



## Formation of PCDD/Fs in the Cooling Down Process of Incineration Flue Gas

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### ABSTRACT

Total concentrations (11.8–29.3 ng I-TEQ/g approximately) of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the fly ash discharged from a laboratory waste incineration process (375 kg/h) have frequently been found to exceed the limit set by Taiwan's EPA (1.0 ng I-TEQ/g). PCDD/Fs can generally be decomposed in incineration chambers at the temperature range of 1173–1273 K. The main objective of this work was thus to determine how the PCDD/Fs in fly ash are formed when the incineration flue gas is cooling down. The results show that concentrations of total (290 mg/kg) and leachable (9.4 mg/L) copper in the deposited ashes on the internal walls of the cooling towers are greater than those of other toxic elements. To better understand how the relatively high PCDD/Fs concentrations in the cooling towers and bag filter ashes are associated with copper species during the cooling process of the flue gas, the chemical structure of these were studied by synchrotron X-ray absorption near edge structure (XANES) spectroscopy. Notably, it seems that a high fraction of CuO in the cooling tower ashes may lead to relatively high PCDD/F concentrations in the fly ashes. In contrast, copper in the form of CuSO<sub>4</sub> may depress the formation of PCDD/Fs. The correlation of molecule-scale data for copper species with the PCDD/F concentrations of ashes in the commercial-scale waste incineration process can provide useful information for the reduction of PCDD/F.

**Keywords:** XANES; CuO; Fly ash; PCDD/Fs.

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### INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are found frequently in the combustion processes such as waste incineration, boiler, coal-fired power generation, electric arc furnace, and iron ore sintering plant (Huang and Buekens, 1996; McKay, 2002; Suzuki *et al.*, 2004; Thomas and McCreight, 2008; Wang *et al.*, 2009; Lin *et al.*, 2010; Chen *et al.*, 2011; Chiu *et al.*, 2011; Kuo *et al.*, 2011). PCDD/Fs formed in the incineration processes may be associated with the originals in the feedstock or re-formation through the de novo synthesis at the temperature range of 523–673 K (Huang and Huekens, 1996; McKay, 2002; Suzuki *et al.*, 2004; Chin *et al.*, 2012). Generally, formation of PCDD/Fs in the incineration flue gas and fly ash may be caused by organic precursors such as chlorinated phenols, chlorinated benzenes, and polychlorinated benzenes (McKay, 2002). In addition, the de novo synthesis proceeds, to some extent, with the availability of active hydrocarbon, chloride and catalytic active species such as CuO and Fe<sub>2</sub>O<sub>3</sub>

which may assist formation of PCDD/Fs via chlorination of aromatic rings (McKay, 2002; Cunliffe and Williams, 2009; Kuo *et al.*, 2011). Copper might accelerate formation PCDD/Fs in a Deacon-type reaction path (Thomas and McCreight, 2008).

By synchrotron X-ray absorption spectroscopy, local chemical structure information such as bond distance, coordination number, and oxidation state of select elements in the complex solid or liquid can be determined (Lin and Wang, 2000; Hsiao *et al.*, 2001a, b; Lin and Wang, 2001; Huang *et al.*, 2003; Hsiao *et al.*, 2007; Liu and Wang, 2008; Huang *et al.*, 2009; Tian *et al.*, 2009; Chiu *et al.*, 2011). The molecule-scale data turn out to be very useful in revealing speciation of active sites and reaction paths in catalysis processes.

Total concentrations of PCDD/Fs in the fly ash discharged from a laboratory waste incineration process (375 kg/h) have frequently been found exceeding the Taiwan EPA limit (1.0 ng I-TEQ/g). The temperatures of the flue gas exited from the secondary combustion chamber to the cooling tower-I were rapidly decreased from 1273 to 523 K in two seconds. It is thus of great importance and interest to learn how PCDD/Fs are formed when the incineration flue gas is cooled down prior to the baghouse filtration. In the present work, fate of copper in the cooling towers and baghouse filter ashes in the commercial-scale laboratory waste

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incineration process was studied. Specifically, to better understand how copper species are associated with the relatively high concentration of PCDD/Fs in the fly ash, chemical structure of copper in the cooling towers and baghouse filter ashes was studied by XANES.

## METHODS

An incineration process integrated with plasma-assisted melting and inorganic wastewater treatments was designed and constructed in 1994 to treat laboratory organic solid and liquid wastes from universities in Taiwan. Fig. 1(a) shows the flow diagram of the laboratory waste incineration process. Liquid or solid wastes were injected with screw

feeder and nozzles, respectively into the primary and secondary combustion chambers which were operated at the temperatures of 1173 and 1273 K, respectively. The hot flue gas was cooled down rapidly from 1273 to 453 K with two cooling towers in series. The baghouse filters were used to remove particulates and activated carbon (containing captured PCDD/Fs) from the flue gas at the temperature range of 423 K. The cooling towers may preserve chemical species that affect formation of PCDD/Fs during cooling. The deposited ashes on the internal wall of the cooling tower-I were sampled at the points of every 80 cm from the bottom of the cooling tower (see Fig. 1(b)). The cooling towers and baghouse filters ash samples were also collected for tracking of PCDD/Fs and copper species.

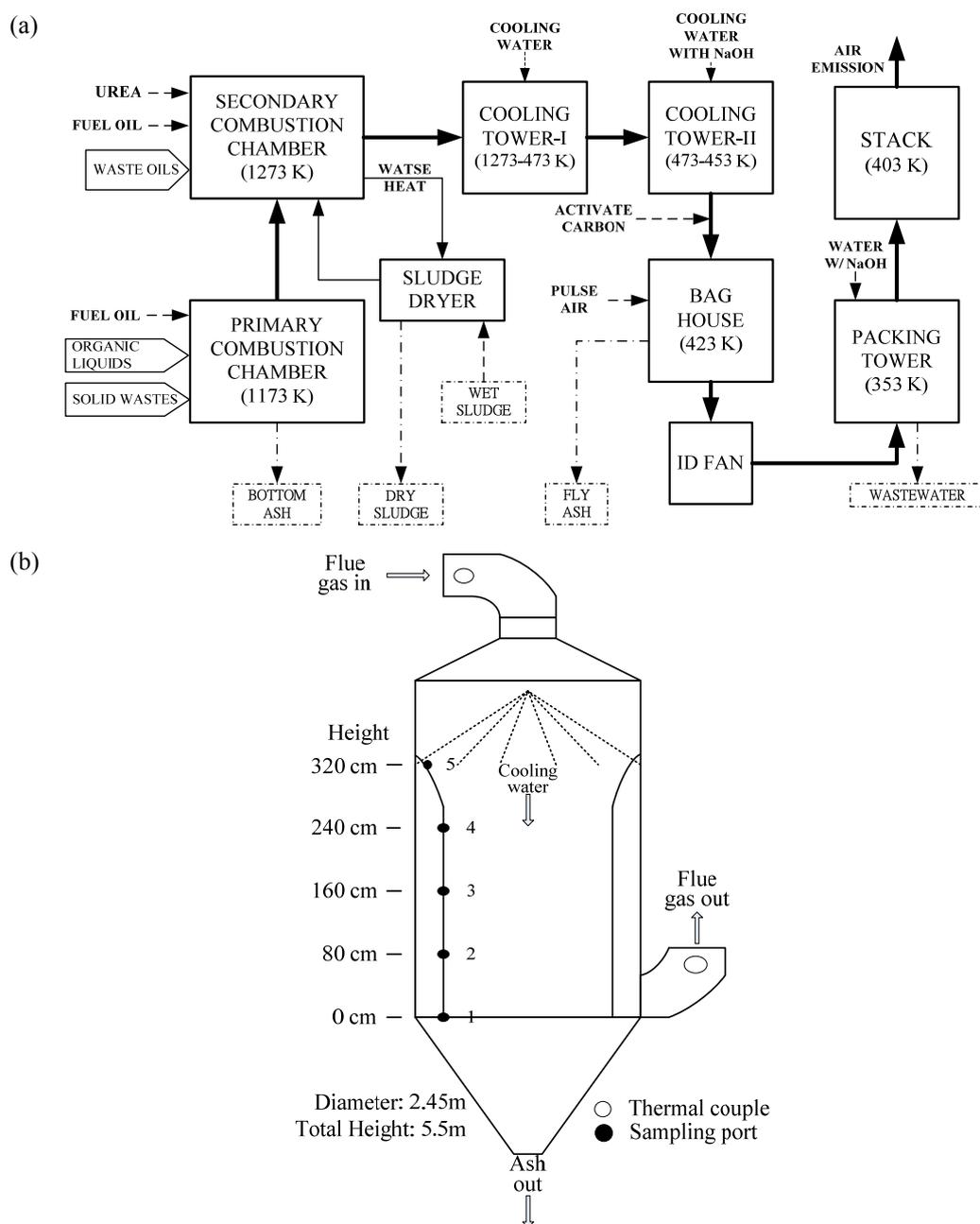


Fig. 1. (a) Flow diagram of the laboratory waste incineration process and (b) sampling points in the cooling tower-I.

Leaching concentrations of toxic metals in the ashes were determined following the toxicity characteristic leaching procedure (Taiwan EPA, 2009), which were obtained on an inductively coupled plasma emission spectrometer (Varian, Model VISTA-MPX). The ash samples were sized with a 9.5 mm sieve prior to extraction. Concentrations of toxic metals in the ash samples were also measured by X-ray fluorescence spectroscopy (Spectro, Model XEPOS).

Synchrotron XANES spectra of copper in the ash samples and copper model compounds such as Cu, Cu<sub>2</sub>O, Cu<sub>2</sub>S, CuCl, CuO, CuCl<sub>2</sub>, CuS, Cu(OH)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, CuSO<sub>4</sub>, and CuSiO<sub>2</sub> were recorded on the Wiggler beam line of the Taiwan National Synchrotron Radiation Research Center (NSRRC). The electron storage ring was operated at energy of 1.5 GeV. Beam energy was calibrated by the adsorption edge of a copper foil at energy of 8979 eV. The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter. The absorption edge was determined at the half height (precisely determined by its derivative) of the XANES spectrum after pre-edge baseline subtraction and normalization to the maximum above-edge intensity (Huang et al., 2007).

Concentrations of PCDD/Fs in the ashes were determined according to the Taiwan EPA standard method (NIEA M801.12B). The ash samples were pretreated with freeze-drying, cracking and crushing to pass through an 18 mesh (< 1 mm) sieve. The sieved ash samples (10 g) were extracted by Soxhlet extraction using 20 µL of toluene and internal spiking standard solutions of PCDD/Fs (100 ng/mL) for 22 hours (4 cycle/h). The extracted samples were transferred to a clean tube with a dichloromethane solution and dried in nitrogen at 298 K. The sample tubes were purified with dichloromethane, standard cleanup solution, sulfuric acid, and hexane. Cleaning of silica gel, aluminum oxide and activated carbon/diatomite columns was also carried out. The cleaned samples with 1–2 µL of PCDD/Fs standard solution were analyzed by high-resolution gas chromatography (GC) integrated with mass

spectrometry (MS) (Hewlett-Packard 6970 Series gas, CA) for determination of 17 congeners of PCDD/Fs. The capillary GC column (DB-5MS fused silica capillary column (L = 60 m, ID = 0.25 mm, film thickness = 0.25 µm)) was programmed with three heating stages: (1) 423–483 K at a heating rate of 20 K/min, (2) 483–503 K at 1.5 K/min, and (3) 503–583 K at 15 K/min. The MS equipped with an electron impact source and selected ion monitoring was operated at a resolution of 10,000.

## RESULTS AND DISCUSSION

Concentration and distributions of toxic metal elements (i.e., As, Hg, Cr, Pb, Cd and Cu) in the ash deposited on the internal wall of the cooling tower-I are shown in Fig. 2. The temperatures of the flue gas exited from the secondary combustion chamber at 1273 K was fast cooled down (473 K) in two seconds in the cooling tower-I. It is clear that concentrations of copper are much greater than those of other toxic metals in the cooling tower ashes. Note that during the rapid cooling, Hg and Cr are concentrated at the bottom of the cooling towers.

Concentrations of the PCDD/F congeners in the cooling tower-I and baghouse filter ashes are shown in Fig. 3. Hepta and Octa chlorinated PCDD/Fs are the main PCDD/F species in ashes. A consideration of the international toxicity equivalency actor suggests that the main congeners which are contributed to the total toxicity equivalency quantity of the PCDD/Fs are 2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, and 1,2,3,7,8-PeCDD in the cooling towers and baghouse filter ashes. Concentrations of total and leachable related to PCDD/Fs concentration in the cooling towers and baghouse filter ashes for two separated runs are shown in Table 1. It seems that concentrations of PCDD/Fs in the ashes are not correlated to their total copper concentrations. To better understand how the relatively high concentration of PCDD/Fs in the ashes is associated with copper species, chemical structure of copper in the cooling towers and baghouse

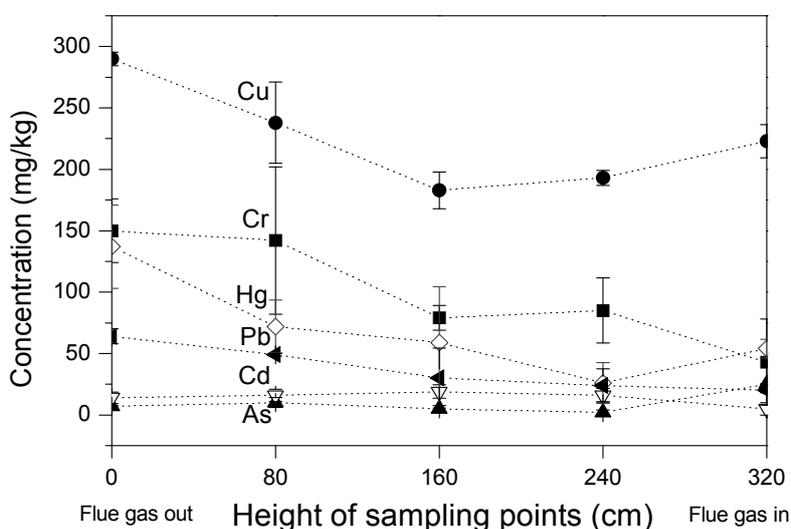
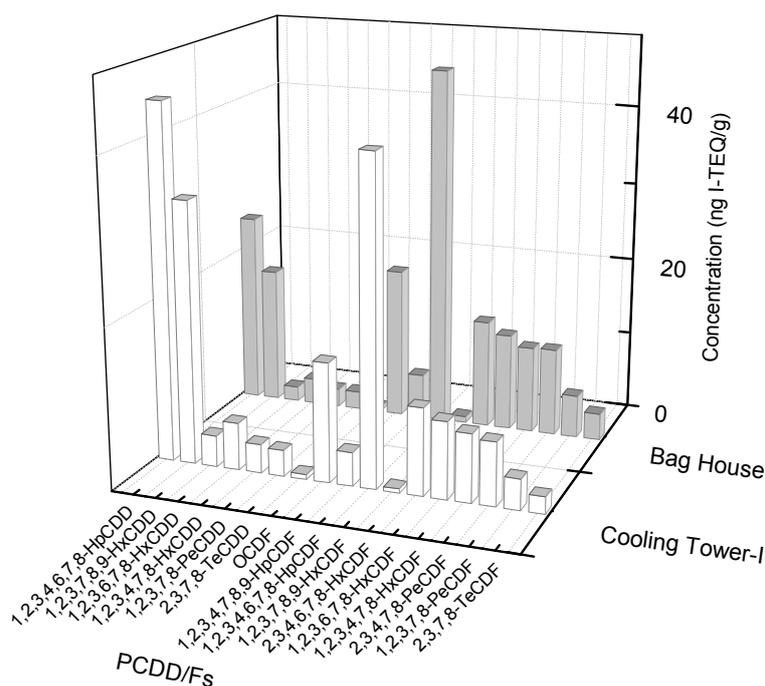


Fig. 2. Total concentrations of toxic metals in the cooling tower-I ashes (deposited on the wall).



**Fig. 3.** Distribution of PCDD/F congeners in the cooling tower-I and baghouse filter ashes.

**Table 1.** Concentrations of total and leachable copper related to PCDD/F concentrations in the cooling towers and baghouse filter ashes.

Run #		Cooling tower-I ash (1323→523 K)	Cooling tower-II ash (523→453 K)	Baghouse filter fly ash (453→423 K)
1	Total copper conc. (mg/kg)	290	680	340
	Leachable copper conc. (mg/L)	9.4	12	15
	PCDD/Fs (ng I-TEQ/g)	11.8	0.147	13.1
2	Total copper conc. (mg/kg)	618	530	491
	Leachable copper conc. (mg/L)	0.05	1.6	1.3
	PCDD/Fs (ng I-TEQ/g)	20.2	0.980	29.3

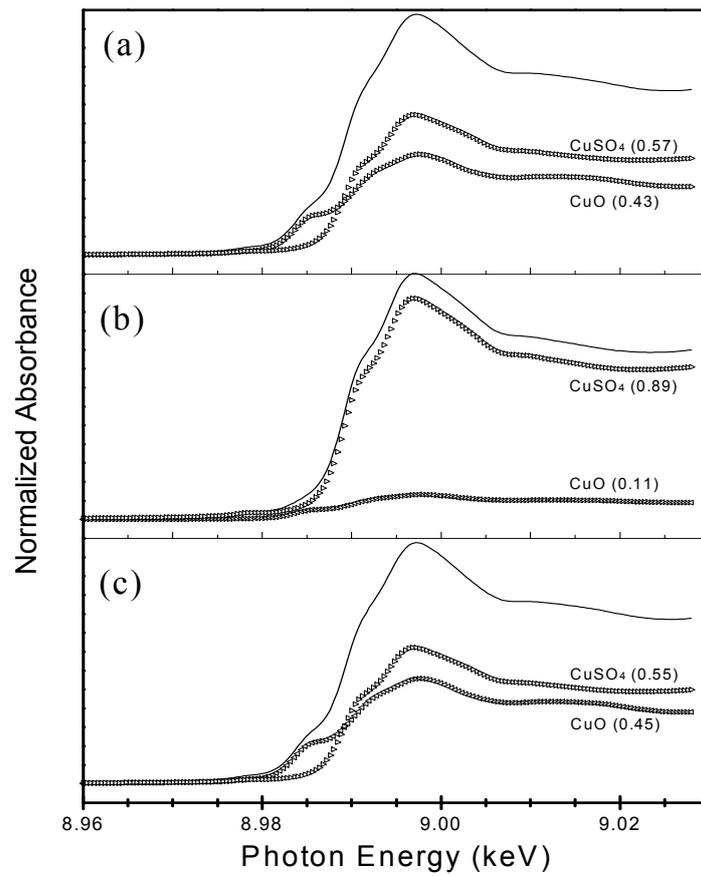
filter ashes has been studied by XANES. The pre-edge XANES spectra of copper in the ashes are shown in Fig. 4. Two shoulder at 8.990–8.994 and 8.983–8.987 keV are observed, which can be attributed the 1s-to-4p transition, suggesting the existence of the Cu(II) species. The component-fitted XANES spectra of copper in the ashes indicate that  $\text{CuSO}_4$  (55–89%) and  $\text{CuO}$  (11–45%) are the main copper species in the cooling towers and baghouse filter ashes. Note that  $\text{CuSO}_4$  is much more soluble in water than  $\text{CuO}$ . Table 1 also shows that the ashes which have relatively high leachable copper concentrations have less PCDD/F concentrations therein.

To learn how copper species play the key role in the formation of the relatively high PCDD/F concentrations in ashes, correlations of concentrations and fractions of  $\text{CuO}$  and  $\text{CuSO}_4$  with concentrations of PCDD/Fs in the cooling towers and baghouse filter ashes are shown in Fig. 5. The correlation between total concentrations of PCDD/Fs and fractions and concentrations of  $\text{CuO}$  or  $\text{CuSO}_4$  in the ash obtained from the commercial-scale incineration data suggest that the high PCDD/F concentrations may be associated with  $\text{CuO}$  in the ashes. Copper as  $\text{CuSO}_4$  can

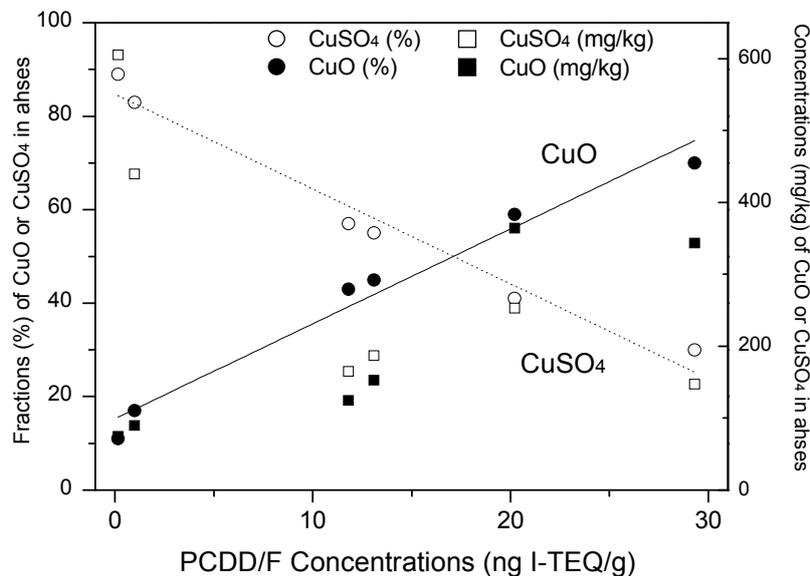
depress formation of PCDD/Fs in the ashes. It is also worth noting that the molecule-scale data obtained from synchrotron X-ray absorption spectra are well correlated with the findings from the full-scale laboratory waste incineration operation, which may be useful in process improvements for reduction of PCDD/F concentration in the fly ash.

## CONCLUSIONS

High-concentration copper has been found in the cooling tower and baghouse filter ashes during the cooling of the incineration flue gas. By component fitted XANES, it is found that  $\text{CuSO}_4$  and  $\text{CuO}$  are the main copper species in the ashes. The total concentrations of PCDD/Fs can be well correlated with fractions and concentrations of  $\text{CuO}$  or  $\text{CuSO}_4$  in the ashes obtained from the commercial-scale incineration data. It seems that the high PCDD/F concentrations may be associated with  $\text{CuO}$  in the ashes. Nevertheless, copper as  $\text{CuSO}_4$  can depress the formation of PCDD/Fs, which may be useful in reduction of PCDD/Fs in ashes by increasing the fraction of  $\text{CuSO}_4$  in the flue gas cooling process. This work is also an example



**Fig. 4.** Component fitted XANES spectra of copper in the (a) cooling tower-I, (b) cooling tower-II, and (c) baghouse filter ashes.



**Fig. 5.** Correlation between PCDD/Fs and (a) fractions and (b) concentrations of CuO or CuSO<sub>4</sub> in ashes.

for applications of the molecule-scale X-ray absorption spectroscopy in developing a key correlation between copper species (CuO and CuSO<sub>4</sub>) and the high-concentration PCDD/Fs found in the fly ash from the commercial-scale laboratory waste incineration process.

#### ACKNOWLEDGEMENTS

The financial supports of Taiwan National Science council and National Synchrotron Radiation Research Center (NSRRC) are gratefully acknowledged. We also

thank Jyh-Fu Lee of NSRRC and Ray-Lin Wong of National Cheng Kung University for their assistances in EXAFS and chemical analyses, respectively.

## REFERENCES

- Chen, W.S., Shen, Y.H., Hsieh, T.Y., Lin, C.W., Wang, L.C. and Chang-Chien, G.P. (2011). Fate and Distribution of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in a Woodchip-fuelled Boiler. *Aerosol Air Qual. Res.* 11: 282–289.
- Chin, Y.T., Lin, C., Chang-Chien, G.P. and Wang, Y.M. (2012). PCDD/F Formation Catalyzed by the Metal Chlorides and Chlorinated Aromatic Compounds in Fly Ash. *Aerosol Air Qual. Res.* 12: 228–236.
- Chiu, J.C., Shen, Y.H., Li, H.W., Lin, L.F., Wang, L.C. and Chang-Chien, G.P. (2011). Emissions of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans from an Electric Arc Furnace, Secondary Aluminum Smelter, Crematory and Joss Paper Incinerators. *Aerosol Air Qual. Res.* 11: 13–20.
- Chiu, Y.M., Huang, C.H., Chang, F.C., Kang, H.Y. and Wang, H.P. (2011). Recovery of Copper from a Wastewater for Preparation of Cu@C Nanoparticles. *Sustain. Environ. Res.* 21: 279–282.
- Cunliffe, A.M. and Williams, P.T. (2009). De-novo Formation of Dioxins and Furans and The memory Effect in Waste Incineration Flue Gases. *Waste Manage.* 29: 739–748.
- Hsiao, M.C., Wang, H.P. and Yang, Y.W. (2001). EXAFS and XANES Studies of Copper in a Solidified Fly Ash. *Environ. Sci. Technol.* 35: 2532–2535.
- Hsiao, M.C., Wang, H.P., Huang, Y.J. and Yang, Y.W. (2001). EXAFS Study of Copper in Waste Incineration Fly Ashes. *J. Synchrotron Radiat.* 8: 931–933.
- Hsiao, M.C., Wang, H.P., Huang, C.H., Chang, J.E. and Wei, Y.L. (2007). Tracking of Copper in Contaminated Soils. *J. Electron. Spectrosc. Relat. Phenom.* 156–158: 208–210.
- Huang, H. and Buekens, A. (1996). De Novo Synthesis of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans – Proposal of a Mechanistic Scheme. *Sci. Total Environ.* 193: 121–141.
- Huang, H.L., Wang, H.P., Chang, J.E. and Wei, Y.L. (2007). Speciation and distribution of copper and zinc in MCM-41. *J. Electron. Spectrosc. Relat. Phenom.* 156–158: 357–360.
- Huang, H.L., Wang, H.P., Eyring, E.M. and Chang, J.E. (2009). Recovery of Nanosize Zinc from Phosphor Wastes with an Ionic Liquid. *Environ. Chem.* 6: 68–72.
- Huang, Y.J., Wang, H.P. and Lee, J.F. (2003). Speciation of Copper in ZSM-48 during NO Reduction. *Appl. Catal., B* 40: 111–118.
- Kuo, Y.C., Chen, Y.C., Yang, C.W., Mou, J.L., Shih, T.S. and Tsai, P.J. (2011). Identification the Content of the Windbox Dust Related to the Formation of PCDD/Fs during the Iron Ore Sintering Process. *Aerosol Air Qual. Res.* 11: 351–359.
- Lin, K.S. and Wang, H.P. (2000). Shape Selectivity of Trace By-products for Supercritical Water Oxidation of 2-chlorophenol Effected by CuO/ZSM-48. *Langmuir* 16: 2627–2631.
- Lin, K.S. and Wang, H.P. (2001). Catalytic Oxidation of 2-chlorophenol in Confined Channels of ZSM-48. *J. Phys. Chem. B* 105: 4956–4960.
- Lin, W.Y., Wu, Y.L., Tu, L.K., Wang, L.C. and Lu, X. (2010). The Emission and Distribution of PCDD/Fs in Municipal Solid Waste Incinerators and Coal-fired Power Plant. *Aerosol Air Qual. Res.* 10: 519–532.
- Liu, S.H. and Wang, H.P. (2008). Fate of zinc in an Electroplating Sludge during Electrokinetic Treatments. *Chemosphere* 72: 1734–1738.
- McKay, G. (2002). Dioxin Characterization, Formation and Minimization during Municipal Solid Waste (MSW) Incineration: Review. *Chem. Eng. J.* 86: 343–368.
- Suzuki, K., Kasai, E., Aono, T., Yamazaki, H. and Kawamoto, K. (2004). De Novo Formation Characteristics of Dioxins in the Dry Zone of an Iron Ore Sintering Bed. *Chemosphere* 54: 97–104.
- Taiwan EPA (1994). Toxicity Characteristics Leaching Procedure (TCLP), NIEA R201.13C.
- Thomas, V.M. and McCreight, C.M. (2008). Relation of Chlorine, Copper and Sulphur to Dioxin Emission Factors. *J. Hazard. Mater.* 151: 164–170.
- Tian, S.L., Yu, M.J., Wang, W., Wang, Q. and Wu, Z.Y. (2009). Investigating the Speciation of Copper in Secondary Fly Ash by X-ray Absorption Spectroscopy. *Environ. Sci. Technol.* 43: 9084–9088.
- Wang, Y.H., Lin, C. and Chang-Chien, G.P. (2009). Characteristics of PCDD/Fs in a Particles Filtration Device with Activated Carbon Injection. *Aerosol Air Qual. Res.* 9: 317–322.

Received for review, March 5, 2012

Accepted, May 28, 2012