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DIOXIN MONITORING BY A CELL-BASED Ah RECEPTOR BIOASSAY FOR A LOW-TEMPERATURE THERMAL DECHLORINATION PROCESS

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1. Introduction

The Special Measures Law on Dioxin Control was enacted in 1999 from the viewpoint that dioxin control measures had to be taken urgently in Japan, and the target value for fly ash was set at 3 ng TEQ/g [1)]. To comply with this law, over fifty municipal governments introduced a low-temperature (below 400 deg. C.) treatment of fly ash under oxygen-deficient condition (i.e. the Hagenmaier process [2)]; the HM process) for dechlorination of dioxins. The aim of this study is to confirm the reduction of dioxin-like activity of fly ashes treated by the HM process by cell-based bioassay measurement of Ah-R dependent activity as DR-CALUX® and the feasibility of monitoring during the HM process by the cell-based Ah receptor bioassay.

2. Materials and Methods

The materials and methods used were as previously reported [3)].

2.1. Materials

Fly ash samples were collected from six different plants (Plants A, B, C, D, E, and F) between 1999 and 2002. The details of the plants are shown in Table 1. The monitoring experiment by a bioassay was conducted at Plant D from October 28, 2002 to December 13, 2002.

2.2. Experimental Methods

Fly ash samples as raw fly ash or fly ash treated under normal conditions were collected at the inlet or the outlet of the HM process. The raw fly ashes obtained at the inlet of the HM process were treated with laboratory apparatus as fly ash under normal or intermediate dechlorination conditions. The normal conditions were 400 deg. C. and 120 min, and the intermediate conditions were 300 deg. C. and 30 min as shown in Table 2. The treatment equipment and procedure were as previously reported [3)].

2.3. Analysis

(1) Clean-up

The raw or treated fly ash samples were pretreated with hydrochloric acid and extracted with toluene in a Soxhlet apparatus for 16 h. The toluene extracts were concentrated, and extracts from each of the fly ash samples were cleaned up by the following method A or method B.

Method A: Column with activated silica gel. The unspiked extracted samples were passed through a

column (10 mm ϕ) filled with 3 g of heat-activated (24 h) silica gel 60 (Merck) with 200 mL of *n*-hexane. The eluate was evaporated to 5 mL, 50 μL of dimethyl sulfoxide (DMSO) was added, and then the sample volume was reduced to 50 μL by passing nitrogen gas over the samples slowly. Finally, it was diluted into the medium (0.4 %).

Method B: Reflux treatment with 44 % sulfuric acid/silica gel. The samples were refluxed with 50 g of 44 % sulfuric acid/silica gel in 100 mL of *n*-hexane for 60 min at 69 deg. C.

Copper treatment for removal of sulfur. Twelve grams of fly ashes for the monitoring experiment was extracted with 240 mL of toluene in a Soxhlet apparatus for 16 h. Before the extraction, 6 g of powdered Cu (150 - 250 μm) was added in the Soxhlet apparatus to remove sulfur. After the extraction, method B was applied to monitoring samples for clean-up.

(2) DR-CALUX®

The raw and treated fly ash samples were analyzed according to the guidelines from the BioDetection Systems (www.biodetectionsystems.com). The luciferase activity was measured by using LucLite™ (Packard) and the TopCount NXT® Microplate Scintillation & Luminescence Counter (Packard).

(3) Chemical analysis

Chemical analysis of dioxins was conducted based on the Japanese Industrial Standard (JIS) K 0311 and JIS K 0312.

3. Results and Discussion

The comparison of chemical analysis values (TEQ) and DR-CALUX® values (CALUX-TEQ) is shown in Figure 1. The CALUX-TEQ values are higher in general than the TEQ values for the samples owing to the existence of other dioxin-like compounds except PCDDs, PCDFs, and coplanar PCBs in the fly ashes. However, the CALUX-TEQ values by method B are close to the values of chemical analysis compared with method A owing to the removal of PAHs in the fly ash. The result of the long-term monitoring experiment by the HM process at Plant D is shown in Figure 2. The time needed for monitoring from sampling to the end of the DR-CALUX® analysis was just 4 days. The values for the raw fly ashes based on DR-CALUX® were 1 - 10 ng CALUX-TEQ/g. The values for the treated fly ashes were below approximately 0.01 ng CALUX-TEQ/g. A treatment efficiency of over 99 % was thus obtained. We confirmed the routine performance of the HM process at plant D for over one month.

4. Acknowledgements

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5. References

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Table 1 Details of the municipal solid waste incineration plants from which the fly ash samples were obtained

Plant	HM process	Type of solid waste	Operation type	Furnace type	Cooling type	Slaked lime	Activated carbon	Dust collector*	Year of sampling
Plant A 300t/d×2	Yes	Domestic waste	Continuous	Stoker	Boiler	Yes	Yes	ESP	2000
Plant B 300t/d×2	Yes	Domestic waste Ordinary business waste	Continuous	Stoker	Boiler	No	Yes	ESP	1999 2000
Plant C 200t/d×3	Yes	Domestic waste Ordinary business waste Bulky combustible waste	Continuous	Stoker	Boiler	Yes	Yes	FF (#1, #2) ESP (#3)	2000
Plant D 200t/d×3	Yes	Domestic waste Ordinary business waste Bulky combustible waste Sewage sludge	Continuous	Stoker	Boiler	No	Yes	ESP (‘99, ‘00) FF (‘02)	1999 2000 2002
Plant E 50t/16h×3	No	Domestic waste	Semi-continuous	Stoker	Water spray	Yes	No	ESP	2001
Plant F 25t/16h×2	No	Domestic waste Bulky combustible waste	Semi-continuous	Fluidized bed	Water spray	No	No	ESP	2001

* ESP: electrostatic precipitator, FF: fabric filter.

Table 2 Laboratory experimental conditions for dechlorination treatment

	Plant A	Plan B	Plant C	Plant D	Plant E	Plant F
Raw fly ash	a	(a)	a	(a)	a	a
Fly ash treated under normal conditions	a	(a)	a	(a)	b	b
Fly ash treated under intermediate conditions	b	(a)	b	(a)	b	b

a: Samples were collected form the municipal solid waste incineration plants in Table 1.

b: Samples were made with laboratory apparatus. The normal conditions for the laboratory experiment were 400 deg. C. and 120 min, and the intermediate conditions were 300 deg. C. and 30 min.

( ): Sampling and chemical analysis were conducted in 1999, and the bioassay was conducted in 2000.

The Hagenmaier process treats fly ash for dechlorination under the following conditions:

1) less than 1 vol % of the atmospheric oxygen in the heating drum,
2) 350 - 400 deg. C. of the heating temperature,
3) 30 - 60 min of the retention time, and
4) less than 100 deg. C. of the discharge temperature of the treated fly ash.

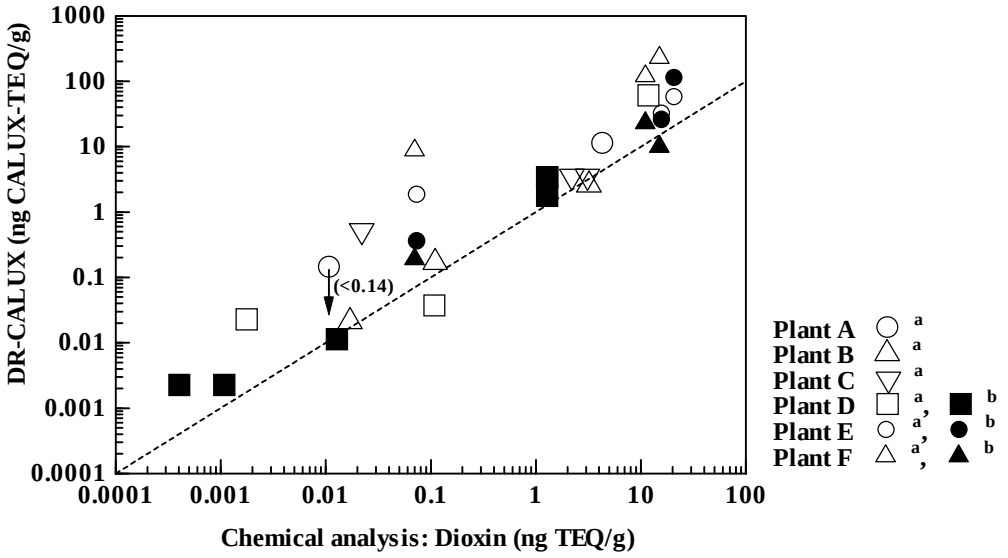

Fig.1 Comparison of TEQ values between chemical analysis and DR-CALUX results for fly ash samples

Clean-up for DR-CALUX
[a] Activated silica column treatment (nonoxidative method)
[b] Reflux treamtment with 44 % sulfuric acid/silica gel (oxidative method)

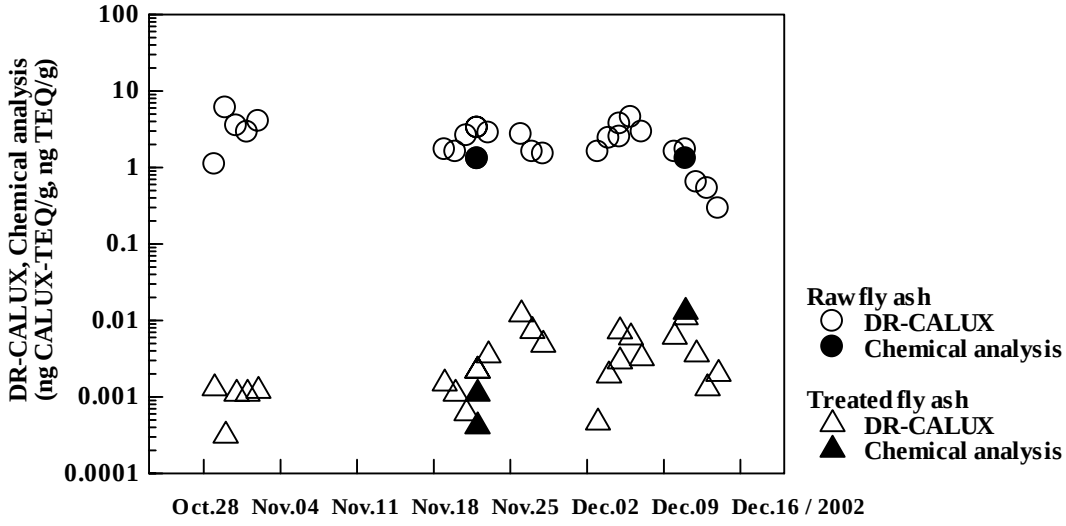

Fig.2 Dioxin monitoring results during the Hagenmaier process at Plant D using DR-CALUX and chemical analysis