Chemosphere 180 (2017) 130–140

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Dioxins degradation and reformation during mechanochemical treatment

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HIGHLIGHTS

- The chloride ions contained in fly ash negatively influence upon PCDD/Fs-degradation during MCD.
- A novel additive, a mix of calcium oxide and aluminium metal, was proposed.
- Dechlorination is the major mechanism for PCDD/Fs degradation and CaO-Al promotes the degradation of PCDD.

ARTICLE INFO

Article history:
Received 4 January 2017
Received in revised form
22 March 2017
Accepted 1 April 2017
Available online 4 April 2017

Handling Editor: Jun Huang

Keywords:
Mechanochemical dechlorination and destruction (MCD)
Milling additives
Polychlorinated dibenzo-p-dioxins (PCDD) and −dibenzofurans (PCDF)
Fly ash
Water-washing

ABSTRACT

Mechanochemical dechlorination and destruction of polychlorinated dibenzo-p-dioxins and -furans (PCDD/F) on fly ash from Municipal Solid Waste Incineration was tested with and without additives (CaO and CaO/aluminium powder). The first results disappointed because of obvious PCDD/F-reformation and a second test series was conducted after removing soluble salts (NaCl, KCl …) by thorough two-stage water washing. This second test series was successful and demonstrated good destruction results, especially with combined CaO/aluminium powder as additive. In a third test series salt was again added to the water-washed fly ash, and the first, poor results were largely reconstituted. For all tests a fairly complete (94 out of 136 congeners) isomer-specific analysis was conducted and analysed, allowing to differentiate between, e.g., 2,3,7,8-substituted PCDD/F and congeners formed following the chlorophenol route. The first became more important in the samples series Fly Ash, Milled Fly Ash, milling with added CaO, and milling with CaO/aluminium-addition. The second follow the opposite trend. This isomer-specific analysis will form the basis for further study using Principal Component Analysis.

1. Introduction

Municipal solid waste incineration (MSWI) fly ash (FA) has been classified as hazardous waste, for it contains contaminants such as heavy metals and dioxins. The most common method of FA elimination is landfill, after immobilization of heavy metals by cement-based solidification/stabilization. However, this treatment does not destroy any polychlorinated dibenzo-p-dioxins (PCDD) and −furans (PCDF) present and these (PCDD/F) are listed as Persistent Organic Pollutants (POPs) subject to the for elimination stipulated by the Stockholm Convention (Stockholm Convention, 2001). Therefore, it is important to develop and demonstrate methods to render FA harmless in an environmentally sound manner. Thermal treatment is effective, yet encounters strong public opposition. For two decades, several alternative non-thermal techniques were proposed, including base-catalysed decomposition, bioremediation, photocatalytic UV degradation (Sayler et al., 1977; Tiernan et al., 1992; Weber, 2007) and in addition, mechanochemical (MC) processing emerged as treatment method. The compression, impaction, friction and shear accompanying grinding operations effectively changes structure and properties of the materials being grinded: MC-methods showed their outstanding performance for decomposing chlorinated (Wei et al., 2009; Lu et al., 2012), brominated (Zhang et al., 2012, 2014) and fluorinated (Zhang et al.,

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http://dx.doi.org/10.1016/j.chemosphere.2017.04.004
0045-6535/

2013; Yan et al., 2015; Zhang et al., 2016a) persistent organic pollutants (POPs) and were applied tentatively for decomposing PCDD/F present in FA (Yan et al., 2007; Mitoma et al., 2011; Mao et al., 2012; Cagnetta et al., 2016). MC-treatment operates under relatively benign conditions, and requires no heating. Industrial procedures were developed in Japan (Radicalplanet Technology) and New-Zealand (Bulley and Black), featuring a planetary mill with capacity of 500 L per vessel and a vibration mill for treating 110 m^3 of soil per week.

Preferably, dechlorination additives should be introduced during or before milling, to react with the toxic substrates and convert organic chlorine into inorganic chlorides. Conventional calcium oxide (CaO) is commonly used as MC-additive (Nomura et al., 2005; Peng et al., 2010; Zhang et al., 2010; Nomura et al., 2012, 2013), since it is efficient, and widely available at low cost. Thorough degradation, however, requires typically 12–24 h of milling, so that low removal rates and considerable operating costs still limit its application. Also, the amount of CaO consumed is substantial, raising landfill requirements. Regularly, other additives have also been studied, striving to attain higher removal efficiency in shorter milling time. These include: pure metals (calcium, magnesium, sodium, potassium, aluminium, etc.), metal oxides (lime, alumina, magnesia, etc.), metal hydroxides (sodium, potassium or calcium hydroxide), as well as associated additives, such as quartz (SiO_2), acting as a plasma-former during milling (Kaupp, 2009; Delogu, 2011). Such studies sometimes combined different additives, such as silica-assisted CaO (Wei et al., 2009; Lu et al., 2012; Xu et al., 2015; Cagnetta et al., 2016), metal plus a hydrogen source (Birke et al., 2004), or a mixture of Ca and CaO (Mitoma et al., 2011), etc. Often, such mixes show better results than the single additives, even if the reasons for such synergy or their mode of action are not clarified yet.

A previous paper (Mao et al., 2015) reported on experimental testing involving five different additive systems, i.e. CaO, CaO/SiO_2, CaO/Al_2O_3, CaO/Al (metal) and Fe/SiO_2 (milled under N_2), comparatively tested to destroy hexachlorobenzene (HCBz), also a Persistent Organic Pollutant listed in the frame of the Stockholm Convention. From these systems, the duo CaO/Al (metal) emerged as the best option, with substantially complete destruction of HCBz already after only 3 h of milling.

In this study the three options (using no additive, and addition of either CaO or CaO/Al metal) were compared, to demonstrate the former result. Milling was conducted on raw fly ash, water-washed fly ash and - to corroborate the eminent effect of water-washing - water washed fly ash, doped with solid NaCl/KCl before being milled. Moreover, in each case the dioxins signature was established, expecting to identify differences in mechanism in the presence and absence of those additives and salts. Such mechanistic study could assist in further rationalising our quest to optimise milling conditions. Successful treatment could promote further the industrial applications of mechanochemical dechlorination and destruction (MCD), by reducing milling time as well as the extension of waste volume after treatment, meanwhile expanding the varieties of treatable substrates, ranging from pure POPs to complex toxic and POP-contaminated industrial waste.

2. Materials and methods

2.1. Sampling and pre-treatment

The fly ash (FA) was sampled from the baghouse filter of a circulating fluidised bed (CFB) MSWI plant located at Hangzhou city, Zhejiang province, China. This incinerator has a capacity of 800 tons per day and typically operates at a temperature not exceeding 850–950 °C. After passing through a waste heat boiler, the flue gas is treated by semi-wet spray neutralisation. Then activated carbon is injected and again separated from flue gas in a baghouse filter, after adsorbing gas phase dioxins.

This FA-sample was used in milling tests, straight, or else added with CaO or with CaO + aluminium metal (CaO/Al). Another part of FA first was washed with deionised water, to remove water soluble salts such as sodium chloride (NaCl), potassium chloride (KCl) and calcium chloride ($CaCl_2$). For this purpose, a two-stage washing process with a water/solids ratio of 10/1 was adopted and optimised (Chen et al., 2016). At each stage, the suspension was vibrated for 30 min at 25 °C, using a horizontal water bath oscillator with speed of 250 rpm.

Both the raw FA and the washed fly ash (WFA) were dried for 24 h at 105 °C and then sealed in a brown bottle, for future use. Part of the washed fly ash was mixed with 8.7% of solid NaCl and 2.8% of solid KCl, to restore the original chlorine content to that of raw FA and named CWFA (cf. Part 3.3). Its performance during milling will be compared with that of the original FA and of WFA, according to the following test scheme (Table 1):

Table 1 presents the testing programme together with the composition of the mill feed for seven different tests. Test 1 (blank test) consisted of milling FA without any additives. In the first set of experiments (samples 2, 4, 6) CaO (purity AR, Sinopharm Chemical Reagent Co., Ltd., China) was added. In the second set (samples 3, 5, 7), FA, together with calcium oxide also aluminium metal powder (100–200 mesh, purity 4N, Sinopharm Chemical Reagent Co., Ltd., China) was introduced into the mix, to investigate their joint effect on PCDD/F-detoxification. Tests 1–3 involved the original fly ash and test 4–5 water-washed fly ash. To confirm the effect of washing out the water-soluble salts, the original Cl-content was restored during tests 6–7 by metered addition of solid NaCl + KCl.

2.2. The grinding experiments

The experiments were performed using a new type of planetary ball mill with a commercial name of all-dimensional planetary ball mill (QXQM-2, Changsha Tencan Powder Technology Co., Ltd, Changsha, Hunan, China), equipped with four stainless steel grinding pots, each of 250 mL capacity. Compared with the planetary ball mill, this unit adds a dimension of rotation. The whole entity consisting of disk and all pots slowly rotates (1 rpm) around a main spindle to avoid sedimentation and wall sticking, making powders to be ground more completely. A Scheme of the ball mill is presented in the supplementary materials.

Test Procedure: An amount of 14 g of each sample enters into each pot, together with 210 g of stainless balls, so that the weight ratio of ball to sample equals 15:1, only half of the 30:1 referred to in former research (Yan et al., 2007). The pots rotate at a speed of 600 rpm, and their ratio of rotation and revolution speed of disks equals 2:1. The mill operates for 20 h, with a 30-min cooling interval after every 30 min (Nomura et al., 2006). After MCD, the

Table 1
Testing scheme applied to FA, WFA and CWFA.

Sample	Raw Materials		Additives		Initial Concentration	
	Type	Weight, g	CaO, g	Al, g	PCDD/F, ng g^{-1}	WHO-TEQ, pg g^{-1}
1	FA	14	–	–	531	4442
2		12	2	–		
3		12	1.6	0.4		
4	WFA	12	2	–	597	4980
5		12	1.6	0.4		
6	CWFA	12	2	–	528[a]	4407[a]
7		12	1.6	0.4		

[a] Calculated, after adding 8.7% of NaCl and 2.8% of KCl.