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# Effects of gaseous $NH_3$ and $SO_2$ on the concentration profiles of PCDD/F in flyash under post-combustion zone conditions

Yaghoub Hajizadeh [1], Jude A. Onwudili, Paul T. Williams *

*Energy Research Institute, University of Leeds, Leeds LS2 9JT, UK*

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The influence of gaseous ammonia and sulphur dioxide on the formation of 2378-substituted PCDD/F on a reference flyash from a municipal waste incinerator has been investigated using a laboratory scale fixed-bed reactor. The reference flyash samples (BCR-490) was reacted under a simulated flue gas stream at temperatures of 225 and 375 °C for 96 h. The experiments were carried out in two series: first with simulated flue gas alone, and then with injection of $NH_3$ or $SO_2$ gas into the flue gas just before the reactor inlet. It was found that the injection of gaseous ammonia into the flue gas could decrease the concentration of both PCDD and PCDF by 34–75% from the solid phase and by 21–40% from the gas phase. Converting the results to I-TEQ values, it could reduce the total I-TEQ values of PCDD and PCDF in the sum of the flyash and exhaust flue gas by 42–75% and 24–57% respectively. The application of $SO_2$ led to 99% and 93% reductions in the PCDD and PCDF average congener concentrations, respectively in the solid phase. In the gas phase, the total reductions were 89% and 76% for PCDD and PCDF, respectively. Moreover, addition of $SO_2$ reduced the total I-TEQ value of PCDD and PCDF in the flyash and exhaust flue gas together by 60–86% and 72–82% respectively. Sulphur dioxide was more effective than ammonia in suppressing PCDD/F formation in flyash under the conditions investigated.

## 1. Introduction

The emission of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) during combustion processes and in particular, the incineration of municipal solid wastes is still of serious concern to the public due to the adverse health effects of these toxic compounds. Particularly, the 2378-substituted PCDD/F congeners have been prominently portrayed as being highly toxic. De novo synthesis is a well researched formation route for PCDD/F in flyash within the post-combustion zone during combustion or incineration. Prevention of PCDD/F formation during the waste incineration process rather than removal of the already formed PCDD/F by end-of-pipe flue gas cleaning systems seems to be a promising technique. With the application of these techniques, the need is reduced for further treatment of the adsorbed or trapped PCDD/F on solid residues before disposal.

One of the encouraging techniques for in-process suppression of PCDD/F formation involves the use of chemical inhibitors. Over the last two decades several nitrogen compounds and/or in combination with sulphur compounds, have been examined as potential inhibitors for PCDD/F formation during waste incineration and other combustion processes. Among others, the PCDD/F suppressing effects of some solid inhibitors including urea, ethylenediammine tetraacetic acid (EDTA), monoethanolamine (MEA), and triethanolamine (TEA), and some gaseous inhibitors such as ammonia ($NH_3$), sulphur dioxide, amido sulphonic acid and dimethylamine (DMA) have been reported (Addink et al., 1996; Ruokojarvi et al., 1998, 2001; Tuppurainen et al., 1999; Samaras et al., 2000; Xhrouet et al., 2002; Kuzuhara et al., 2005; Marie-Rose et al., 2009; Williams, 2005).

In literature, various mechanisms have been proposed for the suppression of PCDD/F formation in the presence of nitrogen- and sulphur containing compounds. Most of the mechanisms involve reducing the ability of metals to catalyse PCDD/F formation. The proposed mechanisms of PCDD/F inhibition by nitrogen compounds include alteration of acidity of flyash e.g. by ammonia; formation of stable metal nitride bonds; and formation of stable metal-ammonia co-ordination compounds (Ismo et al., 1997; Tuppurainen et al., 1998; Kuzuhara et al., 2005). However, some mechanisms also involve the reaction of the nitrogen-based additives and their degradation products with PCDD/F precursors. For example, during combustion $NH_i$ and CN radicals may form and can become attached to potential aromatic rings or may even be inserted into the rings forming aromatic amines, nitriles and pyridine-like structures (Kasai et al., 2008). Recently, Marie-Rose et al. (2009) proposed that

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* Corresponding author.
*E-mail address:* p.t.williams@leeds.ac.uk (P.T. Williams).

[1] Present address: Faculty of Health, Isfahan University of Medical Sciences, Isfahan, Iran.

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PCDD/F could be removed from flue gas via oxidation by $NO_2$, produced from the prior oxidation of the ammonia additive.

The main suggested mechanisms involved in the suppression of PCDD/F by sulphur-containing compounds can be summarized as follows: (i) homogenous reduction of $Cl_2$ at high temperature to HCl which is less active than $Cl_2$ in the chlorination reactions; (ii) conversion of metal oxide/chloride catalyst to metal sulphates which show less catalytic activity, therefore reducing the catalytic activity of the 'Deacon Reaction'; and (iii) $SO_2$ sulphonates the phenolic precursors which prevents chlorination and bi-aryl synthesis, and promotes the formation of sulphur analogues of PCDD/F (Ogawa et al., 1996; Tuppurainen et al., 1998; Ryan et al., 2006; Ke et al., 2010). In addition, Addink et al. (1996) showed that sulphur-based inhibitors were capable of changing the number of chlorine atoms built into PCDD/F molecules but not the position of chlorination.

The variation of mechanisms as well as the inhibitory effects of additives on PCDD/F formation could be due to a number of factors. These could include the type and configuration of plant (Addink et al., 1996), the concentration and form of application of the particular additive (Furrer et al., 1998; Bechtler et al., 1998; Ruokojarvi et al., 2004; Kuzuhara et al., 2005), the point of application within the plant (Kasai et al., 2008), the operating temperature of the plant (Jansson et al., 2008; Weber et al., 1999, 2002; Lundin and Marklund, 2007; Cunliffe and Williams, 2007) as well as composition of the fuels.

It would appear that the catalytic activity of metals during de novo synthesis of PCDD/F would involve both solid–solid as well as gas–solid interactions on the flyash. However, operating temperature has consistently appeared to be an important factor affecting the formation of PCDD/F in flyash (Weber et al., 1999, 2002; Lundin and Marklund, 2007; Cunliffe and Williams, 2007; Jansson et al., 2008). Hence, temperature may also influence the ability of additives in suppressing PCDD/F formation. For example, Ruokojarvi et al. (1998) separately examined the inhibitory effects of gaseous compounds such as $SO_2$ and $NH_3$ on PCDD/Fs formation. The additives were sprayed directly into the flue gas stream at the temperatures of 670 and 410 °C respectively. The total PCDD/Fs concentration was reduced by 42–78% with the large amount being reduced in particulate phase. Similarly, Ruokojarvi et al. (2004) reported that spraying gaseous ammonia into the flue gas during the combustion of light heating oils in a pilot-scale incinerator could reduce the PCDD/F concentration in the flue gas by 68% at 410 °C. In the same vein, Addink et al. (1996) reported that the addition of sodium sulphide reduced PCDD/F concentration on flyash by 80–90% during the thermal treatment of flyash in a fixed-bed reactor at around 300 °C.

In most cases, studies showed that PCDD/F congeners were subjected to desorption/volatilization and degradation/dechlorination at temperatures of about 500 °C (Weber et al., 1999; Cunliffe and Williams, 2007). On the contrary, lower temperatures have been found to favour de novo formation of PCDD/F (Lundin and Marklund, 2007; Jansson et al., 2008; Lundin et al., 2011). The combination of these reactions could lead to shifts in the degree of chlorination of the PCDD/F in relation to temperature. A plausible consequence of such changes in the degree of chlorination may involve increases in the concentrations of the most toxic 2378-substituted congeners. For example, Cunliffe and Williams (2007) reported that treatment of incinerator flyash under inert (nitrogen) gas at 375 °C for 4 d resulted in almost 200 times increase in the concentration of the highly toxic 2378-TCDD compared to the unreacted flyash sample.

This paper describes the changes in the concentration profiles of the toxic 2378-substituted PCDD/F congeners in a reference flyash sample in relation to temperature under simulated flue gas conditions. The selected temperatures of 225 and 375 °C are respectively, within the window for dioxin formation via de novo synthesis. Experiments have been carried out with a laboratory scale static-bed reactor. Most importantly, the effects of the injection of gaseous ammonia and sulphur dioxide into the flue gas, on the concentrations of the PCDD/F congeners have been studied under these conditions. In addition, changes in the total toxic equivalency of PCDD/F in the treated samples are reported.

## 2. Materials and methods

### 2.1. Experimental procedures

A laboratory scale fixed-bed reactor was developed and used to investigate the influence of gaseous ammonia and sulphur dioxide on PCDD/F formation on MWI flyash at the temperature windows of the post combustion zone. It has been accepted that the most effective temperature zone for PCDD/F formation via de-novo synthesis is between 200 and 400 °C (McKay, 2002; Stanmore, 2004). Hence, experiments were carried out at temperatures of 225 and 375 °C, respectively. A schematic diagram of the experimental reactor is shown in Fig. 1. The reactor consisted of a tubular stainless steel reactor with a removable quartz lining surrounded by a temperature-controlled cylindrical furnace. The reactor was of 25 cm height, 48 mm inner diameter with a purge gas inlet at the top, and equipped with a thermocouple to detect the sample bed temperature. BCR-490 reference flyash sample was used for this study.

The metal contents of the applied reference flyash were analyzed via acid digestion and flame atomic absorption spectrometry methods before the experiments. The major metals found were iron (12.3 mg/g), magnesium (9.13 mg/g)) and lead (7.50 mg/g). In addition, small amounts of copper (0.68 mg/g) was found which could be a source of metal catalyst for promotion of PCDD/F forma-

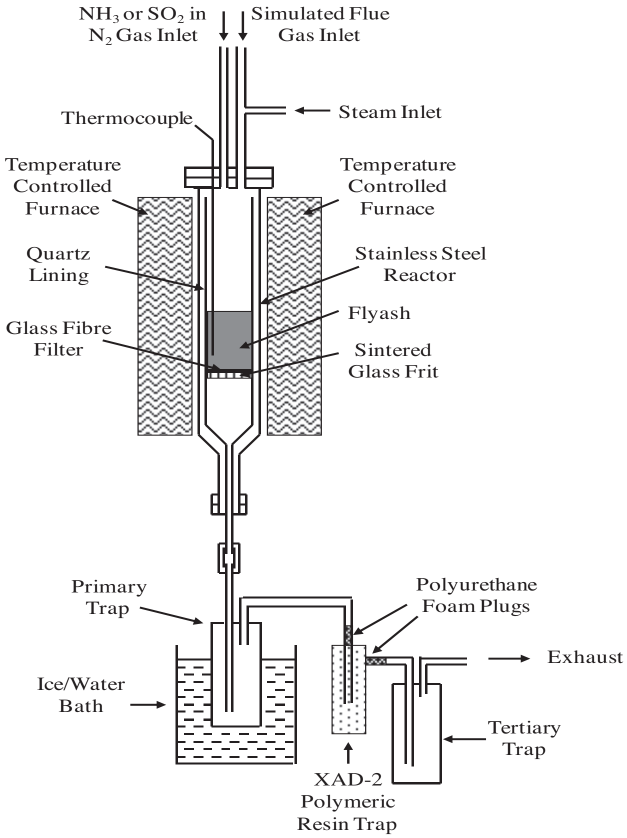

**Fig. 1.** Schematic diagram of the experimental reactor for thermal treatment of flyash.