



Project Summary

Characterization of PCB Transformer/Capacitor Fluids and Correlation with PCDDs and PCDFs in Soot

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Dielectric fluids in transformers and capacitors often contain polychlorinated biphenyls (PCBs) or chlorobenzenes. These substances may generate polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) under certain conditions of combustion/pyrolysis. When electrical equipment containing these fluids is involved in an accidental fire, the resulting smoke, soot, and residues may be contaminated with PCDDs, PCDFs, and other chlorinated hydrocarbons.

The full report contains a review of several laboratory studies investigating the sources of PCDDs and PCDFs as well as the conditions under which they are formed. In addition, some data from sites of actual fire incidents are available and are discussed. Chlorobenzenes and PCBs do not form PCDDs and PCDFs when heated in the absence of oxygen. During fires, the dielectric fluid of transformers or capacitors may be leaked or vented from ruptured casings. With exposure to oxygen, PCBs can produce PCDFs and chlorobenzenes can produce PCDDs. The particular isomers of PCDDs and PCDFs formed are related to the number of chlorine substituents in the reacting material.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In August 1982, the U.S. Environmental Protection Agency (EPA) decided to permit the continued use of electrical transformers containing polychlorinated biphenyls (PCBs) based on the reported low frequency of leaks and spills of PCBs from this equipment relative to the high costs of replacing or securing these transformers. Under Section 6(e)(2)(B) of the Toxic Substances Control Act (TSCA), EPA can authorize a use of PCBs provided that the use "will not present an unreasonable risk of injury to health or the environment." EPA determined that the continued use of PCBs-contaminated transformers (50-500 ppm PCBs) and non-PCB transformers (<50 ppm PCBs) did not present unreasonable risks to public health.

A closer evaluation of the fire-related risks posed by the continued use of PCB transformers, and the costs and benefits of actions designed to reduce those risks followed the 1982 determination. EPA issued a Proposed Rule on October 11, 1984, concerning PCB transformers. EPA determined that fires involving transformers containing >500 ppm PCBs present risks to human health and the environment. The extreme toxicity of materials which can be formed during fires involving PCB transformers, and the potential for human and environmental exposures to these compounds, contributed to EPA's proposed rule.

Considering the extensive comments received during the public comment pe-

riod for the Proposed Rule, EPA modified the Final Rule concerning:

- Evaluation of the use of PCB transformers in or near industrial buildings separately from the use of PCB transformers in or near commercial buildings.
- Relative probabilities of failures and fires in different types of PCB transformers installations, placing more stringent controls on those transformers that EPA believes pose higher risks of failures and fires.
- Increased emphasis on the prevention of PCB transformer fires through increased electrical protection, and decreased emphasis on the use of isolation measures to minimize the spread of already formed and/or released contaminants.

On July 9, 1985, EPA promulgated its Final Rule on PCBs in electrical transformers, the culmination of a long fact-finding and rule-making process that began shortly after the transformer fire at the State Office Building in Binghamton, NY, February 5, 1981.

Summary and Conclusions

An estimated 74,000 tons of PCBs are still in use in U.S. transformers and capacitors. On July 9, 1985, the EPA promulgated its Final Rule on PCBs in electrical transformers. This rule specifies that PCBs at any concentration may be used in transformers (other than in railroad locomotives and self-propelled railroad cars) subject to the following conditions:

- 1) the use of higher secondary voltage (>480 volts) network PCB transformers in or near commercial buildings after October 1, 1990, is prohibited.
- 2) the installation of enhanced electrical protection on lower secondary voltage network PCB transformers and higher secondary voltage radial PCB transformers in use in or near commercial buildings is required by October 1, 1990.
- 3) further installation of PCB transformers in or near commercial buildings is prohibited after October 1, 1985.
- 4) the registration of all PCB transformers with fire-response personnel and building owners is required by December 1, 1985.

5) the markings of the exterior of all PCB transformer locations is required by December 1, 1985.

6) the removal of stored combustibles located near PCB transformers is required by December 1, 1985.

There are still many uncertainties of the scope and nature of the hazards created in PCB transformer and capacitor fires. One potential hazard is the generation of highly toxic substances such as PCDDs and PCDFs from the pyrolysis of PCBs and chlorobenzenes. This report identifies 30 fire incidents involving PCB transformers and capacitors in the United States and western Europe that occurred from September 1978 through February 1985. The following questions are addressed in this study:

- Are PCDDs and PCDFs formed in PCB transformers under normal operating conditions?
- How are the constituents of the transformer fluids related to the type and amount of PCDDs and PCDFs formed?
- What are the temperature and other reaction conditions that favor the formation of the PCB combustion products?

The July 9, 1985 rule provides for a gradual phaseout of some PCB transformers while recognizing the potential for additional fire accidents in the interim. Moreover, PCB capacitors are not covered under the July 9, 1985 rule and, since they have also been involved in fire incidents, capacitors are potential release sources for PCBs and combustion by-products into the environment.

The full report presents and evaluates the available literature and published data on analyses of transformer fluids and soot generated in fires. Even though there have been at least 30 reported incidents, a wide variety of problems that hinder the analysis and evaluation of the data remain, including:

- *Limitation of Analytical Data.* Very few analytical data have been generated for each PCB fire incident. Because of the high cost of isomer analysis and the large number of isomers that characterize the PCBs, PCDFs, and PCDDs, few analyses are actually performed for any specific isomer in the aftermath of a PCB fire incident.
- *Differences in Sampling and Analytical Protocols.* Sampling and analysis protocols for contami-

nants generated in transformer fires are not yet fully standardized, and thus a wide variety of sampling and analytical methodologies are often employed. Some data are based on the analysis of soot and are reported on a weight/weight basis. Other data are based on the analysis of wipe samples and reported on a weight/area basis. Thus, it is very difficult to compare one fire incident with another, or to evaluate the significance of the data in one incident relative to that of another.

- *Lack of Background Data.* Very few background data are available on: (a) composition of transformer fluids and, (b) composition and levels of PCBs, PCDFs, chlorobenzenes, and PCDDs in the environment.

Despite these problems, the following conclusions may be made from analysis of the data from the literature on PCB transformer fires:

- 1) PCDFs and PCDDs are not formed in transformers containing PCBs under normal operating conditions. Their formation requires thermally stressful conditions and the presence of oxygen.
- 2) Electrical arcing in transformers do not lead to the formation of PCDFs and PCDDs.
- 3) A temperature zone between 600°C and 680°C may be regarded as optimal for the formation of PCDFs.
- 4) The amount and the specific PCDF isomers formed are related to the concentration of and type of PCB homologs in the transformer fluid.
- 5) Chlorobenzene diluents in the transformer fluids are required for the formation of PCDDs.

The Binghamton, NY transformer fire accident was the first to capture major media and scientific attention. In that fire, both PCDDs and PCDFs were found in the generated soot, leading to the concern that these compounds were being formed *in situ* in PCB transformers and capacitors under normal operating conditions. The available evidence does not support this concern. Analyses conducted by the Electric Power Research Institute (EPRI) and EPA of samples of dielectric fluids taken from in-service transformers and capacitors and those involved in fire accidents showed no appreciable difference in PCDF values from stock material. No PCDDs were de-

tected. Under normal use conditions, it does not appear that PCDFs are generated to any significant extent in the transformer.

Correspondingly, a second concern was whether PCDDs and PCDFs are formed during electrical discharges associated with transformer performance. To investigate this issue, experiments involving the arcing of electrical energy through various transformer fluids were performed. There was no appreciable difference in PCDF levels before and after electrical arcing. The supposition is that the level of oxygen is very low in the transformer and, thus, does not offer the environment for combustion resulting in the formation of PCDFs and PCDDs.

The amount and the specific PCDD and PCDF isomers formed in a PCB transformer fire appear to be related to the concentration of and type of PCB homologs in the transformer fluids. This supposition is supported by recent estimations on the boiling points for dioxins and furans that indicate that the boiling temperatures for tri-CDDs and tri-CDFs and the higher chlorinated PCDDs and PCDFs range from 375°C to 537°C. A first approximation of the thermodynamic conditions would favor the formation of tri- and higher chlorinated PCDFs and PCDDs. Combustion studies conducted by EPA and EPRI also provide evidence that the concentration of and type of PCB homologs in the transformer fluids are probably related to the amount and the specific PCDD and PCDF isomers formed in a PCB transformer fire. The EPA study indicated that the optimal conditions for PCDF formation from PCBs are a temperature near 675°C and a residence time of 0.8 second or longer. The EPRI study demonstrated that tetra- and penta-CDF yields are roughly proportional to PCB concentrations in the starting material, but it indicated that significant dibenzofuran destruction begins to occur at approximately 550°C.

A final issue pertains to the question of the use of diluents in transformer fluids. Of the 30 reported fire incidents involving PCB transformers and capacitors, unequivocal evidence of PCDDs formation was found only in the Binghamton, NY fire. The Binghamton, NY transformer contained chlorobenzenes as a diluent, adding to the evidence that the pyrolysis of chlorobenzenes leads to the formation of PCDDs. Such evidence has also been found in chemical manufacturing processes and

in metal recovery sites involving PCB transformers. Chlorobenzenes should be carefully evaluated for use as transformer fluids or diluents.

Fire Incidents Involving PCB Transformers and Capacitors

PCBs have been used extensively as dielectric fluid in capacitors and transformers since the 1950s. An estimated 74,000 tons of PCBs are still used in U.S. transformers and capacitors. At least 30 fire incidents involving PCB transformers and capacitors have occurred in the past 7 years as identified in Table 1.

There are no Federal guidelines to define acceptable cleanup levels for toxic releases from PCB transformer and capacitor fires. Current regulations state, however, that all spills and leaks of PCBs or dioxins-contaminated material should be cleaned up to preexisting background levels whenever there is a threat of contamination to water, food, feed, or humans. NIOSH has detected background levels in urban areas of up to 0.5 mcg PCBs/100 cm² of surface area. Following the occurrence of PCB-related fire incidents, several states and

other countries have established contamination cleanup criteria. These criteria are presented in Table 2.

Correlation of Combustion/Pyrolysis Products Generated and Constituents of Transformer Fluids

The ability to predict the type and the quantity of toxic contaminants that may form in a PCB transformer/capacitor fire is of prime importance in the development of prevention and control measures. Because of the scarcity and generally poor quality of data obtained from PCB transformer fire incidents, pyrolytic studies under laboratory-controlled conditions have been employed.

EPA, through a contract with Midwest Research Institute, Kansas City, MO, conducted a study to evaluate thermal degradation products using a bench-scale thermal destruction system. The results indicated that both temperature and oxygen significantly affected PCDF yield. Statistical analysis showed a linear relationship for PCDFs formed versus the concentration of PCBs.

Table 1. Fire Incidents Involving PCB Transformers or Capacitors Since 1978

Location	Date
Norrälja, Sweden	September 25, 1978
Cincinnati, Ohio	December 3, 1980
Binghamton, New York	February 5, 1981
Stockholm, Sweden	August 25, 1981
Danviken, Sweden	1981
Boston, Massachusetts	January 1982
Skövde, Sweden	March 19, 1982
Miami, Florida	April 13, 1982
Arvika, Sweden	May 1982
St. Paul, Minnesota	June 22, 1982
Imatra, Finland	August 3, 1982
Helsinki, Finland	August 1982
Surahammar, Sweden	September 23, 1982
Hallstahammar, Sweden	November 8, 1982
Railway Locomotive, Sweden	Winter 1982/83
Kaukopää, Sweden	1982
Kisa, Sweden	April 25, 1983
San Francisco, California	May 15, 1983
Halmstad, Sweden	August 15, 1983
Chicago, Illinois	September 28, 1983
Bofors, Sweden	December 21, 1983
Columbus, Ohio	March 1984
Södertälje, Sweden	April 27, 1984
Finspang, Sweden	May 24, 1984
Hofors, Sweden	September 13, 1984
Vetlanda, Sweden	October 10, 1984
Reims, France	January 14, 1985
Oslo Lysverker, Norway	January 1985
Sandnes, Norway	February 1985
Raufoss, Norway	February 1985

Table 2. Contamination Cleanup Criteria

Location	Contaminant	Air	Surface
Binghamton, NY Building	PCDDs/PCDFs PCBs	10 pg/m ³ of 2,3,7,8-TCDD/TCDF 200 ng/m ³ of PCBs	3 pg/m ² of 2,3,7,8-TCDD/TCDF 60 mcg/m ² of PCBs
Inside Vault	PCDDs/PCDFs PCBs	80 pg/m ³ of 2,3,7,8-TCDD/TCDF 1 mcg/m ³ of PCBs	24 ng/m ² of 2,3,7,8-TCDD/TCDF 1 mg/m ² of PCBs
San Francisco, CA	PCDDs/PCDFs PCBs	10 pg/m ³ of 2,3,7,8-TCDD/TCDF 200 ng/m ³ of PCBs	3 pg/m ² ^a 60 mcg/m ² of PCBs
Inside Vault	PCDDs/PCDFs PCBs	80 pg/m ³ of 2,3,7,8-TCDD/TCDF 1 mcg/m ³ of PCBs	24 ng/m ² of 2,3,7,8-TCDD/TCDF 1 mg/m ² of PCBs
Sante Fe, NM	PCDDs/PCDFs	--	1 ng/m ² of 2,3,7,8-TCDD/TCDF
Finland	PCDDs/PCDFs	--	5 ng/m ² of 2,3,7,8-TCDD/TCDF
Sweden	PCDDs/PCDFs	--	50 ng/m ² of total TCDF

^aSum of all PCDD/PCDF isomers Cl₄ - Cl₇ with Cl substitution in the 2,3,7, and 8 positions.

A study showed that askarel fluid mixtures of 60% PCBs and 40% trichlorobenzenes were combusted under varying flame temperatures. The results of this study indicated that the optimal temperature for the formation of PCDFs and PCDDs is approximately 600°C. This finding is in fair agreement with the work done at the Midwest Research Institute, where the optimal temperature for PCDF formation from pyrolysis of PCBs was approximately 675°C.

Under optimal conditions, PCDFs are formed from mineral oil or silicone oil contaminated with PCBs at ≥5 ppm. PCDFs were also formed from a trichlorobenzene dielectric fluid that contained no detectable PCBs. These results supported earlier laboratory work and analytical results of soot material from transformer and capacitor fires, which determined that chlorobenzenes are required for PCDD formation.

EPRI has also supported a major study of the thermal conversion of various transformer fluid formulations to PCDFs and PCDDs. Fluids that have been studied include mineral oil, tetrachloroethylene (TCE), and silicone oil, all spiked with Aroclor 1254. One hundred mcl samples were either pyrolyzed (heated in an oxygen-deficient environment) or combusted (injected into a flame or heated under conditions resulting in self-ignition). Pyrolyses were conducted using a simple thermostatically controlled apparatus, capable of accommodating glass or quartz tubes of diameters up to 6 cm within its 9-cm-long heated region. To simulate more accurately certain catastrophic incidents, py-

rolyses were conducted at atmospheric pressure.

Results of the EPRI study support the proposition that tetra- and penta-CDF yields are roughly proportional to PCB concentrations in the starting material. An interesting feature of the mineral oil/Aroclor 1254 data is the clear and reproducible differences between the patterns of tetra-CDFs and penta-CDFs formed by pyrolysis of neat Aroclor 1254 versus those formed by pyrolysis of the 5,000-ppm mixture. For example, 2,3,7,8-TCDF and co-eluters comprise 16-21% of the tetra-CDF mixture formed from neat Aroclor, but they comprise 45-55% of the mixture from mineral oil/Aroclor. Furthermore, combustion of biphenyl in TCE produced decreasing net dibenzofuran as the residence time was varied from 18 seconds to 6 seconds and the wall temperature maintained at 450°C. In contrast, at 550°C, there is a net increase in dibenzofuran yield as residence time decreases. This suggests that at the higher temperature, significant dibenzofuran destruction is occurring. There are also large effects on dibenzofuran yield in the presence of different solvents. Typically, yields obtained with combustion in TCE are much higher than those obtained in silicone or mineral oil. Some sharp differences on the effects of particular variable parameters on dibenzofuran yields have also been noted.

Both EPA's and EPRI's pyrolytic and combustion studies support the proposition that the amount and the specific PCDF isomers are related to the concentration of and the PCB homologs in the

transformer fluid. Additional supporting data include EPA's data on the transformer oil and the generated soot in the Binghamton, NY fire incident. The data on the transformer oil and soot from the Binghamton fire are presented in Table 3.

Penta-CDF concentration was approximately 7% of the total PCDFs in oil. Penta-CDF concentration increased to 31% in the soot after the fire. This finding corresponds to the 52% of pentachlorobiphenyls in the transformer oil. Similar observations can be made for the hexa- and hepta-CDF concentrations in soots relative to the concentrations of hexa- and hepta-chlorinated biphenyls. The Binghamton, NY fire data also appear to indicate that the higher chlorinated biphenyls are more likely to convert to chlorinated dibenzofurans and the lower chlorinated PCBs are more likely to decompose in a transformer fire.

The finding of PCDDs in the Binghamton, NY fire incident raised concerns that PCDDs may be generated in PCB transformers. Analyses of subsequent PCB transformer fire incidents, however, identified only one other incident where PCDDs have been identified. It appears that the presence of chlorobenzene is a requirement for the formation of PCDDs, and fires involving transformers without chlorobenzenes do not generate PCDDs.

Table 3. *Correlation of Analytical Data on Transformer Oil and the Generated Soot from the Binghamton, NY Incident*

	PCBs	PCDFs
	Isomer/Total PCBs	Isomer/Total PCDFs
Tetrachloro-	0.15	0.013
Pentachloro-	0.52	0.31
Hexachloro-	0.28	0.45
Heptachloro-	0.04	0.21
Octachloro-	0.001	0.02

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The complete report, entitled "Characterization of PCB Transformer/Capacitor Fluids and Correlation with PCDDs and PCDFs in Soot," (Order No. PB 87-145 785/AS; Cost: \$18.95, subject to change) will be available only from:

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