Detoxification of Polychlorinated Biphenyls (PCBs) at the Chiba Works

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ABSTRACT Chemical treatment of polychlorinated biphenyls (PCBs) was approved domestically in 1997 and full-fledged treatment is expected to begin, but currently there is no facility in Japan that can treat high-concentration PCBs on a commercial scale. Recently the authors have installed in the Chiba Works a treatment facility based on the PCB treatment technology of Nuclear Fuel Industries, Ltd., an affiliated company of Furukawa Electric, and carried out in-house treatment of PCBs contained in the electric capacitors stored in the Works.

1,561 kg of PCBs collected from 91 capacitors was treated during the period, with the result that the concentration of PCBs and dioxins in the waste gas was on the safe side of the standard, and that the contamination of the yielded byproducts were confirmed by elution tests with every batch to be at a sufficiently low level. The facility could treat up to 40 liters of 100 % PCBs per batch, and four batches a day, demonstrating satisfactory performance as a treatment facility of commercial scale. The treatment took six months including the installation work, treatment, and the removal of the facility, and the entire treatment program was carried out without any accident or mishap.

1. INTRODUCTION

Recently, polychlorinated biphenyls (PCBs) have become an object of public concern such that the ballast for fluorescent lamps containing the substance left decommissioned in schools and the like broke down. PCB is derived from biphenyl by substituting the hydrogen with chlorine, and theoretically has 209 isomers according to the number and position of the chlorine attached to. Because PCB has such properties as chemical as well as thermal stability, decomposition resistance, high boiling point, flame resistance, and high electrical insulation, the substance was widely used as insulating oil for transformers and capacitors.

With the outbreak of the Kanemi-oil decease, however, the use of PCB-containing equipment was banned as a rule in 1972, imposing the companies to store these equipment at their own expense. The reason being that the substance, upon entry into human body due to its solubility in oil, readily accumulates there to have a long-term toxicity. Although Kaneka Corporation once incinerated its own stocks, neither construction of an

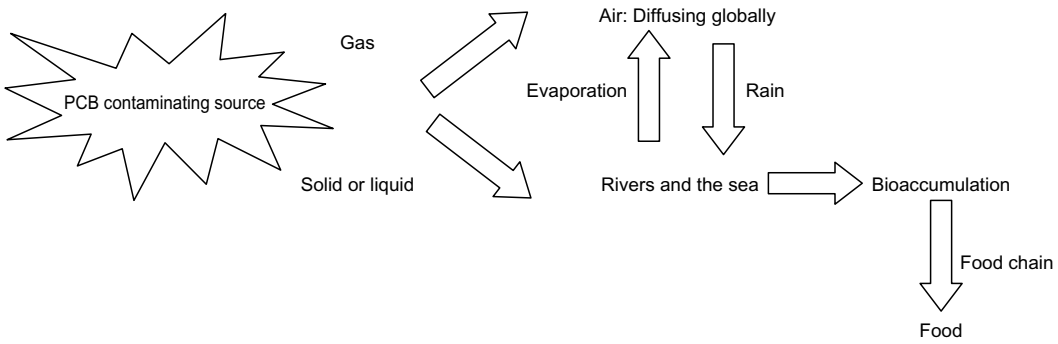

Figure 1 Behavior of leaked PCBs in the environment.

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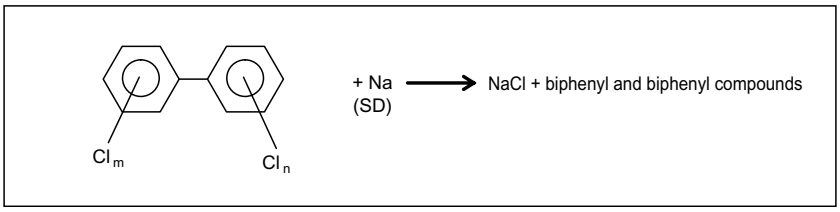

Figure 2 Reaction principle of OSD method.

Table 1 Disposal standards of PCB waste.

PCB waste	Standard
Waste oil	0.5 mg/l or below
Waste acid or alkali	0.03 mg/l or below
Waste plastics or metals	0.5 mg/kg or below for cleaning fluid, or 0.1 μg/100 cm^2 or below for surface concentration, or 0.01 mg/kg or below for volume concentration
Sludge and the like	0.003 mg/l by elution test

incineration facility nor treatment was possible due to local residents' campaign. In 1998, the Waste Disposal and Public Cleaning Law was revised to approve several chemical treatment methods of PCB including the Ontario Hydro Technologies' Sodium Dispersion (OSD) method owned by Nuclear Fuel Industries, Ltd., and the treatment program has just begun domestically. This revision is based on the investigations conducted in 1992 by the Ministry of Health and Welfare, with the result that about 7 % of high-voltage transformers and capacitors were found to be either lost or disappeared [1]. It was recognized that a preemptive move was necessary because, as shown in Figure 1, if the PCBs leaked, these might flow into rivers and the sea leading to bioaccumulation.

But since PCBs contain dioxins also, there was fear that defective handling or treatment might cause serious social issues, so that the State and its related organizations were going to take a very cautious approach. Using the country's first facility of commercial scale for treatment of high-concentration PCBs designed and manufactured by Nuclear Fuel Industries, Ltd., we have passed the strict examination by the related organizations to obtain a permit, thereby carrying out in-house detoxification treatment of high-concentration PCBs that were collected from the capacitors stored in the Chiba Works.

2. TREATMENT TECHNOLOGY (OSD METHOD)

Under the metal-sodium-dispersion oil declorination (OSD) method, as shown in Figure 2, the Na-dispersion oil (hereafter called "SD": sodium dispersion) comprised of fine metal Na particles dispersed in oil is mixed with PCBs to dechlorinate the PCB with Na thus generating NaCl, thereby reducing the PCB concentration below the specified level. The residual Na after the reaction is converted into NaOH by adding water. The treated liquid is separated into oil (recycled oil), NaOH, NaCl, and byproducts such as biphenyl and biphenyl compounds. This technology with a track record of over ten years in Canada has been improved, validation tested, and confirmed by Nuclear Fuel Industries, Ltd. to meet the Japanese treatment standards shown in Table 1, the severest in the world; and the technology was approved for its safety in 1998, together with the technologies of other six companies, through the evaluation by the committees of the Ministry of Public Welfare, the Environment Agency, and the Ministry of International Trade and Industry (all are then-current names).

3. TREATMENT OBJECT

The Chiba Works has stored electrical capacitors --mainly 100-kVA capacitors of the company's brand-- in storage containers and has long been keeping them in a stringent way. Whereas Nuclear Fuel Industries, Ltd. can treat not only metals and plastics but also impregnating materials such as paper using a solvent cleaning method called "S-DEC method", disposal standard for paper and the like are not specified yet, so that only aqueous PCBs collected from capacitors were treated this time, keeping paper and metal containers in continued storage.

4. TREATMENT FACILITY AND PROCESS FLOW

To avoid the risks of transferring PCB-contaminated materials, we used a mobile facility of containerized type, which features installation of the treatment facility near to the place of storage.

The major treatment units comprise, as shown in Photo 1 and Figure 3, oil-removing unit in which the oil is removed from capacitors, liquid treatment unit A in which dechlorination of PCBs is effected, liquid treatment unit B in which the treated oil is separated into recycled oil and byproducts, and liquid treatment unit C which stores the recycled oil and supplies cleaning oil. All these units are connected by piping in ducts to prevent leakage of oil in case of accidents. Steps are provided at every doorway to make the floor of units an oil retaining wall, thus preparing for eventualities of oil leakage from tanks. Moreover, these units are designated as a general handling site for dangerous materials under the Fire Defense Law, so that

Photo 1 Appearance of treatment facility.

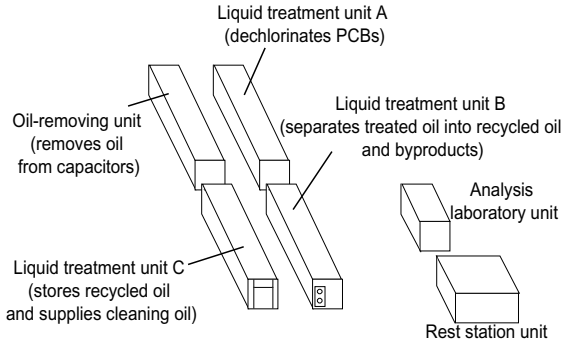

Figure 3 Configuration of treatment units.

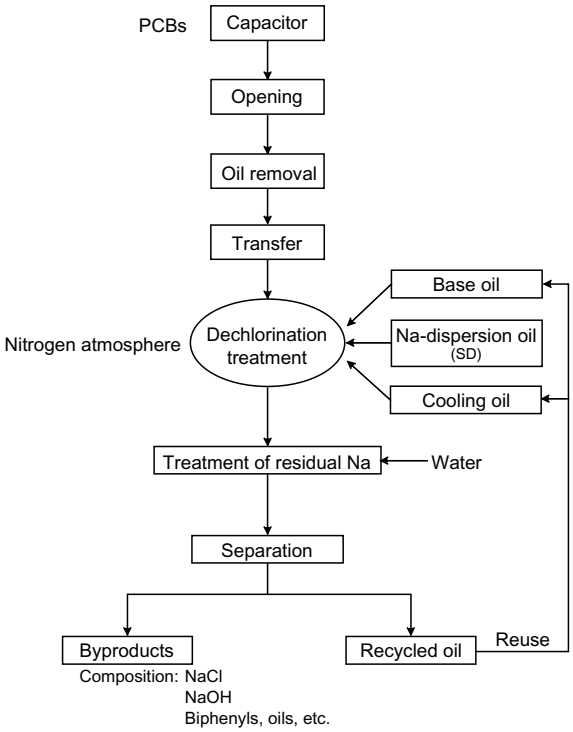

Figure 4 Process flow of treatment.

every unit has a lightning rod and a surrounding reserved space 5 m in breadth.

An analysis laboratory unit for PCB analysis was installed outside the reserved space to carry out analysis.

Whereas this treatment facility can treat low-concentration PCBs, below will be described the process flow for high-concentration PCBs, in which the current treatment was carried out. As illustrated in Figure 4, SD is mixed with a heated oil called “base oil”, into which the 100 % PCB removed from the capacitors is poured at normal pressures. A cooling jacket is used together with the charging of cooling oil to control the temperature, since a substantial amount of heat is generated.

When the treatment reaction is completed, water is charged to convert the residual Na into NaOH, and subsequently the byproducts and the recycled oil are separated through centrifugal separation.

5. ANALYSIS METHOD

5.1 PCB Analysis of Oil and Byproducts

After dechlorination, the oil was analyzed using a flow control analysis method to confirm the completion of treatment as well as an official analysis method specified in Notification No. 192 of the Ministry of Health and Welfare (enforced in 1992, revised in 1998) which is based on the high-resolution gas chromatography and high-resolution mass spectrometry analysis (HRGC-HRMS). The byproducts after centrifugal separation was confirmed by an elution test with every batch, and subsequently liquid conditioned in accordance with Notification No. 13 of the Ministry of the Environment, followed by analysis using the official analysis method specified in Notification No. 59 of the Environment Agency (1971). The flow control analysis was carried out, after refining the samples based on a simple method, using the high-resolution gas chromatography and low-resolution mass spectrometry analysis (HRGC-LRMS), taking an analysis time of about 45 min. In the elution test, the byproducts were shaken with water for six hours since they are defined as sludge in the Waste Management Law, and the eluted amount into the water was analyzed using the HRGC-LRMS method.

5.2 PCB Analysis of Waste Gas and Atmospheric Environment

We analyzed the gas waste for PCBs and dioxins, and the atmospheric environment for PCBs.

PCBs were analyzed using the HRGC-LRMS and HRGC-HRMS methods, and dioxins were analyzed in accordance with JIS K 0311 (Method for determination of tetra- through octa-chlorodibenzo-p-dioxins, tetra- through octa- chlorodibenzofurans and coplanar polychlorobiphenyls in stationary source emissions).

Samples of the waste gas were taken at the exhaust openings of the oil-removing unit and the liquid treatment unit A. The HRGC-HRMS method was applied to these samples every time they were taken on the first day, whereas, from then on, to bulk samples taken all through the treatment time. Meanwhile, samples of the atmospheric environment were taken at the south corner of the treatment site outside the reserved space, since

it was known that north wind was dominant during the treatment time and that the adjacent residential areas were located to the south-east and to the south.

5.3 Soil Analysis

Samples were taken within the facility site based on the four-point method before and after the facility installation, and they were analyzed in accordance with the Attached Table No. 3 of Notification No. 59 of the Environment Agency (December, 1971).

6. PROCESS OF PERMISSION AND RESULTS OF TREATMENT

6.1 Process of Permission

As shown in Table 2, it took more than one year to get permission since the negotiation began in March 2000, partly because of arrearages due to amending of laws. The treatment began after the completion test of the treatment facility finished, and safely ended in March 2002, including the removal of the facility. Currently, the treatment site has been turned into a parking lot as before.

6.2 Results of In-house Treatment

1,561 kg of PCBs collected from 91 capacitors that had been stored were treated this time with the treatment results shown in Table 3.

The type of the PCBs was KC-300, most of which belonged to biphenyl trichloride manufactured by Kaneka Corporation. KC-300 was used as a thermal medium and a high-temperature lubricant besides an insulating oil for capacitors, accounting for the largest portion in the marketplace.

6.2.1 PCB Analysis Results of Oil and Byproducts

The byproducts after treatment were elution tested batch by batch, and the results were, as shown in Table 3, all less than 0.001 mg/l --low enough in comparison with the standard of 0.003 mg/l. Meanwhile, the results of the official analysis method were less than 0.0005 mg/l. The recycled oil was tested using the HRGC-HRMS method, before delivery for reuse, with the results of 0.062 mg/kg over the standard value of 0.5 mg/kg. Meanwhile, the results of the HRGC-LRMS method were less than 0.1 mg/kg.

6.2.2 Measurement Results of Waste Gas and Atmospheric Environment

Tables 4 and 5 show the results of waste gas measurements. The results of the first and consecutive measurements were sufficiently low in terms of all PCBs in comparison with the standard, while they were satisfactorily low in terms of dioxins in comparison with the severest standard applicable to incineration furnaces.

The measurement results of atmospheric environment shown in Table 6 were all less than 0.1 μg/m^3 --low enough in comparison with the standard value of 0.5 μg/m^3.

Table 2 Process of permission and treatment.

Time	Contents
March 2000	Negotiation began with Environment and Life Dept. of Chiba Pref. and Fire Dept. of Ichihara City
September 2000	Submission of prior consultation documents based on the Agreement on Prevention of Environment Pollution (To Environment and Life Dept. of Chiba Pref. and Environment Dept. of Ichihara City)
September 2000	Submission of application for Installation Permission of General Treatment Site for Hazardous Substances (Based on Fire Defense Law)
January 2001	Acquired Installation Permission of General Treatment Site for Hazardous Substances
June 2001	Examination by Expert Committee of Chiba Prefecture
July 2001	Acquired Installation Permission of Disposal Site for Industrial Wastes (Permission No.: 13-5-1)
August 2001	Installation Announcement for Specific Facilities Based on Water Pollution Control Law accepted
September 2001	Installation Announcement for Specific Facilities Based on Special Measures against Dioxins accepted
September 2001	Installation work of the treatment facility began
November 2001	Completion test (By Chiba Pref. and Fire Dept. of Ichihara City)
November 2001	Treatment of high-concentration PCBs began
March 2002	Submission of decommissioning announcement documents based on each law. Return of permission documents based on the Law Concerning Disposal of Industrial Wastes
March 2002	Removal of facility completed

6.2.3 Measurement Results of Working Environment

The liquid treatment unit A and the oil-removing unit were measured as shown in Table 7. All the results were below the administrative concentration.

6.2.4 Results of Soil Analysis

As shown in Table 8, PCB was not detected before the installation of the facility as well as after the removal of the facility, posing no problems. The lower limit of quantitative analysis was 0.0005 mg/l.

6.2.5 Material Balance

The treatment carried out here included the trial run using non-PCB-contaminated oil, facility performance test, cleaning of piping after treatment of high- concentration PCBs using an oil, and treatment of this cleaning oil. Table 9 shows the entire material balance. Whereas some weights were estimated using material density, the recovery rate was found to be a satisfactory value of 98.4 %.

6.2.6 Treatment Capacity

The facility could treat 40 liters of 100 % PCB per batch, and four batches a day, demonstrating satisfactory performance as a treatment facility of commercial scale. Moreover, through the treatment of the cleaning oil for the piping, the facility was confirmed to be capable of treating low-concentration PCB-contaminated oil also.

Table 3 Results of treatment.

Batch No.	Treatment day	Treated PCB volume (l, kg)		PCB concentration in reactor when treatment ended (mg/kg)		Elution test results for byproducts (mg-PCB/l)	
				Standard: Less than 0.5		Standard: Less than 0.003 *2	
		(L)	(kg)*1	HRGC-LRMS	HRGC-HRMS	Elution test	Official method
1	1st day	10	14	< 0.1	Measured at the time of disposal (0.062 mg/kg) *4	< 0.001	< 0.0005
2	2nd day	20	28	< 0.1		< 0.001	
3	3rd day	20	28	< 0.1		< 0.001	
4	4th day	20	28	< 0.1		< 0.001	
5	5th day	40	56	< 0.1		< 0.001	
6	6th day	40	56	< 0.1		< 0.001	
7	7th day	34	47	< 0.1		< 0.001	
8	8th day	20	28	< 0.1		< 0.001	
9	9th day	34	47	0.17		< 0.001	
10	10th day	34	47	0.16		< 0.001	
11	11th day	34	47	Not measured *3		< 0.001	
12		34	47	Not measured *3		< 0.001	
13	12th day	34	47	Not measured *3		< 0.001	
14		34	47	< 0.1		< 0.001	
15	13th day	34	47	< 0.1		< 0.001	
16		34	47	< 0.1		< 0.001	
17	14th day	34	47	< 0.1		< 0.001	
18		34	47	< 0.1		< 0.001	
19	15th day	33	46	< 0.1		< 0.001	
20		33	46	< 0.1		< 0.001	
21		33	46	< 0.1		< 0.001	
22		33	46	< 0.1		< 0.001	
23	16th day	20	28	0.11		< 0.001	
24	17th day	40	56	< 0.1		< 0.001	
25	18th day	40	56	< 0.1		< 0.001	
26	19th day	40	56	0.13		< 0.001	
27	20th day	40	56	< 0.1		< 0.001	
28	21st day	40	56	< 0.1		< 0.001	
29	22nd day	30	41	< 0.1		< 0.001	
30	23rd day	40	56	< 0.1		< 0.001	
31	24th day	40	56	< 0.1		< 0.001	
32	25th day	30	41	< 0.1		< 0.001	
33	26th day	40	56	< 0.1		< 0.001	
34	27th day	30	41	< 0.1		< 0.001	
35	28th day	25	35	< 0.1		< 0.001	
	Total	1,131	1,561				

*1 The weight (kg) is 1.36 times the volume (l).
*2 Ministerial Ordinance No. 5 of General Administrative Agency in 1973. (Defined as sludge in the Waste Management Law)
*3 Only byproducts were confirmed based on the test results of up to batch No. 10.
*4 In compliance with Notification No. 192 of Ministry of Health and Welfare.

7. IN CONCLUSION

We have operated a treatment facility for high-concentration PCBs, the first domestic provision of commercial scale, and completed the treatment operation without any accident or mishap. The treatment carried out here demonstrated that the metal-sodium-dispersion oil declorination method is capable of coping with large-scaled treatment facilities to be installed hereafter.

Whereas the State is going to take a leading part in installing the treatment facilities, thus altering the general situations envisioned at the outset, it is our hope that our achievements could help promote PCB treatment programs to be implemented hereafter.

Table 4 PCB concentrations in waste gas.

Measurement place	Measurement method	Measurement day	Results $\mu g/m^3N$	Standard $\mu g/m^3N$
Treatment unit A	HRGC-LRMS	First day of treatment	< 0.5	< 100 *1
	HRGC-HRMS	First day of treatment	0.067	
		From second day until end of treatment	3.2	
Oil-removing unit	HRGC-LRMS	First day of oil removal	< 0.6	
	HRGC-HRMS	First day of oil removal	0.47	
		From second day until end	2.3	

*1 Temporary allowable limit for emission specified in Document No. 141 of Environment Agency, 1973. (Averaged value for incineration facilities of liquid PCBs)

Table 5 Dioxins concentrations in waste gases.

Measurement place	Measurement method	Measurement day	Results ng-TEQ/m^3N	Standard ng-TEQ/m^3N
Treatment unit A	HRGC-HRMS	First day of treatment	0.0050	< 0.1*1
		From second day until end of treatment	0.00092	
Oil-removing unit	HRGC-HRMS	First day of oil removal	0.0074	
		From second day until end	0.0012	

*1 Emission standard specified in Special Measures against Dioxins. (Incineration furnace)

Table 6 PCBs concentrations in atmospheric environment.

Measurement time	Measurement method	Measurement results $\mu g/m^3$	Standard $\mu g/m^3$
First day of oil removal	HRGC-LRMS	< 0.1	< 0.5 *1
3rd batch		< 0.1	
8th batch		< 0.1	
15th and 16th batch		< 0.1	
Day of no treatment		< 0.1	
23rd batch		< 0.1	
26th batch		< 0.1	
29th batch		< 0.1	
34th batch		< 0.1	

*1 Temporary allowable limit for emission specified in Document No. 141 of Environment Agency, 1973.

Table 7 Measurement results of working environment.

Measurement place	Measurement day	Measurement result $\mu g/m^3$	Administrative concentration $\mu g/m^3$
Liquid treatment unit A	13th and 14th batch	< 10	< 100*1
Oil-removing unit	2nd day of oil removal	Max 18 (Five A measurements)	
		33 (B measurement)	

*1 Work evaluation standard based on Industrial Safety and Health Law, specified in Notification No. 79 of Ministry of Labor

Table 8 Results of soil analysis.

	Measurement result	Lower limit of quantitative analysis
Before facility installation	Not detected	0.0005 mg/L
After facility removal	Not detected	

Table 9 Material balance.

Input (kg)		Output (kg)	
PCB	1,561	Byproducts	10,903
SD	3,052	Recycled oil	9,840
Water	2,063		
Oil (cooling oil, base oil, etc.)	14,399		
Total	21,075		20,743

REFERENCES

1) Ministry of Health and Welfare: On the Promotion of PCB Treatment (Interim Report), 1997. (in Japanese)