

APPLICATION OF IRON OXIDE CATALYST TO DETOXYFY DIOXINS IN FLY ASH AND POSSIBILITY OF CALUXTM ASSAY FOR SAVING ANALYSIS COST AND TIME

Yasuhiko Fujii¹, Toshiki Matsui¹, Junko Fujino², Masafumi Nakamura²,
Hiroko Kitagawa², Hiroshi Murata², Tomoko Okita¹, Tomoyuki Imai¹

¹Toda Kogyo Corporation, 1-4. Meijishinkai, Otake, Hiroshima, 739-0652, Japan

²Hiyoshi Corporation, 908 Kitanoshocho, Omihachiman, Shiga, 523-8555, Japan

Introduction

In Japan 78% of municipal solid waste (51.2 million tons in 1997) was disposed by 1843 incinerators (1997)¹. Dioxins (DXNs) such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are generated in the course of the disposal by these incinerators. DXNs are chiefly discharged in exhaust gas or ashes. In January 1997, the Ministry of Health and Welfare published "New Guideline" that proposed emission standard for DXNs calling for concrete reductions in the amount of DXNs in exhausts². "New Guideline" also indicated the necessity of restricting the total amount of the emissions of DXNs. Therefore, in the near future emphasis would be placed on detoxifying fly ash containing high concentration of DXNs and it would be expected that the disposal of fly ash could be a more significant problem³. Japanese companies involved in constructing incinerators have started to develop new detoxifying technology for dechlorination of chlorinated organic compounds in ash and to introduce them into incinerator systems⁴. We have already reported on the efficiency of the iron oxide catalyst for dechlorination of the polychlorinated hydrocarbons^{5,6}. However, optimizing the conditions by conventional analyzing methods can be costly and time consuming, thereby restricting the development of new disposal technology. In this study we report on the efficacy of iron oxide catalysts in the detoxification of DXNs during heating treatment of fly ash originating from municipal incinerators. We also report on the effectiveness of the CALUXTM assay⁷ in terms of costs and times compared with HRGC/MS, especially for development of new disposal and detoxification technology.

Material and Method

Materials

Fly ash samples from the dust catcher of the municipal solid incinerators were obtained from a city in Tochigi prefecture and analyzed by public method and by the CALUXTM assay. DXNs-TEQ of this ash was 6.9ng-TEQ/g by public method and 5.1 ng-CALUX·TEQ/g by the CALUXTM assay. TIC-8048 (α -FeO(OH), BET;86.3m²/g) and TIC-0018 (α -Fe₂O₃, BET;111.6m²/g) used as catalyst were obtained from Toda Kogyo Corporation. The mixing weight ratio of catalyst to ash was 1:20 or 0:20. Ash and catalyst were mixed by placing both in a polyethylene bag and shaking by hand.

Experimental method

Figure 1 shows rotary kiln in batch operation. The total kiln volume is 10 L and available volume is 2 L. We treated fly ash in this rotary kiln in batch operation. The weight of the ash was 400 g. The temperature of the ash during the operation was 303°~307° C and the retention time of the treatment was 45 or 60 minutes. The operations were carried out with controlled flow of air (0 or 1 L/min). The samples treated in the various conditions indicated in Table 2 were analyzed by HRGC/MS and by the CALUXTM assay.

HRGC/MS Public method

JIS K 0311 (1999) was applied to extraction, purification and HRGC/MS analysis of the ash samples.

CALUX™ Assay

The CALUX™ assay uses a patented recombinant mouse cell line that contains the luciferase reporter gene under control of dioxin responsive elements⁷. When these cells are exposed to environmental ligands such as DXNs, luciferase protein is synthesized. The amount of light produced by the luciferase protein is directly related to DXNs-TEQ. The CALUX™ assay method used has been described previously⁸.

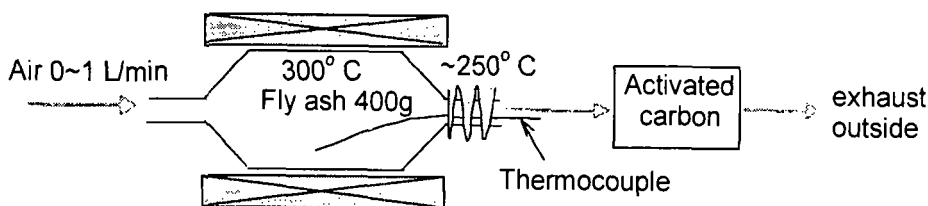


Figure 1. Diagram of rotary kiln used in experiment.

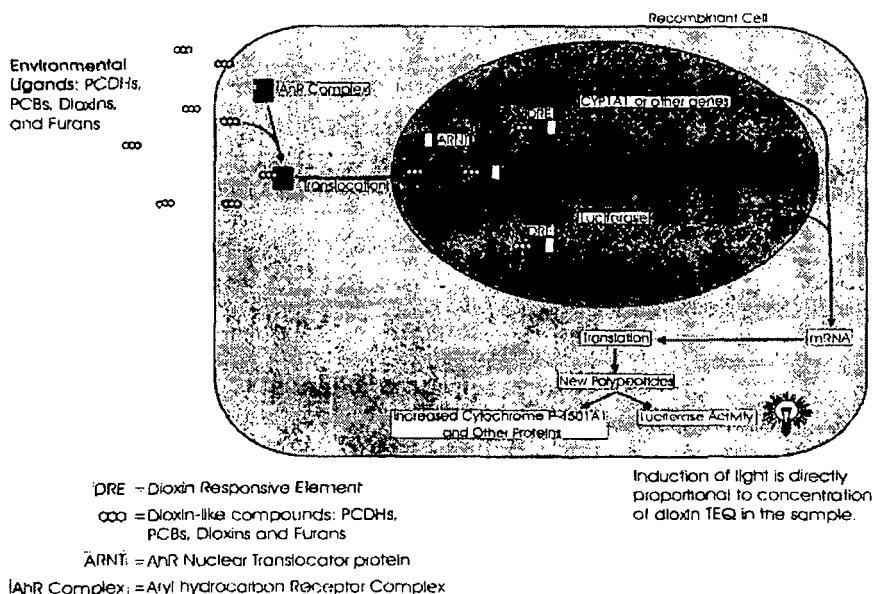


Figure 2. Mechanism of the CALUX™ assay

Results and Discussions

Table 1 and Figure 3 show the distributions of DXNs congeners of the different treatments. Table 2 shows the experimental conditions and DXNs-TEQ data from the public method and CALUX™ assay. Under conditions with no supplemental supply of air (0 L/min) at a

temperature of 300° C (Run 1, Run 2 and Run 4), DXNs-TEQ were 6.7 ng-TEQ/g, 5.3 ng-TEQ/g and 3.2 ng-TEQ/g, respectively. These results indicated that the addition of the iron oxide catalyst enhanced detoxification of DXNs. The ratio of DXNs congeners was characterized by the increase of PCDFs in Run 1. Huang et. al, 1995⁹ and Hagenmaier et. al., 1989¹⁰ pointed out that de novo synthesis of DXNs could contribute to this increase. On the other hand, with the addition of TIC-0018 (Run 4), all DXNs congeners were reduced. These results suggested that the formation of DXNs was depressed by the presence of this catalyst.

Table 1. HRGC/MS analysis results of the heating treatment of fly ash

	Fly ash	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
TeCDDs	34	42	30	28	17	13	23
PeCDDs	36	32	24	20	13	12	19
HxCDDs	38	15	13	13	8.8	8.3	11
HpCDDs	21	4.7	4.9	4.8	2.9	2.5	3
OCDDs	8.7	1.6	1.9	1.7	1.2	0.64	1.1
TeCDFs	65	130	84	68	40	20	110
PeCDFs	40	54	38	24	21	12	68
HxCDFs	29	13	11	9.6	8	5.7	24
HpDFs	13	2.6	3	2.5	1.5	1	3.5
OCDFs	1.8	0.16	0.2	0.2	0.14	0.096	0.25
PCDDs	138	95	74	68	43	36	57
PCDFs	149	200	136	104	71	39	206
PCDFs/PCDDs	1.08	2.1	1.85	1.55	1.65	1.06	3.6
Total DXNs	287	295	210	172	114	75	263

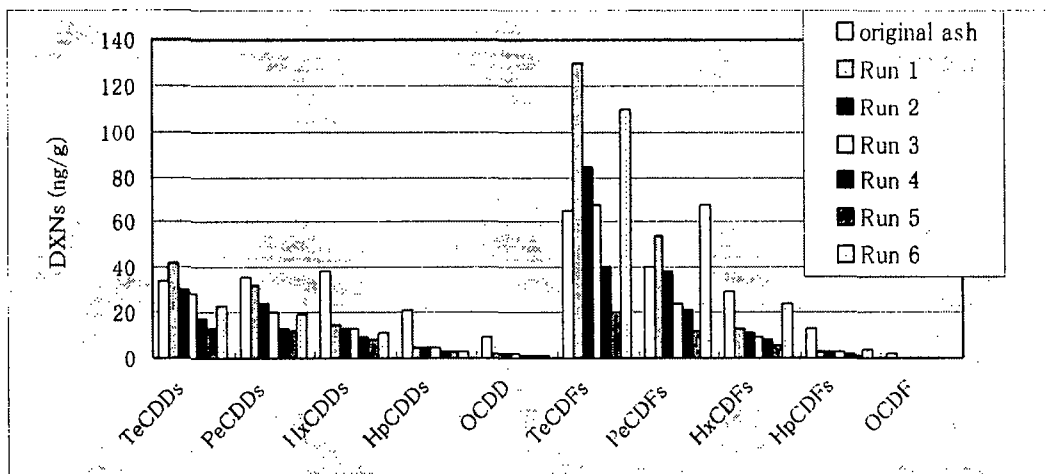


Figure 3. The Distributions of DXN congeners

Under conditions including a supply of air (1 L/min) at a temperature of 300° C (Run 3, Run 5 and Run 6), DXNs-TEQ were 4.5 ng-TEQ/g, 2.5 ng-TEQ/g and 6.5 ng-TEQ/g, respectively. These results also indicated that the addition of the iron oxide catalyst enhanced detoxification of DXNs. Especially in Run 5, all of the DXN congeners were lower than the original fly ash.

This result indicates the superiority of the addition of the iron oxide catalyst to the treatment for detoxifying DXNs. The DXNs-TEQ of Run 1 was almost equal to that of Run 6, so it may be concluded that DXNs-TEQ was scarcely affected by supply of air (in the range of 0 to 1 L/min) in the absence of iron oxide catalyst. In contrast under the conditions of the addition of iron oxide catalyst TIC-8048 and TIC-0018, from the results of Run 2, Run 3, Run 4 and Run 5, as a result of supply of air, DXNs were decreased about 20%. This indicated that supply of air was necessary for better treatment in the case of the addition of iron oxide.

The results from the CALUXTM assay were showed in Table 2. From these data, it was confirmed that DXNs-CALUX· TEQ/g were also diminished by the addition of TIC-8048 or TIC-0018. Moreover the supply of air enhanced the detoxification of DXNs. These data also indicated that the results from the CALUXTM assay were strongly correlated with those from HRGC/MS, thereby from the standpoint of its rapidity and costs the CALUXTM assay was appropriate to analyze DXN-TEQ in the case of development of new technology.

Conclusions

The effect of detoxifying DXNs was confirmed in the course of heating treatment of fly ash by the addition of iron oxide catalyst, TIC-8048 and especially TIC-0018. But the subject to define the mechanism of this detoxification of DXNs in ash remains. So it is necessary to further examine the relationship between exhaust gases from the treatment and the concentration of DXNs remaining.

We previously reported the strong correlation of CALUXTM results with HRGC/MS data⁸. In this study the HRGC/MS data and CALUXTM results were also strongly correlated. Based on these results the CALUXTM assay will be useful for optimizing the methods and conditions for the detoxification of DXNs. The advantages of the CALUXTM assay over HRGC/MS: rapidity, convenience and lower cost; should aid in the development of these detoxification methods.

Table 2. Treatment conditions and results of the heating treatment of the fly ash

Run	weight of the ash (g)	type of iron oxide -	weight of iron oxide (g)	supply of air (L/min)	temperature of ashes (°C)	retention time (min)	cooling time (min)	DXNs-TEQ	
								public method (ng-TEQ/g)	CALUX TM assay (ng-CALUX-TEQ/g)
1	400	-	-	0	303	45	20	6.7	3.0
2	400	TIC-8048	20	0	303	45	20	5.3	2.0
3	400	TIC-8048	20	1	307	45	20	4.5	1.6
4	400	TIC-0018	20	0	303	60	20	3.2	2.3
5	400	TIC-0018	20	1	303	60	20	2.5	0.8
6	400	-	-	1	303	60	20	6.5	1.4

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