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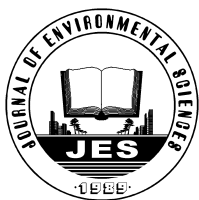
Characterization of mechanochemical treated fly ash from a medical waste incinerator

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Abstract

The mechanochemical treatment of fly ash generated from a medical waste incinerator was subjected to grinding for 2 hr at 400 r/min in a planetary ball mill. The treated fly ash was characterized by a suite of analytical methods including High Resolution Gas Chromatograph/High Resolution Mass Spectrometer, Mastersizer 2000 Particle Size Analyzer, QUADRASORB™ SI Surface Area Analyzer, Scanning Electron Microscopy and X-ray diffraction. Results showed that abatement efficiency of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) in terms of total concentration averagely amount to 76% which was relatively higher than that of I-TEQ concentration averagely amount to 56%; the most concentration of toxic congeners as well as isomers of PCDDs/Fs decreased after mechanochemical treatment. The treated fly ash was characterized by a more homogeneous distribution of concaves as well as the significant decreasing in overall particle size and great enlargement in surface area. The major crystallization phases or intensities were considerably changed by mechanochemical treatment, of which a new phase containing chlorine formed may be a possible factor suggesting chlorination reaction occurring on the crystalline surface.

Key words: PCDDs/Fs; characterization; fly ash; mechanochemical treatment

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Introduction

Numerous studies have been carried out to identify suitable disposal methods for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) (Weber et al., 2002; Flanagan and May, 1993; Volkering et al., 1997; Hawk and Fuller, 1997; Weber and Sakurai, 2001). With either biodegradable methods or some chemical detoxification methods, low detoxification efficiency or long time or expensive costs are the limitations for the detoxification of PCDDs/Fs. Since Hall et al. (1994) observed mechano-chemical (MC) process to dechlorination of DDT by milling with CaO, MC dechlorination has attracted more and more attentions, which has been applied in some organochlorine compounds such as poly (vinyl chloride), chlorinated benzenes, pentachlorophenol, PCBs (polychlorinated biphenyls), dioxins (Mio et al, 2002; Tanaka et al., 2003; Birke et al., 2004; Nomura et al., 2005).

Chemistry occurring at surface under impact is commonly referred as mechanochemistry, which has long been studied and formerly has numerous practical applications in the field of material processing and mining. The standard mechanochemical treatment is normally realized by mechanical agitation of a material within a mill. As MC treatment of organic toxic wastes is a non-combustion technology that requires no heating process or off-gas treatment, it is expected to be more environmental friendly than conventional heating processes.

Since high energy impact between surfaces occurring, for example, stainless balls can produce transient temperature rises of large magnitude and even generation of triboplasma (Annegret et al., 1996), it is hence induces considerable chemical activation, resulting in reactions between the mill charge components. A large amount of energy is released during MC transformation. Some reactions, such as the transformation of calcite into aragonite are induced in the laboratory by a pressure increase up to a maximum of 4.24×10^5 Pa. The same pressures are present during ultra grinding of calcium carbonate, which induces the same transformation (Plescia et al., 2003). An important phenomenon is the formation of amorphous phases during MC transformation. For example, it is well known that quartz grains tend to be covered by coating of amorphous and colloidal silica (Lin et al., 1975). By a continuous and long milling, quartz can change wholly into an amorphous state, as though it has undergone melting, and ultra milling of phyllosilicates leads to progressive release of OH ions, which occurs by heating phyllosilicates at 550–700°C.

MC treatment of DDT (2,2-bis (4-chlorophenyl)-1,1,1-

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trichloroethane), 1,2,3-trichlorobenzene, PCBs, HBB (hexabromobenzene) and OCDD/OCDF (octa-chlorinated dibenzo-*p*-dioxin/octa-chlorinated dibenzofuran) by ball milling in the presence of calcium oxide have been carried out (Annegret et al., 1996; Tanaka et al., 2005; Zhang et al., 2001, 2002; Nomura et al., 2005). Results from these studies demonstrated that the chlorinated aromatic compounds can be thoroughly degraded by MC treatment. The final product is innocuous products, such as graphite like product and some light weight molecular (CH_4, C_2H_6, CO_2) and $CaCl_2$. By investigation of chlorine balance in MC treatment, dechlorination was verified as a major pathway engaging in degradation mechanism (Nomura et al., 2005; Tanaka et al., 2003).

Basic metal oxide plays an important role in dissociating organic chlorine of chlorinated compound to ion-stated chlorine. Many metal oxides (CaO, MgO, CaH_2, Fe_2O_3, δ-MnO_2) have been chosen as reduction agent for degradation of chlorinated compound (Pizzigallo et al., 2004; Nomura et al., 2005; Tanaka et al., 2003). Pizzigallo et al. (2004) demonstrated the simulated soil abiotic compoents (e.g., smectite containing Fe(III), birnessite containing δ-MnO_2) can promote the transformation of aromatic molecules by manual grinding, which implied organic chlorinated compound can be directly degraded without assistance of extra metal oxide.

A question was raised if the toxic organic compounds of PCDDs/Fs and PCBs contained in fly ash can be directly degraded by MC treatment. As calcium compound is the second richest component in fly ash, further more, some minor component of fly ash such as Mg, Fe, Cu, Mn, Ti may also be active in oxidation of organic compound. Fly ash from waste incineration process catalyze the de novo synthesis of PCDDs/Fs at 250–450°C in the presence of oxygen (Hagenmaier et al., 1987), which demonstrated that fly ash can also catalyze the dechlorination/hydrogenation of PCDDs/Fs and other chlorinated aromatic compounds in the same temperature range, but under oxygen deficient conditions. Consequently, direct MC treatment of fly ash can verify the above hypotheses.

In the present study, MC treatment of fly ash generated from a medical waste incinerator was carried out to evaluate the influence of the MC treatment on the PCDDs/Fs contained in fly ash. A series of measurements on PCDD/F isomeric concentration, particle size distribution, surface area, morphology observation for the original fly ash and MC treated fly ash were performed to characterize any changes in their chemical and physical properties.

1 Material and methods

1.1 Fly ash

As the PCDD/F concentration of fly ash of medical waste incineration (MWI) is generally higher than that of municipal solid waste incineration, the former is more harmful to environmental than latter one. Thus, fly ash sampled from a MWI containing high concentration of PCDDs/Fs was chosen to be tested in this work. The fly ash was sampled from the cyclone of a MWI system with disposal capacity of 750 kg/hr, in which no activated carbon was injected into flue gas to control the PCDD/F emission. The original fly ash were dried at 60°C in an oven for 12 hr. I-TEQ and total PCDD/F concentrations of the original fly ash were 15.61 ng ITEQ/g and 183.04 ng/g, respectively.

The elemental composition of the fly ash was given as follows (Table 1): the carbon content was measured by a carbon analyzer (CS600, Leco, USA), the sulphur content was measured by automatic sulphur analyzer (5E-8S, Kaiyuan Analytical Instrument Co., China). The main composition was tested by fluorescence X-ray spectrometer (PW2400, Philips, Holland). Ion chromatography was (792 basic IC, Metrohm, Switzerland) used to analyze chloride ions content. Main composition of the fly ash was measured as C: 18.25%, K_2O: 0.52%, Na_2O: 1.68%, Fe_2O_3: 1.48%, MgO: 2.27%, CaO: 27.31%, TiO_2: 3.46%, Al_2O_3: 6.01%, SiO_2: 23.35%, Cl^-: 8.82%, S: 0.59%.

1.2 MC reactor

The MC reactor was a planetary ball mill (XQM-0.4L, Kexi, China) with four stainless steel pots (100 cm³), and 20 stainless steel balls (10-mm diameter) were arranged in each pot. The pots are situated on a rotating disk, which enables the pots and the disk to rotate in opposite directions. Under atmospheric pressure, 400 r/min for 2-min rotation in clockwise proceeding with a 2 min counter clock rotation and repeated for 2 hr (Fig. 1). The both test and analysis was duplicated to guarantee the results in line with the requirement of quality control.

1.3 Analysis of isomers of PCDDs/Fs

A portion of each milled fly ash was sampled from the pots, and spiked with known amounts of ¹³C isotopically labeled internal standard solution, the sample was then extracted by refluxing with toluene (purity 99.5%; Baker J T, USA) for 24 hr for the extraction of PCDDs/Fs. The procedure for clean-up was conducted in accordance with USEPA method 1613B. Both the original and MC treated fly ash were analyzed to PCDDs/Fs.

All analysis were performed on a high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS) using an Agilent 6890 N gas chromatograph coupled to a JMS-800D mass spectrometer (JMS-800D, JEOL Co, Japan) operated in EI mode. Chromatographic separation was carried out on a 60 m DB-5 quartz capillary column. The temperature program for GC oven was: initial temperature 150°C, held for 1 min; 150–190°C at 25°C/min; 190–280°C at 3°C/min held for 20
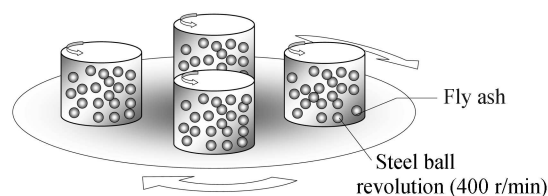

Fig. 1 Scheme of MC treatment.

Fly ash

Steel ball revolution (400 r/min)

min. Carrier gas: helium (99.999%), 1.2 mL/min; 1 µL of the extract was automatically injected in split less mode. Mass spectrum condition: ion source temperature 280°C; interface temperature 280°C; SIM (selective ion monitoring mode); the mass spectrometer was operated at the ionization energy of 38 eV with a resolution higher than 10,000. All the isotope standards were obtained from Wellionton Laboratory, Canada. In the analysis of PCDDs/Fs, ^{13}C-labeled PCDDs/Fs were used as internal standards.

The parameters of retention time and order of eluting for analysis of isomer of TeCDs/TeCFs (tetra-chlorinated dibenzo-p-dioxins/tetra-chlorinated dibenzo-furans) to OCDD/OCDF was chosen based on the work of John et al. (1991). As one chromatography column can not thoroughly separate all the individual isomers, some values in this article was presented as total concentration for the co-eluting isomers.

1.4 Analysis of particle size distribution, surface area, morphology and mineralogy

Both original and MC treated fly ash were measured for the following parameters. The particle size distribution was measured by particle size analyzer (Matersizer-2000, Malvern, US). The surface area was measured by surface area analyzer (QUADRASORB[TM] SI, Quantachrome, USA). The morphology was detected using a scanning electron microscopy (S-570, HITACHI, Japan). The crystalline minerals were identified using X-ray diffraction (XRD) (D-max-2550TC, Rigaku, Japan). The XRD technique used Cu K_α radiation (copper tube operated at 40 kV and 200 mA) on a diffractometer operated at 2θ 0.02°. Crystalline phases were identified by comparing intensities and positions of Bragg peaks with those listed in the joint committee on powder diffraction standards (JCPCS) data files.

2 Results and discussion

2.1 Comparison of PCDD/F homolog

The weight ratio of 1:200 (OCDD/OCDF: CaO) and rotational speed of 700 r/min was chosen for MC treatment of OCDD and OCDF by Nomura et al. (2005), who observed that high percentage of OCDD and OCDF degraded rapidly in early period, and low chlorinated homolog were produced, after 2 hr, 100% OCDD and OCDF were thoroughly degraded. In our work, 400 r/min as the maximal milling speed of the planetary mill was tested, and the weight ratio of calcium to total PCDDs/Fs for FA0 is around 1.49×10^7, which was calculated based on the main composition and total concentration of PCDDs/Fs of original FA. Provided the calcium in the FA was in the form of calcium oxide, they will be quite sufficient to the reaction.

It was observed that the total concentration and I-TEQ concentration of FA1 averagely decreased to 42.47 ng/g and 6.74 ngI-TEQ/g, respectively, which means that the reduction efficiencies for total and I-TEQ concen-

tration of the MC treatment were 76.8% and 56.8%, respectively. Homolog of tetra-octa chlorinated PCDDs/Fs pattern of original and MC treated FA is given in Fig. 2. It can be observed that the reduction of PCDD concentration was greater than that of PCDF concentration, the order of reduction extent and efficiencies in bracket corresponding with homolog were illustrated as octa-chlorinated dibenzo-furan (OCDF) (86.3%) > octa-chlorinated dibenzo-dioxin (OCDD) (86.1%) > tetra-chlorinated dibenzo-furan (TCDF) (58.7%) > tetra-chlorinated dibenzo-dioxin TCDD (55.2%) > penta-chlorinated dibenzo-dioxin (PeCDD) (54.8%) > hepta-chlorinated dibenzo-furan (HpCDF) (50.0%) > haxan-chlorinated dibenzo-furan (HxCDF) (38.8%) > haxan-chlorinated dibenzo-dioxin (HxCDD) (33.2%) > penta-chlorinated dibenzo-furan (PeCDF) (19.2%) > hepta-chlorinated dibenzo-dioxin (HpCDD) (8.4%).

2.2 Comparison of isomer patterns

The PCDD/F isomer patterns were given by Figs. 3 and 4. Comparing FA0 with FA1, it was observed that low chlorinated isomers generally decreased greater than high chlorinated except for OCDD and OCDF. For chlorinated isomers with same chlorination number, the most of them decrease with varied extent, but to some of the isomers did not change in their concentration after MC treatment, and there were still quite few isomers rose in their concentration after MC treatment. The most of the toxic congeners of PCDDs/Fs were reduced after MC treatment with corresponding extent but to 2378TCDF, of which, the concentration increased with some extent. It can be observed the alpha position (1,4,6,9-position) as well as the beta position (2,3,7,8-position) are reduced to approximately same extent in PCDDs/Fs. Nomura et al. (2005) found tetra-, penta-, hexa- and heptachlorodibenzodioxins and -furans were simultaneously degraded, which suggests that a consecutive dechlorination reaction did not occur. In this study, high chlorinated homolog reduced significantly, the next is low chlorinated homolog such as TCDD and TCDF, which can be also concluded that the consecutive dechlorination reaction did not occur.
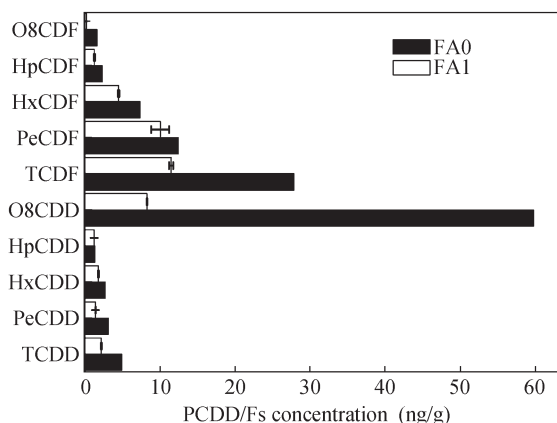

Fig. 2 Comparison of tetra-octa homolog pattern of PCDDs/Fs for original fly ash (FA0) with MC treated fly ash (FA1).
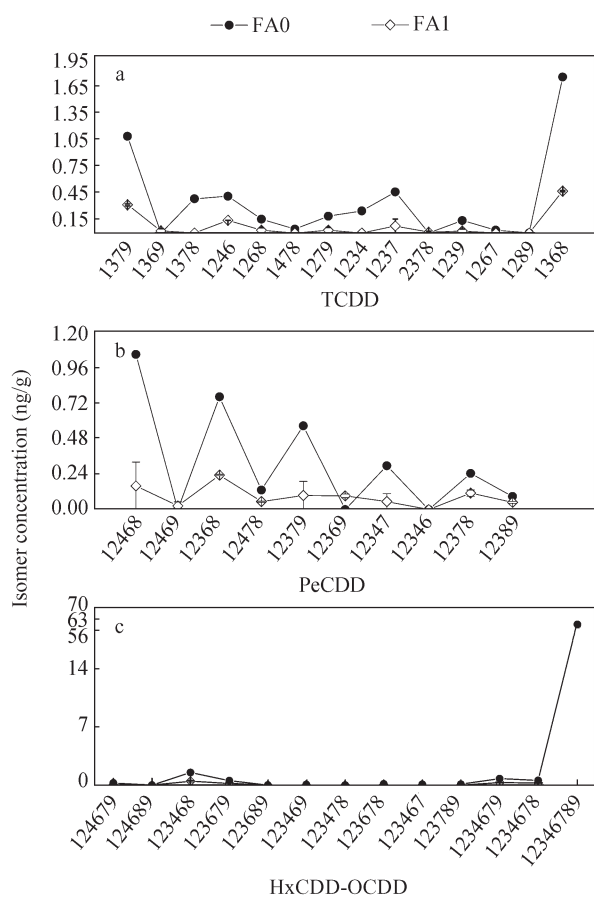
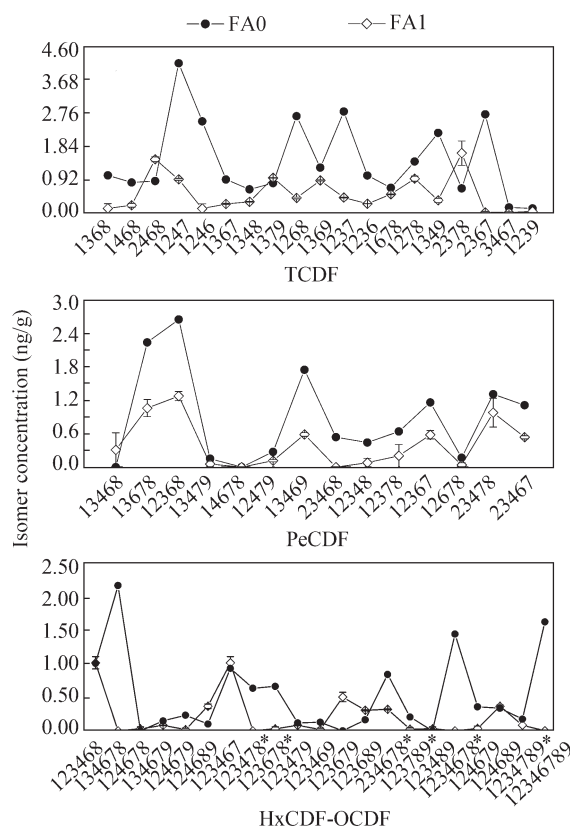**Fig. 3** PCDD isomer pattern of untreated FA0 and FA1.

Fig. 4 PCDF isomer pattern of FA0 and FA1.

2.3 Degree of chlorination for PCDDs/Fs

Many previous literatures (Nomura et al., 2005; Tanaka et al., 2003; Zhang et al., 2001) shown that dechlorination mechanism was mainly engaged in degradation of chlorinated organic compounds. To see how far the dechlorination of PCDDs/Fs has proceeded, the degree of chlorination (d_c) of PCDDs/Fs was calculated by Eq. (1), which is defined as the sum of the products of the mole fraction f_j and the number of chlorine atoms n_j for each homologue.

$$d_c = \sum_{j=4}^{8} f_j \times n_j \tag{1}$$

The degree of chlorination varies from 4.79 for FA0 to 4.64 for FA1. Although the reduction of d_c was not so significant, it still can be concluded from the data that the dechlorination reaction occurs in the degradation mechanism.

2.4 Comparison of particle size distribution

Previous studies have demonstrated that the particle size distribution of the fly ash probably ranged between 2 and 1000 μm (Chang and Chung, 1998). Furthermore, it was reported that over 95% of the particle size distributions of FA were smaller than 149 μm (Mangialardi et al., 1999). In our study, the results were shown in Fig. 5.The three types of diameter describe the overall particle size distribution, i.e, d(0.1), d(0.5), d(0.9), which are in turn represent the particle size of 10%, 50% and 90% of the FA as below. The respective value of FA0 that in turn was 14.210, 51.543 and 146.467 μm. After MC treatment, it was observed that the particle size distributions of parallel samples were changed into Gaussian distribution, and the overall particle sizes were considerably reduced in similar extent, in term of d(0.1), d(0.5), d(0.9) are reduced to 2.422, 11.007 and 62.653 μm for FA1, respectively.

2.5 Comparison of FA morphology and surface area

Figure 6 shows the SEM photography (i.e., 2000 times) of the untreated and MC treated FA to facilitate the understanding and comparison of incineration processes
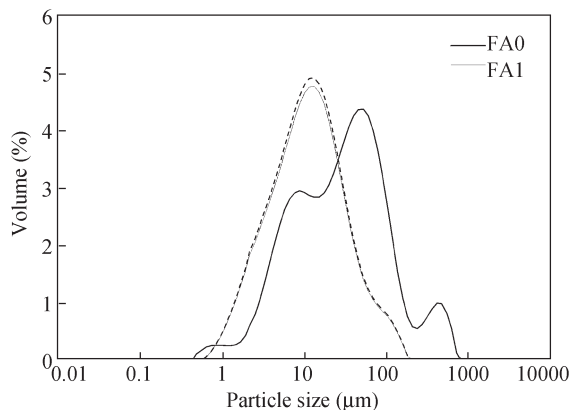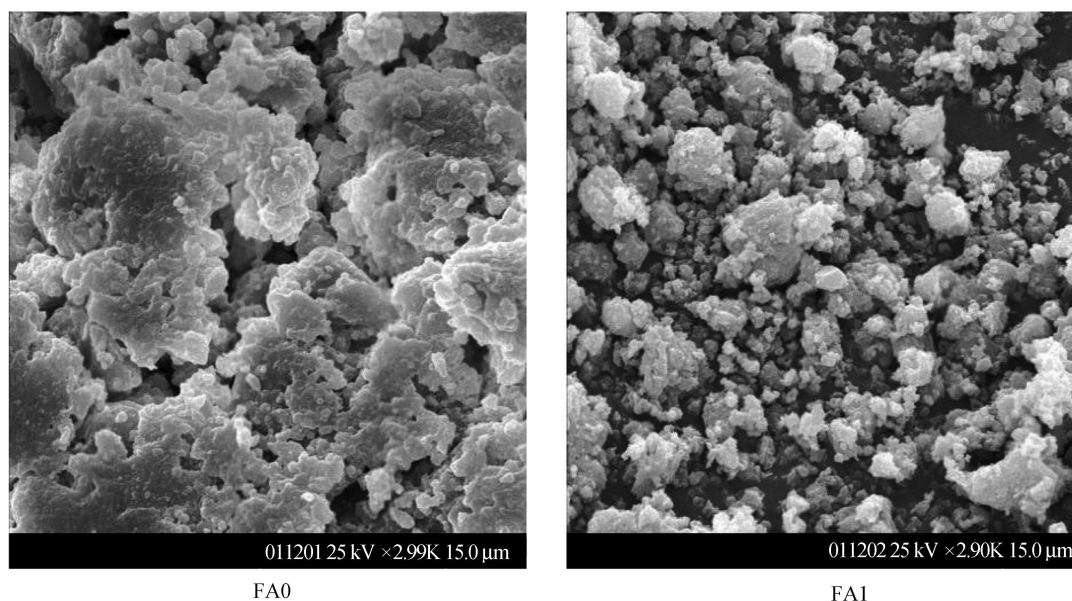

Fig. 5 Particle size distribution of untreated and MC treated FA: FA0 to FA1.

Fig. 6   SEM of untreated FA (FA0) and MC treated FA (FA1).

affecting ash surface structure. Clearly the morphology of the original FA is variable and complex as a result of incineration processes. The shape of FA0 was rippling schistose shape which can be seen in Fig. 6. The both types of treated FA is characterized by more uniform distribution of concaves, agglomerations as well as the similar decreasing in overall particle size by MC treatment. It was elucidated why the particle size distribution became to Gaussian distribution after MC treatment.

The surface area of the untreated and MC treated FA were analyzed as 5.027 m^2/g for FA0, and 61.300 m^2/g for FA1, respectively.

2.6 Comparison of FA mineralogy

In order to identity the possible change in the crystalline phase, XRD was carried out on the untreated FA (FA0) and MC treated FA (FA1). XRD results are shown in Fig. 7. As the composition of FA from MWI is fairly complicated, only the major phases of FA were identified. The complex mineralogy of FA results from several processes, including vaporization, melting, crystallization, vitrification, condensation and precipitation, which occur during the flue gas combustion and treatment (Li et al., 2004; Chang and Wey, 2006) The JCPDS card shows the reflections of seven major minerals in original FA in compare to eight minerals in MC treated FA. The result is coincident with the main composition indicated in Table 1.

According to Bragg peak intensities in XRD results in Fig. 7, the major minerals of original FA (FA0), i.e., halite NaCl, anhydrite $CaSO_4$, calcite $CaCO_3$, Mayenite $Ca_{12}Al_{14}O_{33}$; after MC treatment, halite NaCl remains the richest phase, and the phase of ferrocichterite $Na_2CaFe_5Si_8O_{22}(OH)_{22}$ which was minor in FA0 become second richest phase in FA1, the new phase of wadalite $Ca_{5.67}Mg_{0.24}(Al_{4.44}Fe_{0.48}Si_{2.08}O_{16})Cl_{2.76}$ formed in FA1 was in the third abundance, which may be a factor suggesting dechlorination reaction occurred. The other
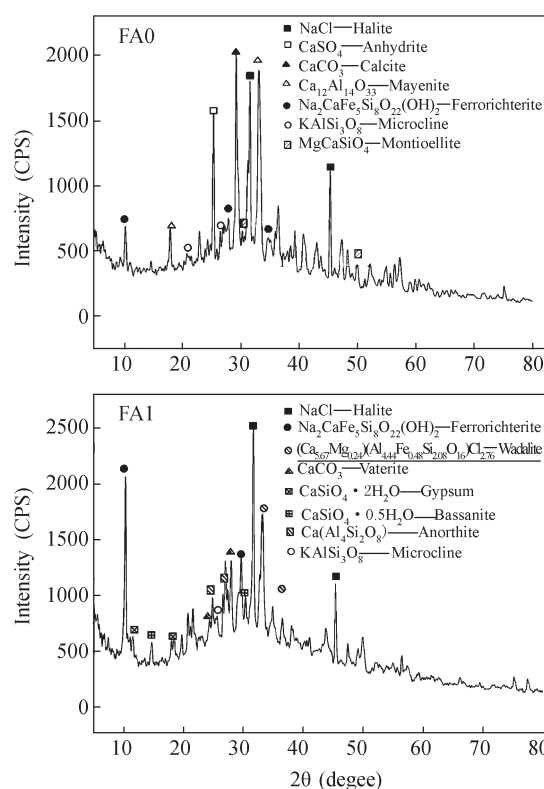

Fig. 7   XRD results of untreated FA (FA0) and MC treated FA (FA1).

phase changes including: calcite $CaCO_3$ vaterite $CaCO_3$, anhydrite $CaSO_4$ gysum $CaSO_4 \cdot 2H_2O$, bassanite $CaSO_4$ $0.5H_2O$. Generally, the major crystallization phases or intensity were changed by MC treatment, which may as well induce chlorination reaction on the crystalline surface.

The most previous studies for MC treatment of chlorinated aromatic compound were based on pure chemical and calcium oxide (Nomura et al., 2005; Tanaka et al., 2003; Annegret et al., 1996), which was quite different from our study. Tanaka et al. (2003) explored the variation

of CaO during trichlorobenzene (TCB) sample grounded with CaO. The $CaCO_3$ and CaOHCl were detected as major products of chlorination and degradation of TCB by XRD. However, CaO and CaOHCl were not detected in either untreated FA or MC treated FA. CaO can be generated by ultra grinding of $CaCO_3$ (Plescia et al., 2003), CaO hence may act as an intermediate product induce the chlorination reaction. Further more, is there any possible that metal oxides (such as MgO, Al_2O_3, Fe_2O_3) are generated as intermediates in MC treatment to cause dechlorination reaction? The XRD results dose not answer the question where chlorine in wadalite ($Ca_{5.67}Mg_{0.24}(Al_{4.44}Fe_{0.48}Si_{2.08}O_{16})Cl_{2.76}$) come from. Does it derive from organic chlorine or inorganic chlorine? In future work, single factor experiment should be carried out by simulated FA which contains controllable composition being grounded with aromatic compound to track the degradation mechanism.

3 Conclusions

The main focus in this work was to investigate the behavior of PCDDs/Fs contained in fly ash by mechanochemical treatment. The MWI fly ash was milled by a planetary mill without addition of reductive agents such as CaO or Fe. The experimental results are summarized as follows:

(1) The PCDDs/Fs of MWI fly ash was observed decreasing after MC treatment, specifically, removal efficiency of PCDDs/Fs in terms of total concentration and I-TEQ concentration for PCDDs/Fs were respectively amount to 76% and 56%. (2) The reduction of PCDD concentration was greater than that of PCDF concentration, and high chlorinated homolog reduced significantly, the reduction intensity of chlorinated homolog from great to weak are in order as OCDF > OCDD > TCDF > TCDD > PeCDD > HpCDF > HxCDF > HxCDD > PeCDF > HpCDD. (3) The MC treated FA is characterized by a more homogeneous state of concaves, agglomerations, and decreasing in overall particle size as well as enlargement of surface area. (4) The major crystallization phases or intensity were changed by MC treatment, of which some new phases containing chlorine formed may be a possible factor suggesting chlorination reaction occurring on the crystalline surface.

Acknowledgments

References

Annegret H, Jack H, Reinhold H, Paul M, 1996. Mechanochemical reaction of DDT with calcium oxide. *Environmental Science and Technology*, 30: 3401–3407.

Birke V, Mattik J, Runne D, 2004. Mechanochemical reductive dehalogenation of hazardous polyhalogenated contaminants. *Journal of Materials Science*, 29: 5111–5116.

Chang B, Chung T, 1998. Dioxin contents in fly ashes of MSW incineration in Taiwan. *Chemophere*, 36: 1959–1968.

Chang Y, Wey Y, 2006. Comparison of the characteristics of bottom and fly ashes generated from various incineration processes. *Journal of Hazardous Material*, 138(3): 594–603.

Flanagan P, May J, 1993, Metabolite detention as evidence for naturally occurring aerobic PCB biodegradation in Hudson River sediments. *Environmental Science and Technology*, 27: 2207–2212.

Hagenmaier H, Kraft M, Brunner H, 1987. Catalytic effects of fly ash from waste incineration facilities on the formation and decomposition of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. *Environmental Science and Technology*, 21: 1080–1084.

Hall K, Rowlands A, Hart J, Ebell G, Donecker P, Street R et al., 1994. Destruction of toxic materials. *Nature*, 367: 223.

Hawk M, Fuller L, 1997. Electrolytic oxidation studies of 2,2'-dichlorobiphenyl using rutherium oxide electrodes, persulfate oxidizers, and UV irradiation. *Waste Management*, 17: 489–495.

John R, Henry S, Luz P, Benjamin L, Jacques H, Yoshito M, 1991. Gas chromatographic separations of all 136 tetra- to octa-polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans on nine different stationary phases. *Journal of Chromatography*, 541: 131–183.

Li M, Xiang J, Hu S, Sun L S, Li P S, Sun X X, 2004. Characterization of solid residues from municipal solid waste incinerator. *Fuel*, 83: 1397–1405.

Lin L, Nadiv M, Grodzian, 1975. Changes in the state of solids and mechanochemical reactions in prolonged comminution processes. *Minerals Science Engineering*, 7: 313–331.

Mangialardi T, Paolini E, Polettini A, Sirini P, 1999. Optimization of the solidification/stabilization process of MSW fly ash in cementitious matrices. *Journal of Hazardous Material*, 70: 53–70.

Mio H, Saeki S, Kano J, Saito F, 2002. Estimation of mechanochemical dechlorinated rate of poly(vinyl chloride). *Environmental Science and Technology*, 36: 1344–1348.

Nomura Y, Nakai S, Hosomi M, 2005. Elucidation of degradation mechanism of dioxins during mechanochemical treatment. *Environmental Science and Technology*, 39: 3799–3804.

Pizzigallo R, Napola A, Spagnuolo M, 2004. Mechanochemical removal of organo-chlorinated compounds by inorganice components of soil. *Chemosphere*, 55: 1485–1492.

Plescia P, Gizzi D, Beneditti S, Camilucci L, Fanizza C, De Simone P et al., 2003. Mechanochemical treatment to recycling asbestos-containing waste. *Waste Managemnt*, 23: 209–218.

Tanaka Y, Zhang Q, Saito F, 2003. Mechanochemical dechlorination of trichlorobenzeneon oxide surface. *Journal of Physical Chemistry*, B107: 11091–11097.

Volkering F, Breure M, Rulkens H, 1997. Microbiological aspects of surfactant use for biological soil remediation. Biodegradation in Hudson River sediments. *Environmental Science and Technology*, 8: 401–417.

Weber R, Sakurai T, 2001. Low temperature decomposition of PCB by TiO_2-based V_2O_5/WO_3 catalyst: evaluation of relevance of PCDF formation and insights into the first step of oxidative destruction of chlorinated aromatics. *Application Catalyst*, 34: 113–127.

Weber R, Takasuga T, Nagai K, Shiraishi H, Sakurai T, Matuda T et al., 2002. Dechlorination and destruction of PCDD, PCDF and PCB on selected fly ash from municipal waste incineration. *Chemosphere*, 46: 1255–1262.

Weber R, Yoshida S, Miwa K, 2002. PCB destruction in subcritical and supercritical water. Evaluation of PCDF formation and initial steps of degradation mechanisms. *Environmental Science and Technology*, 36: 1839–1844.

Zhang Q, Saito F, Ikoma T, 2001. Effects of quartz addition on the mechano-chemical dechlorination of chlorobiphenyl by using CaO. *Environmental Science and Technology*, 35: 4933–4935.

Zhang W, Matsumoto H, Saito F, 2002. Debromination of hexabromobenzene by its co-grinding with CaO. *Chemosphere*, 48: 787–793.