

MECHANOCHEMICAL DECOMPOSITION OF POLYCHLORINATED BIPHENYLS IN SOIL USING BALL MILLING EQUIPMENTS

Lu SY*, Mao QJ, Yan JH, Li XD

State Key Laboratory of Clean Energy Utilization, 38 Zhejiang University Road, Hangzhou, China

Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous persistent contaminants, and are defined as one of the 12 Persistent Organic Pollutants (POPs) subject to the Stockholm Convention⁶. In China, large amounts of PCBs were produced in the past decades¹, as well as the inappropriate treatment of PCBs products, poses a substantial threat of release of PCBs to the environment. A considerable amount of these contaminants can be held in soil in the form of residual saturation and lead to long-term contamination of groundwater².

The current best available remediation technology for PCBs is incineration. However, temperatures of more than 1200°C are required for their safe destruction. These technologies are available only in highly industrialized countries and inappropriate for on-site remediation. Therefore, during the last two decades several alternative non-combustion technologies have been proposed for destruction of PCB³. Recently, the mechanochemical (MC) approaches - having an excellent decomposition performance with a high degree of safety - have been applied to this field.

Planetary mills are chosen for laboratory-scale use. Planetary mills normally feature three or four drums rotating around a common central axis and simultaneously around their own axes. The grinding balls in the drums are subjected to superimposed rotational movements, the so-called Coriolis forces. The difference in speeds between the balls and drums produces an interaction between frictional and impact forces, which releases high dynamic energies⁴. However, the power consumption for maintain pot's revolution cannot be used as effective kinetic energy, Thus, an opinion exists that scaling up for large volumes in a planetary mill is intrinsically impossible⁵. Horizontal ball mill is horizontal cylindrical rotation device. Inside the chamber, there are stage liners and ripple liners as well as steel balls. The shell rotates so as to generate centrifugal force, and this force brings ball to a certain height and then balls drop down by gravity, the impact yields the force to grind the material.

Grinding a mixture of PCBs and CaO with or without quartz was conducted in a planetary ball mill and a horizontal ball mill respectively. Effects of milling time and additives on the degradation efficiency of PCBs were investigated. Laboratory-scale milling in a planetary ball mill leads to the application of medium-scale milling in a horizontal ball mill. Formation of PCDD/Fs during mechanochemical destruction of PCBs was evaluated. The results demonstrate that the problem of PCDF formation can be overcome.

Thus, the aim of the paper is to confirm the effective MC degradation of PCBs, and to test possibilities of the medium-scale horizontal mill for PCBs destruction. Results of grinding of PCB will be presented as an example of laboratory degradation of PCBs and expanded scale degradation of PCBs in a horizontal ball mill.

Materials and methods

The experiments were performed using a planetary ball mill (XQM-0.4L), equipped with thirty $\Phi 9$ mm stainless steel grinding balls in a stainless steel grinding vial within 1 L capacity, and expanded in using a horizontal ball mill, equipped with a $\Phi 450 \times 550$ mm cylindrical mill chamber containing about twenty kilogram stainless steel grinding balls. Grinding ball diameters are between 25-65 mm.

PCB-polluted soil was collected from the topsoil in the locations for the mandatory storage of electrical transformers in Hangzhou, China. These PCBs contaminated soil has a homogeneous homologue distribution of M1CB to D10CB. The CaO (purity 98%; Lotus Chemicals Co., China) and quartz (25~50 mesh, Chemicals Co., China) were used as the additives for MC treatment.

The Test I were performed by grinding of 5 g PCB contaminated soil and 5 g CaO, and the Test II were performed by grinding of 2.5 g PCBs contaminated soil, 2.5 g CaO and 5 kg quartz, in the planetary ball mill, at 400 r/min for various lengths of time, ranging from 1 h to 20 h. Samples of test I were called as P1, samples of test II were called as P2 in this paper.

The Test III were performed by grinding of 5 kg PCB contaminated soil and 15 kg CaO, and the Test IV were performed by grinding of 5 kg PCBs contaminated soil, 5 kg CaO and 10 kg quartz, in a horizontal ball mill, at 40 r/min for various lengths of time, ranging from 2 h to 20 h. Samples of test III were called as H1, samples of test IV were called as H2 in this paper.

GC-MS Analysis: 1 g (for sample P1, P2)/10 g (for sample H1, H2) soil was extracted by hexane. The extracts were injected into a GC-MS (CP-3800/1200L, Varian, USA) for the qualitative analysis of the reaction products generated during the MC experiments. All reaction products were identified in comparison with NIST 2005 databases.

PCB and PCDD/Fs Analysis: After spiking with the ^{13}C -labelled standard mixture (PCBs and PCDD/Fs) for quantification, 1 g/10 g soil was extracted using an Accelerated Solvent Extractor (ASE 200) device. The extraction conditions were: mixture of *n*-hexane: dichloromethane(50:50) (V:V) at a temperature of 185 °C and a pressure of 1500 psi. Three static cycles of 60 min were applied for complete extraction. The clean up procedure was conducted according to USEPA method 1613B and 1668A.

PCB and PCDD/Fs analysis were performed with a high resolution mass spectrometer (JMS-800, JEOL Co., Japan) coupled with a high resolution gas chromatograph (Agilent 6890, USA). The PCBs chromatographic separation was achieved by splitless injection of 1 μL on a 60 m DB-5 quartz capillary column. The gas chromatography oven was programmed as follows: initial temperature 90 °C, held for 1.5 min, increased to 170 °C at 20 °C/min, held for 7 min, increased to 260 °C at 3 °C/min and held for 10 min. Carrier gas: helium (99.999%), 1.2 ml/min. For the PCDD/Fs, chromatographic separation was achieved by splitless injection of 1 μL on a 60 m DB-5 quartz capillary column. The GC oven was programmed as follows: initial temperature 150 °C, held for 1 min, increased to 190 °C at 10 °C/min, increased to 280 °C at 3 °C/min, held for 20 min. Carrier gas: helium (99.999%), 1.2 ml/min. The MS was operated in SIM mode with a resolution higher than 10,000.

Results and discussion

As for the horizontal ball mill, the results in Fig.1 present the concentration levels of total PCBs in soil samples as a function of grinding time, results on WHO-TEQ concentration of the PCBs are given in Fig.2,. The total PCBs concentration of original sample was measured as 1813 $\mu\text{g/g}$ and WHO-TEQ concentration of the

initial PCBs was 11.5 ng/g. The total as well as the WHO-TEQ concentration of PCBs always decreased with time, for both planetary ball mill and horizontal ball milling, shown in Table 1. The destruction efficiency describes the ability of MC means to destroy PCBs during the experimental time, it was calculated as:

$$\frac{PCB_{original} - PCB_t}{PCB_{original}} \times 100\% \quad (1)$$

Table 1 Destruction efficiency of total PCBs and WHO-TEQ concentration

Milling for 20h	Samples	Destruction efficiency of total PCBs	Destruction efficiency of WHO-TEQ
The planetary ball mill	P1	95%	94%
	P2	98%	98%
The horizontal ball mill	H1	65%	73%
	H2	74%	78%

It indicated that the mechanical energy produced in a planetary ball mill is highly effective in the destruction of PCBs, the use of a horizontal ball mill represents a cheap but effective way for the destruction of hazardous polyhalogenated pollutants.

For the same grinding time period the destruction efficiency of H2 was always higher than that of H1. This suggests that PCBs decompose more efficiently while being ground with the aid of quartz. The addition of quartz allows breaking down the agglomerates and therefore reduces the powder sticking on the pot, improving the destruction of PCBs.

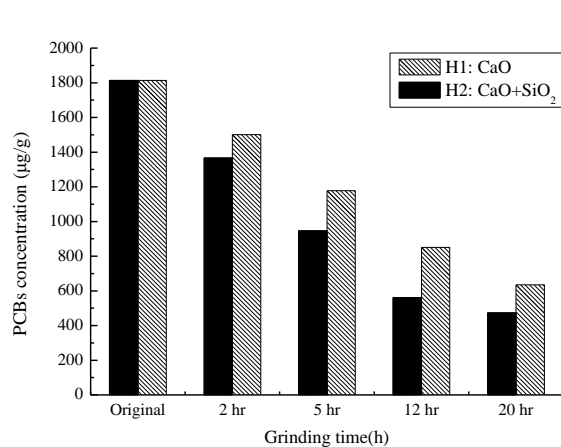


Figure 1

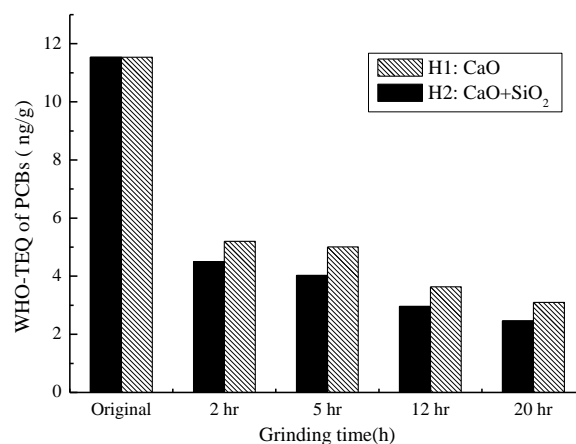


Figure 2

PCBs destruction exhibits a special challenge because PCBs are PCDF precursors and can easily be oxidized into the more toxic PCDFs. Therefore, the formation of PCDD/Fs during destruction of PCBs is an important criterion for evaluation of a PCB-destruction technology³.

The results in Fig.3 present the concentration of toxic PCDD/Fs congeners in soil of H1 as a function of grinding time. The TEQ concentration of PCDD/Fs in original sample was measured as 378 pg/g. After 20 h grinding, the TEQ concentration was decreased to 196 pg/g. The TEQ degradation efficiency of PCDD/Fs was relatively low compared to the degradation efficiency of PCB. As shown in Fig.4, highly chlorinated PCDF congeners have been formed in a few hours time at the beginning, which might be caused by the conversion of

PCBs to PCDFs. The TEQ concentration increased at first 5 h, and then decreased with grinding time. A considerable amount of PCDFs (mainly H₆~O₈CDFs) was formed at the beginning. Since PCDFs have similar chemical structures to PCBs, when prolonging the reaction time PCDFs underwent dechlorination reaction themselves. PCDD congeners were not detected in our results. Under MC conditions, concentration of PCDD/Fs decreased due to dechlorination reaction. The distribution of penta-chlorinated PCDF congeners were decreased and tetra-, hexa-, hepta- and octa-chlorinated congeners were increased after 20 h grinding. H1 showed a slightly higher selectivity in the dechlorination of P₅CDF.

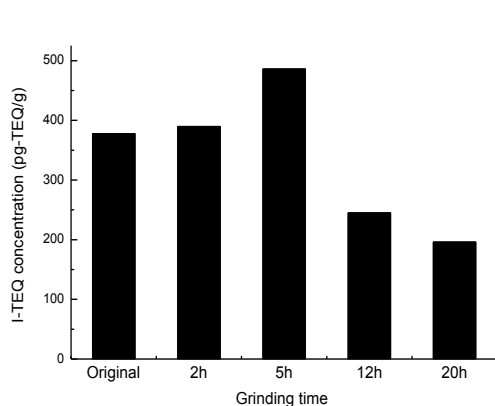


Figure.3 I-TEQ concentration of PCDD/Fs

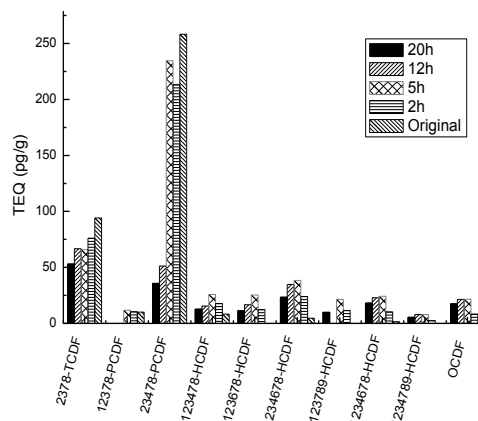


Figure.4 PCDF congeners

The experimental results are summarized as follows:

- (1) The MC means showed high destruction efficiency for total PCBs and WHO-TEQ concentration after 20 h grinding for both the planetary and horizontal ball mill.
- (2) The addition of SiO₂ will help to improve the MC reaction.
- (3) The problem of PCDF formation can be overcome in MC reaction of PCBs.
- (4) The idea of using gravitational field instead of centrifugal acceleration field will highly reduce the enormous energy required. Only by using this type of mill, MC means can be scaled up to an industrial scope or even commercialized.

Acknowledgements

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