Mechanochemical treatment of fly ash and *de novo* testing of milled fly ash

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Introduction

Mechanochemical (MC) methods have been proposed to destruct PCDD/F in the fly ash. They require no heating or off-gas treatment and do not generate secondary pollution (1). Nomura et al. (2) studied the degradation of OCDD/F by MC treatment and found that dechlorination is a major pathway in the degradation mechanism; the dibenzo-p-dioxin and dibenzofuran structures dechlorinate, fracture and degrade further. Though numerous studies focused on the effect of dechlorination and degradation by MC treatment, few considered the chemical reactivity of the carbon structures formed during the MC treatment. In the present study, the MC treatment of fly ash was carried out without any additive or preliminary treatment and the destruction efficiency (DE) of PCDD/F were estimated. The physical and chemical properties of the original fly ash and MC treated fly ash were comprehensively characterised and the evolution in fly ash composition during milling is considered. Moreover, de novo synthesis experiments were performed, to explore the chemical reactivity of the residual carbon structures in the treated fly ash.

Materials and methods

The fly ash used in this experiment was sampled from the baghouse filter of an externally circulating fluidised bed municipal solid waste incineration plant(Cixi, Ningbo), in which hydrated lime was injected into the flue gas, to neutralise the acid gases, as well as activated carbon, to adsorb PCDD/F.

The MC reactor is an all-dimensional planetary ball mill (QXQM-2, Changsha Tencan Power Technology Co., Ltd, China). Revolution speed was set as 350 rpm, and the machine stops every 15 min for 5 min in case the pots are overheated. After running for 0 h, 1.5 h, 3 h, and 6 h, 1g of the ground fly ash is sampled and denoted as samples FA0, FA1.5, FA3, FA6. After that a *de novo* test was conducted. The reaction temperature was set at 350°C. The PCDD/F present in the off-gas were continually collected by both the XAD-2 resin and toluene for 1h.

All original and MC treated fly ash were measured for the following structural and compositional parameters. The structure of the carbon was determined by Raman spectroscopy (LabRamHRUV Jobinyvon Co. France).

The concentration of PCDD/F was detected by HRGC/HRMS refer to method USEPA 1613. The original, MC treated and de novo fly ash were analysed for PCDD/F.

The degradation efficiency of PCDD/F for total concentration and I-TEQ concentration was calculated by Eq.(1) and Eq.(2), respectively. And C (pg/g) and C' (pg-TEQ/g) are PCDD/F total(through 4-8 chlorinated PCDD/F homologue) and I-TEQ concentration.

$$\eta_{S\,total} = \frac{C_{FA0} - Cs}{C_{FA0}} \times 100\%, \quad S=0,\ 1.5,\ 3,\ 6 \tag{1}$$

$$\eta_{SITEQ} = \frac{C'_{FA0} - C's}{C'_{FA0}} \times 100\%, \quad S=0,\ 1.5,\ 3,\ 6 \tag{2}$$

It was reported that dechlorination is a major factor in the degradation of chlorinated organic compounds(3). In our study, the degree of chlorination (dc) was calculated by Eq. (3), which is defined as the sum of the products of the mole fraction fi and the number of chlorine atoms ni for each homologue.

$$d_c = \sum_{i=4}^{8} f_i \times n_i \qquad (3)$$

Results and discussion

Raman spectrum. Two peaks appear in all samples at a wavelength of 1580 and 1355 cm^{-1} in the Raman spectrum (Fig. 1). These are characteristic of graphite and amorphous carbon: the peak at 1580 cm-1 represents the G bond, corresponding to graphite, and a broad peak at 1355 cm-1 corresponds to the characteristic D bond peak of amorphous carbon (4, 5). Tanaka et al. (6) milled mixtures of CaO and aramid (an aromatic polyamide) and found that amorphous carbon and graphite appeared already after 1 h in the milled sample and distinctly intensified with time rising. In the present experiment the fly ash colour deepened with MC treatment proceeding and finally turned black; therefore graphite is expected to be the final degradation product. To verify the hypothesis, the ID/IG value in the Raman spectrum was calculated. This value decreased from 2.42 to 1.76 with time increasing, indicating that the fraction of graphite augmented.

The total PCDD/F concentration and I-TEQ of the raw fly ash were 6.45 ng/g and 0.213 ng I-TEQ/g, respectively. Fig. 1 monitors the evolution of PCDD, PCDF, PCDD/F and I-TEQ concentration during the MC treatment. After 6 h of milling total concentration and I-TEQ finally reduced by 41.7% and 30.6%, respectively. During degradation different trends appeared for PCDD/F and I-TEQ. Fig.2 shows the tetra-octa chlorinated PCDD/F homologue profiles, both for original and MC treated FA.

Most studies on the MC treatment of chlorinated aromatic compounds showed that calcium oxide is an efficient additive (2, 6, 7). Plescia et al. (8) generated CaO by ultra-milling of CaCO3, while in the present experiments free CaO was not detected, as by Peng et al. (9). Hence CaO may act as an intermediate inducing chlorination. The main reason for destruction of chlorinated organic compounds is the breaking of C-Cl bonds (10). Thus, lower chlorinated intermediates are probably produced while higher chlorinated PCDD/F degrade. Nomura et al. (2) observed tetra- through heptachloro-PCDD/F, formed from MC treatment of OCDD/F, to peak simultaneously and decrease with rising grinding time. The same was also reported by Mitoma et al. (11), while no additives were added during MC-treatment, which can explain that in Figure 3 the amount of TCDD/F increased from 0 to 1.5 h. Another reason maybe is that additional formation from PCDD/F precursors in fly ash, such as chlorinated organic compounds (chlorobenzenes, chlorophenols) or PAH, accompanied by dechlorination of high chlorinated PCDD/F. With rising grinding time, the degree of chlorination lessened marginally, from 4.72 for FA0 to 4.62 for FA6, as shown in Table 1.

Table 1. Degree of chlorination of PCDD/F for original and MC treated sample

FA$_0$	FA$_{1.5}$	FA$_3$	FA6
5.09	5.02	5.01	5.12

The particle size of fly ash, the amount and species of organic compounds, as well as the structure of the carbon formed all modify during milling; hence, the reactivity of carbon was explored experimentally during four *de novo* tests at fixed conditions of 350 °C, 1 h.

Fig. 4 shows the PCDD/F-yield (ng/g) from a de novo synthesis test, conducted on the four samples of fly ash, i.e. the original sample, as well as those obtained after 1.5, 3, and 6 h of milling. Remarkably, the yield from milled fly ash is much lower than that from raw fly ash: after 6 h of milling, the total concentration and I-TEQ value for FA$_6$ attains just 36.8% and 45.4%, respectively, of that obtained from raw fly ash. The ratio of PCDD/PCDF rises remarkably with grinding time, from 2.6 for to 48, 56 and 59, suggesting that de novo reactions starting from carbon or graphite become much more predominant and that precursor routes dwindle in importance. The mole average degree of chlorination of the PCDD/F

synthesized from milled fly ash is very low.

Table 4. PCDD/F formed after de novo reaction

	dc	PCDD (ng/g)	PCDF (ng/g)	PCDD/PCDF(-)	I-TEQ(ng/g)
FA0	4.21	1.75	82	2.6	1.04
FA1.5	4.27	0.53	30	48	0.48
FA3	4.21	0.68	57.2	56	0.51
FA6	4.24	0.53	30.3	59	0.47

According to a recent review (12) carbon in fly ash consists of aliphatic and aromatic compounds and macromolecular carbon. Due to the weak C-C bond energy hydrocarbon chains can be broken easily and the resulting molecules volatilise (6). Also, some benzene is formed during ball grinding, and condenses, forming amorphous and graphite-like structures, while the colour of the samples turns black (10).

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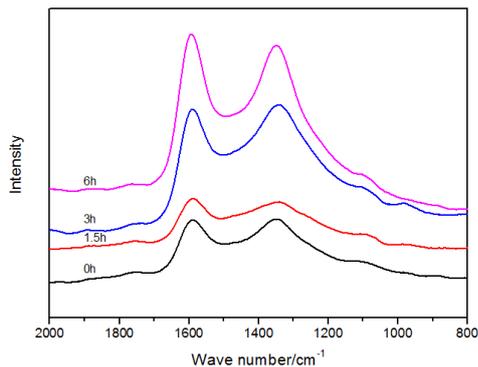
Fig.1 Raman spectrum of milled fly ash samples.
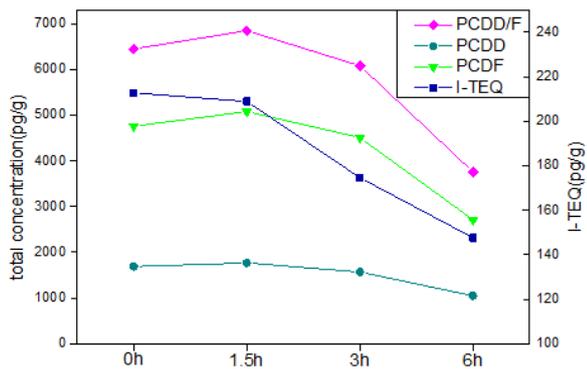
Fig. 2. Time trends for PCDD/F with time increasing.
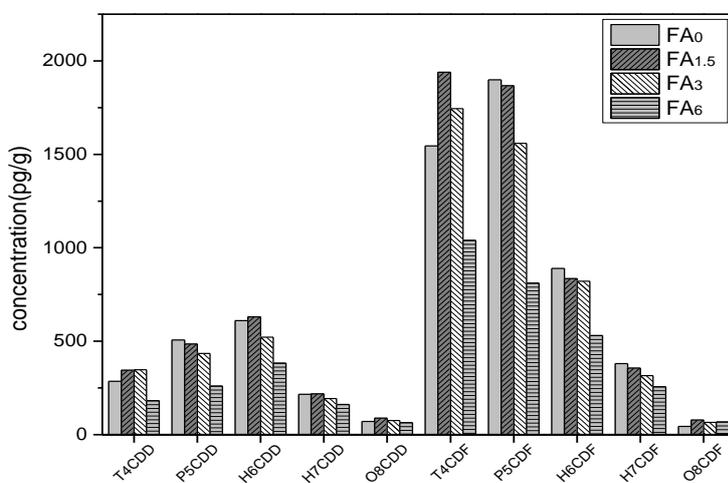
Fig. 3. Homologue pattern of PCDD/F for original fly ash (FA$_0$) and MC treated fly ash
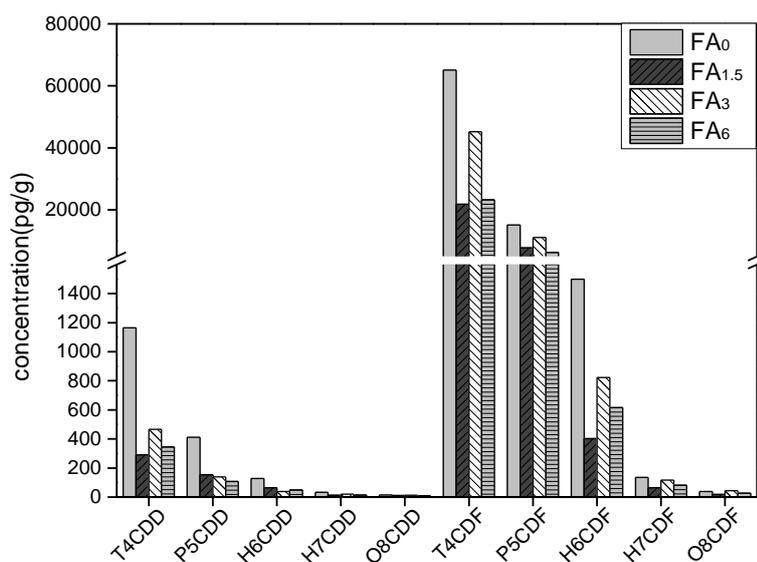
Fig. 4. Time trends of PCDD/F formed from milling residue after de novo reaction