Inhibition Behavior of PCDD/Fs Congeners by Addition of N-containing Compound in the Iron Ore Sintering

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ABSTRACT

PCDD/Fs are typical toxic persistent aromatic compounds that greatly reduce air quality and harm human health. In this study, urea's suppressive effect on PCDD/Fs and their congener emissions was investigated via sintering pot tests, and the inhibition mechanisms were studied. The results showed that the I-TEQ values for the total PCDD/Fs decreased from 0.50 to 0.20, 0.12 and 0.20 ng I-TEQ Nm⁻³ after adding solid 0.02, 0.035 and 0.05 wt.% urea particles, respectively, to the iron ore sintering mixture, but these values increased for the low-chlorinated TeCDFs (from 0.003 to 0.009, 0.006 and 0.006 ng I-TEQ Nm⁻³) and TeCDDs (from 0.014 to 0.020, 0.018 and 0.020 ng I-TEQ Nm⁻³). Moreover, the average I-TEQ values for the chlorine substituents in the PCDFs and PCDDs decreased, indicating that urea inhibited chlorination or enhanced dechlorination. The potential mechanisms by which urea suppresses the total PCDD/Fs and hydrodechlorinates the high-chlorinated PCDD/Fs are discussed.

Keywords: PCDD/Fs; Congeners; Urea; Active radical; Iron ore sintering.

INTRODUCTION

In 1977, Dutch scientists first detected the presence of dioxins in the exhaust gas and fly ash of waste incineration, which aroused widespread concern and in-depth research in the environmental field (Kasai *et al.*, 2008). Dioxins are typical toxic persistent aromatic compounds, including polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), also referred to as "PCDD/Fs" (Dvořák *et al.*, 2010; Yabar *et al.*, 2013; Liao *et al.*, 2016; Zhan *et al.*, 2019). PCDD/Fs are highly toxic that can cause reproductive and developmental problems, damage the immune system, interfere with hormones, and induce cancer as well (Shen *et al.*, 2018). Studies have shown that the average concentrations of PCDD/Fs in the air of some cities in China were between 0.036 and 0.060 pg I-TEQ Nm⁻³ (Tang *et al.*, 2017; Xing *et al.*, 2017). Owing to the great harm of PCDD/Fs to the ecological environment, air quality, and human health, PCDD/Fs have been included into the Annex C compounds of the Stockholm Convention (Yu *et*

al., 2016; Li *et al.*, 2018; Xu *et al.*, 2019). Previous studies generally concluded that the formations of PCDD/Fs are a heterogeneous reaction (200–500°C) and a homogeneous reaction (500–800°C) (Chen *et al.*, 2018). Furthermore, three general formation pathways were proposed as follow: (i) *de novo synthesis by catalytic metals (Cu/Fe)*; (ii) *precursor pathway*; (iii) *the rearrangement reactions of chlorophenols and chlorobenzenes* (Harjanto *et al.*, 2002; Zhang *et al.*, 2016; Xuan *et al.*, 2017; Chen *et al.*, 2019; Ma *et al.*, 2019). So far, municipal waste incineration, iron ore sintering industry, electric steelmaking industry, non-ferrous metal recycling industry, cement production industry, etc. are the potential sources of PCDD/Fs emission (Kuo *et al.*, 2011; Yang *et al.*, 2019).

Among them, iron ore sintering is an essential process in the long steelmaking process and the primary emission source of pollutants as well (Chen *et al.*, 2016; Chun *et al.*, 2017; Rezvanipour *et al.*, 2018). The process of the iron ore sintering is presented in Fig. 1. As shown in this figure, first of all, the raw materials including iron ores, fuels, fluxes, solid waste, recirculated material, etc. are mixed and pelletized with water, then placed on a slow-moving bed to sinter into a lump at temperatures over 1300°C (Thompson *et al.*, 2016; Kumar *et al.*, 2018). Utilizing a high-power draft fan to draw the exhaust gas from the sintering bed, then the exhaust gas passes through a series of wind boxes and enters an electrostatic

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Fig. 1. Schematic diagram of the iron ore sintering process.

precipitator for dust removal. Afterward, the exhaust gas is desulfurized and released via a stack (Ooi *et al.*, 2008a; Abreu *et al.*, 2015; Ji *et al.*, 2017). Meanwhile, the pollutants, like NO_x , PCDD/Fs, etc., are released into the atmosphere as well.

Previous studies showed that PCDD/Fs formed in the sintering process exhibited typical characteristics of *de novo* synthesis (Drage *et al.*, 2014; Liu *et al.*, 2017; Yang *et al.*, 2017). PCDD/Fs can be generated in the drying zone, where the temperature between 200 and 650°C, a large amount of carbon source, chlorides and catalytic metal (Cu^+/Fe^+) are essential for the *de novo* synthesis (Nakano *et al.*, 2005). According to the formation mechanism of PCDD/Fs in the sintering process, injection inhibitors have been extensively studied and confirmed to be an effective method to control the formation of PCDD/Fs (Yan *et al.*, 2014). At present, there are three types of inhibitors, i.e., nitrogen (N)-containing inhibitors, S-containing inhibitors, and alkaline inhibitors. However, due to the negative effect on SO_2 emission levels in the flue gas and quality of sinter, S-containing and alkaline inhibitors were restricted in utilization during the sintering process (Qian *et al.*, 2018). The N-containing inhibitors, especially urea, added in sintering raw mixture have no negative impact on the production process and product quality. Hence, it was widely used to reduce the emission of PCDD/Fs during the iron ore sintering (Nakano *et al.*, 2005). Several studies reported that the addition of 0.02–0.05 wt.% urea into the iron ore sintering mixtures could reduce the emission of PCDD/Fs by about 50–65% (Southern *et al.*, 2000; Xhrouet and Pauw, 2005; Anderson *et al.*, 2007; Ooi *et al.*, 2008b). Furthermore, in our previous studies, we also indicated that the PCDD/Fs emission reduction rate was 72.1% after adding 0.5 wt.% urea aqueous solution into the sintering mixtures in sintering pot tests (Long *et al.*, 2011).

Similarly, experiments to reduce exhaust gas pollutant emission in municipal solid waste incineration showed that adding a certain amount of urea could achieve PCDD/Fs emission reduction (Peng *et al.*, 2016; Ma *et al.*, 2018). A previous study in a full-scale municipal solid waste incinerator indicated that urea concentration in the splayed water was

set at 0.1 wt.% with a splaying rate of 2000 kg h^{-1} , the international toxic equivalent (I-TEQ) value of the PCDD/Fs in the flue gas was reduced by about 50% (Kasai *et al.*, 2008). Ruokojärvi *et al.* (2001) also reported that total PCDD/Fs concentration decreased by a maximum of 74% when 1 wt.% of the fuel input of urea was injected into the flue gas in a pilot-scale plant. Moreover, Ruokojärvi *et al.* (2001) discovered that the emission ratios of low-chlorinated TeCDD and TeCDF were increased by 34% and 52%, respectively, when 0.1 wt.% urea was added in the flue gas of municipal solid waste incineration.

In view of the above, the present papers showed that the addition of urea within the formation temperature range of PCDD/Fs can reduce the total PCDD/Fs emissions in municipal solid waste incineration and urea has a different suppression efficiency on PCDD/Fs congeners. However, most studies focused on the total PCDD/Fs emissions after the addition of urea during the iron ore sintering, the different inhibitory behavior of urea on PCDD/Fs congeners and the differential inhibition mechanism of PCDD/Fs was still unclear. To fill the current knowledge gap, in this study, the suppression effect of the addition of urea into the sintering mixture on PCDD/Fs emission was analyzed. The influence of urea on the suppression efficiency differences of PCDD/Fs congeners was investigated. Finally, the studies allowed demonstrating the dechlorination mechanism of urea on PCDD/Fs molecules.

MATERIAL AND METHODS

Materials

In this study, a commercial sintering plant (located in Jiangsu Province, China) provided the raw materials for the sintering pot tests. The main chemical compositions and the added mass ratio of the raw materials were shown in Table 1. The ferrous materials were the iron ore fines (including Cara ore, Pilbara blend ore, Yankee ore, SFHT ore and Meishan concentrate) and recycling materials (blast furnace dust and miscellaneous ore or other by-products). Fluxes included

Table 1. Chemical compositions and the mass ratio of all raw materials (mass fraction, %).

Raw material	TFe*	SiO ₂	CaO	MgO	Al ₂ O ₃	P ₂ O ₅	C	Mass ratio
Pilbara blend ore	62.10	3.45	0.08	0.10	2.33	0.23	–	13.04
Yankee ore	58.84	4.64	0.09	0.12	1.58	0.11	–	14.30
SFHT ore	59.74	11.06	0.09	0.17	1.20	0.11	–	3.15
Cara ore	66.27	2.05	0.11	0.12	1.41	0.09	–	15.56
Meishan concentrate	56.10	4.84	3.48	1.21	0.95	0.27	–	9.68
Return fines	56.80	5.30	10.12	1.77	1.80	0.18	–	27.81
Blast furnace dust	38.48	7.46	2.74	1.34	2.98	0.14	30.63	1.61
Mixed ore	47.65	4.22	13.22	2.47	1.16	0.48	11.78	3.19
Dolomite	0.35	3.37	30.80	19.60	0.68	0.23	–	3.84
Limestone	2.91	3.10	53.10	0.30	0.64	0.02	–	0.96
Lime	0.51	3.76	82.00	0.84	1.81	0.02	–	3.23
Coke fines	1.07	5.49	0.78	0.15	4.10	0.07	88.20	3.63

*The total Fe in the raw material; C is the fixed carbon.

limestone, dolomite, and active lime. Fuel was the coke fine. The binary basicity ($w(\text{CaO})/w(\text{SiO}_2)$) and coke fine content were fixed at 1.90 and 3.63 wt.%, respectively. Industrial solid urea (containing 46.7 wt.% nitrogen) was used as an inhibitor in the experiments, and its average particle size was 1–2 mm. The solid urea particle was directly added into the mixing process at the rates of 0.020, 0.035 and 0.050 wt.% of the total sintering mixtures.

Methods

Sintering Pot Tests

The sintering pot tests were carried out to simulate a commercial sintering process. Sintering pot process included proportioning, mixing, granulation, charging, ignition, sintering, cooling and PCDD/Fs detection, as shown in Fig. 2. During the mixing, the solid urea was injected into the sintering mixtures according to the set mass proportion and mixed evenly. Next, the mixtures were granulated to large particles with the addition of water. After the granulation process completed, 3 kg sinter particles with the diameter of 10–16 mm were added into the bottom of the sintering pot as hearth layer, and then approximately 98 kg sintering mixtures with the moisture of $6.8 \pm 0.2\%$ were charged into a sintering pot with the height of 720 mm and the diameter of 300 mm. After charging, the mixtures in the sintering pot were ignited by a liquefied gas burner for 2 min with draft fan negative pressure of 7 kPa at the temperature of $1100 \pm 50^\circ\text{C}$. Simultaneously, PCDD/Fs testing devices were conducted. The igniter was moved away after ignition completing, the negative pressure of the draft fan was raised to 14 kPa and the temperature of the flue gas at the bottom of the grate was measured during the sintering and maintained till the end of the sintering process. When the temperature of the flue gas reached its maximum value, PCDD/Fs testing devices were closed and the sintering pot test ended (Jiang *et al.*, 2015; Cheng *et al.*, 2017). Compared with the commercial sintering process, the sintering pot test was a discontinuous process and one sintering time was about 30 min. The collection time of PCDD/Fs for one sample was 1 h. Therefore, to ensure reproducibility, four identical sintering pot tests were done for each group of samples and the sampling of PCDD/Fs lasts for 2 h (1 h for one sample).

Mechanism for Sampling

In this experiment, PCDD/Fs sampling device for flue gas in the iron ore sintering process adopted the instrument recommended in HJ 77.2–2008 and the specific method for taking samples from the sintering process refers to the previous research (Qian *et al.*, 2016). The sampling and analysis of PCDD/Fs samples were completed by the Centre Testing International Group Co., Ltd. (CTI). The CTI was a laboratory accredited by the China National Accreditation Service for Conformity Assessment (CNAS) and has the China Metrology Accreditation (CMA) qualification. The sampling device mainly included a sampling tube, gas adsorption unit, filter membranes, condensing device, flow measurement, control device, etc. The specific introduction could refer to our previous study (Long *et al.*, 2011).

Using adsorption materials and filter membranes to collect the PCDD/Fs, including gas-, solid- and liquid-phase samples. In addition, four sampling internal standard substances (¹³C-123478-HxCDD, ¹³C-23478-PeCDF, ¹³C-123478-HxCDF, and ¹³C-1234789-HpCDF) were added before sampling and the recovery rate of the internal standard substances was required to be 70–130%, otherwise, the sample needed to be resampled.

Analysis Method

The collected PCDD/Fs were transported to the dioxin test laboratory under dark for analysis after each sintering pot test. Before sample extraction, several purified internal standard substances, like ¹³C-2378-TCDF, ¹³C-12378-PeCDF, etc., were added into the sample. The mean recoveries of internal standard substances were required to be 40–130%. For each collected sample, first of all, it was pre-treated with toluene extraction, concentrated to 3 mL by using a rotary evaporator (Eyela, Tokyo, Japan) and then purified with a multilayer silica gel, which was composed of acid, alkali, and neutral silica gel. Finally, the purified extract was condensed to 20 µL by a nitrogen blower, and then further condensed to near-dryness with using a nitrogen stream, readied for analysis. PCDD/F detection congeners adopted isotope dilution high-resolution gas chromatography/high-resolution mass spectrometry, using a 6890 Series Gas Chromatograph (Hewlett-Packard, USA), coupled to an

Fig.2. Schematic diagram of the sinter pot experiment.

AutoSpec Premier (Waters, USA). Besides, a DB-5 quartz capillary column was used to carry out the chromatographic separations. Injections were done using the splitless mode with a column oven temperature program. The temperature could be adjusted between 50–350°C. The initial temperature was 150°C (kept 3 min), 20°C min⁻¹ to 230°C (kept 18 min), 5°C min⁻¹ to 235°C (kept 10 min), then 4°C min⁻¹ to 330°C (kept 3 min). The carrier gas was the helium (99.999% purity) (Xhrouet *et al.*, 2001; Kuo *et al.*, 2012; Wu *et al.*, 2016). The I-TEQ values were calculated using I-TEF_{WHO-05} (Van den Berg *et al.*, 2006).

Statistical Methods

The emission concentration of PCDD/Fs calculated in this paper was the arithmetic mean value of two parallel samples for each group of samples.

The removal rate (δ) of PCDD/Fs was calculated through Eq. (1):

$$\delta = \frac{C1 - C2}{C1} \times 100\% \quad (1)$$

where C1 is the PCDD/Fs concentration without urea (ng I-TEQ Nm⁻³); C2 is the PCDD/Fs concentration with urea (ng I-TEQ Nm⁻³).

The chlorination degree of PCDD/Fs (q_c , average I-TEQ number of chlorine atom) was calculated according to Eq. (2):

$$q_c = \sum_{i=4}^8 w_i \times n_i \quad (2)$$

where w_i is the I-TEQ weight percentage of PCDDs and PCDFs; n_i is the number of the chlorine atom.

RESULTS AND DISCUSSION

Concentrations of PCDD/Fs

For all experiment samples, the recovery rates of sampling internal standard substances were 87.1–102.4% (non-urea), 96.7–106.0% (0.02% urea), 96.3–105.0% (0.035% urea), 76.8–88.5% (0.05% urea) within 70–130%. The internal standard substance recovery rates of all samples after

purification were in the range of 40–130%. The results of the analysis showed that the samples were not significantly contaminated.

The effect of urea addition on PCDD/Fs emission concentration and the detection results of 17 targeted PCDD/Fs congeners were analyzed according to the accumulation of international toxic equivalency factors (I-TEFs), as listed in Table 2. The I-TEQ value without urea was 0.5 ng I-TEQ Nm⁻³. After 0.020, 0.035 and 0.050 wt.% urea added into the sintering mixtures, the emission of I-TEQ values reduced to 0.20, 0.12 and 0.20 ng I-TEQ Nm⁻³ respectively, and the reduction efficiencies were 60.0, 76.0 and 60.0%, separately, which was similar to the results of previous studies (Anderson *et al.*, 2007; Ooi *et al.*, 2008a). The results showed that urea has an obvious inhibitory effect on the emission of PCDD/Fs, which further proves that the addition of urea in mixtures can reduce the PCDD/Fs emission during the iron ore sintering.

Different Inhibition of PCDFs and PCDDs

The emission I-TEQ values of PCDFs and PCDDs were presented in Fig. 3(a). In the case of non-urea, the value of PCDFs and PCDDs were 0.380 and 0.120 ng I-TEQ Nm⁻³, the ratio of PCDFs/PCDDs was 3.15, which was a typical emission distribution of PCDD/Fs during the iron ore sintering process (Xhrouet and Pauw, 2005). Previous studies showed that the formation of PCDFs congeners was dominated by *de novo synthesis* (Huang and Buekens, 1995; Chen *et al.*, 2019) and most PCDDs were synthesized through the precursor pathway (Weber and Hagenmaier, 1999). Therefore, the *de novo synthesis* was the primary formation route of PCDD/Fs during the iron ore sintering process.

With addition of 0.020, 0.035 and 0.050 wt.% urea into the iron ore sinter mixtures, the emission of I-TEQ values were 0.167, 0.098, 0.131 ng I-TEQ Nm⁻³ for PCDFs and 0.037, 0.027, 0.067 ng I-TEQ Nm⁻³ for PCDDs, separately. The PCDFs/PCDDs-ratios became 4.45, 3.68 and 1.95, respectively. Fig. 3(b) presented the inhibition efficiency of PCDFs and PCDDs calculated in different experiments. As illustrated in this figure, the reduction ratios of PCDFs (PCDDs) increased from 56.2% to 74.3% (from 68.9% to 78.0%) with augmenting urea ratio from 0.020% to 0.035%. The inhibition effect of PCDDs was more obvious than that

Table 2. Analyzing results of PCDD/Fs (ng I-TEQ Nm⁻³).

Classification	Congener	I-TEQ*			
		Non-urea	0.02% urea	0.035% urea	0.05% urea
PCDFs	2378-TeCDF	0.0034	0.009	0.006	0.0064
	12378-PeCDF	0.0055	0.006	0.004	0.0045
	23478-PeCDF	0.17	0.085	0.06	0.07
	123478-HxCDF	0.039	0.018	0.0097	0.011
	123678-HxCDF	0.049	0.022	0.011	0.013
	234678-HxCDF	0.068	0.017	0.012	0.016
	123789-HxCDF	0.023	0.003	0.0026	0.0045
	1234678-HpCDF	0.019	0.0059	0.0032	0.0043
	1234789-HpCDF	0.0025	0.0006	0.00051	0.00065
	OCDF	0.00082	0.00016	0.00017	0.00018
PCDDs	2378-TeCDD	0.014	0.02	0.005	0.02
	12378-PeCDD	0.045	0.01	0.005	0.02
	123478-HxCDD	0.014	0.0015	0.0009	0.0042
	123678-HxCDD	0.021	0.002	0.0005	0.01
	123789-HxCDD	0.013	0.0015	0.0016	0.0066
	1234678-HpCDD	0.012	0.0021	0.00088	0.0054
	OCDD	0.0016	0.00036	0.00016	0.00079
	Total PCDD/Fs (PCDDs + PCDFs)	–	0.50	0.20	0.12
I-TEQ inhibition	–	0%	60.0%	76.0%	60.0%
q _c -PCDFs	–	5.58	5.39	5.35	5.37
q _c -PCDDs	–	5.52	4.72	4.5	5.21

* International toxic equivalent, which is calculated by multiplying the measured value of the concentration of each PCDD/Fs congener by the international toxic equivalency factor (I-TEF) and then adding them up.

Fig. 3. Emission value and suppression efficiency of PCDD/Fs: (a) emission of I-TEQ values of PCDDs and PCDFs; (b) suppression efficiency of PCDDs and PCDFs.

of PCDFs. However, when the addition ratio of urea increased to 0.050%, the reduction efficiency of PCDFs (PCDDs) reduced to 65.7% (44.5%), and the inhibition effect of PCDFs was more obvious than that of PCDDs. This phenomenon can be explained by two reasons: (i) When the proportion of urea added is low (0.020 and 0.035%), urea preferentially inhibits PCDD/Fs formation of dioxins precursors, like chlorobenzenes, chlorophenols, etc., and (ii) with the increase in the addition amount of urea (0.050%), more urea molecules and their decomposition products can inhibit the activity of the catalyst that catalyzes the formation of PCDD/Fs and reduce the number of Cl ions, thereby inhibiting the de novo synthesis of PCDD/Fs (Ruokojärvi *et al.*, 2004).

Different Inhibition Behavior of PCDD/Fs Congeners

Distribution of PCDD/Fs Congeners

The PCDFs congeners emission concentration and their homologous profiles of 2,3,7,8-substituted PCDFs were showed in Fig. 4. As shown in the figure, the emission concentration of PeCDFs and HxCDFs occupied the dominant position of PCDFs emission in all samples. Compared with the non-urea test, the emission I-TEQ values of HxCDFs reduced from 0.179 ng I-TEQ Nm⁻³ to 0.060, 0.035 and 0.045 ng I-TEQ Nm⁻³ with adding 0.02, 0.035 and 0.05% urea. The corresponding distribution proportions dropped from 47.1% to 36.0, 36.1 and 34.1%. The HpCDFs and OCDF emission concentrations and distribution ratios

Fig. 4. PCDFs congeners emission concentration and distribution proportions of the 2,3,7,8-substituted PCDFs: (a) I-TEQ values of PCDFs congeners emission concentration; (b) PCDFs fingerprint.

were also significantly decreased. For PeCDFs, the emission I-TEQ values also reduced from 0.176 ng I-TEQ Nm⁻³ (in non-urea test) to 0.091, 0.054 and 0.075 ng I-TEQ Nm⁻³, while their distribution ratios have increased. Nevertheless, the emission I-TEQ values of low-chlorinated TeCDF increased from 0.003 ng I-TEQ Nm⁻³ (in non-urea test) to 0.009, 0.006 and 0.006 ng I-TEQ Nm⁻³ respectively, and the distribution ratios also augmented from 0.89% to 5.4, 6.1 and 4.9%. These results were similar to the previous study on inhibition congeners of PCDD/Fs from fly ash by the addition of urea (Yan *et al.*, 2013).

The effectual trend of urea on the emission concentrations and the congener profiles of 2,3,7,8-substituted PCDDs were the same as that of PCDFs, as shown in Fig. 5. The PeCDD and HxCDDs were the dominant congeners and the emissions of I-TEQ values were 0.045 and 0.048 ng I-TEQ Nm⁻³ in the non-urea test. The emission of I-TEQ values and distribution proportions of PeCDD, HxCDDs, HpCDD, and OCDD were significantly decreased after adding urea. Among them, the percentages of PeCDD reduced from 37.3% to 26.7, 18.8

and 29.9% and HxCDDs declined from 39.8% to 13.3, 9.4 and 31.0%. However, emission concentration and distribution proportions of low-chlorinated TeCDD have increased. The I-TEQ values increased from 0.014 ng I-TEQ Nm⁻³ (in the non-urea test) to 0.020, 0.018 and 0.020 ng I-TEQ Nm⁻³, respectively, and their distribution proportions augmented from 11.6% to 53.4, 67.8 and 29.9%. The distribution proportions occupied the dominant position of PCDDs.

Differences in Inhibition of PCDD/Fs Congeners

The inhibitory efficiencies of urea on PCDDs and PCDFs congeners were compared in Figs. 6(a) and 6(c), in which the inhibitory efficiencies on the low-chlorinated TeCDF and TeCDD were negative, while, in contrast, the inhibitory efficiencies for other congeners were above 50%. This phenomenon can be inferred that the urea or its decomposition products promoted the dechlorination reaction of high-chlorinated PCDFs or PCDDs, which resulted in the formation of TeCDF and PeCDFs so that the distribution proportions were significantly increased. Moreover, compared with the

Fig. 5. PCDDs congeners emission concentration and distribution proportions of the 2,3,7,8-substituted PCDDs: (a) I-TEQ values of PCDDs congeners emission concentration; (b) PCDDs fingerprint.

Fig. 6. The efficiency of PCDDs and PCDFs congeners suppression and average I-TEQ number of chlorine substituents after adding urea: (a) the efficiency of PCDFs congeners suppression; (b) the average I-TEQ number of chlorine substituents of PCDFs congeners; (c) the efficiency of PCDDs congeners suppression; (d) the average I-TEQ number of chlorine substituents of PCDDs congeners.

non-urea test, the average I-TEQ number of chlorine substituents of PCDFs and PCDDs decreased after the addition of urea, indicating that the chlorination process of PCDD/Fs was inhibited by urea, as shown in Figs. 6(b) and 6(d). To conclude, the dechlorination reaction might be a possible reason for the decrease in the average I-TEQ number of chlorine substituents.

Inhibition Mechanisms

Reduction Emission Mechanism of PCDD/Fs

The inhibition mechanisms of urea have investigated in our previous reports (Long *et al.*, 2011; Qian *et al.*, 2018). The mechanisms can be summed up into three aspects: (1) The passivation of Cu^+ , (2) the decrease of Cl_2 amount, and (3) active radicals impede the formation of PCDD/Fs or attack the molecular bonds of PCDD/Fs. For the first mechanism, it is identified that the urea reacted with Cu^+ to generate some stable complexes, such as $[\text{urea-Cu}]^+$ or $[(\text{urea})_2\text{-Cu}]^+$, thereby weakening the activity of metal catalysis (Luna *et al.*, 2000). For the second mechanism, the NH_3 formed by urea can react with Cl_2 through Reaction (1) (Long *et al.*, 2011). The NH_3 can also react with HCl through

Reaction (2). The decrease of HCl concentration is beneficial to suppress the Deacon reaction (Eq. (3)) (Chen *et al.*, 2019), thereby inhibiting the generation of Cl_2 . A decrease in the amount of Cl_2 will significantly affect the *de novo* synthesis.

Urea can be decomposed at 135°C through Reactions (4)–(7) and the effective decomposition reaches 100% at 600°C (Guerriero *et al.*, 2009; Okamoto, 1999). Reactions (4)–(6) shows that the active radicals, including N-containing active group ($\text{NH}_2\cdot$) and hydrogen radical ($\text{H}\cdot$), are formed during the urea pyrolysis process (Chen and Isa, 1998; Koebel and Strutz, 2003). Therefore, the third mechanism is that the active edge sites on the surface of the fly ash can be replaced by the N-containing active group ($\text{NH}_2\cdot$), which prevents the generation of PCDD/Fs, as shown in Fig. 7. Meanwhile, the C-O bond on the PCDD/Fs molecules can be attacked by hydrogen radical ($\text{H}\cdot$), then the C-O bond is broken to form polychlorinated biphenyl or Polystream (Okamoto, 1999), as shown in Fig. 8.

Fig. 7. Schematic diagram of active group ($\text{NH}_2\cdot$) inhibited the formation of PCDD/Fs.

Fig. 8. Schematic diagram of the hydrogen radical ($\text{H}\cdot$) attacked C-O bond on PCDD/Fs molecular.

(R3) bond in the polychlorinated biphenyl molecules to promote the hydrodechlorination reaction (Fueno *et al.*, 2002; Altarawneh *et al.*, 2009).

(R4) The molecular structures of PCDD/Fs include C=C bond, C-C bond, C-H bond, C-Cl bond and C-O bond,

(R5) and their bond energies are showed in Fig. 9. Among them,

(R6) while the C=C bond is the highest (611 kJ mol^{-1}),

(R7) Therefore, when the PCDD/Fs molecules are attacked by $\text{H}\cdot$, C-Cl bonds will be easier to break than other bonds.

In addition, the remaining NH_3 can be enriched in the over-wet layer and react with SO_2 through Reactions (8–9). In this work, after adding urea, the desulfurization efficiencies were 56.3 (0.02% urea), 58.0 (0.035% urea) and 56.4% (0.05% urea), respectively.

Studies indicated that there are many chlorine atoms in the benzene ring of high-chlorinated PCDD/Fs, causing the increase of steric hindrance and weakening the interaction between C and Cl atoms so that the C-Cl bond is vulnerable by the hydrogen radical (Zhang *et al.*, 2004; Yang *et al.*, 2006).

(R9) In addition, a previous study (Lu *et al.*, 2010) suggested that the chlorine atoms in the longitudinal (1,4,6,9) positions are preferentially removed than the chlorine atoms on lateral (2,3,7,8) positions. However, the Cl atoms of low-chlorinated PCDD/Fs are mainly distributed in lateral positions among the 17 congeners of PCDD/Fs, so it is difficult for low-chlorinated PCDD/Fs to dechlorinate the Cl atoms. In comparison, the chlorine atom numbers of high-chlorinated

Mechanism of Dechlorination Reaction

The hydrogen radical generated directly in the pyrolysis process of urea has a strong activity, $\text{H}\cdot$ can attack the C-Cl

Fig. 9. The dissociated energy of the chemical bond of PCDD/Fs.

PCDD/Fs are more significant than that of low-chlorinated PCDD/Fs in longitudinal positions. Therefore, the longitudinal chlorine atoms of high-chlorinated PCDD/Fs are easy to remove by the hydrodechlorination reaction under the attack of hydrogen radical. Then the high-chlorinated PCDD/Fs was continuously converted to low-chlorinated PCDD/Fs after gradual dechlorination. The above demonstrated why urea had a more obvious inhibitory efficiency on high-chlorinated than that of low-chlorinated and the concentrations of TeCDD and TeCDF were increased after the addition of urea into the iron ore sintering mixture. Taking the high-chlorinated OCDD and OCDF as examples, a dechlorination reaction occurred when the hydrogen radical attacks Cl atom of PCDD/Fs, as shown in Fig. 10. Therefore, based on the results that the addition of urea reduced the average I-TEQ number of chlorine substituents, it was suggested that the

hydrodechlorination reaction might be the main mechanism for the increase of low-chlorinated PCDD/Fs.

CONCLUSIONS

In this study, urea was selected as an inhibitor to reduce the emission of PCDD/Fs during iron ore sintering. The I-TEQ values for the PCDD/Fs were evaluated, and the inhibition mechanisms were identified. The following conclusions were drawn:

- (1) After adding 0.02–0.05 wt.% urea particles into the iron ore sintering mixture, the I-TEQ values for the total PCDD/Fs were reduced by 60.0–76.0%, and the average I-TEQ value for the chlorine substituents decreased, indicating that urea inhibits the chlorination of PCDD/Fs.
- (2) The mechanisms driving the reduction in PCDD/F emission can be divided into three categories: (i) the poisoning of Cu⁺; (ii) the decrease in Cl₂ and (iii) the effect of active radicals, which impede the formation or weaken the molecular bonds of PCDD/Fs.
- (3) With the incorporation of urea, the I-TEQ values for the emitted high-chlorinated PCDD/Fs decreased sharply, whereas those for the low-chlorinated ones rose, suggesting that the hydrodechlorination reaction may be the primary mechanism driving the increase in low-chlorinated PCDD/Fs.

ACKNOWLEDGMENTS

This work was supported by the Key Program of National Natural Science Foundation of China (U1660206 and 51674002). One of the authors (L.X. Qian) also acknowledges the scholarship offered by the China Scholarship Council (CSC) via the Joint-Training Ph.D. Program (Grant No. 201908340086).

Fig. 10. Schematic diagram of hydrogen radical (H·) attacked Cl atoms on PCDD/Fs molecular.

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Received for review, February 3, 2020

Revised, May 13, 2020

Accepted, May 15, 2020