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FORMATION OF PXDD/FS (CL OR BR) IN NON-COMBUSTION TREATMENT OF POPS CONTAMINATED SOIL AND ITS PREVENTION

M. Lu[2], T. Lv[1], G. Cagnetta[2], K. Zhang[2], S. Sheng[1], C. Wu[1], J. Huang[2], G. Yu[2]
[1]*CSD Emerging Environmental Technology Center (CETC) (Beijing) Co. Ltd.*
[2]*School of Environment, Tsinghua University*

Introduction

Unintentionally produced persistent organic pollutants (UPOPs) include polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs) are well-known to be generated and released from waste incineration and other industrial thermal processes [1]. The formation mechanism of UPOPs, especially PCDD/Fs has been extensively investigated [2-4]. Facing this issue, the development of alternative non-combustion technologies for POPs degradation has been prompted by international organizations [5-6].

Various non-combustion technologies have been proposed (Fig. 1) [7], however some of them were suspected to have potential to generate UPOPs if the precursors exist and the conditions are in favor of de novo reaction. Nevertheless, owing to data deficiency, detailed assessment with respect to PXDD/Fs (X=Cl or Br) formation of non-combustion technologies is lacking.

In this work, Mechanochemical Degradation technique (MCD) as a promising non-incineration technology, was applied to chlorinated/brominated contaminated soil remediation through loading mechanical forces to induce a chemical reaction in a pilot-scale multi-level successive high-energy milling process. The formation of PXDD/Fs (X=Cl or Br) during the process was investigated, with the key affecting factor identified. In addition, the countermeasures for the prevention of UPOPs were proposed.

Materials and methods

1. Equipment and materials

The multi-level successive high-energy mill (Fig. 2) in series connects 3 levels ball milling reactors, and the volume of each single mill is 60 L. This high-energy mill is a horizontal stirred mill assembled spiral-type stirring blades loading a number of 5 mm diameter steel balls. The main parameters controlled for pollutants destruction include rotation speed, milling time and mass of feedstock.

Clean soil took from the farmland and were collected under the shade to dry, then crush through an 80 mesh sieve. Natural compositions of soil were recognized as dehalogenation removal agents for MCD, such as SiO_2 [8] and CaO [9], accounted for 60 wt. % and 3 wt. % respectively. 100 ppm or 500 ppm target pollutants (PCB and BDE-209) mixed into 15 kg-25 kg clean soil homogenously as feedstock to simulate POPs contaminated soil.

2. Testing method

Using gas chromatography-mass spectrometry (GC-MS QP2010 PLUS, SHIMADZU) for PCB and BDE-209 qualitative and quantitative internal standard; using gas chromatography (Agilent 6890) with external standard.

Analysis of PCDD/Fs were conducted following the HJ 77.1 and HJ 77.3. All the solvents used for analysis were pesticide residue analysis grades, and were purchased from DUKSAN (Geyonggi-do, South Korea). PCDD/Fs were quantitatively determined by an HRGC-HRMS (Agilent 6890N, JEOL JMS-800D).

Results and discussion

The multi-level successive high-energy mill with horizontal stirred ball milling chambers refer to simulation results of IsaMill horizontal stirred ball mill [10], and taking into account the actual daily capacity and other factors, the filling rate in each level was determined between 50%-70%. After the batch experimental study, 15 kg polluted soil and 20 kg milling balls under 400 rpm rotation speed can achieve practical application of POPs disposal with total fill rate of 69%. As a consequence, the removal percentage of PCB and BDE-209 in soil can reach to 90%-97% within 120 min milling time.

1. Formation of PXDD/Fs

Behind high disposal proportion of pollutants, however, the potential risk of secondary-pollution caused by dioxins formation might be always present in the whole MCD process resulting from high local temperature. Urakaev [11] reported the instantaneous (10^{-8}-10^{-9} s) local high temperature in ball mills might be up to 1000 K because of collision impact and attrition. Addink and Olie [3] certified that the lowest temperature of PCDD/PCDFs de novo formation is 473 K. Shaub [12] analyzed concentrations of PCDDs formed from chlorphenol under 500-1500 K temperature in incinerators. It has been found that in 1000 K-1100 K temperature zone concentration of PCDDs achieved a peak value. Thus, these findings indicate that high local temperature during MCD can provide the major requisite to release PXDD/Fs (Cl or Br) with presence of dioxin precursors and products after degradation for de novo formation. In order to estimate the emission of dioxins during MCD for contaminated soil remediation, concentrations of PXDD/Fs (Cl or Br) in treated soil have been analyzed with assembled circulation system passing through the rotation axis. Tap water was injected into hollow axis of each mill, and the temperature of closed loop water would reflect heating-up of rotation axis during MCD process.

When temperature of discharge water from closed loop grew up to 353 K to 363 K, concentration of PCDD/Fs in soil increased from initial 140 ng TEQ/kg to 5500 ng TEQ/kg after 60 min grinding. Similarly, brominated dioxin-like compounds (PBDD/Fs) in BDE-209 contaminated soil after 60 min MCD raised 800 times (240000 ng TEQ/kg) than initial polluted soil (600 ng TEQ/kg). These surprising results demonstrate heating process occurred during milling and dioxin formation took place with POPs degradation. Jayasundara [10] and Yang [13] simulated flow velocity distribution of particles in an IsaMill high speed stirred mill using the Discrete Element Method (DEM). Their findings show that fastest flow velocity with high kinetic energy arises near blades and rotation axis (Fig. 3), which increases the possibility of collision and attrition between particles and blades. In other words, possibility of collision and attrition might consume much kinetic energy to grow the internal energy, and then cause high temperature zone. On the other hand, speeding up flow velocity might also raise the partial high pressure (1-10 GPa) [11] so that local temperature soars instantaneously. Therefore, temperature growth of axis has certified above-mentioned simulation results. Sharp increase of PXDD/Fs verified prediction of Weber's [7] on potential dioxin formation of non-combustion technologies. Breaking the public recognition, non-combustion technologies indeed present risk on secondary-pollution of UPOPs.

2. Prevention of PXDD/Fs

We have proclaimed that high local temperature nearby rotation axis and blades might lead to promoting of UPOPs formation. In accordance with this discussion, an efficient controlling approach is cooling down the temperature of MCD system. Cooling system was assembled with a flow of 273 K-283 K water passing through every axis continuously. The discharge water was always controlled below 308 K.

Comparing to initial PXDD/Fs concentration of contaminated soil (Fig. 4), PXDD/Fs TEQ was not only without obvious increase but also much lower than initial concentration. To be specific, when 100 ppm PCB oil mixed into 15 kg clean soil, PCDD/Fs concentration of soil raised from 0.43 ng TEQ/kg to 140 ng TEQ/kg because of inherent PCDD/Fs in PCB oil [14]. After MCD treatment with cooling system, PCDD/Fs concentration of final remediated soil after 120 min was only 7.2 ng TEQ/kg. Destruction of 132.8 ng TEQ/kg PCDD/Fs indicates cooling system was helpful to restrain formation of UPOPs, and more important that MCD could destruct UPOPs as well. Similar results can be found out for BDE-209 contaminated soil. Concentration of PBDD/Fs was 600 ng TEQ/kg since 100 ppm pollutant mixed into clean soil. However, after MCD remediation, only 0.47 ng TEQ/kg PBDD/Fs can be detected with corresponding 97% BDE-206 removal percentage, which had approximately same concentration as clean soil.

Conclusion

Based on framework of numerous announced non-combustion technologies, there is always concern on potential risk of unexpected UPOPs which are by-products accompanying to combustion technologies. In this study, MCD for polluted soil remediation in pilot-scale gives a success model for non-combustion POPs disposal technology. Moreover, it has been confirmed that MCD non-combustion technology is not "SAFE" for avoiding UPOPs by-products formation unless applying temperature controlling. Under low milling temperature MCD process can not only remove POPs pollutants but also destruct inherent toxic UPOPs.

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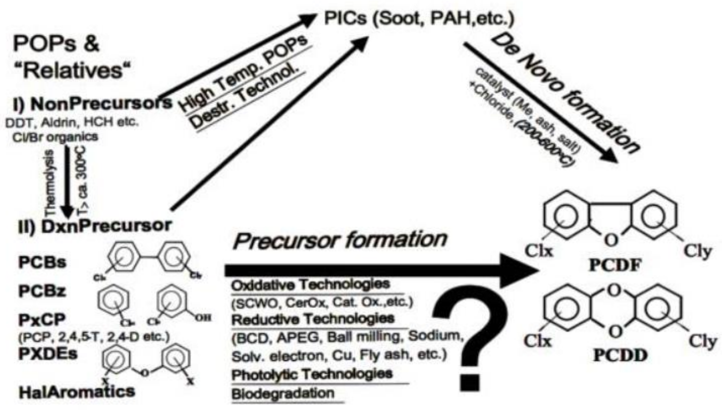
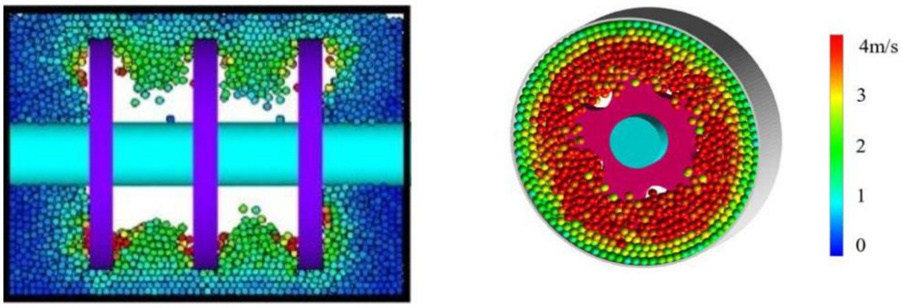


Fig. 1 Potential relevance of PCDD/PCDFs formation pathways for POPs destruction technologies [7]

Fig. 2 Appearance of multi-level successive high-energy mill



(a) (b)

Fig. 3 Flow velocity distribution of particles in IsaMill from the views of horizontal (a) and vertical (b) sections [10]

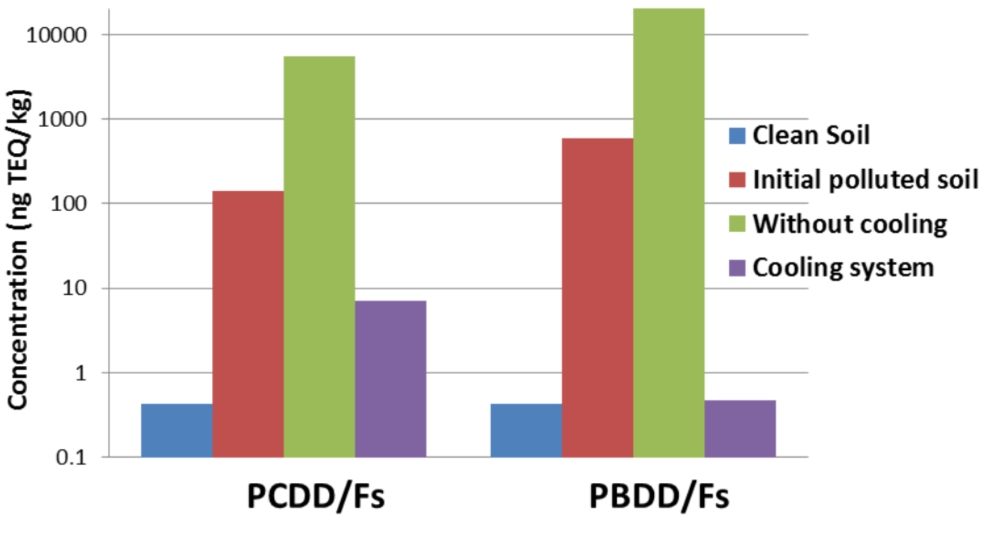


Fig. 4 Concentration of PXDD/Fs (Cl or Br) under different water system.