***De novo* Formation of PCDD/F during Sintering: Effect of Temperature, Granule Size and Oxygen Content**

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(Received on July 11, 2017; accepted on November 10, 2017; J-STAGE Advance published date: December 27, 2017)

Integrated iron and steel industry is the major industrial source of dioxins or, more precisely, of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF). Their main source is the sintering plant (preparing iron ore fines as feed for the blast furnace) and EAF for steelmaking. The influence of temperature (300–600°C), feed granule size (4 fractions, from 0.5–1 to 4–8 mm) and oxygen content (5 to 15 vol.%) on PCDD/F-formation has been investigated during *de novo* tests, involving a feed composed from the various sintering raw materials in their typical proportions. These experiments were conducted using a lab-scale vertical tube reactor and PCDD/F in off-gas and residue were collected together for analysis. Some CuCl₂ catalyst was wetly added, to ensure that PCDD/F-formation activity was well measurable. The experimental results show that dioxins peak at 350°C, a granule size of 2 to 4 mm and the highest O₂ concentration tested (15 vol.%). Within each homologue group, the isomer signature has been further scrutinized, with special emphasis on the seventeen 2,3,7,8-substituted PCDD/F, as well as on the seven PCDD-congeners and two TCDF usually associated with chlorophenol precursor routes, with the purpose to throw more light on the mechanism of PCDD/F-formation. For the first time ever, a complete congener-specific analysis is presented for sintering effluent and discussed. From this study and a number of former and ongoing studies, it is clear that iron oxide is responsible for the high PCDF/PCDD-ratio and the relatively low level of chlorination of PCDF and PCDD.

KEY WORDS: PCDD/F; sintering raw material; *de novo* synthesis; isomer signature.

1. Introduction

In China, the amount of crude steel production has steadily risen, nearly attaining 803.8 million tons in 2015. On the basis of the inventory of dioxins emissions to the Chinese environment in 2004, the dioxins emission from iron and steel industry and other metallurgical process is 45.6% of the total, the largest contribution. Iron ore sintering has been recognized as main industrial source of dioxins.¹⁾ In the European Union, iron ore sintering has overtaken municipal solid waste incineration (MSWI) as most significant source of PCDD/F.²⁾

Relative to the position of the flame front, the sintering bed is divided into four reaction and heat exchange zones, from top to bottom: air preheating in the sintered zone, coke ignition and sintering zone (flame front), pre-heating zone, and wet quenching zone.³⁾ Presumably, most PCDD/F is generated in the pre-heating zone, few cm in front of the flame zone, where temperature rapidly drops from >650 to <200°C.^{3–5)} PCDD/F-formation in the sintering bed has been attributed to two factors: (1) transition metal salts and chlorides volatilize in the flame zone and transfer

with combustion gas, subsequently condense, and react with (2) volatilized organic compounds, coke or soot in a temperature and oxidation window, favorable for PCDD/F-formation (from 500 down to 200°C). Therefore, the zone for PCDD/F-formation is still driven by the flame front and the cooling effect of the dried raw materials, yet bounded by the quenching effect exerted by the moist layer at the bottom. As this layer grows thinner, various pollutants are no longer sorbed in the moist bed and gradually break through. This observation forms the basis of the recirculation of final and dirty off-gas to the first zones of the belt. According to these views, the bulk of the PCDD/F output originates in the bulk of the burden, representing by far the largest part of the iron ore material.

During the European Union (E.U.) R&D-project “Minimization of dioxins in thermal industrial processes: mechanisms, monitoring and abatement” (MINIDIP) an alternative hypothesis was tested: given the erratic and extremely low activity of feed and grate siftings and the rapidly rising activity of fly ash, collected in the successive fields I, II, and III of the electrostatic precipitator, most experimental effort was directed towards the study and testing of these fractions. Systematically, the influence of temperature, time, and oxygen were established and the effect of various suppressants was tested.^{1,6)} Moreover, a Computer Fluid Dynamics study

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DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2017-392>

simulated the temperature, oxygen, and dioxins formation rates over the full-scale sintering plant, yet concluded that the highest rates of formation experimentally encountered could not explain more than few percent of the emission values encountered.⁷⁾ A systematic comparison of fingerprints suggested that the typical sintering fingerprint, with PCDF >> PCDD and a homologue contribution rapidly descending with rising chlorination, fits best with a temperature of formation of 350°C or higher.⁶⁾

A large number of research papers and reviews focus on MSWI and model/real fly ash for guidance to study the formation of dioxins.^{8–15)} Two main formation pathways have been proposed: *de novo* synthesis and precursor pathway. *De novo* synthesis is based on a catalytic partial oxidation of carbon or soot and at times characterized by a ratio of PCDF to PCDD larger than unity.^{3,14)} Precursor synthesis is supported by fast condensation of chlorophenols (CP) to PCDD and PCDF congeners, or, following a longer route, starting from chlorobenzenes (CBz) or other suitable structures situated within Polycyclic Aromatic Hydrocarbons (PAH). Both theories have been linked by the observation that the *de novo* route also abundantly generates precursors, such as CP and CBz. Conversely, most *de novo* products may be integrated into carbonaceous structures and convert into novel PCDD/F forming matrices. The evolution of PCDD/F, PCB (polychlorinated biphenyls), CBz, CP and PAH from fly ash samples varies strongly with the experimental conditions (reaction temperature and time, oxygen and moisture content, addition of various inhibitors and activated charcoal) was systematically investigated during the E.U. program MINIDIP.^{1,6)}

Studies on iron ore sintering are rather less abundant.^{1,3–6,16,17)} Some form of *de novo* synthesis is generally considered to be the main PCDD/F-formation pathway,^{1,3)} yet the impact of solid fuel (coke, anthracite, or in numerous tests activated carbon) and of various oily reverts is not easily ascertained, given the numerous factors of influence to consider. Several studies from a group around Prof. Kasai found that the impact of raw materials (ore, coke, *etc.*) on *de novo* synthesis was rather limited, whereas adding sintering fly ash increased dioxins generation markedly.^{16,17)} The addition of HCl to the inlet air promoted dioxins formation in the sinter mixture, however, moisture in the gas had less effect.¹⁷⁾

The concept of suppressing PCDD/F-formation by adding suitable inhibitors has been first proposed by Karasek and his research group.¹⁸⁾ Several important studies or reviews were prepared by Tuppurainen,¹⁹⁾ Pandelova²⁰⁾ and Liu.²¹⁾ Sulfur and nitrogen compounds and caustic materials may all reduce PCDD/F-formation, yet their effect is difficult to predict. Sulfur compounds are undesirable in an iron & steel context. Ammonia and urea compounds combine with sulfur and nitrogen oxides and with hydrogen chloride, forming fogs constituted by ammonium salts. Japanese iron & steel producers and also China Steel (Taiwan) propose a thorough off-gas cleaning, comprising deep filtration and nitrogen removal (DeNOx) catalysis, removing particulate matter (mainly salt), as well as nitrogen oxides and dioxins.

This study has experimentally investigated the influence of temperature, granule size and oxygen content on *de novo* formation of PCDD/F, starting with a synthetically

composed sintering belt feed. The optimum conditions of formation were established, as well as the homologue profile of PCDD/F (P = 4 to 8). More importantly, the entire isomer signature is scrutinized, with special emphasis on those congeners associated with 2,3,7,8-substituted PCDD/F and chlorophenol precursor routes, hoping to throw more light on the mechanism of PCDD/F-formation. Temperature, granule size and oxygen concentration all are identified as major experimental factors. A systematic comparison with other iron oxide bearing streams from iron & steel industry (continuous casting, hot rolling and cold rolling, sintering fly ash, some of these tests featuring the addition of suppressants and of CaO and Ca(OH)₂) is being prepared.

2. Material and Methods

2.1. Experimental Materials

The sintering bed feed is synthetically composed of iron ore fines (68.6 mass%), returned sinter (15.0 mass%), coke breeze (3.8 mass%), limestone (3.0 mass%), dolomite (3.0 mass%), slaked lime (3.0 mass%), serpentine (1.0 mass%), water (2.5 mass%), CuCl₂ (0.1 mass%). All these materials were loaded into a sintering ore granulator and homogenized for about 5 min of dry mixing, and then an aqueous solution of copper chloride was added into the granulator for wet mixing during 10 min with the rest of the feed. The elemental analysis of experimental samples are shown in **Table 1**.

The size of the resulting granulate ranged from 0.05 to 8 mm. The granulated raw material was sieved in six different granule size (GS) by an automatic screener, namely, GS1 < 0.5 mm, GS2 0.5–1 mm, GS3 1–2 mm, GS4 2–4 mm, GS5 4–8 mm, GS6 > 8.0 mm. The total mass of raw material was 10.0 kg, and the weight contribution of fractions GS1 to GS6 accounted for 0.2%, 7.5%, 28.0%, 34.8%, 19.7% and 9.7% of the total raw material, respectively.

2.2. Experimental Set-up and Procedure

De novo formation tests of PCDD/F were conducted on raw sintering feed material packed in a vertical tube furnace system, as shown in **Fig. 1**. The apparatus comprises a quartz glass tubular reactor (height 60 cm, diameter 4.5 cm),

Table 1. Elemental analysis of experimental samples, wt.%.

	B1	B2	B3	B4
C	8.14	7.91	7.89	7.85
O	44.36	44.03	44.33	47.33
Mg	1.86	2.30	2.45	1.61
Al	1.89	1.61	2.39	1.83
Si	5.09	4.07	4.10	4.13
Cl	0.11	0.10	0.08	0.11
Ca	2.24	1.65	2.02	1.91
Fe	35.34	37.50	35.76	34.40
Cu	0.22	0.21	0.23	0.26
Zn	0.73	0.61	0.67	0.54
Other	0.06	0.03	0.08	0.04
Sum	100.00	100.00	100.00	100.00

Fig. 1. Experimental system for studying *de novo* PCDD/F-formation: 1. Gas cylinder and mass flow meter, 2. Temperature controller, 3. Tubular furnace and tubular reactor, 4. XAD-II resin, 5. Thermocouple, 6. Ice bath, 7. Toluene, 8. Quartz tube and sample.

Table 2. Experimental conditions (A2 = B2 = C2).

Expt.	Granule size (mm)	Temperature (°C)	Time (min)	N ₂ :O ₂ :CO ₂ (vol.%) [*]		
				N ₂	O ₂	CO ₂
A1	1.0–2.0	300	45	80	10	10
A2	1.0–2.0	350	45	80	10	10
A3	1.0–2.0	400	45	80	10	10
A4	1.0–2.0	500	45	80	10	10
A5	1.0–2.0	600	45	80	10	10
B1	0.5–1.0	350	45	80	10	10
B2	1.0–2.0	350	45	80	10	10
B3	2.0–4.0	350	45	80	10	10
B4	4.0–8.0	350	45	80	10	10
C1	1.0–2.0	350	45	80	5	15
C2	1.0–2.0	350	45	80	10	10
C3	1.0–2.0	350	45	80	15	5

^{*}Total flow 300 ml/min. In bold: the standard test.

a temperature controller and a thermocouple for monitoring the reaction temperature of the sample bed.

In each experiment, 30 g of granulated raw material was positioned in the middle of the quartz reactor tube, after the furnace temperature reached the temperature set value. The temperature of sample and atmosphere would mount rapidly to designated value in 5 minute, this process was monitored by the thermometer which was inserted into the sample. In the preheating stage, the water mixed with the sample would evaporate quickly, and then it would be absorbed by the silica wool which was positioned in front of the XAD-II resin. For each test the reaction time selected for *de novo* formation of PCDD/F in a synthetic gas stream (total flow of 300 ml/min) was 45 min; the residence time was 3.2 s, which was the ratio of the filling volume of raw material to the input gas flow rate. The void fraction of the bed was 0.37–0.39 for different sample. Both the oxygen and carbon dioxide concentration were varied between 5 and 15 vol.% of oxygen in the total gas flow, with standard value of 10% oxygen. The ten experimental conditions tested are listed

in Table 2.

All tests were conducted in duplicate/triplicate, except for two tests (A5 and C3). Test A2 (= B2 = C2) as benchmark sample was conducted 3 times, with the purpose of establishing a statistically valid error analysis. The arithmetic average of the duplicated results was used in our further analysis. The variability of PCDD, PCDF and PCDD/F of the benchmark samples defined as a percentage of the standard deviation to the average value, is 6.4%, 3.8% and 4.0%, respectively.

2.3. Sample Analysis

The PCDD/F evolving in the gas phase were absorbed by XAD-II resin and then by toluene in consecutive gas scrubbing bottles. After the test, the cooled test residues were collected together with the absorbed volatiles for further PCDD/F analysis. On the basis of earlier studies, it is believed that at 350°C the contribution of the solid residue to the total value of PCDD/F is relatively minor.

The granule size of the raw materials were characterized by Energy Dispersive Spectrometry (EDS) supplied the elemental analysis. The clean-up procedure of the PCDD/F samples followed the US EPA method 1613 (U.S. EPA, 1999). A HRGC/HRMS analysis separated, identified and quantified the various PCDD/F congeners using a gas chromatograph coupled to a mass spectrometer. A DB-5ms (60 m length × 0.25 mm ID, 0.25 μm film thickness) capillary column separated 38 PCDD and 56 PCDF individual congeners or combinations out of 136 PCDD/F congeners (P = 4 to 8).

The GC temperature program was optimized as follows: splitless injection of 1 μl at 150°C, initial oven temperature of 150°C maintained for 1 min, then raised at a rate of 25°C min⁻¹ to 190°C, and finally increased at 3°C min⁻¹ 151°C to 280°C as final temperature and held for 20 min. Clean-up procedure and analysis method of PCDD/F were described in detail in a previous paper.²²⁾ The toxic equivalents (TEQ) were calculated by the North Atlantic Treaty Organization (NATO) factors, in agreement with the industrial practice in the E.U. and China. The contribution of PCB to WHO-TEQ values usual in Japan was not established, but typically remains marginal, at few %.

3. Results and Discussion

3.1. Influence of Temperature, Granule Size and Oxygen on PCDD/F-formation

Temperature is a major factor of influence in dioxins formation.^{6,15)} In this test program, the optimal temperature of formation of PCDD and PCDF, PCDD/F and I-TEQ is identified (Fig. 2(a)) as 300 and 350°C, respectively. These values could have been depressed, however, by adding 0.1 mass% of CuCl₂ to the charge. Without such an addition, activity remains too low for realizing convincing PCDD/F-output values. Surprisingly, also granule size significantly impacts upon the yield of PCDD, PCDF and I-TEQ (Fig. 2(b)). Within the range investigated (5 to 15 vol.%), PCDD, PCDF, I-TEQ rise together with the oxygen content (Fig. 2(c)). The applied basicity “CaO/SiO₂” of iron ore sinters in the present study is significantly low compared to a standard condition. CaO is an alkali compound, which could

Fig. 2. Influence of temperature, granule size and oxygen content on PCDD/F-formation and I-TEQ, (a) Temperature, (b) Granule size, (c) Oxygen content.

reduce the concentration of HCl available for PCDD/F formation. In the previous study, 90% suppression had been observed by using $\text{Ca}(\text{OH})_2$ or NaOH in the sinter plant ESP dust heating tests.²³⁾ However, tests in a full-scale sinter plant had no significant effect.³⁾ The chlorination degree of PCDD/F from tests with various suppressants added including alkali compounds does not change significantly compared with those without additive.⁶⁾

3.1.1. Influence of Temperature

Figure 2(a) shows the PCDD and PCDF-yield during thermal treatment of feed raw material at different temperatures: 300, 350, 400, 500, and 600°C. As usual during *de novo* tests, there is an optimum temperature of formation. Within the range of temperatures tested, the yield

Table 3. The formation rate and toxicity reduction factor of temperature-dependence samples.

Formation rate (pg/30 g min)	A1	A2	A3	A4	A5
ΣPCDD	38.1	35.0	23.2	11.9	4.5
ΣPCDF	110.8	267.9	212.7	100.0	38.9
$\Sigma\text{PCDD/F}$	148.8	302.9	236.0	112.0	43.4
$\Sigma\text{I-TEQ}$	2.0	4.5	3.8	1.7	0.8
TRF*	76.2	67.7	61.7	67.0	56.5

*Toxicity reduction factor = $\Sigma\text{PCDD/F} : \Sigma\text{I-TEQ}$

of PCDD/F and I-TEQ peak at 350°C, with a value of 454.3 pg/g and 6.7 pg I-TEQ/g respectively, designating that 350°C is the optimum temperature for PCDD/F-formation on raw sintering materials, after addition of copper chloride which act as catalyst and as chlorine source simultaneously. The formation rate and toxicity reduction factor of temperature-dependence samples are shown in **Table 3**.

The trend was similar to those found in previous studies on sintering raw material,¹⁷⁾ fly ash of sinter plant,⁶⁾ and MSWI.^{15,24)} Generally, the optimum for PCDD/F-formation ranges between 300 and 370°C. Compared with the sintering raw material tested in this study, fly ash from sinter plant generated much more PCDD/F, by more than 2–4 orders of magnitude.^{6,17)} Considering the addition of CuCl_2 required for accelerating the formation of PCDD/F, the real PCDD/F-formation from clean sintering raw material during industrial production would be even less. Conversely, PCDD/F-formation is stimulated by returning heavy metal and chloride rich fly ash to the feed.

3.1.2. Influence of Granule Size

Within the experimental range investigated, the total amount of PCDD/F and I-TEQ attains a maximum of 684.7 pg/g and 8.0 pg/g, respectively, both for the 2–4 mm sample B3. The lowest values were reached for B1, representing 18.6% and 18.0% of the B3 value, respectively (Fig. 2(b)).

Agglomerated sintering feed material features a core, including iron ore fines, returned sinter, limestone, dolomite and serpentine, covered externally with small particles, like coke breeze and other raw material.^{25,26)} A sample of 30 g of fractions B1 to B4 were washed and sieved using a 80-mesh (0.212 mm) sieve. The mass loss during this washing process was 8.8 g (B1), 10.3 g (B2), 10.9 g (B3), and 8.3 g (B4), respectively. There is almost no correlation ($R^2 = 0.24$) for the four samples between the experimentally established PCDD/F-yield and the mass, lost during the aforementioned washing and sieving. However, a strongly positive correlation ($R^2 = 0.98$) was found for the three finer samples B1, B2 and B3, suggesting that the weight amount of material covering the core could be a key factor, linking PCDD/F-formation to the external coating by small particles.

In *de novo* test, CuCl_2 plays an important role both in the chlorination of carbon and the oxidative breakdown of carbonaceous material. CuCl_2 had been identified as the strongest catalyst because it could act as catalyst and as chlorine source simultaneously.^{11,13)} Liao also evaluated

the interaction of Fe_2O_3 and CuCl_2 on dioxin formation: no particular synergistic effect occurred when the $[\text{Fe}]:[\text{Cu}]$ ratios rose from 1:1 to 10:1, indicated that CuCl_2 was much stronger than Fe_2O_3 in catalysis.²⁷⁾ According to linear correlation of B1-3, the PCDD/F-yield of B4 would be less than B1. However, it is second only to B3. The elemental analysis of four granule size raw materials was conducted by means of an EDS analysis. The result showed that C, O, Cl, Fe content were equal, but the Cu content of B4 was slightly greater than that of B1-3 (Table 1). This would explain why B4 deviated the linear correlation of B1-3.

3.1.3. Influence of Oxygen Concentration

The yield of PCDD, PCDF, PCDD/F and I-TEQ (Fig. 2(c)) show a slowly growing pathway, with rising O_2 content. The reaction order in oxygen is 0.50 (PCDD), 0.35 (PCDF), and 0.36 (PCDD/F). Reaction order is the basic reaction kinetics. A bigger reaction order means the greater influence of oxygen concentration on PCDD/F formation rate. A correlation analysis was conducted to identify the relationship between target parameters and the O_2 -concentration. The following parameters are studied: (1) PCDD; (2) PCDF; (3) PCDD/F; (4) Σ I-TEQ; (5) PCDF/PCDD and (6) Cl-PCDD/F. The O_2 -concentration correlates positively with all six parameters, with R^2 value: PCDF/PCDD (0.48) < PCDD (0.89) < PCDD/F (0.99) < Σ I-TEQ (0.99) < PCDF (0.99) < Cl-PCDD/F (1.00).

The PCDF/PCDD ratio > 1 suggests that PCDD/F form through *de novo* synthesis,^{1,3,16)} even though recent work has suggested that the nature and speciation of the catalytic metal may be a determining factor. The ratio of PCDF/PCDD is similar for almost all samples in a range of 7.7 to 9.8, except for samples A1 (300°C) and B1 (350°C, 0.5–1 mm), of 2.9 and 5.6, respectively.

The changing trend of the influence of three variables on total amount of PCDD/F is similar to the PCDF/PCDD ratio. Except for sample A5 which is 4.73, the average chlorination degree (Cl-PCDD/F) for all samples is between 4.99 and 5.30. The Cl-PCDD/F fluctuated with the temperature increasing, however, it goes up constantly as the granule size increased. The Cl-PCDD/F increases a bit for rising O_2/CO_2 ratio just like the granule size influenced on it. It indicates that oxygen and granule size increasing would promote chlorination (Table 4).

Table 4. The PCDD/PCDF-ratio and Cl-PCDD/F-values of all samples.

	A1	A2	A3	A4	A5
PCDF/PCDD	2.91	7.66	9.15	8.39	8.64
Cl-PCDD	6.42	6.20	6.26	6.65	5.64
Cl-PCDF	4.90	4.94	5.13	4.88	4.63
	B1	B3	B4	C2	C3
PCDF/PCDD	5.62	9.78	9.23	9.44	8.18
Cl-PCDD	6.22	5.97	6.12	5.91	6.06
Cl-PCDF	4.77	5.11	5.21	4.94	5.03

3.2. Homologue Group Profiles and Principal Component Analysis

Figure 3(a) shows signatures of the ten homologue groups, from TCDD through OCDF (basis: PCDD + PCDF = 100%). All samples, except A1 and B1, are largely dominated by PCDF; TCDF and PeCDF account for 55% (A1) to 75% (A5). The signatures from samples B1–B4 strongly shift, suggesting that rising granule size enhances chlorination. Conversely, samples C1–C3 indicate almost no difference in homologue group profiles, suggesting a uniform PCDD/F-formation pathway when oxygen content is varied. All samples largely dominated by PCDF and a relative abundance of a homologue group dominated by TCDF followed by the PeCDF, HxCDF and OCDF are a typical sintering signature.^{6,16,27)} Compared with the previous study with/without CuCl_2 addition, the isomer distribution in this study is similar with non- CuCl_2 addition, rather than adding CuCl_2 . One possible reason is that without gaseous HCl supply in the present experimental decreases the chlorine source for dioxin formation, thus reducing chlorination.¹⁷⁾

Principal component analysis (PCA) is used to illustrate the similarities and differences between congener distributions and *de novo* formation (Fig. 3(b)). The matrix used for statistically investigating the complete congener signature representing all 136 PCDD/F-congeners in all 10 different test conditions. Before statistical analysis, no transformation of data is performed. Two main clusters (A and B) are observed in the loading diagram separated by factor 1 and factor 2. Factor 1 explains 75.2% of the total variance, and factor 2 explains 18.6% of the total variance. Cluster a only includes sample A4 and A5 and Cluster b includes all other

Fig. 3. PCDD/F homologue group profiles (a) and Principle component analysis of all 136 congeners (b).

samples. It suggests that temperature is the main variable which could influence the PCDD/F-formation dramatically, high temperature over 500°C lead to distinctly different pathways.

3.3. Isomer Distribution Pattern

Comprehensive isomer distribution patterns were already investigated in our earlier work, conducted at 350°C and covering 11 Model Fly Ash systems, featuring five metal chloride and five metal oxide systems, and a blank sample at distinct levels of oxygen (0, 6, 10, 21 vol.%) in nitrogen. In another study, samples were collected at distinct temperature levels in a MSWI-boiler, comparing high-temperature, end of post-combustion levels with concentrations at the inlet of a baghouse filter and stack. Still another study was dedicated to the possible interference and synergy between iron (III) oxide and copper chloride. All these studies concluded that these signatures vary considerably as a function of operating conditions and catalytic systems.

This study is part of a much more comprehensive study, confronting PCDD/F-levels and signatures both from original samples and *de novo* test results, and covering a variety of distinct iron and steel plant conditions: sintering mix (the present study), sintering fly ash, as well as iron oxides from continuous casting, hot rolling and cold rolling. Some of these test series featured the addition of suppressants and of CaO and Ca(OH)₂.

As in previous studies, most attention goes to TCDD, PeCDD, and HxCDD. Also 2,3,7,8-substituted PCDD/F are important, because of their toxic equivalency (TEQ) value and impact on regulated emissions. In earlier work, no significant link was found between the signatures from 2,3,7,8-substituted PCDD/F, suggesting that chlorination proceeds as a stochastic process, rather than following common modes or mechanisms of chlorination.

In this study, there is much more harmony between the selectivity of these 2,3,7,8-substituted congeners, expressed by their Hagenmaier profile according to the following ranking (R): 2,3,7,8-TCDD (1.00) vs. 1,2,3,4,7,8-HxCDF (0.95), 1,2,3,6,7,8-HxCDF (0.93), 1,2,3,7,8-PeCDF (0.91), 1,2,3,4,7,8-HxCDD (0.87), 1,2,3,7,8,9-HxCDD (0.74), 1,2,3,4,7,8,9-HpCDF (0.71), 1,2,3,7,8-PeCDD (0.69), 2,3,4,7,8,+1,2,4,8,9-PeCDF (0.66), and 1,2,3,4,6,7,8-HpCDD (0.62). The remaining five congeners show no correlation, or even marked anti-correlation (1,2,3,4,6,7,8-HpCDF: -0.74).

Several 2,3,7,8-substituted PCDD/F become much more important (**Table 5**) with rising temperature (cf. Table). The largest rise (ratio of value at 600°C to value at 300°C) is found for 2,3,7,8-TCDD (4.0), 1,2,3,7,8,9-HxCDD (3.8), 1,2,3,4,7,8-HxCDD (3.5), and 1,2,3,7,8-PeCDD (2.1).

Conversely, their relative importance or selectivity declines with rising granule size. The effect of oxygen is imperceptible.

In earlier studies, chlorophenol condensation route (CP route) were mainly associated with seven PCDD-congeners, namely 1,3,6,8- and 1,3,7,9-TCDD, 1,2,4,6,8+1,2,4,7,9-, 1,2,3,6,8-, 1,2,3,7,9-PeCDD and 1,2,3,4,6,8-HxCDD, and also with two PCDF-congeners: 1,2,3,4+1,2,3,6+1,2,3,8+1,4,6,9+1,6,7,8+2,3,6,8-TCDF a composite peak and 2,4,6,8-TCDF. These are easily and

Table 5. Hagenmaier profile.

PCDD	A1	A2*	A3	A4	A5	B1	B3	B4	C2	C3
2 378	1.50	2.28	3.71	4.08	5.98	3.35	2.10	2.10	2.53	2.55
12 378	4.61	5.75	11.68	6.60	10.00	7.12	6.60	7.40	6.01	6.22
123 478	4.55	9.08	9.43	8.44	16.05	11.99	7.52	7.33	8.99	7.79
123 678	3.96	8.98	7.96	7.39	3.42	7.29	6.27	7.08	6.61	8.18
123 789	5.77	4.38	5.05	6.67	21.83	7.80	7.14	4.17	12.27	4.09
1234 678	42.02	41.32	42.62	47.91	46.35	40.53	40.05	37.56	41.25	46.15
PCDF	A1	A2*	A3	A4	A5	B1	B3	B4	C2	C3
2 378	2.46	2.26	2.51	1.84	1.91	2.38	2.06	1.73	2.18	2.38
12 378	2.47	3.17	3.55	5.26	5.44	3.15	2.39	2.43	2.70	3.02
23 478+ 12 489	6.54	7.05	5.96	9.18	8.50	6.61	6.26	5.83	6.01	7.12
123 478	6.49	8.21	9.59	10.62	11.85	8.61	8.01	7.43	7.93	7.14
123 678	5.57	6.60	7.91	10.40	10.51	7.10	5.82	5.75	6.41	6.60
234 678+ 123 689	11.16	8.48	6.95	11.04	7.43	8.14	7.96	7.33	7.98	10.68
123 789+ 123 489	2.72	1.66	1.38	3.42	2.47	1.79	1.33	1.32	1.19	2.67
1234 678	75.52	82.41	79.80	59.45	56.41	82.29	85.06	85.72	83.85	70.68
1234 789	5.06	2.91	3.95	9.43	8.55	4.02	1.68	1.65	1.97	5.51

*A2=B2=C1.

rapidly synthesized by condensation of chlorophenol and chlorophenoxy radicals, e.g., 2, 4, 6-trichlorophenol.^{28–30)}

In this study, A correlation matrix between these nine entities shows a fairly good internal correlation between the CP-route TCDD, PeCDD, and HxCDD, yet the agreement with 2,4,6,8-TCDF is modest and that with 1,2,3,4⁺-TCDF non-existent (**Fig. 4**). This chlorophenol condensation dips at 350°C, yet provides a more substantial contribution to PCDD, at the lowest (300°C), as well as the high temperatures (400, 500 and 600°C). **Figure 5** shows this evolution. Rising granule size reduces the relative importance of the CP-route.

Also other congeners can be examined for their dependence on temperature, granule size and oxygen. Systematically, all congeners were confronted with all other congeners, statistically establishing those congeners strongly related in their selectivity, or else strongly anti-correlated. These exercises were repeated for (1) all data, (2) temperature-related data, (3) granule size-related data, and (4) oxygen-related data. Each set of data responds differently to this examination. All data and temperature-related data largely bring a similar message, for fingerprint variability is largely dependent on temperature. The teachings from varying granule size are less convincing and those from oxygen mainly reflect experimental error.

Considering the complete set of data confirms that the selectivity of 2,3,7,8-TCDD is strongest linked (R) with 1,2,3,4,7,8- and 1,2,3,6,7,8-HxCDF (0.95 and 0.93), while the more alike 1,2,3,4,7,8-HxCDD (0.87) and 1,2,3,7,8-PeCDD (0.69) only occupying the 8th and 18th position, respectively. Remarkably, the best related TCDD-isomer of 2,3,7,8-TCDD is its antagonist 1,4,6,9-TCDD (0.82), in the 9th position. All major antagonists are PCDF-congeners. This link could be fortuitous.

Fig. 4. Sum of CP-route congeners as a function of the sum of 1,3,6,8- and 1,3,7,9-TCDD.

Fig. 5. Effect of temperature on the selectivity of CP-route.

The CP-route isomers 1368- (1) and 1379-TCDD (0.89) are related most to their peers, 1,2,3,4,6,8-HxCDD (0.89), 1,2,3,6,8- (0.85) and 1,2,4,7,9+1,2,4,6,8-PeCDD (0.84). Their strongest antagonists include the four 1,2,4,X-TCDD (-0.93) with $X = 6, 7, 8$ and 9 , 1,2,7,8-TCDD (-0.89) in position 3, 1,2,3,7+1,2,3,8-TCDD (-0.85) in position 4, and 1,2,3,6-TCDD (-0.77) in position 9.

The composite peak 1,2,3,4+1,2,6,9-TCDD is clearly antagonistic to the CP-route. Closest come 1,2,7,8-TCDD (0.72), and 1,2,4,6+1,2,4,7+1,2,4,8+1,2,4,9 (0.68), in rank 1 and 2. 1,2,3,6-TCDD is somewhat similar, yet prefers 1,2,4,6+1,2,4,7+1,2,4,8+1,2,4,9- (0.78), and 1,2,3,9-TCDD (0.75). Also 1,2,3,7+1,2,3,8- and 1,2,3,9-TCDD clearly antagonistic to the CP-route.

4. Conclusion

The influence of temperature, granule size and oxygen content was systematically varied to study their effect on PCDD/F-formation during a set of ten *de novo* tests, most of these in duplicate or triplicate. Because the raw sintering material produced a low amount of PCDD/F formation, the aqueous solution of CuCl_2 was added to accelerate the reaction in the present study.

The optimum temperature for I-TEQ, PCDF, and PCDD/F-formation starting from raw sintering materials is 350°C.

PCDD already peak at the lowest temperature, 300°C. With rising granule size the total amount of PCDD/F firstly increased up to 2–4 mm and then decreased. The weight of material covered on the core could be a key factor, to explain the influence of granule size on PCDD/F-formation. Also O_2 concentration boosts PCDD/F-formation.

Homologue group profiles show an influence of temperature. In addition, a strong shift from low to higher-chlorinated PCDF is observed with rising granule size.

Meanwhile, a scrutiny of fingerprints were obtained at all the samples. The study focused on the chlorophenol routes and 2,3,7,8-substituted PCDD/F for investigating formation mechanisms of PCDD/F congeners. Based on the method of statistical correlation, two formation pathways and other mechanisms were proposed.

Actually, dioxins formation from the sintering raw material was less than fly ash. Further studies should focus on the PCDD/F-formation of sintering fly ash and the synergies in sintering raw material and fly ash.

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