

TREATMENT OF DIOXIN CONTAMINATED SOIL BY BCD PROCESS

Seiji Kashiwagi and Hisayuki Toda

Ebara Corporation, 4-2-1 Honfujisawa, Fujisawa-shi, Kanagawa-ken 251-8502, Japan

Introduction

In Japan, Dioxins Special Measures Law was established in 1999 and the environmental standard for dioxins (PCDDs/DFs) was established to be 1000pg-TEQ/g. Even if the environmental standard is met, investigation is required if TEQ concentration is above 250pg-TEQ/g.

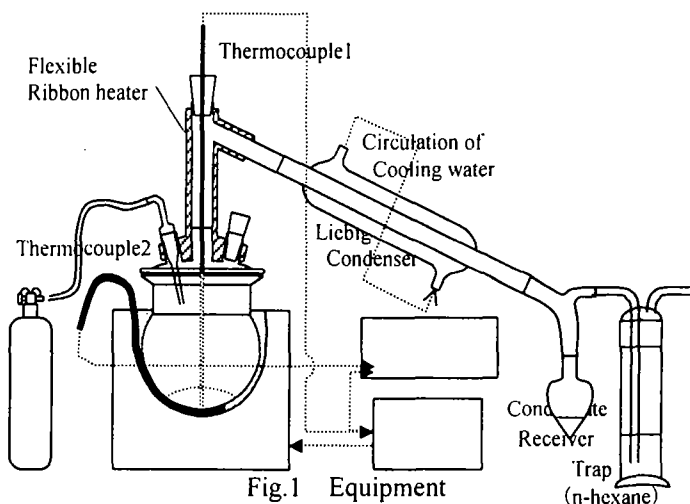
The BCD process is a chemical dechlorination, and is effective to remediate soils contaminated by persistent organic chlorinated compounds such as PCBs and PCDDs/DFs¹⁾. In the treatment method reported here, NaHCO₃ is added to a contaminated soil, and the remediation is conducted at 350 - 400°C under nitrogen atmosphere.

We have already reported remediation tests on a PCDDs/DFs contaminated soil and have demonstrated that the BCD is a valid technology²⁾. We here report the results of the laboratory tests conducted to gain knowledge of changes in concentration of PCDDs/DFs and TEQ in low-temperature short-time treatments, effects of NaHCO₃ addition on the decomposition of PCDDs/DFs, and the decomposition behavior in the treatment. We also report the results of treatability test of the contaminated soil using a 10kg/h-continuous treating plant.

Materials and Methods

PCDDs/DFs contaminated soil (7800pg-TEQ/g) was employed. The soil was a silt base with fine-grain sands. It was air-dried in a hood overnight (moisture content after drying: about 13%), this was followed by removal of sands whose size was over 8mm in diameter before testing. Fig.1 shows the equipment used for the tests.

70g dry-weight of soil was placed in an iron flask, and then the flask was heated by a heating mantle. The



temperature was controlled by a heater controller with a thermocouple inserted into the soil in the flask through a branched glass tube. In order to avoid moisture condensation inside the branched tube, the tube and the lid of the flask were heated to about 200°C. Nitrogen atmosphere was maintained in the flask. Gases evolved were trapped in hexane through a Liebig condenser.

Upon completion of heating, the flask was removed from the heater and was allowed to cool. The resulting soil was then analyzed.

10 - 11ml of water condensate was obtained from each run. The lid of the flask, the branched tube and the condenser were washed by acetone and toluene and the washes were combined with the condensate for analysis.

Table1 summarized test conditions employed.

Table1 Test conditions

	Run1	Run2	Run3	Run4	Run5	Run6
Temperature (°C)	215	240	400	400	400	400
Time (min)	10	10	60	60	60	60
NaHCO ₃ (%)	3	3	3	1	0.5	0
Nitrogen flow rate (ml/min)	100					

Results and Discussion

1. Changes of Concentrations and TEQ in Low-temperature Short-time Treatment

Fig.2 and Table2 show analysis results of the untreated soil as well as the treated soil obtained from Run1 and Run2. The concentrations of PCDDs/DFs were reduced in Cl₅ - Cl₈ chlorinated compounds. On the other hand, the concentrations of T4CDDs were found to be increased in Run1 and Run2. The concentrations of T4CDFs were almost unchanged in both tests, suggesting that decomposition and formation were occurring simultaneously.

Comparing the total concentrations for Cl₄ - Cl₈ chlorinated compounds, the levels for the treated soils in Run1 and Run2 were smaller than those for the untreated soil, indicating that decomposition was occurring at low-temperature short-time treatment. In comparison of

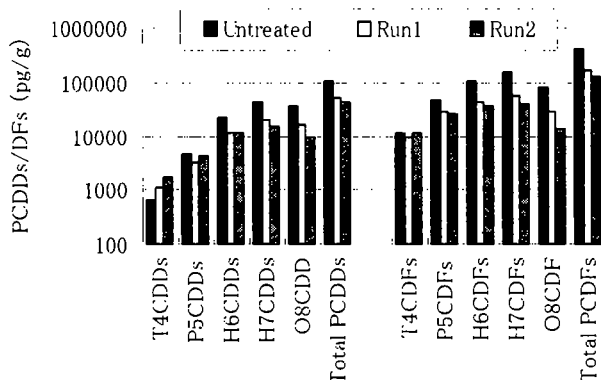


Fig.2 Congener patterns before and after treatment

Table2 The PCDDs/DFs level and TEQ in the soil (R1, R2)

	Concentration (pg/g)			WHO-TEQ (pg/g)		
	PCDDs	PCDFs	Total	PCDDs	PCDFs	Total
Untreated	110000	400000	510000	1400	6400	7800
Run1	51000	170000	220000	800	3100	3900
Run2	42000	130000	170000	920	2600	3500

TEQ for PCDDs/DFs, the level in Run2 was smaller than that in Run1 as in the case of actual concentration. However, the PCDDs level in Run2 was larger than that in Run1. This is due to the contribution of 2,3,7,8-T4CDD and 1,2,3,7,8-P5CDD formed by dechlorination of the high chlorinated compounds.

2. Effects of NaHCO₃ Added

Analysis results of the treated soils in Run3 - Run6 are summarized in Fig.3 and Table3.

There was a clear difference between Runs 3, 4 (NaHCO₃ added: 3%, 1%) and Runs 5, 6 (NaHCO₃ added: 0.5%, 0%). The former showed lower PCDDs/DFs concentrations throughout all the chlorinated compounds. Also observed were marked decreases of Cl₆ - Cl₈ compounds.

The results showed that NaHCO₃ was involved in dechlorination of highly chlorinated compounds, rather than it promoted desorption of PCDDs/DFs from soil³⁾. It was also found that 3% addition of NaHCO₃ was more effective in reducing TEQ than 1%.

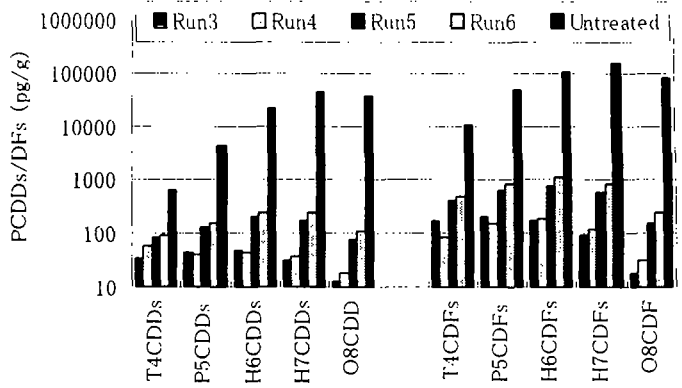


Fig.3 Effect of added NaHCO₃ amount on the treatment

Table3 The PCDDs/DFs level and TEQ in the soil (R3 - R6)

	Concentration (pg/g)			WHO-TEQ (pg/g)		
	PCDDs	PCDFs	Total	PCDDs	PCDFs	Total
Run3	180	650	830	7.5	11	19
Run4	210	590	800	42	13	55
Run5	670	2600	3300	16	45	61
Run6	850	3600	4500	18	62	80
Untreated	110000	400000	510000	1400	6400	7800

3. Behavior of PCDDs/DFs in the treatment

Fig.4 shows the congener distribution patterns of the untreated soil, Run3 soil and Run3 condensate.

Each congener distribution pattern for the condensate was similar to that for the treated soil, however different from that for the untreated soil. The treated soil and the condensate evenly contained Cl₄ - Cl₈ compounds, and were not distributed in favor of low Cl compounds. Thus, it is concluded that dechlorination of PCDDs/DFs in soil proceeds rapidly and then, decomposition and partial desorption of PCDDs/DFs occur at the same time.

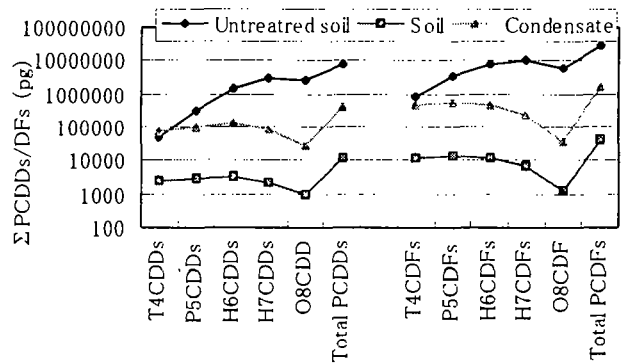


Fig.4 Congener pattern - before and after treatment

4. Percent decomposition of PCDDs/DFs

Fig.5 shows relative percentages of PCDDs/DFs decomposed and that remained in the treated soil and the condensate.

With the total amount of each chlorinated compound in the untreated soil being 100%, the percent decomposition was obtained by subtracting percentages of the chlorinated compound in the treated soil and the condensate. Percent decomposition increased as the number of chlorine atoms increased, and it was higher in PCDFs than in PCDDs. On the other hand, the amount of T4CDDs in condensate increased about 1.7 times the initial level.

Table 4 summarizes relative percentages of PCDDs/DFs, actual concentration, and TEQ expressed as total of Cl₄ - Cl₈ compounds combined in the soil and condensate in Run3. With input PCDDs/DFs amount being 100%, the soil and the condensate contained 0.16% and 5.7% respectively, therefore, percent decomposition of PCDDs/DFs in this system was found to be about 94%.

On the other hand, percent decomposition in TEQ was about 91%.

The treated soil in Run3 was 19.0pg-TEQ/g

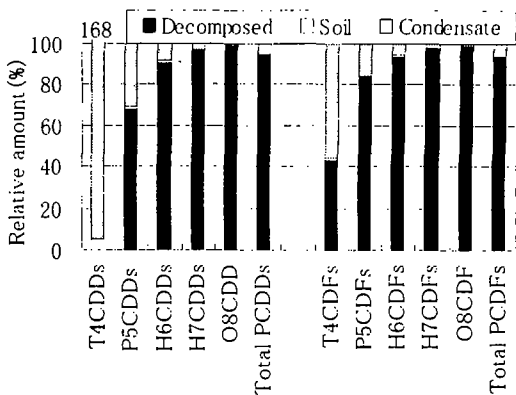


Fig.5 Percent decomposition of congeners

Table 4 Abundance of PCDDs/DFs in soil and condensate from Run3

		Soil	Condensate	Soil + Condensate	Input (PCDDs/DFs)
Total amount of PCDDs/DFs	pg	58100	2090000	2150000	36700000
	Percentage (%)	0.16	5.7	5.9	100
WHO-TEQ	pg-TEQ	1330	49500	50800	562000
	Percentage (%)	0.24	8.8	9.0	100

that sufficiently met the environmental standards.

The PCDDs/DFs concentration of condensate was about 4000ng-TEQ/L. We have already reported that PCDDs/DFs could be converted into innocuous substances by treating with an alkali such KOH in high boiling oil⁴⁾.

5. Results of Soil Treatability Test in a Pilot Plant

The schematic illustration of test equipment is shown in Fig.6. Treatment conditions were as follows: temperature; 400°C, residence time; 60min, NaHCO₃ added; 3%. The amount of soil used for test was 75kg. Treating 6500pg-TEQ/g contaminated soil brought the concentration down to 14pg-TEQ/g, and the exhaust gas was 0.000058ng-TEQ/m³ (NTP), resulting in extremely low environmental burden.

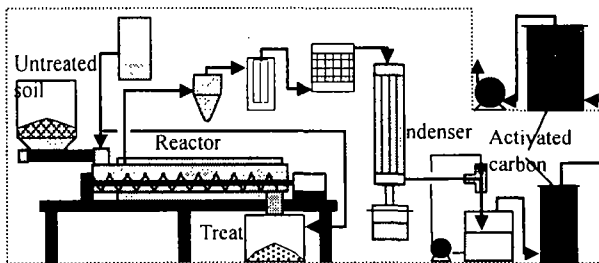


Fig.6 Pilot plant flow

References

1. US EPA (1991) Innovative Treatment Technologies, EPA/540/9-91/002
2. Rappe, C., Anderson, R., Öberg, L., van Bavel, B., Uchida, R., Taniguchi, S., Miyamura, A., Toda, H. (1998) Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Battelle Press, CI-6, 195
3. Chen, A., Gavaskar, A., Alleman, B., Massa, A., Timberlake, D., Drescher, E. (1997) Journal of Hazardous Materials, 56, 287
4. Toda, H., Miyamura, A., Shinmura, H., Taniguchi, S., Uchida, R., Takada, M., Hosomi, M., Murakami, A., Rappe, C. (1998) Organohalogen Compounds, 36, 27