Gas-phase and particle-phase PCDD/F congener distributions in the flue gas from an iron ore sintering plant

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ABSTRACT

The activated carbon injection-circulating fluidized bed (ACI-CFB)-bag filter coupling technique was studied in an iron ore sintering plant. For comparison, the removal efficiencies under the conditions without or with ACI technology were both evaluated. It was found that the polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) removal efficiency for total international toxic equivalence quantity (I-TEQ) concentration was improved from 91.61% to 97.36% when ACI was employed, revealing that ACI was very conducive to further controlling the PCDD/F emissions. Detailed congener distributions of PCDD/Fs in the gas-phase and particle-phase of the Inlet and Outlet samples were determined. Additionally, the PCDD/F distribution for the Fly ash-with ACI sample of was also studied.

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Introduction

Due to their severe toxicities, persistence, and potential to accumulate in the tissues of organisms, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are classified as persistent organic pollutants (POPs) and targeted for international source reduction by the Stockholm Convention (Su et al., 2014a, 2014b; Kaivosoja et al., 2012; Lu et al., 2012). PCDD/Fs are unintentionally formed during various thermal and chemical processes, including those in municipal solid waste incinerators (MSWIs) (Chang et al., 2011; Choi and Lee, 2007; Liu et al., 2013), metallurgical facilities (Su et al., 2014a, 2014b; Kuo et al., 2012; Lee et al., 2009; Lenoir et al., 2012), power generation (Zhang et al., 2013) and some chemical processes (Li et al., 2014). Among them, iron ore sintering plants are recognized as the most important PCDD/F emission source in many countries (Kuo et al., 2012).

In the past few years, the emission standards for PCDD/Fs have become increasingly stringent globally. The Chinese government has promulgated a new regulation that reduces the emission limit from 1.0 ng I-TEQ/Nm³ (I-TEQ: international toxic equivalence quantity) to 0.1 ng I-TEQ/Nm³ starting in July 2014 and January 2016 for newly-built and existing MSWIs with a daily capacity of 100 ton, respectively. For the control of PCDD/F emissions, various end-of-pipe treatment technologies have been developed, such as catalytic decomposition using SCR catalysts (Su et al., 2015; Dvořák et al., 2010; Jones and Ross, 1997), spraying of powdered activated carbon (PAC) into flue gas (Chang et al., 2009) and installing a fixed-bed adsorption system (Hung et al., 2011). Among the air pollutant control devices (APCDs) applied, activated carbon injection (ACI) into flue gas has been considered as the most convenient strategy due to its simplicity in engineering and high efficiency (Chi and Chang, 2005; Lin and Chang, 2008; Wang et al., 2009). So far, ACI...
technology has become the most widely used method for reducing PCDD/F emissions at most MSWIs (Chang et al., 2009).

As the most important PCDD/F emission source, iron ore sintering plants have received far less concern, especially in developing countries. In most iron ore sintering plants, great attention has been paid to fly ash control by bag filter or electrostatic precipitator technologies, and SO2 control through dry, semidry, or wet methods, whereas PCDD/Fs could only be removed simultaneously during the desulfurization and dedusting processes (Guerriero et al., 2009b; Kuo et al., 2012).

For PCDD/F emissions of iron ore sintering plants, increasing attention has been paid to emission monitoring, and a total PCDD/F concentration of the flue gas is commonly reported (Guerriero et al., 2009a). However, in the flue gas, PCDD/Fs are semi-volatile in the forms of gas-phase and particle-phase, and both are collected simultaneously in standard isokinetic sampling procedures. Different APCDs might show different control performances for gas-phase and particle-phase PCDD/Fs. For example, the gas-phase PCDD/Fs could be substantially removed using ACI technology, whereas the particle-phase PCDD/Fs could be easily removed during the dedusting process. Hence, detailed analysis of the gas-phase and particle-phase PCDD/F congener distributions for flue gas samples collected from the field plants at the inlet and outlet of the APCDs would be highly useful for the practical application of PCDD/F removal methods. Kuo et al. have reported the gas-phase and particle-phase partitioning of PCDD/F congeners in the flue gas of an iron ore sintering plant, and found that the gas phase dominated in the collected samples (Kuo et al., 2012).

China, as the largest developing country in the world, contributes nearly half of the steel production of the world. Accordingly, the PCDD/F emission from the steel industry accounts for the largest proportion. Meanwhile, the sintering process generates the overwhelming majority of PCDD/Fs in the steel industry (Wu et al., 2015). However, in China, existing APCDs may not meet the emission standard of 0.5 ng I-TEQ/Nm$^3$ for newly-built and existing iron ore sintering plants starting October 2012 and January 2015, respectively. The technique of coupling existing APCDs with ACI is of great importance for further control of PCDD/Fs at present, and is very meaningful for potentially more stringent standards in future.

Recently, multiple pollutant collaborative control technology using a circulating fluidized bed (CFB) has become increasingly popular due to its advantages of not producing wastewater, simplicity, and lower investment (Sheng et al., 2012). Also, detailed analysis of the gas-phase and particle-phase PCDD/F congener distributions for flue gas samples collected from an iron ore sintering plant at the inlet and outlet of APCDs has been rarely reported in China (Tian et al., 2012). Recently, we studied the simultaneous control of PCDD/Fs and NOx from the flue gas of a MSWI with a pilot plant (Liu et al., 2015). However, significant differences exist between the PCDD/F emissions from MSWI and iron ore sintering processes. Herein, we researched the PCDD/F emissions in the flue gas from an iron ore sintering plant located in northern China. In the plant, a CFB reactor and bag filter were built to remove the SO2, fly ash, and PCDD/Fs, and ACI technology was employed for better PCDD/F control. The PCDD/F congener distributions in the gas- and particle-phases were systematically studied with and without ACI technology.

1. Experimental

1.1. Characterization of activated carbon

Commercial coconut shell activated carbon (AC) used in the ACI technology was purchased from the Chengde Jibeiyanshan Activated Carbon Corporation in Hebei province. The BET special surface area was measured as 1050 m$^2$/g, and its H-K micropore width was 0.50 nm.

1.2. Description of the ACI-CFB-Bag filter technique

In the ACI-CFB-Bag filter technique (Fig. 1), the flue gas was first introduced to an electrostatic separator to remove the particulate matter (PM). The flue gas was then sent to a circulating fluidized bed (CFB) with two cyclones. Meanwhile, lime and activated carbon were injected into the CFB deSO2 reactor. After the desulfurization, the flue gas passed through the bag filter, the fly ash was collected. Finally, the purified gas was emitted through the stack. The emissions of SO2 and PM were recorded using an online analyzer. The sampling points were located at the inlet of the CFB reactor, and the outlet of the bag filter.

At the inlet of the CFB reactor, the gas flow was 500,000 m$^3$/hr and the temperature was 110–130°C. The concentrations of SO2 and PM were 416.7 and 55.3 mg/m$^3$, respectively. At the outlet of the bag filter, the concentrations of SO2 and PM were 36.2 and 5.2 mg/m$^3$ with the corresponding removal efficiencies of 91.3% and 90.6%, respectively.

1.3. PCDD/F sampling

The gas sampling points for PCDD/Fs were located at the inlet of the CFB reactor and the outlet of the bag filter. For convenience, the samples were named Inlet and Outlet samples. The fly ash sample was collected at the fly ash tank under the bag filter.

The sampling and analysis procedures were conducted according to previous reports (Liu et al., 2015). The gas samples were collected using an automatic isokinetic sampling system, Isostack Basic, following the EU standard method EN-1948. The sampling system is composed of a heated probe, a filter box with a quartz fiber filter, and a water-cooled XAD-2 adsorbent trap. The quartz fiber filter was used to collect particle-bound pollutants, and XAD-2 adsorbent resin was used for trapping the vapor-phase contaminants. Five surrogate target compounds (Wellington Laboratories, Guelph, Canada) were added into the XAD-2 resin in the adsorbent sampling cartridge before sampling. The fly ash sample was collected from the bag filter during the collection of the gas samples.

1.4. PCDD/F analysis

Seventeen homologs of 2,3,7,8-substituted PCDD/Fs were analyzed using method EU 1948. The samples were spiked with defined amounts of $^{13}$C$_{12}$-PCDD/F internal standards and then extracted with toluene for about 24 hr in a Soxhlet apparatus. The extracts were subjected to a series of cleanup steps by adsorption chromatography, including an acidic silica gel column, a multilayer silica gel column, and a basic...
alumina column. The final extracts were then concentrated to 20 μL and spiked with 1.0 ng of 13C12-PCDD/F internal standards for the recoveries of the internal standards to be estimated before the instrumental analysis.

The PCDD/F analyses were performed by an Agilent 6890 gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) coupled with an Autospec Ultima high-resolution mass spectrometer (Waters, Milford, MA, USA). The gas chromatograph was equipped with a DB-5 ms fused-silica column (60 m × 0.25 mm i.d. × 0.25 μm) to achieve chromatographic separation. The mass spectrometer was tuned and operated at ≥10,000 resolution with 38 eV EI energy. Selected ion monitoring (SIM) mode was used for data acquisition.

The removal efficiency for PCDD/Fs is defined as follows:

$$\eta(\%) = \frac{C_{\text{inlet}} - C_{\text{outlet}}}{C_{\text{inlet}}} \times 100\%.$$  

2. Results and discussion

2.1. PCDD/F congener distributions for Inlet and Outlet samples

In this study, the sampling points for PCDD/Fs were located at the inlet of the CFB reactor and the outlet of the bag filter, and the samples were named Inlet and Outlet samples for convenience. The 1-TEQ concentrations were calculated according to the international toxic equivalence factors (I-TEF). The concentrations of Cpg, Cpg-PCDFs, Cpg-PCDDs, and Cpg-1-TEQ, and the corresponding values of particle-phase and total concentrations are summarized in Table 1.

For Inlet samples, Cpg was much lower than Cpp, and the Cpg/Cpp and Cpg-1-TEQ/Cpp-1-TEQ ratios were 0.06 and 0.22, respectively. It is reasonable that the removal efficiency of particle-phase...
PCDD/Fs was higher than that of the gas-phase PCDD/Fs, since the particle-phase PCDD/Fs are all attached on the particle matter (PM), and the PM could be removed by the bag filter with very high removal efficiency. For gas-phase PCDD/Fs, a large part was captured first during the desulfurization process with or without ACI, a portion was transformed into particle-phase PCDD/Fs, and its further removal was then accomplished by the dedusting process with the bag filter. Most PCDD/Fs could be captured by activated carbon due to its suitable pore size in comparison to the molecular size of PCDD/Fs. However, a small portion of PCDD/Fs still existed in the gas phase during the adsorption process. PCDFs apparently dominated in both the gas phase and particle phase, and the $C_{PCDF}/C_{PCDD}$ ratios for gas-phase, particle-phase, and total samples were 15.33, 5.46, and 5.70, respectively. The $C_n/C_p$ and $C_p$I-TEQ/$C_p$I-TEQ values of outlet without ACI were 0.05 and 0.02, and the $C_n$ and $C_p$I-TEQ o were 1.54 ng/Nm$^3$ and 0.35 ng I-TEQ/Nm$^3$ with the corresponding removal efficiency of 97.51% and 91.61%, respectively. For comparison, the $C_n/C_p$ and $C_p$I-TEQ/$C_p$I-TEQ values of outlet with ACI were 0.19 and 0.04, and the $C_n$ and $C_p$I-TEQ o were 0.56 ng/Nm$^3$ and 0.11 ng I-TEQ/Nm$^3$ with the corresponding removal efficiency of 99.09% and 97.36%, respectively. It can be seen that the removal efficiencies for the total concentrations and the total I-TEQ concentrations were both apparently higher when ACI technology was employed.

Fig. 2 – Congener profiles of PCDD/Fs for gas phase and particle phase of Inlet samples. PCDD/Fs: polychlorinated dibenzo-p-dioxins and dibenzofurans.

Fig. 3 – Congener profiles of PCDD/Fs for gas phase and particle phase of outlet without ACI samples. PCDD/Fs: polychlorinated dibenzo-p-dioxins and dibenzofurans; ACI: activated carbon injection.
Detailed gas-phase and particle-phase congener profiles of the seventeen 2,3,7,8-substituted PCDD/Fs obtained from the flue gas collected at the inlet of the CFB reactor are illustrated in Fig. 2. For the gas-phase sample, the top three congeners in abundance were 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDF, and 1,2,3,4,7,8-HxCDF with the concentrations of 1.05, 0.77, and 0.39 ng/Nm³, respectively. In sequence, the top three I-TEQ congeners were 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,7,8-PeCDF with the I-TEQ concentrations of 0.53, 0.039, and 0.038 ng I-TEQ/Nm³, illustrating that 2,3,4,7,8-PeCDF contributed 70% of the I-TEQ concentration of the gas sample. For the particle-phase sample, the top three congeners were 1,2,3,4,6,7,8-HpCDF, 2,3,4,6,7,8-HxCDF, and 1,2,3,6,7,8-HxCDF, and their concentrations were 21.45, 8.04, and 4.34 ng/Nm³, respectively. Meanwhile, the top three I-TEQ congeners were 2,3,4,7,8-PeCDF, 2,3,4,6,7,8-HxCDF, and 1,2,3,6,7,8-HxCDF with the I-TEQ concentrations of 0.89, 0.80, and 0.43 ng I-TEQ/Nm³. In addition, it can be seen that the concentrations of PCDFs were apparently higher than those of PCDDs for both gas-phase and particle-phase samples.

During the desulfurization process, most of PCDD/Fs could be removed simultaneously. It is of interest to investigate removal efficiencies for the gas-phase and particle-phase PCDD/Fs, and their congener distributions after the desulfurization process. As shown in Fig. 3, each congener in the gas-phase was reduced below 0.025 ng/Nm³. The highest concentration and I-TEQ concentration correspond to OCDF and 2,3,4,7,8-PeCDF with the values of 0.024 ng/Nm³ and 0.004 ng I-TEQ/Nm³, respectively. For the particle-phase of outlet without ACI, the concentration of each congener was below 0.5 ng/Nm³, with the I-TEQ concentration below 0.25 ng I-TEQ/Nm³. 2,3,4,7,8-PeCDF contributed the highest concentration and I-TEQ concentration with the values of 0.47 ng/Nm³ and 0.24 ng I-TEQ/Nm³, accounting for nearly 70% of the I-TEQ concentration for the particle-phase PCDD/Fs.

As discussed above, most PCDD/Fs could be removed during the desulfurization process. However, PCDD/F emissions must be strictly controlled due to their high toxicities, and the strategy of using existing APCDs to remove PCDD/Fs may not meet the increasingly strict requirements. Hence, the ACI technology was employed for further PCDD/F removal. As illustrated in Fig. 4, for the gas-phase PCDD/Fs, each congener was reduced to a great extent, with concentrations below 0.05 ng/Nm³. The top two congeners in abundance were the octo-chlorinated OCDD and OCDF with the concentrations of 0.04 and 0.02 ng/Nm³, whereas 2,3,4,7,8-PeCDF gave the

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**Fig. 4** – Congener profiles of PCDD/Fs for gas phase and particle phase of outlet with ACI samples. PCDD/Fs: polychlorinated dibenzo-\(p\)-dioxins and dibenzofurans; ACI: activated carbon injection.
ACI-total samples were 0.35 and 0.11 ng I-TEQ/Nm³, and their concentrations of outlet without ACI-total and outlet with when ACI technology was not used. However, the total I-TEQ congeners showed notable decrease after the treatment, even samples are summarized in Fig. 5. It can be seen that all the Inlet-total, outlet without ACI-total, and outlet with ACI-total respectively (Table 1). The results revealed that the ACI technology was effective for further PCDD/F removal.

The ACI-CFB-bag filter coupling technique has been proved to be an efficient strategy for PCDD/F removal. When ACI was not used, the PCDD/F removal efficiency for total I-TEQ concentration was 91.61%. For further PCDD/F removal, the ACI technology was employed, and the removal efficiency for total I-TEQ concentration was greatly improved to 97.36%, while the corresponding removal efficiency for gas-phase and particle-phase PCDD/Fs reached 99.47% and 96.93%, respectively. Detailed congener distributions of PCDD/Fs in the gas phase and particle phase of the inlet and outlet samples were determined. Additionally, the PCDD/F distributions for the sample of Fly ash-with ACI revealed that the concentration of PCDFs was higher than that of PCDDs, and the total I-TEQ concentration was 0.63 ng I-TEQ/g.

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REFERENCES


