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PCDD/F emissions during startup and shutdown of a hazardous waste incinerator

Min Li, Chao Wang, Kefa Cen, Mingjiang Ni, Xiaodong Li*

State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou, Zhejiang Province, 310027, China

HIGHLIGHTS

- A completed startup-shutdown procedure has been investigated.
- The PCDD/F concentrations increase visibly during startup-shutdown procedure.
- De novo synthesis is the major pathway of PCDD/F formation in present study.
- Memory effect occurs in BF at the end of startup procedure.
- PCDD/Fs in flue gases are dominated in solid phase at BF inlet.

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ABSTRACT

Compared with municipal solid waste incineration, studies on the PCDD/F emissions of hazardous waste incineration (HWI) under transient conditions are rather few. This study investigates the PCDD/F emission level, congener profile and removal efficiency recorded during startup and shutdown by collecting flue gas samples at the bag filter inlet and outlet and at the stack. The PCDD/F concentration measured in the stack gas during startup and shutdown were 0.56–4.16 ng I-TEQ Nm^{-3} and 1.09–3.36 ng I-TEQ Nm^{-3}, respectively, far exceeding the present codes in China. The total amount of PCDD/F emissions, resulting from three shutdown-startup cycles of this HWI-unit is almost equal to that generated during one year under normal operating conditions. Upstream the filter, the PCDD/F in the flue gas is mainly in the particle phase; however, after being filtered PCDD/F prevails in the gas phase. The PCDD/F fraction in the gas phase even exceeds 98% after passing through the alkaline scrubber. Especially higher chlorinated PCDD/F accumulate on inner walls of filters and ducts during these startup periods and could be released again during normal operation, significantly increasing PCDD/F emissions.

1. Introduction

According to the Stockholm Convention, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are Unintentional Persistent Organic Pollutants (UPOPs). They comprise 210 different congeners, distributed over 8 homologue groups, featuring 1 to 8 chlorine atoms, but only 17 PCDD/F congeners substituted at the 2,3,7,8 positions by chlorine atoms are considered toxic (Olie et al., 1977; Rappe et al., 1987; McKay, 2002), potentially causing a range of health problems (Schuhmacher et al., 1997; Zhou et al., 2006).

In China the three types of waste incineration, namely municipal solid waste incineration (MSWI), medical waste incineration (MWI), and hazardous waste incineration (HWI), represent the top three PCDD/F emission sources (UNEP, 2005; Yu et al., 2008). Previous studies showed that most MSWI and HWI can meet the state limit under normal operating conditions (Hoyos et al., 2008; Gao et al., 2009; Rivera-Austrui et al., 2011; Yan et al., 2011; Chen et al., 2014; Wang et al., 2014; Karademir, 2014). Transient or unstable operating conditions, however, have significant effects on PCDD/F emission levels. For MSWI, the emission levels and congener distributions of PCDD/F at transient conditions (startup and shutdown) have already been investigated in numerous studies. Their results revealed that mainly the startup significantly affects the PCDD/F concentrations; plant shutdown was regarded as less problematic (Neuer-Etscheidt et al., 2006; Wang et al., 2007), and the formation of PCDD/F by de novo synthesis under transient

* Corresponding author.
E-mail address: lixd@zju.edu.cn (X. Li).

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operating conditions was higher than that under steady-state conditions (Guo et al., 2014; Syc et al., 2015). More attention should be paid to PCDD/F emissions from the startup (Guo et al., 2014). However, corresponding studies on HWI under transient operating conditions have been rare.

Hazardous waste arises in a wide variety of types, compositions and calorific values. Also, the content of chlorine and heavy metals is generally higher than for municipal solid waste, which accelerates the formation of PCDD/F, specifically under conditions of poor combustion or unstable operation (Wang et al., 2015; Chen et al., 2008a,b; Lin et al., 2014). Karademir and Korucu (2013) and Lin et al. (2014) investigated PCDD/F emission levels and congener profiles in the flue gas of HWI during cold startup process by collecting flue gas samples at the air pollution control devices (APCDs) and the stack. Both results showed that PCDD/F concentration could rise significantly during startup and low combustion temperature might cause high PCDD/F values in raw gas. Karademir and Korucu (2013) also found that PCDD/F formation by de novo synthesis occurred in electrostatic precipitator because the operating temperatures (approximately 200 °C) remained within the de novo synthesis temperature window.

The present study investigates the PCDD/F emission of a HWI plant during a complete shutdown-startup cycle, in order to obtain more information on PCDD/F formation and removal during different operating periods.

2. Materials and methods

2.1. Sampling arrangements

The hazardous waste incinerator (50 t/d) investigated in this study has operated since 2009. The incineration system consists of a rotary kiln and a secondary combustion chamber. Due to erratic combustion, poor gas phase mixing and short residence time, a rotary kiln cannot deliver regular and complete combustion gas. Gas phase combustion has to be completely burned by the secondary combustion chamber, ensuring sufficient temperature, time, turbulence (3 T's) and oxygen for completing combustion. The APCDs include an acid extracting tower, activated carbon injection (ACI), a baghouse filter (BF) and an alkaline scrubber (AS) for controlling pollutant emissions. Flue gas samples were collected simultaneously at the inlet and outlet of BF and the stack during the startup.

The startup of a hazardous waste incinerator is often a cold startup process, occurring after plant revision and repair. It proceeds as follows: (1) heating up the furnace and second combustion chamber with diesel oil, until a suitable temperature for incineration (850 °C) is reached; (2) starting gradually to feed waste with high calorific value until the design load and temperature is reached. Once the combustion chamber temperature exceeds 850 °C, liquid waste with high calorific value is fed as auxiliary fuel to continue heating the chamber volume and inner walls.

During sampling campaigns, two different types of liquid waste were fed into the furnace through mechanical pump. The liquid waste was stored in fiberglass-reinforced plastics, and a tank of liquid waste is about 700 kg, which can be pumped for nearly 2 h. The calorific values of liquid waste 1 and liquid waste 2 were 6600 kcal kg^{-1} and 6400 kcal kg^{-1}, respectively, and the chlorine contents were 4.23% and 17%, respectively. And generally, the calorific value of the solid waste fed during Startup 4 was approximately 3500 kcal kg^{-1}, chlorine content was below 4%. Moreover, the solid waste often has a complex composition and fluctuating calorific value, so it is deemed unsuitable during Startup 2 and 3.

The temperature evolution in different sections of the hazardous waste incinerator during the startup is shown in Fig. 1 a. During the heating-up period, diesel oil is burned to raise gradually the chamber temperature. When the temperature of the secondary combustion chamber reached 600 °C, flue gas samples were for the first time collected at the BF inlet, BF outlet, and the stack simultaneously (Startup 1). The hazardous liquid waste 1 was fed into the rotary kiln furnace while the secondary chamber temperature was above 850 °C. Meanwhile, flue gas samples were collected for the second time at the same three points (Startup 2). As shown in Fig. 1 a, the temperature of the rotary kiln and secondary combustion chamber decreased sharply after feeding liquid waste 1, which then recovered loosely with the help of auxiliary burners. During the third time of flue gas sampling (Startup 3), hazardous liquid waste 2 was fed. Again temperature decreased rapidly and then increased slowly with the help of auxiliary burners, similar to the Startup 2 stage. Flue gas samples were collected concurrently at the BF inlet, BF outlet and the stack for the fourth time, 24 h after the incinerator started up (Startup 4). The temperature in the secondary combustion chamber remained variable within a span of 1100–1300 °C. During this period, solid waste rather than liquid waste was fed as a fuel. Moreover, the ACI started to work after feeding liquid waste 1.

The temperature evolution during shutdown is shown in Fig. 1 b at different positions. The shutdown process of the hazardous waste incinerator being studied occurs when the plant prepares for revision. At the beginning of shutdown, waste feeding stops and also injection of activated carbon halts. The shutdown continues until chamber temperature has descended to ambient temperature. The temperature in the secondary combustion chamber far exceeded 850 °C before shutdown, then declined distinctly after waste feeding was stopped. Meanwhile, flue gas samples were collected simultaneously at the BF inlet and the stack for the first time (Shutdown 1). During shutdown period, the temperature of the secondary combustion chamber decreased and fluctuated strongly, which might have been due to the high induced-draught fan, used for shortening the shutdown time. The second and third sampling (Shutdown 2 and Shutdown 3) were performed at the same sampling points.

2.2. Sample collection and analysis

Flue gas sampling was conducted using isokinetic samplers (KNJ, Korea), complying with US EPA Method 23; the specific sampling method was described by Chen et al. (2008a,b). The gas-phase sample was collected by absorption on XAD-2 resin, whereas the particle-bound sample was collected by a fibre glass filter and by rinsing the sampling probe thereafter. Due to the high particle concentration, the fibre filters were replaced three or four times in each flue gas sampling to make the samples more realistic. Twelve flue gas samples were collected during startup and nine flue gas samples were collected during shutdown.

These flue gas samples were spiked with known amounts of US EPA Method 23 internal standard solution before sampling to check the PCDD/F sampling efficiency. After sampling, filters and XAD-2 resin were stored and maintained in the dark until being transferred to the laboratory. For a better understanding of PCDD/F distributions between the gas and particulate phases before and after BF and the stack during the startup, the XAD-2 and fibre filter samples collected in the Startup 2 and Startup 4 stages were separately Soxhlet extracted with toluene for 24 h. While, the other flue gas samples were extracted with toluene together. After extraction, the toluene extract was concentrated to nearly 1 mL by rotary evaporator and replaced by 5 mL hexane. Then, the hexane solvent was treated with concentrated sulphuric acid. After being subjected to a series of clean-up columns including a hybrid silica gel column (sulphuric acid and sodium hydroxide silica gel) and an aluminum oxide column, the eluate was then concentrated to 1 mL