MELAMINE AS SUPPRESSANT OF PCDD/F FORMATION IN THE SINTERING PROCESS

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1. INTRODUCTION

Combustion processes, particularly those associated with the incineration of chemical and municipal wastes have been shown to be important sources of dioxin emissions, i.e. polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). One of the potential contributors, owing to the fundamental requirement for its operation of a variety of high temperature processes, is the steelmaking industry, where iron ore sintering process has been identified as the only noteworthy emission source[1-3]. Addition of urea directly into the sinter bed of an iron ore sintering plant has been shown to suppress the formation of PCDD/Fs in the sintering process[3]. Further to this, PCDD/F suppression has also been demonstrated with other nitrogen-containing substances such as ammonium hydroxide, triethylamine, ethanolamines and ethylenediaminetetra-acetic-acid[4-7] suggesting that the inhibition occurs before precursors form on the surface of particulates. It has also been proposed that the amines deactivate the surface of catalysts by forming nitrides[6], found through a comparative study of different nitrogen inhibitors for PCDD/Fs, including monoethanolamines. This paper describes an investigation of the PCDD/F suppressant properties of melamine (1,3,5-triazine-2,4,6-triamine) using a bench-scale sintering apparatus.

2. EXPERIMENTAL

2.1 Experimental programme: A series of eight experiments was performed using the same iron ore blend. The ore blend contained a base mixture of five high-grade iron ores, coke breeze (3.3%-wt) as fuel and additions of limestone and olivine to achieve a lime:silica ratio of 1.6 in the sinter product. Urea was added at a concentration of 0.02% of the raw sinter mix, which has been found to be the optimum addition rate from both plant studies and sinter pot experiments. Melamine was used at five different addition rates viz., 0.005%, 0.01%, 0.015%, 0.02% and 0.05% of the raw sinter mix. The melamine nitrogen equivalent to 0.02% urea is 0.013%. A second series of sinter pot experiments using both melamine and urea at three different ratios viz., 3:1 and 1:3 (blends normalised to a total nitrogen equivalent rate of 0.02% urea) was also performed. Both melamine and urea were added to the raw sinter blend in the form of fine powders prior to pelletising the mix. The chloride content of the sinter mix also influences the dioxin emission; therefore, 223 mg of potassium chloride was added to each mix in order to provide a constant background concentration of 105 mg/kg of chloride.

2.2 Raw mix preparation and firing: The sinter pot studies were performed using an experimental sinter pot, which has a raw sinter mix capacity of 1.0 kg; the bed diameter and height are 100 mm and 150 mm, respectively. On each day of operation sufficient mixture was prepared for single test firing by mixing the raw materials and additives in a drum mixer/pelletiser together with the requisite amount of water to give the required moisture content (6%-wt). The resulting micropellets were loaded into the sinter pot and fired following a standard procedure. A series of steering experiments, described elsewhere, led to the tests whose results are described here[8]. The sampling duration was also determined from this earlier experimentation.

2.3 Measurement of dioxin emissions: Sampling of PCDD/Fs in the exhaust gas was conducted using polyurethane foam (PUF) cartridges according to US EPA Method 23 connected in series to a suction fan. For optimum PCDD/F emission sampling the temperature of the exhaust gas was reduced to less than 70^{o}C using a water tube heat exchanger. The efficiency of trace organic sampling using the PUF was assessed using US EPA sampling standard, which were spiked on the surface of the exhaust gas filter. The recovery of US EPA sampling standards ranged from 91% to 104% for all the experiments. The PCDD/F analyses were performed according to a UKAS-accredited procedure (ISO 17025).

3. RESULTS

The congener-specific PCDD/F emission released from a standard raw sinter mix containing potassium chloride is shown in Figure 1, while the results obtained with melamine and urea additions are presented in Tables 1 and 2, respectively. Figure 2 shows bed thermal profiles, waste gas composition and bed pressure variations with time during a typical experiment. Throughout this work, the process variables remained close to those shown implying that sintering conditions were reproducible.

Figure 1 shows the relative abundances of targeted PCDD and PCDF emissions obtained from the sinter pot experiments. The relative abundances are typical to those observed in a sinter plant supporting the view that trends observed in pot experiments should be reflected in a full-scale plant. A detailed comparison between PCDD/F emissions obtained from both plant studies and sinter pot experiments has been reported elsewhere[8].

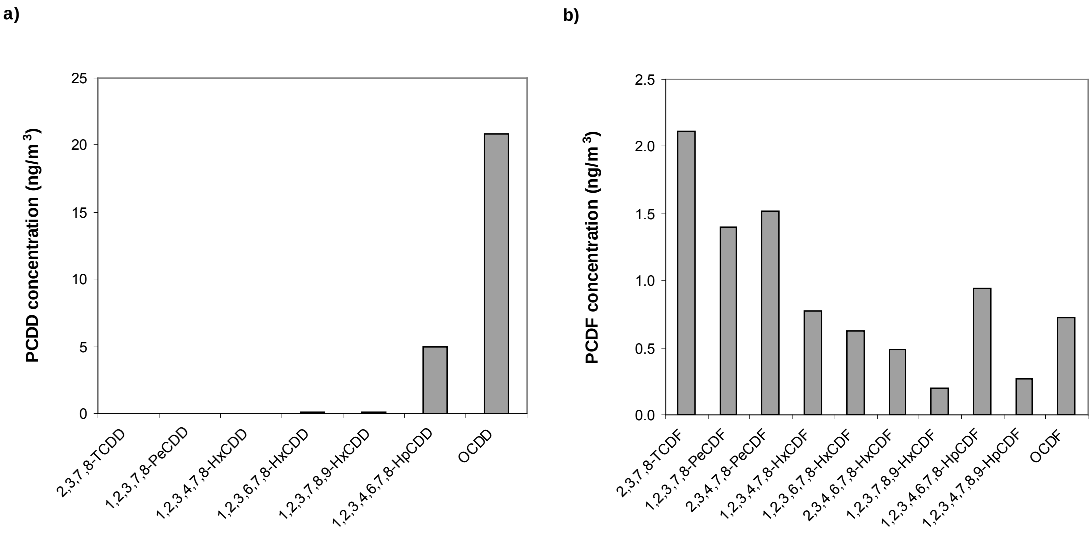


Figure 1. Mean (a) PCDD and (b) PCDF emission concentrations obtained during the sintering of a raw standard iron ore mix containing potassium chloride.

3.1 Effect of melamine and urea upon dioxin suppression: As may be seen from Table 1, the addition of 0.02% solid urea resulted in 54% suppression of PCDD/F emissions (Table 1). This result was in good agreement with the data obtained during full scale plant trials at a UK sinter plants which demonstrated that similar additions rate of urea to the raw sinter feed was capable of suppressing the formation of dioxins by 55 to 60%[9].

From Table 1, it may be seen that the highest level of PCDD/F reduction was attained with 0.015% melamine, whereby PCDD/F formation was reduced by 64%. Since 0.015% melamine has approximately the amine group (-NH_2) equivalent of 0.02% urea (0.013% is the amine group equivalent to 0.02% urea), it is believed that the mechanism of PCDD/F suppression is related to the number of amine groups present in a compound and gaseous ammonia formed as a result of degradation and volatilisation. The additional 10% suppression over urea observed with melamine at 0.015% addition rate may possibly be due to the compound being less volatile than urea. As the melamine concentration was increased to 0.02%, equivalent to 0.031% urea on a nitrogen basis, the dioxin suppression efficiency was reduced to 39%. The boiling or decomposition point for melamine and urea are 280^{o}C and 135^{o}C, respectively. Therefore, irrespective of the mode of operation of the suppressant, melamine may persist longer and its effect may possibly extend over a greater part of the bed. From Table 1 it may be seen that the formation of each of the targeted isomers is reduced by a similar amount at each suppressant addition level. This suggests that the action of urea and melamine is to reduce the activity of catalyst in the bed rather than the formed compounds.

As shown in Table 2, the addition of a blend of melamine and urea did not result in additional PCDD/F inhibition compared to using melamine alone. The level of inhibition was also quite similar for each targeted congener supporting the hypothesis that PCDD/F inhibition was determined by the presence of amino groups irrespective of the compound used.

Table 1. Suppression of targeted PCDD/F congeners with optimum urea and with varied melamine additions

	Average PCDD/F base emission concentration (ng/m^3)	**Suppression efficiency for each targeted compound (%)**				
		0.005% melamine	**0.01% melamine**	**0.015% melamine**	**0.02% melamine**	**0.02% urea**
2,3,7,8-TCDD	<LOD*	NA**	NA**	NA**	NA**	NA**
1,2,3,7,8-PeCDD	0.01	6.3	43.8	56.3	25.0	43.8
1,2,3,4,7,8-HxCDD	0.04	27.3	63.6	50.0	22.7	59.1
1,2,3,6,7,8-HxCDD	0.08	50.9	73.6	47.2	11.3	71.7
1,2,3,7,8,9-HxCDD	0.07	48.6	100.0	43.2	18.9	70.3
1,2,3,4,6,7,8-HpCDD	4.9	35.2	67.6	44.2	11.5	64.0
OCDD	21	23.7	54.2	31.9	<5%	56.4
2,3,7,8-TCDF	2.1	22.2	46.3	66.9	30.3	56.7
1,2,3,7,8-PeCDF	1.4	17.6	42.4	64.2	36.1	48.8
2,3,4,7,8-PeCDF	1.5	13.1	46.1	62.4	33.6	54.5
1,2,3,4,7,8-HxCDF	0.77	<5%	38.8	53.5	25.0	33.4
1,2,3,6,7,8-HxCDF	0.62	<5%	41.4	53.8	25.7	35.6
2,3,4,6,7,8-HxCDF	0.49	<5%	35.4	51.1	22.6	30.9
1,2,3,7,8,9-HxCDF	0.20	<5%	44.6	54.0	23.8	30.7
1,2,3,4,6,7,8-HpCDF	0.94	<5%	36.5	50.7	29.4	36.2
1,2,3,4,7,8,9-HpCDF	0.27	16.2	51.6	52.6	30.5	43.2
OCDF	0.73	13.9	55.8	63.6	50.4	61.0
		Overall I-TEQ reduction				
		20.0	**51.4**	**64.2**	**38.6**	**54.2**

*<LOD=less than the limit of detection **NA=data not available due to the absence of a base emission value

Table 2. Suppression of individual targeted PCDD/F congeners using various ratios of melamine and urea inhibitors at a fixed N equivalent rate

	Average PCDD/F base emission concentration (ng/m^3)	**Suppression efficiency for each targeted compound (%)**		
		100% urea	**25% melamine + 75% urea**	**75% melamine + 25% urea**
2,3,7,8-TCDD	<LOD*	NA**	NA**	NA**
1,2,3,7,8-PeCDD	0.01	40.0	<5%	<5%
1,2,3,4,7,8-HxCDD	0.04	58.3	36.1	61.1
1,2,3,6,7,8-HxCDD	0.08	48.7	32.9	46.1
1,2,3,7,8,9-HxCDD	0.07	58.2	31.3	55.2
1,2,3,4,6,7,8-HpCDD	4.9	76.7	51.7	61.3
OCDD	21	74.6	50.0	59.3
2,3,7,8-TCDF	2.1	61.5	62.8	75.3
1,2,3,7,8-PeCDF	1.4	64.5	68.3	72.5
2,3,4,7,8-PeCDF	1.5	61.4	63.7	68.0
1,2,3,4,7,8-HxCDF	0.77	58.4	61.9	62.6
1,2,3,6,7,8-HxCDF	0.62	56.4	62.2	61.8
2,3,4,6,7,8-HxCDF	0.49	53.9	57.6	58.8
1,2,3,7,8,9-HxCDF	0.20	60.7	59.7	62.2
1,2,3,4,6,7,8-HpCDF	0.94	67.8	68.2	67.5
1,2,3,4,7,8,9-HpCDF	0.27	78.7	75.4	75.7
OCDF	0.73	77.0	74.5	72.9
		Overall I-TEQ reduction		
		59.6	**59.8**	**66.5**

*<LOD=less than the limit of detection **NA= data not available due to the absence of a base emission value

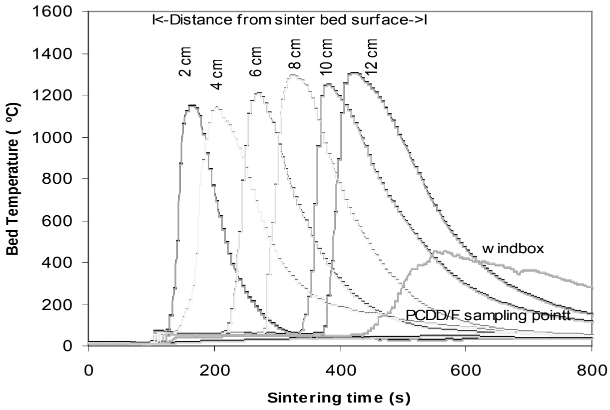
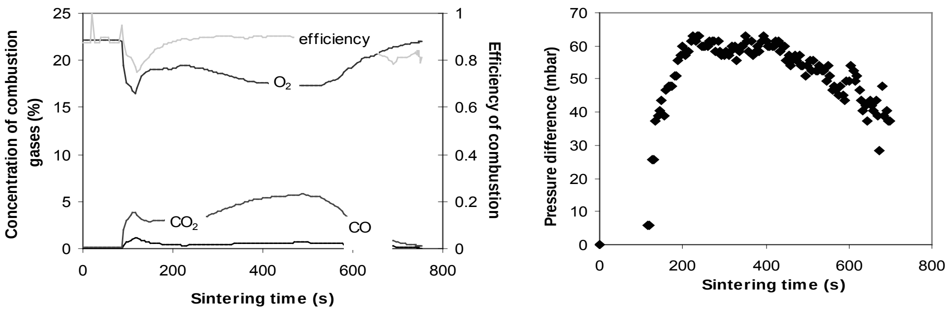


Fig. 2: Temperature (top), combustion products (left) and pressure drop (right) for a representative sinter pot trial



4. SUMMARY

A comparative study was carried out to investigate the effect of melamine and urea upon dioxin emissions in iron ore sintering. The results indicated that similar dioxin suppressions (ca. 60 %) were obtained using either urea or melamine when the nitrogen content was kept constant. Therefore, it is concluded that the effect of nitrogen-containing compounds upon dioxin suppression in iron ore sintering can be directly correlated to the amount of $–NH_2$ groups introduced in the raw sinter mix, irrespective of the nitrogen-containing suppressant used. This study was carried out to provide further understanding of the mechanism of PCDD/F inhibition using two different nitrogen-containing suppressants. A full-scale implementation of melamine addition for the abatement of PCDD/Fs would require further comparative evaluation on cost, availability, handle-ability and toxicity of the additive.

5. REFERENCES

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