PCDD/F Formation in Milled Fly Ash: Metal Chloride Catalysis

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ABSTRACT

Mechanochemical treatment reduces the particle size of fly ash and disperses catalytic metals, raising the potential reactivity of fly ash to form and destroy 'dioxins', i.e., polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD + PCDF or PCDD/F). To test this issue, model fly ash (MFA) samples were artificially composed by mixing silica, sodium chloride, and activated carbon, and doping this matrix with five selected catalytic metal chlorides administered as $CuCl_2 \cdot 2H_2O$, $CrCl_3 \cdot 6H_2O$, $FeCl_3$ (anhydrous), $ZnCl_2$ and anhydrous $CaCl_2$. Without additives, these samples were first finely milled for 0 (blank), 1 and 8 h, and the effect on the formation of PCDD/F was investigated during de novo tests. These simulate the conditions prevailing in deposits in the heat-recovery zone of an incinerator, where dioxins are formed and destroyed, and the tests were conducted at the same temperature, reaction time and air flow rate. Metal chlorides produce specific and distinct homologue and isomer patterns. The isomer signatures of 2,3,7,8-PCDD/F, precursor route, and other congeners were recognised and are studied in some detail. Principal component analysis (PCA) was applied to the 2,3,7,8-PCDD/F-congeners, indicating $CuCl_2$ as major contributor of WHO2005-TEQ values. Surprisingly, for $CuCl_2 \cdot 2H_2O$ the total yield of dioxins reduced drastically with milling. Since this study revealed various unexpected results, as well as experimental limitations, some suggestions for further ongoing work are formulated.

Keywords: Mechanochemical treatment; Metals doped-MFA; De novo test; Dioxins; Congeners.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (dioxins, PCDD/F), are highly toxic pollutants and released into the atmosphere from different industrial processes, including municipal solid waste incineration (MSWI) (Cheruiyot *et al.*, 2016). PCDD/F are ubiquitous in the air due to their stability, persistence, bio-accumulative and lipophilic nature, also dioxins are dispersed globally through long range transport mechanism (Wu *et al.*, 2009) and mostly high chlorinated PCDD/F remain in atmosphere, as these are easily captured by particles (Lee *et al.*, 2016).

Thus, to avoid environmental pollution and health impacts, feasible and cost- effective pollution control technologies have been adopted vigorously in past few decades. One such example is injection of activated carbon in most MSWIs on a wider scale to adsorb gaseous dioxins (Everaert *et al.*, 2003; Hajizadeh *et al.*, 2011; Kawashima *et al.*, 2011). For

the flue gas emissions control and fly ash treatment, many technologies have been investigated e.g., biodegradation (Mori and Kondo, 2002), catalytic destruction of PCDD/F (Yu *et al.*, 2016), adsorption on carbon materials (Li *et al.*, 2016) and thermal treatment (Hung *et al.*, 2016).

However, MSWI fly ash is burdened by heavy metals and dioxins; its PCDD/F-load varies with waste composition, combustion conditions, and pollution control techniques used (Weber *et al.*, 2001; Kao *et al.*, 2006; Vehlow, 2015). Fly ash contains all ingredients necessary for forming dioxins, including carbon, precursors like chlorophenols CP, chlorobenzenes CBz, polycyclic aromatic hydrocarbons PAHs (Cheruiyot *et al.*, 2015), chlorides, and metal catalysts. Precursors condense to PCDD and PCDF (PCDD/F) (Altarawneh *et al.*, 2007). De novo synthesis assumes chlorination and subsequent oxidation of carbonaceous structures (Stieglitz and Vogg, 1987; Addink and Olie, 1995; Olie *et al.*, 1998).

Numerous metal chlorides and oxides were tested as catalysts for PCDD/F and other organic compounds (Stieglitz *et al.*, 1989; Lou *et al.*, 2009; Li *et al.*, 2016; Yu *et al.*, 2016). De novo tests with $FeCl_3$, $CaCl_2$ and $CdCl_2$ formed PCDD/F at blank level (< 0.5 ng g^{-1}), $MgCl_2$, $ZnCl_2$, $SnCl_2$, $MnCl_2$, $NiCl_2$ and $HgCl_2$ generated some PCDD/F at low

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levels (< 10 ng g^{-1}), yet PbCl$_2$ and moisture-free FeCl$_3$ reached 25–60 ng g^{-1}, still to be compared with 4900 ng g^{-1} PCDD/F formed with CuCl$_2$ (Vogg *et al.*, 1987). CuCl$_2$ has the highest formation potential (Pekárek *et al.*, 2001; Takaoka *et al.*, 2005) and is industrially preferred as catalyst for the Deacon reaction, converting HCl into Cl$_2$ (Olie *et al.*, 1998).

De novo and precursor routes were studied by Chin *et al.* (2012), the output of dioxins concentration was 8.8, 25.5 and 369.5 ng g^{-1} 2,3,7,8-PCDD/F for 10 wt.% of FeCl$_2$, ZnCl$_2$ and CuCl$_2$, respectively. Eleven catalytic samples doped with different metal chlorides and oxides have been investigated to form PCDD/F and other organic compounds (Fujimori *et al.*, 2009) and ranked as follows: ZnO < PbO < ZnCl$_2$ < Blank < PbCl$_2$ < Fe$_2$O$_3$ < CuO < FeCl$_2$•4H$_2$O < FeCl$_3$•6H$_2$O < Cu$_2$(OH)$_3$Cl < CuCl$_2$•2H$_2$O

Speciation and the presence of other co-catalysts influence the activity of zinc (Fujimori *et al.*, 2011). Metal chlorides show much higher activity than their oxides, yet their relative activity varies strongly from metal to metal, also with presence of oxygen (O$_2$) in the system, as well as PCDD or PCDF homologues (the target group considered). CuCl$_2$ was found most active catalyst and CrCl$_3$, NiCl$_2$, and ZnCl$_2$ were second most active in chlorides category, whereas CuO and Cr$_2$O$_3$ were found most active oxides (Zhang *et al.*, 2016).

PCDD/F are persistent organic pollutants (POPs) and are threat to the environment. These compounds should be decomposed in a safe way and with environment friendly technologies according to Stockholm Convention, Yet, some destruction techniques initially form supplemental PCDD/F (Mitoma *et al.*, 2011). So, suitable methods should decompose dioxins in contaminated substances (fly ash, soil) to appropriately low levels.

Mechanochemical (MC) treatment has been successfully applied for the destruction of many hazardous compounds safely and cleanly: it is solvent-free and operates without heat-treatment, while changing the basic properties (structure and physicochemical) of fly ash by exerting mechanical stress (Heinicke, 1984). Numerous halogenated compounds, including dioxins and furans successfully are destroyed (Cagnetta *et al.*, 2016, Mubeen *et al.*, 2017).

The present study focuses on de novo tests, conducted comparatively after milling model fly ash (MFA) samples, doped with five metal chlorides (0.2 wt.% Cu, Cr, Fe, Zn and Ca), in order to investigate their effect and that of milling on PCDD/F formation. The non-milled sample (noted as 0 h milling) acts as a blank. In principle, milling for 1 or 8 h should augment the fineness and homogeneity of the powders constituting MFA and distribute the catalytic metal at a micron scale, enhancing catalytic activity. Hence, model fly ash (MFA) was grinded at different treatment times to investigate whether additional PCDD/F formation occurred. Homologue and isomer patterns of the dioxins formed by de novo tests were determined and examined to try to identify the mechanism of PCDD/F-formation and destruction at work, after brief or extensive sample milling. To our best knowledge, there is no earlier such study focusing on catalytic effects and concomitant PCDD/F output in samples pre-treated by milling.

METHODS

Preparation of MFA

Fly ash preparation method and level of mixing greatly influences upon the results of consecutive de novo tests and that the mobility of the catalytic metal (induced by thermal pre-treatment) also is important (Kuzuhara *et al.* (2003).

Samples of model fly ash (MFA) composed from activated carbon (2.5 wt.%, 200–400 mesh) as source of carbon, sodium chloride (NaCl; 10 wt.% Cl) as source of chloride, and metal compound dopes (0.2 wt.% of each metal). The matrix material was silica (SiO$_2$; 120–200 mesh). To prepare fly ash, materials were selected to simulate the composition of fly ash in real incinerators. Activated carbon, sodium chloride and silica were mixed with the metal species selected, by grinding them together in an agate mortar for about 10 min (0 h, blank sample) to ensure complete mixing. The resulting MFA was subjected to further milling for 1 and 8 h. The materials used for preparing MFA, and the milling apparatus are represented as supplementary material (S.1, S.2, Table S.1, and Fig. S1), together with the composition of each metal-doped MFA before and after grinding, as analysed by XRF (S.4, Table S.2). A surprising observation after milling was a gain of the sample's physical weight; TGA/DSC tests and SEM/EDX compositional mapping (see Fig. S.3) were conducted to verify this issue further, and these unexpected weight increases were explained by the wear and attrition of milling balls and housing. Unfortunately, this brought a number of novel elements (Fe, Cr, Ni, Mn…) in the MFA samples.

Experimental Procedure

Fig. 1 shows a schematic diagram of the experimental apparatus used for the de novo tests. A sample of 2 g of model fly ash (MFA) is placed into a vertical quartz tube (53 cm height × 5 cm I.D.) and fixed by glass wool. The glass wool was first rinsed by acetone and dried at 100°C. Then, the tube is placed in a preheated electric furnace at 300°C and exposed for 1 h to a flow (300 mL min^{-1}) composed of 10% oxygen and 90% nitrogen to simulate the operating conditions in the post-combustion zone of a MSWI. During the test, the evolving PCDD/F in the carrier gas were absorbed on XAD-2 cartridges and in toluene washing bottles. These represent the gas-phase PCDD/F-compounds, while those remaining in the solid residue were collected as solid-phase compounds, then both phases were combined for further pre-treatment. In these tests, the two phases (gas and solid residue) were analysed collectively, following the EPA method 1613 (US EPA, 1994). The method of clean-up and analysis are given in the supplementary material (S.3), briefly, analyses were performed by means of High Resolution Chromatography with a DB-5MS column (60 m × 0.25 mm × 0.25μm) coupled with High Resolution Mass Spectrometry (JMS-800D, JEOL, Japan). The mean recoveries of standards for PCDD/F range from 55 to 125%, which are all within the acceptable 25 to 150% range. The target compounds were all tetra- to octa-CDD/F as well as the seventeen 2, 3, 7, 8-substituted PCDD/F. A blank test involving no MFA was run at the same experimental

conditions and no PCDD/F were detected.

RESULTS AND DISCUSSION

PCDD/F Formation during De Novo Tests

Table 1 shows the PCDD/F-output (in ng g^{-1} MFA) from five metal chlorides in blank (0 h) and milled samples. As expected, CuCl$_2$ is by far the most potent catalyst for dioxin formation, with a total PCDD/F yield much larger than for CrCl$_3$, FeCl$_3$, ZnCl$_2$ and CaCl$_2$. The reactivity shown in Table 2 agrees reasonably well with previous studies (Vogg *et al.*, 1987; Kuzuhara *et al.*, 2003; Fujimori *et al.*, 2009; Chin *et al.*, 2012; Zhang *et al.*, 2016), even though metal concentration and procedures selected to prepare and test the model fly ash differ in all earlier studies.

Surprisingly, the PCDD/F-output of CuCl$_2$-doped MFA markedly decreases with milling time and after 1 and 8 h

drops to only 15 and 3.4%, respectively, of the blank yield. The other metals selected respond differently to milling, as shown in Table 3.

Average chlorination level apparently was not much affected by prolonged milling time for all catalysts (Table 1). The Cl-PCDD and Cl-PCDF was calculated as weight average chlorination level (Eq. (1)) and CuCl$_2$ consistently remained the dominant chlorinating agent at 0, 1 and 8 h.

$$d_c = \sum_{j=4}^{8} f_j \times n_j \qquad (1)$$

Milling proceeds without any dedicated cooling to remove the heat generated by the Joule effect. When fly ash particles at high velocity collide with a solid surface, a triboplasma appears, i.e., quasi-adiabatic energy accumulation, and the
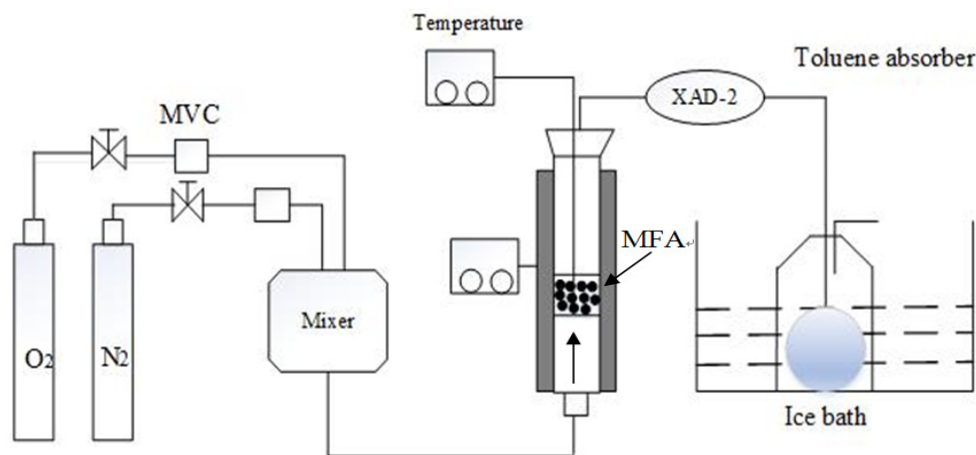

Fig. 1. Schematics of the de novo test apparatus.

Table 1. PCDD/F yield (ng g^{-1}) from metal doped MFA samples milled at 0, 1 and 8 h.

	PCDD(ng g^{-1} MFA)			PCDF (ng g^{-1} MFA)		
Time, h	0	1	8	0	1	8
CuCl$_2$	660	70.1	11.0	1698	276	68.9
CrCl$_3$	0.92	1.14	0.70	9.09	10.1	6.04
FeCl$_3$	0.37	0.85	0.65	2.25	7.26	6.43
ZnCl$_2$	0.50	0.41	0.47	1.49	1.63	1.17
CaCl$_2$	0.18	0.54	0.16	0.62	0.80	0.35
	PCDD/F (ng g^{-1}MFA)			Ratio-PCDF/PCDD		
Time, h	0	1	8	0	1	8
CuCl$_2$	2358	346	79.9	2.58	3.93	6.28
CrCl$_3$	10.0	11.3	11.3	9.86	8.86	8.59
FeCl$_3$	2.62	8.11	7.08	6.04	8.59	9.97
ZnCl$_2$	1.99	2.04	1.63	2.99	3.99	2.51
CaCl$_2$	0.80	1.33	0.51	3.44	1.48	2.26
	Cl-PCDD			Cl-PCDF		
Time, h	0	1	8	0	1	8
CuCl$_2$	7.58	7.64	7.58	6.93	6.63	6.58
CrCl$_3$	6.22	6.32	5.99	5.01	5.28	4.83
FeCl$_3$	5.56	4.88	4.89	4.76	4.49	4.91
ZnCl$_2$	6.61	6.03	6.71	5.68	5.67	5.55
CaCl$_2$	6.06	5.63	5.59	5.67	5.65	5.21

Table 2. Order of reactivity of metal chlorides for PCDD/F output in MFA, selected studies.

	PCDD/F output (ng g⁻¹)						Reference
Met. C.*	CuCl$_2$	CrCl$_3$	FeCl$_3$	ZnCl$_2$	CaCl$_2$	Reactivity Order	
N.A. *	4900	-	60	< 10	< 0.5	CuCl$_2$ > FeCl$_3$ > ZnCl$_2$ > CaCl$_2$	Vogg et al., 1987
N.A. *	2600	-	3.6	-	4.6	CuCl$_2$ > FeCl$_3$ > CaCl$_2$	Kuzuhara et al., 2003
0.2 %	45312	-	6256	10.15	-	CuCl$_2$ > FeCl$_3$ > ZnCl$_2$	Fujimori et al., 2009
10 %	369.5	-	-	25.5	-	CuCl$_2$ > ZnCl$_2$	Chin et al., 2012
0.1 %	10100	419.9	-	110	-	CuCl$_2$ > CrCl$_3$ > ZnCl$_2$	Zhang et al., 2016
0.2 %	2358	10.0	2.62	1.99	0.80	CuCl$_2$ > CrCl$_3$ > FeCl$_3$ > ZnCl$_2$ > CaCl$_2$	Present Work

Met. C.* = metal concentration; N.A. * = Not Available.

Table 3. Chlorophenol precursor route and reactivity of metal chlorides for PCDD/F formation in MFA milled for different time (0, 1 and 8 h), averaged for and over five catalytic systems.

	CuCl$_2$			CrCl$_3$			FeCl$_3$			ZnCl$_2$			CaCl$_2$			Average,%			St. Dev.%		
Time, h	0	1	8	0	1	8	0	1	8	0	1	8	0	1	8	0	1	8	0	1	8
TCDD	20	25	41	24	20	24	28	29	21	40	42	49	58	10	25	34	25	32	15	12	12
PeCDD	41	48	41	39	35	34	41	42	37	51	52	53	40	34	61	43	42	45	5	8	11
HxCDD	37	41	31	28	23	27	29	28	23	28	26	28	32	28	46	31	29	31	4	7	9
TCDF	26	24	20	17	18	17	17	17	17	11	11	11	13	12	7	17	16	15	6	5	5

	Average						St. Dev.				
	CuCl$_2$	CrCl$_3$	FeCl$_3$	ZnCl$_2$	CaCl$_2$		CuCl$_2$	CrCl$_3$	FeCl$_3$	ZnCl$_2$	CaCl$_2$
TCDD	29	23	26	43	31		11	2	4	5	24
PeCDD	43	36	40	52	45		4	3	3	1	14
HxCDD	37	26	27	27	35		5	2	3	1	10
TCDF	23	17	17	11	11		3	0	0	0	3

Reactivity of metal chlorides for PCDD/F formation											
Time, h	0	1	8		0	1	8		0	1	8
CuCl$_2$	100	11	1.7		100	16	4.1		100	15	3.4
CrCl$_3$	100	124	76		100	111	66		100	112	67
FeCl$_3$	100	230	176		100	323	286		100	310	270
ZnCl$_2$	100	82	94		100	109	79		100	103	82
CaCl$_2$	100	300	89		100	129	56		100	168	64

local spot temperature inside the material being milled may reach ca. 3000 K in sub-microscopic deformation zones (Heinicke, 1984; Monagheddu et al., 1999). Moreover, milling due to heat and mass transfer, significantly affects physical and chemical properties of solid materials at different scale and prompts size reduction (Balaz et al., 2013). Therefore, MFA lost its reactivity to generate PCDD/F, to some extent.

The PCDF/PCDD-Ratio

Huang and Buekens (1995) and Sakurai et al. (1996) linked the PCDF to PCDD ratio to de novo vs. precursor formation. In these tests, all ratios are > 1; CuCl2 and FeCl$_3$ show a PCDF to PCDD ratio rising with milling (see Table 1). Among all five selected catalysts CrCl$_3$ and FeCl$_3$ showed the highest PCDF to PCDD ratio that slightly increased with further milling, contrary to the results of Zhang et al. (2016). CaCl$_2$ and ZnCl$_2$ showed the lowest ratio, suggesting their preference towards the precursor route. CuCl$_2$ showed an average of 0.3 of PCDF/PCDD ratio for 0, 1 and 8 h milled samples that is in good agreement with previous study by Addink et al. (1991). In the original Cu-doped sample, hexa- and hepta- CDD are dominant PCDD congeners, after 1 and 8 h milling treatment, their value greatly reduced and high chlorinated PCDF become dominant.

Homologue Profiles

The signatures of isomer groups starting from TCDD to OCDF are represented by homologue group profiles, relating PCDD/F with specific sources (Fujimori et al., 2009). Fig. S.2 shows such signatures for five catalytic systems, obtained after no milling and for 1 and 8 h of treatment (PCDD + PCDF = 100%). Homologue profiles look very similar, for CrCl$_3$ and FeCl$_3$ samples (0, 1 and 8 h). Conversely, CuCl$_2$ and CaCl$_2$ homologue profiles change with milling time. At present, it is difficult to decide, which factor has a major effect on reduced/enhanced reactivity of MFA. Relevant factors could be:

- the changed composition of milled material (see Table S.2),
- the reduced reactivity due to oxidation of carbon (Wei et al., 2009)
- the low BET surface area, the formation of aggregates, and the reduction of particle size with prolonged milling time (Chen et al., 2016),
- high plasma temperature and collision velocity (Heinicke, 1984), and

- silica as grinding medium (Lu *et al.*, 2012).

2,3,7,8-PCDD/F Profiles

The 2,3,7,8-PCDD/F are represented by their Hagenmaier profile (Table 4). Should the isomer signature be determined by thermodynamic equilibrium, then each line would show a specific constant value. The minimum and maximum and average values encountered are given as supplementary materials (Table S.3). A rapid scrutiny shows that the figures for $CrCl_3$ and $FeCl_3$ samples tend to score lower, except for 1,2,3,4,6,7,8-TCDF, where they are very high, and that the results for PCDD and PCDF are not necessarily similar. Again, $CaCl_2$ shows extreme variations. Table S.4 lists the seventeen contributions to the WHO-TEQ values for MFA milled samples (0, 1 and 8 h) in pg WHO-TEQ g^{-1} MFA. $CuCl_2$ being most potent catalyst for toxic congeners yield, however toxicity potential of Cu-doped MFA gradually decreased with milling time (66% after 1 h and total reduction was > 94% after 8 h milling treatment).

2,3,7,8-PCDD/F profiles of metal doped MFA before and after milling treatment were evaluated to find similarities and differences by Principal component analysis (PCA) (Fig. 2). The seventeen 2,3,7,8-PCDD/F for $CuCl_2$ milled for 0, 1 and 8 h tend to behave similarly; it implies that although milling did not change 2,3,7,8-PCDD/F profiles, it reduces the toxicity potential of MFA. Other metal doped MFAs tend to behave similarly (low toxicity potential) with respect to each other but with a marked difference with Cu. PCA analysis was applied to various other profiles and on standardised data as well, yet there are individual differences in each catalytic system.

Isomer Distribution

A complete range of isomers is present in thermal fingerprints, whereas the condensation of chlorophenoxy-radicals and chlorophenol generates specific PCCD/F isomers such as (PCDD) 1,3,6,8- and 1,3,7,9-TCDD, 1,2,4,7,9+, 1,2,4,6,8-, 1,2,3,6,8-, 1,2,3,7,9-PeCDD and 1,2,3,4,6,8-HxCDD, and (PCDF) 2,4,6,8-TCDF and 1,2,3,8+, 1,2,3,6+, 1,4,6,9+, 1,6,7,8+, 1,2,3,4+, 2,3,6,8-TCDF. In this study, particular attention is given to the 2,3,7,8-substituted PCDD/F and to those PCDD/F derived from chlorophenols. The chlorophenol precursor route is better represented in PCDD than in PCDF. Table 3 shows its different representatives on the basis of the aforementioned congeners**.** The values recorded in Table 3 suggest that the chlorophenols route supplies a sizeable part of the PCDD and contributes less to the PCDF: on average 30 ± 13% to TCDD, 43 ± 8% to PeCDD, 30 ± 6% to HxCDD, and only 16 ± 5% to TCDF. The effect of milling shows no obvious pattern, with on average a rather limited impact on the internal distribution, as suggested by the values and their large standard deviation, when averaged over the five distinct catalysts (Table 3). Table 3 also assesses any marked differences between the five catalytic systems. The richest homologue group is PeCDD, followed by TCDD; $ZnCl_2$ leads in both and $CrCl_3$ is lowest. The values show a low standard deviation, with the exception of $CuCl_2$ with values rising with milling time and especially $CaCl_2$ with a singular comportment marked by an erratic evolution. Since milling treatment could influence the reactivity of MFA (Kuzuhara 2003), a systematic comparison of fingerprints could be helpful to verify how these metal chlorides in differently milled samples affect the congener distribution. A complete data set representing percent isomer profile for each metal chloride in 0, 1 and 8 h milled samples is recorded in supplementary material (Table S.5). The congener output from five selected metal chlorides in 0 h milled samples, is

Table 4. 2,3,7,8-PCDD/F Hagenmaier profile for milled MFA at 0, 1 and 8 h.

HAGENMAIER Profile	$CuCl_2$			$CrCl_3$			$FeCl_3$			$ZnCl_2$			$CaCl_2$		
	0 h	1 h	8 h	0 h	1 h	8 h	0 h	1 h	8 h	0 h	1 h	8 h	0 h	1 h	8 h
2378	3.05	2.25	2.35	2.08	2.29	2.22	2.94	2.39	2.36	2.44	2.92	2.22	2.50	1.86	3.73
12378	16.3	11.6	13.3	6.23	6.27	5.56	5.56	6.32	6.54	9.60	9.20	8.98	14.3	9.61	2.17
123478	3.35	3.86	5.09	7.34	7.25	8.98	8.20	7.85	8.22	5.51	5.26	4.85	4.65	4.74	4.46
123678	7.38	6.36	6.52	6.70	7.11	8.22	8.23	8.33	8.93	10.3	8.30	8.51	8.23	7.91	10.6
123789	9.37	8.23	10.6	4.29	3.89	3.74	5.73	4.11	4.90	6.55	6.69	6.56	5.42	6.67	6.71
1234678	48.0	48.2	47.0	40.0	38.6	42.0	36.2	46.2	40.6	45.4	47.7	47.3	51.7	46.4	47.0
12346789	66.0	78.2	75.1	39.8	40.0	36.6	53.8	36.2	39.1	39.1	14.4	47.2	24.8	27.7	29.7
2378	2.29	1.31	1.19	2.12	1.84	2.08	2.36	2.19	2.00	6.55	5.09	4.45	7.09	6.19	21.9
12378	3.05	2.37	1.97	2.87	2.55	3.14	3.13	3.02	2.87	15.2	5.51	5.59	5.91	5.90	7.10
23478+	9.68	9.00	7.26	5.59	6.49	7.01	7.57	7.12	6.72	10.6	11.2	10.7	15.8	11.5	15.0
123478	6.94	7.07	6.60	7.42	7.32	8.04	8.01	7.14	7.64	11.2	11.1	11.6	10.6	10.9	12.7
123678	6.67	7.14	6.45	5.94	5.62	6.82	6.40	6.60	6.44	10.4	11.1	10.9	10.7	11.0	11.7
234678+	17.7	17.4	11.6	7.55	7.32	8.26	8.62	10.7	7.65	14.3	12.7	12.3	14.2	13.3	11.7
123789+	5.26	4.57	4.16	1.31	1.39	1.52	1.43	2.67	1.21	2.73	2.58	2.55	2.43	2.41	2.46
1234678	45.9	56.3	57.9	85.0	85.6	84.2	82.7	70.7	85.7	46.6	58.5	57.7	56.9	60.2	70.1
1234789	10.4	7.50	7.11	1.95	1.82	2.88	4.21	5.51	1.61	7.48	9.09	9.56	16.3	8.69	7.49
12346789	39.3	42.0	32.5	1.39	1.90	0.94	1.19	3.38	0.90	2.84	3.39	3.40	3.07	3.07	3.03
*Geomean 6 PCDD	9.06	7.96	8.96	6.91	6.93	7.23	7.82	7.57	7.80	8.56	8.49	7.97	8.53	7.69	7.02
*Geomean 9 PCDF	8.03	7.13	6.24	5.13	5.01	5.82	6.13	6.63	5.12	10.6	9.58	9.42	11.0	9.81	12.0

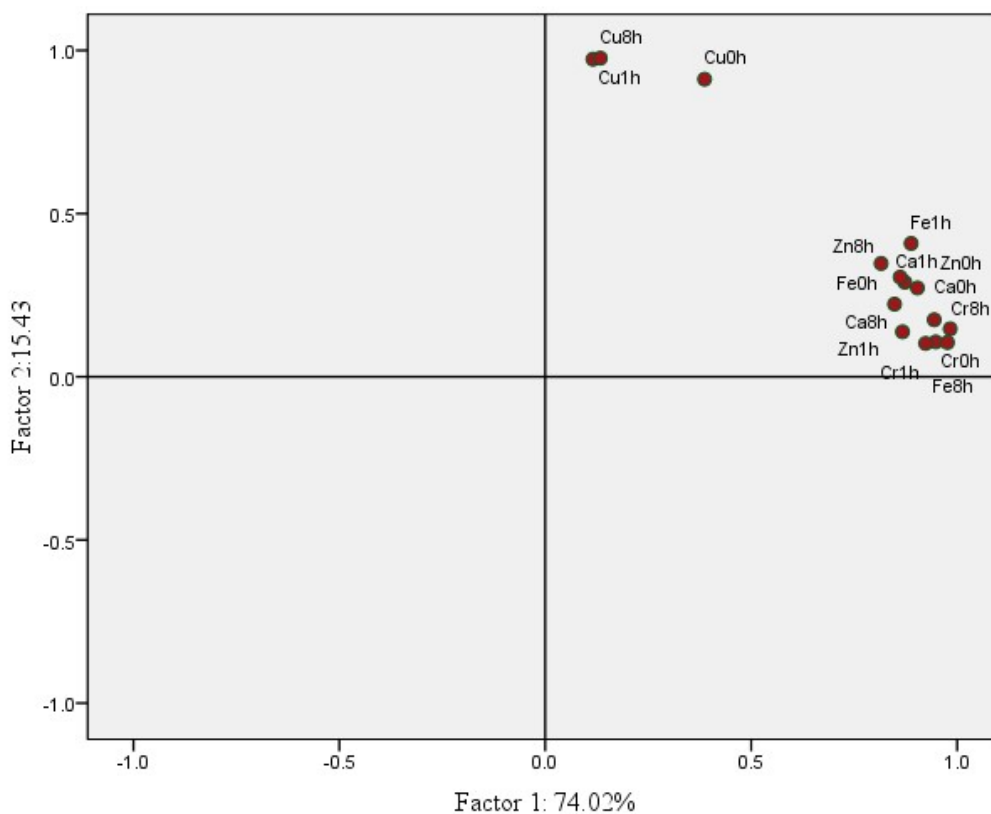*Geomean = geometrical average.

Fig. 2. PCA of the profiles of metal doped MFA, milled at 0, 1 and 8 h. The total variance explained by factor 1 and factor 2 is 89.45%.

given in Fig. 3. $CuCl_2$ produced specific congeners that are evenly distributed while $CrCl_3$ and $FeCl_3$ were closer in congener's distribution pattern. There was also less variation between $ZnCl_2$ and $CaCl_2$ congeners that later on greatly increased with milling augmentation.

Milling treatment brings in many changes in MFA e.g., particle size reduction, oxidation of carbon and also introduces Fe, Ni, Cr, Mn etc. (supplemental metals) due to attrition from milling balls and housing.

DISCUSSION

High intensity ball milling of metal doped MFA for 1 and 8 h brings in numerous physical and chemical changes, not only reducing average particle size and affecting other physical parameters as well as speciation, but also changing the composition of milled fly ash by attrition of the milling equipment (see Table S.2). The reason could be, SiO_2 has more hardness value on moh's scale compared to stainless steel pots, and this causes shear abrasion along the walls of pots during high intensity milling. The evolution of the reactivity of fly ash with milling treatment time could be tentatively attributed to many different factors, related to catalyst particle size and speciation, different impact on formation and destruction, etc.

Inside the mill, local temperature reaches up to several thousand degrees, which is unfavourable for de novo synthesis of dioxins (Shaub and Tsang, 1983). Cagnetta *et al.* (2016) argue that $CuCl_2$ is a sensitive catalyst, preferably

it is trapped inside the matrix and/or converted into an amorphous material and so that longer milling augmentation decreased $CuCl_2$ catalytic potential.

Future work could try and explain which factor has a major effect on the reduced reactivity of MFA or on the output of PCDD/F. However, in some cases (selected metal chlorides other than Cu), reformation could be explain by the fact that attrition increases the formation of Cu and Fe compounds that produced more dioxins. However, looking at the different fingerprints (dominant distribution of TCDD, HxCDD and TCDF homologues) of Zn and Ca-doped MFA after milling with respect to blank sample, it is difficult to elucidate which particular catalytic compounds were generated. Another possible explanation for reformation of dioxins is hot-spot theory, when MFA powder is compressed by hitting of balls with milling pot, temperature increases up to thousands of K in a microscopic area (~ 1 μm^2) for a very short time ($\sim 10^{-9}$ s) on the contact surface (Urakaev and Boldyrev, 2000). However, near the contact surface temperature rise is less and last longer, also other ingredients (Carbon, Chlorine, possible metal chlorides and precursors) for de novo formation are available, reformation reaction seems to occur (Cagnetta *et al.*, 2016).

CONCLUSION

The effect of milling treatment time on metal doped MFA activity to generate dioxins (PCDD + PCDF) via de novo synthesis was evaluated after testing at a single temperature,
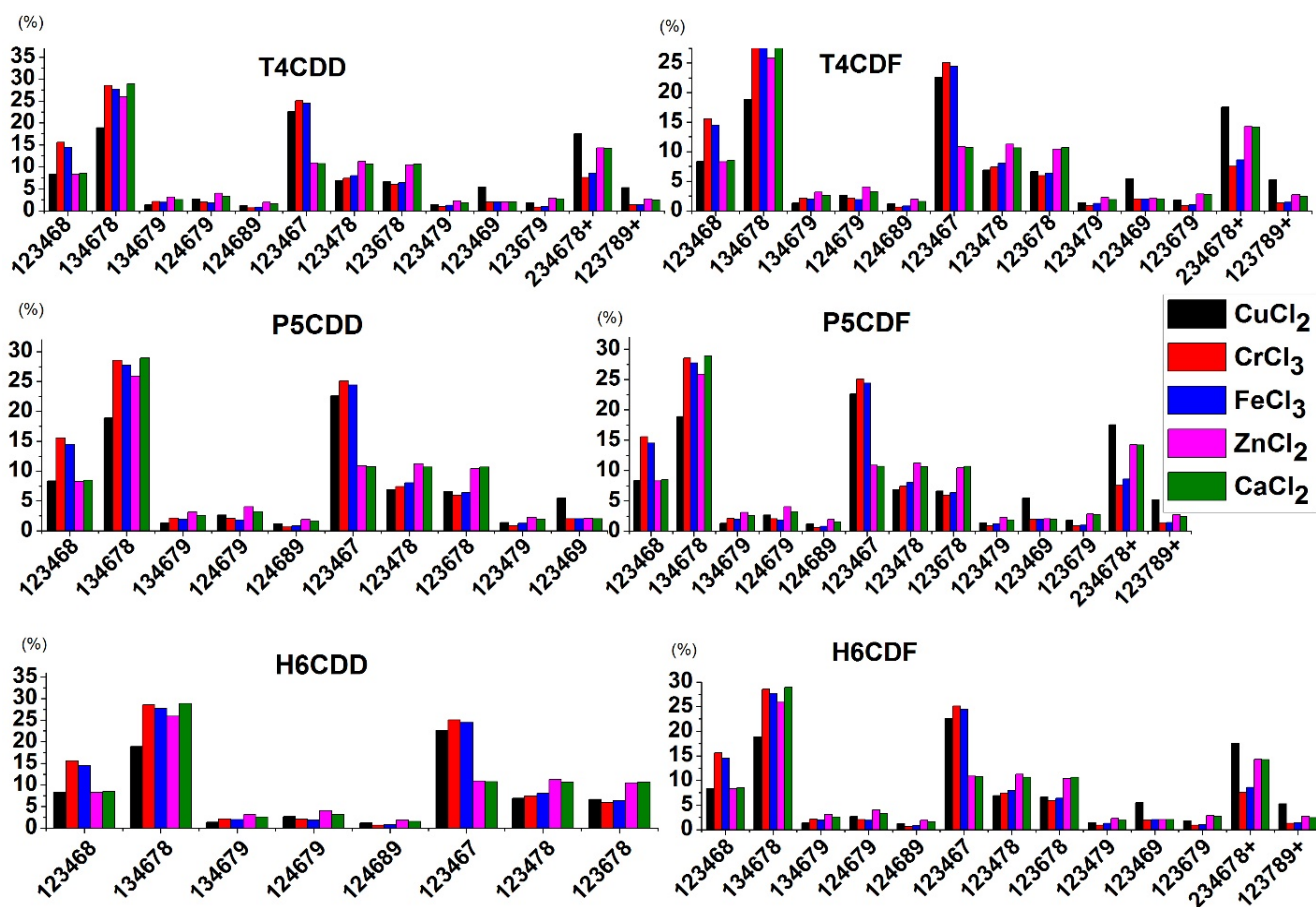
Fig. 3. PCDD/F congener profiles of metal doped MFA (0 h Milled).

gas flow rate and reaction time. Milling affects Model Fly Ash samples by reducing their average particle size, enhancing their homogeneity and the dispersion of the catalytic agent (see Fig. S.3). When testing blank samples, CuCl$_2$ is, as expected, a much more potent catalyst than CrCl$_3$, FeCl$_3$, ZnCl$_2$ and CaCl$_2$, both in synthesis and in chlorination activity. The PCDD/F yield from milled MFA samples varies greatly; the main results are summarized in Tables (1, 2, 3 and 4). PCDD/F-output markedly decreases with prolonged milling time for all type of MFAs. WHO2005-TEQ concentration of Cu-doped MFA was significantly affected by milling time, while other selected metals have low toxic potential as compared to Cu and total yield of their WHO2005-TEQ (ng g^{-1}) was not much high (Table 1). Apparently average chlorination degree did not changed with milling, except CrCl$_3$ showed a slight decrease from 5.18 (0 h) to 4.95 (8 h). Homologue and congener profiles of all MFA showed variation with milling time, either distribution decreased (e.g., OCDF in CuCl$_2$ from 0 to 8 h), increased (e.g. OCDD in CrCl$_3$ from 1 to 8 h), or remained almost constant (e.g., 1289-PCDF in all MFAs). Congener patterns that dominate after 8 h in CaCl$_2$ strongly indicate precursor route of formation for PCDD/F. The other parameters of milling treatment such as milling speed, milling ball materials and reaction atmosphere during mechanical treatment will also be considered in future work and de novo test conditions (temperature, time and atmosphere),

and also the formation and destruction of other potential precursors, such as PAH, PCB, PCN, CP and CBz. For further clarification, focusing on mechanisms involved in formation and destruction of dioxins in milled fly ash, results from present study may provide a source of comparison for future work.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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