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Dechlorination of Mineral Insulating Oil Contaminated with Polychlorinated Biphenyls

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Abstract

Polychlorinated Biphenyls (PCB) were widely used as fire retardants and insulating material in the manufacture of transformers and capacitors. This was due to their ability to withstand exceptionally high temperatures. Because of their classification as a human carcinogen, the EPA banned their use in 1979, with the exception of their regulated use for a specific purpose. Transformers and Capacitors which were manufactured prior to 1979 contain oil, which may contain certain levels (ppm) of PCB. Therefore, all oil-filled equipment with PCB contamination must be disposed of. Because of their highly regulated use and disposal, all oils from transformers/power supplies need to be sampled and tested prior to disposal of the oil and the carcass. The Stockholm Convention on POPs, which was adopted in May 2001 with the objective of protecting human health and the environment from POPs, came into force on 17th May 2004. Accordingly, those mineral insulating oils which are contaminated by PCB due to retro-filling need to be treated by the PCB dechlorination procedure. This paper presents a case study of PCB dechlorination of mineral insulating oil. In this study, the dechlorination of about 65 kL of PCB-contaminated mineral insulating oil was carried out using the sodium dispersion method. After the dechlorination process, the PCB contamination levels have been decreased from 21.06 mg/kg to less than 2 mg/kg, which is the requirement as per IS 335:2018. It was recommended to reclaim or reuse the dechlorinated oil.

Keywords: Dechlorination, Mineral Transformer Oils, Poly Chlorinated Biphenyl, Sodium Dispersion

1. Introduction

Polychlorinated Biphenyls (PCB) are colourless and odourless liquids in different forms. They were synthetically manufactured by catalytic chlorination of biphenyls. This process produces a complex mixture of different molecular combinations of PCB, forming up to 209 structures known as congeners, with a general chemical formula of $C_{12}H_{10-n}Cl_n$ [1-3] (Figure 1).

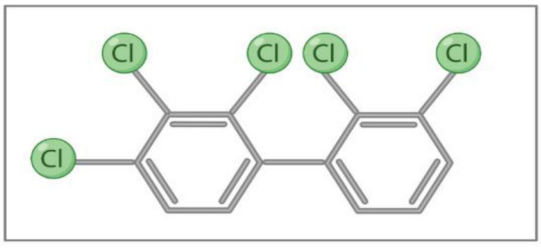


Figure 1. Molecular structure of PCB.

They were marketed as Aroclors in the United Nations, Kaneclor in Japan, Fenclor in Italy, Pyralene in France, and Clophen in West Germany, *etc*. PCBs were used in many applications, such as capacitor dielectric fluid for transformer insulation and coolant, air and gas compressor lubricant, plasticisers, heat transfer systems in paint, surface coating materials, *etc*.[2-5].

PCB were widely used as a fire retardant and insulating material in high-rated transformers and capacitors, prior to the 1980s. These compounds have a significant potential for pollution due to their high chemical stability, toxic characteristics, and capacity to stay in the environment. These substances fall into the category of Persistent Organic Pollutants (POPs). If these materials are left untraced or unidentified, they will continue to contaminate food, water, soil, and biological materials for a very long time. Therefore, proper care should be taken while collecting and disposing of the PCB[4-6]. To mitigate these issues, an international treaty, was signed at Stockholm Convention on "Persistent Organic Pollutants", was signed in the year 2001 to protect human health and the environment from toxic chemicals that persist in the environment, bio-accumulate in organisms and travel

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long distances. More than 160 nations have participated and committed to removing these types of harmful materials from their nations as a result of this agreement. India is also a signatory to this convention and is obliged to eliminate these types of materials[7-9]. Several mechanisms have been developed to destroy PCB, and some of the important methods are listed.

1.1 Biological methods

The biological methods, like anaerobic and aerobic oxidative methods, are used to reduce the concentration of poly chlorinated biphenyls[10,11].

1.1.1 Anaerobic Reductive De-chlorination (ARD)

ARD is a microbial process in which the chlorine atoms in the PCBs are removed by bacteria in oxygen-free environments, and the PCBs are converted to biodegradable, non-toxic compounds[12].

1.1.2 Aerobic Oxidative Degradation (AOD)

In the AOD process, microorganisms participate in the biodegradation of PCBs in the presence of an oxygen atmosphere by producing enzymes, which modify the organic pollutant into simpler compounds[13].

1.2 Chemical Methods

Chemical methods such as sodium neutralisation, incineration and plasma arc methods are also used for the destruction of PCBs.

1.2.1 Sodium Neutralisation Method

In this method, dispersed sodium metal in mineral transformer oil is used for reacting with the PCB in the contaminated oil to form sodium chloride salt and biphenyls[14].

1.2.2 Incineration

The PCB contaminated oil is incinerated in rotary kilns that operate at high temperature[15].

1.2.3 Plasma Arc

The plasma arc is used to decompose the PCB to an atomic level. Experiments have been carried out at temperature range above 1,800 K[16].

1.2.4 Microwave Method

PCB contaminated siloxane transformer oil and hydrocarbon engine oil were investigated through the application of Microwave (MW) irradiation[17].

1.3 PCB Dechlorination Work Undertaken by Central Power Research Institute (CPRI)

Central Power Research Institute (CPRI) has been identified as the nodal organisation by MoEFCC (Ministry of Environment, Forest and Climate Change) for destroying the PCB contaminated mineral insulating oils in the Indian power sector through the sodium neutralisation process (Chemical Method) as per the guidelines of UNIDO. CPRI has taken up sponsored projects from UNIDO entitled "Reduction and Elimination of PCBs, prioritizing the Power sector in India" and "A management service for the treatment of transformer mineral oil containing PCB using mobile PCB dechlorination system in India" with the objectives of finding out the inventory of PCB contaminated mineral oils in the Indian power sector and further to destroy the targeted 750 MT of PCB contaminated transformer oils.

The present paper details a case study taken up by CPRI on the dechlorination of PCB-contaminated transformer oil drawn from a Generator Transformer as part of the above project.

2. Materials and Methods

CPRI identified a 250 MVA (15.75/220 kV) Generator Transformer (GT) having an estimated quantity of 66.6 kL of PCB-contaminated oil for the dechlorination process. The contaminated transformer oil was drained from the GT and stored in an MS storage tank to carry out the PCB dechlorination process. The general chemical equation for the dechlorination of PCB by the dispersed sodium process is given in Equation 1.

$$Ar\ PCB(Cl)+Na \rightarrow Ar(H) + NaCl \qquad \text{Equation (1)}$$

where, Ar represents a hydrocarbon molecule. Sodium metal in the form of bricks (Figure 2), preserved in mineral oil (density of 0.88 g/ml), was used for preparing the dispersed sodium in mineral oil.



Figure 2. Sodium metal bricks.

The other chemicals used for this process were Iso-Octane of HPLC grade, Sulphuric Acid 98 % and ultra-high pure nitrogen.

Sodium dispersion required for dechlorination activity was prepared in batches by a specially designed sodium dispersion unit manufactured by M/s NPO Dekanter, Russia, as shown in Figure 3. The maximum batch size is 340 kg. The sodium dispersion unit is working on a constant dispersion and stirring principle in which the transformer oil and the sodium metal are stirred at a proportion of 60:40, respectively, at a constant speed of 35 RPM and at a temperature of 105°C in a nitrogen environment. This process is continued for about 25 h for each batch, until the sodium metal size is less than 10 microns.



Figure 3. Sodium metal bricks.

An optical microscope capable of measuring less than 10 microns was used for measuring the particle size of the dispersed sodium in the mineral oil (Figure 4).

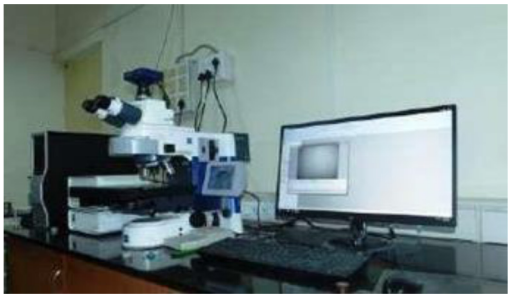


Figure 4. Optical microscope.

A Gas Chromatograph (GC) equipment of make Perkin Elmer was used for evaluating the PCB content of transformer oil before and after the dechlorination of PCB contaminated oil as per IEC 61619 standard[18-20]. This equipment uses the Electron Capture Detector (ECD) for the evaluation of PCB compounds (Figure 5).



Figure 5. GC-ECD equipment.

The PCB dechlorination unit basically contains an electrically controlled reaction chamber and other accessories with an associated safety system. The total unit is built inside a compact container (Figures 6, 7). This PCB-contaminated oil is heated to a temperature of 120°C, and a sample was drawn from the reactor to check the initial concentration of PCB content. Based on the initial concentration of PCB content in the oil, the calculated amount of sodium dispersed in oil (NaD) was added from the sodium storage tank to the reactor.



Figure 6. PCB dechlorination unit.

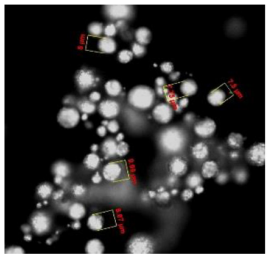


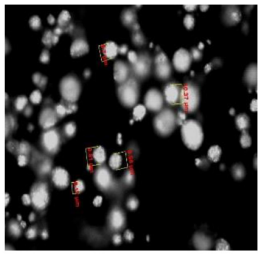
Figure 7. Reactor of the PCB dechlorination unit.

3. Results and Discussion

3.1 Sodium Dispersion

Around 680 kg of sodium dispersed in oil was prepared using the sodium dispersion unit stationed at CPRI, Bengaluru. The details of the sodium dispersion prepared are given in Table 1. Optical microscope image analysis is carried out to measure the particle size for the sodium-dispersed oil, and an optical image of the size of the particle is given in Figures 8 & 9.





Figures 8, 9. Particle sizing in the range 2-10 µm.

Table 1. Details of sodium dispersed in oil

Batch No.	Batch size Kg	Na, Kg	Qty Oil, Kg	Na, microns
1	340	136	204	2-10
2	340	136	204	2-10

3.2 PCB Dechlorination Plant at Site

Preliminary arrangements were made at the site for levelling the PCB dechlorination plant and other electrical connections with a step-down transformer as shown in Figures 10 and 11.



Figure 10. Levelling done for placing the PCB de-chlorination unit.



Figure 11. The step-down transformer is connected to the PCB unit.

The electrical connections of all the accessories, like the electrical heater, pump, compressor, valves, sensors, *etc*., to the control panel were checked before the commencement of operation.

The laboratory setup was made for the PCB extraction from the contaminated transformer oils. The GC-ECD used for the PCB testing was calibrated using PCB standards 1242, 1254 and 1260 Aroclor before examining the test samples.

3.3 PCB Dechlorination Process

The PCB-contaminated transformer oil was drained from the chosen Generator Transformer (Figure 12) and stored in 3 Nos. of MS Storage Tanks of 20 kL capacity.



Figure 12. PCB contaminated 250 MVA, 15.75/220 kV generator transformer.

PCB dechlorination process was carried out by loading a known volume of PCB-contaminated oil into the reactor. The oil was passed through a set of pre-heaters and a de-gasifier, where water and volatile compounds were removed. The PCB dechlorination reaction was carried out at a temperature of 120°C with nitrogen purging into the reactor.

The basic principle of the reaction is that the sodium metal dispersed in the transformer oil reacts with the PCB content in the contaminated transformer oil, and this will strip off the chlorine atoms attached to PCB to form a sludge that contains sodium salt and other harmless organic products. After the completion of the reaction, the excess sodium in the reaction vessel is neutralised by adding water, and the hydrogen gas released during the neutralisation is purged with nitrogen and vented out to the atmosphere. The treated oil containing sludge in the reaction vessel is transferred to the settling tank.

In the present case, the samples were drawn at every one hour during the reaction and analysed using GC-ECD to check the level of PCB content. The reaction was continued till the PCB content was reduced to 2 ppm in the oil. After the completion of the reaction, the treated oil containing sludge was kept for one day for settling, and the settled sludge at the bottom of the tank was removed by gravity. The

sludge generated in the PCB dechlorination contains sodium chloride, sodium hydroxide, water, and biphenyls, and this was drained into barrels and kept in safe custody for disposal. The treated oil from the settling tank was drained to separate barrels for re-use in the transformer after reclamation.

The general technical issues, like agglomeration and settling of sodium dispersed in the mineral oil, dust settling on the sensor indicating the sodium dispersed oil level, suction pump clogging, *etc*., as given in Figures 13-16, were addressed during the dechlorination process.



Figure 13. Sodium dispersion storage tank level sensor.



Figure 14. Sodium dispersion settled in a 100 l drum.



Figure 15. Vacuum pump open and cleaned.



Figure 16. Vacuum filter removed and cleaned.

The PCB dechlorination activity was carried out in 16 batches. The batch-wise details are given in Table 2. The PCB analysis was carried out for the PCB-contaminated oil before dechlorination, and it was found to be 21.06 ppm (Figure 17).

The PCB analysis was carried out for the transformer oil after dechlorination for all 16 batches, and the results were found to be less than 2 ppm. The PCB results and the quantity of oil taken for each batch are given in Table 2, and the chromatograms are given in Figures 18 to 20.

The Generating Transformer was flushed with new transformer oil, and the PCB concentration of the flushed oil was found to be 0.50 ppm after 2nd flushing and 0.23 ppm after 3rd flushing, which were within the acceptable limit. A total of 64,691 l' oil was de-chlorinated in 16 batches with various batch sizes around 4 kL. With this activity, the 250 MVA, 15.75/220 kV Generator Transformer became PCB-free as indicated by the chromatogram of flushed oil in Figure 21.

Table 2. Details of PCB content evaluated for 16 batches

Batch No.	Quantity (l)	PCB Content after treatment
1	4008	0.38
2	4008	0.15
3	4020	0.12
4	4018	0.12
5	4008	0.18
6	4018	0.31
7	4044	0.23
8	4008	0.26
9	4008	0.34
10	4018	0.29
11	4008	0.86
12	4018	0.2
13	4018	0.22
14	4008	0.71
15	4008	0.06
16	4473	0.39

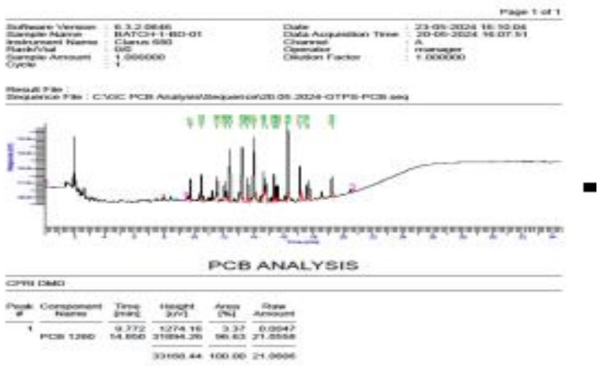


Figure 17. Chromatogram of contaminated mineral insulating oil.

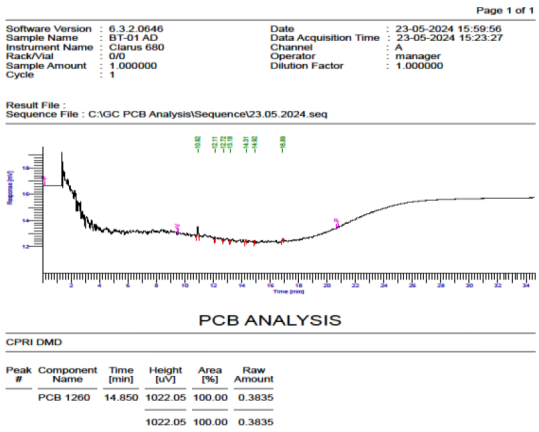


Figure 18. Chromatogram of batch 1 - PCB chromatogram – after dechlorination.

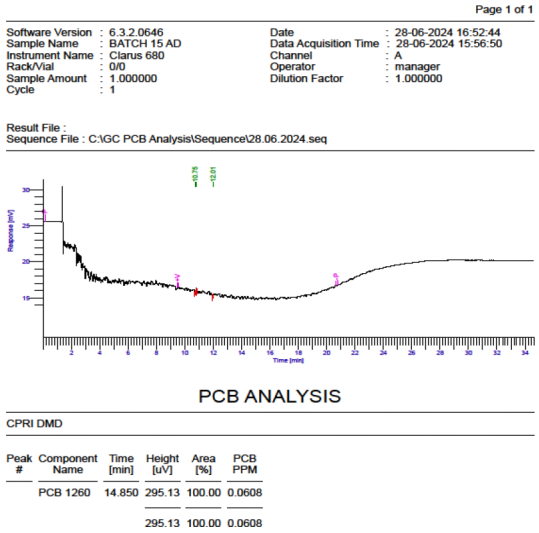


Figure 19. Chromatogram of batch 15 - PCB chromatogram – after dichlorination.

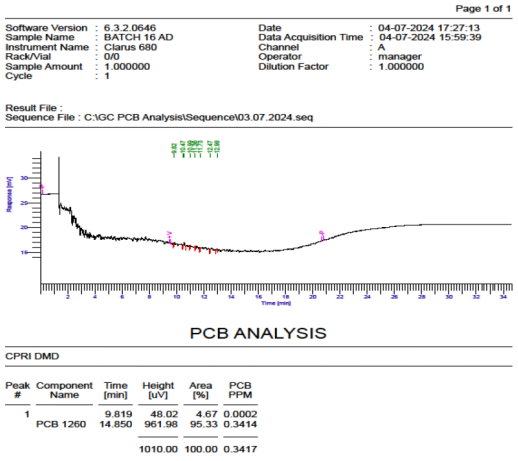


Figure 20. Chromatogram of batch 16 - PCB chromatogram – after dichlorination.

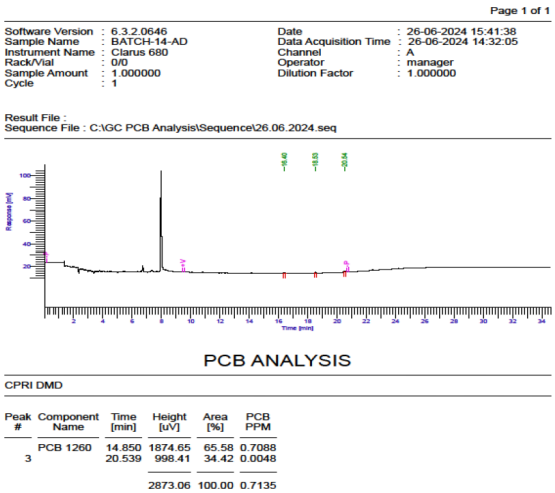


Figure 21. Chromatogram of PCB analysis for flushing oil.

In the dechlorination process of 64, 691 l of the PCB-contaminated transformer oil, 836 l of sludge and 5768 l of water were collected. These items were recommended to be disposed of as per the state pollution control board norms.

4. Conclusions

CPRI has carried out the dechlorination of 64,691 l of PCB-contaminated transformer oil from a Generating Transformer using the sodium neutralisation method. The sodium neutralisation process is a rapid method in which the PCB-contaminated oil can be dechlorinated at the average rate of 2000 l/day. The dechlorination was carried out in 16 batches. The PCB contamination in the original transformer oil was found to be 21 ppm. The PCB content was reduced to less than 2 ppm after the dechlorination process. The sludge and the water obtained from the process were non-toxic. The water generated in the process can be treated and reused. The sludge is disposed of as per pollution norms, and the mineral insulating oil recovered is treated and reused in low rated transformer. This helps to conserve the mineral insulating oil for further continued use.

5. Acknowledgement

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Author Contribution:

Dr. Ann Pamla Cruze - writing-original draft preparation; Dr. V. Saravanan - Original draft editing and review. All authors have read and agreed to the published version of the manuscript.