

## Chemical Remediation of PCB-contaminated Soil using BCD Continuous Treatment Pilot Plant

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## **1. Introduction**

Because PCBs are toxic compounds which are difficult to decompose, the conventional method for treating soil contaminated by PCBs mainly involves excavating the contaminated soil and disposing in an isolated landfill or water-barrier landfill in Japan. That containment-type of treatment, however, raises difficulties in some cases because it is very costly and requires a disposal site for receiving the contaminated soil. In addition, it will be necessary to carefully monitor and maintain these landfill sites over the long-term in order to ensure these sites remain safe. Accordingly, an improved technology to decontaminate PCB-contaminated soil is required.

In the United States of America, the Environmental Protection Agency has developed the Base Catalyzed Decomposition (BCD) Process, which decontaminates the soil itself through the dechlorination decomposition of PCBs in the contaminated soil. Some contaminated areas in the U.S. have already adopted this process on a commercial scale.

In the preceding paper, we reported the results of a batch-wise laboratory test on artificial contaminated soil <sup>1)</sup>. This time we conducted a series of tests to decontaminate actual contaminated soil using a pilot plant, and we obtained favorable treatment results. This paper reports the pilot test results.

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## 2. Experimental plant

Fig. 1 shows a flow diagram of the experimental pilot plant. The plant consists of a set of preliminary treatment equipment including a screen, a meter and a mixer, and main treatment equipment including a feeder, a reactor, a cyclone, a filter, a condenser, activated carbon adsorbers, and a gas pump. Those units are installed in a container. A nitrogen gas generator is attached to the plant to maintain an inert atmosphere in the reaction space. The container is fabricated in a module having external dimensions of 6.3 m (length) x 3.2 m (width) x 3.5 m (height) and weighing approximately 10 tons. The pilot plant can be transferred on a trailer for treatment at the polluted site. The air inside of the container is exhausted by a ventilation fan through the activated carbon adsorber. The reactor is a screw conveyer, which is heated by an external electric heater. The reactor is provided with three sampling openings on a side wall. The retention time of the soil up to the sampling opening is 0.25 hour, 0.5 hour, and 1.0 hour, respectively. Thermocouples are inserted from the top of the reactor at the position of sampling openings to determine the soil temperature within the reactor.

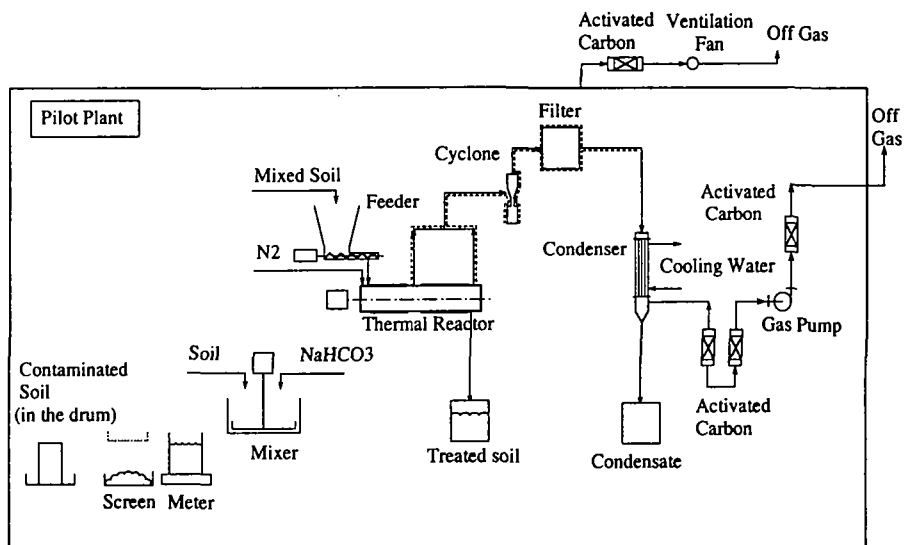


Fig.1 The Flow Diagram of the Pilot Scale Experimental Plant in BCD Soil Treatment

## 3. Experimental methods

A single batch feed (operating time ranging from 4 to 5 hours) of soil (10 mm opening pass) and NaHCO<sub>3</sub> were weighed and blended in the mixer. The mixed soil was charged into the hopper on the feeder. After the reactor temperature reached a specified level, the feeder was started to continuously charge the soil into the reactor. The retention time of the soil in the reactor was controlled to 1 hour by adjusting the screw rotational speed with an ON-OFF timer. The soil discharged from the reactor was cooled in a vessel equipped with water-cooled jacket and was taken out after completing the experiment. During the experiment, N<sub>2</sub> gas was introduced from two places in the reactor, and a gas discharge pump was kept operating to discharge the gas from the reactor via the four-

stage activated carbon adsorber to maintain the reactor atmosphere at a reduced pressure. The condensate was stored in a receiving tank. The condensate in the receiver tank was discharged after the experiment to be stored in a sample bottle.

The soil was subjected to a chemical analysis and elution test before and after treatment. The analysis of the soil was conducted using mainly ECD/GC, which is an officially accepted method, and GC/MS was also applied to part of soil for comparison. The condensate was analyzed by GC/MS.

Table 1 shows the analytical condition of ECD/GC, and Table 2 shows the analytical condition of GC/MS. The elution test was carried out by the method specified in the "Environmental Standard relating to Contamination of Soil" (Notification No.46 of the Environment Agency in Japan, August 23, 1991).

The total quantity of PCBs in the condensate was extracted by n-hexane followed by concentration. The concentrate was then transferred into a liquid phase reaction experimental unit to decompose the PCBs.

Fig. 2 shows a schematic drawing of the liquid phase reaction experimental unit.<sup>2)</sup> A hydrogen donor (C-heavy oil) of 150 ml, a carbon catalyst, and NaOH were added to the PCBs extracted from the condensate.

The mixture was then heated to 350°C on a mantle heater in a nitrogen gas atmosphere. Sampling was conducted at a specified interval to determine the PCBs concentration. After confirming that the PCBs concentration became ND (1 mg/l or less), heating was stopped to complete the experiment.

Table 1 ECD/GC Conditions

GC	Shimazu GC-14B
MS	ECD
Fillers	Silicon OV-1 2% Chromosorb WAW 80/100
Column	Glass 3mm $\phi$ $\times$ 3m
Column Temp.	195°C
Det. Temp.	230°C
Inj. Temp.	230°C
Carrier Gas	N <sub>2</sub> 40 ml/min

Table 2 GC/MS Conditions

Instrument	HP5890/HP5971A
Column	HP-5MS Silica Capillary Column 30m $\times$ 0.25mm $\times$ 0.25 $\mu$ m
Inj. Temp.	250°C (Splitless)
Column Temp.	70°C (3.5min hold) 25°C/min 180°C (2.5min hold) 5°C/min 280°C (15min hold)
Carrier Gas	He 1 ml/min
Mass Range	50 ~ 550 m/z
Ion Source Temp.	280°C

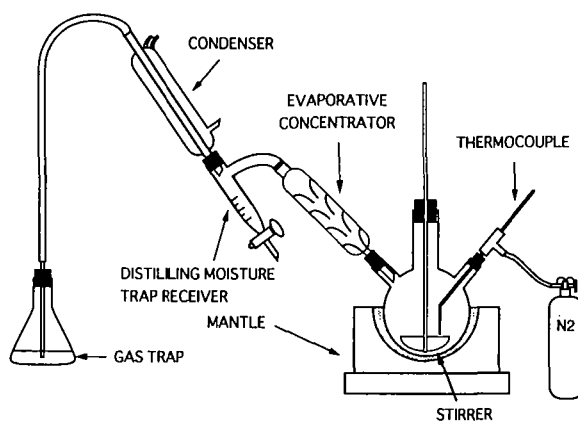


Fig.2 Experimental Apparatus for BCD liquid phase reaction

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## 4. Results and Discussion

Table 3 shows the properties of soil used in the experiment. The soil had a neutral pH value and contained 7.3% of organic matter.

Table 3 The Properties of the Soil used in the Experiment

Ignition loss (%)	7.3
C (%)	6.4
H (%)	0.83
pH	7.1

Table 4 shows the PCBs concentration in the soil before and after treatment. The soil treatment conditions were: three soil temperature levels, 280°C, 330°C, and 380°C; three NaHCO<sub>3</sub> concentration levels, 0%, 3%, and 6%; and one soil retention time, 1 hour.

For the case of a retention time of less than 1 hour, the study was examined using the sampling openings at the side wall of the reactor.

Table 4 Experimental Conditions & Results of Analysis of PCBs in the Soil

	Temperature of Soil (°C)	Amount of NaHCO <sub>3</sub> Adding (%)	Untreated Soil		Treated Soil		Removal Ratio (%)
			Content of PCBs (mg/kg)	Leaching Solution by Notification NO.46 of the Environment Agency in Japan (mg/ℓ)	Content of PCBs (mg/kg)	Leaching Solution by Notification NO.46 of the Environment Agency in Japan (mg/ℓ)	
Run 1	330	6	49	ND	0.26	ND	99.5
Run 2	330	3	32	ND	0.038	ND	99.9
Run 3	330	0	44	ND	0.074	ND	99.8
Run 4	380	3	51	ND	0.022	ND	99.95
Run 5	280	3	72	ND	0.26	ND	99.6

N.D.: less than 0.0005mg/ℓ

The PCBs concentration in the soil before treatment was in the range of from 32 to 72 mg/kg, which indicates that the soil has a relatively low level of contamination. The PCBs concentration in the soil after treatment was a maximum of 0.26 mg/kg, and the analysis gave a removal rate of 99.5 to 99.95%. Even when no NaHCO<sub>3</sub> was added, the PCBs concentration in the soil after treatment was as low as 0.074 mg/kg, and the influence of the difference in experimental conditions was not clear. According to the results of the laboratory test<sup>1)</sup>, the effect of adding NaHCO<sub>3</sub> was clear for highly contaminated soil. Some soils may not need the addition of chemicals.

The result of the elution test gave ND (0.0005 mg/l or less) of the PCBs analysis for the soil after treatment in all experimental runs. The elution test on the soil before treatment also gave ND result, which presumably comes from the weakly contaminated soil.

Table 5 shows the relationship between PCBs concentration and retention time. The correlation was derived from Run 2 where the soil was sampled from sample openings on the side wall of the reactor. At a retention time of 0.25 hour, the PCBs concentration was 1.9 mg/kg, which was slightly high level. At a retention time of 0.5 hour, however, the PCBs concentration decreased to 0.31 mg/kg.

Table 5 Relationship between Retention time and Concentration of PCBs in the Soil (RUN2)

( Comparison between GC/MS and ECD/GC )

	Retention time (h)	0	0.25	0.5	1.0
GC/MS	Biphenyl (mg/kg)	0.0044	0.054	0.052	0.023
	PCBs (mg/kg)	36	2.0	0.47	0.035
ECD/GC	PCBs (mg/kg)	32	1.9	0.31	0.038

Therefore, if the target level is 1 mg/kg or less, then the retention time may be selected as 0.5 hour. The result was compared to that of GC/MS, and there was no significant difference in the analytical values between GC/ECD and GC/MS.

Fig. 3 shows the concentration of each of PCBs congeners in soil for each retention time. Because all retention times except for zero hour gave extremely low concentration levels, the figure adopted a magnification of ten times the actual value. The figure suggests that the concentration decreases as a total with longer retention times while the lower chlorinated biphenyls increase to some extent.

Fig. 4 shows the total PCBs content in the soil and the condensate before and after treatment during Run 2 in terms of PCBs congeners. As can be seen in the figure, the soil before treatment has a distribution resembling KC-400, centering on tetra-chlorinated biphenyl. The condensate, however, contains biphenyl, mono-chlorinated biphenyl, and di-chlorinated biphenyl, and a decreased

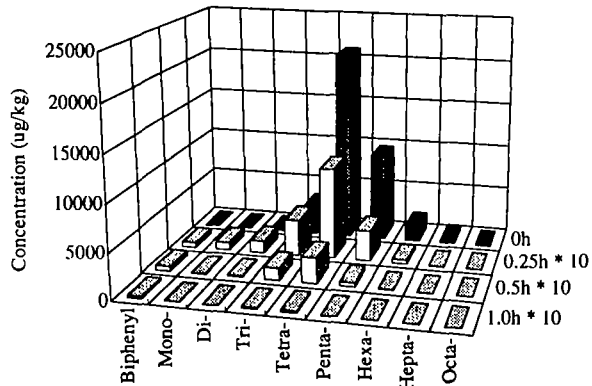


Fig.3 Concentration of each of PCBs Congeners in Treated Soil for each Time

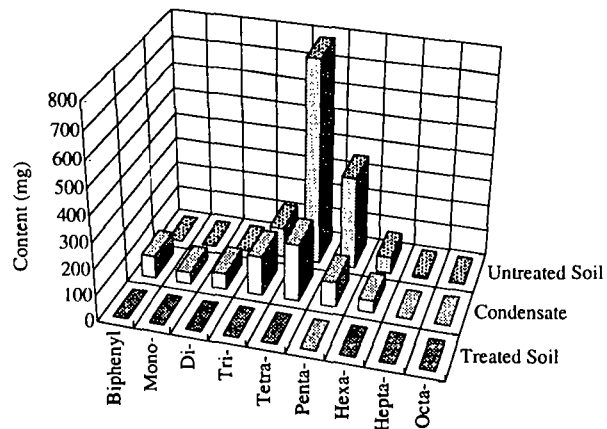


Fig.4 Content of each of PCBs Congeners in Soil and Condensate

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amount of higher chlorinated biphenyls such as tetra-chlorinated biphenyl. The phenomenon suggests that a part of PCBs is dechlorinated in the reactor. Because lower chlorinated biphenyls show lower boiling points, the thermal desorption on the soil will be enhanced for the lower chlorinated ones.

The experiment of Run 1 through Run 5 treated 187 kg of soil. The total amount of PCBs recovered from the condensate was as small as 3.2 g, so the recovered PCBs were treated at one time in a liquid phase reactor unit using a 300 ml glass flask.

Fig. 5 shows the concentration of each of PCBs congeners with time. The figure indicates that the PCBs are dechlorinated with time to become lower chlorinated biphenyls. The result was similar to the result of the liquid phase laboratory reactor test<sup>2)</sup> using KC-400 as reference material. Within 1 hour, the decomposition proceeded to ND (1 mg/l or less) level, corresponding to 99.99% of decomposition rate in the liquid phase reaction.

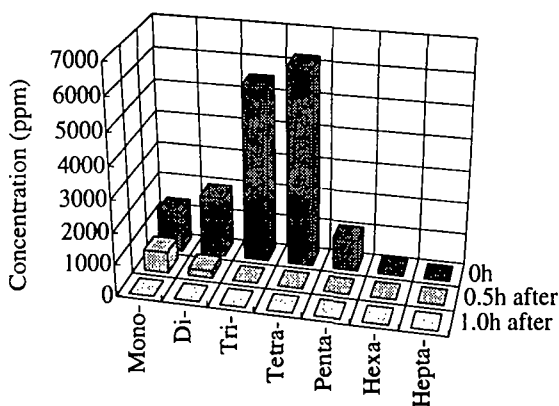


Fig.5 Result of Decomposition Test of PCBs extracted from Condensate

## 5. Conclusion

- 1) A pilot-scale treatment plant installed in a mobile-type container was used to continuously treat actual PCB-contaminated soil, and the reaction time of 30 minutes satisfied environmental regulations in Japan.
- 2) It was proved that part of the PCBs is thermally desorbed in the soil reactor and that part of the PCBs is subjected to dechlorination decomposition within the reactor.
- 3) The PCBs that become lower chlorinated biphenyls were collected in the condenser and decomposed in a laboratory-scale liquid phase reaction unit. In the liquid phase reactor, the PCBs in the condensate were decomposed to the ND level within 1 hour.

## 6. References

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- 2) S. Taniguchi, M. Takada, M. Hosomi, A. Murakami, R. Uchida, S. Iimura, K. Iwasaki and K. Usukura (1994) : Chemical Decomposition of Organic Chlorine Compounds. Lecture Bulletin of The Fifth Waste Academy Study Seminar, pp503-506.