REDUCTIVE HEATING DECOMPOSITION OF POLYCHLORINATED BIPHENYLS IN SOIL

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Abstract

A reductive heating kiln treatment was applied to confirm the reduction of polychlorinated biphenyls (PCBs) in contaminated soil. It is confirmed that the 94% of initial PCBs amount in contaminated soil is decomposed at 550℃ under an oxygen deficient atmosphere, and biphenyl, which is considered as the dechlorination product of PCBs, is also detected in the exhaust gas from the kiln.

Introduction

To destruct POPs, such as PCBs in soil, incineration is efficient way, but it expenses energy and needs high temperature. However, there is potential for formation of dioxins according to the incinerating condition. The bio-remediation costs lower than other process cost but it takes long terms for remediation because of its very slow reaction rate. Solvent washing needs relatively lower energy and temperature for treatment, but in case of silt it takes many times to reach the decontamination level and thus this method will costs expensive.[1]

Then the reductive heating and sodium particle dispersion (RH-SP) process has been applied to POPs contaminants to develop an on-site decontamination process at a lower temperature. This process consists of soil treatment by reductive heating process and dechlorination of POPs absorbed oil by metallic sodium particle dispersion process. It was carried out to develop an on-site decontamination process for POPs polluted soil,sludge,sediment and other kind of wastes at lower temperatures. The exhaust gas volume is considerably smaller than using secondary combustion system.[2,3]

The process flow of RH-SP process is schematically shown in Figure 1. POPs contaminated solids are supplied into the reductive heating kiln and heated to about 600℃ in oxygen deficient atmosphere purged with nitrogen to dechlorinate organic chlorides. The process gas from the kiln is sent to oil scrubber, where POPs are absorbed into oil and then the cleaned gas is exhausted through the activated carbon filter. Organic chlorinated compounds are dechlorinated with metallic sodium dispersion metnod.[4,5,6]

This paper reports on the treatment of PCBs contaminated soil with RH-SP process using a laboratory-scale equipment and GC-MS analysis of gas absorbed oil to confirm the PCBs removal and chemical formula of by-products.

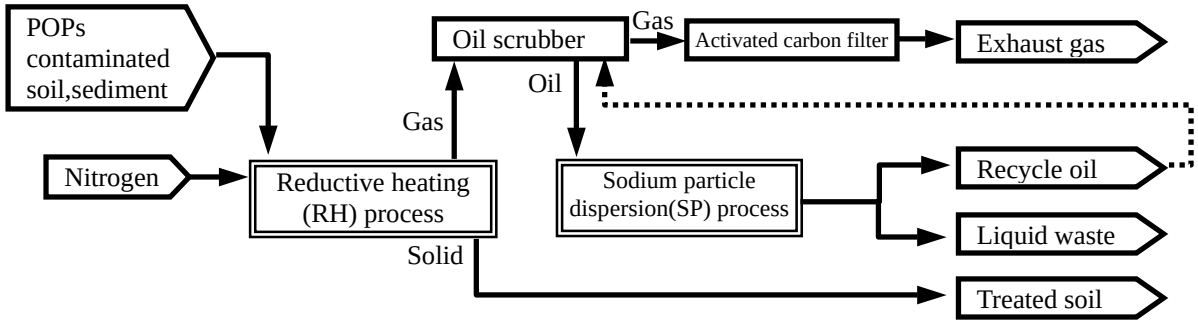

Figure 1 Schematic diagram of reductive heating and sodium particle dispersion (RH-SP) process

Materials and Methods

It is shown in Figure 2 that the schematic flow of the test equipments which consist of reductive heating unit, oil absorber, activated carbon absorber and distiller. Also the experimental conditions are shown in Table 2. The operation procedure was as follows: A fixed quantity of soil samples were supplied into a Reductive Heating kiln,

and heated in an hour with a temperature of 550℃. During the heating the atmosphere in the kiln was purged with nitrogen gas for deoxidization. The process gas was sent to the gas cleaning unit. PCBs and dioxins were absorbed in oil (normal paraffin), and then the gas was exhausted via activated carbon filter. The absorbed oil was distilled under a vacuum pressure of (4kPa) at 100℃, and then separated PCBs concentrated oil. PCBs were measured by GC/ECD and GC/MS. Dioxins were measured by GC/MS. Products in PCBs concentrated oil were measured by GC/MS as shown in Table 1.

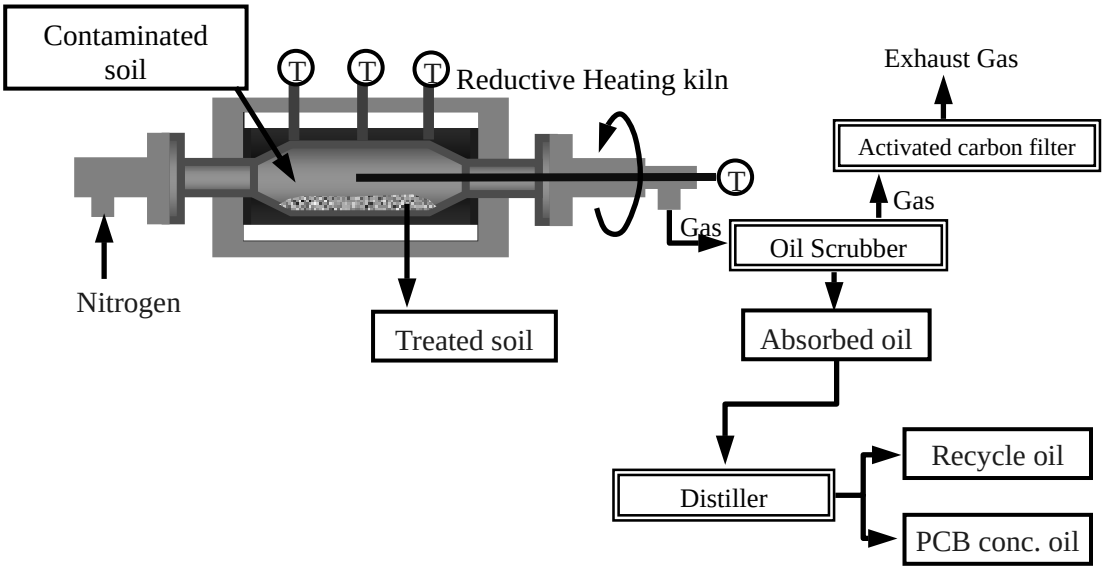

Figure 2 Schematic flow of the test equipments

Table 1 Analytical method of products in PCBs concentrated oil

Equipment	Agilent 6890 GC , 5973N Mass spectrometer
Column	DB-1 60m , ID 0.25mm , 0.25 μ m thickness
Temp.	Oven 40℃(5min)→10℃/min→300℃
Mode	EI (70 eV , 230℃)

Results and Discussion

The results of experiment are shown from Table 2 to Table 4. Soil samples contain 3400 mg-PCBs/kg, and the isomer pattern was similar to Kanechlor KC-300, of which trichlorinated biphenyl rate was 49%. After an hour reductive heating, PCBs of treated soil leachate was lower than 0.0005mg/L and dioxins of treated soil was 70 pg-TEQ/g. This confirms the Japanese soil environmental standard. The longer heating time and the lower PCBs level of treated soil. Higher than 99.7% PCBs and 98.7% dioxins were removed from the soil samples. PCBs level of absorbed oil was 50~69 mg/kg.

Table 2 Treatment conditions and PCBs concentration in soil

Case	Conditions		Soil samples		Treated soil		Japanese Standard	Removal Rate
	Temp.	Time	Conc.	Conc. (leachate)	Conc.	Conc. (leachate)		
	[℃]	[h]	[mg/kg]	[mg/L]	[mg/kg]	[mg/L]	[mg/L]	[%]
1	550	1	3,400	0.0024	10	< 0.0005	< 0.003	99.7
2	550	3			4.2	< 0.0005		99.9
3	550	6			0.019	< 0.0005		99.999

Table 3 Dioxins concentration in soil

Case	Soil samples		Treated soil		Japanese Standard	Removal Rate
	Conc.	TEQ	Conc.	TEQ		
	[pg/g]	[pg-TEQ/g]	[pg/g]	[pg-TEQ/g]	[pg-TEQ/g]	[%-TEQ]
1	140,000,000	57,000	210,000	70	1,000	98.7
2			-	-		-
3			61	0.0075		99.999987

Table 4 PCBs and dioxins concentration in absorbed oil

Case	PCBs Conc.	Dioxins	
		Conc.	TEQ
	[mg/kg]	[pg/g]	[pg-TEQ/g]
1	50	—	—
2	69	1,500,000	460
3	69	—	—

PCBs balance of case 2 as shown in Figure 3 indicates that PCBs in absorbed oil were 5.9% of initial amount in soil, and thus 94% of initial PCBs amount were reduced in this process.

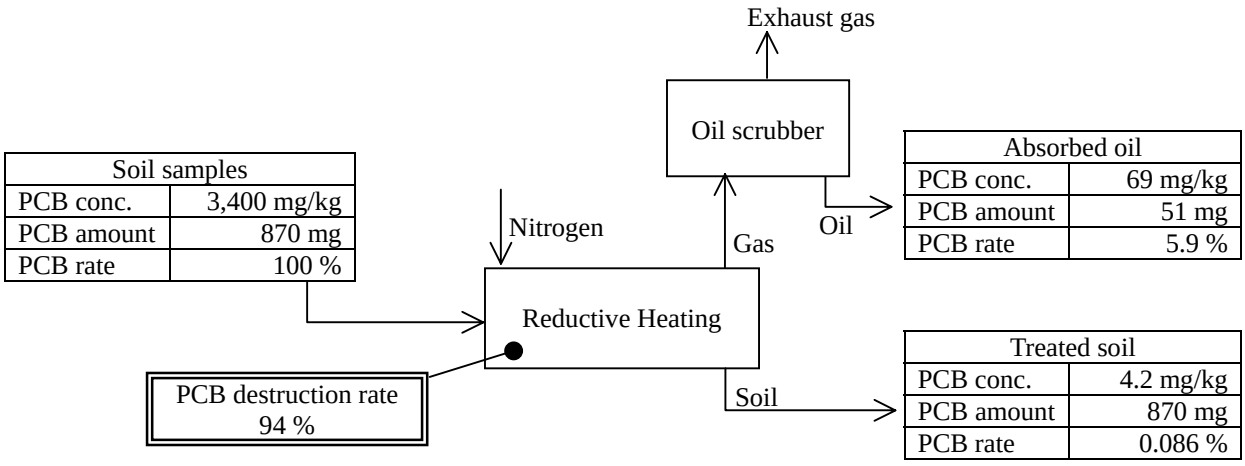

Figure 3 PCBs balance of case 2

Distillation result of case 2 as shown in Table 5, indicates that PCB level of concentrated oil was 440 mg/kg and PCBs level of distilled oil was lower than 0.001mg/kg, also the volume of contaminated oil was decreased into 13% of absorbed oil.

Table 5 Distillation result of case 2

	Unit	Absorbed oil	Concentrated oil	Distilled oil
Sample amount	g	200.1	26.3	162.4
Volume rate	%	100	13.1	81.16
PCB conc.	mg/kg	69	440	< 0.001
PCB amount	mg	14	12	< 0.0002
DXNs conc.	pg/g	1,500,000	10,000,000	2,300
DXNs TEQ	pg-TEQ/g	460	3,300	0.32
DXNs amount	pg-TEQ	92,000	87,000	52

GC/MS total ion chromatogram of PCBs concentrated oil as in Figure 4 shows that; Large peaks indicates the saturated hydrocarbons, that of formula describes as $C_{11\sim13}H_{24\sim28}$. Other peaks indicate biphenyl, methyl-naphthalene, dimethyl-naphthalene and PCBs. Biphenyl is considered to be a major PCBs dechlorination product. Alkyl-naphthalene is also considered to be a contaminant of pre-treated soil.

Table 6 Result of GC-MS

Peak No.	Identified substances
1	C11H24
2 - 4	C12H26
5	Methyl-naphthalene
6	C13H28
7	Biphenyl
8	Dimethyl-naphthalene
9	PCBs

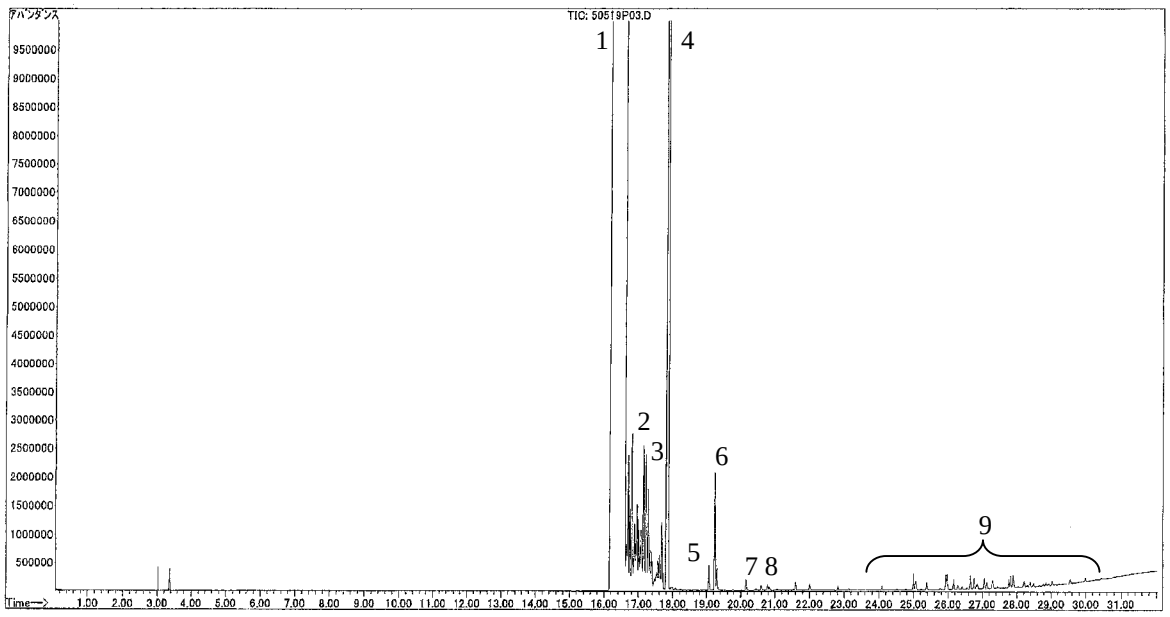

Figure 4 Gas chromatogram of PCBs concentrated oil

Conclusion

The treatment of PCBs contaminated soil with the RH-SP process was conducted and it is concluded that : 99% of initial PCBs in contaminated soil were removed by reductive heating , and 94% of initial PCB amount were dechlorinated in the reductive heating process; Biphenyl, PCBs and alkyl-naphthalene were detected in gas absorbed oil by GC-MS analysis, and it is considered that biphenyl is a major dechlorination product of PCBs and alkyl-naphthalene is also considered as a contaminant of pre-treated soil.

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