Utilization and Improvement of the Adsorption Method for Sampling PCDD/Fs from a Sinter Plant

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ABSTRACT

In this work, the Adsorption Method for Sampling (AMESA) is developed to collect long-term samples of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) from stacks. However, the variation of in duration might affect the analytical results due to the memory effect in the AMESA. This research is one of the very few reports of using AMESA in sinter plants. Eight long-term AMESA (LA) samples were collected, followed by 16 parallel short-term AMESA (SA) and manual (SM) samples. The LA reports good correlations ($R = 0.82–0.83$) between PCDD/F emissions and the recovery feedstock, which can be further used for emission reduction. However, the breakthrough effects of the highly chlorinated PCDD/Fs is in the range of 6–14% in LA samples, and these are further improved by increasing the glass wool and adsorbent (with higher specific surface area, lower pore size, and higher polarity) packing, and finally reduced to 5.17%. For the short-term sampling, a maximum difference of 170% occurred between SA and SM, if the sampling strategy suddenly changed from LA to SA. The PCDD/F memory effect remained for the first 8 SA samples, with the dominant 1,2,3,4,6,7,8-HpCDD and OCDD. Therefore, five post-washings for the AMESA system took place to successfully reduce the PCDD/F residual mass to >0.2% of a normal LA. Unfortunately, these residuals were still equal to 51.4% of a normal SA. Therefore, it is not suggested that AMESA replace the current manual sampling method without any modification. According to this study, both the breakthrough and memory effects could be inhibited. Finally, a new inspection system, including both AMESA and short-term samples, is then proposed for improving the PCDD/F control strategy in Taiwan.

Keywords: PCDD/Fs; Adsorption method; Sinter plant; Memory effect; Breakthrough.

INTRODUCTION

Polychlorinated dibenzo-p-dioxins and dibenzofurans, denoted as PCDD/Fs in this paper, have been extensively studied after they were first discovered in the flue gases and fly ash of municipal solid waste incinerators in 1977 (Olie and Vermeulen, 1977). Emissions of the PCDD/Fs from various sources have become a serious issue in many countries. The US EPA (EPA, 2003, 2006) has thus established and legislated emissions regulations for municipal solid waste incinerators (MSWIs), hazardous and medical waste incinerators, cement kilns, sinter plants, metallurgical processes, and secondary aluminum smelters. Recent studies (Wang et al., 2003a, c; Lin et al., 2006; Li et al., 2007; Lin et al., 2007; Wang et al., 2010; Wang, 2010) have shown that most of the aforesaid combustion sources contribute to the PCDD/F emissions in Taiwan, and thus monitoring the POP emissions in flue gases is needed in order to address this issue. Due to the stringent regulations for MSWIs, the sinter plants have become a dominant emission source of PCDD/Fs in Taiwan. A number of studies have reported the PCDD/F emissions from iron ore sintering in Taiwan and around the world over the last two decades (Lahl, 1994; Eduljee and Dyke, 1996; Everaert and Baeyens, 2002; Wang et al., 2003c; Aries et al., 2006; Ooi and Lu, 2011; Kuo et al., 2012). The PCDD/F emissions from sinter plants were first found to be around 1 ng I-TEQ Nm$^{-3}$ (Anderson and Fisher, 2002), similar to the results (0.995–2.06 ng I-TEQ) reported in the earliest report that was carried out in Taiwan (Wang et al., 2003c). In order to reduce the adverse health effects of PCDD/F emissions are number of removal strategies have...
been developed (Shih, et al., 2009). The deactivation of de novo and chlorination catalysts can be achieved with the use of nitrogen- or sulphur-containing additives, while the chlorine content can be removed by alkali inhibitors (Ooi and Lu, 2011; Lehtanska and Wielgosinski, 2014). The selective catalytic reduction process designed for nitrogen oxide reduction (DeNOx) has been shown to destroy PCDD/F compounds with 50–99% removal efficiencies (Wang et al., 2003c; Chang et al., 2007; Chang et al., 2009). Multi-layer reactors with bead-shaped activated carbon have also been shown to reduce PCDD/F emissions to less than 0.1 ng I-TEQ (Hung et al., 2011). These techniques have been developed due to the more stringent regulations that were introduced in 2010 in Taiwan, with inspection systems for flue gas emission also becoming more important in recent years.

In Taiwan, the PCDD/F levels from the combustion sources are obtained by the manual sampling (MS) method over several hours, and those sources are regularly checked at least twice a year, although usually less than ten time during normal operations. However, some studies (Lothgren and van Bavel, 2005; Neuer-Etscheidt et al., 2006; Tejima et al., 2007; Wang et al., 2007) show that PCDD/F levels in the flue gas, especially during the start-up and shut-down periods of the incinerators, could be higher compared to those seen in normal operations, with the amount of PCDD/F emissions during the start-up accounting for between 41% (Tejima et al., 2007) and 60% (Wang et al., 2007) of the annual PCDD/F emissions under normal operations. Nevertheless, the PCDD/F emissions cannot even be immediately controlled when unstable operations occur, such as when there are abnormal conditions or the related air pollution control devices are broken. The results of start-up and shut-down operations reveal that PCDD/F emissions from the incinerator cannot be reliably measured using the conventional MS technique, since these short-term spot measurements represent only a small part of the yearly operation time of the plant during the normal operating conditions.

An alternative method of dioxin and furans, called the Adsorption Method for Sampling (AMESA), has thus been developed for long-term monitoring of PCDD/F emissions, since it is difficult to achieve continuous online monitoring of PCDD/Fs, and using this approach the flue gas is automatically collected under isokinetic conditions for periods ranging from four hours up to four weeks (Mayer et al., 2000). AMESA long-term sampling of PCDD/Fs was certified by the German certification agency, TÜV, in 1998, and by the UK certification agency, MCERT, in 2005, and it can also be used to monitor emissions of other POPs (Reinmann, et al., 2006). Cost analysis of long-term AMESA shows higher sampling frequencies are more cost-efficient than the MS method (Reinmann, et al., 2004), and can also reduce the related manpower demands, and it has been widely used in Europe to comply with Directive 2000/76/EC for PCDD/Fs and PCBs.

The AMESA was first widely used to examine the emissions of MSWI, which were the main contributors of PCDD/Fs in the ambient air fifteen years ago. However there have been very few studies that explored the use and modification of this approach with regard to sinter plants. Since the memory effect has been reported as an important secondary and continuous impact from unstable operations (during the start-up of incinerators) (Neuer-Etscheidt et al., 2006; Wang et al., 2007; Chen et al., 2008; Guo et al., 2014) and aged air pollution control devices (Lothgren and Andersson, 2008; Li et al., 2011), a long-term observation check is needed for localization of the AMESA sampling method. The current research focuses on the practicality of using AMESA with regard to short- and long-term sampling, with the standard MS also being used for a short period for comparison purposes. Additionally, the particle loading, size distribution, sampling breakthrough and long-term memory effect were analyzed. Furthermore, various physical modifications (multi-washing process, sample packing and adsorbent material) were tested to improve the sample quality and representativeness of the results. Finally, and based on these results, a comprehensive sampling strategy was proposed for the PCDD/F emissions from a continuously operating sinter plant.

MATERIALS AND METHODS

Sampling
This study tested the AMESA in a sinter plant in order to achieve the following: (1) a comparison between parallel short-term AMESA and MS; (2) carry out continuous long-term sampling for 168 hours and examine its breakthrough effect; (3) clarify the PCDD/F memory effect in an AMESA system after long-term sampling; (4) reduce the above drawbacks for AMESA so that it can be put in practical use in sinter plants. The overall experimental design is as shown in Fig. 1.

The AMESA employed in this study is produced by Environment S.A Deutschland, and was certified for PCDD/F sampling from an MSWI, as mentioned above. Eight long-term AMESA flue gas samples were taken from a sinter plant, followed by a sequence of sixteen pairs of the parallel short-term AMESA and MS samples. The above design could stand for the commercial monitoring strategy that shifts the continuous long-term AMESA monitoring (LA, 168 h/sample) to a shorter sampling duration (SA, 3 h/sample) with higher frequency when the abnormally high PCDD/F levels occur. The samples were further analyzed for PCDD/Fs using U.S. EPA modified Method 23 and European Union EN 1984 for MS and AS, respectively. On the other hand, the short-term manual (SM) sampling system is commonly used for PCDD/F sampling in flue gas rather than the AMESA system.

Fig. 2 shows the AMESA sampling train configuration, which consists of a sampling unit and control cabinet. A cooled titanium probe (≤ 50°C and diameter for 60 mm) is used following by a water cooling water system, steam measurement, quartz wool (9 g) filter for particle collection, and two-stage XAD-2 filled (50 g) cartridge for adsorbing gaseous and condensate phases of PCDD/Fs in the sampling unit, while the control cabinet is make-up of compressed air, cooling water supply, power supply and working computer, which makes it possible to extract the flue gas isokinetically and automatically. Prior to sampling, a known amount of
Fig. 1. Experimental flow chart for AMESA practical use test in a sinter plant.

Fig. 2. Functional principles of AMESA system.
isotope pre-labeled surrogate standards (SS) was spiked into the XAD-2 cartridge to monitor the collection efficiency. An automatic leakage test was performed to ensure the non-contamination of the cartridge in the AMESA system before and after the sampling cycle, and trip blanks and field blanks were also taken and determined. Notably, the breakthrough effect of PCDD/Fs was a significant concern, since the sinter plant in this study, equipped with an electrostatic precipitator (ESP), was expected to emit fine particle and particle-bound PCDD/Fs. The above two-stage XAD-2 cartridge set was then used to identify the breakthrough amount, using the following Eq. (1).

\[
\text{Breakthrough} = \frac{\text{Cartridge.1}}{\text{Cartridge.1} + \text{Cartridge.2}} \times 100\%
\]  

In this Cartridge.1 and Cartridge.2 represent the PCDD/F concentrations in the 1st and 2nd sample cartridges, respectively. The PCDD/F emissions in the flue gas are assumed to be completely collected by the above two-stage cartridge set, and the preliminary test showed less than 1% mass of PCDD/Fs could pass this collector.

The particle mass-size distributions were measured using an in-stack cascade impactor (CI-700-K, Apex Instruments, Inc., USA) with isokinetic sampling that following USEPA method 5. The aerodynamic diameters of 50 wt% accumulation PM (Dp 50) on eight-stages were F (dead-end filter), 0.333, 0.730, 1.41, 2.42, 4.59, 12.1, and 16.0 µm, respectively. Furthermore, the particle distributions were modified by spline fitting from the eight-stage raw mass concentrations. The spline curve fitting was done by utilizing the computer program documented in Appendix A of State of California Air Resources Board (CARB) Method 5, which has been well verified using linear and quadratic least-square fit of log-normal transform data (CARB, 1990). Additionally, five sequences of system cleaning took place by using acetone, dichloromethane, and toluene to analyze their PCDD/F contents and compared with those in the LA or SA samples to identify the memory effect.

**PCDD/F Analyses**

The flue gas samples were analyzed for seventeen 2,3,7,8-substituted PCDD/Fs following the US EPA Modified Method 23, and this process was performed at the Super Micro Mass Research and Technology Center in Cheng Shiu Institute of Technology. The sample analysis was performed according to the standard procedures. Each sample was spiked with a known internal standard (IS) and subsequently extracted for 24 hours with toluene by a Soxhlet extractor. The extract was then concentrated by nitrogen purging and an alternate standard (AS) was added. The extracts were treated with sulfuric acid, which was followed by a series of clean-up and fractionation procedures. A specific amount of recovery standard solution was finally added to the sample before PCDD/F analysis to estimate the recovery of overall analysis process.

A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used for the measurement of PCDD/Fs. The HRGC (Hewlett Packard 6970 Series) was equipped with a DB-5 fused silica capillary (60 m, 0.25 mm I.D., 0.25 µm film thickness) and splitless injection, and the HRMS (Micromass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI+) source. The analyzer mode was selected ion monitoring (SIM), with a resolving power of 10,000, electron energy of 35 eV, and source temperature of 250°C. The detailed instrumental analysis parameters of PCDD/Fs are given in our previous works (Wang et al., 2003a, b, c, 2010).

**RESULTS AND DISCUSSION**

**Long-Term AMESA (LA) Sampling**

During the LA sampling, the PCDD/F mass concentrations were around 0.279–3.07 ng Nm⁻³, with the mean and RSD of 1.69 ng Nm⁻³ and 61.7% (as shown in Fig. 3). For a toxicity perspective, eight flue gas samples were around 0.036–0.392 ng I-TEQ Nm⁻³, with the mean and RSD of 0.189 ng I-TEQ Nm⁻³ and 62.1%. The PCDD/F levels measured by LA sampling in the current study were close to the results by SM sampling in previous studies, which report normal and optimal emissions as 0.225–0.276 ng I-TEQ Nm⁻³ and 0.069–0.107 ng I-TEQ Nm⁻³, respectively (Chen et al., 2012). All PCDD/F emissions from the focal sinter plant during sampling season (about eight weeks) met the regulations in Taiwan (0.5 ng I-TEQ Nm⁻³), indicating good operating conditions.

Specifically, the sample LA1-LA3 (0.259–0.392 ng I-TEQ Nm⁻³) had higher PCDD/F levels than the following LA4-LA8 (0.036–0.134 ng I-TEQ Nm⁻³). However, the congeners fingerprints of both lower and higher emission were too similar to be distinguished. Their PCDD/F mass concentrations were both dominated by 2,3,4,7,8-PeCDF and 1,2,3,4,6,7,8-HpCDF (as shown in Fig. 4), as also found in previous research (Wang et al., 2003c; Lee et al., 2004; Cavaliere et al., 2011; Chen et al., 2012; Esposito et al., 2014). The PCDDs/PCDFs ratio were only 0.09 to 0.17, indicating that the PCDD/Fs could be formed by de novo synthesis when there were enough carbon sources and metallic catalyst (Kakuta et al., 2007; Ooi and Lu, 2011; Chin et al., 2012). The significantly different emissions raised doubts as to whether the routine short-term manual inspection process that is currently used (and which takes place once or twice per year) is sufficient enough to represent a whole year’s emissions for a continuously operating process, such as sintering.

Furthermore, the operation information, including feeding materials, fuels, air pollution control devices (APCDs), and stack conditions, were compared with the PCDD/F mass and toxicity levels for eight LA samples (as shown in Table 1). The PCDD/F concentrations obviously varied with the different materials and fuel feeding rates. Pearson correlation was then employed to quantify the relationship between PCDD/F emissions and operation conditions. Among the various operation conditions of iron ore sintering processes, the feeding rate of recovery material (RECOV) from the multiple processes of steel production had the most
Samples 1 2 3 4 5 6 7 8 LA sampling for PCDD/F mass concentration ng Nm\(^{-3}\)

<table>
<thead>
<tr>
<th>Cartridge 1</th>
<th>Cartridge 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.93</td>
<td>2.60</td>
</tr>
<tr>
<td>3.07</td>
<td>0.747</td>
</tr>
<tr>
<td>1.12</td>
<td>1.16</td>
</tr>
<tr>
<td>1.08</td>
<td>0.279</td>
</tr>
</tbody>
</table>

Mean: 1.69 ng Nm\(^{-3}\)

Fig. 3. Total PCDD/F (A) mass and (B) I-TEQ concentrations by LA sampling.

Fig. 4. PCDD/F congener profiles of LA samples.
FeCl₃, CuCl₂, Fe₂O₃, and CuO, would act as the catalysts for the particle removal efficiency; (3) the metal contents, such as welded together onto the surface of the rod in ESP, inhibiting of PCDD/Fs; (2) kalium, sodium, and unburned fuel would be RECOV, including (1) chlorine content leading to chlorination Table 5). There are several possible effects due to the use of the correlation coefficient equal to 0.82–0.83 (as shown in positive relation to the PCDD/F and I-TEQ emissions, with LA

<table>
<thead>
<tr>
<th>Samples</th>
<th>LA1</th>
<th>LA2</th>
<th>LA3</th>
<th>LA4</th>
<th>LA5</th>
<th>LA6</th>
<th>LA7</th>
<th>LA8</th>
<th>Average</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDD/F mass conc.</td>
<td>2.21</td>
<td>2.96</td>
<td>3.57</td>
<td>0.844</td>
<td>1.22</td>
<td>1.23</td>
<td>1.17</td>
<td>1.319</td>
<td>1.69</td>
<td>61.7%</td>
</tr>
<tr>
<td>PCDD/F I-TEQ conc.</td>
<td>0.259</td>
<td>0.336</td>
<td>0.392</td>
<td>0.098</td>
<td>0.134</td>
<td>0.133</td>
<td>0.123</td>
<td>0.036</td>
<td>0.189</td>
<td>62.1%</td>
</tr>
</tbody>
</table>

Feeding materials  
Iron ore (MT h⁻¹) 264 279 269 306 323 307 304 300 294 6.7%  
Flux (MT h⁻¹) 12.9 12.4 13.0 15.3 14.2 15.5 14.8 13.4 14 8.0%  
Recovery material (MT h⁻¹) 110.0 118.0 113.1 85.9 83.5 88.6 93.6 97.1 99 12.7%  
Total (MT h⁻¹) 387 409 395 407 421 411 412 410 407 2.4%  

Fuels  
Coke (MT h⁻¹) 6.72 6.46 7.02 8.62 12.14 8.01 7.92 9.86 8 21.2%  
Anthracite (MT h⁻¹) 6.95 7.15 7.06 7.49 2.80 6.82 6.28 4.49 6 24.9%  
Coke-oven gas (Nm³ h⁻¹) 512 515 502 520 507 515 510 509 511 1.0%  

APCD in sequence  
ESP Average temp. (°C) 101 103 101 100 104 100 101 99 101 1.5%  
Electrode rod (mA) 173 172 162 172 152 147 151 150 160 6.6%  
SCR Average Temp. (°C) 352 351 350 354 351 352 352 353 352 0.3%  
Stack conditions  
Average stack temp. (°C) 125 126 124 124 126 122 123 121 124 1.4%  
Dry flow rate (Nm³ h⁻¹) 7624 7636 7651 7620 7627 7640 7649 7639 7636 0.1%  

Table 1. Basic information and operating conditions of the sinter plant during LA sampling.  

positive relation to the PCDD/F and I-TEQ emissions, with the correlation coefficient equal to 0.82–0.83 (as shown in Table 5). There are several possible effects due to the use of RECOV, including (1) chlorine content leading to chlorination of PCDD/Fs; (2) kalium, sodium, and unburned fuel would be welded together onto the surface of the rod in ESP, inhibiting the particle removal efficiency; (3) the metal contents, such as FeCl₃, CuCl₂, Fe₂O₃, and CuO, would act as the catalysts for de novo synthesis for PCDD/F formation; (4) the various compositions of RECOV would lead to unsteady control and react to form extra unburned hydrocarbons, which then acted as the carbon source of PCDD/F formation. Therefore, the higher PCDD/F mass and I-TEQ concentration of samples LA1 to LA3 might be due to the higher recovery material feeding rates than used with LA4 to LA8.

All of the above effects might increase the PCDD/F emissions in a sinter plant; however, the standard SM method could not cover all the sampling duration for eight LA samples (two months). Therefore, the short-duration collection by SM could easily over- or underestimate the real emissions if sampling was carried out during LA1-LA3 or LA4-LA8. The long-term AMESA sampling was thus much more comprehensive and representative of the annual PCDD/F emissions. However, high breakthrough ratios of 6–14% were also found, especially in the higher PCDD/F concentration cases. The fine particle bound PCDD/Fs were the possible reason for these breakthrough ratios, since the ESP has a removal limit with regard to extremely small PM. Furthermore, the subsequent AMESA system captured these escaped PM using only cool probe condensation, without any filtration units, and this caused to the breakthrough problem. Therefore, several design suggestions are made in this study to improve the capability of PCDD/F capture for the first sampling cartridge (cartridge 1).

**Short-Term AMESA (LA) and Manual (SM) Samplings**

In order to simulate the shifting sampling strategy from long- to short-term AMESA sampling, 16 pairs of LA and SM samples were collected immediately after the aforementioned eight LA samples. These manual samples have relatively steady PCDD/F masses and I-TEQ concentrations within 1.01–1.43 ng Nm⁻³ (mean = 1.20 ng Nm⁻³; RSD = 12%) and 0.124–0.179 ng I-TEQ Nm⁻³ (mean = 0.155 ng I-TEQ Nm⁻³; RSD = 9%), respectively (as shown in Fig. 5). All 16 SM samples again indicated good operation of the target sinter plant, showing significantly lower PCDD/F emissions than the regulated standard in Taiwan (0.5 ng I-TEQ Nm⁻³).

Unfortunately, the SA samples, which were parallel to the MS ones, showed extremely high PCDD/F levels in the first two samples (106 and 109 ng Nm⁻³ for mass; 1.61 and 1.56 ng I-TEQ Nm⁻³ for toxicity), and these levels reduced as the number of sampling times increased. This might lead to overestimated and unsteady results, while the mean values and RSDs of PCDD/F mass and TEQ, as obtained by SA, were 15.0, 234%, 0.354, and 132%, respectively. In comparison, the relative percent differences (RPDs = absolute [SA – SM]/0.5[S(A + SM)]) of 16 paired-samples obtained by the two methods (SA and SM) were 3%–196% (mean = 50%) for mass and 0%–170% (mean = 78%) for toxicity, revealing significant differences. The linear correlation coefficients between SA and SM were only 0.0013 and 0.0554, which supported the RPD results.

According to Fig. 5, the higher RPD occurred during the first eight samples, which might be due to the PCDD/F memory residues from the former long-term samplings, with a similar memory phenomenon being found for old filter bags in previous research (Weber et al., 2002; Li et al., 2011). The congener profiles of the samples SA1-SA8 are shown in Fig. 6(A). The highly chlorinated PCDDs, including 1,2,3,4,6,7,8-HpPCDD and OCDD, dominated the mass concentration at the beginning of the SA sampling. The hepta- and octa-chlorinated substituted PCDDs represented 33.4–34.6% and 64.0–66.8%, respectively, of total PCDD/Fs. These results reveal that the PCDD congeners with lower
vapor pressure tended to condense or be adsorbed by the particles, and further accumulated (Li et al., 2011; Tseng et al., 2014a) in the AMESA system during long-term sampling. This memory effect caused by the former LA operation was further reduced as the number of sampling times increased, and was steady from samples 9 to 16, as shown in Fig. 6(B). This memory effect was further confirmed and reduced by the later cleaning experiment. Additionally, the SA and SM samples had higher correlations when the first eight samples of short-term AMESA were excluded. The correlation coefficients were then improved to 0.606 for mass and 0.450 for I-TEQ, with the congener profiles of both short-term methods consistent and similar to those of the LA samples and previous studies, as shown in Fig. 6(B) (Wang et al., 2003c; Guerriero et al., 2009; Cavaliere et al., 2011; Ooi and Lu, 2011; Chen et al., 2012; Kuo et al., 2012; Esposito et al., 2014). The average PCDD/F mass and TEQ levels collected by short-term AMESA were also reduced to 1.23 (RSD = 8%) and 0.167 (RSD = 4%), which were very close to the SM results. These figures thus show that AMESA is practical for application in short-term PCDD/F sample collection, and could replace the standard SM well if the earlier samples with high concentrations were removed. However, the extension of the PCDD/F memory effect still cannot be accurately estimated, and so it is still not suggested that short-term AMESA sample collection directly replace the standard method, and a more comprehensive strategy is proposed in the following section.

**Breakthrough Reduction**

The particle distribution during normal operation of the target sintering process was first analyzed by an in-stack cascade impactor. The results show that the overall PM concentration was 17.1 mg Nm$^{-3}$, higher than the values found for the other emission sources. There were also three peak values within 0.1–0.5, 0.5–2.5, and 2.5–10 µm of PM aerodynamic diameter in the probability density function (PDF), as shown in Fig. 7. The $D_p$ 50 was then calculated as 1.07 µm.
by cumulative distribution function (CDF), indicating the high contribution of fine particles in the flue gas of the sinter plant. Therefore, the breakthrough of fine particle-bound PCDD/Fs was expected. The following parameters were designed to improve the PCDD/F removal efficiency of “cartridge 1” in the two-stage adsorbing unit during the 168-hour \( L_A \) sampling (as shown in Table 2). The increase in glass wool and XAD packing tended to increase both the pathway and resident time when the fine particles passed through the adsorption cartridge, and further inhibited their escape (samples 2 and 3).

The breakthrough effect from the \( L_A \) samplings fell from the original 9.10% in the mass of sample 1 to 7.69% and 6.67% for samples 2 and 3, respectively. With regard to the toxicity, using more glass wool packing could reduce the I-TEQ breakthrough effect from 9.04% to 6.60%. The PCDD/F congener profile of sample 1 (Fig. 8) shows that the lower chlorinated PCDFs were dominant in cartridge 1, indicating the XAD2 had better adsorption ability with regard to gaseous PCDD/Fs. In the following cartridge 2, the amount of dominant 2,3,7,8-\( \text{TeCDF} \) was reduced, while the amount of highly chlorinated congeners increased. In other words, the higher molecular, lower volatile, and particle-bound PCDD/Fs might have passed through the first and even the second cartridge, and then been accumulated at the end of AMESA system.

Changing the adsorbent properties is another design strategy that can decrease the breakthrough ratio. The specific surface area (SSA), pore size (PS), and polarity (POL) of different adsorbents were also tested. The amount of glass wool and adsorbents were kept the same in the improved sample 3. XAD2, XAD16, XAD4, and XAD1180 were used in samples 3–6, as shown in Table 2. The results showed that sample 4 could reduce the breakthrough ratio to 6.29% in mass and 5.54% in I-TEQ, since the packing XAD16 increased by 167% SSA compared to the original XAD2, and also improved the PM removal rate.

Furthermore, the pore size (PS) of XAD4 was only 44.4% that of the original XAD2, and this reduced the opportunities for PM desorption in sample 5, as found in previous absorbent studies (Tseng et al., 2014a, b). The escaped PCDD/F ratio was then reduced by 5.17% in mass and 5.40% I-TEQ when using XAD4 resin. Suzuki proposed using adsorption synthesis on various PS to achieve the target particle size ratio.
Fig. 7. Particle distribution in the flue gas of the tested sinter plant under normal operations.

Table 2. Experimental parameters to reduce the breakthrough effect.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Pre-filtration</th>
<th>Adsorbent</th>
<th>Cartridge 1 Mass (ng)</th>
<th>Cartridge 2 Mass (%)</th>
<th>Breakthrough Mass (%) I-TEQ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Glass wool (g)</td>
<td>Kinds</td>
<td>Amount (g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>XAD2</td>
<td>50</td>
<td>57.8</td>
<td>9.10</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>XAD2</td>
<td>80</td>
<td>44.6</td>
<td>7.69</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
<td>XAD2</td>
<td>80</td>
<td>45.5</td>
<td>6.67</td>
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<tr>
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<td>18</td>
<td>XAD16</td>
<td>80</td>
<td>58.3</td>
<td>6.29</td>
</tr>
<tr>
<td>5</td>
<td>18</td>
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<td>80</td>
<td>62.7</td>
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<tr>
<td>6</td>
<td>18</td>
<td>XAD1180</td>
<td>80</td>
<td>49.1</td>
<td>14.6</td>
</tr>
</tbody>
</table>

Table 3. Specifications of different commercial XAD.

<table>
<thead>
<tr>
<th>Classes</th>
<th>SSA $m^2 g^{-1}$</th>
<th>PS Å</th>
<th>POL mL g$^{-1}$</th>
<th>Resin diameter $\mu m$</th>
<th>$PS/D_{50}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>XAD2</td>
<td>300</td>
<td>90</td>
<td>0.65</td>
<td>250–830</td>
<td>8.41</td>
</tr>
<tr>
<td>XAD16</td>
<td>800</td>
<td>100</td>
<td>1.82</td>
<td>250–830</td>
<td>9.35</td>
</tr>
<tr>
<td>XAD4</td>
<td>725</td>
<td>40</td>
<td>0.98</td>
<td>250–830</td>
<td>3.73</td>
</tr>
<tr>
<td>XAD1180</td>
<td>500</td>
<td>300</td>
<td>1.68</td>
<td>250–830</td>
<td>46.7</td>
</tr>
</tbody>
</table>

Notes:

SSA: specific surface area; PS: pore size; POL: polarity; $PS/D_{50}$: the ratios of pore size/$D_{50}$ (1.07 $\mu m$).

The surface adsorption occurred at $PS/d > 5$, while micropore and ultramicropore adsorption took place at $5 > PS/d > 3$ and $PS/d < 3$, respectively. The higher PS/d values were due to the lower activation energy of the particle desorption from the adsorbent surface, and this caused the PM to escape. In the current study, $D_{50}$ was chosen as the specific diameter of PM in the sintering flue gas, and all the $PS/D_{50}$ ratios of various XAD were thus derived and are shown in Table 3. The lowest $PS/D_{50}$ was for XAD4, supporting its better adsorption and PM removal efficiency. On the other hand, XAD1180 was used in sample 6 and significantly increased the breakthrough, with 1.67 and 3.33 times higher SSA and PS than XAD2. In this case, the drawback of lower PS was more dominant than the benefit of SSA with regard to the PM removal efficiency.

According to Fig. 8, the lower chlorinated PCDD/Fs, including 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, and 2,3,4,7,8-PeCDF, were major congeners in cartridge 1 of each sample. The mass percentages of the higher (Hexa- to Octa-) chlorinated PCDD/Fs increased in cartridge 2, indicating they might have more potential to pass through the adsorbent. Therefore, the lowest breakthrough ratio would be the result of competition among the aforementioned factors. The optimal value then occurred in sample 5 with the use of more packing material and XAD4.

Residue Cleaning for Inhibition of Memory Effect

Post-washing took place in the standard MS sampling process to reduce the residual PCDD/Fs in the AMESA system. All of the samples were amplified five times so that the memory effect could be obtained before and after LA sampling in this study. The improvement target was sample 5, which had been optimized with regard to its breakthrough effect.

The PCDD/F residual fraction in the AMESA sampling units (probe and flexible tube) were quantified by the eluents...
collected from the washing processes after the long-term AMESA sampling. Fig. 9 shows the mass distributions of PCDD/F and I-TEQ in the cartridges and washing eluents. The total PCDD/F and I-TEQ mass in the 1st eluent were equal to 21.8% and 19.7% masses of cartridge 1, respectively, while the total PCDD/F and I-TEQ mass in the 2nd eluent were equal to 0.411% and 0.185% mass of cartridge 1. These results indicate a significant reduction of PCDD/F I-TEQ.

**Fig. 8.** PCDD/F congener profiles in two cartridges of samples 1 to 6.
mass with the washing time, and thus that the residual effect of PCDD/F I-TEQ will be greatly inhibited (lower than 0.4% and 0.2% for mass and I-TEQ) after washing one time.

The absolute PCDD/F mass and I-TEQ of the 2nd eluent had less effective with regard to the long-term AMESA sampling, but might cause interference with the short-term samples. Table 4 shows a comparison between the PCDD/F residues in the 2nd eluent and three short-term AMESA samples, which were collected after the 16 sample at a relatively stable concentration. The PCDD/F and their I-TEQ
masses in the eluent are equal to 51.4 and 37.0% of the short-term samples. These high ratios will definitely increase the PCDD/F and I-TEQ in the following short-term samples. Consequently, the memory effect of the system residues cannot be ignored, and it so the AMESA should not be utilized for short-period sampling.

Using AMESA with the Current Emission Policy

Due to the different sampling mechanisms and residue problems described above, it is suggested that continuous sampling should not directly replace the standard short-term manual sampling as a form of legal inspection. However, the significantly greater representativeness of the monitoring results for continuous emissions that can be obtained by AMESA are valuable. Therefore, a new PCDD/F sampling and control design should be proposed that uses both two methods, AMESA and standard short-term sampling.

As shown in Fig. 10, the monitoring targets should first be chosen based on their potential PCDD/F emissions. In other words, the stacks with emissions that are significantly over the standard values or higher that the PCDD/F emission levels in the historical inspection records should be chosen as the continuous sampling targets. The targets would then be sampled once per two weeks for one year. The sampling frequency could be reduced to once per four weeks if there no records over the related standards are found during the first monitored year (with 26 samples for 52 weeks). Furthermore, a target could be removed from the continuously monitored list if it maintain steady low emissions (under the regulated standards) for the following two years. In other words, an emission source that is identified as a target could improve its air pollution control system or operating conditions, and thus later cease to be a target. On the other hand, penalties will still be incurred if the AMESA finds that emissions are over the related standard and the target does pass the subsequent manual sampling check, as shown in Fig. 10. This strategy can avoid various different biases with regard to punishing high emission sources, since manual
sampling play the decisive role in any judgment, as in the current control strategy. Moreover, the AMESA system could work as remotely and provide comprehensive monitoring of long-term PCDD/F emissions.

**Fig. 10.** A new sampling strategy including both the standard and AMESA sampling.

**Table 5.** Pearson correlation coefficients among various emissions and operating conditions.

<table>
<thead>
<tr>
<th>Pearson Correlation Coefficients</th>
<th>Mass</th>
<th>TEQ</th>
<th>IrO</th>
<th>Flux</th>
<th>RECOV</th>
<th>Coke</th>
<th>Anthracite</th>
<th>COG</th>
<th>ESPT</th>
<th>ESPC</th>
<th>SCRT</th>
<th>StT</th>
<th>DFR</th>
</tr>
</thead>
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<tr>
<td>Mass</td>
<td>1</td>
<td>1</td>
<td>-0.82</td>
<td>-0.54</td>
<td>0.82</td>
<td>-0.64</td>
<td>0.45</td>
<td>-0.36</td>
<td>0.38</td>
<td>0.5</td>
<td>0.56</td>
<td>0.56</td>
<td>0.3</td>
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<tr>
<td>TEQ</td>
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<td>1</td>
<td>-0.83</td>
<td>-0.56</td>
<td>0.83</td>
<td>-0.65</td>
<td>0.46</td>
<td>-0.33</td>
<td>0.39</td>
<td>0.54</td>
<td>0.59</td>
<td>0.59</td>
<td>0.26</td>
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<tr>
<td>IrO</td>
<td>-0.82</td>
<td>-0.83</td>
<td>1</td>
<td>0.66</td>
<td>-1</td>
<td>0.8</td>
<td>-0.54</td>
<td>0.21</td>
<td>-0.07</td>
<td>-0.6</td>
<td>-0.32</td>
<td>-0.32</td>
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<tr>
<td>Flux</td>
<td>-0.54</td>
<td>-0.56</td>
<td>0.66</td>
<td>1</td>
<td>-0.7</td>
<td>0.16</td>
<td>0.18</td>
<td>0.46</td>
<td>-0.44</td>
<td>-0.3</td>
<td>-0.42</td>
<td>-0.42</td>
<td>-0.13</td>
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<tr>
<td>RECOV</td>
<td>0.82</td>
<td>0.83</td>
<td>-1</td>
<td>-0.7</td>
<td>1</td>
<td>-0.78</td>
<td>0.5</td>
<td>-0.24</td>
<td>0.1</td>
<td>0.59</td>
<td>0.33</td>
<td>0.33</td>
<td>0.23</td>
</tr>
<tr>
<td>Coke</td>
<td>-0.64</td>
<td>-0.65</td>
<td>0.8</td>
<td>0.16</td>
<td>-0.78</td>
<td>1</td>
<td>-0.9</td>
<td>0.21</td>
<td>0.18</td>
<td>-0.55</td>
<td>-0.1</td>
<td>-0.1</td>
<td>-0.27</td>
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<tr>
<td>Anthracite</td>
<td>0.45</td>
<td>0.46</td>
<td>-0.54</td>
<td>0.18</td>
<td>0.5</td>
<td>-0.9</td>
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<td>0.58</td>
<td>0.03</td>
<td>0.03</td>
<td>0.09</td>
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<td>COG</td>
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<td>ESPT</td>
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<td>0.85</td>
<td>-0.21</td>
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<tr>
<td>ESPC</td>
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<td>0.54</td>
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<td>0.59</td>
<td>-0.55</td>
<td>0.58</td>
<td>0.38</td>
<td>0.21</td>
<td>0.65</td>
<td>0.65</td>
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<td></td>
</tr>
<tr>
<td>SCRT</td>
<td>0.56</td>
<td>0.59</td>
<td>-0.32</td>
<td>-0.42</td>
<td>0.33</td>
<td>-0.1</td>
<td>0.03</td>
<td>0.04</td>
<td>0.85</td>
<td>0.65</td>
<td>1</td>
<td>1</td>
<td>-0.47</td>
</tr>
<tr>
<td>StT</td>
<td>0.56</td>
<td>0.59</td>
<td>-0.32</td>
<td>-0.42</td>
<td>0.33</td>
<td>-0.1</td>
<td>0.03</td>
<td>0.04</td>
<td>0.85</td>
<td>0.65</td>
<td>1</td>
<td>1</td>
<td>-0.47</td>
</tr>
<tr>
<td>DFR</td>
<td>0.3</td>
<td>0.26</td>
<td>-0.23</td>
<td>-0.13</td>
<td>0.23</td>
<td>-0.27</td>
<td>0.09</td>
<td>-0.58</td>
<td>-0.21</td>
<td>-0.5</td>
<td>-0.47</td>
<td>-0.47</td>
<td>1</td>
</tr>
</tbody>
</table>

Notes:
Mass: PCDD/F mass concentrations by LA; TEQ: I-TEQ concentrations by LA; IrO: iron ore feeding rate; RECOV: recovery material; COG: coke-oven gas; ESPT: temperature of ESP; ESPC: current of ESP; SCRT: temperature of selective catalytic reduction; StT: temperature of stack; DFR: dry flowrate of stack flue gas.
CONCLUSION

This study obtained comprehensive results that could not be achieved with standard short-term sampling during the sintering process. The operation analysis showed a correlation between PCDD/F emissions and the feeding rate of feedstock, which could further be used as one of the effective emission control factors. However, the breakthrough effect (6–14 in mass%) was also found in the sinter flue gas during long-term sampling, since the highly chlorinated and particle bounded PCDD/Fs tended to pass through the adsorbent in the AMESA system, along with the fine particles emitted from the sinter plant. The breakthrough ratio was in this study to 5.17% and 5.4% in mass and I-TEQ by using higher density packing materials and using of XAD4 as the adsorbent.

On the other hand, this study found that the AMESA would receive much higher PCDD/F I-TEQ levels (up to 170%) than the manual method in short-term sampling, due to memory and particle effects in the flue gas of the sintering process. Fortunately, the five-time post-washing strategy designed in this study successfully inhibited the residual memory effect to 0.2% of PCDD/F I-TEQ for a normal long-term AMESA sample. Although the parallel AMESA and MS samples exhibited similar concentrations of PCDD/F I-TEQ after eight short-term samplings, it is suggested that the AMESA system be utilized only for long-term monitoring in order to obtain more steady operations and reliable results. Finally, the breakthrough and memory effects were reduced in this study by the use of long-term sampling, and more comprehensive characteristics of PCDD/F emissions in sintering flue gases were also obtained. Nevertheless, the process PCDD/F control could be improved by the use of a new sampling strategy, including both AMESA and standard short-term samples.

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