REMOVAL OF PCBs FROM CONTAMINATED TRANSFORMER BY CIRCULATIVE FLUSHING OF PCB-FREE INSULATINFG OIL

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Abstract
Here we report removing PCBs from the core and coil assembly of contaminated transformers using a process of circulative flushing with PCB-free insulating oil. The leaching of PCBs from the core assemblies was confirmed by a time dependent increase and eventual plateau of PCB concentrations in the flushing oil. In four transformers (5kVA, 10kVA and two 100kVA), removal of PCBs was completed with no PCBs detected in the core assemblies after 16 hours circulation. Contaminated transformers could be classified to non-PCB status after PCB removal by circulative flushing processes.

Introduction
Polychlorinated biphenyls (PCBs) were often introduced into the insulating oil of capacitors and transformers prior to their prohibition in 1973 in Japan. PCBs themselves and PCBs used in electrical equipment have been collected and securely kept until a 2001 law permitted decomposition of PCBs into harmless constituents by several methods based on chemical reactions. It seems likely that PCBs stored in Japan will be eradicated in near future. However, it was reported by the Japanese government in 2003 that PCBs might be still present as a contaminant in insulating oil. In most cases the contaminated concentration of PCBs is quite low such at mg/kg, but the concern is the large number, approximately 1.2 million, of transformers that are suspected to be contaminated. Due to the large number of transformers and low levels of PCB contamination a more cost effective procedure to decompose PCBs is highly desirable.
The ministry of environment in the Japanese government is thus investigating experiments for PCB decomposition in insulating oil using a commercial incinerator. On the other hand, a simple technique to remove PCBs from contaminated transformers must also be developed to use in conjunction with decomposition of PCBs by incineration. The Environmental Protection Agency of U.S. investigated removing PCBs from the core and coil assembly of contaminated transformers using a process of flushing with PCB-free insulating oil[1]. The investigation also proved experimentally that there is no significant leaching of PCBs into PCB-free oil added to the transformers after flushing. These results suggest contaminated transformers can be reclassified to non-PCB status after the draining and flushing processes is complete. In this study, the four contaminated transformers were tested for removal of PCBs from the assembly through flushing by PCB-free insulating oil.

Materials and Methods
Transformer: Four transformers designated A to D were used in this study (Table 1). The total weight including insulating oil for transformer A (5kVA) and transformer B (10kVA) was 85kg and 103 kg, respectively. Oil quantity for both transformers was around 25L. The total PCB concentration in the original insulating oil was 12mg/kg for transformer A and 27mg/kg for transformer B. Transformer C and D were 100 kVA. The total weight including 270 L insulating oil for both transformers was 555kg. The total PCB concentration in original insulating oil is 10mg/kg for transformer C and 22mg/kg for transformer D.

Flushing experiment: Flushing experiments were carried out in the following steps. First, PCB contaminated oil was drained from the transformer. The core was taken out from the case, and a part of the core assembly was cut as a sample before flushing for PCB analysis. The samples are dielectric paper, primary and secondary copper coil and core steel. In addition, contaminated oil from the inside wall of the case was also collected by wiping with cotton wool. After the sampling, the core was replaced in the case and transformer was set into a heating

bath. PCB-free insulating oil was then introduced to the transformer. The refilled transformer was attached to a flushing machine to circulate oil between transformer and machine (Fig. 1). During circulation, the temperature of flushing oil and transformer were maintained at 80 ℃ by the heating oven and bath respectively. Flow rate for circulation was fixed at 4.0L/min for the 5kVA and 10kVA transformers (oil quantity:25L) and 6.0mL/min for 100kVA transformer (oil quantity:195L) . After flushing, the samples for PCB analysis were taken in the same manner described above.

Table 1. Transformer used in this study

Transformer	Voltage (kVA)	Oil quantity (L)	Total weight (kg)	Core weight (kg)	Original PCB conc. in oil(mg/kg)
A	5	24	85	42	12
B	10	26	103	43	27
C	100	195	555	270	10
D	100	195	555	270	22

PCB analysis: All PCB analysis for transformers was done with the Japanese statutory methods for PCB waste. The basic procedure calls for extracting PCBs in *n*-hexane from the sample, PCBs in *n*-hexane are then cleaned up by DMSO extraction followed by sulfuric acid treatment and silica gel column chromatography. Finally, total PCB were measured by gas chromatography with electron capture detection (GC-ECD). Briefly, dielectric paper was shaken in more than 200mL of water at pH5.8-pH6.3 at 10% (wt) for 6 hours. The filtrate of this mixture was extracted with *n*-hexane. PCBs from dielectric paper in *n*-hexane were measured by basic procedure described above. PCBs in 50g of primary or secondary copper coil were extracted with *n*-hexane and applied to basic procedure. For PCBs on the surface of core steel and inside wall of the case in 500cm^2 was wiped with cotton wool which was moisten with *n*-hexane. The cotton containing PCBs were extracted with *n*-hexane and applied to basic procedure to measure total PCB.
Total PCB concentration of flushing oil was monitored using a rapid immunoassay[2-4]. The flushing oil was taken from a sampling port of the flushing machine at the time described and provided for assay. Briefly, the oil sample was applied to a rapid pretreatment using multi-layer column and evaporator. PCBs separated from oil matrix was then added to the antibody solution to allow binding of the antibody. The degree of binding varies with PCB concentration, allowing the PCB concentration to be estimated from a measurement of the free antibody remaining in solution. The amount of free antibody was determined as absorbance changes of the detection cell using a portable reader after flowing through antibody and PCB mixture to the cell. Total PCB concentration can be calculated as a function of absorbance changes.

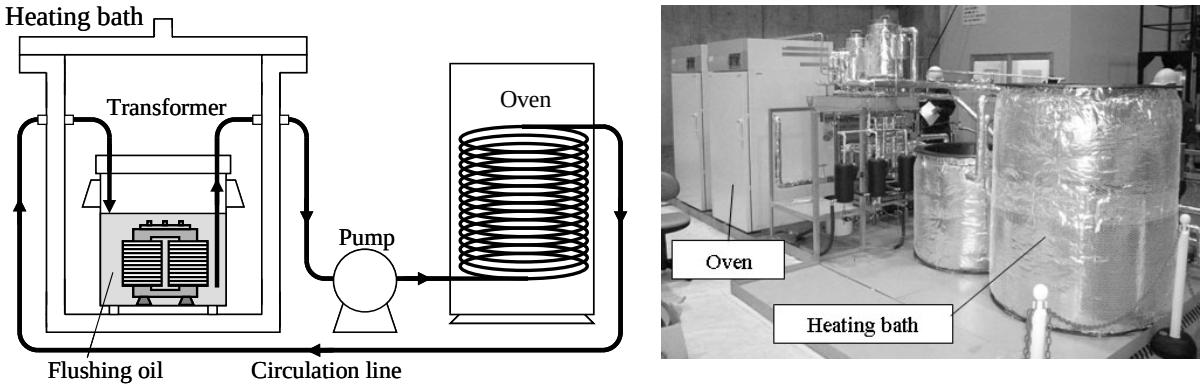

Figure 1. Scheme and photo of flushing machine

Results and Discussion

Effect of temperature for leaching PCBs from transformer assembly to flushing oil: In order to set the oil temperature in the flushing experiment, a preliminary test was performed with small transformer (oil quantity:45L). The original oil (total PCB concentration was 21mg/kg) in this transformer was replaced with 45L of PCB-Free insulating oil. The replaced oil was circulated at 4.0L/min between transformer and flushing machine with temperature control at 30-40℃. Total PCB concentration in flushing oil was monitored by immunoassay (Fig.2). PCB concentration increased with an increase of flushing time until 50 hours when it reached a plateau. The concentration did not change even after 98 hours flushing. However, PCB concentration started to increase again when oil temperature was increased to 80℃ during 98-106 hours. After cooling circulation to 30-40℃ during 106-119 hours, the oil temperature was increased again at 80℃ for 8 hours but an increase of PCB concentration in flushing oil was not observed. These results suggested an increase of flushing oil temperature more efficiently leached PCBs from the core assembly of the transformer. In addition, saturation of PCBs leaching to flushing oil suggested the removal of PCBs from core assembly. Total PCB concentration was measured as less than 0.003mg-PCB/L-solution for dielectric paper and less than 0.01mg-PCB/kg-metal. These concentrations were less than concentrations of the Japanese statutory definition of PCB-contaminant. Therefore, the core assemblies were classified as non-PCB after flushing.

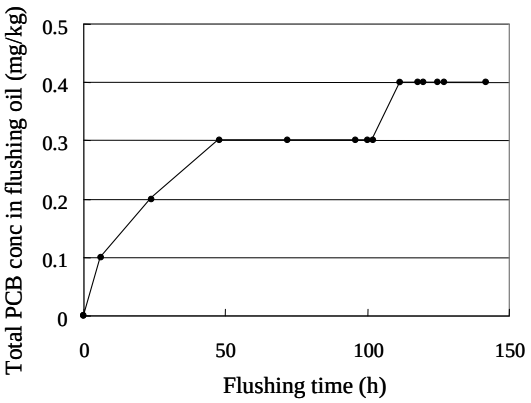

Figure 2. Effect of temperature on leaching of PCBs from core assembly to flushing oil.

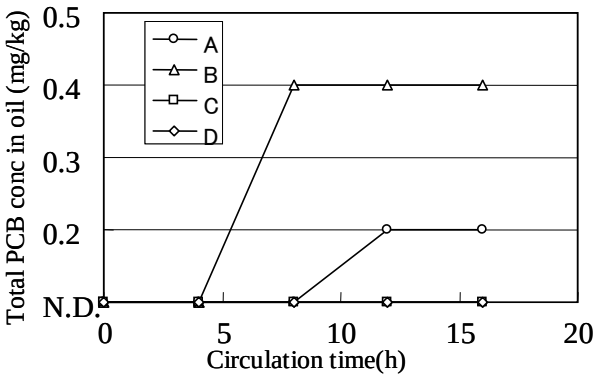

Figure 3. Time course of PCB conc. in flushing oil for four transformers

Leaching profile of PCBs from core assembly to flushing oil: From the results above, temperature for flushing was set to 80℃ for further investigation. First, transformer B in Table 1 was applied to flushing experiment. Total PCB concentration in flushing oil was measured by a rapid immunoassay and a change of concentration for 16 hours circulation was shown in Fig. 3. Total PCB concentration in flushing oil was less than detectable limit (0.2mg/kg) of immunoassay after 4 hours circulation, and increased to 0.4 mg/kg on 8 hours. After 8 hours, the concentration reached to the constant until 16 hours circulation period. From these results, a leaching of PCBs from core and oil assembly could be possibly saturated under these conditions at least 12 hours. Therefore, flushing experiments were performed with transformer A, C and D in the same manner. In transformer A, leached PCBs from assembly could be detected in flushing oil at 0.2 mg/kg after 12 hours circulation, and the concentration did not change until 16 hours circulation. In order to confirm immunoassay results, the same oil samples in Fig. 3 were measured by GC/ECD with GPC (CLNpak EV-G/CLNpak EV-2000, Showa Denko), following sulfuric acid treatment. The same tendency of leaching was observed as well.

Removal of PCBs from core assembly by circulation of flushing oil:

The PCB content of core assemblies was measured to confirm PCB removal by circulation of flushing oil. The PCB contents of the dielectric paper, primary and secondary copper coil, the core steel and the case for all transformers were measured using the Japanese statutory method after 16 hours circulation of flushing oil. The

measurement results are summarized in Table 2.

Table 2. PCB content of transformer assembly after 16 hours circulation by flushing oil.

Assembly	Transformer				Statutory regulation for non-PCB status	Units
	A	B	C	D		
Case	<0.1	<0.1	<0.1	<0.1	≦0.1	μg-PCB/100cm^2-surface area
Core steel	<0.1	<0.1	<0.1	<0.1		
Primary copper coil	<0.01	<0.01	<0.01	<0.01	≦0.01	mg-PCB/kg-material
Secondary copper coil	<0.01	<0.01	<0.01	<0.01		
Dielectric paper	<0.0005	<0.0005	<0.0005	<0.0005	≦0.003	mg-PCB/L-

In all transformers, PCB contents of the core assemblies were actually less than detectable limits of the Japanese statutory methods for PCB waste. These results showed that PCBs in core assemblies could be removed by 16 hours circulation of flushing oil. After treatment, the assemblies were classified as non-PCB in accordance with the Japanese statutory definition for PCB waste.

This study investigated removing PCBs from the core and coil assembly of contaminated transformers using a process of circulative flushing of PCB-free insulating oil after draining of original contaminated oil. The leaching of PCBs from the core assemblies to the flushing oil was confirmed from a circulation time dependent increase and saturation of PCB concentrations in the flushing oil. Washing efficiency was enhanced by a temperature elevation of the flushing oil from 30-40℃ to 80℃. In all four transformers, PCB contents of the core assemblies were less than detectable limits of the Japanese statutory methods for PCB waste. From these results, it was concluded that contaminated transformers with at least up to 27mg/kg PCBs in their oil could be classified to non-PCB status after the draining and circulative flushing process. It seems likely that that the circulative flushing process, in conjunction with a rapid immunoassay based concentration check, will be useful in cleaning and reclassifying contaminated transformers.

References

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