Removal of PCDD/Fs and CBzs by different air pollution control devices in MSWIs

Tong Chen¹⁺, Chen Sun¹, Tianjiao Wang², Mingxiu Zhan³¹, Xiaodong Li¹, Shengyong Lu¹, Jianhua Yan¹

¹ State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou 310027, China
² Institute of Incineration Technology, Everbright Envirotech (China) Ltd., Nanjing 211102, China
³ College of Metrology and Measurement Engineering, China Jiliang University, Hangzhou 310018, China

Abstract

This study investigated the efficiencies with which polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and chlorobenzenes (CBzs) were removed by different air pollution control devices (APCDs) in three municipal solid waste incinerators (MSWIs). These devices were the semi-dry flue gas desulfurization (SDFGD) system, activated carbon (AC) injection, bag filters (BF), the selective catalytic reduction (SCR) reactor, and the wet scrubber. The SDFGD system, AC injection, and BF exhibited similar removal effects on both PCDD/Fs and CBzs, whereas minor effects were found regarding their correlations. Furthermore, it was more difficult to adsorb and remove the lower chlorinated CBzs by AC injection

⁺ Corresponding author. E-mail address: chentong@zju.edu.cn
and BF. However, it was easier to decompose and remove lower chlorinated PCDD/Fs and CBzs by using the SCR reactor. The removal efficiency of CBzs was also considerably lower than that of PCDD/Fs. Moreover, the “memory effect” in the wet scrubbers resulted in an increase in PCDD/Fs and even CBzs. Regrading PCDD/Fs, the concentrations of penta- to hepta-chlorinated PCDD/Fs increased most when flue gas passed through the wet scrubbers. Among CBzs, TrCBzs were the most seriously affected. Given the different removal effects of each unit of APCDs, especially the wet scrubber, the correlation model between PCDD/Fs and CBzs should be distinguished and established separately. Better indicators of PCDD/Fs affected by APCDs were also discussed.

Keywords: Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans; Chlorobenzenes; Air pollution control devices; Correlations; Emission characteristics
INTRODUCTION

Typical organic pollutants, such as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs), chlorobenzenes (CBzs) and chlorophenols, can be found throughout the whole process of municipal solid waste incinerator (MSWI) with various concentration levels. Researchers have found that there are various persistent organic pollutants in the bottom ash, fly ash and the flue gases before and after the air pollution control devices (APCDs) (Dong et al., 2002; Takaoka, 2002; Oh et al., 2007; Yan et al., 2010; Hu et al., 2013; Han et al., 2017; Hsieh et al., 2018). The characteristics and relationships of PCDD/Fs and chlorobenzenes as indicators have also been studied (Ballschmiter et al., 1988; Altwicker et al., 1992; Kato and Urano, 2001; Lavric et al., 2005; Yin et al., 2007; Gullett et al., 2011). In our previous research, the emission characteristics of PCDD/Fs and CBzs in flue gas before the APCDs and in the stack have been investigated along with their correlation models (Chen et al.; Wang et al., 2017a; Wang et al., 2017b). However, the removal efficiencies of PCDD/Fs and CBzs by the semi-dry flue gas desulfurization (SDFGD) system, activated carbon (AC) injection, bag filters (BF), the selective catalytic reduction (SCR) reactor, and the wet scrubber have not been comprehensively studied. Furthermore, influences on the correlation models of PCDD/Fs and CBzs by each APCDs unit have not been investigated.

APCDs play vital roles in controlling pollutant emissions from MSWIs and can substantially affect the characteristics of both PCDD/Fs and CBzs. The common related technologies most commonly used in the MSWIs include SDFGD, wet
scrubbers, selective non-catalytic reduction (SNCR), SCR, AC adsorption, BF, and electrostatic precipitators (ESPs) (Kulkarni et al., 2008; Wielgosiński, 2010; Li Shiyou, 2017; Sida, 2017).

SDFGD and wet flue gas desulfurization are methods commonly employed to control acid gas pollutants, such as HCl, SO₂ and NOₓ. The use of calcium oxide or calcium hydroxide powders can also affect the characteristics of PCDD/Fs and CBzs. The wet scrubber is also a typical deacidification device. Wevers et al. (1992b) found that 71% of PCDD/Fs in the flue gas could be removed by the wet scrubber. However, because of the existence of memory effects, which typically burden clean flue gas but clean dirty flue gas, increasing concentrations of PCDD/Fs could also be found (Trivedi and Majumdar, 2013). SNCR and SCR technologies are widely used in NOₓ reduction. Amino-reductants employed in SNCR systems also suppress the formation of PCDD/Fs (Ruegg and Sigg, 1992; Päivi H. Ruokojärvi et al., 1998; Ruokojärvi et al., 2001; Kuzuhara et al., 2005). Additionally, novel catalysts used in SCR systems nowadays facilitate the joint degradation of NOₓ and PCDD/Fs (Kulkarni et al., 2008; Wielgosiński, 2010).

ESPs and BF employed to remove particulate matters from flue gas. ESP is suitable for use in a range of adverse circumstances at high temperature. However, it is sensitive to particle size and fails to remove gaseous pollutants. ESP is also one of the main sources for the formation of PCDD/Fs. Bag filters are suitable for various flue gases and have high removal efficiencies; however, they are easily damaged because of filter materials. Bag filters are able to remove solid-phase PCDD/Fs...
attached to particles. However, memory effects on PCDD/Fs were found (Trivedi and Majumdar, 2013). AC is used to remove heavy metals, ultrafine particles, PCDD/Fs and other organic pollutants (Wielgosiński, 2010). Bag filters an AC injection are a conventional unit of APCDs in numerous of MSWIs.

APCDs might also have a significant influence on the relationship between PCDD/Fs and CBzs. CBzs as significant precursors and indicators, have an adequate relationship with PCDD/Fs, and can be used to indirectly monitor and control their emissions (Lavric et al., 2005; Gullett et al., 2011). However, the influences of each APCD unit on the relationship of between PCDD/Fs and CBzs remain unknown. In this research, the concentrations, fingerprint characteristics of, and relationships between PCDD/Fs and CBzs before and after the applications of different air purification units of three MSWIs were studied.

METHODS
Sample collection
The sample comprised three stocks in one municipal solid waste incineration plant in eastern China. Each stock had a capacity of 750 t/d. The ACPD system included SNCR, SDFGD, AC injection, BF, steam gas heater (SGH), SCR, wet scrubber, and gas gas heater (GGH). Basic information on each of these is presented in Table 1, and a schematic diagram of APCD system is shown in Fig. 1.

Table 1 The basic information of MSWIs investigated

<table>
<thead>
<tr>
<th>MSWI I, II, and III</th>
<th>stock</th>
<th>capacity /t·d(^{-1})</th>
<th>combustion temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>type of furnace</td>
<td>stock</td>
<td>750</td>
<td>950</td>
</tr>
</tbody>
</table>
operation duration /m 10
APCD system SNCR + SDFGD + AC injection + BF + SGH + SCR + wet scrubber + GGH

Fig. 1 The technological process of flue gas purification system

The original flue gas from the boiler first entered the SDFGD to remove acid gases. Heavy metals, PMs, and PCDD/Fs were then removed through the bag filter with an AC injection. Following the steam gas heater, flue gas entered the SCR reactor. The SCR reactor was put after BF to avoid the destructive effect of PM on the SCR catalyst. Both PCDD/Fs and NO\textsubscript{x} were removed using special catalysts. The acid gas was then removed once again in the wet scrubber at the end to achieve the ultra-low emission standard. After several removals of SO\textsubscript{2}, NO\textsubscript{x}, PM and PCDD/Fs, the emitted flue gas was generally clean.

Flue gas samples were collected simultaneously in the APCD systems of each MSWI. The sample sites were the SDFGD inlet (named 1#), the SCR reactor inlet (2#), the SCR reactor outlet (3#), and the stack (4#), as shown in Fig. 1. The temperature and oxygen content in each of the sampling conditions are listed in Table 2.

Table 2 The main information of experimental conditions

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>MSWI I</th>
<th>MSWI II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace temperature /℃</td>
<td>948±35</td>
<td>908±22</td>
</tr>
<tr>
<td></td>
<td>MSWI III</td>
<td>964±27</td>
</tr>
<tr>
<td>----------------</td>
<td>----------</td>
<td>--------</td>
</tr>
<tr>
<td>Temperature at</td>
<td>1#</td>
<td>2#</td>
</tr>
<tr>
<td>the sampling</td>
<td>198±15</td>
<td>179±9</td>
</tr>
<tr>
<td>Oxygen content at</td>
<td>1#</td>
<td>2#</td>
</tr>
<tr>
<td>the sampling site</td>
<td>198±15</td>
<td>179±9</td>
</tr>
</tbody>
</table>

All flue gas samples were collected in accordance with the US EPA method 23 standard (EPA, 1995) by using an isokinetic sampler (KNJ, Korea). Each sample was collected for approximately 2.0 m$^3$. The part in the particulate phase was collected in the filter, whereas the part of the sample in the gaseous phase was collected in XAD-II resin.

The extraction method employed in previous research was used for all the samples collected (Oh et al., 2007). The samples were extracted stepwise with methylene chloride and toluene and then concentrated separately. This step was undertaken to prevent the losses of semi-volatile compounds such as chlorobenzenes.

The aliquots of the concentrated samples were used for the cleanup and analysis of PCDD/Fs and CBz. The PCDD/F cleanup procedure and analysis were conducted in accordance with the standard of US EPA Method 23a (EPA, 1995). A 6890 Series gas chromatograph (Agilent, USA) coupled with a JMS-800D mass spectrometer (JEOL, Japan), comprised the high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) used for the identification and quantification of PCDD/Fs. The capillary column used was DB-5ms (60 m×0.25 mm I.D., 0.25 μm film thickness). Details of the temperature programming used for the column can be found in previous research (Wang et al. 2017a; Wang et al. 2017b).
The recovery of PCDD/Fs in all samples was within the range required. Based on standards for pollution control at municipal solid waste incinerators in China, the international toxic equivalent factors (I-TEFs) (Bhavsar et al., 2008) were employed to calculate the toxic equivalent values (TEQs) of PCDD/Fs. All concentrations were normalized to dry air, 11% of oxygen content, 101 kPa, and 237 K.

The pretreatment and detection of CBzs were previously described thoroughly by Yan et al. (Yan, 2012). GC-ECD (GC 6890N, Agilent, USA) and involved the use of a DB-5 column (30 m×0.25 mm×0.25 µm).

RESULTS AND DISCUSSION

Effects on the total concentrations of PCDD/Fs and CBzs

The concentration of PCDD/Fs in the flue gas passing through the APCDs in three MSWIs are presented in Fig. 2. The concentrations of PCDD/Fs in the original flue gas of three MSWIs were 1.1, 2.2, and 1.0 ng I-TEQ Nm⁻³, respectively. The original pollutant values emitted were rather low in most Chinese MSWIs. This is primarily due to the new technology designed for the grate. Each column moves as one unit, and shear knives are set in the combustion section to break up caked waste and improve combustion conditions. Excellent operation in time during the combustion also exhibited good effects. Low levels of pollution produced from the furnace assisted the subsequent purification steps.

After applying the SDFGD cleaning system with AC and BF, the concentrations of PCDD/Fs decreased to 0.14 ng I-TEQ Nm⁻³. The SCR reactor then reduced the TEQ value even further to only 0.026 ng I-TEQ Nm⁻³, which is rather lower than the
national standard of 0.1 ng I-TEQ Nm\(^{-3}\). However, the wet scrubber at the end increased the concentration of PCDD/Fs to 0.4 ng I-TEQ Nm\(^{-3}\), resulting in excess emissions. The similar results were also found in MSWI II. For instance, the TEQ value decreased from 2.16 ng I-TEQ Nm\(^{-3}\) to 0.043 ng I-TEQ Nm\(^{-3}\) using the SDFGD with AC and BF and, then fell even further to 0.028 ng I-TEQ Nm\(^{-3}\) through the SCR reactor, but the TEQ value then increased to 0.061 ng I-TEQ Nm\(^{-3}\) because of the effects of the wet scrubber. The results showed that the SDFGD with AC and BF worked effectively in all MSWIs with removal efficiencies of 87.0%, 98.0%, and 98.2%, respectively. This purification system is widely used in nearly all MSWIs. This shows that an effectively functioning system could achieve highly efficient removal efficiencies of PCDD/Fs, especially in newly-built MSWIs. However, the SCR reactor and wet scrubber had different effects on the concentration of PCDD/Fs. SCR is a technology typically used to remove NO\(_x\) coupled with PCDD/Fs to reach near-zero emissions of PCDD/Fs. Among the three MSWIs investigated, the SCR reactor exhibited a high PCDD/F removal efficiency of 81.8% and a low efficiency of 33.5% in two MSWIs. However, in MSWI III, it did not work effectively. The removal efficiency of catalysts in flue gas is largely affected by several complex factors, such as temperature, flue gas velocity, moisture, and oxygen content (Tian Bo, 2010). The rather lower concentrations before SCR in MSWI II and III, which fell to as low as 0.05 and even 0.01 ng I-TEQ Nm\(^{-3}\), respectively, also resulted in weaker removal efficiencies, compared with the experimental results of other studies (Yu et al., 2016a; Yu et al., 2016b). Similarly, the wet scrubber also had different effects on
the removal of PCDD/Fs. In MSWI I and II, the wet scrubber promoted the formation
of PCDD/Fs, whereas the concentrations of PCDD/Fs in flue gas from MSWI III
decreased when flue gas passed through the wet scrubber. The removal effect can be
attributed to alkaline compounds used in the wet scrubber. However, this effect on
PCDD/Fs is limited because the memory effect, which mainly results in high
concentrations of PCDD/Fs, is common in the wet scrubber (Trivedi and Majumdar,
2013). The memory effect is thus a really significant factor in controlling PCDD/Fs.

![Fig. 2 PCDD/F concentrations and TEQ in the flue gas from MSWIs](image)

A similar variation was also found in the total concentrations of CBzs when flue
gas passed through APCDs. As shown in Fig. 3, the average concentration of CBzs in
oral flue gas from the stock was 3.25 µg Nm$^{-3}$, nearly 1,000 times higher than that of
PCDD/Fs. This was similar to results for fluid bed incinerators (Wang et al., 2017a;
Wang et al., 2017b). The SDFGD system with AC and BF had the same effect on
CBzs in all three MSWIs. The removal efficiencies were 48.4%, 51.6%, and 67.5%
for MSWI I, II, and III, respectively. The SCR reactors in MSWI I and II also showed
adequate removal effects on CBzs, which was consistent with the effects on PCDD/Fs.
The concentrations of CBzs in flue gas decreased from 1.27 to 1.04 µg Nm$^{-3}$ for
MSWI I and 1.77 to 0.94 µg Nm\(^{-3}\) for MSWI II, respectively. However, the removal efficiencies were different from those of PCDD/Fs. In MSWI I, the removal efficiency of PCDD/Fs was higher than that of CBzs, whereas the opposite was the case in MSWI II. Furthermore, the concentrations of CBzs were significantly affected by the wet scrubbers. The total concentration of CBzs increased in all MSWIs when flue gas passed through the wet scrubber, especially in MSWI II and III, where the concentrations increased by 6.3 and 5.2 times, respectively. This shows that there the effects of wet scrubbers on PCDD/Fs and CBzs are considerably more complicated.

![Fig. 3 The total concentrations of CBzs in the flue gas](image)

**Effects on the total concentrations of PCDDs, PCDFs and gas-solid phase distribution**

This research also assessed the gas-solid phase distributions of PCDD/Fs in flue gas through all APCDs from three MSWIs. As shown in Fig. 4, gaseous PCDD/Fs accounted for 90% of the total concentration of original flue gas at SDFGD inlets in three MSWIs, and the corresponding TEQ value reached 97%. In MSWI I, the gas-solid distribution of PCDD/Fs changed considerably through the SDFGD system with AC and BF. More highly chlorinated PCDD/Fs with low toxic equivalency
factors were present in the particulate matter, and the AC could not adsorb and remove them easily. Thus, the proportion of gaseous PCDD/Fs fell to 66.3%. A similar trend was also evident in MSWI III, where the proportion of gaseous PCDD/Fs decreased from 98% to 90%. Taking the gas-solid distribution of PCDD/Fs through the SCR reactors and wet scrubbers into account, gaseous PCDD/Fs dominated in all flue gas from stockers, and the SDFGD system with AC and BF had the strongest effect on the gas-solid phase distribution of PCDD/Fs.

Fig. 4 The gas-solid distribution of PCDD/Fs in the flue gas through the APCDs

The investigation of PCDDs and PCDFs in flue gas from three MSWIs is shown in Fig. 5. The ratios of PCDD and PCDF in original flue gas and final emissions from the three MSWIs were all lower than 1.0. In MSWI I, the concentrations of both PCDDs and PCDFs concentrations decreased and then increased when flue gas passed through the APCD system. Following the SDFGD system with AC and BF, the ratio of PCDDs and PCDFs increased to 4.0, including that PCDFs are easier to be remove than PCDDs. However, the ratio of PCDDs and PCDFs decreased to 2.7 in the SCR reactor because of a more adequate removal effect was found on PCDDs than on PCDFs. Both PCDDs and PCDFs increased through the wet scrubber of MSWI I,
especially PCDF. In MSWII, the SDFGD system with AC and BF, the SCR reactor, and the wet scrubber had similar effects on PCDDs and PCDFs. In MSWIII, both PCDDs and PCDFs decreased, especially PCDFs, which differed from the result obtained from MSWI I.

Different APCDs had different effects on PCDDs and PCDFs. More PCDFs could be removed by the SDFGD system with AC and BF, whereas more PCDDs could be removed by the SCR reactor. The wet scrubber also had a relatively strong impact on PCDFs.

![Fig. 5 The concentration of PCDDs and PCDFs in the flue gas](image)

**Effects on CBz homologues**

The concentration fractions of different chlorobenzenes in flue gas at the four sample sites of three MSWIs were also studied. As shown in Fig. 6, the homologue distributions of CBz were the same in all the APCD systems of three MSWIs investigated. These decreased as chlorination increased. Notably, trichlorobenzenes (TrCBzs) contributed most to the total concentration of CBz. For MSWI I, the concentration fractions of tri- to hexa-chlorobenzenes were 48.1%, 28.9%, 18.5%, and 4.5%, respectively. TrCBzs dominated in all flue gas samples, especially flue gas between the SDFGD and BF with the addition of AC. The concentrations of
1,3,5-TrCBz, 1,2,4-TrCBz, and 1,2,3-TrCBz are compared in Fig. 7. This shows that 1,3,5-TrCBz had the lowest concentration in the flue gas of the entire APCD system. The distribution of 1,2,3-TrCBz and 1,2,4-TrCBz varied considerably in different conditions. For instance, we found that the concentration of 1,2,4-TrCBz was higher than that of 1,2,3-TrCBz before the purification of flue gas. However, a different pattern was observed after the purification of flue gas, where the concentration of 1,2,4-TrCBzs in flue gas at the sample position 1# from MSWI II reached 0.78 µg Nm⁻³. The fractions of 1,2,4-TrCBz generally decreased when flue gas passed through the SCR system. Furthermore, 1,2,3-TrCBz contributed most to the TrCBzs with fractions of 47.5% and 62.7% in flue gas after the wet scrubbers of MSWI II and III, respectively.

Fig. 6 The concentration fractions of CBz in the flue gas at different positions
Fig. 7 The concentrations of TrCBz isomers in the flue gas at different positions

**Removal efficiencies of PCDD/Fs and CBzs by the SDFGD system with AC and BF**

The concentration distributions of 17 toxic PCDD/Fs before and after the SDFGD system with AC and BF in three MSWIs were presented in Fig. 8. Before purification, gaseous PCDD/Fs in flue gas from MSWI I primarily consisted of 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,7,8-PeCDF and 1,2,3,4,6,7,8-HpCDF with fractions of 10.1%, 13.4%, 10.8%, and 11.7%, respectively. Fewer differences were found in the distributions of PCDFs. In the solid phase, OCDD contributed a rather high percentage of 50.6% to the total concentrations. 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDF were also the main congeners with fractions of 12.9%, 10.2% and 8%, respectively. After purification, the concentration of low chlorinated gaseous PCDD/Fs decreased; thus, OCDD contributed most to the total concentration with a fraction of 66.2%. Regarding the solid phase PCDD/Fs, most decreased simultaneously except for OCDD. The distributions of PCDD/Fs in flue gas from MWSI II and III were similar to those in MSWI I.
Fig. 8 The distributions of 17 toxic PCDD/Fs through SDFGD system

The removal efficiencies of PCDD/Fs in all three MSWIs were rather similar. For example, the removal efficiencies of each PCDD/F congener in flue gas from MSWI III were greater than 70%, as shown in Fig.9. All gaseous PCDD/Fs were significantly removed, with the efficiencies higher than 90%.
Fig. 9 The removal efficiencies of 17 toxic PCDD/Fs from SDFGD+ AC+ BF

The removal efficiencies of CBzs are shown in Fig. 10. Compared with other CBzs, TrCBzs were difficult to remove with APCDs. For instance, in flue gas from MSWI I and II, the removal efficiencies of teta- to hexa-chlorobenzenes were above 60%, whereas the removal efficiencies of TrCBzs were only 21.8% and 8.7%, respectively. The removal efficiency of TrCBzs in flue gas from MSWI III was 47.8%, whereas the efficiencies of other CBzs reached almost nearly 90%. This could be due to the selection absorption capacity of CBzs by AC. Normally, high chlorinated CBzs have considerably higher boiling points and lower saturated vapor pressure and thus can be much more easily removed. Furthermore, the removal efficiency of all CBzs was affected by the low removal capacity of TrCBzs and the relatively high ratio of TrCBzs to the total number of CBzs. In fact, the activated carbon was chosen based on the adsorption performance of PCDD/Fs not the CBzs, thus the removal efficiency of CBzs might be lower than that of PCDD/Fs.
Removal efficiencies of PCDD/Fs and CBzs by the SCR reactor

The effects on the distributions and removal efficiencies of PCDD/Fs by the SCR reactor of MSWI I are shown in Figs. 11 and 12. OCDD dominated all PCDD/Fs in flue gas before the SCR reactor with a fraction of 66.2%. The main PCDF congeners were 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF with fractions of 6.8% and 5.1%, respectively. The fractions of 1,2,3,4,6,7,8-HpCDF and OCDF increased to 6.0% and 4.1%, respectively, when flue gas passed through the SCR reactor. Thus, PCDFs in flue gas were affected more by the SCR reactor. The removal efficiencies of each PCDD/F congener were clearly different, which could be attributed to their differing oxidation capacities and volatilization (Weber et al., 1999). Furthermore, the removal efficiencies of OCDD and OCDF were lower than those of other low chlorinated PCDDs and PCDFs. The removal efficiencies of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were both higher than 80%. Similarly, the removal efficiencies of 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, and 2,3,4,7,8-PeCDF were all higher than 85%. The removal efficiencies of 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF could even reach as high as 93%.
and 90%, respectively. This result was in accordance with those obtained from pilot tests in full-scale MSWIs (Li et al., 2016). This is because high chlorinated PCDD/Fs have higher vapor pressure and are easily absorbed on the surface of catalysts to be decomposed. Therefore, catalysts need higher oxidation potential to handle the higher chlorination PCDD/Fs (Li et al., 2016).

Fig. 11 The distributions of 17 gaseous PCDD/Fs through the SCR reactor

Fig. 12 The removal efficiencies of 17 gaseous PCDD/Fs through the SCR reactor

The removal efficiencies of CBzs by the SCR reactor of MSWI I are shown in Fig. 13. The removal efficiencies of CBzs decreased as the chlorination level increased, which was similar to the results for PCDD/Fs. However, the removal
efficiencies of all CBzs were considerably lower than those of PCDD/Fs. For instance, the efficiencies of tri- to hexa-chlorobenzenes were all below 25%. CBzs and macromolecular chlorinated benzenes, such as PCDD/Fs, reformed simultaneously in actual flue gas. When flue gas passed through the SCR reactor, both CBzs and PCDD/Fs were decomposed, producing several small-molecule bicyclic or monocyclic compounds (such as CBzs) as degradation products. Some PCDD/Fs could be reductively degraded to the CBzs on SCR catalyst, which could cause the increment of CBzs. Therefore, the removal efficiencies of CBzs were lower than that of PCDD/Fs.

![Graph showing removal efficiencies of different CBzs through the SCR](image)

**Fig. 13 The removal efficiencies of different CBzs through the SCR**

**Memory effects of the wet scrubber**

The wet scrubber is a typical deacidification device. Wevers et al. (1992a) found that 71% of PCDD/Fs in flue gas could be removed through the wet scrubber. However, numerous studies have detected considerably higher levels of PCDD/Fs in the wet scrubber outlet which could therefore be a potential source of PCDD/Fs (Kreisz et al., 1996; Hunsinger et al., 1998; GASS et al., 2000; Sam-Cwan et al., 2001;
Löthgren and van Bavel, 2005). This source is named “the memory effect”. In this research, different chlorinated PCDD/Fs in MSWI I and II increased through the wet scrubber. As shown in Fig. 14, the distributions of PCDDs and PCDFs did not change any great extent, which is in accordance with previous research from Takaoka (2002). Higher chlorinated PCDDs had higher concentration fractions. OCDD dominated among all the PCDDs. Moreover, the fractions of PCDF homologue increased and decreased as chlorination increased and HxCDF contributed most to the total PCDFs.

![Fig. 14 The distributions of PCDDs and PCDFs through the wet scrubbers](image)

The increment of different chlorinated PCDD/Fs is shown in Fig. 15. All the PCDD/Fs clearly increased in MSWI I. The increment of both PCDDs and PCDFs increased and then decreased as chlorination increased. The concentration of HxCDD and PeCDD increased dramatically by 32 and 17 times, respectively among all PCDDs from MSWI I. The same results were found for PCDFs, where penta- and hexa-chlorinated PCDFs increased by almost 20 times. The effects of the wet scrubber in MSWI II were considerably weaker than those in MSWI I. The highest increasing ratios of HpCDD and HpCDF were approximately 5.0.

Due to the strong “memory effect” of wet scrubber, the wet scrubber could...
be installed before the SCR reactor. The PCDD/Fs derived from the “memory
effect” could be degraded on SCR catalyst to achieve higher removal efficiency.
However, the adjustment would increase the consumption of energy on the steam
gas heater due to the low outlet temperature of flue gas at the wet scrubber.
Furthermore, the increasing vapor content in the flue gas after wet scrubber
might affect the destruction behavior of PCDD/Fs by SCR catalyst. Therefore,
the wet scrubber should be installed after the SCR reactor. The PCDD/F control
efficiency can be improved by adjusting the operation temperatures of SCR
system and wet scrubber more or less.

![Graph](image)

**Fig. 15** The increment of different chlorinated PCDD/Fs through wet scrubbers

The effects on different chlorinated CBzs in flue gas were also investigated. As
shown in Fig. 16, the increment ratio through the wet scrubber in MSWI I was almost
around 1.0. However, the concentrations of all CBzs went up dramatically in MSWI II
and III, especially TrCBzs which increased by 8.5 and 7.0 times, respectively.
Fig. 16 The increment of different CBzs under the effects of wet scrubbers

Correlations between PCDD/Fs and CBzs through the APCDs

The concentrations of PCDD/Fs and total CBzs in the three MSWIs through all the APCDs are compared in Fig. 17. In MSWI I, the trends of PCDD/Fs and total CBzs were generally similar. In MSWI II and III, similar trend appeared through the SDFGD with AC injection and BF. The wet scrubbers seriously affected the relationships of PCDD/Fs and CBzs. In all MSWIs, the SDFGD with AC and BF worked effectively and revealed few effects on their correlations. Compared with other CBzs, TrCBzs were far more sensitive to the purification and exhibited significant changes through different purification devices, especially through the SCR reactor and wet scrubbers. The result showed that the correlations between PCDD/Fs and TrCBzs need to be considered separately, before and after the two devices were applied.
The correlations between TEQ and different CBzs through the APCDs were calculated in Table 3. Before the APCDs, all the TEQ values in MSWIs were above 1.0 ng/Nm$^3$. TeCBzs and PCBzs had higher correlation coefficients. 1,2,3,4-TeCBz had the highest correlation with PCDD/Fs and could therefore be an indicator of PCDD/Fs. A linear correlation model (determination coefficient, $R^2 = 0.79$) and a quadratic correlation model ($R^2 = 0.82$) were then established, and are presented in Fig. 18.

**Table 3 The correlation coefficients between TEQ and CBzs through the APCDs**

<table>
<thead>
<tr>
<th></th>
<th>(a) before the APCDs</th>
<th>(b) after the APCDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3,5-TrCBz</td>
<td>0.463</td>
<td>0.05</td>
</tr>
<tr>
<td>1,2,4-TrCBz</td>
<td>0.589</td>
<td>0.822*</td>
</tr>
<tr>
<td>1,2,3-TrCBz</td>
<td>0.568</td>
<td>0.013</td>
</tr>
<tr>
<td>1,2,3,5-TcCBz</td>
<td>0.810**</td>
<td>0.165</td>
</tr>
<tr>
<td>1,2,4,5-TeCBz</td>
<td>0.678*</td>
<td>0.022</td>
</tr>
<tr>
<td>1,2,3,4-TeCBz</td>
<td>0.894**</td>
<td>0.016</td>
</tr>
<tr>
<td>PCBz</td>
<td>0.865**</td>
<td>0.277</td>
</tr>
<tr>
<td>HCBz</td>
<td>0.770*</td>
<td>0.183</td>
</tr>
<tr>
<td>TrCBzs</td>
<td>0.307</td>
<td>0.534</td>
</tr>
<tr>
<td>TeCBzs</td>
<td>0.796*</td>
<td>0.054</td>
</tr>
<tr>
<td>total CBzs</td>
<td>0.672</td>
<td>0.506</td>
</tr>
</tbody>
</table>

**. Significant at 0.01 level (two-tailed); * significant at 0.05 level (two-tailed).
After the APCDs, the emission levels of PCDD/Fs in MSWI II and III were in the range of 0.01 to 0.1 ng I-TEQ Nm$^{-3}$. The significant effects on CBzs by the SCR reactors and wet scrubbers resulted in poorer correlations between PCDD/Fs and CBzs, and the different indicators. Following the purification system, the correlation coefficient between PCDD/Fs and CBzs had already fallen down to 0.51. 1,3,5-TrCBz. Moreover, 1,2,3-TrCBz, 1,2,4,5-TeCBz and 1,2,3,4-TeCBz had correlation coefficients lower than 0.1. However, 1,2,4-TrCBz was found to establish a good correlation quadratic model with PCDD/Fs, as shown in Fig. 19. This raises the possibility that the effects of APCDs, especially the wet scrubber, on PCDD/Fs and 1,2,4-TrCBz, were generally similar, although further detailed research is needed on wet scrubbers. This underlines the importance of establishing different correlation models before and after the APCDs to indirectly monitor the emission of PCDD/Fs.

**Fig. 18 The correlations between 1,2,3,4-TeCBzs and TEQ before the APCDs**
Fig. 19 The correlations between 1,2,4-TrCBzs and TEQ after the APCDs

CONCLUSION

This research investigated the removal of PCDD/Fs in three MSWIs by several typical flue gas purification devices: the SDFGD with AC injection and BF, the SCR reactor, and the wet scrubber. The detailed concentrations and homologue distributions of PCDD/Fs and CBzs were considered along with the correlations between PCDD/Fs and CBzs.

We found that the concentrations of PCDD/Fs largely decreased with the purification device system. However, no trend was found in the concentrations of CBzs, which either decreased by 53.7% or increased dramatically. Among these devices, the SDFGD system with AC injection and BF had a similar effect on both PCDD/Fs and CBzs and fewer effects on their correlations. TrCBzs with low chlorination were the most difficult to adsorb and remove, and therefore dominated throughout the rest of the purification system.

The SCR reactor exhibited different removal efficiencies for PCDD/Fs in flue gas. The removal efficiency of CBzs was considerably lower than that of PCDD/Fs.
The removal efficiencies of PCDD/Fs and CBzs decreased as chlorination increased. This was because less chlorinated compounds were easier to remove. The “memory effect” in wet scrubbers increased concentrations of PCDD/Fs. The concentrations of penta- to hepta-chlorinated PCDD/Fs increased substantially when flue gas passed through the wet scrubbers. Because of the effects of APCDs, especially wet scrubbers, the correlation models between PCDD/Fs and CBzs must be distinguished and established separately to obtain the best monitoring models with the highest correlation coefficients. For instance, 1,2,3,4-TeCBz had the highest correlation with PCDD/Fs in flue gas before the APCDs, while 1,2,4-TrCBz correlated more effectively with PCDD/Fs.

ACKNOWLEDGEMENTS

This research was supported by the National Key R&D Program of China (2018YFC1802100) and the National Key Research and Development Program of China (2017YFC0703100). National Natural Science Foundation of China (Grant No. 51621005). This manuscript was edited by Wallace Academic Editing.

REFERENCES


Päivi H. Ruokojärvi, Ismo A. Halonen, Kari A. Tuppurainen, Juhani Tarhanen, a. and Juhani


Yu Ming-feng, L.X.-d., Li Wen-wei, Chen Tong, Yan Jian-hua (2016b). Catalytic destruction of
### Table 1 The basic information of MSWIs investigated

<table>
<thead>
<tr>
<th>Type of furnace</th>
<th>Stock capacity /t·d⁻¹</th>
<th>Combustion temperature /°C</th>
<th>Operation duration /m</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSWI I, II, and III</td>
<td>750</td>
<td>950</td>
<td>10</td>
</tr>
</tbody>
</table>

**APCD system**

- SNCR + SDFGD + AC injection + BF + SGH + SCR + wet scrubber + GGH

### Table 2 The main information of experimental conditions

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>MSWI I</th>
<th>MSWI II</th>
<th>MSWI III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace temperature /°C</td>
<td>948</td>
<td>908</td>
<td>964</td>
</tr>
<tr>
<td>Temperature at the sampling site /°C</td>
<td>200</td>
<td>204</td>
<td>198</td>
</tr>
<tr>
<td>Oxygen content at the sampling site /%</td>
<td>8.8</td>
<td>9.1</td>
<td>7.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1#</th>
<th>2#</th>
<th>3#</th>
<th>4#</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>180</td>
<td>175</td>
<td>201</td>
</tr>
<tr>
<td>204</td>
<td>181</td>
<td>172</td>
<td>200</td>
</tr>
<tr>
<td>198</td>
<td>179</td>
<td>174</td>
<td>201</td>
</tr>
<tr>
<td>8.8</td>
<td>9.2</td>
<td>9.2</td>
<td>9.3</td>
</tr>
<tr>
<td>9.1</td>
<td>9.2</td>
<td>9.2</td>
<td>9.6</td>
</tr>
<tr>
<td>7.5</td>
<td>8.3</td>
<td>8.3</td>
<td>8.6</td>
</tr>
</tbody>
</table>

### Table 3 The correlation coefficients between TEQ and CBzs through the APCDs

<table>
<thead>
<tr>
<th>Compound</th>
<th>(a) before the APCDs</th>
<th>(b) after the APCDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3,5-TrCBz</td>
<td>0.463</td>
<td>0.05</td>
</tr>
<tr>
<td>1,2,4-TrCBz</td>
<td>0.589</td>
<td>0.822*</td>
</tr>
<tr>
<td>1,2,3-TrCBz</td>
<td>0.568</td>
<td>0.013</td>
</tr>
<tr>
<td>1,2,3,5-TeCBz</td>
<td>0.810**</td>
<td>0.165</td>
</tr>
<tr>
<td>1,2,4,5-TeCBz</td>
<td>0.678*</td>
<td>0.022</td>
</tr>
<tr>
<td>1,2,3,4-TeCBz</td>
<td>0.894**</td>
<td>0.016</td>
</tr>
<tr>
<td>PCBz</td>
<td>0.865**</td>
<td>0.277</td>
</tr>
<tr>
<td>HCBz</td>
<td>0.770*</td>
<td>0.183</td>
</tr>
<tr>
<td>TrCBzs</td>
<td>0.307</td>
<td>0.534</td>
</tr>
<tr>
<td>TeCBzs</td>
<td>0.796*</td>
<td>0.054</td>
</tr>
<tr>
<td>total CBzs</td>
<td>0.672</td>
<td>0.506</td>
</tr>
</tbody>
</table>
**. Significant at 0.01 level (two-tailed); * significant at 0.05 level (two-tailed).
Figure Captions

**Fig. 1** The technological process of flue gas purification system

**Fig. 2** PCDD/F concentrations and TEQ in the flue gas from MSWIs

**Fig. 3** The total concentrations of CBzs in the flue gas

**Fig. 4** The gas-solid distribution of PCDD/Fs in the flue gas through the APCDs

**Fig. 5** The concentration of PCDDs and PCDFs in the flue gas

**Fig. 6** The concentration fractions of CBz in the flue gas at different positions

**Fig. 7** The concentrations of TrCBz isomers in the flue gas at different positions

**Fig. 8** The distributions of 17 toxic PCDD/Fs through SDFGD system

**Fig. 9** The removal efficiencies of 17 toxic PCDD/Fs from SDFGD+ AC+ BF

**Fig. 10** The removal efficiencies of different CBzs from SDFGD+AC+BF

**Fig. 11** The distributions of 17 gaseous PCDD/Fs through the SCR reactor

**Fig. 12** The removal efficiencies of 17 gaseous PCDD/Fs through the SCR reactor

**Fig. 13** The removal efficiencies of different CBzs through the SCR

**Fig. 14** The distributions of PCDDs and PCDFs through the wet scrubbers

**Fig. 15** The increment of different chlorinated PCDD/Fs through wet scrubbers

**Fig. 16** The increment of different CBzs under the effects of wet scrubbers

**Fig. 17** The comparisons between TEQ and CBz through the APCDs

**Fig. 18** The correlations between 1,2,3,4-TeCBzs and TEQ before the APCDs

**Fig. 19** The correlations between 1,2,4-TrCBzs and TEQ after the APCDs
Fig. 8