DEGRADATION OF DIOXIN-LIKE CONGENERS IN FLY ASHES VIA PYROLYSIS

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Introduction

Fly ashes in Taiwan are mainly from municipal waste incinerators (MWIs), electric arc furnaces (EAFs) and secondary metal smelting processes. Typically, they are categorized as hazardous wastes and have to be treated before their releases due to high concentrations of dioxin-like compounds and heavy metals. A study conducted by Taiwan EPA indicates that the amount of fly ash generated by MWIs and EAFs is more than 700 kilotons, accounting for 62% of total annual yield of hazardous wastes in Taiwan (based on 2005)[1]. Pyrolysis typically takes place under high-temperature and O_2-deficient condition. When nitrogen is applied as the carrier gas, dechlorination and dehydrogenation of PCDD/Fs take place significantly, some literatures also tested PCDD/F destruction with different conditions [2,3,4,5]. Furthermore, metal additives, such as Cu, Cu_2O, Fe_2O_3…etc., were also added into the pyrolysis system for enhancing PCDD/F removal [6,7]. Relevant literatures indicated dechlorination of PCDD/Fs can be enhanced with adding basic materials [8,9]. In contrast to metal additives, CaO and $Ca(OH)_2$ are inexpensive and easy to obtain. This study aims to understand the pyrolysis characteristics of dioxin-like congeners (including PCDD/Fs and dioxin-like PCBs) with adding $Ca(OH)_2$ or CaO as basic material.

Materials and methods

Three kinds of fly ashes were evaluated for the removal efficiencies of dioxin-like congeners by pyrolysis in this study. Three types of fly ash including bag filter (BF) ash of MWI, EAF and secondary copper smelter (SCS) with initial concentrations of 3.66, 1.85 and 22.0 ng-TEQ_{WHO}/g, respectively, are tested. Their concentrations are significantly higher than the standard of hazardous materials (1.0 ng-TEQ/g). Lab-scale pyrolysis module used in this study is shown in Figure 1. For controlling pyrolysis temperature, a thermometer is used to detect the temperature of fly ash tested. This study is motivated to understand the removal characteristics of dioxin-like congeners with different ashes and basic additives of $Ca(OH)_2$ or CaO. Typically, 1 g ash was tested at 320^{o}C with 0.1 slpm N_2 as carrier gas. The samples were spiked with known amounts of Method 1613 and Method 1618a labelled standards following quantification standards, and then analyzed for seventeen 2,3,7,8-substituted PCDD/F congeners and twelve dl-PCBs with high resolution gas chromatography (HRGC) (Thermo Trace GC) /high resolution mass spectrometer (HRMS) (Thermo DFS) using a fused silica capillary column DB-5 MS (60 m x 0.25 mm x 0.25 μm, J&W). TEQ concentrations of PCDD/Fs and dl-PCBs are calculated with WHO_{2005}-TEF.

Results and discussion

Removal efficiencies of PCDD/Fs and dl-PCBs with $Ca(OH)_2$ or CaO as additive are shown in Figure 2. As the basic additive in fly ash is increased from 5% to 10%, mass removal efficiencies of dioxin-like congeners increase (Figure 2 (a) and (b)). However, TEQ removal efficiencies were significantly lower than that of mass removal efficiencies. It may be attributed to the significant dechlorination found by the difference of removal efficiencies between highly (6-8 Cl) and lowly (4-5 Cl) Cl-substituted congeners. Significant formation of 2,3,7,8-TeCDD is found for the MWI fly ash as 5% $Ca(OH)_2$ is added. Similar trends are also found for other ashes.

In contrast to $Ca(OH)_2$ as basic additive, degradations of dioxin-like congeners as CaO is added are significantly different, especially for BF ash of MWI. Figure 3 shows the removal efficiencies of seventeen 2,3,7,8-substituted chlorinated congeners with different CaO contents. The removal efficiencies of lowly Cl-substituted congeners, including dioxins and furans decreased while that of highly Cl-substituted congeners increased. Significant formation of 2,3,7,8-TeCDD and 1,2,3,7,8-PeCDD was observed in MWI fly ash and the removal efficiencies of these two congeners interestingly decreased with increasing CaO content. 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF were also observed with the same trend, but were not as significant. However, lowly Cl-substituted PCDD/Fs are of higher TEF and TEQ removal efficiency of dioxin-like congeners of MWI ash slightly decreased from 85.0% to 75.8% as CaO content is increased from 5% to 20%, even though total mass removal efficiency increased with increasing CaO content.

This phenomenon may be attributed to the fact that higher dechlorination potential is found with adding $Ca(OH)_2$ compared with adding CaO. Firstly, the mass removal efficiencies of dioxin-like congeners with adding $Ca(OH)_2$ were higher than that with adding CaO (Figure 2). Secondary, formation of lowly Cl-substituted congeners were significantly found as 5% basic additives was added, but TEQ removal efficiency was significantly increased with increasing $Ca(OH)_2$ content in fly ashes. In contrast to $Ca(OH)_2$, total TEQ removal efficiencies of dioxin-like congeners in fly ashes sampled from MWI and EAF decrease with increasing CaO content in fly ashes (Figure 2 (d)).

Regrading 12 dl-PCBs, removal efficiencies of 2,3',4,4',5-PeCB, 2,3,4,4',5-PeCB and 2,3,3',4,4'-PeCB in fly ash sampled from MWI and EAF were significantly lower than other congeners as $Ca(OH)_2$ was added. Slight formations of 2,3',4,4',5-PeCB, 2,3,4,4',5-PeCB and 2,3,3',4,4'-PeCB in EAF fly ash were found with 5% of $Ca(OH)_2$ content. However, removal efficiencies of dl-PCBs in MWI and EAF ashes increased with increasing $Ca(OH)_2$ content. But SCS ash has different trend. As CaO was added into MWI ash, removal efficiencies of 4-5 Cl-substituted dl-PCBs decreased with increasing CaO content. This is similar to the PCDD/Fs.

Significant difference of dioxin-like congener removal efficiencies from SCS ash was obversed for two kinds of basic additives. As CaO was added into SCS ash, total TEQ removal efficiency increased from -7.8% to 34.7% with increasing CaO content, but there were no significant difference in removal efficiencies of dioxin-like congeners with different $Ca(OH)_2$ content. Removal efficiencies of lowly Cl-substituted congeners in SCS ash were close to that of highly Cl-substituted congeners compared with MWI ash and EAF ash. Table 1 shows copper content and chloride content of fly ashes tested in this study. SCS ash had relatively higher copper content and chloride content. Chlorine can be released from chlorinated aromatics by pyrolysis, but the empty sites of aromatics after dechlorination/dehydrogenation may bond with free chlorine. This may explain why there is no significant differences in removal efficiencies of Cl-substituted congeners in SCS ash between lowly and highly Cl-substituted congeners, but more study is needed to confirm this hypothesis.

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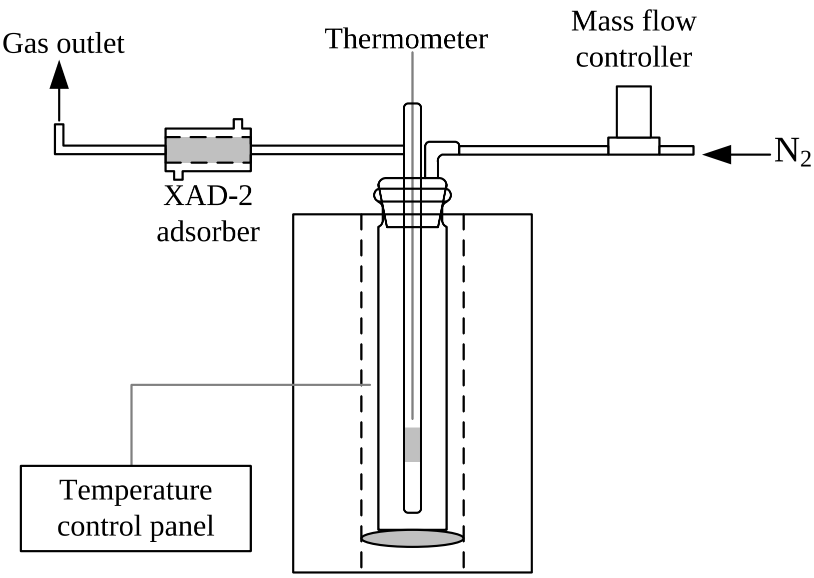

Figure 1. Pyrolysis system applied in this study

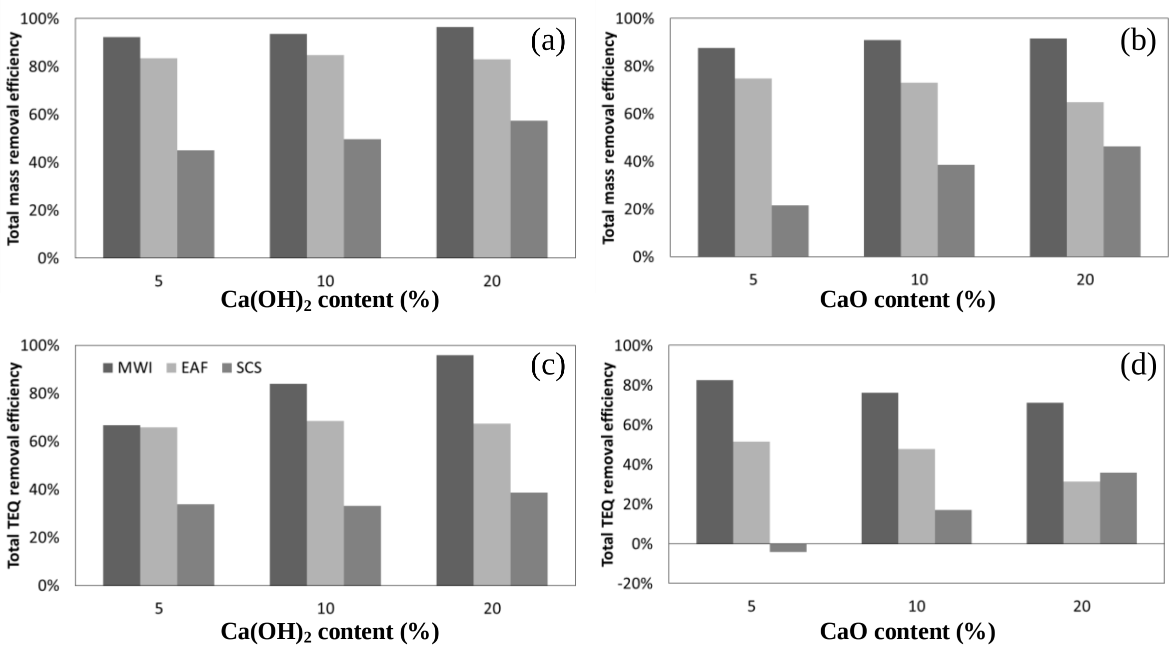

Figure 2. Total mass and TEQ removal efficiencies of dioxin-like compounds with $Ca(OH)_2$ or CaO as additive

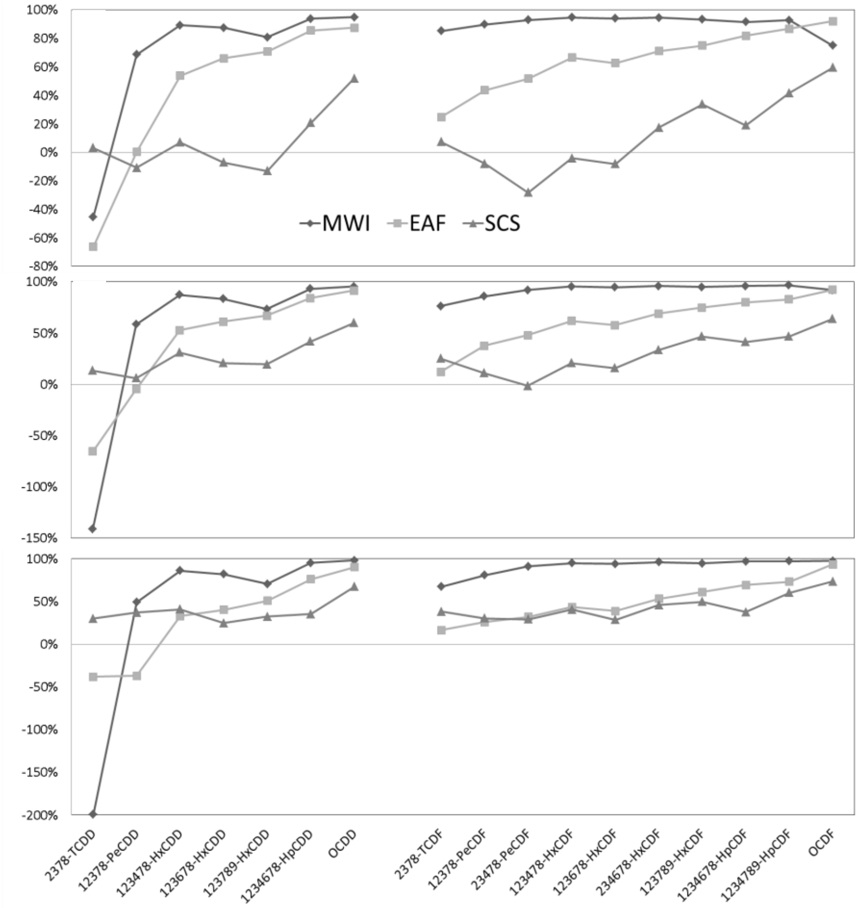

Figure 3. Removal efficiencies of seventeen 2,3,7,8-substituted chlorinated congeners with different contents of CaO: (a) 5%; (b) 10%; (c) 20%

Table 1. Characteristics of fly ashes tested in this study

Ash source	Copper content (%)	Chloride content (μg/g)
MWI	0.06	288
EAF	0.18	4.7
SCS	0.49	770