A NEW DESTRUCTION TECHNIQUE FOR DIOXIN ANALOGUES IN LANDFILLS AND FLY ASH CONCERNING WASTE COMBUSTION BY DCR-DEHALOGENATED METHOD

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Introduction

In recent years, dioxin analogues including polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar PCBs (Co-PCBs) have been the much concern of the public, due to their extremely high toxicity. In Japan, more than 90% of dioxin analogues is surmised to be emitted through the flue gas from several thousands municipal solid waste (MSW) and industrial waste incinerators. The total annual emission in the fiscal year of 1999 was estimated to be ca. 3,000 gTEQ. In Japan, “Dioxins Special Measures Law” was established in July 1999. In the law, the discharge standard for dioxin analogues was set up to be 3 ngTEQ/g. for the bottom ash, fly ash and cinder from the waste incineration facilities with the incineration capacity of more than 50 kg/hour and from the industrial production factories including electric furnace for steel manufacture, sintering facility for crude steel manufacture, zinc recovery facility and aluminum-alloy manufacture facility. In addition, all these incineration ashes were designated as “the special control waste” to be filled in the control type landfill.

In Japan, a great quantity of ash such as bottom ash and fly ash have been filled in the landfill, due to an annual combustion of ca. 80 million tons of solid waste. Consequently , the capable period for the use of MSW and industrial waste landfills are respectively surmised to be only 8 years and 2 years.

From these circumstances, we established a newly safe and economy decomposition method for dioxin analogues in the ash and landfill by DCR-dehalogenated method.

Principle of DCR-dehalogenated method

In Japan, most bottom and fly ash from the solid wasted incineration facility are filled in the final landfill. Therefore, the content of the landfill is manly composed of bottom ash, fly ash, cinder and soil with ca. 20 % of moisture. Therefore, the landfill is heavily contaminated with dioxin analogues. In our newly developed remediation method, the wet landfill was first powdered by “Dispersing by Chemical Reaction” (abbreviated as DCR), consisting essentially of an addition of a special lipophilic CaO covered with a film of hydrophobic substance (commercial name: Hibic Powder) and mixing mechanically. In the DCR process, lipophilic compounds in the landfill are easily gathered on the surface of lipophilic CaO, resulting in a small particle of water to get together, followed by a conversion of CaO to Ca $(OH)_2$[1)]. In general, the fly ash from the solid waste incineration facility shapes roughly a round with a diameter of a few tens mm and its surface is covered with a film of alkaline metal salts. The cover of alkaline metal salts obstructs the decomposition of dioxin analogues by a dechlorination reaction with an alkaline metal such as metal sodium. Therefore, it was necessary the DCR treated matter to pulverize into smaller powder for destruction of the film cover of alkaline metal salts. In addition, our newly developed metal sodium, which was covered with a film of lipophilic matter for an intercept from a chemical reaction with moisture in the air, was used as an agent of dechlorination due to a high cost performance remediation, because this agent was capable of application for cleaning the contaminated landfill without extracting dioxin analogues at a room temperature. We also found a Tower Mill, one of vertical type ball mills, to be the most suitable machine for this remediation method by using the metal sodium.

Addition of Catalyst X and a metal sodium covered with a lipophilic matter film, the DCR treated matter was pulverized into a fine small power with of ca. 3 mm and was dehalogenated under a stream of nitrogen by using the Tower Mill. The dehalogenation reactions of dioxin analogues were shown as follows.

$$\text{PCDD with nCl + nNa} \xrightarrow[\text{nH}]{\text{Catalyst X (Hydrogen donor)}} \text{Dibenzo-p-dioxin + nNaCl}$$

$$\text{PCDF with nCl + nNa} \xrightarrow[\text{nH}]{\text{Catalyst X (Hydrogen donor)}} \text{Dibenzofuran + nNaCl}$$

Materials and Methods

Sample

Landfill sample: In 2000, about 10 m^3 of sample was obtained from the final landfill for a MSW incineration facility and filtered through 30 mm meshes in order to remove scrap plastics, metal, glass, wood, etc. After filtration, the material was thoroughly mixed for 4 hrs. using two mixing machines of twin-header and backhoe. The sample contained 480 pgTEQ/g dry weight of PCDDs and PCDFs.

Fly ash sample: In 2000, about 4 m^3 of sample was gained from the above incineration facility and was thoroughly mixed for 4 hrs. using mixing machines of twin header and backhoe. The contamination level of PCDDs and PCDFs in the mixed sample was 910 pgTEQ/g dry weight.

Contaminated soil sample: In 2002, about 4 m^3 of soil was obtained from the area contaminated with bottom ash and cinder from an industrial waste incineration facility. The sample contained 17.5% of moisture and 25,200 pgTEQ/g dry weight of PCDDs and PCDFs.

Analytical method

The analyses of dioxin analogues were carried out by two analytical companies of Shimadzu-Techno-Research, Inc., Japan and IVE, Inc., Germany. The analyses by Shimadzu- Techno-Research, Inc., and IVE, Inc., were respectively done according to Japanese standard and EU standard of EN 45001.

The outline of Japanese standard method was essentially composed of an addition of internal standards, treatment with 2 M HCl, Soxlet extraction with toluene for 16 hrs., clean-up on a multi-layer silica gel column and alumina column. The cleaned up extract was analyzed for dioxin analogues in EI-SIM mode at a resolution of 10,000 using HRGC-HRMS. On the other hand, the outline of EU standard method was essentially composed of an addition of internal standards, Soxlet extraction with toluene for more than 18 hrs., clean-up on a multi-layer silica gel column and a macro-alumina column, followed by a gel permeation chromatography, HPLC on Neucleosil 5-Nitro and a micro-alumina column chromatography. The final extract was analyzed for dioxin analogues in EI-SIM mode at a resolution of 10,000 using HRGC-HRMS. A calculation of 2,3,7,8-TCDD toxicity equivalency quantity (TEQ) of the dioxin analogues in analyzed samples was carried out on the basis of TEFs by WHO.

As above described, there was a considerable difference in the procedure of Japanese and EU standards. However, we confirmed that the two methods gave a good coincidence in the crosscheck data of 3 samples (Table 1).

Results and Discussion

Result concerning the landfill sample

The moisture of sample gives an adverse effect for dechlorination of dioxin analogues by metal sodium. Therefore, the removal of moisture is essentially the most important for our remediation method. As shown in Table 2, the removal rate of moisture increased with an increase of added amount of a special lopophilic CaO (Hibic Power, HP) in the process of DCR. From the result, it was found the most suitable addition amount of HP to be 30 % versus the original weight of landfill sample. In this case, the landfill sample contained 2.79 % of moisture after DCR treatment. However, we confirmed the moisture to be completely removed for 30 min in a mixing process by using a Tower Mill.

After the DCR treatment, the landfill sample was the powder of particle with a diameter of ca. 38.5 mm on the average. As shown in Table 3, however, the Tower Mill was adjusted the sample particle to pulverize into smaller one with a diameter of 4 mm on the average, meaning one original particle to be divided into 890 fine particles. This steered the remediation of contaminated landfill to success. In Test No. 4 to 6, dioxin analogues in the landfill sample were destroyed in the range of 99.84 to 99.95 % by our remediation technique. Consequently, the contamination level decreased from 480 pgTEQ/g dry weight to 0.25 - 0.78 pgTEQ/g dry weight. These levels were all lower than the average level (1.8 pgTEQ/g) of PCDDs and PCDFs in the soil at our background area. Therefore, it is insisted that the diminished level to be safe for Japanese people.

Result concerning the fly ash sample

In the case of fly ash sample, we used a new Catalysis Y having a higher boiling point than Catalysis X. As shown in Table 4, the contamination level of dioxin analogues were diminished from 910 pgTEQ/g to 0.080 – 0.33 pgTEQ/g with an average of 0.27 pgTEQ/g, showing the level to be equal to only 1/7 of the average dioxin analogues level in the backgrounds. The destruction rate was 99.95 to 99.991 % with an average of 99.97 %. From this result, the contamination level in the treated fly ash sample is apparently safe for us.

Result concerning the soil sample

As well as the cases of landfill and fly ash samples, our remediation method gave an excellent destruction efficiency for the soil samples with a heavy contamination level of 21,000 to 28,000 pgTEQ/g dry weight, showing the maximum destruction rate to be 99.92%.

References

1. Bolsing, F. (2000) in: Remediation Engineering of Contaminated Soils (Wise, D.L. et al., Ed.), Marcel Dekker, Inc., pp. 849-929

Table 1. Crosscheck data of dioxin analogues in three samples by Shimadzu-Techno-Research, Inc. and IVE, Inc.

Sample	Concentration of PCDDs and PCDFs (pgTEQ/g dry weight)	
	Shimadzu-Techno-Research Inc.	IVE, Inc.
Sample 1	23	27
Sample 2	7.4	7.4
Sample 3	21	31

Table 2. Alteration of moisture content in the landfill sample by DCR in four trials

Test No.	Addition of Hp (%)	Moisture content (%)		Removal rate (%)
		Before DCR	After DCR	
1	10	28.4	12.9	54.6
2	20	29.2	7.65	73.8
3	30	28.9	2.79	90.3
4	40	32.8	2.33	92.9

Table 3. Destruction of dioxin analogues in the landfill sample by our new method

Test No.	Sample (kg)	Size[a)] (mm)	Na (g)	Catalysis (g)	R. T.[b)] (hr)	Concentration (pgTEQ/g)		Destruction Rate (%)
						Before	After	
1	19	4	240	240	2.0	480	87	81.9
2	19	4	300	1,400	2.0	480	28	94.2
3	19	4	300	1,400	2.0	480	21	95.6
4	19	4	300	1,400	2.0	480	0.78	99.84
5	19	4	300	1,400	2.0	480	0.25	99.95
6	19	4	300	1,400	2.0	480	0.30	99.91

Amount of HP: 5.7 kg a): Sample particle size b): Reaction time

Table 4. Destruction of dioxin analogues in the fly ash sample by our new method

Test No.	Sample (kg)	Size[a)] (mm)	Na (g)	Catalysis (g)	R. T.[b)] (hr)	Concentration (pgTEQ/g)		Destruction Rate (%)
						Before	After	
1	14	4	800	400	2.0	910	0.33	99.96
2	14	4	800	400	2.0	910	0.080	99.991
3	14	4	800	400	2.0	910	0.041	99.95
Average	14	4	800	400	2.0	910	0.27	99.97

Amount of HP: 1 kg a): Sample particle size b): Reaction time