Identification the Content of the Windbox Dust Related to the Formation of PCDD/Fs during the Iron Ore Sintering Process

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ABSTRACT

This study measured the contents of the ionic and elemental constituents, and the chemical compounds containing in windbox (WB) dusts collected from a commercial iron ore sintering plant, then the results were used to identify possible PCDD/Fs formation pathways in the WB. We found that the abundance in both KCl and NaCl may provide a suitable condition for de novo synthesis of PCDD/Fs in the WB. Al, Fe, K, Ca, and Pb were the top five contents in WB16 dusts, but the co-existence of the above five metal contents warrants the need for further investigation on their roles in PCDD/F formation processes in the future. Although a low concentration of Cu was detected, it might be of importance to PCDD/Fs formation inside the WB. A total of 29 chemical compounds were identified. Among them, several oxygenated organic compound might be associated with PCDD/F formations at the beginning stage, but the roles of aromatic oxygenates on the formation of PCDD/Fs required further investigation. Finally, possible *de novo* synthesis pathways of PCDD/Fs were proposed based on the above findings. However, the above pathways are required further laboratory studies for validation before possible formation suppression approaches can be determined.

Keywords: Iron ore sintering; Windbox dusts; Chemical contents; PCDD/Fs; *de novo* synthesis.

INTRODUCTION

It is well known that dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) generate toxicological effects and associated adverse health implications to organisms (U.S. EPA, 2003; Lin *et al.*, 2010a; Ning and Sioutas, 2010). PCDD/Fs were first found in the fly ash of a municipal solid waste incinerator (MSWI) (Olie *et al.*, 1977). Since then, attention has been paid on many other emissions sources by environmental science researchers (Wang *et al.*, 2003; Lee *et al.*, 2004; Kao *et al.*, 2006; Hu *et al.*, 2009; Lin *et al.*, 2010b; Chuang *et al.*, 2010a, 2010b; Wang *et al.*, 2010a, 2010b; Wu *et al.*, 2010; Yu *et al.*, 2010; Chiu *et al.*, 2011;

Chen *et al.*, 2011). Among them, the iron ore sintering process is considered as the most important PCDD/F emission source in many countries (Lahl, 1993, 1994; Alcock *et al.*, 1999; Anderson and Fisher, 2002; Aries *et al.*, 2006; Shih *et al.*, 2006, 2008, 2009; Chen *et al.*, 2010). For example, PCDD/Fs emitted from the sintering process contributed to 19.6%, 11–34%, 8.4% and 30.7% of the total annual PCDD/F emissions in Europe (Quaß *et al.*, 2000), United Kingdom (Anderson and Fisher, 2002), Japan (Japan Ministry of the Environment, 2005) and Taiwan (Taiwan Environmental Protection Administration, 2008), respectively.

Kasai and his colleagues (Kasai *et al.*, 2001a) have investigated that the PCDD/Fs congener profiles of exhaust gases of windboxes. They found that the concentration of PCDFs were 10 times in magnitude higher than PCDDs. The above pattern is similar to that of PCDD/F emissions from municipal waste incinerators. The *de novo* synthesis has been considered as an important

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formation pathway of PCDD/Fs during the iron ore sintering process according to the results obtained from several field and laboratory investigations (Kasai *et al.*, 2001a, 2001b; Xhrouet *et al.*, 2001; Cieplik *et al.*, 2003; Kuzuhara *et al.*, 2003; Suzuki *et al.*, 2004; Kasama *et al.*, 2006; Tsubouchi *et al.*, 2006). For example, a series of laboratory sinter-pot studies have identified that the *de novo* synthesis could be occurred in the drying zone of the sinter bed (Cieplik *et al.*, 2003). More recently, the concept of the two-stage release of PCDD/Fs from the rear half part of the sinter strand has been proposed by Kasama *et al.* (2003). Here, the formation of PCDD/Fs at the end of the wet zone and the beginning of the drying zone of the sintering bed was considered as the first stage. As the melting zone touching the bottom of the sintering bed (i.e., "the burn through point"), PCDD/F formation inside the corresponding windbox (WB) was considered as the second stage, and also the peak formation stage, of PCDD/Fs via the *de novo* synthesis process. In order to elucidate the *de novo* synthesis process occurred in WB, Tsubouchi *et al.* (2006) conducted a study focused on investigating functional groups containing in WB dust. Several functional groups, such as carboxyl, lactone/acid anhydride, and ketone/ether/phenolic groups, were identified by using temperature-programmed desorption (TPD) and temperature-programmed oxidation (TPO) techniques. Possible *de novo* pathways for synthesis of PCDD/Fs on the WB dust have been proposed based on their results. Briefly, the surface oxygen functional groups found in the WB dust may involve in the formation of PCDD/Fs by catalyzed carbon gasification under *de novo* condition in the WB towards the end of the sinter strand (Kasama *et al.*, 2006). However, due to the limitation of both TPD and TPO, detailed information regarding the oxygenated organic compounds still remains unclear. In addition, beside the oxygenated organic compounds, the investigation of other contents containing in WB dusts might also be important for better understanding the *de novo* synthesis pathway of PCDD/Fs in the WB.

It is known that directly suppressing PCDD/F formations during the sintering process is considered as a better approach for reducing PCDD/F emissions than end-of-pipe treatment methods (Chen *et al.*, 2008). Therefore, if the contents containing in WB dusts can be identified, then the information may help researchers to determine PCDD/Fs formation pathways and eventually to initiate potential suppression methods in the future. The aim of this research was set out to meet the above purpose.

METHODS

Conducting WB Dust Sampling

The whole study was conducted in a commercial iron ore sintering plant located in southern Taiwan with a Dwight-Lloyd type sintering process. The sintering machine was installed with 18 WBs (inner diameter of 1,025 mm) with an effective sintering area of 315 m^2 and total air suction capacity of 11,000–12,000 Nm^3/min. The raw mix materials used in this sintering process including blending ore, coke breeze, fluxes (marble limestone and serpentine), and return fines (minipellet, blast furnace returning fine, sintering plant returning fine, and slurry).

Dust samplings were carried out in the sixteenth WB (denote as WB16) of the sinter plant. The location of WB16 represents the phase of the "the burn through point" in the sintering process, and is the exact location for the occurrence of the second PCDD/F formation stage (i.e., the peak formation) in the *de novo* synthesis process (Kasama *et al.*, 2006).

All WB dust samplings followed the modified USEPA method 5 (U.S. EPA, 2001). A silica glass microfiber thimble (25 mm O.D., 90 mm length, Whatman, Maidstone, UK) was used for collecting dust samples with a sampling velocity of 1.5×10^{-2} Nm/dry min and sampling time of 1 hr. All samples were collected at the same sampling positions. Total ten dust samples were collected. Among them, four, three, and three samples were designated for the analyses of the ionic constituents, metal contents, and the types of functional forms, respectively. All silica glass microfiber thimbles were baked at 500°C for 24 hrs before sampling to eliminate the organic compounds originally containing in the filter.

Sample Analyses

For water-soluble ionic constituent analyses, each sample was cut into small pieces, then placed into 500 mL flask and mixed with 200 mL double deionized (d.d.) water. Each flask was heated at 70°C for 2 hr for extracting water-soluble ions, then subsequently filtrated by a quantitative filter paper (No. 3 filter, 15 cm in diameter) (Advantec, Tokyo, Japan). The extracts were analyzed for cation (Na$^+$, K$^+$, NH$_3^+$, and Ca^{2+}) and anion (F$^-$, Cl$^-$, Br$^-$, SO$_4^{2-}$, NO$_3^-$, and NO$_2^-$) using an ion chromatograph (ICS-1000, Dionex, Sunnyvale, CA, USA) with a IonPac CG12A guard column (4 × 250 mm, Dionex, Sunnyvale, CA, USA) and AS4A-SC analytical column (4 × 250 mm, Dionex, Sunnyvale, CA, USA), respectively. All sample analyses were completed within a week after sampling. This study yielded detection limits for the analyzed ionic constituents ranging from 0.01 to 0.05 mg/L.

For the determination of the concentrations of various elemental constituents, another three filter samples were used. Each sample was mixed with 10 mL acid mix (6 mL HCl, 2 mL HF, 2 mL HNO$_3$) and then placed for 30 min. The mixtures were subsequently pretreated by a microwave digestion system (MLS-1200 mega, Milestone, Italy) with programmed operation conditions set at 250 W for 6 min, 400 W for 6 min, 650 W for 6 min, and 250 W for 6 min. Sixteen elements (S, Cu, Ni, Cr, Mo, V, Ti, Co, Al, Pb, Zn, As, Fe, K, Mg, and Ca) were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 3300 DV, Perkin-Elmer, Norwalk, CT, USA). This method detection limits for sulfur and other analyzed elements were 5 ppm and 0.1 ppm, respectively.

To determine the chemical compounds containing in WB dust, three remained samples were pretreated by Soxhlet extraction process for continuously 24 hr using toluene as the solvent. The extracts were concentrated and

qualitatively analyzed for chemical compounds using a gas chromatography-mass spectrometry (GC/MS) (HP 6890/5973, Hewlett Packard, Palo Alto, CA, USA) with a HP-5MS column (0.25 mm I.D., 60 m length, 0.25 μm film thickness, Hewlett Packard, Palo Alto, CA, USA). The splitless mode was used for sample injection and the oven temperatures were set at 100°C for 10 min, 10 °C/min to 280°C, and held for 20 min. The analyzer mode of the selected ion monitoring (SIM) was used with mass resolution of R = 1,000. The compound identification was done by spectrum matching and library (NIST05 MS) searching. All library-matched species exhibited a degree of match better than 90%.

RESULTS AND DISCUSSION

Ionic Constituents Containing in WB Dusts

Table 1 shows the contents of ionic constituents containing in WB dusts. High Cl^- and SO_4^{2-} contents were found among the analyzed anions in the present study. The above result was quite comparable to that conducted by Tsai *et al.* (2007), although their dust samples were collected from the stack rather than from the windbox. In principle, the high Cl^- contents were quite expectable since the iron ore and coke used in this sintering process contains ~200 and 100 mg/kg of water-soluble chlorides (Nakano *et al.*, 2005). But for SO_4^{2-}, its high content might be contributed mostly by the sulfur content containing in the fuels (such as coke oven gas (COG) and coke breeze for igniting the burner). The above inference could be supported by Hu *et al.* (2008). They estimated that ~90% of sulfur in the steel manufacturing process were derived from fuels. For a sintering process, sulfides could be decomposed and oxidized to form gaseous SO_2 or SO_3. Subsequently, oxidation of SO_2 might occur at the particle surface to form SO_4^{2-} (Mamane and Pueschel, 1979). Therefore, it is no so surprising to see that abundant SO_4^{2-} could be found in WB dusts.

For cation analysis, results show that the concentrations

Table 1. Mean concentrations and their SDs (values in parenthesis) of ionic contents containing in the WB16 dust (n = 4).

Cation/Anion		mmol/g
cation	Na^+	2.59 (2.43)
	K^+	4.72 (2.80)
	NH_3^+	ND
	Ca^{2+}	0.0101[*]
anion	F^-	0.826 (0.0947)
	Cl^-	2.62 (1.25)
	NO_2^-	0.212[§]
	Br^-	ND
	SO_4^{2-}	2.82 (1.35)
	NO_3^-	ND

[*] only one sample was detected for Ca^{2+}
[§] only one sample was detected for NO_2^-

of both K^+ and Na^+ were higher than that of other analyzed cations. It might be because the involved raw materials for the iron ore sintering process, such as iron ore and return fines, were abundant in both K^+, and Na^+ (Cieplik *et al.*, 2003; Nakano *et al.*, 2005). The above results were also comparable to that conducted by Tsai *et al.* (2007). Several laboratory studies have used alkali chlorides as raw material additives (act as catalysts and chlorine sources) to investigate the formation of PCDD/Fs during iron ore sintering process. They found that the alkali chlorides, such as NaCl and KCl, might catalyze the *de novo* synthesis (Kasai *et al.*, 2001b; Cieplik *et al.*, 2003; Kuzuhara *et al.*, 2003; Nakano *et al.*, 2005). Table 2 show the comparison between the amounts of alkali chlorides added in the above reference studies and the contents of K^+, Na^+ and Cl^- found in the present study. It can be seen that the concentrations of the contents of Na^+, K^+ and Cl^- found in this study were at least 88, 16 and 9 times in magnitude higher than that of previous studies, respectively. This result indicates that the abundance in both KCl and NaCl may provide a suitable condition for *de novo* synthesis of PCDD/Fs inside the WB16.

Elemental Constituents Containing in WB Dusts

Table 3 shows the content of elemental constituents containing in WB16 dusts. We found that Al, Fe, K, Ca, and Pb were the top five elements in the WB16 dust samples and they accounted for 98.6% of the total analyzed elemental constituents. The above result is quite comparable to the results conducted by Tsubouchi *et al.* (2006) and Tsai *et al.* (2007). In principle, high Al, Fe, K, Pb and Ca concentrations found in the WB dust samples might be because: 1. fluxes, iron ore fines and coke breeze used in the iron ore sintering process could contain a variety of impurities, including Al_2O_3, and K_2O (Cieplik *et al.*, 2003; Nakano *et al.*, 2005; Sammut *et al.*, 2010); 2. the use of limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)$) as fluxes in the sintering process (Cieplik *et al.*, 2003); and 3. the return fine used in the sintering process usually contains Pb compounds (Sammut *et al.*, 2010). Among these five metal contents, several studies have shown that the existence of Fe and K might lead to the increase in PCDD/Fs formation (Hinton and Lane, 1991; Nganai *et al.*, 2009; Fujimori *et al.*, 2009). To the contrary, the existence of Pb (chloride and oxide) and Ca (oxide) might inhibit the formation of PCDD/Fs (Qian *et al.*, 2005; Fujimori *et al.*, 2009). But for Al, conflict roles (i.e., either act as a catalyst or inhibitor) have been found in PCDD/F formation processes (Hinton and Lane, 1991; Gullett *et al.*, 1992; Qian *et al.*, 2005). In this study, the co-existence of the above five metal contents warrants the need for further investigation in their roles on PCDD/F formation processes.

In this study, the concentration of Cu found in WB16 dusts was 0.0308 mmol/g (Table 3). Although its concentration was much lower than that of Fe (6.69 mmol/g) and K (2.65 mmol/g), it was comparable to the result (0.0180 mmol/g) obtained from Tsai *et al.* (2005). The Cu presents in coal predominantly as chalcopyrite ($CuFeS_2$) which might decompose and react with sulfur

Table 2. Amount of alkali chlorides (served as catalysts and chlorine sources) added in PCDD/Fs formation experimental studies and the ionic contents of K^+, Na^+ and Cl^- found in the present study.

Sources	Amount added
Kasai *et al.* 2001	NaCl 0.08% (Na – 0.317 mg/g, Cl – 0.483 mg/g)
	NaCl 0.17% (Na – 0.674 mg/g, Cl – 1.03 mg/g)
Cieplik *et al.*, 2003	NaCl 0.0075 mg/g (Na – 0.00297 mg/g, Cl – 0.00453 mg/g)
Kuzuhara *et al.*, 2003	KCl (K – 11.1 mg/g, Cl – 10 mg/g)
Nakano *et al.*, 2005	NaCl 0.33 mg/g (Na – 0.131 mg/g, Cl – 0.199 mg/g)
This study (ionic contents in the WB16 dust)	Na^+ – 59.6 mg/g K^+ – 184 mg/g Cl^- – 91.7 mg/g

Table 3. Mean concentrations and their SDs (values in parenthesis) of elemental constituents containing in WB16 dusts (n = 3).

Elemental constituents	mmol/g
As	0.00156 (0.000348)
Co	0.00180 (0.000403)
V	0.00220 (0.00167)
Mo	0.00786 (0.00311)
Ni	0.00972 (0.000189)
Ti	0.00984 (0.00102)
Cr	0.0112 (0.0107)
Cu	0.0308 (0.0120)
Zn	0.0370 (0.00919)
S	0.0664 (0.0332)
Mg	0.202 (0.135)
Pb	0.314 (0.0890)
Ca	0.572 (0.185)
K	2.65 (0.653)
Fe	6.69 (1.25)
Al	21.1 (11.3)

during the coke making process, then condense upon the surface of coke breeze (Coles *et al.*, 1979; Khare *et al.*, 2010). Therefore, Cu found in the present study might originate from the coke breeze which was used as a fuel in the sintering process. Table 4 compares Cu contents containing in the WB16 dust and that containing in the fly ash collected from different combustion processes. The Cu content in WB16 dust was higher than that of thermal power plant fly ash, but was close to the upper value of

MSWI fly ash (Wiles, 1996; Aunela-Tapolaa *et al.*, 1998; Ferreira *et al.*, 2003; Nakano *et al.*, 2005, Smolk-Danielowska, 2006; Sushil and Batra, 2006; Smichowski *et al.*, 2008; Cobo *et al.*, 2009). It is know that Cu plays a crucial role on the formation of PCDD/Fs in the fly ash for both the thermal power plant and MSWI. Moreover, laboratory study suggests that the small amount of Cu (0.0127 mg/g) could significant increase the formation of PCDD/Fs (Olie *et al.*, 1998). Therefore, it could be expected that Cu might also play an important role on PCDD/Fs formation inside the WB.

Chemical Compounds Containing in WB Dusts

Table 5 shows the contents of chemical compounds containing in WB16 dusts. Eleven classes of organic compounds were detected, including alkane, alkene, aldehyde, alkyl benzene, alcohol, acid, ester, phthalate ester, phenols, phenoxy compound, and PAHs, above containing 3, 7, 1, 2, 2, 1, 4, 6, 1, 1, and 1 chemical compounds for each individual class, respectively. However, no chlorinated compound was detected might be because chlorinated compounds were presented in the gaseous form under either complete or incomplete combustion situations (Ismo *et al.*, 1997).

Table 5 also compares the results obtained from the present study and that obtained from Tsubouchi *et al.* using TPD and TPO techniques (Tsubouchi *et al.*, 2006). Noted that the study conducted by Tsubouchi *et al.* was not able to provide the detailed specific compound information due to the limitations of their adopted analytical methods. Therefore, only functional groups were provided in their

Table 4. Comparisons of Cu contents containing in the investigated WB dusts of the selected iron ore sinter plant and those in the stack flue gas dust of an iron ore sinter plant, and in the fly ash of thermal power plants, MSWIs and hazard waste incinerator.

Sources	Sampling location	Sample type	Cu content
This study	Iron ore sinter plant	WB16 dust	0.0308 mmol/g (1.97 mg/g)
Tsai *et al.*, 2007	Iron ore sinter plant	Stack flue gas dust	0.0180 mmol/g (1.15 mg/g)
Aunela-Tapola *et al.*, 1998	Thermal power plant	fly ash	0.000281 mmol/g (0.0180 mg/g)
Smołka-Danielowska, 2006	Thermal power plant	fly ash	0.000375 mmol/g (0.0240 mg/g)
Sushil and Betra, 2006	Thermal power plant	fly ash	0.00130 mmol/g (0.0830 mg/g)
Smichowski *et al.*, 2008	Thermal power plant	fly ash	0.00125 mmol/g (0.0799 mg/g)
Wiles, 1996	MSWI	fly ash	0.00937–0.05 mmol/g (0.6–3.2 mg/g)
Ferreira *et al.*, 2003	MSWI	fly ash	0.00853 mmol/g (0.546 mg/g)
Cobo *et al.*, 2009	Hazard waste incinerator	fly ash	0.00740 mmol/g (0.474 mg/g)

Table 5. Comparison of the chemical classes found in this study and the functional groups found in a study conducted by Tsubouchi *et al.* (2006).

Sources	Sampling location	Resutls		Detail information of results
Tsubouchi *et al.*, 2006	WB21 dust (total 23 WBs)	the information associated with functional groups		carboxyl group lactone/acid anhydride ketone/ether/phenolic group
This study	WB16 dust (total 18 WBs)	11 chemical classes of compounds	Alkane	8-hexylpentadecane; octadecane; 2-methyloctadecane; nonadecane; eicosne; heneicosane; docosane; tricosane; tetracosane; hexacosane; hentriacontane; tetratriacontane; tetratetracontane
			Alkene	[(E)-2-phenylethenyl]benzene; [(Z)-2-phenylethenyl]benzene; octadec-1-ene; docosa-1,21-diene; tricos-1-ene; (Z)-tricos-9-ene; (6E,10E,14E,18E)-2,6,10,15,19,23-hexamethyltetracosa-2,6,10,14,18,22-hexaene
			Aldehyde	Benzaldehyde
			Alkyl benzene	2-phenylethylbenzene; 1-methyl-4-(phenylmethyl)benzene
			Alcohol	phenylmethanol; octadecan-1-ol
			Acid	Hexadecanoic acid
			Ester	1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1, 4a-dimethyl-7-(1-methylethyl)-, methyl ester; 1-Cyclohexene-1-carboxylic acid, 4-(1,5-dimethyl-3-oxohexyl)-, methyl ester; tetradec-13-enyl acetate; phenylmethyl benzoate
			Phthalate ester	dibutyl benzene-1,2-dicarboxylate; dioctyl benzene-1,2-dicarboxylate; bis(2-methylpropyl) benzene-1,2-dicarboxylate; 2-O-butyl 1-O-(2-methylpropyl) benzene-1,2-dicarboxylate; 2-(2-ethylhexoxycarbonyl)benzoic acid; bis(6-methylheptyl) benzene-1,2-dicarboxylate
			Phenols	2,6-bis(1,1-dimethylethyl)-4-methylphenol
			Phenoxy compound	1,3-bis[3-(phenoxy)phenoxy]benzene
			PAHs	Fluoranthene

study (Tsubouchi *et al.*, 2006). But in the present study, the specific compounds belong to each individual chemical class were identified and provided by the present study.

As shown in Table 5, linear alkanes with high molecular weight (from C_{15} to C_{44}) and a group of phthalate esters were found in WB dusts. These compounds might mainly come from lubricants (which were used in the sinter plant for lubricating the wheel bearing of the sintering strand) (Totten, 2006). The above inference can be confirmed by the detected compound of the 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) from WB16 dusts, since the BHT is widely-used anti oxidation additive in lubricants.

Several oxygenated organic compound were identified from WB16 dusts, including aldehyde, alcohol, organic acid, ester and phenols etc. (Table 5). According to mechanisms proposed by Tsubouchi *et al.* (2006), the O-containing species may play an important role on PCDD/Fs formation at the beginning stage. Moreover, several aromatic oxygenates, such as phenylmethanol, benzaldehyde, 2,6-bis(1,1-dimethylethyl)-4-methylphenol, and 1,3-bis[3-

(phenoxy)phenoxy]benzene, were also observed in WB16 dusts (Table 5). These compounds were quite similar to those found in the MSWI fly (Jay and Stieglitz, 1995; Cains *et al.*, 1997). The aromatic oxygenates could be degraded into phenols if the alkali and alkaline earth bases could also be found in the dust (Jay and Stieglitz, 1995). In the present study, although the co-existence of alkali metals and the aromatic oxygenates could be confirmed in WB16 dusts, no phenols were identified from the WB16 dust samples. It might be because phenols have a high reactivity on the carbon surface and hence they became undetectable in WB16 dusts (Jay and Stieglitz, 1995). Finally, it should be noted that the detected 1,3-bis[3-(phenoxy)phenoxy]benzene has a similar structure as that of diphenyl ether. Wiater and Louw investigated the reactions of diphenyl ether with Cl and Br atoms at 477°C (Wiater and Louw, 1999). Their results indicate that the phenoxy radicals can be formed via the reaction of diphenyl ether with chlorine atoms. Then, the generated phenoxy radical might react with another phenoxy radical

to form dibenzofuran. Here, it should be noted that the temperature of WB16 is very close to 477°C. However, whether the aromatic oxygenates found in the present study will contribute to the formation of PCDD/Fs via the above pathway require further investigation in the future.

Possible *de novo* Synthesis Pathways of Organic Chlorine Compounds

According to theory proposed by Huang and Buekens, the gasification of carbon could be critical for the *de novo* synthesis in the low-temperature condition (Huang and Buekens, 1996). In principle, the gasification of carbon includes two steps: 1. the absorption of gases on carbon surface, and 2. the catalyzed carbon gasification. For the first step, the oxygen could dissociatively chemisorb on metallic sites and subsequently migrate to the carbon site to form complex at temperatures between 400–500°C. Moreover, other researchers have shown that certain metals, such as Cu and Cr, can act as the dissociation center for the O_2 chemisorption (Mckee, 1970; Baker and Chludzinski, 1981). As described in Table 3, more abundant elemental metal, including Cu and Cr, can be found in the WB16 dust. In addition, the temperature of the flue gas in the WB at the latter phase of the sinter strand (i.e., WB16 in this study) usually falls to the range 400–500°C. Particularly, abundant oxygen content could also be found in the flue gas due to the high suction air flow rate passing through the sintering bed. Therefore, the absorption of gases on carbon could be happened in WB16. This inference could be confirmed by the observation of several O-containing species, including carboxyl acids, alcohols, aldehydes, ketone, and esters, contained in the dust samples in the present study. For the second step, the metal mediated catalyzed carbon gasification takes place and the O-containing species are decomposed into carbon active sites and CO_2/or CO. The activities of metallic oxides for carbon gasification, while presented in sequence, were: Pb > V > Mn > Co > Cr > Cu > MO > Ag > Cd > Fe > Pt > Ni > Zn (Mckee, 1970). According to the elemental analysis results of the present study, high concentrations of Pb, Cr and Cu were observed in the WB16 indicating that the occurrence of the gasification of O-containing species in the WB16 could be possible. In addition, the carbon active site could then react with HCl to form covalent C-Cl bonds (Takeda *et al.*,

2006). Here, HCl could be formed during the combustion process since the Cl content was originally containing in the cokes (Kasai *et al.*, 2001a). Yet, it is true that HCl might be converted to Cl_2 under the temperature range between 340 and 400°C via the Deacon reaction. Although Cl_2 measurements were not conducted in the present study, the result of high-level of Cl^- content contained in the WB16 dusts (see Table 1) indicating that the Cl-containing intermediate could be formed in the WB16. Therefore, it infers that these Cl-containing intermediates could be further converted into organic chlorine compounds, including PCDD/Fs. Based on the above inferences, the proposed pathways for the *de novo* synthesis of organic chlorine compounds were summarized in Fig. 1. The further studies were needed to confirm the above inferences.

CONCLUSIONS

Based on ionic constituents found in WB dusts, our study suggests that the abundance in both KCl and NaCl may provide a suitable condition for de novo synthesis of PCDD/Fs in the WB16. After analyzing elemental constituents, we found that Al, Fe, K, Ca, and Pb were the top five contents in WB16 dusts. However, the co-existence of the above five metal contents warrants the need for further investigation on their roles in PCDD/F formation processes. Although the concentration of Cu was much lower than that of Fe, it might play an important role on PCDD/Fs formation inside the WB. In the present study, 11 classes of organic compounds were detected, and in total 29 chemical compounds were identified. Among them, several oxygenated organic compound may play an important role on PCDD/Fs formation at the beginning stage. On the other hand, whether the aromatic oxygenates found in the present study will contribute to the formation of PCDD/Fs required further investigation in the future. The results obtained from the present study can be used as a basis for laboratory studies to further elucidate possible formation pathways of PCDD/Fs in WBs in the future.
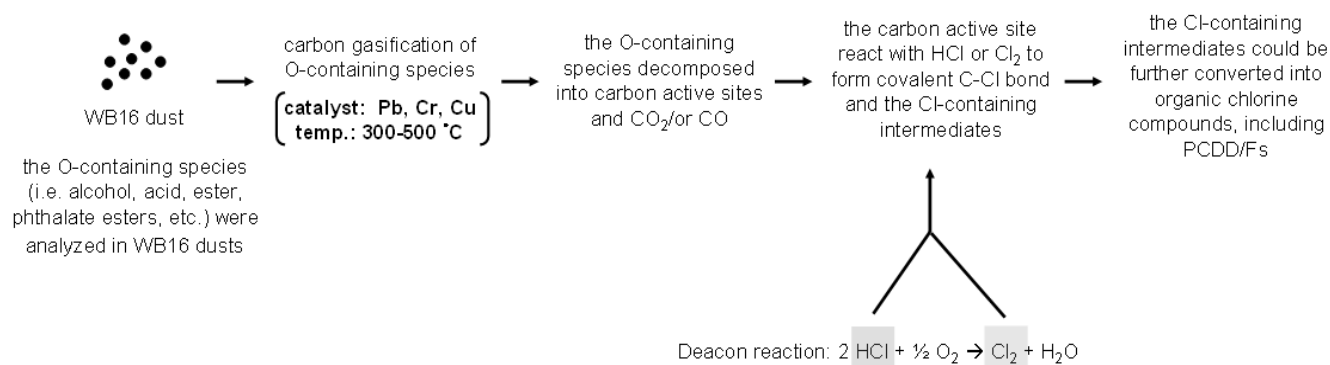
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Fig. 1. The possible *de novo* synthesis pathway of organic chlorine compound.

REFERENCES

Alcock, R.E., Gemmill, R. and Jones, K.C. (1999). Improvements to the UK PCDD/F and PCB Atmospheric Emission Inventory Following an Emissions Measurement Programme. *Chemosphere* 38: 759–770.

Anderson, D.R. and Fisher, R. (2002). Sources of Dioxins in the United Kingdom: The Steel Industry and Other Sources. *Chemosphere* 46: 371–381.

Aries, E., Anderson, D.R., Fisher, R., Fray, T.A.T. and Hemfrey, D. (2006). PCDD/F and "Dioxin-like" PCB Emissions from Iron Ore Sintering Plants in the UK. *Chemosphere* 65: 1470–1480.

Aunela-Tapolaa, L.A., Frandsen1, F.J. and Häsänen, E.K. (1998). Trace Metal Emissions from the Estonian Oil Shale Fired Power Plant. *Fuel Process. Technol.* 57: 1–24.

Baker, R.T.K. and Chludzinski, JJ. Jr. (1981). Catalytic Gasification of Graphite by Chromium and Copper in Oxygen. *Carbon* 19: 75–82.

Cains, P.W., Mccausland, L.J., Fernandes, A.R. and Patrick, D. (1997). Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans Formation in Incineration: Effects of Fly Ash and Carbon Source. *Environ. Sci. Technol.* 31: 776–785.

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.

Chen, Y.C., Tsai, P.J. and Mou, J.L. (2008). Determining Optimal Operation Parameters for Reducing PCDD/F Emissions (I-TEQ Values) from the Iron Ore Sintering Process by Using the Taguchi Experimental Design. *Environ. Sci. Technol.* 42: 5298–5303.

Chen, Y.C., Tsai, P.J., Wang, L.C., Shih, M. and Lee, W.J. (2010). An Integrated Approach for Identification of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans (PCDD/Fs) Pollutant Sources Based on Human Blood Contents. *Environ. Sci. Pollut. Res. Int.* 17: 759–769.

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 Aluminium Smelter, Crematory and Joss Paper Incinerators. *Aerosol Air Qual. Res.* 11: 13–20.

Chuang, S.C., Chen, S.J., Huang, K.L., Chang-Chien, G.P., Wang, L.C. and Huang, Y.C. (2010b). Emissions of Polychlorinated Dibenzo-*p*-dioxin and Polychlorinated Dibenzofuran from Motorcycles. *Aerosol Air Qual. Res.* 10: 533–539.

Chuang, S.C., Chen, S.J., Huang, K.L., Wu, E.M.Y., Chang-Chien, G.P. and Wang, L.C. (2010a). Gas/Particle Partitioning of Dioxins in Exhaust Gases from Automobiles. *Aerosol Air Qual. Res.* 10: 489–496.

Cieplik, M.K., Carbonell, J.P., Munõz, C., Baker, S., Krüger, S., Liljelind, P., Marklund, S. and Louw, R. (2003). On Dioxin Formation in Iron Ore Sintering. *Environ. Sci. Technol.* 37: 3323–3331.

Cobo, M., Gálvez, A., Conesa, J.A. and Montes de Correa, C. (2009). Characterization of Fly Ash from a Hazardous Waste Incinerator in Medellin, Colombia. *J. Hazard. Mater.* 168: 1223–1232.

Coles, D.G., Ragaini, R.C. and Ondov, J.M. (1979). Chemical Studies of Stack Fly Ash from a Coal-fired Power Plant. *Environ. Sci. Technol.* 4: 455–459.

Debrincat, D. and Loo, C.E. (2007). Factors Influencing Particulate Emissions during Iron Ore Sintering. *ISIJ Int.* 47: 652–658.

Ferreira, C., Ribeiro, A. and Ottosen, L. (2003). Heavy Metals in MSW Incineration Fly Ashes. *J. Phys. IV France.* 107: 463–466.

Fujimori, T., Takaoka, M. and Takeda, N. (2009). Influence of Cu, Fe, Pb, and Zn Chlorides and Oxides on Formation of Chlorinated Aromatic Compounds. *Environ. Sci. Technol.* 43: 8053–8059.

Gullett, B.K., Bruce, K.R., Beach, L.O. and Drago, A.M. (1992). Mechanistic Steps in the Production of PCDD and PCDF during Waste Combustion. *Chemosphere* 25: 1387–1392.

Hinton, W.S. and Lane, A.M. (1991). Characteristics of Municipal Solid Waste Incinerator Fly Ash Promoting the Formation of Polychlorinated Dioxins. *Chemosphere* 22: 473–483.

Hu, C.Q., Zhang, C.X., Han, X.W. and Yin, R.Y. (2008). Sulfur Flow Analysis for New Generation Steel Manufacturing Process. *J. Iron. Steel Res. Int.* 37: 12–15.

Hu, M.T., Chen, S.J., Lai, Y.C., Huang, K.L., Chang-Chien, G.P. and Tsai, J.H. (2009). Characteristics of Polychlorinated Dibenzo-*p*-dioxins/Dibenzofuran from Joss Paper Burned in Taiwanese Temples. *Aerosol Air Qual. Res.* 9: 369–377.

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.

Ismo, H., Kari, T. and Juhani, R. (1997). Formation of Aromatic Chlorinated Compounds Catalyzed by Copper and Iron. *Chemosphere* 34: 2649–2662.

Japan Ministry of the Environment. (2005). Dioxins Emissions Inventory.

Jay, K. and Stieglitz, L. (1995). Identification and Quantification of Volatile Organic Components in Emissions of Waste Incineration Plants. *Chemosphere* 30: 1249–1260.

Kao, J.H., Chen, K.S., Chang-Chien, G.P. and Chou, I.C. (2006). Emissions of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans from Various Stationary Sources. *Aerosol Air Qual. Res.* 6: 170–179.

Kasai, E., Aono, T., Tomita, Y., Takasaki, M., Shiraishi, N. and Kitano, S. (2001a). Macroscopic Behaviors of Dioxins in the Iron Ore Sintering Plants. *ISIJ Int.* 41: 86–92.

Kasai, E., Hosotani, Y., Kawaguchi, T., Nushiro, K. and Aono, T. (2001b). Effect of Additives on the Dioxins Emissions in the Iron Ore Sintering Process. *ISIJ Int.* 41: 93–97.

Kasama, S., Yamamura, Y. and Watanabe, K. (2006). Investigation on the Dioxin Emission from a Commercial Sintering Plant. *ISIJ Int.* 46: 1014–1019.

Khare, P. and Baruah, B.P. (2010). Chemometric Analysis of Trace Elements Distribution in Raw and Thermally Treated High Sulphur Coals. *Fuel Process. Technol.* 91: 1691–1701.

Kuzuhara, S., Sato, H., Kasai, E. and Nakamura, T. (2003). Influence of Metallic Chlorides on the Formation of PCDD/Fs during Low-temperature Oxidation of Carbon. *Environ. Sci. Technol.* 37: 2431–2435.

Lahl, U. (1993). Sintering Plants of Steel Industry – The most Important Terminal PCDD/F Source in Industrialized Regions. *Organohalogen Compd.* 11: 311–314.

Lahl, U. (1994). Sintering Plants of Steel Industry-PCDD/F Emission Status and Perspectives. *Chemosphere* 29: 1939–1945.

Lee, W.S., Chang-Chien, G.P., Wang, L.C., Lee, W.J. and Tsai, P.J., Wu, K.Y. and Lin, C. (2004). Source Identification of PCDD/Fs for Various Atmospheric Environments in a Highly Industrialized City. *Environ. Sci. Technol.* 38: 4937–4944.

Lee, W.S., Chang-Chien, G.P., Wang, L.C., Lee, W.J., Wu K.Y. and Tsai, P.J. (2005). Emissions of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans from Stack Flue Gases of Electric Arc Furnaces and Secondary Aluminum Smelters. *J. Air Waste Manage. Assoc.* 55: 219–226.

Lin, L.F., Shih, S.I., Su, J.W., Shih, M., Lin, K.C., Wang, L.C. and Chang-Chien, G.P. (2010a). Dry and Wet Deposition of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans on the Drinking Water Treatment Plant. *Aerosol Air Qual. Res.* 10: 231–244.

Lin, W.Y., Wu, Y.L., Tu, L.K., Wang, L.C. and Lu, X. (2010b). The Emission and Distribution of PCDD/Fs in Municipal Solid Waste Incinerators and Coal-fired Power Plant. *Aerosol Air Qual. Res.* 10: 519–532.

Mamane, Y. and Pueschel, R.F. (1979). Oxidation of SO_2 on the Surface of Fly Ash Particles under Low Relative Humidity Conditions. *Geophys. Res. Lett.* 6: 109–112.

McKee, D.W. (1970). Metal Oxide as Catalysts for the Oxidation of Graphite. *Carbon.* 8: 8623–8635.

Nakano, M., Hosotani, Y., Kasai, E. (2005). Observation of Behavior of Dioxin and some Relating Elements in Iron Ore Sintering Bed by Quenching Pot Test. *ISIJ Int.* 45: 609–617.

Nganai, S., Lomnicki, S. and Dellinger, B. (2009). Ferric Oxide Mediated Formation of PCDD/Fs from 2-monochlorophenol. *Environ. Sci. Technol.* 43: 368–373.

Ning, Z. and Sioutas, C. (2010). Atmospheric Processes Influencing Aerosols Generated by Combustion and the Inference of their Impact on Public Exposure: A Review. *Aerosol Air Qual. Res.* 10: 43–58.

Olie, K., Addink, R. and Schoonenboom, M. (1998). Metal as Catalysts during the Formation and Decomposition of Chlorinated Dioxins and Furans in Incineration Processes. *J. Air Waste Manage. Assoc.* 48: 101–105.

Olie, K., Vermeulen, P.L. and Hutzinger, O. (1977). Chlorodibenzo-*p*-dioxins and Chlorodibenzofurans are Trace Components of Fly Ash and Flue Gas of some Municipal Incinerators in the Netherlands. *Chemosphere* 6: 455–459.

Qian, Y., Zheng, M., Liu, W., Ma, X. and Zhang, B. (2005). Influence of Metal Oxides on PCDD/Fs Formation from Pentachlorophenol. *Chemosphere* 60: 951–958.

Quaß, U., Fermann, M.W. and Bröker, G. (2000). Steps towards a European Dioxin Emission Inventory. *Chemosphere* 40: 1125–1129.

Sammut, M.L., Noack, Y., Rose, J., Hazemann, J.L., Proux, O., Depoux, M., Ziebel, A. and Fiani, E. (2010). Speciation of Cd and Pb in Dust Emitted from Sinter. *Chemosphere* 78: 445–450.

Shih, M., Lee, W.J., Shih, T.S., Huang, S.L., Wang, L.C., Chang-Chien, G.P. and Tsai, P.J. (2006). Characterization of dibenzo-*p*-dioxins and Dibenzofurans (PCDD/Fs) in the Atmosphere of Different Workplaces of a Sinter Plant. *Sci. Total Environ.* 366: 197–205.

Shih, T.S., Lee, W.J., Shih, M., Chen, Y.C., Huang, S.L., Wang, L.C., Chang-Chien, G.P. and Tsai, P.J. (2008). Exposure and Health Risk Assessment of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans (PCDD/Fs) for Sinter Plant Workers. *Environ. Int.* 34:102–107.

Shih, T.S., Shih, M., Lee, W.J., Huang, S.L., Wang, L.C., Chen, Y.C. and Tsai, P.J. (2009). Particle Size Distributions and Health-related Exposures of Polychlorinated Dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) of Sinter Plant Workers. *Chemosphere* 74: 1463–1470.

Smichowski, P., Polla, G., Gómez, D., Fernández Espinosa, A.J. and López, A.C. (2008). A Three-step Metal Fractionation Scheme for Fly Ashes Collected in an Argentine Thermal Power Plant. *Fuel* 87: 1249–1258.

Smołka-Danielowska, D. (2006). Heavy Metals in Fly Ash from a Coal-Fired Power Station in Poland. *Pol. J. Environ. Stud.* 6: 943–946.

Sushil, S. and Batra, V.S. (2006). Analysis of Fly Ash Heavy Metal Content and Disposal in Three Thermal Power Plants in India. *Fuel* 85: 2676–2679.

Suzuki, K., Kasai, E., Aono, T., Yamazaki, H., Kawamoto, K. (2004). *De Novo* Formation Characteristics of Dioxins in the Dry Zone of an Iron Ore Sintering Bed. *Chemosphere* 54: 97–104.

Taiwan Environmental Protection Administration. (2008). The Project of Emission Investigation and Draft Control Strategy of Air Toxic Pollutants (Dioxins and Heavy Metals) from the Stationary Sources.

Takeda, M., Ueda, A., Hashimoto, H., Yamada, T., Suzuki, N., Sato, M., Tsubouchi, N., Nakazato, Y. and Ohtsuka, Y. (2006). Fate of the Chlorine and Fluorine in a Sub-bituminous Coal during Pyrolysis and Gasification. *Fuel* 85: 235–242.

Totten, G.E. (Eds.) (2006). *Handbook of Lubrication and Tribology*, Vol. 1, 2nd ed., Taylor & Francis, Boca Raton.

Tsai, J.H., Lin, K.H., Chen, C.Y., Ding, J.Y., Choa, C.G. and Chiang, H.L. (2007). Chemical Constituents in Particulate Emissions from an Integrated Iron and Steel Facility. *J. Hazard. Mater.* 147: 111–119.

Tsubouchi, N., Kuzuhara, S., Kasai, E., Hashimoto, H. and Ohtsuka, Y. (2006). Properties of Dust Particles Sampled from Windboxes of an Iron Ore Sintering Plant: Surface Structures of Unburned Carbon. *ISIJ Int.* 46: 1020–1026.

U.S. EPA. (2001). Determination of Particulate Emission from Stationary Sources. 40 CFR, Part 60, Appendix A.

Method 5.

U.S. EPA. (2003). National Primary Drinking Water Standards. EPA816-F-03-016.

Wang, L.C., Lee, W.J., Chang-Chien, G.P., Lin, B.T. and Tsai, P.J. (2003). Effects of Chlorine Content in Feeding Wastes of Incineration on the Emission of Polychlorinated Dibenzo-*p*-dioxins/dibenzofurans. *Sci. Total Environ.* 302: 185–198.

Wang, M.S., Chen, S.J., Lai, Y.C., Huang, K.L. and Chang-Chien, G.P. (2010a). Characterization of Persistent Organic Pollutants in Ash Collected from Different Facilities of a Municipal Solid Waste Incinerator. *Aerosol Air Qual. Res.* 10: 391–402.

Wang, Y.F., Hou, H.C., Li, H.W., Lin, L.F., Wang, L.C., Chang-Chien, G.P. and You, Y.S. (2010b). Dry and Wet Depositions of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in the Atmosphere in Taiwan. *Aerosol Air Qual. Res.* 10: 378–390.

Wiater, I. and Louw, R. (1999). Reactoins of Diphenyl Ether with Chlorine and Bromine Atoms around 750 K – Relevance for Gas-phase "Dioxin" Formaton. *Eur. J. Org. Chem.* 1: 261–265.

Wiles, C.C. (1996). Municipal Solid Waste Combustion Ash: State-of-the-knowledge. *J. Hazard. Mater.* 47: 325–344.

Wu, Y.L., Li, H.W., Chien, C.H., Lai, Y.C. and Wang, L.C. (2010). Monitoring and Identification of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in the Ambient Central Taiwan. *Aerosol Air Qual. Res.* 10: 463–471.

Xhrouet, C., Pirard, C. and De Pauw, E. (2001). *De Novo* Synthesis of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans on Fly Ash from a Sintering Process. *Environ. Sci. Technol.* 35: 1616–1623.

Yu, K. M., Lee, W.J., Tsai, P.J**,** Fang, K. and Lin, M. (2010). Emissions of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans (PCDD/Fs) from Both of Point and Area Sources of an Electric-Arc Furnace-Dust Treatment Plant and their Impacts to Vicinity Environments. *Chemosphere* 80: 1131–1136.