

# Application of Multilayer AC-adsorption System for PCDD/F Removal – Effect of BAC Modification

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## Introduction

PCDDs (Polychlorinated dibenzo-*p*-dioxins) and PCDFs (Polychlorinated dibenzofurans) are commonly known as persistent organic pollutants (POPs). Activated carbon (AC) could effectively remove air pollutants, such as PCDD/Fs, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and heavy metals (Hg in particular) from incineration processes<sup>1</sup>. AC can generally be applied in three ways, i.e. entrained flow or called activated carbon injection (ACI), fixed bed and moving bed adsorption<sup>2</sup>. AC injection with a BF system is widely employed due to easy handling, effectiveness, and low capital cost<sup>3</sup>. Although ACI technology can effectively reduce PCDD/F emission from flue gases, previous study indicates that it may actually increase the total PCDD/F discharge (including that in fly ash and flue gas) from MWIs<sup>4</sup>. Moreover, powder AC injected cannot be recovered. Fixed-bed adsorption is batch-type operation and the rich organic materials adsorbed in carbon bed with long-term operation may lead to fires. For better controlling PCDD/F emission, a multilayer AC-adsorption system is developed in this study. Results obtained from both laboratory and pilot-scale tests are presented. Moreover, bead-shaped AC (BAC) modified by NaOH is applied as adsorbent in the multilayer AC-adsorption system and possible influence on PCDD/F removal is investigated.

## Materials and methods

The multilayer AC-adsorption system developed in this study adopts commercial BAC with average diameter of 0.72 mm, specific surface area of 1,140 m<sup>2</sup>/g and pore diameter of 19.3 Å as adsorbent. Fig. 1 shows the test module including multilayer AC-adsorption system and vapor-phase PCDD/F collection. Laboratory-scale system and pilot-scale module with multilayer AC-adsorption bed are tested for PCDD/F removal in this study. Regarding to lab-scale test (Case 1), each layer of reactor is designed with 10 cm of height and 2.5 cm of inner diameter, and 5 g BAC is used (2 cm of bed height) for each layer. Gas flow rate is 10 slpm (liter/min). Three-layer adsorption system is used and three temperatures including 120, 150 and 180°C are tested. Case 2 is the pilot-scale test which is carried out in a sinter plant located in southern Taiwan. The size and BAC weight of each layer are the same as that described in Case 1. In this case, characteristics of PCDD/F removal achieved with BACs modified with/without NaOH are investigated. By the way, dual-layer AC-adsorption system is adopted here.

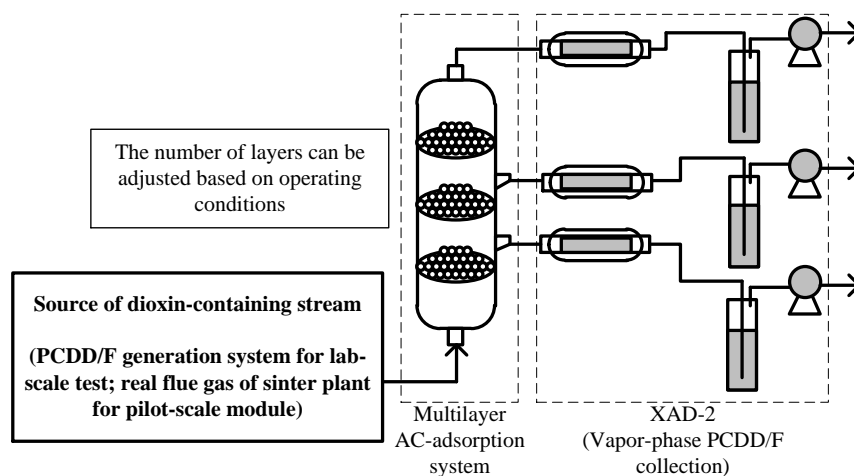


Figure 1 Multilayer AC-adsorption system

The multilayer AC-adsorption system is applied to remove vapor-phase PCDD/Fs and is installed after PM control device. XAD-2 resin is applied to collect the vapor-phase PCDD/Fs of the gas streams at the inlet of system and outlets of each layer. The XAD-2 samples were spiked with known amounts of Method 23 internal standards following internal quantification standards, and then analyzed for seventeen 2,3,7,8-substituted PCDD/F congeners with high resolution gas chromatography (HRGC) (Thermo Trace GC) /high resolution mass spectrometer (HRMS) (Thermo DFS) using a fused silica capillary column DB-5 MS (60 m x 0.25 mm x 0.25  $\mu\text{m}$ , J&W).

## Results and discussion

### *Case 1 – Laboratory-scale test*

PCDD/F removal achieved with three-layer AC-adsorption system is investigated in this case. Inlet TEQ concentration is controlled at 410 ng I-TEQ/Nm<sup>3</sup>. Three temperatures of 120, 150 and 180°C are tested. Adsorption is an exothermic reaction. Therefore, increasing temperature of adsorption system reduces the adsorptive capacity of adsorbent. Moreover, previous study indicates that desorption of PCDD/Fs from filter cake of bag filter would be significant if the operating temperature exceeds 165°C<sup>5</sup>. TEQ concentrations of vapor-phase PCDD/Fs at each adsorption layer are shown in Fig. 2. At outlet of the 1<sup>st</sup> layer, the TEQ concentrations are significantly decreased from 410 to 0.934-1.05 ng I-TEQ/Nm<sup>3</sup>. The effect of operating temperatures is not significant in the 1<sup>st</sup> layer. After passing through 2<sup>nd</sup> and 3<sup>rd</sup> layers, the TEQ concentrations are further decreased to lower than 0.1 ng I-TEQ/Nm<sup>3</sup>, the lowest emission standard of Taiwan. In this case, the effect of operating temperature on PCDD/F removal is not significant and multilayer AC-adsorption system can effectively control PCDD/F emission even with a relatively high inlet PCDD/F concentration (410 ng I-TEQ/Nm<sup>3</sup>).

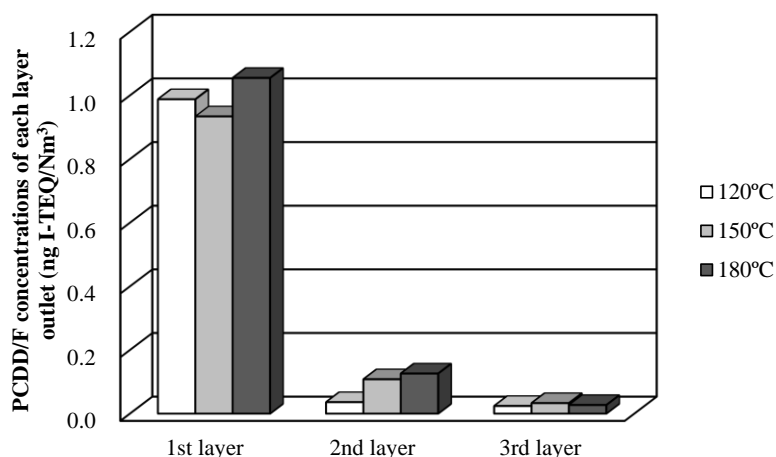


Figure 2 Removal efficiencies achieved with three-layer AC-adsorption system of lab-scale test

### *Case 2 – Pilot-scale test in a sinter plant*

In Taiwan, iron ore sintering process is regarded as one of the most important anthropogenic sources for PCDD/F emission. In general, dioxins can be generated during thermal process, requiring the installation of additional air pollution control devices (APCDs) to reduce the emission. Taiwan government has set 0.5 ng I-TEQ/Nm<sup>3</sup> as the PCDD/F emission limit for sintering process. However, previous study indicates that the PCDD/F removal efficiencies of a sinter plant achieved with the electrostatic precipitator (EP) and wet scrubber were relatively low, being 41.4% and 68.4%, respectively<sup>6</sup>.

The results achieved with the lab-scale test have proved that multilayer AC-adsorption system can effectively remove PCDD/Fs, but PCDD/F formation in AC-adsorption system may be significant as real flue gas is introduced into the system. In real plants, the composition of flue gas is complex and may contain incomplete combustion products, water vapor, catalytic metals and Cl-containing compounds and may lead to PCDD/F formation in the AC-adsorption system if temperature is appropriate. For avoiding PCDD/F formation, BAC is modified with NaOH. Hence, 0, 5 and 10% NaOH-impregnated BACs are evaluated and compared in Case 2. Flow rate and temperature are controlled at 20 slpm and 130±5°C, respectively. Average inlet PCDD/F concentration is 2.58 ng I-TEQ/Nm<sup>3</sup>. Fig. 3 shows the PCDD/F removal efficiencies achieved with dual-layer AC-adsorption system. Higher than 98.8% of total PCDD/F removal efficiencies is achieved and all PCDD/F concentrations of the flue gas streams treated with raw BACs and NaOH-impregnated BACs are lower than 0.1 ng I-TEQ/Nm<sup>3</sup>.

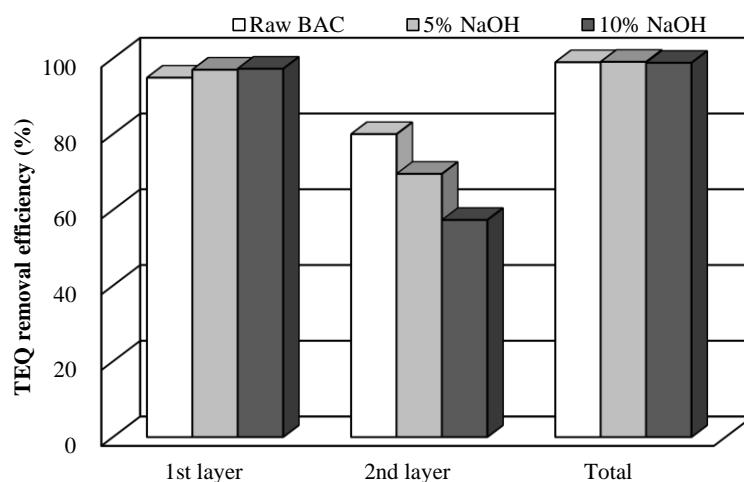


Figure 3 Removal efficiencies achieved with dual-layer AC-adsorption system

However, mass balance of PCDD/Fs is significantly different among three kinds of BACs used. Tab. 1 lists the TEQ PCDD/F flow rates including inlet, outlet and adsorption by three BACs. The definitions of adsorption rates and mass balance achieved with BACs are listed as following formulas:

$$\text{Adsorption rate (ng I-TEQ/hr)} = \frac{\text{PCDD/F concentration of BACs (ng I-TEQ/g)} \times \text{BAC weight (g)}}{\text{Total test time (hr)}}$$

$$\text{Mass balance (\%)} = \frac{(\text{Emission rate} + \text{Adsorption rates of 1}^{\text{st}} \text{ and 2}^{\text{nd}} \text{ layer BACs})(\text{ng I-TEQ/hr})}{\text{Inflow rate (ng I-TEQ/hr)}} \times 100\%$$

The results clearly indicate that mass balance achieved with NaOH-impregnated BACs is lower than that of raw BAC. Moreover, PCDD/F formation is found in the raw BACs of 1<sup>st</sup> layer, resulting in higher total PCDD/F rate (including adsorption and emission) than inflow PCDD/F rate even at a temperature of 130±5°C. Temperature window for significant PCDD/F formation is of the range 200-450°C. However, the test periods in the literature were commonly less than 60 minutes. In this case, pilot-scale system is continuously operated for 13 hours and BACs are not replaced. Therefore, formation of PCDD/Fs is observed on the BACs of pilot-scale module. In contrast, the mass balances of PCDD/Fs achieved with NaOH-impregnated BACs are significantly lower than 100% and decrease with increasing NaOH content in BACs. Previous study indicates that alkaline-impregnated powder activated carbon (AIPAC) applied in ACI+BF system can inhibit PCDD/F formation potential in fly ash<sup>7</sup>. Furthermore, the results obtained in this case indicate that NaOH may destroy PCDD/Fs adsorbed on BACs.

However, further studies are needed to clarify the possible mechanisms. The results obtained in this study indicate that multilayer AC-adsorption system is effective in removing PCDD/Fs from gas streams. In addition to this application, this system has also been applied to simultaneously remove PCDD/F and mercury from the exhaust of small-scale pyrolysis system which is applied to remediate contaminated soil. It is expected that the applicable field of multilayer AC-adsorption system can be further extended.

Table 1 TEQ PCDD/F flow rates achieved with the pilot-scale test (130±5°C, 13 hours)

NaOH content (%)	Inlet PCDD/F rate (ng-TEQ/hr)	PCDD/F adsorption rate (ng-TEQ/hr)		Emission rate (ng-TEQ/hr)	Mass balance (%)
		1 <sup>st</sup> layer	2 <sup>nd</sup> layer		
0 (raw BACs)	2.71	3.36	1.00	0.028	162%
5	3.29	2.33	0.125	0.030	75.5%
10	3.29	1.82	0.093	0.038	59.3%

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