Chemical Remediation of PCB-contaminated Soil

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1. Introduction

Polychlorinated biphenyls(PCBs) are refractory and harmful chemical substances.
Until recently PCBs-contaminated soil has been mostly disposed by isolated landfill after stabilized solidification by cement. However, owing to an increase of the contaminated soil, the disposal has been at a deadlock. Accordingly, development of technologies enabling remediation of the contaminated soil has been expected.
The United States Environmental Protection Agency(US-EPA) established a technology called Base Catalyzed Decomposition (BCD) Process which chemically decomposes PCBs and remedies PCB-contaminated soil. Since the early literature contained few quantitative reports of PCB-contaminated soils remedied in BCD process, the present authors examined them. This report summarizes test results on several PCB-contaminated soil samples by the BCD process.

2. Outline of the BCD Process

Being ground and sieved after excavation, PCBs-contaminated soil is mixed with sodium bicarbonate. The mixture is heated to 300-350°C in a heated reactor where higher chlorinated biphenyls are converted to lower chlorinated biphenyls containing volatile compounds and are recovered as liquid condensate together with vapor and volatile organic substances. Non-condensable gases are treated by activated carbon adsorbent prior to vent to the atmosphere.
An oil layer containing PCBs in the condensate is separated from water through an oil separater. The PCBs oil is sent to an oil reactor and PCBs is decomposed by the liquid phase BCD process. Treated oil can be utilized as low grade fuel oil as the PCBs concentration is confirmed within the acceptable level.
Major features of the BCD soil treating process are ;
1) The process utilizes safe and less expensive reagent (NaHCO3) and that results in low operating costs.
2) The process can treat various chlorinated organic compounds such as pentachlorophenol (PCP) and benzene hexachloride (BHC) other than PCBs.
3) Smaller amount of spent gas is generated from the process than from calcination processes. Furthermore, any dioxin is not produced.
4) A mobil unit (loaded on three or four trailers) makes possible to remedy contaminated soil at site.

3. Experimental

3-1 Apparatus
The structure of the apparatus used for the experiments is shown in Fig.1.
The apparatus consists of a reaction flask, a mantle heater, a ribbon heater, a condenser, a flask for condensate, two gas traps and an activated carbon trap.

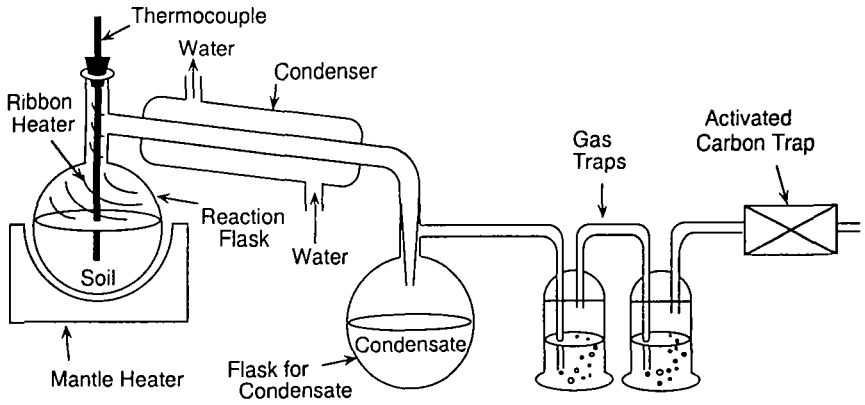

Fig.1 Experimental apparatus

3-2 Methods
Experiments were carried out in a way that after being well mixed with NaHCO3 and water, a soil sample was heated in a reaction flask with a mantle heater. The upper part of the reaction flask was heated at around 200°C with a ribbon heater. Vapor and gases generated from the reaction flask were condensed in a cooler condenser then adsorbed through two gas traps and an active carbon trap.
The start of the reaction was defined when the temperature at the core of the soil sample measured by a thermocouple reached a predetermined level.
After a laps of a predetermined reaction time, the mantle heater was turned off and let the sample cool down.
The content of PCBs in the treated soil sample and the distilled sample were determined after the samples cooled down. PCBs were determined by using a gas chromatographic instrument with an electron captive detector (GC/ECD).

Experiment 1:
Different five soil samples (A, B, C, D and E) was treated at 335°C of reaction temperature, 1 hours of reaction time and 6% of NaHCO3.
The concentration of PCBs in each untreated and treated soil sample was measured.
Samples A, B and C were prepared by means of artificial contamination of a clean soil sample with acetone solution of a standard PCB sample followed by air drying.Samples D and E were PCB-contaminated soil obtained from the field.

Experiment 2:
Soil sample B was treated at 6% of NaHCO3 and without NaHCO3.
The content of PCBs in each treated soil at 290, 330 and 380°C of reaction temperature was mesured.

Experiment 3:
Soil sample B was treated at 335°C of reaction temperature, 0, 3 and 6% of NaHCO3. The content of PCBs in each treated soil at every 0.5 hours of reaction time was mesured.

Experiment 4:
Artificially contaminated Soil samples by KC-300, KC-400 and KC-500 ware treated at 335°C of reaction temperature, 3% of NaHCO3, and 1 hour of reaction time.
The content of each of the PCB congeners in untreated soil, condensates and gases was mesured. The analytical instrument used was GC/MS (HP5890 Series II /5971).
Besides, the content of chlorine in soil and condensate after and before treatment was mesured.

4 Results and Discussion

4-1 Experiment 1:

A table1 shows the concentration of PCBs in untreated and treated soil samples. Based on the PCBs concentration of the soil samples, above 99.79% of PCBs removal rates were achieved. Soil samples containing high concentration of PCBs demonstrated a removal rate as high as 99.98%. All of the treated soil samples met the environmental standard on soil for the leaching tests in Japan, namely any PCBs were not detected in the leaching test (below 0.0005mg/l).

Table 1 Results of contaminated soil treatment (Experiment 1)

Sample	Type of PCBs	PCBs concentration in soil				Removal per cent (%)
		Raw soil		Treated soil		
		Concentration in soil (mg/kg)	Concentration by leaching test (mg/l)	Concentration in soil (mg/kg)	Concentration by leaching test (mg/l)	
A	Kanechlor KC-300: equivalent to Aroclor 1242	50	0.018	0.10	ND	99.79
B		2500	0.25	0.44	ND	99.98
C	Kanechlor KC-300: equivalent to Aroclor 1242	3600	0.56	0.44	ND	99.98
D		110	0.0044	0.017	ND	99.98
E		22	0.0016	0.046	ND	99.79

ND : < 0.0005 mg/l

4-2 Experiment 2:

Fig. 2 shows the relation between PCBs concentration in soil after the treatment and treating temperatures on the soil sample B. PCBs concentration in soil reduced with an increase of reaction temperature for both with 6% of NaHCO3 and without NaHCO3.
Reaction temperature had a great influence on the PCB removal, namely PCBs concentration showed a decrease of more than 90 % with an increase of temperature by 40-50°C.

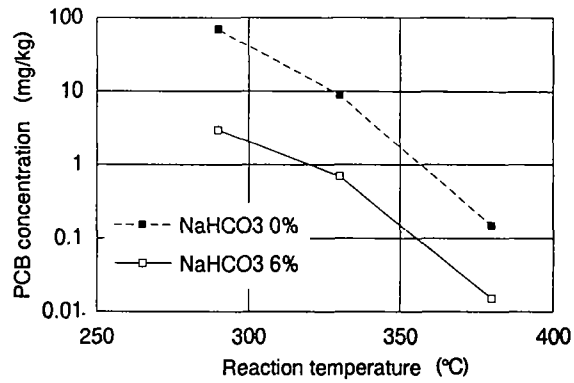

Fig.2 Relationship between PCB concentration in treated soil and reaction temperature (Experiment 2)

4-3 Experiment 3:
Fig. 3 shows the relation between PCBs concentration in treated soil and reaction time on the sample B.
PCBs concentration reduced with an increase of reaction time. However, the effectiveness of prolonged reaction time for 0.5-2 hours was not so significant as an increase of reaction temperature.
A comparison of test results at the same reaction temperature and the same reaction time in Figs. 3 and 4 demonstrates the effectiveness of NaHCO3 addition on PCB removal, because the PCBs concentration in treated soil with NaHCO3 was less than 1/10 of that from without NaHCO3.

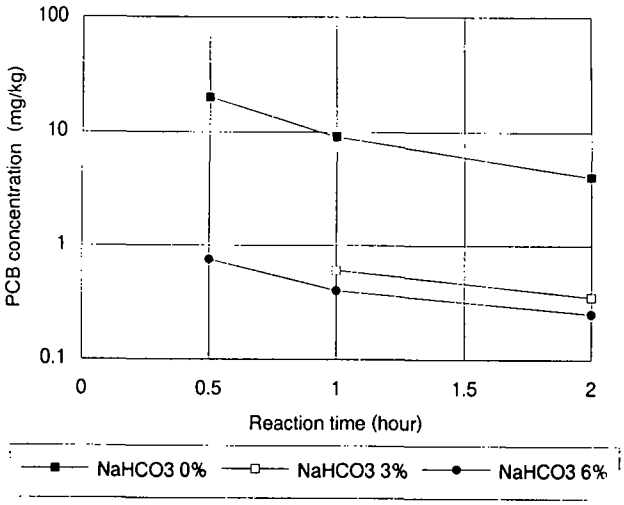

Fig.3 Relationship between PCB concentration in treated soil and reaction time (Experiment 3)

4-4 Experiment 4:
Figs. 4(KC-300), 5 (KC-400) and 6 (KC-500) show the total quantity of each of PCB congeners in untreated soil samples,condensates and gases.
The PCBs concentration in gases is shown in 100 times of actual measurements since the concentration is too low to show. An increase in biphenyl, mono-chlorinated biphenyl and di-chlorinated biphenyl indicates occurrence of de-chlorination reactions as shown in the figs. 4 , 5 and 6.
The fact that smaller amount of PCBs existing in condensates from KC-400 and KC-500 than that from KC-300 may suggest that higher chlorides are more susceptible of destruction. That is because more volatile lower chlorides such as KC-300 are distilled off without destruction before the temperature of the test apparatus reached 300°C.
Table 2 shows the content of inorganic chlorine in treated soil and organic chlorine in untreated soil. The total quantity of chlorine after treatment was nearly equal to that before treatment. Chlorine generated from dechlorination reactions of PCBs was found to stay in soil as an inorganic chloride (NaCl).

Table 2. Content of de-chlorinated chlorine

	Untreated	Treated				Rate of
	Chlorine in soil (mg)	Chlorine in condensate etc. (mg)	Inorganic chlorine in soil (mg)	Total chlorine (mg)	Rate of collection (%)	de-chlorination (%)
KC-300	130	65	54	120	92.3	41.5
KC-400	130	36	80	120	92.3	61.5
KC-500	120	45	88	130	108	73.3

Condensate etc. = condensate + washed liquid
Rate of collection = 100 * chlorine after treatment / chlorine before treatment
Rate of de-chlorination = 100 * inorganic chlorine in treated soil/ chlorine in untreated soil

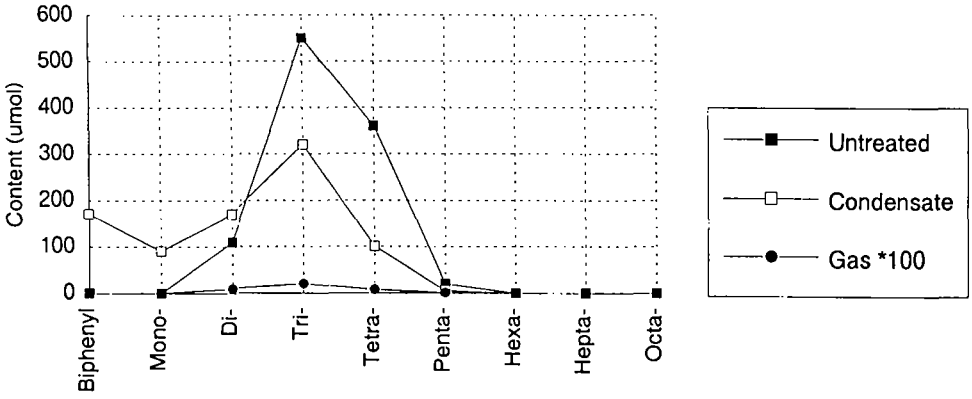

Fig.4 Treatment of KC-300 by BCD process (Experiment 4)

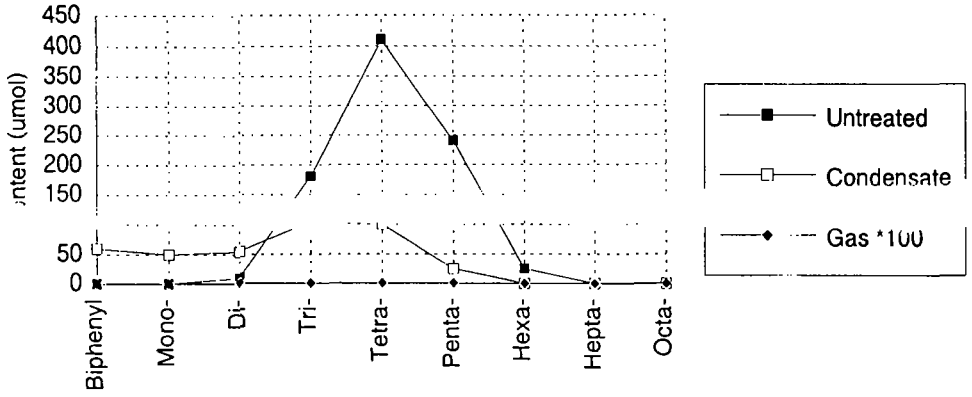

Fig. 5 Treatment of KC-400 by BCD process (Experiment 4)

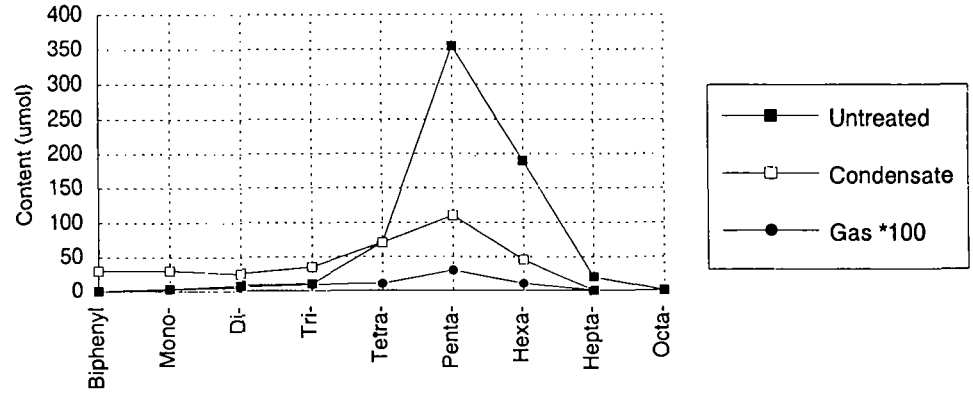

Fig.6 Treatment of KC-500 by BCD process (Experiment 4)

5 Conclusion

Tests on PCB-contaminated soil treatment by the BCD process led to the following conclusions;
1) Treated soil samples met the environmental standard in Japan on soil as any PCB was not detected at the leaching tests (below 0.0005mg/l).
2) PCBs concentration in the treated soil samples reduced as an increase of treating temperature. Removal rate as high as above 99.79% was achieved at 335°C of reaction temperature.
3)The PCBs concentration in treated soil with NaHCO3 was less than 1/10 of that from without NaHCO3. The effectiveness of NaHCO3 addition on PCB removal was demonstrated
4) It was also found that PCBs underwent partly de-chlorination and degradation reactions and were converted to lower chlorinated compounds.
The total quantity of chlorine after treatment was nearly equal to that before treatment. Chlorine generated from dechlorination reactions of PCBs was found to stay in soil as an inorganic chloride (NaCl).

6,References

1)Rogers C.J.,A.Kornel,and H.L.Sparks(1991):Base Catalyzed Decomposition of Toxic and Hazardous Chemicals. In:HAZPAC '91:Hazardous Waste Management in the Pacific Basin. Randol International,Golden,CO,233-244.
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