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Plasma Melting and Decomposing Technology for Treating PCB-contaminated Wastes

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Abstract

A plasma melting/decomposing technology is introduced as a method for thermally decomposing highly toxic and chemically stable polychlorinated biphenyls (PCBs). The technology is capable of efficiently melting and decomposing PCB-contaminated wastes that are charged into a plasma melting furnace as encased in containers taking advantage of the combined effects of plasma arcs and a molten slag bath. Verification tests of mixed and individual processing of various kinds of PCB-containing wastes demonstrated that the process was capable of operating stably, melting and decomposing the toxic substance as encased in containers and producing recyclable slag having homogeneous quality. The concentrations of the dioxins and PCBs in the slag, fly ash and exhaust gas discharged from the furnace were found to be well below the respective regulation limits. Thus, the technology proved capable of safely treating a variety of PCB-containing wastes minimizing the danger of contamination of operators.

1. Introduction

Polychlorinated biphenyls (PCBs) are incombustible, electrically insulating, high in boiling points and chemically stable at high temperatures. Owing to the chemical stability, PCBs were used for various applications such as the insulating oil for transformers and condensers, the heating medium of heat exchangers and non-carbon copy paper. However, their toxicity became widely known in Japan in 1968 when many people were intoxicated with PCB-contaminated food oil, and eventually, the Japanese Government banned the production of PCBs in 1972. While 5500 t of liquid PCBs stored by Kaneka Corporation was decomposed by incineration at high temperatures, the PCBs that did remain in the form of final products were not treated but kept sealed according to the new regulation.

Since PCBs do not decompose quickly, they continue to spread in the atmosphere and the sea even after they were banned, and constitute one of the causes of global environmental pollution; there are reports that PCBs have been found in mother's milk even in such places as the arctic regions where PCBs were never used. In view of the situation, the possibility of contamination caused by the leakage of PCBs from PCB-containing products, which have been stored for more than 30 years, or their misplacement has become a serious concern.

2. Current Situation of PCB Treatment

The proposal of the Stockholm Convention on Persistent Organic Pollutants (POPs) was adopted to eliminate or reduce the global contamination with PCBs and other pollutants through international cooperation. The convention entered into force in May, 2004 when the number of ratifying countries reached 50. Japan ratified the convention, and in July, 2001 put the Law for Special Measures for the Promotion of Adequate Treatment of Wastes Containing Polychlorinated Biphenyls (hereinafter referred to as the PCB Special Measures Law) in force. According to the law, the detoxification treat-

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Table 1 Quantity of PCB-containing objects in stockpile and use

	In stockpile	In use
[1] High-voltage transformers	16 496	1 689
[2] High-voltage condensers	220 345	30 502
[3] Low-voltage transformers	30 412	616
[4] Low-voltage condensers	1 146 383	17 510
[5] Pole-mounted transformers	1 713 291	1 967 000
[6] Ballasts	4 170 839	868 256
[7] PCB	12 955 ton	55 kg
[8] PCB-containing oil	142 261 ton	3 kg
[9] Copy paper	679 ton	–
[10] Waste cloth	215 ton	–
[11] Sludge	17 698 ton	–
[12] others	199 873	42 067

ment of PCBs will have to be completed by 2016. To alleviate the burden of the treatment costs on small- and medium-size companies, the Fund for the Treatment of Wastes Containing Polychlorinated Biphenyls was established. Japan Environmental Safety Corporation, the successor of the Japan Environment Corporation, is now responsible for the construction of regional PCB treatment facilities and their operations. **Table 1** shows the counting of all the PCBs and PCB-containing products and wastes in stockpile and in use in Japan (as of July 15, 2001), notified in accordance with the PCB Special Measures Law.

Regarding the objects listed in Table 1, Japan Environmental Safety Corporation is constructing regional PCB treatment plants to treat all the [1] high-voltage transformers, [2] high-voltage condensers, [3] low-voltage transformers, [4] low-voltage condensers, [7] PCBs and [8] PCB-containing oil in the country by the time limit set forth by the law. The regional PCB treatment plants will wash PCB containers clean of PCBs, and chemically decompose PCBs collected thus far and those in the form of oil sealed in transformers and condensers to detoxify them.

Since the [5] pole-mounted transformers are owned by electric power companies, those companies are responsible for their treatment. The regional treatment plants will also treat some of the PCBs extracted from the transformers. However, it is difficult to chemically treat all of the outstanding items of Table 1, namely the [6] ballasts, [9] pressure-sensitive copy paper, [10] waste cloth, [11] sludge and [12] other equipment and objects, and furthermore, the pits and containers used for storing them; the treatment is costly as well. Furthermore, secondary pollutants arise from the PCB treatment process, so there is a drive to find technologies that will cope with the treatment and all these derivative problems. In view of the situation, Nippon Steel Corporation and Kobelco Eco-Solutions Co., Ltd. have jointly developed the plasma melting and decomposing technology for PCBs as a method different from chemical decomposition methods. This paper introduces the developed technology.

3. Plasma Melting and Decomposing Technology

3.1 Basic principles

By the developed technology, objects containing or contaminated with PCBs and encased in steel drums are charged into a plasma melting furnace without having to be removed from the drums, and melted and decomposed efficiently by the heat of the plasma arcs and molten slag bath working in combination.

The PCBs in the upper part of a steel drum are directly heated by the plasma arcs and decomposed. Those in the lower part of it are soaked in the molten slag bath, heated to 1400℃ or higher and decomposed as well. As the melting advances and the steel drum melts down, objects lighter than the slag such as the sludge, concrete, waste cloth and copy paper float on the surface of the molten slag and are directly heated by the plasma arc irradiation and decomposed. Objects heavier than the molten slag, such as the ballasts, sink into the molten slag and are melted and decomposed by the heat. **Fig. 1** schematically illustrates the plasma melting furnace.

3.2 Process flow

Fig. 2 shows the basic process flow of a plasma melting furnace system. The PCB wastes encased in steel drums are transported to a plasma melting plant, and charged into the furnace as encased, drum by drum. The melting process in the furnace is monitored through a camera (see **Photo 1**), and the plasma torches are manipulated so that the melting process proceeds adequately. When a steel drum and its content melt down and decompose completely, another drum is charged, and thus, PCBs and PCB-containing objects do not accumulate inside the furnace; this facilitates measures against operation troubles and ensures thorough decomposition.

PCBs and combustibles decompose into CO_2 and H_2O inside the

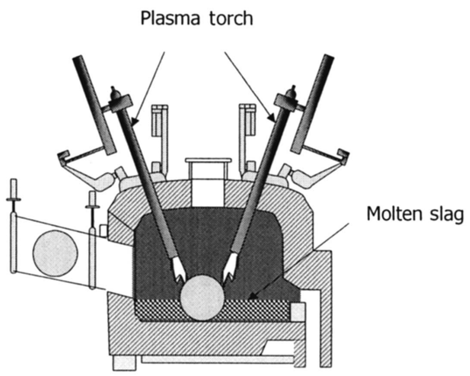

Fig. 1 Schematic illustration of plasma melting furnace

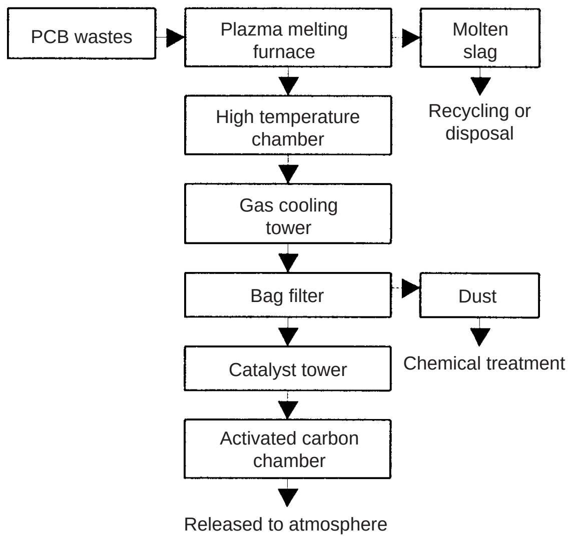

Fig. 2 Basic flow

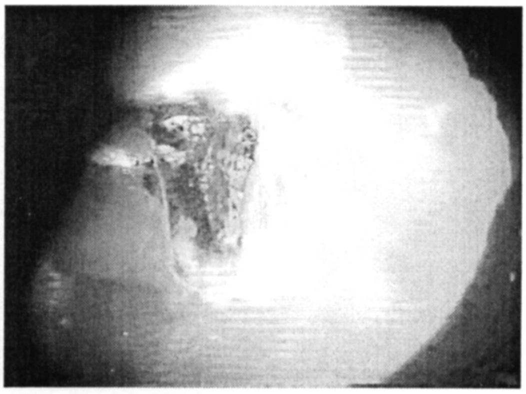

Photo 1 Melting state in the plasma melting furnace

furnace, and incombustibles turn into molten slag. The furnace exhaust gas is cooled by water spray to about 200℃ in a gas cooling tower, rid of HCl and SO_X by slaked lime injection at bag filters and of NO_X by ammonia injection at a catalytic converter. Dioxins in the exhaust gas are adsorbed by activated carbon injected at the bag filters, and then decomposed and removed by catalysts at a catalytic converter. An activated carbon chamber is provided at the final stage of the gas treatment equipment as the final safety measure.

The molten slag is discharged from the furnace, subjected to a final inspection as to the existence or otherwise of residual PCBs, and when approved, discharged to outside the system for recycling or final disposal. The solids collected by the bag filters are also subjected to the final inspection, and when approved, chemically treated to inhibit the elusion of heavy metals, and then discharged to outside the system for final disposal.

3.3 Advantages

The developed technology, which is characterized by the melting and decomposing of the toxic substance by the plasma arcs and molten slag, has the following advantages:

(1) Non-transfer plasma torches ensure stable operation with treatment objects of widely different shapes and properties.
(2) The system has a high PCB decomposition capacity and excellent safety.
(3) The objects are handled and treated as encased in steel drums, and therefore contamination during handling is minimized.
(4) Virtually no pre-treatment is required.
(5) The slag and solids discharged from the system are homogeneous and stable.
(6) The system is self-contained and causes no secondary pollution.

4. Verification Tests of PCB-contaminated Waste Treatment

In view of the application of the plasma melting furnace system to the commercial treatment of PCB-containing wastes, we carried out a series of verification tests.

4.1 Test plant

The test plant shown in **Photo 2** had a capacity for 1 t/day.

4.2 Test conditions

Two types of tests were carried out: mixed treatment tests in which the kinds of PCB-containing wastes were mixed in the ratios according to Table 1 and sealed in 20-l steel drums similar to those used for the storage of the PCB-containing wastes; and individual treatment tests in which each kind of waste was sealed separately in the 20-l steel drums. The mixed treatment tests were carried out continuously for five days under a constant operation condition, and the individual treatment tests for one day for each kind of waste. For the mixed treatment tests, the sludge, waste cloth and copy paper were put into the drums after weighing to the respective mixing ratios. The ballasts were put into the drums unit by unit, without breaking into pieces. Common concrete blocks and resin pellets available in the market were put into the drums as substitutes for the concrete and resin containers used for the storage of the wastes. **Tables 2** and **3** show the amounts of wastes charged into the furnace per 8-hour operation. Besides the wastes, basicity adjustment chemicals were also put into the drums to control the properties of the slag.

The furnace was operated for eight hours per day, from 10 am to 6 pm. The wastes were charged into the furnace drum by drum: a first drum was charged at 10 am, subsequent drums were charged at equal intervals, and the slag was discharged at intervals of 4 h. The furnace temperature was set at 1400℃ or higher, and the furnace pressure was controlled to be lower than the atmospheric pressure to prevent the leakage of the furnace gas to outside the system.

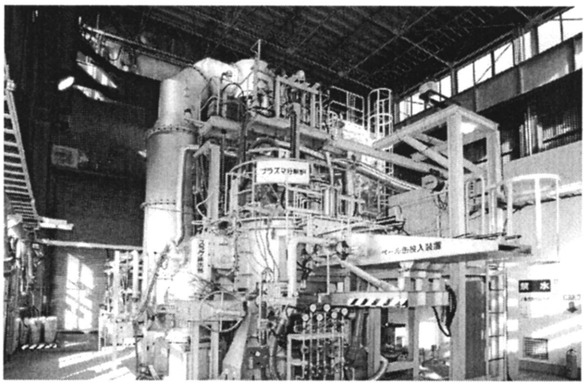

Photo 2 Overview of test plant

Table 2 Kind and weight of wastes of mixed test

(kg)

	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5
Ballasts	96	96	96	96	96
Copy paper	4.5	4.3	4.3	4.4	4.3
Waste cloth	1.3	1.3	1.3	1.3	1.3
Sludge	116	116	116	116	116
Concreat block	67	68	68	64	65
Plastic pelets	2.9	2.9	2.9	2.9	2.9
Pail cans	32	32	32	32	32
Total	319	320	320	317	318

Table 3 Kind and weight of wastes of individual tests

(kg)

	RUN 1	RUN 2	RUN 3	RUN 4
Ballasts	315			
Copy paper		140		
Sludge			208	
Waste cloth				130
Pail cans	18	56	52	52
Total	333	196	260	182

Photos 3 to **6** show the PCB-containing wastes used for the tests.

4.3 Results

Fig. 3 shows the changes over time of the molten slag temperature, exhaust gas volume and furnace pressure during Run 4 as a typical example of the mixed treatment tests. The molten slag temperature was higher than 1400℃ and the furnace pressure was kept negative stably throughout the 8-h operation; the situation was the same with all the test runs. **Tables 4** and **5** show the balance and ratio of PCB decomposition. The PCB decomposition ratio was maintained at 99.9999% or more in all the test runs.

The test results confirmed the capability of the plasma melting and decomposing technology to safely treat stocked PCB-containing wastes as encased, without pre-treatments such as mixing with additives. **Tables 6** and **7** show the analysis results of dioxins in the

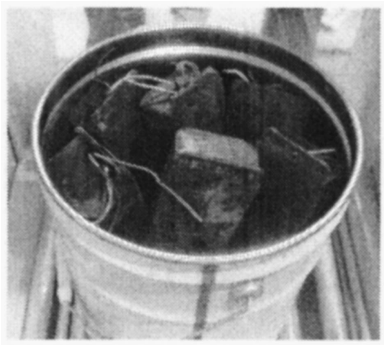

Photo 3 Ballasts containing PCB

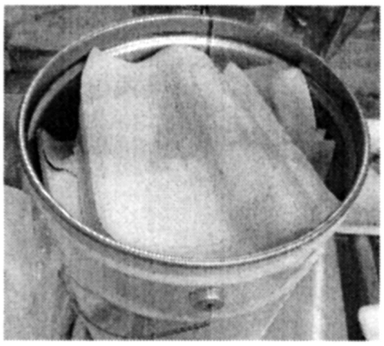

Photo 4 Copy paper containing PCB

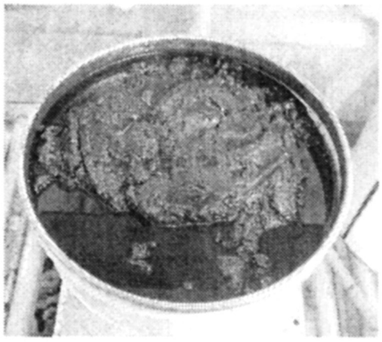

Photo 5 Sludge containing PCB

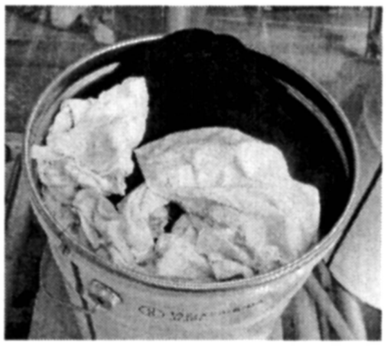

Photo 6 Wastes cloth containing PCB

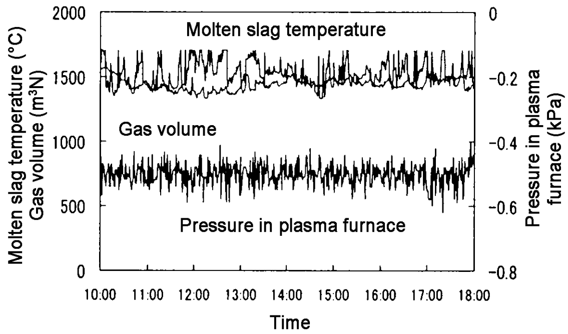

Fig. 3 Chart of molten slag temperature, gas volume and furnace pressure(RUN4)

Table 4 Balance of PCB decomposition of mixed test

				RUN 1	RUN 2	RUN 3	RUN 4	RUN 5
Input	PCB wastes	Amount	kg/8h	319	320	320	317	318
		PCB concentration	%	1.3	1.3	1.3	1.3	1.3
Output	Slag	Amount	kg/h	30.25	27.75	29.75	39.25	28.5
		PCB concentration	mg/kg	0.000027	0.000023	0.000025	0.00019	0.0000072
	No. 1 bag filter dust	Amount	kg/h	9.68	8.32	9.13	7.50	7.34
		PCB concentration	mg/kg	0.00016	0.000044	0.0000043	0.00019	0.0000049
	No. 2 bag filter dust	Amount	kg/h	11.41	8.88	9.68	8.13	7.49
		PCB concentration	mg/kg	0.000069	0.000049	0.000017	0.00020	N.D.[*1]
	Catalyst tower gas	Volume of dry gas	m^3N/h	1 790	1 860	1 790	1 780	1 820
		PCB concentration	$\mu g/m^3N$	0.0051	0.0038	0.0016	0.019	0.0016
PCB decomposition			%	99.999998	99.999998	99.999999	99.999991	99.999999

[*1] N.D.: not detected

Table 5 Balance of decomposition of individual tests

				RUN 1 Ballasts	RUN 2 Copy paper	RUN 3 Sludge	RUN 4 Waste cloth
Input	PCB wastes	Amount	kg/8h	333	196	260	182
		PCB concentration	%	1.5	0.65	27	21
Output	Slag	Amount	kg/h	63	5.5	5.8	3.8
		PCB concentration	mg/kg	N.D.[*1]	0.0000028	0.000017	0.0000092
	No. 1 bag filter dust	Amount	kg/h	5.7	6.1	5.5	7.5
		PCB concentration	mg/kg	0.00089	0.0071	0.00074	0.0025
	No. 2 bag filter dust	Amount	kg/h	5.2	6.2	5.3	5.8
		PCB concentration	mg/kg	0.00018	0.00095	0.0013	0.0082
	Catalyst tower gas	Volume of dry gas	m^{3}N/h	1 450	1 640	1 620	1 700
		PCB concentration	μ g/m^{3}N	0.019	0.023	0.012	0.024
PCB decomposition			%	99.9999944	99.999945	99.9999965	99.9999978

[*1] N.D.: not detected

Table 6 DXNs concentration of mixed test

		RUN 1	RUN 2	RUN 3	RUN 4	RUN 5
Slag	ng-TEQ/g	0	0	0	0.00000071	0
No. 1 bag filter dust	ng-TEQ/g	0.000031	0.00000018	0	0.0000011	0
No. 2 bag filter dust	ng-TEQ/g	0.00000020	0.00000016	0	0.00000079	0
Catalyst tower gas	ng-TEQ/m^{3}N	0.00029	0.0000061	0.0000056	0.0046	0.0000043

Table 7 DXNs concentration of individual tests

		RUN 1 Ballasts	RUN 2 Copy paper	RUN 3 Sludge	RUN 4 Waste cloth
Slag	ng-TEQ/g	0	0	0	0
No. 1 bag filter dust	ng-TEQ/g	0.0036	0.0038	0.10	0.068
No. 2 bag filter dust	ng-TEQ/g	0.0019	0.00000072	0.016	0.093
Catalyst tower gas	ng-TEQ/m^{3}N	0.041	0.044	0.00023	0.068

Photo 7 Crushed slag after air cooling

slag, bag filter dust and furnace exhaust gas. The dioxin concentration was well below the lower limit set forth by the regulation. These results show that the plasma melting and decomposing technology is fully capable of completely detoxifying PCBs.

Photo 7 shows the slag discharged from the plasma furnace, cooled, and crushed for taking samples for analysis. The slag was quite homogeneous without non-melted original objects, and was good for recycling. Note that iron in the original objects was mostly oxidized by the plasma arc and mixed in the slag, and thus no metal/slag separation was observed.

5. Summary

Various waste PCBs and PCB-containing objects were test processed in a test plant of a plasma arc melting and decomposing furnace in mixtures and individually. The test results confirmed that the plasma arc furnace was capable of stably melting and decomposing the treatment objects as encased in steel drums, that the slag discharged from the furnace was homogeneous and had characteristics suitable for recycling, and that the dioxin and PCB concentrations in the slag, bag filter dust and exhaust gas were far lower than the respective lower limit of regulations. Thus, we have confirmed that the plasma melting technology is a safe technology capable of processing a variety of PCB-containing objects and minimizing the contamination of operators with PCBs.

The tests described herein were carried out using a test plant designed in consideration of the actual treatment of PCB-containing wastes, and the tests supplied valuable data for developing commercial plants based on the test plant. We are willing to promote the safe detoxification of PCBs by the technology and thus significantly contribute to the conservation of the global environment.