in test B and test C. Inhibitor C shows better control effects on surface chlorine content.

As shown in Fig. 7c, carbon source and chlorine source are two key factors for de novo synthesis, and the formation of PCDD/Fs could change the proportions of organic chlorine and oxidized carbon. Fig. 7 shows the XPS analysis results of C and Cl, based on the information in Avantage software, aiming to study the chemical states of ashes and the influence of de novo synthesis by inhibitors. The formation of PCDD/Fs (mainly PCDF) from unburned carbon matrix in ashes was identified as de novo synthesis (Huang and Buekens, 1995; Stanmore, 2004). De novo synthesis can be mainly divided into two steps: (1) Chlorine is transferred from metal chloride to carbon matrix (organic Cl); (2) Chlorinated

carbon matrix is oxidized, releasing CO, CO<sub>2</sub> and few PCDD/Fs at the same time (Stieglitz et al., 1997; Stieglitz et al., 1993).

Focusing on the first step, the Cl 2p spectra is divided into four peaks as: metal Cl 2p<sub>3/2</sub>, metal Cl 2p<sub>1/2</sub>, organic Cl 2p<sub>3/2</sub> and organic Cl 2p<sub>1/2</sub>. Metal chlorine dominates in every sample (from 94.08% to 97.14%). Inhibitor B successfully decreased the proportion of organic chlorine from 4.11% to 2.86%. Inhibitor C slightly increased the proportion of organic chlorine to 4.29%. The results show that inhibitor B and inhibitor C hindered the chlorination process by reducing proportions of organic chlorine and reducing surface chlorine content, respectively. The proportion of organic chlorine in quench tower ash was the highest (5.92%) due to the abundance of chlorine source.

Focusing on the second step, the C 1s spectra is divided into three peaks as: C–C/phenyl, C=O/COOR and C–O/C–O–C, and the carbon in the surface of fly ash was mainly organic. The oxygen reaction of carbon matrix to form PCDD/Fs was found leading to the escape of gaseous CO and CO<sub>2</sub> from fly ash (Schwarz and Stieglitz, 1992). The utilization rate of carbon source was limited, and the main part was lost in the form of CO and CO<sub>2</sub> (Wikstrom et al., 2003). Thus this process could lead to a decrease of proportions of oxidized carbon in fly ash. Interestingly, both the highest and lowest values were found in inhibition conditions, which may explain the distinct difference of inhibition efficiencies on PCDFs. Inhibitor C increased the proportion of oxidized carbon from 15.05% to 19.12%, which means that more oxidized carbon was intercepted in fly ash without further reaction to form gaseous carbon (CO/CO<sub>2</sub>) and PCDD/Fs. In laboratory research, thiourea was found delaying the release of CO, and reducing the emission of PCDD/Fs, which is consistent with this study (Fu et al., 2015). While inhibitor B decreased the proportion of oxidized carbon from 15.05% to 14.43%. Compared with normal condition, inhibitor B accelerated the oxidation process, and more dioxin dominated by PCDF is generated despite the good control of chlorine source.

## 4. Conclusions

In this study, flue gas at quench tower outlet, quench tower ash, fly ash and flue gas in stack were sampled, and inhibitors (Ca(OH)<sub>2</sub> & (NH<sub>4</sub>)<sub>2</sub>H<sub>2</sub>PO<sub>4</sub>; CH<sub>4</sub>N<sub>2</sub>S & (NH<sub>4</sub>)<sub>2</sub>H<sub>2</sub>PO<sub>4</sub>) were injected into the flue gas to cooperate with the quench tower for further inhibition. The quench tower was found mainly hindering de novo synthesis, with CP-route dominant in quench tower ash. Ca(OH)<sub>2</sub> & (NH<sub>4</sub>)<sub>2</sub>H<sub>2</sub>PO<sub>4</sub> effectively controlled organic chlorine from 4.11% to 2.86% and inhibited precursors synthesis, but failed to inhibit the oxidation process of de novo

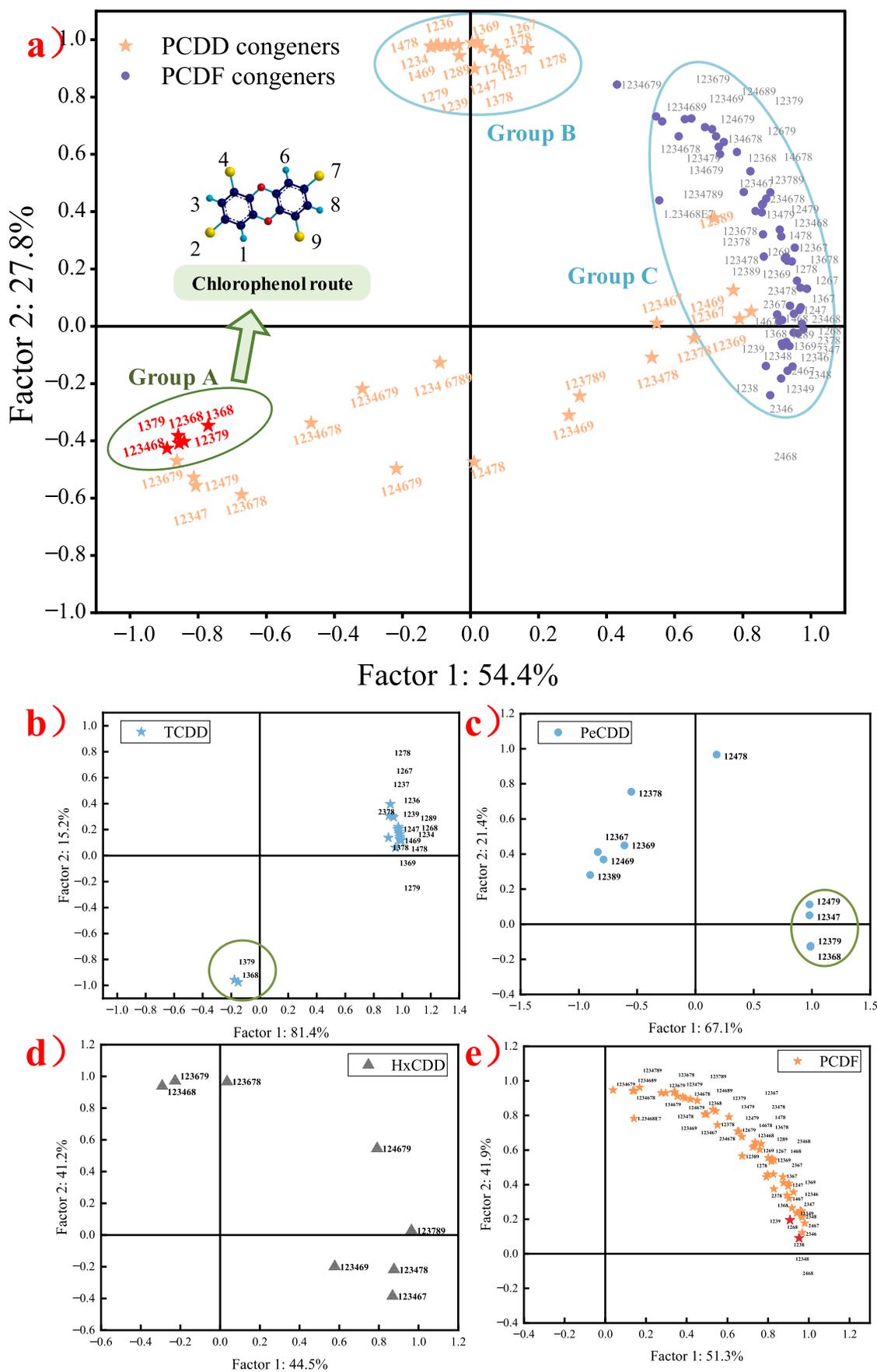


Fig. 6. (a) Principal component analysis results of all PCDD/Fs congeners (b) PCA of TCDDs (c) PCA of PeCDDs (d) PCA of HxCDDs (e) PCA of PCDFs congeners.

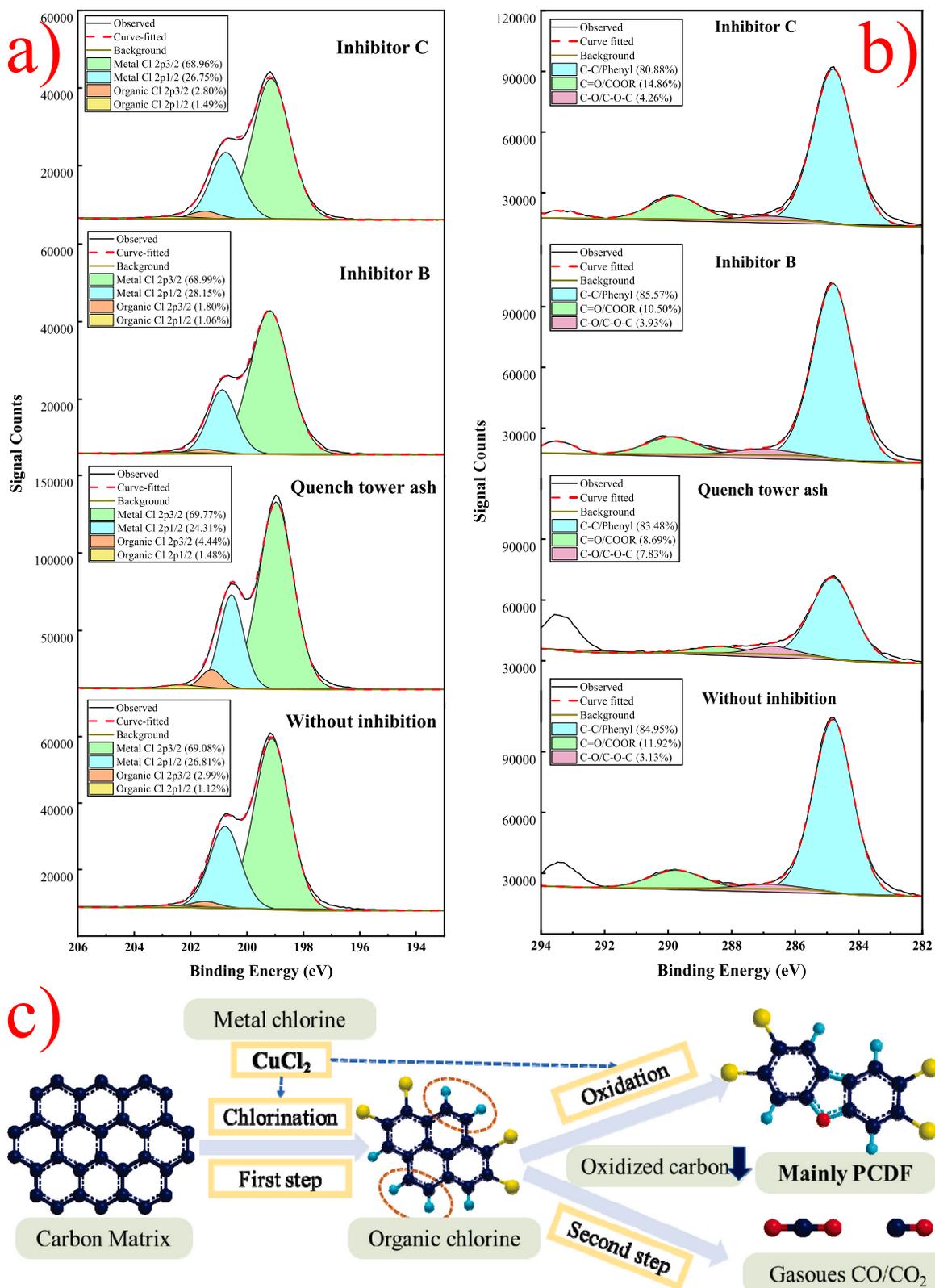


Fig. 7. (a) XPS analysis on chlorination process by results of Cl (b) XPS analysis on oxidation process by results of C (c) The influences of chlorine source, carbon source and metal catalysts on de novo synthesis.

synthesis, causing the increase of PCDFs. Cooperating well with the quench tower,  $\text{CH}_4\text{N}_2\text{S}$  &  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  has realized 81.7% inhibition efficiency of PCDD/Fs I-TEQ emissions by hindering catalysts and chlorine source.

Although the formation pathways and inhibition mechanisms in

HWIs were studied, effect of variation of hazardous waste on PCDD/Fs formation has not been further figured out. Based on this HWI study, three suggestions are helpful for PCDD/Fs emission control. Firstly, characteristics (especially chlorine) of hazardous waste should be carefully concerned due to their importance on PCDD/Fs emission levels

in HWIs. In addition, suitable inhibitors can cooperate with the quench tower to further reduce PCDD/Fs emissions. Finally, PCDD/Fs emission pressure urges for deeper research including laboratory, pilot and full-scale experiments focusing on the PCDD/Fs formation and migration mechanisms in HWIs.

### Credit author statement

**Fengyu He:** Formal analysis, Investigation, Conceptualization, Methodology, Software, Validation, Writing- original draft, Visualization, Data curation. **Yaqi Peng:** Writing-review & editing, Formal analysis. **Fei Wang:** Project administration, Funding acquisition, Supervision. **Yuhang Dong:** Resources. **Ken Chen:** Investigation, Formal analysis. **Shengyong lu:** Resources, Methodology.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

### Acknowledgement

This study is supported by the National Key Research and Development Program of China (No. 2019YFC1907000), the National Nature Science Foundation of China (No. 51976188), the Science and Technology Plan Project of Zhejiang Province (No. 2021C03162) and the Key Project of Innovation of Science and Technology of Ningbo City (No. 2018B10023).

### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2022.120261>.

### References

Agency, U.S.E.P., 2017. Method 23—determination of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from stationary sources. United States Environmental Protection Agency. [https://www.epa.gov/sites/default/files/2017-08/documents/method\\_23.pdf](https://www.epa.gov/sites/default/files/2017-08/documents/method_23.pdf).

Altarawneh, M., Dlugogorski, B.Z., Kennedy, E.M., Mackie, J.C., 2009. Mechanisms for formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). *Prog. Energy Combust. Sci.* 35 (3), 245–274. <https://doi.org/10.1016/j.pecs.2008.12.001>.

Altwickler, E.R., Milligan, M.S., 1993. Formation of dioxins - competing rates between chemically similar precursors and de-novo reactions. *Chemosphere* 27 (1–3), 301–307. [https://doi.org/10.1016/0045-6535\(93\)90306-](https://doi.org/10.1016/0045-6535(93)90306-).

Babushok, V.I., Tsang, W., 2003. Gas-phase mechanism for dioxin formation. *Chemosphere* 51 (10), 1023–1029. [https://doi.org/10.1016/s0045-6535\(02\)00716-6](https://doi.org/10.1016/s0045-6535(02)00716-6).

Ballschmitter, K., Braunmiller, I., Niemczyk, R., Swerev, M., 1988. Reaction pathways for the formation of polychloro-dibenzodioxins (PCDD) and polychloro-dibenzofurans (PCDF) in combustion processes. 2. chlorobenzenes and chlorophenols as precursors in the formation of polychloro-dibenzodioxins and polychloro-dibenzofurans in flame chemistry. *Chemosphere* 17 (5), 995–1005. [https://doi.org/10.1016/0045-6535\(88\)90070-7](https://doi.org/10.1016/0045-6535(88)90070-7).

Bo, X., Guo, J., Wan, R., Jia, Y., Yang, Z., Lu, Y., Wei, M., 2022. Characteristics, correlations and health risks of PCDD/Fs and heavy metals in surface soil near municipal solid waste incineration plants in Southwest China. *Environ. Pollut.* 298, 118816. <https://doi.org/10.1016/j.envpol.2022.118816>.

Chen, T., Gu, Y.-l., Yan, J.-h., Li, X.-d., Lu, S.-y., Dai, H.-f., Cen, K.-f., 2008. Polychlorinated dibenzo-p-dioxins and dibenzofurans in flue gas emissions from municipal solid waste incinerators in China. *J. Zhejiang Univ. - Sci.* 9 (9), 1296–1303. <https://doi.org/10.1631/jzus.A0720144>.

Chen, T., Zhan, M.X., Lin, X.Q., Li, X.D., Lu, S.Y., Yan, J.H., Buekens, A., Cen, K.F., 2014. Inhibition of the de novo synthesis of PCDD/Fs on model fly ash by sludge drying gases. *Chemosphere* 114, 226–232. <https://doi.org/10.1016/j.chemosphere.2014.03.123>.

Chen, Z., Lin, X., Lu, S., Li, X., Yan, J., 2019. Suppressing formation pathway of PCDD/Fs by S-N-containing compound in full-scale municipal solid waste incinerators. *Chem. Eng. J.* 359, 1391–1399. <https://doi.org/10.1016/j.cej.2018.11.039>.

China, 2005. Technical specifications for Centralized Incineration Facility (HJ/T 176-2005). Ministry of ecology and environment of the People's Republic of China. [www.mee.gov.cn/yw/gz/fgzb/bz/bzwb/other/hjbhgc/200505/t20050524\\_67081.shtml](http://www.mee.gov.cn/yw/gz/fgzb/bz/bzwb/other/hjbhgc/200505/t20050524_67081.shtml).

China, 2020. Standard for Pollution Control on Hazardous Waste Incineration. Ministry of ecology and environment of the People's Republic of China. <https://www.mee.gov.cn/yw/gz/fgzb/bz/bzwb/gthw/gtwwrkzcbz/202012/W020201218699412566946.pdf>.

Fu, J.-Y., Li, X.-D., Chen, T., Lin, X.-Q., Buekens, A., Lu, S.-Y., Yan, J.-H., Cen, K.-F., 2015. PCDD/Fs' suppression by sulfur-amine/ammonium compounds. *Chemosphere* 123, 9–16. <https://doi.org/10.1016/j.chemosphere.2014.10.073>.

Fujimori, T., Nakamura, M., Takaoka, M., Shiota, K., Kitajima, Y., 2016. Synergetic inhibition of thermochemical formation of chlorinated aromatics by sulfur and nitrogen derived from thiourea: multielement characterizations. *J. Hazard Mater.* 311, 43–50. <https://doi.org/10.1016/j.jhazmat.2016.02.054>.

Gao, H., Ni, Y., Zhang, H., Zhao, L., Zhang, N., Zhang, X., Zhang, Q., Chen, J., 2009. Stack gas emissions of PCDD/Fs from hospital waste incinerators in China. *Chemosphere* 77 (5), 634–639. <https://doi.org/10.1016/j.chemosphere.2009.08.017>.

Gullett, B.K., Lemieux, P.M., Dunn, J.E., 1994. Role of combustion and sorbent parameters in prevention of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran formation during waste combustion. *Environ. Sci. Technol.* 28 (1), 107–118. <https://doi.org/10.1021/es00050a015>.

Guo, X.X., Ma, Y.F., Lin, X.Q., Li, X.D., Xiang, Y.F., Wu, A.J., 2020. Reduction of polychlorinated dibenzo-p-dioxins and dibenzofurans by chemical inhibition and physisorption from a municipal solid waste incineration system. *Energy Fuel.* 34 (9), 11237–11247. <https://doi.org/10.1021/acs.energyfuels.0c01918>.

Huang, H., Buekens, A., 1995. On the mechanisms of dioxin formation in combustion processes. *Chemosphere* 31 (9), 4099–4117. [https://doi.org/10.1016/0045-6535\(95\)80011-9](https://doi.org/10.1016/0045-6535(95)80011-9).

Isabel, M., Ana Font, R., Francisca Gomez-Rico, M., 2019. Inhibition effect of polyurethane foam waste in dioxin formation. *Waste Manag.* 97, 19–26. <https://doi.org/10.1016/j.wasman.2019.07.034>.

Kuzuhara, S., Kasai, E., 2003. Formation of PCDD/Fs during oxidation of carbonaceous materials at low temperatures. *Tetsu To Hagane-J. Iron Steel Inst. Jpn.* 89 (8), 811–818. <https://doi.org/10.2355/tetsutohagane.1955.89.8.811>.

Li, M., Wang, C., Cen, K., Ni, M., Li, X., 2017. PCDD/F emissions during startup and shutdown of a hazardous waste incinerator. *Chemosphere* 181, 645–654. <https://doi.org/10.1016/j.chemosphere.2017.04.044>.

Lomnicki, S., Dellinger, B., 2003. A detailed mechanism of the surface-mediated formation of PCDD/F from the oxidation of 2-chlorophenol on a CuO/silica surface. *J. Phys. Chem. A* 107 (22), 4387–4395. <https://doi.org/10.1021/jp026045z>.

Lu, S.Y., Xiang, Y.F., Chen, Z.L., Chen, T., Lin, X.Q., Zhang, W.F., Li, X.D., Yan, J.H., 2021. Development of phosphorus-based inhibitors for PCDD/Fs suppression. *Waste Manag.* 119, 82–90. <https://doi.org/10.1016/j.wasman.2020.09.019>.

Luijk, R., Dorland, K., Smith, P., Govers, H.A.J., 1992. The halogenation of dibenzo-p-dioxin and dibenzofuran in a model fly ash system. *Organohalogen Compd.* 8, 273–276.

Ma, H.T., Du, N., Lin, X.Y., Liu, C.F., Zhang, J.Y., Miao, Z.Z., 2018. Inhibition of element sulfur and calcium oxide on the formation of PCDD/Fs during co-combustion experiment of municipal solid waste. *Sci. Total Environ.* 633, 1263–1271. <https://doi.org/10.1016/j.scitotenv.2018.03.282>.

Ma, P., Ma, Z., Yan, J., Chi, Y., Ni, M., Cen, K., 2011. Industrial hazardous waste treatment featuring a rotary kiln and grate furnace incinerator: a case study in China. *Waste Manag. Res.* 29 (10), 1108–1112. <https://doi.org/10.1177/0734242X11410116>.

Ma, Y.F., Lin, X.Q., Chen, Z.L., Li, X.D., Lu, S.Y., Yan, J.H., 2019. Influences of P-N-containing inhibitor and memory effect on PCDD/F emissions during the full-scale municipal solid waste incineration. *Chemosphere* 228, 495–502. <https://doi.org/10.1016/j.chemosphere.2019.04.161>.

Ma, Y.F., Wang, P.Y., Lin, X.Q., Chen, T., Li, X.D., 2021. Formation and inhibition of Polychlorinated-rho-dibenzodioxins and dibenzofurans from mechanical grate municipal solid waste incineration systems. *J. Hazard Mater.* 403. <https://doi.org/10.1016/j.jhazmat.2020.123812>.

McKay, G., 2002. Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review. *Chem. Eng. J.* 86 (3), 343–368. [https://doi.org/10.1016/s1385-8947\(01\)00228-5](https://doi.org/10.1016/s1385-8947(01)00228-5).

Milligan, M.S., Altwickler, E.R., 1995. Mechanistic aspects of the de-novo synthesis of polychlorinated dibenzo-p-dioxins and furans in fly-ash from experiments using isotopically labeled reagents. *Environ. Sci. Technol.* 29 (5), 1353–1358. <https://doi.org/10.1021/es00005a030>.

Moreno, A.I., Font, R., Gomez-Rico, M.F., 2019. Inhibition effect of polyurethane foam waste in dioxin formation. *Waste Manag.* 97, 19–26. <https://doi.org/10.1016/j.wasman.2019.07.034>.

Olie, K., Addink, R., Schoonenboom, M., 1998. Metals as catalysts during the formation and decomposition of chlorinated dioxins and furans in incineration processes. *J. Air Waste Manag. Assoc.* 48 (2), 101–105. <https://doi.org/10.1080/10473289.1998.10463656>.

Pulido, Y.F., Suarez, E., Lopez, R., Menendez, M.I., 2016. The role of CuCl on the mechanism of dibenzo-p-dioxin formation from poly-chlorophenol precursors: a computational study. *Chemosphere* 145, 77–82. <https://doi.org/10.1016/j.chemosphere.2015.11.042>.

Qian, Y., Zheng, M.H., Liu, W.B., Ma, X.D., Zhang, B., 2005. Influence of metal oxides on PCDD/Fs formation from pentachlorophenol. *Chemosphere* 60 (7), 951–958. <https://doi.org/10.1016/j.chemosphere.2004.12.068>.

- Raghunathan, K., Gullett, B.K., 1996. Role of sulfur in reducing PCDD and PCDF formation. *Environ. Sci. Technol.* 30 (6), 1827–1834. <https://doi.org/10.1021/es950362k>.
- Ren Zhang, H., Fan, Y., Zhou, H., Cao, R., Gao, Y., Chen, J., 2021a. Suppressing the formation of chlorinated aromatics by inhibitor sodium thiocyanate in solid waste incineration process. *Sci. Total Environ.* 798, 149154. <https://doi.org/10.1016/j.scitotenv.2021.149154>.
- Ren Zhang, H., Zhou, H., Fan, Y., Cao, R., Gao, Y., Chen, J., 2021b. Effect of urea on chlorinated aromatics formation mediated by copper and iron species in combustion flue gas. *Chemosphere* 280, 130963. <https://doi.org/10.1016/j.chemosphere.2021.130963>.
- Ryan, S.P., Gullett, B.K., Tabor, D., Oudejans, L., Touati, A., 2005. Determination of the vapor pressures of select polychlorinated dibenzo-p-dioxins and dibenzofurans at 75–275°C. *Chem. Eng. Sci.* 60 (3), 787–796. <https://doi.org/10.1016/j.ces.2004.09.039>.
- Ryu, J.-Y., Mulholland, J.A., Chu, B., 2003. Chlorination of dibenzofuran and dibenzo-p-dioxin vapor by copper (II) chloride. *Chemosphere* 51 (10), 1031–1039. [https://doi.org/10.1016/s0045-6535\(02\)00844-5](https://doi.org/10.1016/s0045-6535(02)00844-5).
- Schwarz, G., Stieglitz, L., 1992. Formation of organohalogen compounds in fly-ash by metal-catalyzed oxidation of residual carbon. *Chemosphere* 25 (3), 277–282. [https://doi.org/10.1016/0045-6535\(92\)90543-z](https://doi.org/10.1016/0045-6535(92)90543-z).
- Shao, K., Yan, J.H., Li, X.D., Lu, S.Y., Wei, Y.L., Fu, M.X., 2010. Inhibition of de novo synthesis of PCDD/Fs by SO<sub>2</sub> in a model system. *Chemosphere* 78 (10), 1230–1235. <https://doi.org/10.1016/j.chemosphere.2009.12.043>.
- Sidhu, S.S., Maqsood, L., Dellinger, B., Mascolo, G., 1995. The homogeneous, gas-phase formation of chlorinated and brominated dibenzo-p-dioxin from 2,4,6-trichlorophenols and 2,4,6-tribromophenols. *Combust. Flame* 100 (1–2), 11–20. [https://doi.org/10.1016/0010-2180\(94\)00057-y](https://doi.org/10.1016/0010-2180(94)00057-y).
- Soler, A., Conesa, J.A., Ortuno, N., 2018. Inhibiting fly ash reactivity by adding N- and S-containing compounds. *Chemosphere* 211, 294–301. <https://doi.org/10.1016/j.chemosphere.2018.07.177>.
- Stanmore, B.R., 2004. The formation of dioxins in combustion systems. *Combust. Flame* 136 (3), 398–427. <https://doi.org/10.1016/j.combustflame.2003.11.004>.
- Stieglitz, L., Bautz, H., Roth, W., Zwick, G., 1997. Investigation of precursor reactions in the de-novo-synthesis of PCDD/PCDF on fly ash. *Chemosphere* 34 (5–7), 1083–1090. [https://doi.org/10.1016/s0045-6535\(97\)00410-4](https://doi.org/10.1016/s0045-6535(97)00410-4).
- Stieglitz, L., Eichberger, M., Schleihauf, J., Beck, J., Zwick, G., Will, R., 1993. The oxidative-degradation of carbon and its role in the de-novo-synthesis of organohalogen compounds in fly-ash. *Chemosphere* 27 (1–3), 343–350. [https://doi.org/10.1016/0045-6535\(93\)90311-r](https://doi.org/10.1016/0045-6535(93)90311-r).
- Tuppurainen, K., Asikainen, A., Ruokojarvi, P., Ruuskanen, J., 2003. Perspectives on the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans during municipal solid waste (MSW) incineration and other combustion processes. *Accounts Chem. Res.* 36 (9), 652–658. <https://doi.org/10.1021/ar020104+>.
- Tuppurainen, K., Halonen, I., Ruokojarvi, P., Tarhanen, J., Ruuskanen, J., 1998. Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: a review. *Chemosphere* 36 (7), 1493–1511. [https://doi.org/10.1016/s0045-6535\(97\)10048-0](https://doi.org/10.1016/s0045-6535(97)10048-0).
- VandenBerg, M., Birnbaum, L., Bosveld, A.T.C., Brunstrom, B., Cook, P., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R., Kennedy, S.W., Kubiak, T., Larsen, J.C., van Leeuwen, F.X.R., Liem, A.K.D., Nolt, C., Peterson, R.E., Poellinger, L., Safe, S., Schrenk, D., Tillitt, D., Tysklind, M., Younes, M., Waern, F., Zacharewski, T., 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect.* 106 (12), 775–792. <https://doi.org/10.1289/ehp.98106775>.
- Wang, Qian, L.X., Yu, Z.W., Chun, T.J., Long, H.M., Wu, X.J., Li, J.X., 2020. Inhibition behavior of PCDD/fs congeners by addition of N-containing compound in the iron ore sintering. *Aerosol Air Qual. Res.* 20 (11), 2568–2579. <https://doi.org/10.4209/aaqr.2019.12.0660>.
- Wang, C., Xu, J., Yang, Z., Zhang, Z., Cai, Z., 2019. A field study of polychlorinated dibenzo-p-dioxins and dibenzofurans formation mechanism in a hazardous waste incinerator: emission reduction strategies. *J. Clean. Prod.* 232, 1018–1027. <https://doi.org/10.1016/j.jclepro.2019.06.020>.
- Wang, P.Y., Xu, S.X., Chen, Z.L., Chen, T., Lin, X.Q., Ma, Y.F., Zhang, M.M., Li, X.D., 2020. Inhibition of polychlorinated dibenzo-p-dioxins and dibenzofurans by phosphorus-containing compounds in model fly ash. *Chemosphere* 257. <https://doi.org/10.1016/j.chemosphere.2020.127168>.
- Wang, Q., Jin, Y., Li, X., Chen, J., Lu, S., Chen, T., Yan, J., Zhou, M., Wang, H., 2014. PCDD/F emissions from hazardous waste incinerators in China. *Aerosol Air Qual. Res.* 14 (4), 1152–1159. <https://doi.org/10.4209/aaqr.2013.03.0069>.
- Wang, X., Ma, Y., Lin, X., Wu, A., Xiang, Y., Li, X., Yan, J., 2022. Inhibition on de novo synthesis of PCDD/Fs by an N-P-containing compound: carbon gasification and kinetics. *Chemosphere* 292, 133457. <https://doi.org/10.1016/j.chemosphere.2021.133457>.
- Weber, R., Hagenmaier, H., 1999. PCDD/PCDF formation in fluidized bed incineration. *Chemosphere* 38 (11), 2643–2654. [https://doi.org/10.1016/s0045-6535\(98\)00472-x](https://doi.org/10.1016/s0045-6535(98)00472-x).
- Wiater, I., Born, J.G.P., Louw, R., 2000. Products, rates, and mechanism of the gas-phase condensation of phenoxy radicals between 500–840 K. *Eur. J. Org. Chem.* 2000 (6), 921–928. [https://doi.org/10.1002/\(sici\)1099-0690,200003\)2000:6<921::Aid-ajoc921>3.0.Co;2-p](https://doi.org/10.1002/(sici)1099-0690,200003)2000:6<921::Aid-ajoc921>3.0.Co;2-p).
- Wikstrom, E., Ryan, S., Touati, A., Telfer, M., Tabor, D., Gullett, B.K., 2003. Importance of chlorine speciation on de Novo formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. *Environ. Sci. Technol.* 37 (6), 1108–1113. <https://doi.org/10.1021/es026262d>.
- Xing, Y., Zhang, H., Su, W., Wang, Q.H., Yu, H.B., Wang, J.Q., Li, R., Cai, C.Q., Ma, Z.L., 2019. The bibliometric analysis and review of dioxin in waste incineration and steel sintering. *Environ. Sci. Pollut. Control Ser.* 26 (35), 35687–35703. <https://doi.org/10.1007/s11356-019-06744-0>.
- Xu, S.X., Chen, T., Buekens, A., Li, X.D., 2018. De novo formation of PCDD/F during sintering: effect of temperature, granule size and oxygen content. *ISIJ Int.* 58 (3), 566–572. <https://doi.org/10.2355/isijinternational.ISIJINT-2017-392>.
- Yang, L., Liu, G., Zheng, M., Zhao, Y., Jin, R., Wu, X., Xu, Y., 2017. Molecular mechanism of dioxin formation from chlorophenol based on electron paramagnetic resonance spectroscopy. *Environ. Sci. Technol.* 51 (9), 4999–5007. <https://doi.org/10.1021/acs.est.7b00828>.
- Yearbook, 2021. China Statistical Yearbook (chapter 8)-15. <http://www.stats.gov.cn/tjsj/ndsj/2021/indexch.htm>.
- Zhan, M.X., Xu, S., Cai, P., Chen, T., Lin, X., Buekens, A., Li, X., 2019. Parameters affecting the formation mechanisms of dioxins in the steel manufacture process. *Chemosphere* 222, 250–257. <https://doi.org/10.1016/j.chemosphere.2019.01.126>.
- Zhang, G., Hai, J., Cheng, J., 2012. Characterization and mass balance of dioxin from a large-scale municipal solid waste incinerator in China. *Waste Manag.* 32 (6), 1156–1162. <https://doi.org/10.1016/j.wasman.2012.01.024>.
- Zhang, H., Lan, D.Y., Lu, F., Shao, L.M., He, P.J., 2020. Inhibition of chlorobenzenes formation by calcium oxide during solid waste incineration. *J. Hazard Mater.* 400. <https://doi.org/10.1016/j.jhazmat.2020.123321>.
- Zhang, M., Buekens, A., Olie, K., Li, X., 2017. PCDD/F-isomers signature - effect of metal chlorides and oxides. *Chemosphere* 184, 559–568. <https://doi.org/10.1016/j.chemosphere.2017.05.176>.
- Zhang, M.M., Buekens, A., 2016. De novo synthesis in iron ore sintering. *Int. J. Environ. Pollut.* 60 (1–4), 111–135.
- Zhao, Y., Zhan, J., Liu, G., Ren, Z., Zheng, M., Jin, R., Yang, L., Wang, M., Jiang, X., Zhang, X., 2017. Field study and theoretical evidence for the profiles and underlying mechanisms of PCDD/F formation in cement kilns co-incinerating municipal solid waste and sewage sludge. *Waste Manag.* 61, 337–344. <https://doi.org/10.1016/j.wasman.2016.12.008>.
- Zimmermann, R., Blumenstock, M., Heger, H.J., Schramm, K.W., Ketrup, A., 2001. Emission of nonchlorinated and chlorinated aromatics in the flue gas of incineration plants during and after transient disturbances of combustion conditions: delayed emission effects. *Environ. Sci. Technol.* 35 (6), 1019–1030. <https://doi.org/10.1021/es000143l>.