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Reducing PCDD/F formation by adding sulfur as inhibitor in waste incineration processes

Moo Been Chang*, Yao Chiang Cheng, Kai Hsien Chi

Graduate Institute of Environmental Engineering, National Central University, Chungli 320, Taiwan

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Abstract

The results obtained in this study indicate that addition of sulfur in incineration processes could effectively reduce PCDD/F formation. PCDD/F formation is reduced dramatically (54.1%) when S/Cl molar ratio is controlled at about 2 in a laboratory-scale system (LSS). The XRD analysis of the fly ash confirms the existence of vulcanized metals such as Cu_2SO_4, Cu_2S, SnS and ZnS. The results suggest that the sulfur added would poison Cu-based metals and render the Deacon reaction catalyst less active, thereby reducing PCDD/F formation. In addition, the results obtained from the tests conducted in an industrial waste incinerator (IWI) indicate that the efficiency of reducing PCDD/F formation by adding sulfur was 51.6% at S/Cl mole ratio of 0.4. The results indicate that adding too much sulfur would actually increase particle concentration and also increase PCDD/F yield. This study demonstrates the effectiveness of adding sulfur as an alternative technology for reducing PCDD/F emissions from waste incineration processes. The efficiency of reducing PCDD/F formation by addition of sulfur is strongly influenced by S/Cl mole ratio.

Keywords: Dioxin; Industrial incinerator; Inhibition; Sulfur

1. Introduction

Concerns over formation of polychlorinated dibenzo-*p*-dioxions (PCDD) and polychlorinated dibenzofurans (PCDF) in municipal and industrial waste incineration processes have led to increasingly stringent regulatory limitations on their emissions globally. Numerous factors (such as oxygen contents, temperature, catalytic metal, chlorine source, and residue carbon) would affect PCDD/F formation in the waste incineration process (Dickson et al., 1992; Stieglitz and Vogg, 1987; Milligan and Altwicker, 1993). De Novo synthesis and precursor reaction are two major mechanisms which had been identified for PCDD/F formation during waste incineration processes. In addition, Cu and Fe have been recognized as effective catalysts in PCDD/F formation from carbon, and copper is approximately 20 times stronger as a catalyst compared with iron (Addink and Olie, 1995).

* Corresponding author. Tel./fax: +886 3 4226774.
E-mail address: mbchang@ncuen.ncu.eu.tw (M.B. Chang).

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To effectively remove PCDD/Fs from flue gases, three methods have been commonly used as engineering practice to either inhibit PCDD/F formation or to remove PCDD/Fs from gas streams. They include: (1) applying activated carbon to adsorb PCDD/Fs, (2) decomposition with De-dioxin catalysts, (3) addition of inhibitors. Among the three methods mentioned above, spraying of powdered activated carbon (PAC) into gas streams or installing a fixed-bed activated carbon system to adsorb PCDD/Fs from waste gas streams is considered as the simplest one. Nevertheless, some problems exist in controlling PCDD/F emissions from incinerators with activated carbon injection (ACI). Previous study (Chang and Lin, 2001) indicates that ACI technology can effectively reduce the flue gas PCDD/F concentrations, but actually increases the total PCDD/F discharge (including those existing in fly ash and flue gas) from municipal waste incinerators (MWIs) because it brings extra carbon source to the system. Additionally, SCR can be used as a decomposer to remove residual PCDD/Fs and as a denitrificator to reduce NOx as well. SCR is optional, depending on the efficiency needs to be achieved for NOx and dioxins. However, it is essential to raise the temperature of the waste gases entering SCR to 250–400 °C for effective NOx and PCDD/F removal (Kim et al., 2001). As a result, applying SCR for controlling PCDD/F emissions can be energy-consuming and costly to install and operate in incineration processes.

Inhibition of PCDD/F formation could be more cost-effective than the end-of-pipe control methods for reducing PCDD/F emission from combustion/incineration processes, however, detailed investigations are quite limited. Significantly lower levels of PCDD/F emissions were typically measured from coal-fired combustors compared with those from municipal/industrial waste incinerators. Griffin (1986) proposed that the high sulfur content of coal was the major cause leading to the low PCDD/F emission from coal combustion. Measurements of PCDD/F emissions from coal combustion have suggested that these sources were relatively insignificant (Rigg et al., 1995). Possible reaction mechanisms for reducing PCDD/F formation by adding sulfur-containing compounds could be summarized as follows: (1) decrease of chlorination lowers its reactive capability in generating dioxins (Raghunathan and Gullett, 1996; Bruce et al., 1991), (2) depletion of molecular chlorine (Cl_2) by SO_2 through gas-phase reactions and poisoning of Cu catalysts by SO_2 to form $CuSO_4$ which have been identified as major mechanisms of sulfur inhibition (Gullett et al., 1992), (3) sulfur might vulcanize phenolic precursors to form sulfur-containing compounds such as dibenzothianthrene and dibenzthiophene which were structurally similar to PCDD/Fs (Tuppurainen et al., 1998). Ogawa et al. (1996) and Tuppurainen et al. (1998) elucidate the mechanism of inhibiting PCDD/F formation by adding sulfur. The first postulated role of sulfur is to convert the chlorinating agent (Cl_2) into HCl that is less likely to undergo aromatic substitution to produce PCDD/Fs or their precursors (as shown is reaction (1)). The second possible role played by sulfur is to react with Deacon reaction catalysts, such as CuO to alter their ability to produce Cl_2 (as shown in reaction (2)). Note that the Deacon reaction for chlorine production is probably a two-step mechanism (as shown in reactions (3) and (4)).

$$Cl_2 + SO_2 + H_2O \rightarrow 2HCl + SO_3 \quad (1)$$

$$CuO + SO_2 + 1/2O_2 \rightarrow CuSO_4 \quad (2)$$

$$2Cu + 1/2O_2 \rightarrow Cu_2O \quad (3)$$

$$Cu_2O + 2HCl \rightarrow 2Cu + H_2O + Cl_2 \quad (4)$$

In this study, a laboratory-scale experimental apparatus (LSS) and industrial waste incinerator (IWI) are used individually to investigate the inhibition of PCDD/F formation by adding elemental sulfur.

2. Experimental

This study consists of two parts in which one involves adding different amounts of elemental sulfur into the fly ash to evaluate its effectiveness in inhibiting PCDD/F formation in incineration process with a laboratory-scale experimental setup. The second part involves mixing appropriate amounts of elemental sulfur with industrial wastes being incinerated in an industrial waste incinerator (IWI) for evaluating its effectiveness in inhibiting PCDD/F formation. A brief description is provided below.