

Effect of Liquid Inhibitor De-dio™ on Dioxin-Furan Emission from Medical Waste Incineration Plant

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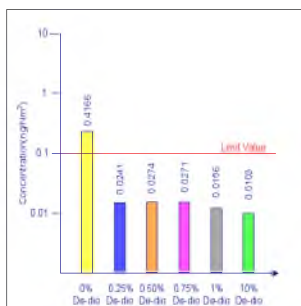
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Graphical abstract



Abstract

The aim of the study was to investigate the effects of liquid inhibitor (known as De-dio™) on the emission of dioxin-furan from medical waste incineration plants. Various concentrations of De-dio™ solutions were tested on the medical waste incinerator combustion chamber with an injection flow rate of 1.5 L/min. The sampling protocol of US EPA Method 23 was adopted to collect the sample using a modified US EPA Method 5 sampling train. The flue gas emission was collected before and during the injection of the chemical. The result showed that the De-dio™ was able to reduce or minimize the formation of dioxin-furan to meet its regulatory limits. The study illustrates that the higher the concentration of De-dio™ solution, the lower the dioxin-furan emission was observed in the flue gas.

Keywords: Inhibitors; dioxin-furan; incineration; medical waste

Abstrak

Tujuan kajian ini adalah untuk mengkaji kesan perencat cecair (dikenali sebagai De-dio™) pada pelepasan dioksin-furan dari loji pembakaran sisa perubatan. Kepekatan pelbagai larutan De-dio™ telah diuji ke atas sisa pembakaran keabuh pembakaran sisa perubatan dengan kadar aliran suntikan 1.5 L / min. Protokol pensampelan Kaedah US EPA 23 telah digunakan untuk pensampelan yang diubah suai daripada US EPA Kaedah 5 rangkaian persampelan. Emisi gas serombong diambil sebelum dan semasa suntikan bahan kimia tersebut. Keputusan menunjukkan bahawa De-dio™ dapat mengurangkan atau meminimumkan pembentukan dioksin-furan untuk memenuhi had peraturan. Kajian ini mendapati kepekatan De-dio™ yang lebih tinggi, mengakibatkan pelepasan dioksin-furan yang rendah dalam gas serombong.

Kata kunci: Perencat; dioksin-furan; pembakaran; sisa perubatan

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1.0 INTRODUCTION

Polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzo-furan (PCDF) are commonly known as dioxins and furans (DF), respectively. Both originate from many combustion related sources, including waste incineration, bushfire, and diesel burning emission. Today it is known that PCDD/F are mainly formed through heterogeneous reactions taking place in the downstream regions (200–400°C) of HCl-containing flue gases waste combustion processes. Due to the toxic nature of these compounds, stringent stack emissions limits of 0.1 ng ITEQ/Nm³ have been set for the flue gas by several countries including Malaysia. Many of the research efforts are given on methods of controlling the emissions of these chemicals in incineration process.

To date, the emission control techniques employed is concerned mainly with the end-of-pipe or secondary control such as wet/dry scrubbing, fabric filtration, activated carbon adsorption.

Previous study indicates that activated carbon injection can effectively reduce the flue gas PCDD/F concentration (Chang and Lin, 2001). This approach is focused on the removal of PCDD/F from flue gases after their formation by means of gas cleaning devices, increasing their installation and operation costs.

A second approach, the so-called primary measure technique, has been developed for toxic emissions reduction. This technique includes measures and actions for controlling the PCDD/F formation, such as optimization of the combustion processes. This approach may include the addition of some selected compounds in the post combustion zone aiming in reducing the formation of PCDD/F and their precursors; it is known as inhibition and differs from the flue gas cleaning methods as it deals with the prevention of PCDD/F. Inhibitors can be used to reduce PCDD/F formation, thus avoiding the problem of waste containing these substances. A variety of chemicals, both inorganic and organic compounds have been shown to inhibit PCDD/F formation (Dickson *et al.*, 1989;

Addink *et al.*, 1993; Addink *et al.*, 1996; Ogawa *et al.*, 1996; Ragunathan and Gullet, 1996; Tuppurainen *et al.*, 1999 and Chang *et al.*, 2006).

Various inorganic and organic compounds have been studied for their PCDD/F prevention ability. One group includes basic compounds such as NH₃, CaO, NaOH, KOH, and Na₂CO₃ which might change the acidity of the fly ash surface. Another group of inhibitors includes compounds that are likely to form some kind of complexes with the transition metal species, responsible for catalyzing the PCDD/F reaction pathways. Sulfur compounds such as Na₂S, Na₂S₂O₃, CS₂, SO₃ and SO₂ are capable of reducing the PCDD/F concentration. Furthermore, low PCDD/F emissions have been observed during coal combustion, which were attributed to the high sulfur content of coals.

Functionalized amines (ethanolamine, EDTA, trimethylamine) and nitrogen compound, such as urea can also be effective as inhibitors (Dickson *et al.*, 1989; Addink *et al.*, 1996). In most of the studies presented here, the experiments were performed in laboratory scale conditions, where fly ash samples were impregnated with the inhibitors and the reactants, and were heated to the desired temperature. However, in full-scale studies, the inhibitors were injected into the flue gas at the post combustion zone. By such a method, PCDD/F inhibition potential is affected by several operating parameters such as the location and the temperature of the inhibitor injection, the contact surface area between the active metal sites and the inhibitor molecules and the concentration of the compound.

Preliminary studies using this technique with various inhibitors added to the post combustion zone and applied on a pilot scale reactor showed positive results (Dickson *et al.*, 1989; Tuppurainen *et al.*, 1999). However, all attempts for scale-up on a full scale plant using the same inhibitors failed completely due to a number of technical difficulties and problems such as oxidation of the inhibitors to CO.

In summary, various inhibitors have been successful in preventing PCDD/F formation, but only a few have been tested in real scale incinerators, as also presented in a comprehensive review articles of Buekens and Huang (1998) and Ruokojärvi *et al.* (2004). The ideal inhibitor for a full-scale waste incinerator would be a non-toxic compound of low cost, and easy to use, but such a compound is still to be discovered.

In this study, we performed a series of experiments for the prevention of PCDD/F formation at selected medical waste incineration plants. The objectives of this work were to study the ability of liquid inhibitor (known as De-dioTM) to prevent or minimize PCDD/F formation when applied to the combustion chamber. In addition, the study was to investigate the effect of the liquid inhibitor concentration on the PCDD/F prevention capability.

2.0 EXPERIMENTAL

2.1 Plant Selection

The study on the effectiveness of De-dioTM liquid inhibitor in minimizing of DF formation in incineration process was conducted at selected medical waste incineration plants. These incinerators are designated as plant A, B, C, D, E and F, operating at different incineration capacities.

Table 1 presents the full description of the each of medical waste incineration plants tested and the concentration of De-dioTM applied or injected in the combustion chamber.

Table 1 Description of the incineration plant and concentration of De-dioTM applied

Incinerator Id.	Incineration Capacity (kg/hr)	Sample Id.	Concentration of De-dio TM Applied (%wt)
A	250	A1	0
		A2	10
		A3	10
		A4	1
		A5	1
B	250	B1	0
		B2	10
		B3	1
		B4	1
		B5	1
C	200	C1	0
		C2	10
		C3	10
		C4	1
		C5	1
D	200	D1	0
		D2	10
		D3	10
		D4	1
		D5	1
E	200	E1	0
		E2	10
		E3	1
		E4	1
F	80	F1	0.25
		F2	0.50
		F3	0.75

2.2 Stack Sampling

The stack sampling protocol of US EPA Method 23: "Determination of Polychlorinated Dibenzop-Dioxins, Polychlorinated Dibenzofurans and Polychlorinated Biphenyls from Stationary Sources" was adopted to collect the sample using a modified US EPA Method 5 sampling train. A measured volume of air sampled (i.e 3.0 – 3.3 Nm³) from stack was withdrawn isokinetically through a filter and XAD2 resin.

In this study, the stack sample was collected before and during the injection of De-dioTM in the combustion chamber of the incinerator. Approximately, 1.5 L/min of the liquid inhibitor with various concentrations (i.e 0.25%, 0.50%, 0.75%, 1% and 10%) were injected inside the combustion chamber of the incineration plant.

2.3 Sample Analysis

The analysis of the PCDD/Fs collected both in the filter and XAD2 resin was performed in the United Kingdom using a high resolution mass spectrometry, a VG70S with Opus data system equipped with a fused silica capillary column DB-5 MS (60m x 0.32 mm x 0.25µm). The mass spectrometer was operated at 6,000 resolving power (10% valley definition) at 28eV and at 8kV accelerating potential. The sample was analyzed in accordance with US EPA Method 1613.

3.0 RESULTS AND DISCUSSION

3.1 Overall Dioxin Furan Emission

Table 2 presents the results on the application of different concentrations of liquid inhibitor on the emissions of DF which showed that there was a reduction in the emission of the pollutant

with increasing concentration of De-dioTM introduced in the combustion chamber. The percent of limit of the DF emission with and without the introduction of the inhibitor ranged from 5 to 37% and 11 to 1918%, respectively, which illustrates that the variability of the DF emission concentration in the former was less than the

latter case. Interestingly, the study indicates that not only the concentration of DF emission was lower but also it was much more contained with the application of the inhibitor.

Table 2 Result on the application of various concentration of De-dioTM on dioxin-furan emission.

Incinerator Id and Capacity (kg/hr)	Sample Id.	Concentration of De-dio TM applied (%)	Concentration of Dioxin-Furan (ng ITEQ/Nm ³)		Percent of Limit*
			Actual	Corrected to 11% O ₂	
A (250 kg/hr)	A1	0	0.0236	0.0738	74 %
	A2	10	0.0073	0.0170	17 %
	A3	10	0.0076	0.0185	19 %
	A4	1	0.0052	0.0168	17 %
	A5	1	0.0052	0.0371	37 %
B (200 kg/hr)	B1	0	0.9398	1.9180	1918 %
	B2	10	0.0035	0.0146	15 %
	B3	1	0.0097	0.0202	20 %
	B4	1	0.0093	0.0187	19 %
C (200 kg/hr)	C1	0	0.0090	0.0106	11 %
	C2	10	0.0038	0.0059	6 %
	C3	10	0.0042	0.0047	5 %
	C4	1	0.0086	0.0106	11 %
	C5	1	0.0051	0.0082	8 %
D (200 kg/hr)	D1	0	0.0477	0.0598	60 %
	D2	10	0.0049	0.0096	10 %
	D3	10	0.0051	0.0069	7 %
	D4	1	0.0147	0.0177	18 %
	D5	1	0.0047	0.0075	8 %
E (200 kg/hr)	E1	0	0.0293	0.0206	21 %
	E2	10	0.0053	0.0051	5 %
	E3	1	0.0090	0.0088	9%
	E4	1	0.0085	0.0102	10%
F (80 kg/hr)	F1	0.25	0.0079	0.0241	24 %
	F2	0.50	0.0090	0.0274	27 %
	F3	0.75	0.0089	0.0271	27 %

* With limits of 0.1ng ITEQ/Nm³ @corrected at 11% oxygen, Pressure = 101.325kPa

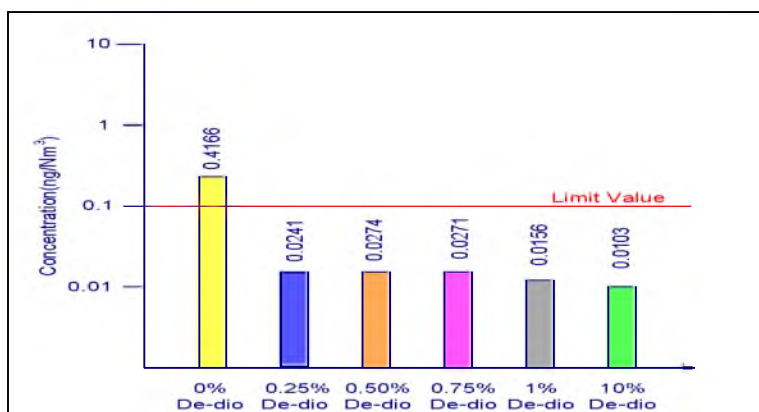


Figure 1 Average concentration of dioxin-furan emission with and without application of De-dio

Figure 1 presents the average DF emission concentration with and without the application of the inhibitor for all the plants A to F which clearly showed that the plants were able to comply the stipulated limits of DF emission even with the application of 0.25% of the De-dio™. The 10% inhibitor presented the lowest DF emission average concentration of 0.0103 ng ITEQ/Nm³ compared to the others. While without inhibitor recorded an average DF concentration of 0.4166 ng ITEQ/Nm³ which was thirty times higher than the limits stipulated for such facility. This value is similar to emission values observed from a hazardous waste incinerator (2.9 ng/Nm³) and from a municipal waste incinerator (3.0 ng/Nm³) (Verhulst *et al.*, 1996) The result shown that, without application the De-dio, incinerators A-F does not comply with specification requirement of emission of dioxin furan.

Figure 1 also indicate that application of De-dio on incinerator A-F could reduce dioxin furan formation to some extent and proves to be helping that incinerators comply the emission limit stated. Inhibitions of dioxin furan formation on the basis of limit value concentration were 24% when 0.25% De-dio were applied, 27% when 0.50% and 0.75% De-dio were applied, 16% when 1% De-dio were applied and 10% when 10% De-dio were applied.

The result illustrates that the higher concentration of De-dio solution used, the higher efficiency of that solution in reducing

dioxin furan. Then the lower dioxin furan emission from incinerator A-F was obtained. However, 1% of De-dio seems to be the most possible concentration to be applied in controlling the formation of dioxin furan from the incineration processes.

The Specific Congener of Dioxin Furan Emission

Figure 2 presents the patterns of the specific PCDD/Fs congener distribution for tests operated on incinerator B with and without application of De-dio solution which showed that sample B2, B3 and B4 has similar dioxin furan patterns profiles. The profiles were different from the profile of sample B1, a sample tested on incinerator B without application of De-dio.

As in Figure 2 the major congeners for sample B1 were 2,3,4,6,7, 8-PeCDF, 1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-HxCDF. The concentration of 2,3,4,6,7, 8-PeCDF alone exceeded the limits of 0.1 ng/Nm³ permitted for emission of dioxin furan for such facility. The major congeners for sample obtained with the inhibitors i.e B2, B3 and B4 were 2,3,7,8-TCDD, 1,2,3,4,6,7,8-HpCDD, 2,3,4,7,8-PeCDF and 1,2,3,4,6,7,8-HpCDF. The concentrations of 2,3,4,6,7,8-PeCDF for each sample B2, B3 and B4 were in between 0.0010 – 0.0030 ng/Nm³, where the value was lower compared sample B1, without the application of De-dio.

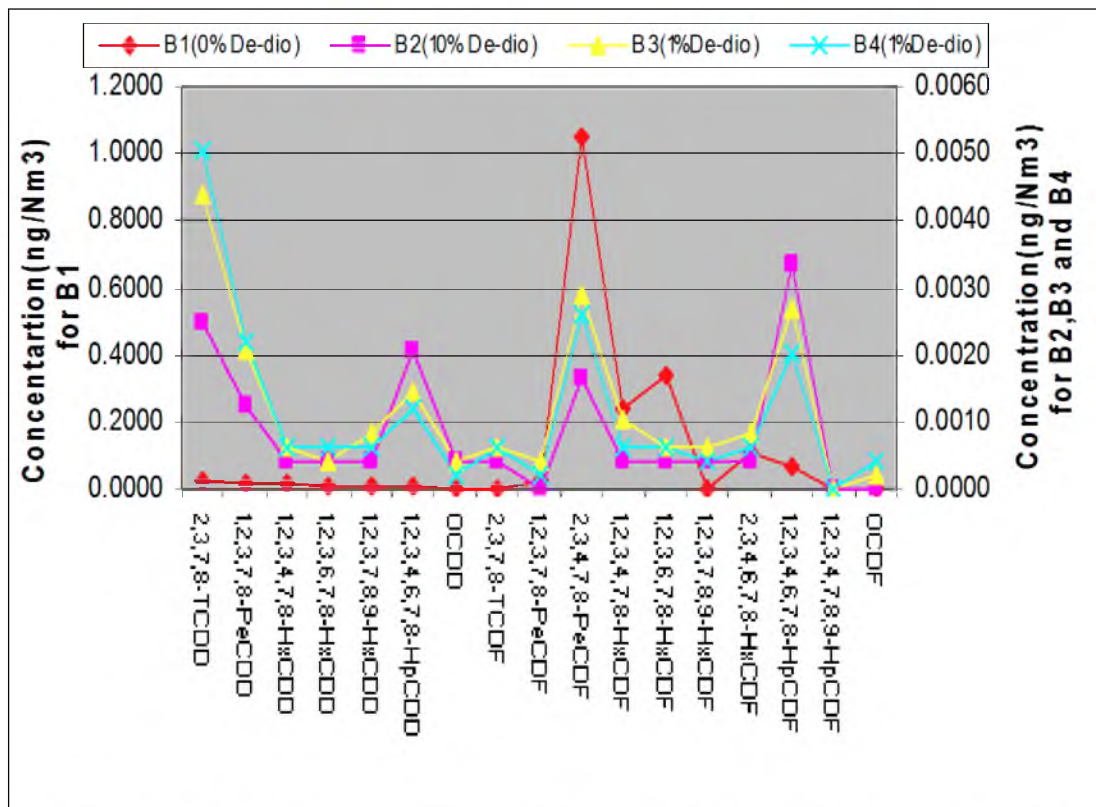


Figure 2 2,3,7,8-substituted PCDD/Fs congener patterns from incinerator B with and without application of De-dio

■4.0 CONCLUSION

The application of liquid inhibitor is seen to be innovative in minimizing the formation of PCDD/F in an incinerator. The results showed that the use of De-dio able to minimize the concentration of dioxin furan generated in medical waste incineration plants where the study showed that all the incinerators were able to achieve the dioxin-furan emission standard of 0.1 ng/Nm³ or better, despite of their difference in the incineration capacity.

In addition, a considerably small amount i.e. 1.5L/min of De-dio solution was injected in the combustion chamber in the study and yet the dioxin-furan emissions obtained were consistently below the regulatory limits for all the incinerators tested. The study also illustrates that the higher purity of the De-dio solution used, the lower the dioxin-furan emission obtained. However, 1% purity of De-Dio seems to be the most possible concentration to consider if the continuous use of the chemical is to be adopted in controlling dioxin-furan emission from incineration processes.

References

- [1] Addink, R., Paulus, R. W. L., Olie, K. 1993. Inhibition of PCDD/PCDF formation during de novo synthesis on fly ash using N- and S-compounds. *Organohalogen Compds.* 12: 27.
- [2] Addink, R., Paulus, R. W. L., Olie, K. 1996. Prevention of Polychlorinated Dibenzo-p-dioxins/Dibenzofurans Formation on Municipal Waste Incinerator Fly Ash Using Nitrogen and Sulfur Compounds *Environ. Sci. Technol.* 30(7): 2350.
- [3] Buckens, A., Huang, H. 1998. Comparative Evaluation of Techniques for Controlling the Formation and Emission of Chlorinated Dioxins/Furans in Municipal Waste Incineration. *J. Hazard. Mater.* 62: 1.
- [4] Chang, M. B., Lin, J. J. 2001. Memory Effect of the PCDD/F Emissions from Municipal Waste Incinerator in Taiwan. *Chemosphere.* 45: 1151–1157.
- [5] Chang, M. B., Cheng, Y. C., and Chi, K. H. 2006. Reducing PCDD/F Formation by Adding Sulfur as Inhibitor in Waste Incineration Processes. *Science of the Total Environment.* 366: 456–465.
- [6] Dickson, L., C. Lenoir, D., Hutzinger, O., Naikwadi, K. P., Karasek, F. W. 1989. *Chemosphere.* 19(8/9): 1435.
- [7] Ogawa, H., Orita, N., Horaguchi, M., Suzuki, T., Okada, M., Yasuda, S., 1996. Dioxin Reduction by Sulfur Component Addition. *Chemosphere.* 32(1): 151–157.
- [8] Ragnathan, K. and Gullett, B. 1996. Role of Sulfur in Reducing PCDD and PCDF Formation. *Journal of Environment Science Technology.* 30(6): 1827–1834.
- [9] Ruokojärvi, P. H., Asikainen, A. H., Tuppurainen, K. A., Ruuskanen, J. 2004. Chemical inhibition of PCDD/F Formation in Incineration processes. *Science of the Total Environment.* 325(1–3): 83–94.
- [10] Tuppurainen, K., Aatamila, M., Ruokojärvi, P., Halonen, I. and Ruuskanen, J. 1999. Effect of Liquid Inhibitors on PCDD/F Formation. Prediction of Particle-phase PCDD/F Concentrations Using PLS Modelling with Gas-phase Chlorophenol Concentrations as Independent Variables. *Chemosphere.* 38: 2205–2217.
- [11] Verhulst, D., Buckens, A., Spencer, P. J., Erriksson, G. 1996. Thermodynamic Behavior of Metal Chlorides and Sulfates under the Conditions of Incineration Furnaces *Environ. Sci. Technol.* 30: 50.