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Suppression of dioxins after the post-combustion zone of MSWIs

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ABSTRACT

Thiourea was selected as representative of combined S- and N-inhibitors and injected after the post-combustion zone of two full-scale municipal solid waste incinerators (MSWIs) using a dedicated feeder. Firstly, the operating conditions were scrutinised by monitoring the concentrations of SO_2, NH_3 and HCl in the clean flue gas. The suppression experiment showed that in MSWI A thiourea could reduce the total I-TEQ value in flue gas by 73.4% from 1.41 ng I-TEQ/Nm^3 to 0.37 I-TEQ/Nm^3, those in fly ash by 87.1% from 14.3 ng I-TEQ/g to 1.84 I-TEQ/g and the total dioxins emission factor by 87.0 wt.%, with a (S + N)/Cl molar ratio of 9.4. The suppression efficiencies of PCDD/Fs in flue gas and fly ash in MSWI B could be up to 69.2% and 83.0% when the (S + N)/Cl molar ratio attained 7.51. Furthermore, the congener distributions of dioxins were also analysed in the flue gas and fly ash, before and after addition of thiourea, to find cues to some suppression mechanism. In addition, the filtered fly ash was explored by the Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS) analysis of fly ash. These results suggest that poisoning the metal catalyst and blocking the chlorination are most probably responsible for suppression.

1. Introduction

In 2013, the number of MSWI plants operating in China has reached 166, with a total disposal capacity of 158,000 ton/d (NBSC, 2014). However, every project proposal for a newly planned municipal solid waste (MSW) incinerator has received fierce opposition from the public, with reference to the harmful flue gas emissions into the atmosphere, including heavy metals in fly ash, acid gases, persistent organic pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs). Especially, the polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), or "dioxins" are a frequent public concern, labeled by some as "Poison Substance of the Century" (Gullett et al., 1990; Gao et al., 2009; Ni et al., 2009). They were first discovered and reported in fly ash and flue gas from MSW incineration by Olie et al. (1977).

Three theories were considered for dioxins formation during waste incineration (Hutzinger et al., 1985; Tuppurainen et al., 1998; McKay, 2002; Stanmore, 2004): (i) survival, from PCDD/Fs originally present in the furnace feedstock, MSW; (ii) formation from precursor compounds (Babushok and Tsang, 2003; Evans and Dellinger, 2005); (iii) formation from *de novo* synthesis starting from carbon in fly ash, (Cunliffe and Williams, 2009). Also, a large number of studies have been conducted regarding the possible formation and destruction of PCDD/Fs and the addition of chemical suppressants has been proven to be one of the most effective ways for reduction of their formation.

As early as 30 years ago, SO_2 has been observed to strongly suppress PCDD/Fs formation, possibly via reducing elemental chlorine at the source (Griffin, 1986). Also in laboratory tests continuous feeding of S- or N-compounds was found to be effective. Few suppression tryouts have been completed at full-scale, however, especially for N-compounds. Until now, mixing inhibitors with waste has been an acceptable and convenient way to suppress PCDD/Fs formation, and it was applied in some circumstances. As reported, the suppression efficiency by adding S-compounds into medical waste incinerators could reach 51.6% when the S/Cl molar ratio was 0.4 in the flue gas. Additionally, the suppression value would increase to 54.4% when the S/Cl molar ratio was 1.3 by mixing FeS and $(NH_4)_2SO_4$ with waste (Chang et al., 2006; Wu et al., 2012). The suppression efficiencies were significantly affected by aggregates of factors, such as stability of the incineration system (Aurell et al., 2009a, 2009b), the injection temperature and method (Tuppurainen et al., 1999; Ruokojârvi et al., 2004; Shao et al., 2010a, 2010b), the characteristics of the inhibitors (Samaras

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et al., 2000; Pandelova et al., 2007), their amount (Chang et al., 2006) and the extent and quality of the contact surface between inhibitors and flue gas (Ruokojârvi et al., 2001). Considering the complex composition of waste in China, it is better not to mix inhibitors directly with waste, in case pre-reactions between them are possible (Hunsinger et al., 2007). Moreover, the high temperature in the furnace and during post-combustion seems not to be beneficial for PCDD/Fs suppression. Therefore, injection of inhibitors after the post-combustion region with a specific and dedicated feeder could be a much better way than high temperature suppression. Firstly, the feeder could control the flow rate of inhibitor powder more easily. Secondly, the inhibitor would suppress the formation of PCDD/Fs directly. The suppression effect of injecting thiourea with the Selective Non-Catalytic Reduction (SNCR) system has been investigated, showing a reduction of 55.8 and 90.3 wt.% of dioxins in flue gas and fly ash, respectively (Lin et al., 2015). Injection with a SNCR system addresses a high temperature flue gas. A higher suppression efficiency could be expected when an injection position was adopted at a lower temperature, at the entrance of the convection section.

As to the suppression mechanism, poisoning the metal catalyst and blocking the chlorination are widely accepted for S-inhibitors (Raghunathan and Gullett, 1996; Gullett et al., 1992; Addink and Altwicker, 1998). Similarly, N-inhibitors could undergo complex reactions with the metal catalyst, forming strongly bonded organometallic nitride complexes resulting in irreversible deactivation of catalytic sites (Tuppurainen et al., 1999; Luna et al., 2000). The suppression mechanism of combined S- and N-compounds, which have shown high inhibition efficiency was also investigated in laboratory, indicating that they combine the effect of S-inhibitors and N-inhibitors (Chen et al., 2014; Fu et al., 2015). Moreover, the high temperature suppression tests in a full-scale incinerator plant showed that poisoning the metal catalyst and blocking chlorination are probably responsible for suppression (Lin et al., 2015). However, until now no tests were conducted to specifically certify the possible suppression of the heterogeneous synthesis of PCDD/Fs by injecting these compounds into the dioxins synthesis temperature window of full-scale incinerator plants.

In this study, thiourea was selected as representative of S- and N-inhibitors and it was injected into the dioxins synthesis temperature window of two full-scale MSWI plants with a feeder. These two MSWI plants, with 800 and 600 ton/d MSW disposal capacity, are named MSWI A and MSWI B, respectively. Both are based on a circulating fluidised bed design. At first, the operation condition of MSWI A and MSWI B was checked by monitoring the concentrations of SO_2, NH_3 and HCl in the clean flue gas. The corresponding (S + N)/Cl molar ratios was calculated and analysed. Then the suppression efficiency of dioxins as well as their congener distribution were also investigated in flue gas without and with addition of thiourea, in both of the MSW incinerators. In addition, the possible suppression mechanism regarding the heterogeneous synthesis of PCDD/Fs was explored by analysing the fly ash using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS).

2. Materials and methods

2.1. MSWI

The tests were carried out in two full-scale circulating fluidised bed (CFB) MSW incinerators situated in Zhejiang province. The disposal capacities of these two incinerators were 34 and 25 t/h per line and they are referred to MSWI A and MSWI B, respectively. MSWI A eliminates MSW without any addition of auxiliary fuel (coal), despite the high moisture content of MSW. It included a furnace, a secondary combustion chamber, a cyclone separator, a secondary combustion chamber and an air pollution control device (APCD). The APCDs include a semi-dry spray neutraliser, an activated carbon (AC) contacting chamber and finally a baghouse filter, to control both gaseous and particulate pollutants. Details of the description of MSWI A can be found in a previous paper (Lin et al., 2015). Compared with MSWI A, a secondary combustion chamber is not present and the arrangement of heat exchangers in the boiler system are much more compact in MSWI B. Each MSW incinerator has a SCNR system, installed at the inlet of the cyclone separator to reduce the emission of NO_x. It comprises 4 sets of spraying nozzles, through which an aqueous ammonia solution is injected into the flue gas. The injection temperature of aqueous ammonia in the flue gas varies between 850 and 950 °C and the injection pressure of the nozzle varies between 0.15 and 0.60 MPa.

The injection position of the inhibitors should not point at the heating surface directly to avoid erosion (Boonsongsup et al., 1997; Iisa et al., 1999; Glarborg and Marshall, 2005; Hunsinger et al., 2007; Hunsinger and Andersson, 2014). Moreover, the high negative pressure inside the boiler should be taken into account to ensure the continuous injection of inhibitor by the feeder.

2.2. Experimental set-up

The suppression effect of thiourea was determined by comparing the PCDD/F concentration in the cleaned flue gas and the fly ash separated, with (inhibition tests) and without (normal condition) thiourea injection. The amount of thiourea injected was controlled at 34 and 25 kg/h for MSWI A and B, respectively, accounting for 0.1 wt.% of the MSW for disposal. In the meanwhile, thiourea was injected into the flue gas after the low temperature superheater at a flue gas temperature of 450 °C. For MSWI A, the amounts of AC and lime injected into the flue gas were set at 150 and 3000 mg/Nm^3, respectively. As shown in Table 1, the flow of fly ash and stack gas amounted to 2.55 t/h and 120,000 Nm^3/h, respectively. As to MSWI B, the flow rates of AC and lime were 175 and 2500 mg/Nm^3 and the emission amounts of fly ash and stack gas were 2.00 t/h and 100,000 Nm^3/h, respectively.

The operating temperature of the incineration system is shown in Table 2. The combustion chamber temperature of both MSW incinerators was higher than 850 °C, showing a sound treatment temperature for MSW. However, compared with MSWI B, the combustion condition was not stable with a fluctuating temperature for MSWI A. Therefore, the emission level of PCDD/Fs was expected to be rather high in the MSWI A.

The tests were conducted with the MSWI operating normally, avoiding any uncontrolled factors. The inhibition tests were conducted after 24 h of operating at normal conditions. The sampling of PCDD/Fs in flue gas was performed after 5 h of continuous injection of thiourea and lasted for 6 h (3 h for one sample). The gaseous compounds were monitored continually at the stack during the

Table 1
Experimental design conditions.

Parameters	MSWI A		MSWI B	
	Normal condition	Inhibition tests	Normal condition	Inhibition tests
No.	A-1	A-2	B-1	B-2
Waste (t/h)	34	34	25	25
Fly ash (t/h)	2.55	2.55	2.00	2.00
Stack gas (Nm^3/h)	120,000	120,000	100,000	100,000
Inhibitor (kg/h)	0	35	0	26
AC (mg/Nm^3)	150	150	175	175
Lime (mg/Nm^3)	3000	3000	2500	2500