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Topics:
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Fires
Transformers
Pollution control
Insulating oils

EPRI CS/EA/EL-4480
Project 2028
Proceedings
March 1986

Proceedings: 1985 EPRI PCB Seminar

Prepared by
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Palo Alto, California

REPORT SUMMARY

SUBJECTS: Hazardous/toxic substances / Risk assessment / T&D: Substations

TOPICS:
- PCB
- Chemical analysis
- Fires
- Transformers
- Pollution control
- Insulating oils

AUDIENCE: Environmental managers / Distribution engineers

Proceedings: 1985 EPRI PCB Seminar

New regulations have increased the complexity of virtually all phases of PCB management. In this EPRI-sponsored seminar, participants discussed the latest advances in methods and equipment to facilitate and improve PCB disposal, cleanup, replacement, and risk assessment.

BACKGROUND: This industrywide meeting constituted the third EPRI-sponsored seminar to update utilities on equipment and processes for dealing with the complex problems of polychlorinated biphenyl (PCB) management. As in the previous seminars, held in 1981 and 1983, discussion topics ranged from equipment and methods in the initial stages of development to processes now on the market.

OBJECTIVES:
- To provide a forum for discussing equipment and methods for PCB management.
- To avoid unnecessary duplication of research efforts through exchange of information.
- To inform equipment suppliers of utility PCB management needs.

APPROACH: Approximately 460 representatives of utilities, government agencies, research groups, and private industry in the United States and other countries attended a PCB seminar in Seattle, October 22-25, 1985. Major subjects of discussion were PCB destruction, mineral oil decontamination, PCB analysis, PCB spill cleanup and management, risk analysis and management, PCB fires, and retrofill and replacement fluids.

RESULTS: This report contains more than 60 papers presented at the seminar. Those discussing PCB destruction addressed such topics as the thermal treatment of PCBs and PCB-contaminated soils and the sampling and analysis criteria for evaluating the effectiveness of PCB destruction methods. Topics in other discussion areas included processes for removing PCBs from contaminated transformer oil and coolants, equipment for testing PCB-contaminated soils, PCB environmental transport, pyrolysis and combustion of PCB-contaminated transformer fluids, and preventive measures for reducing airborne PCB contamination. Several papers described pilot plant projects or

case studies to demonstrate the use of new equipment, processes, and cleanup methods.

EPRI PERSPECTIVE

The large number of people attending the 1985 PCB seminar reflects the need of all those involved in PCB management to discuss common problems and goals. Participants—nearly 200 of whom were from member utilities—came from the United States, Canada, Great Britain, France, Italy, and Sweden and represented a variety of disciplines. The meeting thus provided for a comprehensive review of the issues faced by those responsible for PCB analysis, risk assessment, and disposal—and by those planning research or developing equipment to make these tasks easier. This report presents the proceedings of the seminar. The proceedings from the 1981 and 1983 seminars are contained in EPRI reports EL-2572 and EL-3581, respectively.

PROJECT

RP2028
EPRI Project Managers: Ralph Komai; Vic Niemeyer; Gil Addis
Coal Combustion Systems Division; Energy Analysis and Environment Division; Electrical Systems Division

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Proceedings: 1985 EPRI PCB Seminar

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Research Project 2028

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NOTICE

ABSTRACT

The 1985 PCB seminar continued EPRI's series providing timely information on PCB research to utilities, regulators, and contractors. The papers in this seminar showed a significant increase in technical level over those presented in the 1981 and 1983 meetings.

Subjects covered in the three and one-half days meeting were:

PCB Destruction
Mineral Oil Decontamination
Analytical Techniques for PCBs
Spill Cleanup and Management
Risk Analysis and Management
PCB Fires and PCDF Analysis
Retrofill and Replacement Fluids
Miscellaneous Subjects

ACKNOWLEDGMENTS

We would like to acknowledge the help of our session chairmen who kept the long meeting on schedule throughout. Ellen Lanum and Claudia Runge did a superb job on meeting arrangements and administration. Babs Ryan and Barbara Cole contributed both to the preparations for the meetings and these proceedings.

Thanks to all.

CONTENTS

PART 1:

BACKGROUND

FIRE INVOLVING PCB TRANSFORMERS
FURTHER REGULATIONS
MANAGING THE RISK

H. C. Manger

The Environmental Protection Agency (EPA) issued a final rule on August 25, 1982, authorizing the indefinite use of certain electrical transformers containing polychlorinated biphenyls (PCBs). At that time, information available to the EPA indicated that fires involving electrical transformers were rare, isolated incidents.

Because of the notoriety of several recent transformer fires and upon reconsideration, EPA has amended the 40 C.F.R. regulations with regards to:

761.3 Definition
761.30 Authorization
761.40 Marking Requirements

The changes established three important dates for action:

October 1, 1985
December 1, 1985
October 1, 1990

October 1, 1985

After October 1, 1985, EPA prohibits the use or storage of PCB transformers where there is exposure to food or feed. In addition, the installation of PCB transformers in or near commercial buildings is prohibited, and defines "in or near commercial buildings".

December 1, 1985

By December 1, 1985, all PCB transformers must be registered with the local fire fighting authority with specific information such as location, principle dielectric fluid, name and telephone number of person to contact in case of a fire.

By the same date, PCB transformers located in a commercial building (commercial buildings are defined) must be registered with building owners, noting the specific location, principle dielectric fluid, and type of the PCB transformer (radial - network). For PCB transformers located near commercial buildings, the same information must be registered with all owners of buildings located within 30 meters of the transformers.

October 1, 1990

EPA has amended authorizations in CFR 40 - 761.30

Prohibitions .

As of October 1, 1990, the use of Network PCB Transformers with high secondary voltages (480 - 480/277 or greater) in or near commercial buildings is prohibited.

Allowed (with "enchanced" protection)

Radial PCB Transformers with high secondary voltages 480V and above, in use, in or near commercial buildings after October 1, 1990 must be equipped with protection to avoid high current faults, and a method to detect and avoid sustained low current faults.

Network and Radial Transformers with voltage less than 480 need only be equipped with protection to avoid high current faults.

These amendments are a result of an EPA Risk Analysis. EPA with data available, as stated in the preamble of the latest rule, "undertook an evaluation of the fire-related risks posed by the continued use of PCB Transformers, and the costs and benefits of measures designed to reduce those risks".

MANAGING THE RISK

Aside from the regulation, the fire incidents publicized and the ensuing costs from fires involving PCB should suggest an evaluation of each specific risk with PCB equipment, particularly in buildings.

Some of the potential cost are:

Litigation Costs and Injury Awards

The potential presence of PCDF's (Furans) and PCDD's (Dioxins) essentially causes every incident to turn into a piece of Agent Orange controversy.

Business Interruption Costs

The building owners in San Francisco and Tulsa have claims against the utilities involved for damages.

Cleanup Costs

In Binghamton, the cost for cleanup exceeded the cost of the building.

Sampling and Analysis Costs

Each dioxin and furan analysis cost as much as $1,000.00.

It is evident that industry generally is not prepared to deal with a PCB fire. In order not to make costly mistakes, one should consider what steps could be taken before a PCB incident, and possibly prepare a plan in order to respond expeditiously to potential PCB fire emergencies.

Examination of the PCB fire incidents suggest that proper pre-incident preparation and post-incident emergency response can greatly reduce the risks and liabilities associated with PCB fires in buildings.

Pre-Incident Preparation should include:

(1) Form a corporate response team to develop pre-incident preparations and plan post-incident actions.

This team should include employees who encompass these disciplines:

Legal
Insurance Claims
Environmental
Operations
Maintenance
Media Relations

(2) Make an inventory of, and collect detailed information about all major PCB equipment installations owned by the Company.

(3) Record the location of all PCB transformers and prepare maps identifying major PCB transformers in public buildings or areas accessible to the general public.

(4) Identify the owners of buildings which contain PCB transformers.

(5) Develop a risk assessment and transformer phase-out prioritization scheme.

(6) Determine the responsibilities and authority of local Fire, Health, EPA and Natural Resource departments. Discuss the plan with the local agencies and determine limits of authority.

(7) Discuss plans and execute contracts in advance with experienced PCB-cleanup service companies.

(8) Prepare operation procedures which will ensure the proper and immediate reporting of all PCB incidents.

If an incident occurs:

(1) Take charge immediately.

When governmental agencies assume control, they may act so slowly that nothing is done by the time the media is involved. Public opinion can then dictate procedures and cleanup levels. One must convince the agencies, preferably in advance, that you can handle all problems.

(2) Call in cleanup companies.

(3) Sample to analyze the extent of the problem promptly. It is important to determine the extent of the problem as soon as possible, not only from a PCB, furan, and dioxin standpoint, but what portion of the building is actually contaminated.

(4) Get in touch with building owners.

Building managers have the primary interest and responsibility for communicating with the tenants of the building and for arranging alternate accommodations if the building must be evacuated during the cleanup. Therefore, the building manager should be kept completely informed, and should be both the spokesman for the tenants and their major source of information.

(5) Get statements from persons who claim exposure or may have been exposed describing their feelings and symptoms.

(6) Follow predetermined plan for press releases. Caution all involved not to make statements which will add confusion and adverse publicity.

How one handles such a serious situation is never cut and dry, nor do I infer that this approach is the only way. However, adopting a well thought out plan in advance can show that you are competent and knowledgeable. It can also provide tangible benefits, such as reducing human and environmental exposure, and can serve to significantly reduce the risks of liabilities associated with PCB accidents.

REFERENCES:

1. PCB Fire Emergency Response and Management by Joseph E. Shefchek, Wisconsin Power and Light Company and Louis Kosek, Public Service Company of Oklahoma

. Proceedings of Pollution Engineering's HAZPRO '85, Baltimore, Maryland

PART 2:

DESTRUCTION

SAMPLING AND ANALYSIS CRITERIA USED TO EVALUATE THE EFFICACY OF POLYCHLORINATED BIPHENYL (PCB) DESTRUCTION

Author: John H. Smith

For PCB Disposal Permits in more than one United States Environmental Protection Agency Region, the Office of Toxic Substances (OTS) has the responsibility to negotiate demonstration conditions for, examine demonstrations for, and write permits for PCB destruction efficacy demonstrations in accordance with Toxic Substances Control Act Section 6(e) regulations. To carry out this responsibility OTS reviews documentation submitted by permit applicants. This documentation includes: existing state and local permits, equipment diagrams, equipment operation procedures used, operating specifications, proposed personnel, PCB destruction validation, waste disposal, a schedule of demonstration activities, and expected use(s) of treated material. This talk discusses information obtained in and prepared by the U.S.E.P.A. Headquarters PCB Disposal Permitting Program.

One of the key factors in evaluating the demonstration of PCB destruction efficacy is the review of the permit application and analysis of the treated and untreated PCB matrix. The PCB Disposal Section evaluates the sampling and analysis of different process materials in order to meet several regulatory objectives.

Sampling of a matrix, from which PCBs are to be destroyed or removed, must be representative of that kind of matrix and the distribution of PCBs in the matrix. Sampling must be controlled such that (1) PCBs are not destroyed in the sampling process, and (2) contaminants interfering with PCB analysis must not be introduced in the sampling process. Samples must be of a large enough size to provide sufficient material for instrumental analysis.

Analysis includes the preparation of the sample for instrumental analysis, the instrumental analysis, interpretation of instrumental data, and reporting of the results of the analysis. As with sampling, contaminants interfering with PCB analysis are not introduced in the analysis process. Minimum quantitation levels must meet regulatory requirements. The maximum level of PCBs in the treatment matrix must be specified in many permits, and thus the permit applicant must demonstrate the repeatable capability to treat and analyze PCBs at the maximum level to be permitted. In all demonstrations the materials from which PCBs have been removed or destroyed must be proven free, at levels required in the regulations, of PCBs by definitive, confirmatory chemical analysis. In many cases waste products from the process must also be analyzed, the specifications of waste product analyses depend on the proposed method of disposal.

Office of Toxic Substances senior officials use the results of the sampling and analysis from the PCB destruction efficacy demonstrations in making final decisions on PCB Disposal Permits.

If the treated material and waste from a PCB disposal process are below designated treatment levels, there are no regulatory requirements for disposal of the treated material. If waste material or material treated as part of PCB disposal does not have a PCB concentration below designated limits, the waste material or treated material must be disposed inthe same manner as the regulatory requirement for the original untreated material. That is, for original untreated material greater than 500 parts per million (ppm) disposal is incineration and for original untreated material between 50 ppm and 500 ppm disposal is in an approved PCB landfill.

According to the regulation (40 CFR 761.60 and 761.70), there are several requirements for a PCB incinerator. Some of the sampling requirements are the monitoring of oxygen, carbon monoxide, carbon dioxide, volatile organic halides, PCBs, polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) in the stack emissions. The temperature and the residence time are also regularly monitored.

The regulation also allows alternative methods of disposal if those methods have been determined equivalent to incineration. Equivalence includes not only destruction eficiency but also potential for environmental exposure to, potential hazards from, and contamination from material from which PCBs are to be removed and PCB disposal processing wastes. As an example, PCB materials treated by mobile alternative methods do not have to be transported. The matrix containing PCBs, once completely treated to below the levels required by regulation, may be reused. The non-PCB wastes generated are generally not hazardous. For separation processes, PCB wastes, in which PCBs have been concentrated to much lower volumes are incinerated.

Alternate technologies demonstrated to the Office of Toxic Substances to date include the general classifications of chemical reduction, physical separation, and solvent washing for metal recovery. The demonstrations of the alternate technologies include representative sampling of the untreated PCB matrix, the treated matrix, and process emissions and wastes. Initial PCB matrix concentrations are quantitated based on the original PCB formulation present. Where the treatment process changes the chemical nature of PCBs, the analytical method for treated material must be quantified based on representative individual PCB compounds at each level of chlorination. If the treatment process does not change the chemical nature of the original PCB formulation, quantitation of the treated material is based on the original PCB formulation. Completeness of PCB disposal in conjunction with metal recovery (and assumed metal reuse) is addressed in a case by case basis. For capacitor casing by solvent rinse, a solvent concentration based on estimated metal surface area is used to determine the equivalence to incinerator removal of PCBs. For the recovery of copper from transformer cores, the content of PCBs in the copper must be below regulated disposal treatment waste levels of 2 ppm for each individual PCB compound.

PYROPLASMA DETOXIFICATION OF ASKAREL FLUIDS

Thomas G. Barton

INTRODUCTION

During the past year, a mobile Pyroplasma™ unit has been undergoing a series of waste destruction demonstrations using organic fluids. This demonstration project has been jointly funded by the New York State Department of Environmental Conservation (NYS/DEC) and the Environmental Protection Agency Industrial Environmental Research Laboratory (EPA/IERL).

The Pyroplasma unit is a plasma based system which uses a Westinghouse high enthalpy plasma device to chemically atomize organic fluids. Following their atomization, the elemental components are allowed to recombine to form fuel gas, acid gas and carbon. A caustic soda scrubber is used to quench the gas, neutralize the acidic products and capture the carbon. A schematic of this process is shown in figure 1.

The entire process is controlled and monitored by a process control computer which provides a continuous check on all operating parameters and provides operator warnings should these parameters deviate from preset values. The computer is also programmed to shut down the process in the event of deviation set by critical parameters. Two onboard gas chromatographs monitor for bulk gas constituents as well as trace residual compounds of interest. The entire mobile unit is housed in a forty-five foot moving van and requires hookup to power, water and sanitary sewer as well as waste fluid and caustic soda supplies to function.

THE TEST PROGRAM

A three stage test program was jointly developed by NYS/DEC, and EPA/IERL in conjunction with Environment Canada and the Ontario Ministry of the Environment. The first stage involved system shakedown with organic solvents as the feed material. The second stage had two main objectives. The first was to determine the ability of the Pyroplasma system to destroy a refractory chlorinated compound.

The second objective was to verify the mechanical operation of the system when using chlorinated feed material and demonstrate the capture of the hydrogen chloride product by the caustic soda scrubbing system.

The third stage involves the destruction of Askarel fluids by the Pyroplasma unit with stack monitoring for residual PCB, dioxin and furan residuals. At the time of writing this abstract, only the first two stages have been completed.

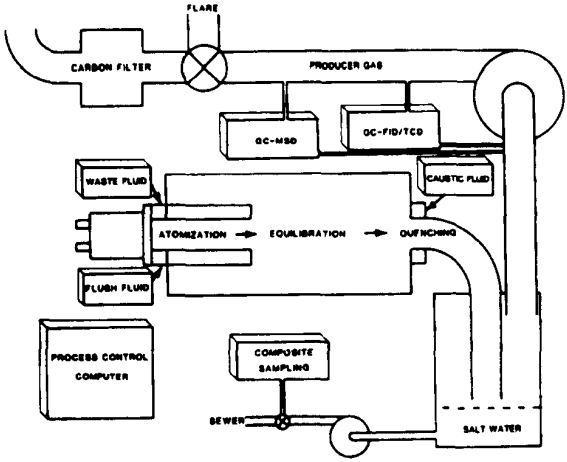

Figure 1. Pyroplasma Process Schematic

RESULTS TO DATE

During the first stage, approximately twelve hours of operation, including a three hour and a four hour test, pyrolyzed over 3000 litres of ethanol. A further eighteen hours of testing were conducted using 3500 litres of methyl ethyl keytone (MEK). Once the operating temperature of the reactor had reached 1000°C, virtually no adjustments by the operator were required. Product gas composition was very constant from run to run. In the ethanol testing the concentrations of the two major components of the product gas, hydrogen and carbon monoxide, varied by only three percent from the mean concentration. During these shakedown tests, no external stack monitoring was conducted.

Theoretical values for the composition of the product gas from the pyrolysis of ethanol were calculated using kinetic equilibria equations. This theoretical composition was then compared with the gas chromatographic analyses of the product gas to determine the accuracy of the computer predictions. Excellent agreement within the 95 percent confidence interval of the experimental data is indicated. This agreement supports the hypothesis that the pyrolytic gas leaving the reactor has a composition close to that defined by kinetic equilibria. As a result, computer modelling based upon such kinetic equations should provide a good estimate of the product gas composition. Discrepancies may be caused by the assumption that the composition of the cooled product gas as analysed by the gas chromatograph is equivalent to the composition of the hot product gas as it leaves the reactor. This hot product gas composition may not be instantaneously "frozen" by the scrubbing water system. During cooling, kinetics would favour an increase in methane and a reduction in hydrogen concentrations. A "reverse shift" to reduce methane concentration to a theoretical value provides higher concentrations of hydrogen and carbon. This calculated product gas composition when compared to the theoretical composition showed differences of less than one percent for the major bulk gas constituents.

During the second stage of testing, a solution containing 38 percent carbon tetrachloride and 62 percent MEK on a mass basis was fed to the reactor at a rate of 2.6 kg/min. This represented a chlorine loading of 36 percent by mass. The reactor exit temperature was maintained at 1000°C with a plasma torch operating power of 300 kW. The product gas had a combustion energy value approximately three times the plasma energy put into the system.

Operational stability was demonstrated during this series of tests. At the 95 percent confidence level, parameters such as feed rates, plasma power and cooling water flows varied by less than four percent, whereas the reactor temperature varied by less than one percent.

The GCA/Technology Division, under contract to EPA provided external monitoring of the scrubber water and flared product gas effluent streams. The scrubber water was analysed for residual CCl_4. The post flare product gas was monitored for CCl_4, HCl, O_2, CO, CO_2 and NO_x. The temperature and flow rate of the flared gas were also monitored. The data collected by GCA are to be considered as preliminary pending review and approval by EPA.

Preliminary results showed that the Pyroplasma system repeatedly achieved for CCl_4 a destruction efficiency greater than 99.9999 percent in triplicate tests. Recovery of HCl by the scrubber system was better than 99.3 percent during these tests. Stack emissions for HCl were also less than 8 g HCl/min and easily complied with the EPA emission requirements of 99 percent removal. On average, the stack loading for NO_x was typically less than 100 ppm and met EPA standards.

During these tests, particulate carbon was captured in the scrubber at a rate approaching 2.5 grams of carbon per litre of scrubber fluid. As this carbon absorbs residual organics, its presence in the water is considered beneficial in the overall objectives of environmental protection. At a detection limit of 5 ppb, no organics were detected in the liquid phase of the scrubber effluent. When this effluent stream is discharged to the wastewater treatment plant, the carbon is physically separated in the plant and sent to the anaerobic digesters for final treatment.

At the time of writing, stage three tests with Askarel fluids are not complete. I hope to be able to report on their success during the Fall meeting in Seattle. The success demonstrated by the Pyroplasma unit with carbon tetrachloride indicates that Askarel fluids should offer little additional technical challenge. However, the controversy surrounding these wastes often creates interesting political challenges.

Thermal Treatment of PCBs and PCB-contaminated Soils

Jimmy W. Boyd, J. M. Huber Corporation

Huber Technology Group (HTG) of J. M. Huber Corporation has developed an Advanced Electric Reactor (AER) which is highly effective for decontaminating soils contaminated with polychlorinated biphenyls (PCB) and similar hazardous materials. The AER has been used to conduct PCB tests under the auspices of the Toxic Substances Control Act (TSCA), and demonstrations with carbon tetrachloride (CCl_4), octachlorodibenzo-p-dioxin (OCDD), and tetrachlorodibenzo-p-dioxin (TCDD).

The AER is a pyrolytic process which rapidly heats wastes to temperatures between 2200°-2500°C using intense thermal radiation in the near infrared. Solid feed is transferred from an air-tight hopper to the top of the AER. Reactants are isolated from the cylindrical graphite reactor core by a gaseous blanket formed by flowing nitrogen inward through the porous core wall. Carbon electrodes heat the core to incandescence. The core transfers heat to the reactants by radiative coupling. Two post reactor treatment zones (PRTZ) immediately below the reactor provide additional high-temperature residence time at about 1370°C and cool the product gas to about 540°C. HTG currently maintains a pilot-scale AER (AER-12) with a 12-inch diameter core and a portable 3-inch AER (AER-3). The AER-12 uses a cyclone, baghouse, caustic scrubber, and activated carbon beds for particle removal and gas polishing. The AER-3 uses one PRTZ, a baghouse, and carbon beds. The technology is designed to be highly mobile and well suited for on-site treatment. A transportable AER with a throughput of 18-27 million kg/yr is readily feasible.

In September 1983, HTG conducted a trial burn treating approximately 6400 kg of soil containing 3000 ug/g PCB. All TSCA requirements were exceeded including PCB destruction and removal efficiencies (DRE) in the range of 99.999998% (7 nines). Even destruction efficiencies (DE) measured in the product gas before downstream cleanup exceeded the TSCA DRE requirement of 6 nines in 3 of 4 tests. Chloride and particulate loading in the gaseous effluent were also well below EPA incinerator standards. Gas-phase polychlorinated dibenzodioxins and furans (PCDD & PCDF) before downstream cleanup were below detection limits of 0.03-0.06 ug/SCM. The AER received EPA certification for destruction of PCBs in May 1984.

AER Tests were also conducted with CCl_4 as a surrogate on soil and with dioxin-contaminated soil taken from Times Beach, Missouri. CCl_4 was chosen for testing based on its refractory properties, reflected by its high position on EPA's

hierarchy of incinerability. CCl_4 tests were conducted to demonstrate the AER's capabilities over a wide range of operating conditions and waste concentrations. DREs >99.9999% were achieved for CCl_4 feed concentrations up to 99%. The Times Beach tests, conducted on site with the AER-3 in November, 1984 was the world's first successful field demonstration of dioxin treatment technology. The Times Beach tests are supported by OCDD tests conducted with the AER-12 and AER-3 at Borger, Texas. On-site tests and tests conducted with the AER-3 in Borger achieved DREs >99.999%. Dioxin concentrations in the process effluent were below detection limits in all cases. Higher DREs could not be demonstrated due to low feed concentrations. However, OCDD tests with the AER-12 resulted in DREs of >99.9999%, indicating that in an actual cleanup operation using a full-scale unit, DREs of greater than 6 nines for dioxins are achievable. A summary of tests conducted is given in Table 1. Detailed results of the PCB and CCl_4 tests are given in Tables 2 and 3, respectively. PCB, dioxin, and CCl_4 concentrations were determined by gas chromatography-mass spectrometry (GC-MS), GC-MS-MS, and GC with electron capture detection, respectively. Other species concentrations were determined using EPA reference methods.

Rotary kiln incineration (RKI) is presently touted as an attractive technology for treatment of soils contaminated with hazardous wastes. The AER has inherent safety and performance advantages over RKI. Safety features include: the absence of combustion air, eliminating the possibilities of explosion and formation of toxic compounds such as PCDDs, PCDFs, and dioxins; high thermal inertia to process time ratio, assuring continued waste destruction and safe clearing of feed from the process in the event of a temporary power failure; operation at low to slightly negative pressures, greatly reducing the probability of an outward gas leak; and the ability to economically equip the AER with high-efficiency gas treatment units such as carbon beds to provide redundant treatment of stack emissions in case of emergency. Performance advantages include: increased gaseous residence time at higher temperatures resulting in improved DEs and DREs and reduced sensitivity to process upsets; pyrolytic decomposition which essentially eliminates normal products of combustion such as NO_x, SO_x, and oxygenated organic species and also eliminates the problems of fuel carbonization on burner surfaces, caking and fouling, and variations in fuel properties; and very low process flow rates which reduce atmospheric emissions and allow using low-cost, off-the-shelf gas scrubbing and cleanup units. AER versus RKI job total cleanup costs for contaminated soils are comparable. Assuming 20,000 ton/site and on-site operation, an overall cost comparison including setup, treatment, site excavation, and site restoration indicates a total cost of $780/ton for the AER and $765/ton for the RKI in 1985 dollars.

Table 1

A SUMMARY OF HAZARDOUS WASTE TESTS CONDUCTED WITH THE AER

Species	Date	Unit	Feed Conc. (ug/g)	Feed Rate (kg/min)	Average DRE
PCB	Nov. 83	AER-12	3000	7.1	99.999997
CCl_4	May 84	AER-12	0.37-100%	1.5-18.5	99.99998
OCDD	Oct. 84	AER-12	17.9	5.4-7.8	>99.99998
OCDD	Oct. 84	AER-3	0.25	0.1	>99.999[a]
TCDDb	Nov. 84	AER-3	0.08	0.1	>99.9992[a]

[a]Dioxins at the process stack were below detection limits for all tests.

[b]Test performed on site.

Table 2

DETAILED RESULTS FOR THE PCB TEST SERIES

Parameter	Test 1	Test 2	Test 3	Test 4
Test Duration (min)	271	271	225	220
Average Feed Rate (kg/min)	7.0	7.1	7.1	7.2
Total Feed Mass (kg)	1910	1930	1610	1580
PCB Concentrations				
Feed (ug/g)	3000	3000	3000	3000
Treated Feed (ug/g)	0.0005	<0.0005	0.0006	0.001
Gaseous Effluent (ug/SCM)	0.23	0.03	0.10	0.30
Stack Gas				
NO_x (mg/SCM)	16.0+26	6.2+4.8	NS	8.0+8.6
Chloride (mg/SCM)	<0.010	<0.016	<0.012	<0.012
Particle Loading (mg/SCM)	<4.5	<7.1	<5.5	<5.8
Reactor Outlet				
PCDDs (ug/SCM)	<0.05	<0.06	<0.03	<0.05
PCDFs (ug/SCM)	<0.05	<0.06	<0.03	<0.05
PCB DE (%)	99.99992	99.99992	99.9996	99.99995
PCB DRE (%)	99.999995	99.9999994	99.999998	99.99994

NS = Not Sampled.

Table 3

DETAILED RESULTS FOR THE CARBON TETRACHLORIDE TEST SERIES

Test	Reactor (°C)	Feedrate (kg/min)	Feed (%CCl4)	Treated Feed (ug/g CCl4)	Stack Gas (ug/SCM)	DE (%)	DRE (%)
1	2100	14.9	1.37	0.69	0.0023	99.99992	99.999992
2	2100	10.0	1.37	0.47	0.0019	99.99996	99.999990
3	2090	3.0	1.37	NS	NS	99.99991	ND
4	2260	10.1	1.37	0.47	0.0071	99.9992	99.99996
5	2260	2.5	1.37	NS	<0.0002	99.9990	>99.999996
6	2420	2.6	1.37	NS	0.0007	99.9997	99.99999
7	2100	2.5	1.37	0.07	0.0004	99.9993	99.999996
8	2080	18.5	0.37	0.14	0.0018	99.99991	99.99998
9	2060	9.8	0.37	NS	<0.0009	99.99992	>99.99998
10	2080	2.0	0.37	0.56	<0.0004	>99.99992	>99.99996
11	2260	10.4	0.37	NS	<0.0004	99.99995	>99.999992
12	2270	2.1	0.37	NS	<0.0004	99.9984	>99.99996
13	2440	2.3	0.37	NS	<0.0004	>99.99987	>99.99997
14	2090	0.5	13.8	NS	<0.0008	99.99998	>99.999991
15	2100	1.4	13.8	0.18	<0.0008	99.99992	>99.999997
16	2090	1.5	99	NS	0.0054	98.3	99.999997
17	2090	1.5	99	NS	0.0027	97.1	99.999999

NS = Not Sampled; ND = Not Determined.

PCB INCINERATOR USING MOLTEN GLASS BATH AS HEAT SOURCE

Larry Penberthy *

The toxicity of polychlorinated biphenyls was grossly overstated during the environmental hysteria of the 1970s. It has since appeared that the culprit was impurity dioxin. Even that has not been demonstrated to be very hazardous to humans (1). Ironically, cigarettes may be burned in closed rooms freely, whereas PCBs are under strict burning regulations with which we must comply.

Dioxins and furans can be formed during burning of PCBs if there is a deficiency in oxygen as in a smokey transformer fire (Figure 1). (2) (3)

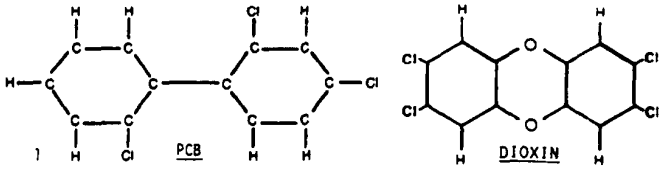

Figure 1. Smokey Transformer Fire

In the presence of excess oxygen, temperature above the cracking point for the carbon-carbon bond, and turbulence, the benzene rings burn to carbon dioxide, never to form benzene again. These considerations of chemistry guided our work in development of a furnace to destroy PCBs. Our long background in electric melting of glass (4) was ideal in providing such a furnace for destruction of PCBs.

Figure 2 shows our engineering and demonstration furnace (6). It is a tunnel, 3 ft sq by 22 ft long. The basin holds five tons of glass which is kept molten by heat from the burning PCBs, supplemented by electric heat as needed. This size can burn 20 gallons per hr of PCBs.

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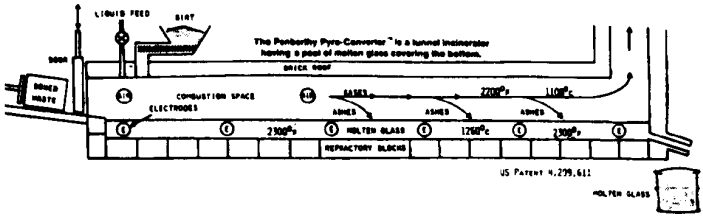

Figure 2. Glass Furnace Incinerator

PCB liquid is sprayed or poured onto the hot glass surface. The organic portions vaporize and burn in air supplied from side jets. The jets are arranged to give high turbulence to the fire. The organics burn to completion and inorganic residues, such as metal oxides or soil, fall on the glass and dissolve in it.

The range of allowable feed material is very broad. The furnace can even handle contaminated mud or soil. Soda ash is added to soil to flux it down to make glass. When the glass level builds up a few inches, the excess is tapped off and sent to beneficial use or to landfill.

Our demonstration furnace is small but is still a practical furnace. It is also practical to build larger furnaces such as 20 ft wide x 50 ft long x 15 ft high, volume 15,000 cu ft (Figure 3). The burning capacity is 150,000,000 BTU/hr, corresponding to 3,000 gallons of PCBs per hour. Intermediate sizes can also be built readily.

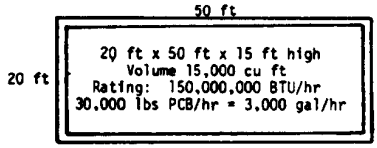

Figure 3. Plan View of Large PCB Furnace

The heating value of PCB-mineral oil mixtures as commonly found in transformers is amply high to reduce electric power consumption to about half a kilowatt-hour per gallon of PCB liquid. Where power costs 8¢ per KWH, the electric cost is thus 4¢ per gallon. This is a lot less than has been rumored.

The chlorine part of the PCB is converted to hydrogen chloride, which must be scrubbed out of the offgas. Figure 4 shows a series of scrubber towers. They are filled with limestone rock. A recirculating water spray absorbs the HCl to form hydrochloric acid which then reacts immediately with the rock to form calcium chloride. When the solution in the first tower rises to commercial concentration (33% $CaCl_2$), it is tapped off to be filtered and sold. The weaker solutions in the second and third towers are moved upstream and fresh water is added to the third tower. The fourth tower contains a Brink filter for mist and particulate removal. This filter is a cylindrical cup of fiber glass 2 ft diameter x 10 ft high. The walls are densely-packed, and are 4.5" thick.

Alternatively the HCl can be captured in water-spray towers to form hydrochloric acid, also a commercial product.

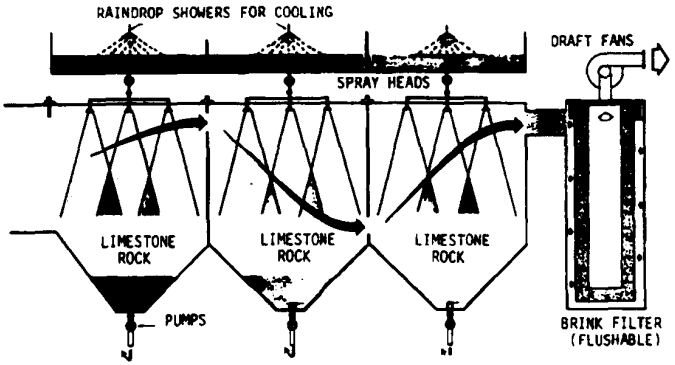

Figure 4. Scrubber Towers

There are several advantages of the Pyro-Converter^{tm} System for the destruction of PCBs:

1. The burning conditions are highly oxidative (12% excess oxygen) and hence products of incomplete combustion cannot form if the temperature is held above the auto-ignition temperature and there is turbulence.
2. There cannot be a flame-out with loss of temperature because electric heat comes on to maintain the correct temperature if the feed stops or if a low-heating-value material is being burned. Even plain water can be "burned".

3. The tunnel can be made as long as required for absolute totality of destruction of the PCBs.

4. The molten glass provides a "home" for any inorganic material that might be in the PCB oil. The glass thus made is a superb non-leaching form for the inorganic residues.

5. Valuable chlorine compounds can be recovered and sold.

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PART 3:

DECONTAMINATION OF MINERAL OIL

NON-SODIUM PROCESS FOR REMOVAL OF PCBS FROM CONTAMINATED TRANSFORMER OIL

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R. L. PETERSON, Galson Research Corporation

INTRODUCTION

Currently acceptable methods of disposing of PCB contaminated oil include either incineration in specially permitted incinerators or use of metallic sodium decontamination processes. Niagara Mohawk Power Corporation (NMPC) through it's contractor Galson Research Corporation (GRC) has developed a non-sodium process for oil decontamination as an alternative to current methods. This patented (1) process has been demonstrated at both laboratory and pilot plant (60 gallon) scales, and a 2200 gallon/batch mobile prototype unit is currently in the start-up phase.

BACKGROUND

Incineration and sodium treatment of PCB contaminated transformer oil have significant disadvantages. Disposal of PCB oil by incineration is expensive and depletes the limited supply of replacement naphthenic transformer oil. Application of the Goodyear process (2) or similar sodium based dechlorination systems is an improvement on incineration in that it allows recovery of the naphthenic oil for re-use. However, such decontamination processes require the expense and hazard of handling potentially explosive metallic sodium. The use of metallic sodium in such processes has resulted in safety related operating problems.

The NMPC process, like the Goodyear process and it's variations, allows recovery of decontaminated transformer oil. Unlike the Goodyear process, the NMPC process does not use metallic sodium, but rather a mixture of potassium hydroxide, glycol and sulfoxide.

APPROACH

The objective of the NMPC study was to find and develop a commercially viable non-sodium process for dechlorination of PCBs and other aromatic halides in transformer oil. Dechlorination of aliphatic halides using potassium hydroxide and alcohol is a standard technique (3). Researchers at General Electric demonstrated that aromatic halides such as PCBs and chlorobenzenes can be dechlorinated in the same fashion as aliphatic halides by use of an alkali metal hydroxide/alcohol mixture if polyethylene glycol is used as the alcohol (4).

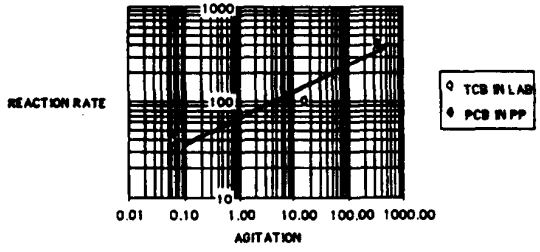
Tests conducted by GRC confirmed that PCBs mixed directly with a hydroxide/glycol reagent were rapidly dechlorinated to <2 ppm. EPA regulations require that chemically decontaminated transformer oils contain < 2 ppm PCB. However, in GRC tests hydroxide/glycol reagents used to dechlorinate PCBs in transformer oil reacted very slowly (6-7 hours from 500 ppm to <2 ppm). This slow rate of reaction made the hydroxide/glycol process questionable from a commercial view point.

The large difference in reaction rate between PCB added directly to hydroxide/alcohol reagent and PCB dissolved in transformer oil indicated that the rate controlling step in the process was the transfer of the PCB from the oil phase into the immiscible reagent phase. The NMPC research therefore focused on methods of improving the rate of extraction of aromatic halides into the hydroxide/alcohol phase. Two major areas of investigation were studied. The first area involved tests of the effects of using varied rates of agitation on reaction rates. The second major area studied the effects of various co-solvents on the reaction rate. Co-solvents tested included sulfoxides, amines, ketones, and various mixtures of alcohols.

RESULTS OF AGITATION TESTING

Initial laboratory testing of the agitation effect used 1,2,4 trichlorobenzene (TCB) in place of PCB. This simplified the analysis of the oil. Mixtures of TCB in the transformer oil were allowed to react at 100°C with agitation supplied by a paddle stirrer turning at either 400 or 2500 rpm. Additional tests of agitation effects were conducted using a 60 gallon pilot plant equipped with a 2 hp high shear mixer with a variable speed 0-7000 rpm motor. Use of this equipment allowed higher agitation rates than were practical in laboratory glassware. The results of both the laboratory and pilot plant (PP) tests are shown in Graph 1.

GRAPH 1 - EFFECTS OF AGITATION ON REACTION RATE



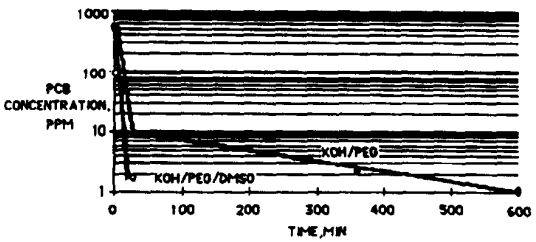
Laboratory and pilot plant results are graphed using reaction rate, calculated as (10,000/time in minutes to reach 2 ppm), and agitation calculated as $(rpm/1000)^3$. While increased agitation produced increased reaction rates, the magnitude of the agitation effect was small. A 90 fold increase in agitation was required to yield a 3 fold increase in reaction rate. These data indicate that changes in agitation are not sufficient to produce the desired improvement in reaction rate.

RESULTS OF CO-SOLVENT/CATALYST TESTING

In an effort to improve the rate of extraction of contaminant from the oil phase into the reagent phase, a variety of co-solvents were tested, including sulfoxides, amines, alcohols and, ketones. The most promising results were obtained with sulfoxides such as dimethyl sulfoxide or sulfolane and amines such as ethylene diamine. The toxicity and potential carcinogenicity of the amine reaction products led to the selection of the sulfoxide series for further development.

The addition of sulfoxide to the hydroxide/alcohol mixture in laboratory testing caused a substantial increase in the overall rate of reaction, as shown in Graph II for the reaction of a mixture of potassium hydroxide (KOH) and polyethylene glycol 400 (PEG) with PCB 1254 in transformer oil at 100°C.

GRAPH II - REACTION OF PCB 1254 IN TRANSFORMER OIL



The reagent with DMSO reached <2 ppm PCB after 30 minutes, vs about 400 minutes for the reagent without DMSO. Much the same result was obtained using sulfolane, a chemically similar and somewhat more expensive sulfoxide commonly used to extract aromatic compounds from crude oil in refining operations. These data formed the basis for the patent (1).

After the laboratory work on co-solvents was completed, additional tests were conducted in a 60 gallon batch capacity pilot plant. These tests confirmed the results of the laboratory experiments, with results in the pilot plant being slightly better than those from laboratory runs, probably due to better agitation.

SCALEUP

The successful results of the pilot plant co-solvent tests led to the construction of a full size 2200 gallon/batch prototype unit. Prototype construction was completed in August 1985, with initial field trials scheduled for September. Field trials with PCB contaminated oil will commence with receipt of EPA and NYDEC permits.

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AN ELECTROCHEMICAL PROCESS FOR DECONTAMINATING PCB-CONTAINING TRANSFORMER COOLANTS

Drs. Michael J. Massey and Fraser M. Walsh*

Environmental Research & Technology, Inc. (ERT) and Tracer Technologies, Inc. (Tracer) are developing an electrochemical technique for the controlled dehalogenation of a wide range of halogenated organics, including PCB's.** Feasibility studies, design, and prototype field test programs are being conducted to integrate this technique into processes tailored to address the full range of PCB problems from fluids contamination to equipment and soils contamination. The present paper focuses on application of the technique to the in-situ decontamination of PCB-containing mineral oils and mineral oil transformers.

CHARACTERISTICS OF ELECTROCHEMISTRY

ERT/Tracer's electrochemical cell consists of pairs of working electrodes operating at a controlled potential in an electrochemical solution. A range of inexpensive non-noble metal materials serve as suitable electrodes. Cell operating voltages range from about 5 to about 15 volts depending upon the overall conductivity of the electrochemical solution. The electrochemical solution consists of the PCB-contaminated fluid, a chemical medium for the proper conductance of current, and a proprietary reagent. Although a variety of sources are feasible, the most convenient

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**Patent pending.

medium is usually a combination of the proprietary reagent and accumulated electrochemical reaction products. The proprietary reagent is an inexpensive, readily available organic chemical.

Products of electrochemical dehalogenation of PCB's are substituted biphenyls and chloride salts. Treatment of the chlorinated benzenes typically present as solvents in a PCB system yields substituted benzenes and chloride salts. Chloride salts can be washed from the electrochemical solution and concentrated to a small volume brine for disposal. Electrochemical reactions involved are rapid, highly specific to halogenated organics, and proceed at least to detection limits of PCB's in organics, viz., about 2 ppm. Reaction systems function well over a tested range of temperatures from room temperature to 95°C.

APPLICATION TO MINERAL OIL DECONTAMINATION

Application of ERT/Tracer electrochemistry to mineral oil decontamination involves simple equipment and avoids the need for extraction equipment to remove PCB's from the mineral oil (see Figure 1). PCB-contaminated mineral oil is mixed with conducting medium (about 1:3 ratio) and fed to two electrochemical cell circuits connected in series. Because mineral oil and conducting medium are largely immiscible, the combination is recirculated between the electrochemical cell and a pump which continuously remixes the two fluids. The first reaction cell removes the bulk of the PCB contamination; the second completes the reaction to detection limits of 2 ppm. The bulk of the conducting medium is then recovered and recycled by simple phase separation. The remainder is recovered with chloride salt reaction products by washing. Buildup of reaction products is regulated by a process blowdown stream.

ERT/Tracer systems for mineral oil treatment are low cost, extremely compact, can be sized to treat either small or large quantities of oil and can be operated unattended. The total system required to treat 500,000 gallons per year of oil containing 250 ppm of PCB would: fit in a 10 ft. by 15 ft. space

with 10 ft. of clearance, cost less than $200,000 in capital, and produce 1,000 to 10,000 gallons per year of concentrated chloride blowdown.. Smaller systems can be made fully portable, with packaging that will pass through conventional doorways. Total treatment costs to a client are expected to be about $1 per gallon.

ILLUSTRATIONS OF MINERAL OIL TREATMENT SYSTEM PERFORMANCE

Laboratory-scale data on the performance of the ERT/Tracer system are presented in Figure 2. Figure 2A indicates that the three chlorinated organic contaminants in mineral oil are all dechlorinated over time. Figure 2B shows that, as PCB dechlorination proceeds, measured accumulations of chloride salt product represent essentially 100% of the chlorine removed from PCB and chlorinated benzenes. Figure 2C illustrates the favorable kinetics involved in the electrochemical reaction, and indicates a lack sensitivity to the presence of either mineral oil or reaction products.

COMMERCIALIZATION PROGRAM AND SCHEDULE

ERT is seeking to complete the commercialization of its mineral oil treatment technology by January 1987. A key contribution to the accomplishment of this objective is a costsharing contract now in progress between ERT and the U.S. Navy for field demonstration of the technology. As a part of this contract, ERT is presently constructing a 10 gallon per hour prototype mineral oil treatment unit. During the fourth quarter, this unit will be installed at Northeast Utilities in Hartford, Connecticut. Shakedown testing will occur there during the first quarter of 1986. The unit will then be modified as needed and moved to the Naval Station in San Diego and operated during the second quarter of 1986. Based upon the results obtained, an EPA-approved commercial demonstration of the system is planned for the third quarter of 1986. Arrangements for the manufacture of process systems will be made during the third quarter of 1986, with target date for the delivery of commercial equipment of first quarter 1987.

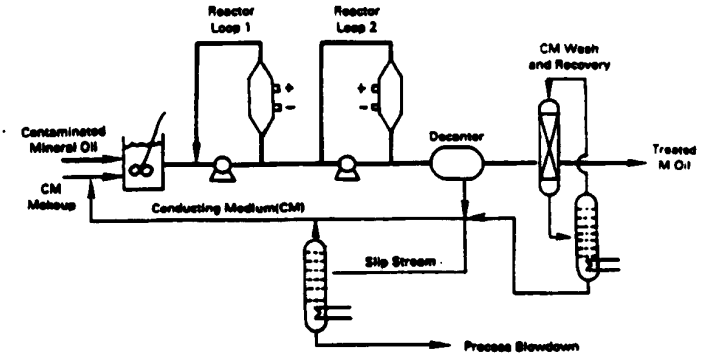

Figure 1. Schematic Flowsheet of ERT/Tracer Process for the Electrochemical Decontamination of PCB-Contaminated Mineral Oil

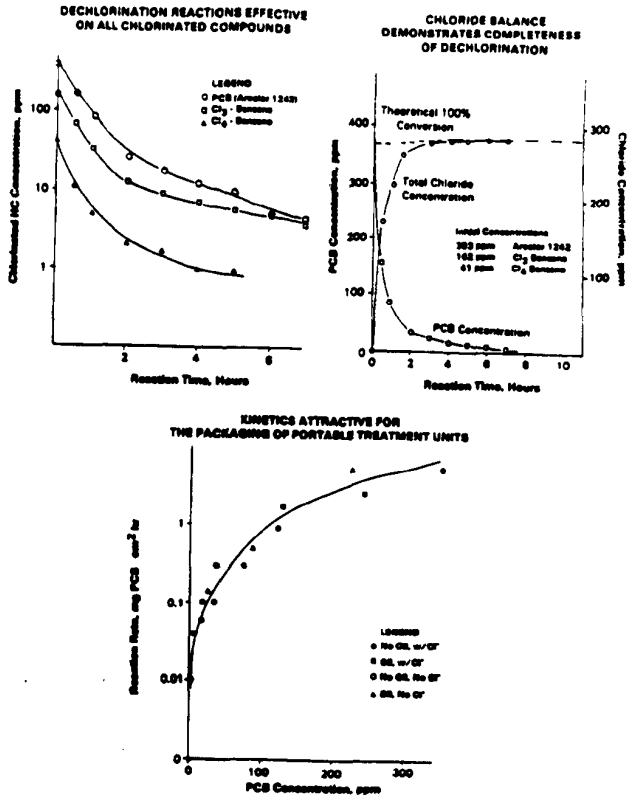

Figure 2. Illustrations of the Performance of ERT/Tracer Process for Electrochemical Decontamination of PCB-Containing Mineral Oil

CHEMICAL DESTRUCTION OF POLYCHLORINATED BIPHENYL

N. S. Chu and S. C. Vick

INTRODUCTION

Polychlorinated biphenyls (PCBs) are widespread environmental pollutants. The molecules are characterized by their extremely high chemical stability, low water solubility, low vapor pressure and nonflammability. These properties render them ideal heat transfer, hydraulic and dielectric fluids. However, the same factors also account for widespread contamination of our environment. Because of the toxicity associated with PCBs and PCB derived products, Congress in 1976 banned the further manufacture and use of PCBs in the United States. However, an estimated 750 million pounds still are in service, awaiting a cost effective, safe means of disposal.

PRIOR PCB DESTRUCTION TECHNIQUES

Although high temperature incineration offers an effective way to dispose of PCBs, of the numerous generally approved waste incinerators in the US, only three have been approved by the EPA for the destruction of PCBs. Furthermore, because an inadequately designed and/or improperly operated incineration process can lead to incomplete destruction and formation of highly toxic compounds such as dioxins and dibenzofurans, incineration continues to incur some public opposition.

Alternatively, PCBs can be destroyed or detoxified by chemical means. The chemical destruction of PCBs contained in contaminated transformer oil has the advantage that it allows the recovery of the valuable transformer fluid, while incineration is simply a disposal strategy which does not allow for recovering valuable components. Several approaches have been studied to destroy PCBs chemically. For instance, Lapiere and co-workers studied the catalytic dehydrochlorination of PCBs using either 61% nickel on Kieselguhr or 10% palladium on charcoal (equation 1) (1). They reported that approximately 90% of the chlorine may be removed from PCBs in five hours at 100-200°C.

$$ArCl_n + xH_2 \xrightarrow{Ni/Pd} ArH_xCl_{n-x} + xHCl \qquad (1)$$

However, the reaction requires the handling of relatively high hydrogen pressure (30-50 atm), and the HCl liberated has to be removed with base to prevent catalyst deactivation and corrosion problems. Sodium (2) or organosodium such as Na-naphthalide (3) and Na-PEG (4) have been used to dehalogenate PCBs at low concentrations. But because sodium and organosodium can react violently with water with increased potential for fire, and poly(ethylene glycol ether) containing sodium alkoxyglycolate ($ROCH_2CH_2ONa$) is hazardous to handle, these processes are not suitable for the destruction of PCBs in high concentrations. Other PCB destruction approaches such as by ultrasonic energy (5), electrocatalytic dechlorination (6), and biodegradation (7) are all still undergoing research and development.

NICKEL CATALYZED REDUCTION OF PCBs

We now wish to report a chemical method which allows the destruction of PCBs in both dilute form such as PCB contaminated transformer fluids and in concentrated form such as Askarel wastes. This chemical method can be carried out in conventional equipment and is, therefore, less capital intensive. In addition, this would provide a mobile service eliminating the potential transportation risks associated with incineration. The process was developed based on a nickel catalyzed zinc reduction of aromatic halides reported by Colon (equation 2) (8).

$$2\ ArCl + Zn \xrightarrow{Ni\text{-}cat} 2\ ArH + ZnCl_2 \qquad (2)$$

Destruction of Pure PCB. Using pure Aroclor® 1260 as a model, we have successfully demonstrated that after reduction, at least 99.5% of the Aroclor® 1260 originally added was destroyed. It was further estimated that of the Aroclor® 1260 destroyed, 95% was converted to biphenyl. The remainder was converted predominately to chloro- and dichloro- biphenyls. These chloro- and dichloro-biphenyls and the minor amounts of remaining PCBs can be recovered together with catalyst components and can be recycled for the next reaction, thus providing for PCB destruction efficiencies approaching 100%. Because solvent and catalyst used for the reaction are recyclable, biphenyl and a concentrated aqueous metal halide solution are the only waste products of the process.

Destruction of PCB in Dilute Form. Similar results were obtained when mixtures containing Aroclor® 1242, trichlorobenzenes and tetrachlorobenzenes were used

(Aroclor® mixtures with chlorobenzene diluents were commonly used in transformers) as well as when Union Carbide Silicone Fluid® L-305 contaminated with PCB (10,000 ppm) was used. Although in the latter case the reaction mixture contained two liquid phases, the destruction of PCBs was just as effective, and the silicone oil recovered after the reaction was free from PCBs (i.e. less than 1 ppm). Gel permeation chromatographic analysis of the recovered silicone revealed no change in molecular weight distribution, showing that the recovered, PCB free silicone fluid would be reusable in transformers.

OPTIMUM CONDITIONS FOR PCB DESTRUCTION

The destruction of PCBs works best when a 50/50 mixture (by weight) of dimethylformamide (DMF) and isopropanol is used. The presence of a protic solvent is essential for the reduction of PCBs. In the absence of a protic solvent, coupling of the aromatic halides will become a major pathway (equation 3) and an insoluble polymer will form due to coupling of the polychlorinated biphenyls and benzenes.

$$2\ ArCl + Zn \longrightarrow Ar\text{-}Ar + ZnCl_2 \qquad (3)$$

Formation of polymers should be avoided because it renders the recovery of unreacted zinc more difficult and because the polymers still usually contain unreacted chloro-groups, the disposal of which might also be a problem. Although water can also be used as a protic solvent as indicated by previous Union Carbide work, alcohol is a much better choice for the current objective. The low mutual solubility of PCBs and water prevents water from being used effectively.

On the other hand, the presence of a polar aprotic solvent is important in order to obtain reasonable reaction rates. Polar aprotic solvents such as DMF, dimethylacetamide (DMAC) and N-methyl-2-pyrolidinone (NMP) all work well as the aprotic solent for this Ni-catalyzed reduction. Solvents such as acetonitrile and tetrahydrofuran do not give as good results, but they may be used together with DMF.

Both the ratio of reduction to coupling reaction and the rate of these reactions depend on the ratio of protic to aprotic solvent used. A mixture of 50/50 percent DMF/isopropanol was found to promote the reduction of PCBs and still give reasonable reaction rates, so that the destruction of PCBs can be completed within a few hours at 70-80°C.

MECHANISTIC CONSIDERATIONS

Based on gas chromatographic (gc) analysis of the reaction, the highly substituted chlorobiphenyls appear to be more reactive toward the Ni-catalyzed reduction. Significant amounts of chloro- and dichlorobiphenyls were found together with biphenyl as long as Aroclor® was present in the reaction mixture. Upon depletion of the high PCB congeners, the mono- and dichlorobiphenyls themselves are consumed. The fact that the same dichlorobiphenyl isomer is always formed no matter which of the three Aroclors® (1242, 1254 or 1260) were used, and that the gc retention time of this dichlorobiphenyl is different from the three dichlorobiphenyl isomers generally present in Aroclor® 1242 suggests that there might be a substitution effect. The two chloro- groups of this dichlorobiphenyl are located in such positions that they are less reactive toward the reduction reactions and therefore are reduced at a much slower rate. The Ni turnover rate for the reduction of biphenyls with 3 or more chloro groups is estimated to be approximately 60 while for chlorobiphenyl and the mentioned dichlorobiphenyl it is about 37. The positions of the two chlorines on the biphenyl skeleton for this dichlorobiphenyl are unknown at the present time.

The mechanism of the Ni-catalyzed reduction is not yet fully understood. However, based on Colon's work and other related literature data, a working hypothesis for the reaction involves:

1. a reduction of Ni(II) to a lower valent state by zinc
2. oxidative addition of aryl halide to the lower valent nickel and
3. reaction of the aryl nickel species with alcohol to form the dehalogenated aromatic compound, regenerating a Ni(II) species.

Transition metals such as palladium and ruthenium are also known to catalyze the reductive dehalogenation of aromatic halides using hydrazine (9), amines (10), formates (11) and alcohols (12) as hydrogen sources. But our current process is more effective and requires no expensive, precious metals as catalyst.

CONCLUSIONS

This technology represents a new approach for PCB destruction via the nickel catalyzed zinc reduction of PCB to biphenyl. By this process, PCBs can be destroyed with efficiencies approaching 100%. The process has the advantage that it destroys PCBs in dilute solutions in transformer fluid but leaves the transformer fluid intact. The recovered PCB free transformer fluid is reusable in transformers, thus limiting the destruction only to the toxic PCBs. This is

in contrast to incineration, which by necessity, must destroy both the PCBs and the transformer fluid. Furthermore, the ease with which the reaction can be carried out, the mild nature of the Ni-catalyst toward water and the recyclability of the recovered reactants and solvents make the technology suitable for the destruction of PCBs in concentrated form. The latter development is important as it represents the first viable technology for the safe and economical chemical destruction of concentrated PCBs. Alternate technologies are useful only for the destruction of dilute solutions. Thus, one process may be used to eliminate the hazard from both concentrated and dilute PCB solutions. Finally, this method of PCB destruction utilizes an inexpensive nickel catalyst and does not require the use of expensive, precious metals as catalysts.

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PART 4:

ANALYTICAL PANEL - PCBs

EVALUATION OF A PORTABLE TEST KIT FOR TESTING PCB CONTAMINATED SOILS AND OILS IN THE FIELD

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McGraw-Edison Company

INTRODUCTION

The McGraw-Edison PCB field test kit was initially developed by the Centec Corp. in Reston, VA. to screen oil samples for PCBs in order to eliminate the need to test every sample received by gas chromatography. The kit was evaluated initially by Centec and independently by the U. S. Army Environmental Hygiene Agency (AEHA)* to determine the effectiveness of the kit. Prior to acquiring the PCB test kit technology, McGraw-Edison made an evaluation of the kit using field samples of PCB contaminated oil. Based on this evaluation and the previous studies, it was determined that the kit could be a feil safe screening tool provided that the interpretation be based on a more conservative Aroclor 1242 calibration curve. McGraw-Edison introduced this curve in late 1983.

Shortly after the kit was introduced the U. S. Air Force, which had been actively using the kit to screen oil samples in the field, expressed an interest in being able to screen soil samples at various remote spill sites in Alaska. Centec, in conjunction with the U.S. Air Force, proceeded to develop and evaluate adaptations to the kit which allowed soil screening. In the process of this evaluation, over 27 different soil types were tested, spiked at 50 ppm, 250 ppm and 1000 ppm, with Aroclor 1260 to determine the effectiveness of the field extraction procedure by correlation of the kit results with gas chromatography. The results of this study indicated a worst case extraction efficiency of 40%. For screening purposes, therefore, when taking into account the worst case extraction efficiency and solvent density, a multiplication factor of four was found necessary to give a safe screening value. The initial study also determined that the test procedure was not subject to interferance from inorganic

*AEHA Pesticide Monitoring Special Study No. 17-44-0609-83, "Laboratory and Field Evaluation of a Commercially Available Field Test Kit", Jan.-July 1983.

chloride in the environment. The results of this study concluded that the developed procedure provided a reliable screening tool for rapidly assessing the extent and level of PCB contamination at suspected spill sites. Because of the complex nature of soils and the potential for contamination by Aroclors other than 1260, namely Aroclor 1242, McGraw-Edison has continued this evaluation to further evaluate the performance characteristics of the kit. This study assesses the effects of soil composition and moisture levels on the kit performance.

REVIEW OF TECHNOLOGY

The method involves chemical dechlorination of the PCB molecule with an organo sodium reagent. The sodium chloride which results is extracted into an aqueous medium and detected with a chloride ion specific electrode. The concentration of chloride is then related mathematically to the concentration of PCB either as Aroclor 1242 or as Aroclor 1260. When testing soils, the PCB is initially extracted from the soil matrix and the solvent extract is then evaluated.

SCOPE OF WORK

This evaluation involves side-by-side PCB analysis using standard laboratory methods and the McGraw-Edison PCB Field Test Kit. A summary is presented depicting both the oil and soil test capabilities of the kit.

Oil samples were tested which had been submitted to our lab for analysis. The samples represented a large variation in PCB concentration, Aroclor blend and oil condition.

The soil evaluation was accomplished in two stages. The first stage involved the evaluation of the soil test method under varying soil conditions. A multidimensional experiment was designed and completed to evaluate the effects of soil type, moisture and PCB concentration on the ability of the PCB Field Test kit to screen for PCB content. The second stage involved the analysis of actual field samples.

OIL TESTING

870 oil samples which were sent to our laboratory for PCB analysis by more than 50 different customers were analyzed by both gas chromatography and the test kit

method. The total PCB concentration by GC was compared to the value obtained with the test kit.

RESULTS FOR OIL SCREENING

Overall the data indicates interpretation as Aroclor 1260 will be more accurate in 96% of samples tested in a typical sample population. In the remaining 4% of the samples interpreted as 1260, the answers will be lower than actual. Interpretation as Aroclor 1242 on the other hand will essentially give no false negatives but will give values that are higher than actual if Aroclor 1260 is present. A false positive or negative means that the kit classified the sample into a higher or lower range than did the G.C.

SOIL SELECTION AND PREPARATION

Soils testing is much more complex than oil evaluations, due to the diverse soil types and conditions encountered in field situations. Soil texture and particle size, ranging from the larger size of sand particles to the minute clay particles, all with varying organic contents, provide an inconsistent unpredictable matrix.

Texture as well as porosity is an important soil characteristic because it will, in part, determine water intake and the accessibility of the extraction solvent to adsorbed PCBs. Surface area and the activity of adsorbtive sites also play an important part in both water and PCB access and removal. Sandy type soils have higher porosity and have relatively low surface area and adsorptive affinity compared to clays which are noted for high surface area and wide range of active adsorbtive sites. Organic soils have very high water holding capacity and strongly adsorb PCB molecules in the lipid portion of cellular residues. Selection of soils from each of the categories sand, clay and organic for the evaluation was, except for sand, a difficult task because of the almost infinite variety of possibilities available and the lack of defined standards. Use of a refined industrial type clay was not practical, for example, because of the extremely high absorbtivity of these materials. Therefore, high clay soil and organic peat were selected and characterized.

Theoretically, the combinations of soil texture, organic content and moisture content contribute to the strength of adsorption of chemicals to soil and accordingly to the extraction efficiency of PCBs from soil.

Each soil was air dried and sieved then contaminated to the desired level using PCB (1242) standards. Oil was added to a level of 5% w/w oil to soil. These soils were used in all subsequent testing. The "wet" soils were spiked to a level considered to be the field moisture capacity for each particular soil type.

Each soil type was spiked with PCB to three different contamination levels (15, 50, 500 ppm 1242). Each of these samples were tested when air dried and also at maximum field moisture capacity.

Soxhlet extraction and subsequent gas chromatographic testing per ASTM D3304 (proposed) was used as the standard analysis method. Throughout this evaluation, D3304 was considered to be 100% efficient in extracting PCBs from soil. The PCB test kit extraction was compared to it in order to determine extraction efficiency.

By evaluating the extraction efficiency of the test kit method using extremes of soil type and moisture content, the minimum extraction efficiency could be determined. Once determined, it could then be compared to the factor of four used in the kit method.

The characterization of the sand, clay and organic soils used in the evaluation are shown in Table I. A blend which contains equal parts of the three basic types was also evaluated.

RESULTS OF THE SPIKED SOIL EXPERIMENTS

A summary of the results for model soils spiked with Aroclor 1242 under air dry and water saturated conditions is shown in Figures 1 and 2, respectively. It was not possible to modify the test soils with the same high moisture levels because of the wide variance in their moisture holding ability. Moisture content of saturated sand is little more than 5% where as the clay soil was around 20% moisture and the organic soil saturated significantly above 20%.

Table I

Soil Type	Organic Matter (%)	Field Moisture Capacity (%)	Air Dried Moisture Level (%)	Particle Size Evaluation Sand (%)	Silt (%)	Clay (%)
Sand	.02		.07	80	13	7
Clay	2.54		2.2	30	27	43
Organic	20.72		54	60	27	13
Blend	6.08		20	53	27	20

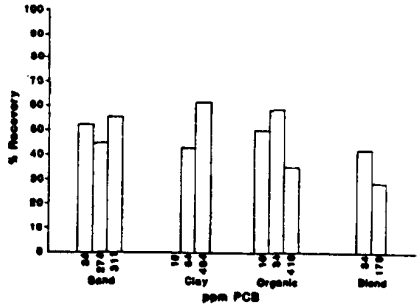

Figure 1. Air Dried Soil

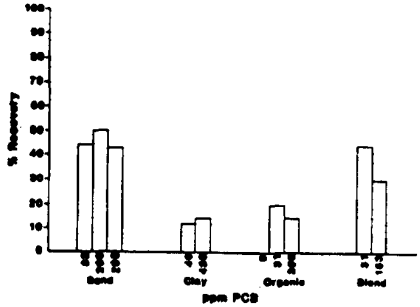

Figure 2. Water Saturated Soil

The results on the air dry soils indicate that all soil types show 40% or greater recovery with the test kit. This implies that using the standard multiplication factor of four with the kit all screening values would be at the level of the expected G.C. result or greater. The results with the spiked soils indicate that the kit will not consistently detect PCB levels below about 20 ppm in some soil compositions, however, the limited experience with air dried field samples indicates a slightly better detection limit than observed with the artificially contaminated samples.

Soils evaluated in a water saturated condition do show a distinct reduction in extraction efficiency. The reduction for sandy soils is only slight but is more pronounced for both clay and organic type soils. Clearly it is more desirable to test air dried or moderately wet soils when screening for PCB's with the test kit in order to obtain optimum results. To more effectively deal with situations of extremely high moisture content, physical removal of the water by desiccant or mechanical techniques will enhance the capabilities of the kit in handling water saturated samples. Since the final step in using the soil test is sending the last sample back to the lab for analysis, no serious problem is anticipated even under the worst case conditions.

FIELD SAMPLES

Soil samples which were sent to our laboratory for PCB analysis were analyzed by both gas chromatography and the test kit method. These samples represented a large variation in soil type, moisture content, Aroclor blend and concentration.

The relative extraction efficiency of the various samples follows the trend established with the synthetic (laboratory prepared) soils. The samples which contained minimal moisture showed excellent extractability. The "wet" samples, however, showed decreased extractability, especially those samples of high clay and high organic content.

CLOR-N-OIL™ TEST KIT AS A PCB SCREENING TOOL

DAVID W. MILLS and KIRT RHOADS

UTAH POWER & LIGHT COMPANY

INTRODUCTION

Utah Power & Light (UP&L) has been faced with the necessity of testing large numbers of transformers and other equipment to determine the PCB content of the dielectric fluid. EPA promulgated marking and disposal regulations of PCBs in 1978 and in 1979 consolidated these into the Use Prohibition Regulations. These regulations established the transformer categories of non-PCB (less than 50 ppm); PCB-contaminated (50-500 ppm); and PCB (greater than 500 ppm).

These regulations have been further refined, mostly as a result of court actions, to include:

Periodic inspection of PCB transformers,
Identification of PCB transformers in food and feed locations,
Removal of such by October 1, 1985,
Identification of PCB transformers in commercial buildings,
Notification of building owners and fire departments by December 1, 1985, and finally,
Removal of some by October 1, 1990.

In addition, UP&L instituted a program to remove and dispose of its PCB transformers by December 31, 1988, a program which requires testing of all Company transformers.

In the scramble to meet all of these requirements, UP&L has investigated every method of testing or screening of PCBs that research has brought to light. So far the Clor-N-Oil™ test kits have been found to be the most effective screening system for UP&L applications given the time limitations imposed by the regulations.

DISCUSSION

The Clor-N-Oil™ test kits were developed by General Electric under contract from the Electric Power Research Institute (EPRI). DEXSIL Chemical Corporation has exclusive license from EPRI to mass-produce the kits for industry-wide use. This kit evaluated by UP&L is designed to give an indication of whether a mineral oil contains more than or less than 50 ppm PCBs. The kit does not measure PCBs but rather measures chlorine content of the oil. It is designed to read positive if the chlorine content of the oil is greater than 21 ppm.

The cut-off point of 21 ppm is based on the chlorine content of the least halogenated Aroclor (1242). In other words, 50 ppm of Aroclor 1242 will contain at least 21 ppm chlorine.

The kit is hand-held and portable. Each kit has its own set of instructions and can be used in the field. The test only takes a few minutes, and the result is an easy-to-read colorimetric determination of the presence of chlorine. The kit will only work on PCB-contaminated mineral oils and Askarel fluids; it will not work on soils, waters, or other material.

One kit will test one oil sample and costs from $3 to $6, depending on quantity purchased at one time. Laboratory Gas Chromatograph (GC) analysis of one sample of mineral oil currently costs $20 to $40. Testing programs can generally be completed much sooner if the test kit is utilized, since it is not necessary to send all samples to the laboratory for GC analysis.

UP&L uses the test kit to screen its distribution transformers for PCB content. In the past, UP&L has not purchased or utilized PCB-type transformers in its distribution plant. It has, however, classified these, by rule, as PCB-contaminated transformers. From our experience, between 80% and 90% of all distribution-type transformers are screened out (classified as non-PCB) by the test kit.

Current computer records show 198,464 distribution transformers in six regions throughout the UP&L system. Some of the regions cover metropolitan areas such as Salt Lake City, and others cover remote areas in Wyoming. In most of the regions, there is considerable irrigated agriculture, with substantial distances between each transformer.

Line crews have been commissioned to collect the samples and deliver them to a central location for testing, or run the test themselves in the field. They take the sample by inserting a piece of polyethylene tubing into the pressure relief valve of the transformer. The oil sample is then collected in new 2-ounce glass vials. They also label the vials and complete the paperwork which will be used to enter the test information into the company-wide computer.

If the samples test positive (50 ppm or greater) with the Clor-N-Oil™ kit, they are sent to a Utah State-certified laboratory to be tested by GC methods. If a sample tests negative, it is sent to a central facility where it is permanently stored in case GC analysis on the sample is needed at some point in the future, such as in the case of an oil spill.

If a sample tests positive with the test kit (over 50 ppm PCB) and negative (less than 50 ppm PCB) by GC methods, it is termed a "false positive." If it is negative by the kit and positive by GC, it is considered a "false negative". False positives are expected but the rate of false negatives should be very low if the kit is to be considered an effective screening tool.

EPA Region VIII has been contacted regarding the use of the test kit as a screening tool. Region VIII said they had no problem with using the kit, but when asked to put this in writing, hesitated. UP&L then inquired further of EPA in Washington D.C. They responded:

> ".....the Agency presently finds gas chromatography to be the minimum acceptable method for determining the concentration and nature of PCBs in most samples. There is no prohibition against the use of test kits utilizing total chlorine analysis as rough field screening devices to determine if further testing is required. However, any analytical errors resulting from such testing would not insulate a company against prosecution should the Agency obtain evidence of a violation of the PCB rule."[1]

Since UP&L intended to use the test kit extensively in a testing program to be completed in 1986, and since EPA took the position that test kit results could not be used to insulate the Company from prosecution should an analytical error be made with the test kit, UP&L decided to study the probability that such an error might occur. The goals and objectives of the study are as follows:

[1] U. S. EPA correspondence to Utah Power & Light Co. dated February 14, 1985, signed by John S. Seitz, Chief Executive Officer, Office of Compliance Monitoring, Pesticides and Toxic Substances Branch.

GOALS AND PROGRAM OBJECTIVES

1. Determine what percent of a large random sample of distribution transformers could be expected to be "screened out," i.e., test negative, with the Clor-N-Oil™ PCB test kit.

2. Determine whether the portion of transformers screened out by the test kit varies with the transformer manufacturer.

3. Determine what portion of those samples testing positive with the test kit will test positive by GC methods.

4. Of those samples testing positive, determine what portion would be expected to test between 50 and 500 ppm; over 500 ppm PCB.

5. Of those samples testing negative with the kit, determine how many would be expected to test positive by GC methods; i.e., the portion that would be false negatives, and compare this false negative rate with that which would be expected from the Clor-N-Oil™ test kit.

6. Evaluate the probability of a false negative with the kit vs. the probability of a false negative by GC methods.

METHODOLOGY

1. There are approximately 198,000 transformers on the UP&L system. Some of these transformers have been installed since the PCB regulations became affective in 1979. It is company policy to rely on the individual manufacturer's non-PCB certification rather than test these transformers. However, 51,032 transformers have been tested with the kit or with both the kit and the GC. The samples taken to date have been taken from transformers selected at random. The number of transformers sampled so far represents approximately 35% of all the transformers to be tested.
2. Records on each transformer sampled indicate the manufacturer as well as other data. This data has been compiled on the computer and is accessible by various sort programs.
3. All samples testing positive are tested by GC methods at a Utah state-certified laboratory. The results of the GC tests are entered into the computer data base along with the other information mentioned in "2" above.

4. The results of the GC tests, once entered into the computer data base, can be sorted into the PCB-contaminated (50-500 ppm PCB) and PCB (over 500 ppm PCB) categories.

5. Ninety-nine samples testing negative with the kit were tested with the GC to determine if any were actually positive.

6. Twenty samples were prepared by an independent Utah State-certified laboratory to accomplish objective 6. They contained 50 ppm of Aroclor 1260 plus or minus 5%. These samples were then tested by GC methods at another laboratory and by the test kit. The number of test kit negatives was compared with the number of negatives by the GC method.

Various computer sort programs were used to accomplish objectives 1 through 4 and a simple tabulation of the test results satisfied Objectives 5 and 6.

RESULTS

1. Of the 51,032 tests run with the Clor-N-Oil™ kit, 4,523, or 8.9%, tested positive. Therefore, 91.1% of all samples tested were "screened out" with the test kit.

2. From the information in Table 1, the test kit seems to be able to screen the transformers made by certain manufacturers slightly better than those made by others. T&R Electric and Standard do not seem to screen as well with the test kit as some of the other manufacturers, since they have a higher rate of false positives. The data shows Northwest to have a 100% positive rate; however, only one Northwest transformer was tested.

   Although there was some variability in the rate of false positives among the various manufacturers, no single manufacturer was considered to have a false positive rate high enough to significantly reduce the usefulness of the test kit as a screening tool.

TABLE I

Manufacturer	Total Tested w/Clor-N-Oil™	No. Testing Pos. w/CNO	Total Test. Pos. w/GC	% Positive by GC
Allis Chalmers	2,244	82	9	0.40
Bullock	1	-	-	-
Chance	42	-	-	-
Central Moloney	4,846	811	43	0.88
Colt	46	1	-	-
Dowzer Electric	28	14	-	-
Delta Star	49	1	-	-
General Electric	14,635	1,986	1,241	8.48
Howard Industry	901	10	4	0.44
Hill	3	-	-	-
Kuhlman	2,512	20	-	-
Larkin	16	-	-	-
Line Material	1,592	32	2	0.13
McGraw Edison	2,213	39	2	0.09
Moloney	1,185	233	14	1.18
Northwest	1	1	1	100.00
Pacific Electric	2	-	-	-
Pennsylvania	393	90	15	3.82
Porter	61	2	1	1.64
Pole Star	262	12	-	-
RTE	3,961	143	2	0.05
Sorenson Electric	33	2	1	3.03
Spokane	3	-	-	-
Square D	2	-	-	-
Standard	233	36	30	12.88
T&R Electric	31	27	15	48.38
Wagner	3,512	119	38	1.08
Westinghouse	12,029	1,466	562	4.67

3. Of the 4,523 samples testing positive with the Clor-N-Oil™ kit, 2,537, or 56.1%, tested negative by GC methods.

4. Of the 4,523 samples testing positive, 1,830, or 40.45%, were between 50 and 500 ppm by GC methods, and 158, or 3.49%, were greater than or equal to 500 ppm by GC method.

5. Of 99 samples testing negative with the kit, 5 were actually found to be positive when tested by GC methods. All were run again by GC and the results confirmed. When the 5 samples were retested with the Clor-N-Oil™ test kit, they all tested positive.

6. Twenty samples prepared by an independent Utah State-certified laboratory were certified to be 50 ppm Aroclor 1260 plus or minus 5%. These samples were tested by both GC methods and with the test kit.

The results were as follows:

a. The GC test results on the 20 known samples were as follows:

TABLE 2

PCB Conc. (ppm)	Frequency
47	2
48	1
49	1
52	1
53	2
54	2
55	1
56	2
57	2
58	2
59	1
61	2
62	1
	20

As can be seen from Table 2 above, the GC test was negative on four samples.

b. The same samples were tested with the Clor-N-Oil™ test kit. Seventeen tested positive and three tested negative.

As can be seen from the data above, the GC test actually did not predict as well as the test kit in terms of false negatives. (4 false negatives versus 3 false negatives.) It must be emphasized that the 50 ppm samples were plus or minus 5% and that 20 is a fairly small sample size.

CONCLUSIONS

1. The test kit is an economical PCB screening tool since over 90% of all samples tested were "screened out".
2. The probability of false negatives with the test kit as determined by the data herein is not higher than the probability of a false negative by GC test methods. However, the rate of false negatives experienced by UP&L (5%) is higher than that experienced by other researchers (1.2%, 2.5%).[1,2] Since all of the false negatives tested positive when retested with the Clor-N-Oil™ kit, the analytical precision of the kit is probably better than indicated by this experiment.
3. There is insufficient variability in the rate of false positives among manufacturers to conclude that the Clor-N-Oil™ kit will not screen the transformers from a particular manufacturer economically.
4. The Clor-N-Oil™ test kit is an analytically acceptable method for screening PCBs in distribution transformer oils.

[1] Riley, Michael T., Detroit Edison Co., "Utility PCB Practices", presented at 1985 T & D Exposition May 14, 1985, Chicago, Illinois (see Table 5), found false negative rate of 1.5% out of 247 tests.

[2] Tehiliani, Vasu H., EPRI "Field Determination of PCB in Transformer Oil, Volume 2: Clor-N-Oil™ PCB Screening Kit", EPRI EL-3766, October 1984, Appendix B, pg. 8-10, found false negative rate of 2% out of 1,506 tests.

Field Testing of the S-Cubed Gas Chromatograph, PCBA-102

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Background

In many field situations, the analysis of polychlorinated biphenyls (PCB) in transformer fluids and in soils must be accomplished under severe time constraints. Often, highly trained analysts are not available. Field instrumentation (PCBA-102) recently developed for EPRI under RP1263-9 by S-Cubed is intented to circumvent both difficulties in the sense that their instrument is highly portable and does not require an experienced analyst operator.

The manufacturers have simplified the sample preparation steps by providing prepackaged reagents. The interpretation of results, which is often the most demanding of the analytical tasks, is performed by pattern recognition software. Furthermore, the amount of time between injections has been significantly reduced, thereby permitting greater sample throughput.

Objectives

The Electric Power Research Institute has elected to support field testing of this instrument. The objectives of the project were to evaluate the S-Cubed PCBA-102 instrument for accuracy and precision, convenience, technical expertise for operation, and the ability to handle PCB's in a variety of matrices.

Study Design

The field test program had two aspects, a series of comparisons between laboratory and field measurements of PCB in soil from a contaminated site and an instrument loan program to utilities where they ran oil or soil samples of their own choosing. The site study was in Sacramento, California. utilization of the PCBA-102 allowed on-site

definition of the contamination zone at a number of transformer substations. Confirmation analyses were performed by conventional laboratory methods.

The instrument loan program allowed the utilities to apply the PCBA-102 to applications of their own choosing. Confirmation analyses by approved EPA methodology were used to evaluate precision and accuracy. Speed and convenience of operation was evaluated by each utility.

Conclusions

The performance of the PCBA-102 during the utility loan program was subject to both instrument downtime and operator error. In general, adequate precision and accuracy was achieved with experienced gas chromatographers as operators. Downtime, imprecision and inaccuracy increased dramatically when inexperienced personnel were asked to perform instrument start-up and operation.

The site study is being conducted in September and October of 1985. Results will be available for the EPRI PCB Seminar in Seattle, Washington.

COMPARISON OF PCB ANALYTICAL METHODS

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The purpose of this work was to evaluate several PCB analytical systems as alternatives to gas chromatography (GC).

Since the promulgation of PCB regulations under the Toxic Substances Control Act, there has been a need for a rapid and accurate method of determining PCB concentrations. Gas chromatography has been the accepted method for PCB analysis. It requires an operator trained in the operation and maintenance of a gas chromatograph, sample preparation, and interpretation of PCB chromatograms. Because of the labor involved, it is an expensive analysis.

Several alternate methods are now available which are faster, portable, and less expensive. These are the McGraw Edison specific ion electrode method, the CLOR-N-OIL colorimetric method, and the S-Cubed PCBA-102 gas chromatograph/computer.

McGraw Edison Chloride Specific Ion Electrode PCB Test Kit

This method is based on the measurement by specific ion electrode of the resultant chloride ion activity when chlorine is chemically removed from the PCB molecule. Any chloride from other sources will also be measured as PCB, which can result in higher results. Time required per analysis is about five minutes, not including meter calibration, which takes about ten minutes. The detection limit is about 6 ppm as Aroclor 1260.

CLOR-N-OIL 50 PCB Screening Kit

This PCB measurement method is the fastest to perform, requiring about five minutes. It gives a quick determination as to whether an oil is over 50 ppm in PCB or not. This analysis is based on color changes caused by different

concentrations of PCB. The color ranges from a deep purple for low PCB concentrations and gradually lighter to colorless for high PCB (over 50 ppm) concentrations.

As with the McGraw Edison method, other chlorinated compounds can contribute chloride, which can give high results.

S-Cubed PCBA-102 Gas Chromatograph

The system is basically a gas chromatograph with an electron capture detector coupled with a computer which is programmed for interpretation of PCB chromatograms and calculation of concentration. As programmed, the PCBA-102 can detect PCB down to 10 ppm. Modification of the sample preparation procedure can extend this dectection limit to 1 ppm, but this requires some calculations by the operator. The PCBA-102 eliminates the need for the operator to analyze the chromatograms.

Addition of a recorder to the PCBA-102 is helpful in that it gives a visual trace of the sample, and would give indication interferences not evident in the numerical printout. Time for analysis is about 12 minutes.

Results

Some two hundred samples were run by the different methods. Of these, seventy-seven were run by all three, which allowed comparison. Results obtained by conventional gas chromatography were used as a basis for comparison.

Results generated from the PCBA-102 were much closer to those obtained by conventional GC than that of the McGraw Edison. They averaged 1.12 times that obtained by regular GC. This is probably due to the fact that the PCBA-102 procedure is basically the same as the conventional GC procedure, the main difference being the computer interpretation and calculation of the results.

For the McGraw Edison, results averaged 1.25 times that obtained by GC. This is in large part probably due to other chlorinated compounds other than PCB (such as trichlorobenzene) in the samples.

No numerical results can be given for the CLOR-N-OIL results, as it tests as only over or under 50 ppm. In any case, the CLOR-N-OIL successfully screened any oil over 50 ppm as determined by GC.

Gas chromatography remains the accepted method for PCB analysis per EPA regulations and ASTM methods. The PCBA-102 appears to be a logical choice as an analytical alternative to GC. Sample preparation and calibration are easier than the other methods. Its weak points are injection of the sample, which requires a consistent technique for reproducible results; and the use of sulfuric acid, which requires care in handling for safety.

The CLOR-N-OIL and McGraw Edison are better suited for screening samples for approximate PCB concentration.

Summary of Results of Comparisons of PCB Methods

Table 1

AVERAGE OF RESULTS OF METHODS RATIOED TO CONVENTIONAL GC ANALYSIS

Method	Average Ratio and Standard Deviation
McGraw Edison	1.25 ± 0.43
S-Cubed PCBA-102	1.12 ± 0.25

Table 2

COMPARISON OF MISCELLANEOUS METHOD PARAMETERS

	GC	PCBA-102	McGraw Edison	CLOR-N-OIL
Time per analysis, minutes	30	12	5	5
Time per calibration, minutes	30	12	10	NA
Frequency of calibration (samples between calibration)	10	10	5	NA
Detection limit, ppm	NA	10	6	NA

DEVELOPMENT OF THE BPA SUBSTATION SOIL PCB TESTING PROGRAM

David C. Plath

INTRODUCTION

Polychlorinated biphenyls (PCBs), because of their stability and resistance to oxidation, were used for years as dielectric fluids in electrical equipment. Due to their chemical stability they have been determined to be a persistent environmental pollutant. As they are relatively nonpolar, they tend to accumulate in fatty tissues and hence are passed through the food chain. Therefore, as stated by Toxic Substances Control Act (TSCA), the Environmental Protection Agency has implemented rules for the handling, storage, and disposal of contaminated materials. Two limits (50 and 500 ppm) have been set which divides insulating fluids into three catagories, non-PCB contaminated fluids, (less than 50 ppm) PCB contaminated fluids (between 50 and 500 ppm), and PCB fluids (over 500 ppm). In addition, a recent ruling (July 1985) of the Washington Department of Ecology has set the lower limit of regulation on waste insulator fluids at 1 ppm.

Since these legislative limits were set, a great deal of work has gone into developing methods for accurately and reliably determining the concentrations of PCBs in a variety of matrices. Major problems have had to be overcome in the clean-up, analysis, and quantitation of PCBs. These include differentiating PCB congeners from coeluting pesticides (2,4-D, PCP, etc.), suppression of the electron capture detector by the elution of the oil matrix, and the quantitation of mixed Aroclor solutions. In addition, the power utilities involved in this analysis had an obligation to limit the cost, and thus the analysis time due to the extraordinary number of samples being handled.

INSTRUMENTATION AND INSTRUMENTAL CONCERNS

At Bonneville Power Administration we became involved in PCB analysis 3 years ago because private laboratories could meet neither our sampling obligations nor our turn-around-time expectations. Now, 3 years later, the capabilities of many west coast laboratories have improved to the point where we now have additional options. Our program has completed over 9000 samples providing a data base on over 4000 pieces of oil-filled equipment. We feel that the problems we have encountered and solved in the course of developing our approach to PCB analysis might provide help to utilities in a similar positon.

Since we were starting on this analysis from scratch, we were in the enviable position of being able to choose the instrumentation and methods to best suit our needs rather than having to adapt existing hardware. Noting the necessity of high resolution to the separation and the quantitation of these complex mixtures, we chose to develop our method around the capillary gas chromatograph. Excepting "on column" injections, the two main methods of sample introduction for capillery chromatography are splitless and split injection. As split injection tends to differentiate between the high and low boiling fractions and would thus tend to skew our results, we chose splitless injection which has been identified in the literature as a more quantitative approach. We were hoping to automate this system, therefore, "on column" injection was not considered because it has not yet been shown to be compatible with autosamplers.

At this point, it should be pointed out that it has been written in several well-respected sources, (Ref. 1 and 2), that the method of injection (a very slow, 5-10 second injection) is essential for a proper splitless injection. While we do not dispute this claim, we have found that due to changes we have made in the flow system of the chromatograph, we are able to achieve less than 5 percent relative standard deviation in replicate injections of both standards and samples when using an autosampler and splitless injection. The changes made involved primarily replacement of tubing connections that were found to develop small leaks, and the use of ultrapure carrier and makeup gases with oxygen scrubbers. As a consequence, our normal ECD background current has dropped from approximately 600 p. amps to 100 p. amps indicating a clean system with very little air leakage. One phenomena that we noted early on in this method

development, was that the response factors for chlorinated hydrocarbons in an ECD were higher when air leaks were evident. While this tended to lower our PCB detection limit it was impossible to reproduce and increase the error of the analysis considerably. Recently, work was presented in the literature that indicates that doping the make-up gas with low levels of oxygen will increase the response of an ECD. Since this would give a reproducible increase, it could be valuable for this analysis, especially for low level work, now that the system leakage has been minimized.

QUALITY ASSURANCE

In order to assure the absolute concentration of PCBs in a sample oil, it is necessary to have a regular quality assurance program. This includes, in our case, both standard oil samples as well as documented standards. Early on in this method development we noted variability in the relative concentrations of individual PCB congeners for standards from different sources. Since this variability would affect the use of single peak or peak group calculations necessary for mixed Aroclor samples we decided that it would be prudent to base our analysis on a well-defined standard. We requested samples of pure Aroclors from the Food and Drug Administration (FDA) that had been well characterized in the literature by Leon Sawyer of the FDA (Ref. 3 and 4). In addition, we received PCB standards and diluent oil from the National Bureau of Standards in order to prepare standard oil samples.

To ensure repeatability with the autosampler without sacrificing sample output, we designed our analysis schedule such that after every six samples run, two standards, nominally 0.1 and 0.5 ug/ml of a single Aroclor were run followed by a blank run of solvent. The Aroclors were then alternated so that in a series of 100 runs there were approximately three sets of each standard run. The solvent runs give an indication if carryover is occurring from sample to sample and when syringes should be cleaned or changed. The absolute magnitude of standard runs indicate the condition of the splitless injection system (i.e., septum leaks, etc.). Of course, when the sample was of a known Aroclor type, the autosampler table was adjusted to reflect this case (standards were shifted).

Once it has been determined that the system is giving reproducible results, it is necessary to determine the accuracy of the data. The signal suppression in the

ECD due to the passing of the transformer oil fraction, has been noted in several articles and was a basis for the development of the ASTM procedure that involves preparation of standard Aroclors with a known transformer oil, (Ref. 5). As reliable sources had noted that the degree of suppression varied with the transformer oil, we chose an alternate route to account for suppression. Using a sample of new Shell transformer oil, representative of the oil used at BPA, and FDA Aroclors, we prepared 5 and 50 ug/g standards of Aroclors 1260, 1254, and 1242 in oil. These standards were then run through our procedure to determine the "recovery" due to suppression. This recovery was found to vary between approximately 50 and 80 percent. As the recovery falls toward the 60 percent level or below, it indicates the existence of air leaks in the detector systems and as such signals the need for corrective maintenance. In a series of 99 autosampler runs, 5 ppm and 50 ppm standards prepared in oil are run three times for each Aroclor type. It should be noted that the oil suppression recovery is a function of retention time and when individual peak areas are used in calculations, as they are for Aroclor mixtures, the suppression recoveries are individually calculated for each peak. Effects such as oil suppression recovery variation are masked when all standards are prepared with oil as in the ASTM procedure. While these effects may not result in different quantitative results by the two methods, they do add to the fundamental understanding of the measurement system as a whole. Sample chromatograms of Aroclors in solvent, in oil, and as mixtures are shown in Appendix B.

If the calculated concentration falls on or near a regulatory limit (50 or 500 ppm), the sample is rerun using standard additions. In most cases this involves using the same stock or standard solutions used in the normal standards. The preparation time for standard additions is less than 5 minutes and with the use of an autosampler the operator time is negligible. Standard Aroclors in oil run by this method show a recovery of 100 percent $\pm$ 5 percent. We consider this accuracy to be more than adequate.

CALCULATIONS

The calculation of mixed Aroclor samples was the next problem to be addressed. Since we had chosen to use the capillary system, we found that for two Aroclor mixtures we had significant non-overlapping regions in the chromatogram from which individual peak areas could be determined for quantitation versus the standard or by standard additions.

For mixtures of Aroclors 1242, 1254, and 1260, this same method can be employed for the determinations of the first and last Aroclors. We are currently investigating the use of a mini computer to "subtract out" the areas due to Aroclors 1242 and 1260 in order to calculate the remaining fraction of Aroclor 1254. Since the overlap of Aroclor types is due to the presence of the same congener in both mixtures (as opposed to different compounds coeluting), it is not possible to completely resolve Aroclor mixtures by capillary GC.

However, it should be possible to calculate by relative peak area ratios the contribution of each Aroclor type to a given peak using peaks in the non-overlapping region as reference.

In the fall of 1982, we participated in an NBS round robin study on the analysis of PCBs in oil. It was our relatively poor performance in this study which prompted the changes in our chromatographic system as well as the adoption of the current quality assurance program. As a result, reanalysis of these samples has shown the system and method to be reproducible and accurate. Stepwise procedures for oil sample preparation and calculations can be found in Appendix A. Instrumental parameters for this analysis are given in Appendix C.

Methodology for the Analysis of PCBs in Substation Soils

The methods currently being used by BPA for the sampling and analysis of PCBs in soil are modifications of those used by EPA. The EPA extraction method (No. 8080) uses a 16-hour Soxhlet extraction with a mixture of acetone and hexane. This extraction is intended to recover PCBs and pesticides from a wet soil sample. Since we are not interested in volatile pesticides, we have modified this procedure. We first dry the sample at 50°C and then sieve it with a 40-mesh screen in order to remove rocks leaving a homogeneous sample that is representative of the true adsorbing matrix. Rocks in the sample (such as substation gravel) being nonporous, will merely dilute the effective PCB concentration by virtue of their weight. A 10 gram sample of this preparation is then Sohlet extracted with 2, 2, 4-trimethyl pentane (iso-Octane) for 6 hours to remove PCBs. We have done serial extractions on samples of known PCB content and established that the first 6-hour extraction will capture 97 percent of the PCBs in the sample. In turn, each additional 6-hour extraction will capture 97 percent of the remaining PCB content.

Next the sample is reduced in volume, in the extraction flask, on a hot plate such that the iso-Octane (boiling point = 90°C) will reflux in the neck of the flask. This reduces the volume without loss of PCBs (boiling point approximately 250°C) without having to resort to the time-consuming, Kuderna-Danish method. In many cases a large percentage of the solvent can be captured in the upper level of the Soxhlet extractor completely eliminating the boil down step.

Finally, the sample is brought to volume with iso-Octane in a 100 ml volumetric flask and analysed by capillary gas chromatography with electron capture detection following the protocol we have established for the analysis of PCBs in transformer oil.

One of the tools we have been using in the analysis of soils is to determine the difference of the soil sample weight before and after extraction. The percentage of iso-Octane "extractables" calculated from this difference can be cautiously used to compare the amount of oil present to the PCB content. This comparison can give information concerning the contamination mode of the PCBs in soil. For example, a soil sample showing a high level of PCBs but a low percentage of oil would indicate either that the source did not contain transformer oil (i.e., a capacitor spill) or that some mechanism was occurring that separated the oil from the PCBs after the soil was contaminated. This information is also of value analytically since the response of PCBs in an electron capture detector is reduced when analysed in the presence of transformer oil through a process previously referred to as suppression. Suppression is accounted for when analysing PCBs in transformer oil by preparing PCB standards in oil and calculating the suppression based on standards prepared in iso-Octane. For soil samples we can determine the extent of suppression visually on the chromatogram and compare this to the expected suppression based on the percentage of iso-Octane extractables. We can then determine if the use of an oil suppression factor is warranted. We have determined in our lab that oil suppression is not a linear function of oil concentration. Therefore, dilution of the sample by a factor of 10 will not cause a corresponding decrease in suppression. Our preliminary findings are that it is a log-log function.

Preparation of Sampling Plans for the Analysis of PCB's in Substation Soils

Faced with the prospect of characterizing the PCB contamination patterns of over 90 of BPA's 450 substations, we first had to decide the extent to which we would sample. Our first calculations, based on Ref. 6 indicated that in order to have a 90 percent chance of finding a PCB "hot spot" of 1 meter radius in a substation of 100 meters length on a side we would need to set up a square sampling grid and take over 3,000 samples just to analyze the surface soil. Obviously, for temporal and financial reasons, this would be unacceptable. Therefore, it was necessary to make some assumptions to reduce this burden.

The first assumption that we made is that a spill would be visible. With our substations being covered with coarse gravel, a stain from an oil spill is generally visible for many years. The next assumption made was that once deposited on soil, PCB contamination would not migrate horizontally. While some reports of airborne PCB migration have been made concerning open hazardous waste dumps, our results of thousands of soil samples (approximately 20 percent of which were taken at the perimeter of highly contaminated fenced capacitor yards) indicate that horisontal migration simply is not occurring at any reasonable level.

One of the "knowns" we had going into this program was that, based on the analysis of PCBs in insulating oil from approximately 4,000 pieces of large oil-filled equipment (transformers and oil circuit breakers), only 2 percent of this equipment was contaminated with PCBs above the 50 ppm level. Also, with the geometric layout of the substations, large areas could be disregarded as potential areas of PCB contamination.

Referring to Figures 1 and 2, it is apparent that with increasing voltage rating (and consequently size) the levels of PCB contamination in general dropped. Since this equipment, greater than 69 kV in voltage rating, occupies the majority of space in the substation yards, we can expect that PCB contamination of the surrounding soil will be minimal. In fact, if oil at the 50 ppm level contaminates soil and comprises 10 percent of its weight, the resultant soil would have a PCB content of 5 ppm. We would consider this level of contamination in a substation to be minimal. Our current practice for construction in areas of PCB contamination of less than 5 ppm is to place this material to the side of the construction and use it as backfill after construction is completed.

It should be emphasized that circuit breaker and transformer oil (from equipment greater than 69 kV in rating) accounts for at least 90 percent of oil used in the BPA system. In addition, this large equipment has the potential for causing much larger spills. Small equipment, on the other hand, has historically shown a higher level of PCB contamination. Figure 3 shows the results of oil analysis in smaller equipment. The most significant result of this figure is that over 16 percent of the small equipment tested showed PCB contamination above 50 ppm. Therefore, spillage from this equipment would have a greater probability of causing significant contamination to the surrounding soil. However, this contamination would be spread over a more limited area than the large equipment due to the smaller amount of fluid in the low voltage equipment.

The previous analysis has resulted in the development of sampling plans which concentrate sampling around the lower voltage equipment and visible oil stains. Figure 4 shows a typical substation with its resultant sampling plan.

The second area of concentrated sampling has been around capacitor yards and houses. Capacitors in the BPA system, with a few exceptions, are isolated in the yard by enclosure with fencing or metal houses. This was done primarily for safety reasons due to the low electrical clearance of this equipment. However, this isolation has also prevented the distribution of PCBs throughout the substation. It has, therefore, been our practice to sample the perimeter of these locations, especially by gateways (in the case of capacitor yards) and close to pads (in the case of capacitor houses). The results of these tests have shown that migration of PCBs horizontally is virtually nonexistent, with the exception of actual tracking of PCB from the locations by substation personnel and the contamination resulting from the past practice of storing failed capacitor cells along the outside of the capacitor yard fences. Results of samples taken within the capacitor yards (during periods of de-energization) have shown levels of PCBs exceeding 10,000 ppm and additional testing would be expected to yield similar results. All soils from these locations are assumed to be highly contaminated but contained.

The Use of Contract Labs

In the summer of 1984, it was learned that our laboratory would be responsible for the testing and profiling of PCBs in soil from 90 of BPA's 450 substations. The

substations identified in this program were those which had or still have capacitor installations as well as those substations containing equipment filled with PCB oil. Since this program would have taxed the laboratory beyond its ability to plan and execute such an undertaking, it was decided the actual sampling and analysis would be performed by contract laboratories. The responsibility for preparing the sampling plans and assuring the quality of the analysis, however, remained in our control.

Since we began contracting analysis, we have noted several quality assurance problems with our contract labs. In general, the problems have not been with basic methodologies because we provided each laboratory with the method we had developed in our lab. Rather, the problem has been that of record keeping during analysis. We have, with some labs, had problems of dilution factor errors due to poor record keeping, the reported results being as much as a factor of 10 below the actual value. I believe this is a record keeping problem which is associated with sample "overload" in the smaller labs.

Many of the labs that we deal with are small organizations which do a variety of analytical work in addition to PCB analysis. PCB analysis in this region has recently increased, drastically overtaxing record keeping systems that were devised for handling fewer samples. Therefore, it is important to keep in mind, when evaluating contract labs, the level of work they are currently doing versus what you will be expecting of them. Their quality assurance procedures should be designed for the increased sample load.

As a quality control procedure we are currently requesting contract laboratories to provide us with duplicate samples of approximately 10 to 20 percent of selected samples following receipt of their report. These samples are then run by the same procedure in our laboratory. The acceptable limit of deviation from our results is $\pm$ 50 to 100 percent, depending on the level of PCBs found. Duplicate analysis by the contract lab is required when these limits are exceeded in order to reconcile the deviations. Since soil samples are not inherently homogeneous we feel these limits are conservative. It is our intention, in the future, to develop a homogeneous soil/PCB standard to use for additional quality control.

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4. Leon D. Sawyer: Quantitation of Polychlorinated Biphenyl Residues by Electron Capture Gas-Liquid Chromatography: Collaborative Study, J. Assoc. Off. Anal. Chem. (Vol. 61, No. 2, 1978).

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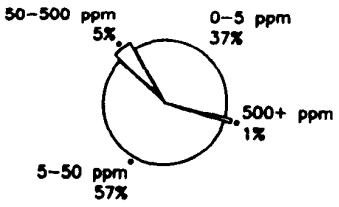
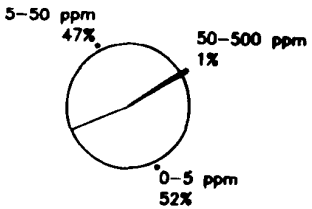
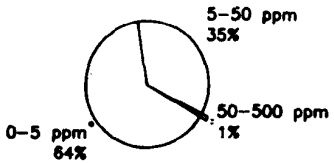


OCB'S OF 69 KV OR LESS
(500 PIECES TESTED)

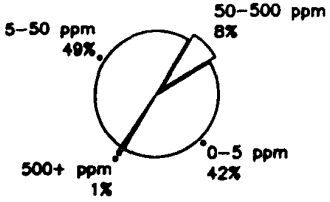


OCB'S 110–130 KV
(409 PIECES TESTED)

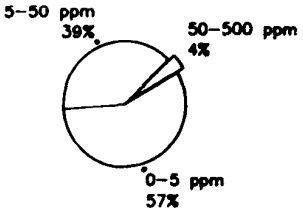


OCB'S OF 220 KV OR MORE
(319 PIECES TESTED)

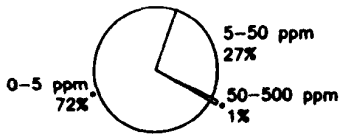
Figure 1. Comparison of PCB's in Oil Circuit Breakers



XFORMERS OF 69KV OR LESS
(162 PIECES TESTED)

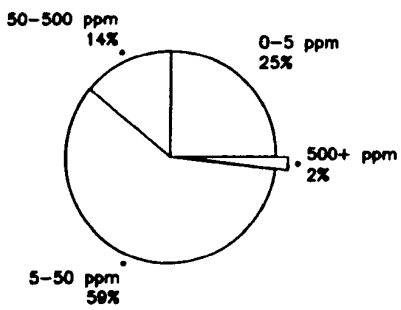


XFORMERS 110–130 KV
(443 PIECES TESTED)

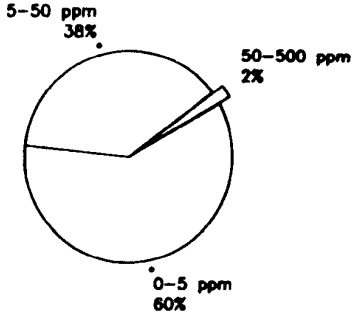


XFORMERS 220 KV OR MORE
(344 PIECES TESTED)

Figure 2. Comparison of PCB's in Transformers



SMALL EQUIPMENT
(1591 PIECES TESTED)



LARGE EQUIPMENT
(1515 PIECES TESTED)

Figure 3. Comparison of PCB's in Large and Small Equipment

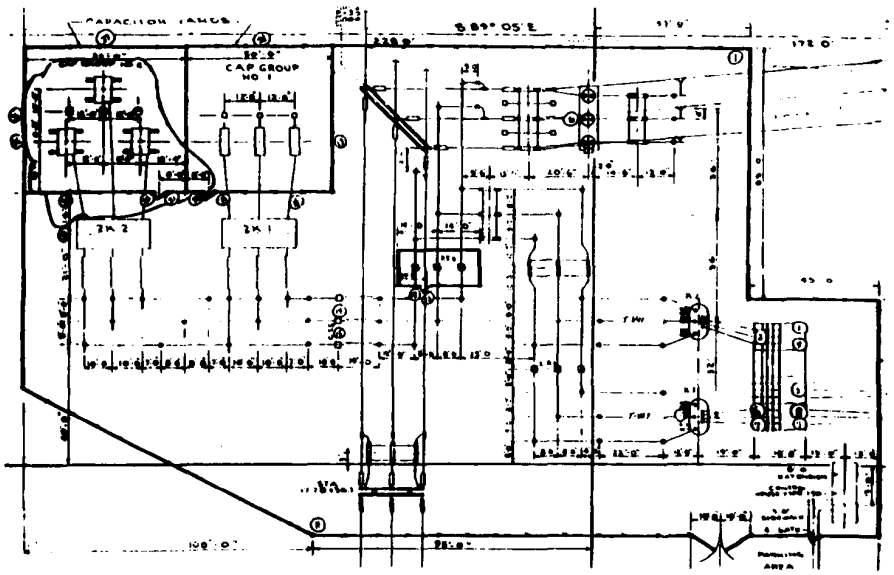


Figure 4.

APPENDIX A

PCB SAMPLE PREPARATION; OIL SAMPLE

1. For each sample to be analyzed prepare two - 20 ml disposable culture tubes with Teflon-faced screw caps. Tube A contains 9 ml of 2, 2, 4-trimethyl pentane. Tube B contains 9.00 ml of 2, 2, 4-trimethyl pentane and 5 ml concentrated H_2SO_4. All volumes are delivered ± 1 percent by automatic pipetting equipment.

2. To Tube A pipette 1.000 ml of oil to be analyzed. Mix well on a vortex mixer.

3. Pipette 1.000 ml of the solution from Tube A into Tube B and mix well on the vortex mixer. Centifuge to separate microdrops of H_2SO_4 and prepare autosampler vial with the supernatent solution.

STANDARD PREPARATION

1. Weigh 0.5000 g to the nearest .0001 g of pure Aroclor standard obtained from FDA. Dilute to 500 ml with 2, 2, 4-trimethyl pentane. Store this solution in the refrigerator away from light. This solution is nominally 1000 ug/ml.

2. Prepare working standard by pipetting 0.5 ml and diluting to 500 ml with 2, 2, 4-trimethyl pentane. This solution is nominally 1.000 ug/ml.

3. Actual standards are prepared by 1:10 and 1:2 dilutions of the working standard with 2, 2, 4-trimethyl pentane. Prepare actual standards in the same type of disposable culture tube and with the same volumetric pipette as the sample solutions. These solutions are nominally 0.1 ug/ml and 0.5 ug/ml.

CALCULATION

1. Single Aroclor Samples

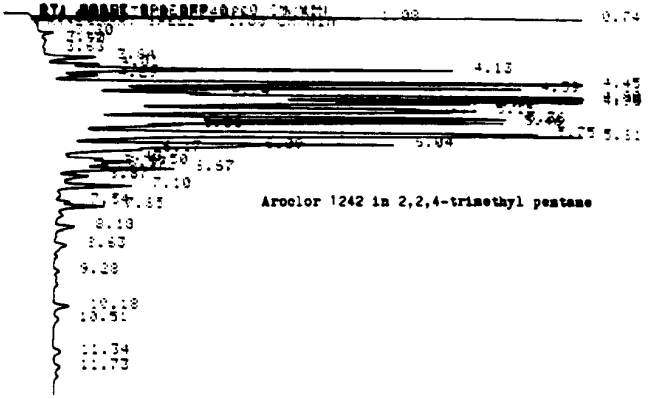
When a sample has been identified as a single Aroclor the calculation is quite straightforward. Linear Regression Analysis is used to prepare a standard curve using the total area of all the peaks due to that Aroclor at both standard concentrations. The same total area is calculated for the sample and using an HP-11C calculator the concentration is "picked" off the curve. This value is then divided by the density of the oil sample (approximately 0.86, an average value determined by measurement of 10 normal oil samples) and multiplied by 100 (the dilution factor). This concentration (now in ug/g) is then divided by the oil suppression recovery. This factor is a "recovery" to account for the suppression of the ECD signal due to the passage of the transformer oil fraction. This factor has been determined on 5 ppm and 50 ppm Aroclor 1260, 1254, and 1242 standards prepared in oil and normally runs about 50-80 percent. When the final calculation is close to a limit the sample should be rerun by standard additions. Therefore, the calculation for a single Aroclor is:

$$\frac{\text{(Concentration of sample from regression analysis) ug/ml}}{\text{.86 g/ml}} \times \frac{\text{dilution factor (100)}}{\text{Suppression Recovery}}$$

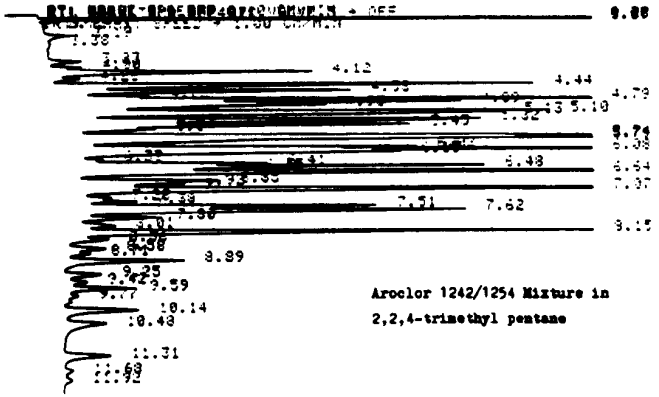
2. Mixed Aroclor Samples

Mixed Aroclor samples are calculated by individual congener peak areas or peak grouping sums chosen from non-overlapping regions of the chromatogram. These areas are compared with the same standard areas using a regression analysis program as for single Aroclor samples. This method is sufficient for two-Aroclor mixtures. For three-Aroclor mixtures 1242 and 1260 can be determined as before. Aroclor 1254 can be determined by subtracting the Aroclor 1260 component of a single congener peak in the overlapping region from the sample peak area. This 1260 component is calculated by multiplying the congener peak area from the sample by the ratio of the same peak in the 1260 standard and another peak from a non-overlapping region of the 1260 standard. This value then subtracted from the cogener peak area will give the congener peak area

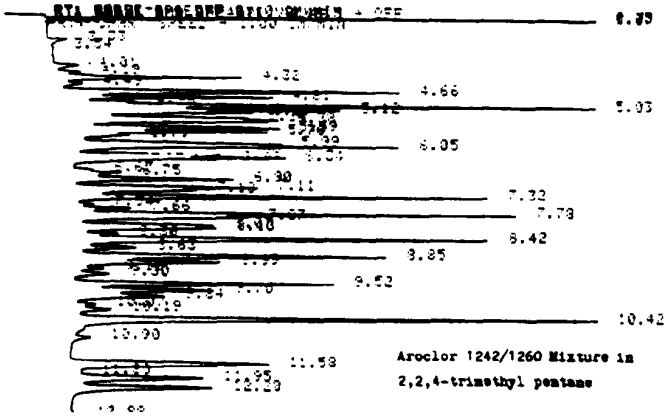
contribution of Aroclor 1254. With this area the concentration can then be caculated by comparing with Aroclor 1254 standards and completing the calculation as for two-Arqclor mixtures. This assumes that relative peak concentrations in a given Aroclor standard are constant. We have found this to be reasonably true for standards.

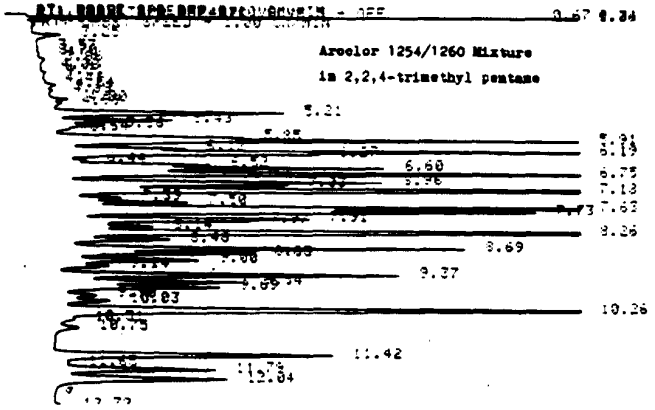


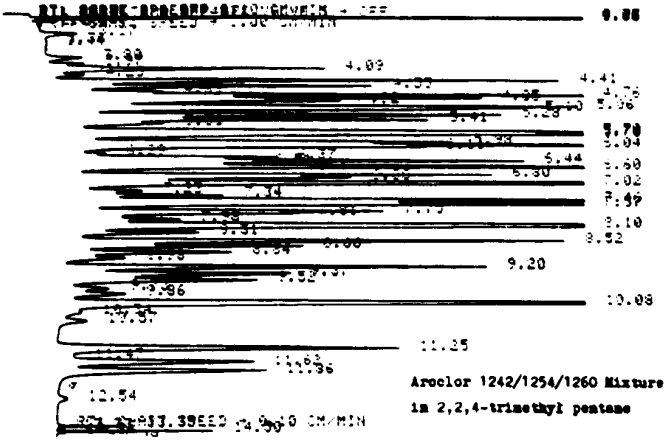
Aroclor 1242 in 2,2,4-trimethyl pentane



Aroclor 1242/1254 Mixture in
2,2,4-trimethyl pentane


4.32
4.66
5.03
6.05
7.32
7.78
8.42
8.85
9.52
10.42
10.90
11.58
Aroclor 1242/1260 Mixture in
2,2,4-trimethyl pentane


Aroclor 1254/1260 Mixture
in 2,2,4-trimethyl pentane
5.21
6.60
7.13
7.62
8.26
8.69
9.37
10.26
11.42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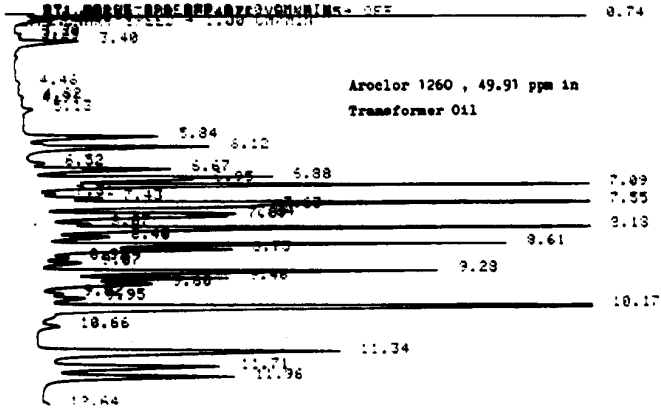
4.09
4.41
5.06
5.70
5.04
5.44
5.60
5.80
7.02
8.10
8.52
9.20
10.08
11.35
11.96
12.54
Aroclor 1242/1254/1260 Mixture
in 2,2,4-trimethyl pentane


0.74
7.40
4.46
4.92
Aroclor 1260 , 49.91 ppm in
Transformer Oil
5.84
6.12
6.32
6.67
6.88
7.09
7.55
8.13
8.61
9.29
10.17
10.66
11.34
11.96

Appendix C

PCB Analysis- Instrumental Parameters

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LIST ANALYSIS
OVEN TEMP LIMIT 405
OVEN TEMP 140
OVEN TEMP ON
DET 2 TEMP LIMIT 405
DET 2 TEMP 325
DET 2 TEMP ON
INJ 1 TEMP LIMIT 405
INJ 1 TEMP 300
INJ 1 TEMP ON
INJ 2 TEMP LIMIT 405
INJ 2 TEMP 300
INJ 2 TEMP ON
DETECTOR B ON
DETECTOR C ON
DELETE RUN TBL
RUN TBL ON
RUN TBL ANNOTATION ON
RUN TIME    0.01 VALVE 9 ON
RUN TIME    0.02 VALVE 9 OFF
RUN TIME    0.10 CHART SPEED 0.1
RUN TIME    0.50 VALVE 6 OFF
RUN TIME    0.50 VALVE 5 OFF
RUN TIME    0.55 OVEN TEMP 240
RUN TIME    3.00 CHART SPEED 1
RUN TIME   13.25 CHART SPEED 0.1
RUN TIME   20.00 VALVE 6 ON
RUN TIME   20.05 VALVE 5 ON
RUN TIME   25.00 STOP
SIGNAL C DEVICE0 12
SIGNAL ON DEVICE0 12
STOP PLOT DEVICE0 12
CHART SPEED 1.00 DEVICE0 12
ATTN 217 DEVICE0 12
%OFFSET 15 DEVICE0 12
ZERO ON DEVICE0 12
SIGNAL B DEVICE0 20
SIGNAL ON DEVICE0 20
STOP PLOT DEVICE0 20
ATTN 290 DEVICE0 20
%OFFSET 0 DEVICE0 20
ZERO ON DEVICE0 20
INTG SIGNAL C
TIME OFF
RUN TIME ANNOTATION ON
OVEN TEMP EQUIB TIME 1.00
DELETE TIME TEMP
VALVE 5 OFF
VALVE 6 OFF
VALVE 9 OFF
PEAK WIDTH 0.04
THRESHOLD 1
REPORT ON DEVICE0 0
REPORT ON
REPORT ANNOTATION ON
DELETE REPORT TBL
REPORT TIME    0.10 AREA SUM ON
REPORT TIME    3.75 AREA SUM OFF
REPORT TIME    6.25 AREA SUM ON
REPORT TIME    8.85 AREA SUM OFF
REPORT TIME    9.95 AREA SUM ON
REPORT TIME   10.10 AREA SUM OFF
REPORT TIME   13.25 AREA SUM ON
AREA
DELETE CALIB
EDIT CALIB -7
EDIT CALIB 0.1
EDIT CALIB -1.5
EDIT CALIB -2.5
EDIT CALIB -3.0
EDIT CALIB -4.--
EDIT CALIB -0.0
```

Instrument: Hewlett Packard 5890A with dual capillary inlets and dual ⁶³Ni electron capture detectors, with autosampler

Column: 25m HP Ultra #2, wide bore, thick phase, 5% phenyl methyl silicone

AN ANALYTICAL METHOD FOR THE ANALYSIS OF CHLORINATED BIPHENYLS IN LIQUIDS AND SOLIDS

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This is a gas chromatographic/electron impact mass spectrometric (GC/EIMS) method applicable to the determination of chlorinated biphenyls (PCBs) in liquid or solid samples of environmental, human, or commercial origin. The PCBs may originate either as contaminants derived from commercial PCB products (e.g., Aroclors) or as synthetic by-products. The PCBs may include any of the 209 congeners from monochlorobiphenyl through decachlorobiphenyl and may be present as single isomers or complex mixtures.

The use of GC/EIMS yields qualitative information which not only readily differentiates among the PCB homologs but also permits elimination of other compounds from quantitation. The other common PCB analysis technique, GC/ECD, does not discriminate between PCBs and many common interferents. Thus, GC/ECD results are less reliable for complex matrices.

A variety of general and specific sample preparation options are presented in this method. In some cases, these options are taken from other standard procedures for PCBs. In other cases, no standard procedure exists and general guidance is given with appropriate literature references. This method takes a different approach from those which rely on Aroclor mixtures for calibration and quantitation. In this method PCBs are detected and quantitated by homolog group. The results can be summed to give a total PCB value comparable to results generated by other methods or they may be presented as 10 individual homolog values. This homolog distribution can provide additional quantitative information on the composition and source of the PCBs. For example, the relative homolog distributions may indicate how closely the sample resembles a commercial mixture.

The method consists of the following steps:

1. The process or product must be sampled such that the specimen collected for analysis is representative of the whole. Statistically designed selection of the sampling position, time, or discrete items should be employed where appropriate. The sample must be preserved to prevent PCB loss prior to analysis. Room temperature storage may be adequate for some samples if biological degradation will not occur. Otherwise, subambient storage is recommended; refrigeration for aqueous samples and freezing for all others.

2. The sample is mechanically homogenized and subsampled if necessary. The sample must then be spiked with four ^{13}C PCB surrogates (4-chloro-$^{13}C_6$-biphenyl; 3,3',4,4'-tetrachloro-$^{13}C_{12}$-biphenyl; 2,2',3,3',5,5',6,6'-octachloro-$^{13}C_{12}$-biphenyl; and decachloro-$^{13}C_{12}$-biphenyl) and the surrogates incorporated by further mechanical agitation.

3. The surrogate-spiked sample is extracted and cleaned up at the discretion of the analyst. Simple dilution or direct injection is permissible. Possible extraction techniques include liquid-liquid partition, liquid-solid partition, thermal desorption, and sorption onto resin columns followed by solvent desorption. Cleanup techniques may include liquid-liquid partition, sulfuric acid cleanup, saponification, adsorption chromatography, high performance liquid chromatography, gel permeation chromatography, or a combination of cleanup techniques. The sample is diluted or concentrated to a final known volume for instrumental determination.

4. The PCB content of the sample extract must be determined by high resolution (preferred) or packed column gas chromatography/electron impact mass spectrometry (HRGC/EIMS or PGC/EIMS) operated in the full scan, selected ion monitoring (SIM), or limited mass scan (LMS) mode.

5. PCBs are identified by comparison of their retention time and mass spectral intensity ratios to those in calibration standards.

6. PCBs are quantitated by the internal standard technique, using response factors for a mixture of 10 PCB congeners. The recoveries of four ^{13}C surrogates are used to monitor for losses in workup and determination.

7. The PCBs identified by the SIM technique may be confirmed by full scan HRGC/EIMS, retention on alternate GC columns, other mass spectrometric techniques, infrared spectrometry, or other techniques, provided that the sensitivity and selectivity of the technique are demonstrated to be comparable or superior to GC/EIMS.

8. The analysis time is dependent on the extent of workup employed. The time required for instrumental analysis of a single sample, excluding instrumental calibration, data reduction and reporting, is typically 30 to 45 min.

9. A quality assurance (QA) plan must be developed for each laboratory.

10. Quality control (QC) measures include laboratory certification and performance check sample analysis, procedural QC (instrumental performance, calculation checks), and sample QC (blanks, replicates, and standard addition).

The method is available through NTIS:

Erickson, M. D., J. S. Stanley, J. K. Turman, and G. Radolovich, "Analytical Method: The Analysis of Chlorinated Biphenyls in Liquids and Solids," U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC, EPA-560/5-85-023 (February 1985).

The work was supported by the U.S. Environmental Protection Agency under Contract No. 68-02-3938.

FIELD MEASUREMENT OF PCB'S IN SOIL AND SEDIMENT USING A PORTABLE GAS CHROMATOGRAPH

Thomas M. Spittler

INTRODUCTION

With the recent increase in activity at hazardous waste sites where cleanup and remedial action is underway, a need has emerged for rapid analaytical methods which can be used in the field. Often there is need to assess the impact and extent of contamination right in the field. This enables a sampling crew to collect meaningful samples for later laboratory analysis.

A second, more pressing need for field data is in the actual cleanup process. Where a problem has been identified and removal is planned, it is logistically difficult to perform adequate analytical work to direct a thorough cleanup prior to the actual cleanup operation. Few pollutants leave adequate visible traces to guide cleanup. Therefore, analytical work must often be performed during the cleanup operation to guide the contaminant excavation and subsequent removal process. Because removal and transportation of hazardous materials to a safe disposal site is often very costly, it would be preferable to remove only the contaminated materials and stop excavation when clean material or soil is finally reached. In order to achieve this end we have devised a field method for extraction and measurement of PCB's from soil and sediment which can be performed in as little as seven minutes after the sample is collected.

EQUIPMENT AND METHODOLOGY

While there are several serviceable small gas chromatographs on the market, we have found that the Model 511-06 made by Analytical Instruments Development is one of the most practical for field work. This instrument is equipped with a sensitive Electron Capture Detector and has a long history of reliable field operation both in our laboratory and elsewhere. A stainless steel column is held in a well-insulated isothermal chamber. If the column and oven are raised to 210 degrees Centigrade on AC power, the unit can maintain these conditions on battery power for a full eight-hour working day. However, it is usually possible to supply some alternative source of elelctrical power such as a battery-inverter supply or a portable generator. Overnight charging of the Ni-Cad batteries will prepare the unit for an 8-hour workday.

The unit has three lecture bottles stored in the power pack base and these can quite easily be manifolded together to supply carrier gas for several days of field operation. Again, an auxiliary carrier gas bottle of moderate capacity is adviseable for longer field use. Overnight charging of the Ni-Cad battery pack will prepare the unit for an 8-hour workday.

For general field use we employ a 3 or 4-foot x 1/8" stainless steel column packed with 3% SE-30 on 80/100 mesh chromosorb W-HP. The column is held at about 200 - 215 degrees centigrade, depending on the particular Arochlor which is to be analysed. Adjustment of temperature and carrier flow as well as proper choice of column length can provide rapid elution of even Arochlor 1260 in as little as seven minutes. Injections are typically made using 1-3 ul of the hexane extract of a soil, sediment or standard sample.

FIELD EXTRACTION TECHNIQUE

A field sample is prepared for analysis as follows. Depending on soil homogeneity, 100 - 400 mg of soil is used for analysis. Typically, 200 mg of soil is weighed (or estimated by volume when high accuracy is not important) and placed in a 2 cc septum vial. To the soil sample are added sequentially 100 ul of water, 400 ul of methanol and 500 ul of hexane. The sample is then agitated for about 60 seconds. This is easily achieved in the field by holding the vial to the tip of a vibrating engraver .

RESULTS AND DISCUSSION

This method has been applied in the field at several PCB spills and cleanup operations. Results of some of this work will be discussed. Also, several samples were analysed by the field technique and then subjected to standard PCB analytical procedures in our laboratory. Finally, a study is underway to more accurately determine the extraction efficiency of the field method on different Arochlors. Results of this work will also be reported at the seminar.

DISTRIBUTION OF POLYCHLORINATED BIPHENYLS WITHIN BONNEVILLE POWER ADMINISTRATION SUBSTATIONS

David W. Baker

INTRODUCTION

The Bonneville Power Administration (BPA) is a federal power distribution and marketing agency for some 30 hydroelectric dams in the Columbia River Basin. The BPA transmission system interconnects public and private electrical utilities in the Pacific Northwest and consists of about 14,200 circuit miles of high voltage transmission lines and approximately 450 substations. BPA also supplies direct service to aluminum reduction plants and other industrial customers with high power loads.

The electrical industry began using polychlorinated biphenyls (PCBs) in capacitors, transformers, and other equipment in 1929 with production continuing until about 1977. The persistence of PCBs in the general environment has created a national concern regarding the impact of these bioaccumulating chemicals both to public health and to sensitive ecological systems. As a result, a voluntary cooperation agreement was recently entered into by BPA with the Environmental Protection Agency (EPA) for the purpose of clarifying mutual responsibilities and commitments for conducting actions required and authorized by the Toxic Substances Control Act (TSCA), PCB Regulations, and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Provisions under this agreement include the implementation of a testing program to determine the extent that soils in BPA facilities have been contaminated over the years by equipment leaks and failures. Because very few Askarel transformers (PCB's over 500 ppm) were used within the BPA system, emphasis of this soil survey is toward the 85 substations where PCB capacitors are now, or have in the past been, in service.

APPROACH AND OBJECTIVES

Sampling procedures and analytical requirements developed to carry out this testing program are presented in the companion report. With hundreds of samples needed to fully characterize an average substation, certain assumptions regarding PCB soil contamination patterns were made to reduce testing requirements. To confirm the validity of these assumptions and their use in sampling plans for the 85 substations, 13 BPA substations were sampled extensively. Type and size of electrical equipment, maintenance history, environmental setting, and past construction practices were factors considered in selecting these substations.

This paper is intended to provide insight into overall PCB soil contamination patterns within fenced BPA substations based on a continuing PCB study which is about one third completed. Results are included on the 13 substations identified for comprehensive sampling and the findings from these substations are reviewed in detail. A total of 15 substations, analyzed according to the reduced sampling protocol, are now completed along with 26 other BPA substations sampled in specific areas for construction projects. This report will not cover those substations tested for construction purposes or those sampled under the reduced plan. Levels of soil contamination will be considered in relation to the general equipment locations within the substations and maintenance history, in order to check basic assumptions used in developing the reduced sampling plans.

It is important to remember that this survey focuses on presenting a worst case scenario for PCB contamination within fenced BPA substations. Samples include those taken from capacitor areas which are generally inaccessible, but traditionally show high levels of PCB contamination (e.g., soil adjacent to capacitor house pads and locations beneath rack-mounted capacitors) and sites used in the past for temporary storage of failed capacitors. Sampling plans and instructions to samplers also call for preferential collection of soil with visual evidence of past oil spills. Sampling is also selective towards oil-filled equipment, such as distribution and metering transformers, known to contain the highest PCB concentrations.

OVERALL RESULTS AND DISCUSSION

Extensive sampling was performed on the following substations to form foundational information on PCB distribution patterns in soil:

BPA Substation	No. PCB Caps	No. Small Oil Filled Equip.*	No. Large Oil Circuit Breakers	No. Power/ Converter Transf.	Total No. Soil/Core Samples
Albany	1782	33	12	7	38
Anaconda	2178	40	7	6	29
Bell	12663	189	35	22	315
Big Eddy	1998	109	12	34	33
Longview	8178	129	34	12	103
Maple Valley	3246	70	9	7	49
McNary	0	77	14	25	33
Olympia	2667	79	21	13	62
Port Angeles	1065	74	17	7	50
Rose	7628	120	31	15	101
Snohomish	3021	108	30	16	59
St. Johns	1764	69	23	11	66
Troutdale	5814	118	18	19	149

Test results for the 13 substations tested under the initial phase of this survey are summarized below:

PCB Contamination Level	Surface Soils (0 to 6")	Soil Cores (Below 12")	Sediment Samples	Total Samples
Less than 1 ppm	468 (66.1%)	283 (89.3%)	31 (50.0%)	782 (71.9%)
1 to 4.9 ppm	148 (20.9%)	17 (5.4%)	17 (27.4%)	182 (16.7%)
5.0 to 49.9 ppm	61 (8.6%)	16 (5.0%)	13 (21.0%)	90 (8.3%)
50 to 499 ppm	10 (1.4%)	1** (0.3%)	0 (0.0%)	11 (1.0%)
Over 500 ppm	21 (3.0%)	0 (0%)	1 (1.6%)	22 (2.0%)
All Concentrations	708	317	62	1087

*Includes distribution/metering transformers and oil circuit breakers less than 69 kV.

**Single core sample exceeding 50 ppm (283 ppm) was from Bell Substation at drill site near capacitor house.

The results from 708 surface soil samples indicate that most (95.6 percent) of the substation locations contain less than 50 ppm PCBs, with two-thirds of these sites having less than 1 ppm. Of the 317 samples taken below the soil surface (12" or more) only 1 (0.3 percent) had more PCBs than the 50 ppm regulatory level. The higher number of sediment samples with 1 to 49 ppm contamination is consistent with the property of PCBs to tightly bind to organic fines which in turn tend to collect in quiescent environments such as electrical manholes and oil/water separator tanks. Overall surface soil and sediment results for the individual facilities tested are given in Table No. 1.

PCBS IN CAPACITOR AREAS

The test results for selected substations having extensive sampling have shown that the highest level of PCB contamination is in locations adjacent to capacitor banks, and of these areas the highest levels are associated with enclosed capacitor houses. Older direct customer service substations, such as Longview, Bell, St. Johns, and Troutdale had certain vintages of lower voltage capacitors which were more prone towards violent failure or leakage. Clean-up of spills within these enclosures is difficult and led to practices which either spread PCBs directly (steam cleaning), or left enough compound within the structure to eventually flow into the soil outside the house. Initial test results have shown that the soil next to capacitor house foundation pads may have extremely high concentrations of PCBs (mostly Aroclors 1242 and 1254). At this point PCBs could be readily tracked by workmen to other substation areas. One example of this phenomena is shown by three Rose Substation sidewalk samples, taken in an area with no history of capacitors or contaminated (over 50 ppm PCBs) oil-filled equipment, showing between 5 and 9 ppm of Aroclor 1242. Apparently, operator personnel caused this pattern of contamination by their daily rounds through contaminated areas.

Fenced capacitor yards with a history of failures will of course have concentrated PCB compound in the soil directly below the capacitors involved, but limited access reduces spread by foot traffic. Core samples (which we define as soil collected deeper than the 0 to 6 inch surface samples) have shown that concentrations of PCBs drop off rapidly with depth, indicating that the contamination appears to be contained at the surface soil through strong

adsorption. An exception was a single core sample exceeding 50 ppm which was from the Bell Substation at a location near a 13.8-kV capacitor house. The sample was taken at 12 inches and tested at 283 ppm. Deeper cores for this drill site at 5, 10, 20, and 25 feet were found to contain 1.04, 39.3, 3.28, and 0.18 ppm PCBs respectively.

Past maintenance practices which included storing ruptured cells at convenient locations (usually near the gate for fenced capacitor yards) no doubt has contributed to contamination beyond restricted access areas. This is illustrated by two samples from Longview Substation, collected next to gates leading to capacitor yards, which were tested and found to have 28,500 ppm (1254) and 22,100 (1242) ppm PCBs.

Results for the capacitor locations in the 13 substations are summarized in Table No. 2. In the case of McNary Substation, no data is shown since this facility has never had capacitors. For those BPA substations with rack-mounted capacitors, most could not be sampled within the fenced capacitor yards because of the reduced electrical clearance during operation. Surface soil PCB contamination profiles, based on 83 and 133 samples from capacitor houses and fenced yard areas respectively, are illustrated in Figure 1. Of these 216 samples more than half (55.6 percent) contained less than 1 ppm PCBs and 86.1 percent were less than the 50 ppm regulatory level.

PCBS IN OIL-FILLED EQUIPMENT AREAS

In addition to PCBs from capacitor cells, another source of soil contamination within substations is from oil-filled equipment. For purposes of assessment, sample data from lower voltage (69 kV and below) areas is being considered separately from those of higher voltages. Of course, within a 230-kV yard, for example, there is often lower voltage metering and station service transformers which typically contain much higher PCB levels than the major breakers or power transformers. As mentioned earlier, a critical element of this survey is to take these factors into account and to preferentially collect samples from sites most likely to have significant contamination. The information developed on the group of 13 substations is summarized in Table 3. This data suggests (see Figure 2) that the lower voltage oil-filled

equipment areas are more contaminated by PCBs than the 115-kV (and above) locations but the limited number of samples for the 69-kV and below areas make this conclusion statistically invalid, as does the overwhelming influence by one facility to this data. It is clear, however, that oil-filled equipment sections within BPA substations are significantly less contaminated than capacitor areas. Only one substation of the 13 showed high PCB levels in surface samples collected near oil-filled equipment (as opposed to seven for capacitor bank locations). The exception was a single Longview sample which contained 1070 ppm PCBs identified as Aroclor 1248. Not withstanding, the sample serves to illustrate the fact that although this survey may provide valuable insights into the extent of PCB contamination within substations, there is always the possibility of undetected hot spots.

SEDIMENT SAMPLES

Although PCBs have a very low solubility in water, they are known under certain circumstances to migrate in runoff water while tightly bound to organic "fines." The analysis of sediments found in electrical manholes and oil water separator tanks, could provide a diagnostic tool related to past levels of substation contamination. Average PCB results for the 62 sediment samples collected from 8 of the 13 substations are presented in Table 1.

PCBS IN OTHER SUBSTATION AREAS

Surface samples from bulk oil storage locations within BPA substations appear to have similar PCB soil contamination levels as the oil-filled equipment areas. The 39 samples collected from 8 of the 13 substations, had no results above 50 ppm and 28 percent between 1 and 49 ppm as shown in Figure 3.

Core samples were taken at two of the substations around oil storage tanks because these areas may have been subjected to spills over the years. Bell substation was extensively sampled in the oil storage area with a total of 12 holes drilled, most of them reaching 50 feet in depth. One drill site showed

heavy oil contamination with fairly low PCB levels down to approximately 15 feet, a maximum of about 6 ppm appearing at 6 feet. However, deeper than 15 feet saw an increase to a maximum of 43 ppm at 30 feet. Below this the PCBs drop off to a minimum of 0.09 ppm at 50 feet. The other core samples showed some agreement but did not have the PCB levels of the described site. It should be noted that the soil is glacial moraine and is thought to account for the depths of penetration. The other substation sampled below surface near oil storage tanks was Port Angeles. Analysis of the soil at the two sample sites showed 0.02 and 0.04 ppm at the surface, and 0.14 and 0.26 ppm at 18 and 16 inches respectively. These results suggest that further work is needed to characterize below surface contamination around oil storage locations.

Surface samples taken in substation areas away from existing or past electrical equipment and storage tanks are referred to as background samples. The sample category diagram (refer to Figure 3) shows less PCB contamination than other substation locations.

CONCLUSIONS

Sampling parameters identified for this system-wide PCB soil survey appear to be valid based on reviewing 1087 sample results from 13 substations. Movement of PCBs away from areas of highest expected contamination (e.g., PCB capacitor installations) has been shown to be limited both horizontally and vertically through the soil. Contamination levels have been demonstrated to be predictable based on the general location within the substation with highest contamination associated with capacitor installations. Tests to date, with very few exceptions, have not shown PCB contamination to exist above the 50 ppm level outside capacitor use areas in BPA substations. Oil contaminated soil samples associated with higher voltage equipment (115 kV and above) appear to have lower contamination than samples collected near lower voltage (69 kV and below) equipment but additional work is needed to confirm this.

Table No. 1
Surface Soil (0 to 6 Inches Depth) and Sediment Results for 13 Substations Tested

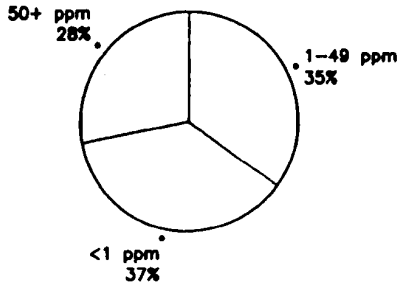
Substation	Total No. Surface Samples	Samples ≥ 50 ppm PCBs	Samples 1 to 49.9 ppm PCBs	Samples < 1 ppm PCBs	Total No. Sediment Samples	Sediment Sample Averages	Type Capacitor Installations
Albany	31	0%	6.5%	93.5%	0	-	Fenced Racks Only
Anaconda	29	6.9%	51.7%	41.4%	0	-	Fenced Racks Only
Bell	96	8.3%	16.7%	75.0%	1	32.5 ppm	Houses and Fenced Racks
Big Eddy	33	0%	3.0%	97.0%	1	ND	Fenced Racks Only
Longview	80	7.5%	63.8%	28.8%	22	4.68 ppm	Houses and Fenced Racks
Maple Valley	44	0%	6.8%	93.2%	5	0.03 ppm	Fenced Racks Only
McNary	33	0%	6.1%	93.9%	0	-	None
Olympia	57	1.8%	28.1%	70.2%	5	0.26 ppm	Fenced Racks Houses Previously
Port Angeles	36	5.6%	11.1%	83.3%	0	-	Fenced Racks Only
Rose	101	3.0%	42.6%	54.5%	1	8.6 ppm	Houses and Fenced Racks
Snohomish	50	0	0	100%	10	0.36 ppm	Fenced Racks Only
St. Johns	48	2.1%	83.3%	14.6%	0	-	Houses
Troutdale	70	11.4%	22.9%	65.7%	17	7.87 ppm	Houses and Fenced Racks

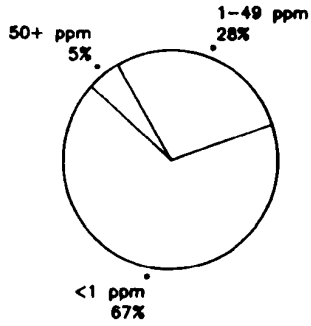
Table No. 2
Surface Soil (0 to 6 Inches Depth)
Results in Relation to General Substation Locations

BPA Substation	Enclosed Capacitor House Areas				Fenced Capacitor Rack Areas			
	Samples in PCB Category			Total No.	Samples in PCB Category			Total No.
	≥ 50 ppm	1 to 49.9	< 1 ppm		≥ 50 ppm	1 to 49.9	< 1 ppm	
Albany	-	-	-	0	0	0	4. 100%	4
Anaconda	-	-	-	0	2 14.3%	8 57.1%	4 28.6%	14
Bell	7 29.2%	3 12.5%	14 58.3%	24	1 5.3%	9 47.4%	9 47.4%	19
Big Eddy	-	-	-	0	0	0	6 100%	6
Longview	3 37.5%	4 50%	1 12.5%	8	2 25%	4 50%	2 25%	8
Maple Valley	-	-	-	0	0	0	16 100%	16
McNary	-	-	-	0	-	-	-	0
Olympia	1 11.1%	3 33.3%	5 55.6%	9	0	1 9.1%	10 90.9%	11
Port Angeles	-	-	-	0	2 25%	2 25%	4 50%	8
Rose	3 30%	6 60%	1 10%	10	0	11 55%	9 45%	20
Snohomish	-	-	-	0	0	0	13 100%	13
St. Johns	1 12.5%	5 62.5%	2 25.0%	8	-	-	-	0
Troutdale	8 33.3%	8 33.3%	8 33.3%	24	0	2 14.3%	12 85.7%	14
Total	23 27.7%	29 34.9%	31 37.4%	83	7 5.3%	37 27.8%	89 66.9%	133

Table No. 3
Surface Soil (0 to 6 Inches Depth)
Results in Relation to General Subetation Locations

BPA Substation	Oil Filled Equipment Areas ≤ 69 kV Samples in PCB Category			Total No.	Oil Filled Equipment Areas ≥ 115 kV Samples in PCB Category			Total No.
	≥ 50 ppm	1 to 49.9	< 1 ppm		≥ 50 ppm	1 to 49.9	< 1 ppm	
Albany	0	0	2 100%	2	0	2 12.5%	14 87.5%	16
Anaconda	-	-	-	0	0	4 40%	6 60%	10
Bell	-	-	-	0	0	2 5.4%	35 94.6%	37
Big Eddy	-	-	-	0	0	1 4.3%	22 95.7%	23
Longview	-	-	-	0	1 4.2%	14 58.3%	9 37.5%	24
Maple Valley	-	-	-	0	0	3 10.7%	25 89.3%	28
McNary	0	0	1 100%	1	0	1 3.7%	26 96.3%	28
Olympia	-	-	-	0	0	9 30%	21 70%	30
Port Angeles	0	0	4 100%	4	0	2 18.2%	9 81.8%	11
Ross	0	0	8 100%	8	0	22 41.5%	31 58.5%	53
Snohomish	-	-	-	0	0	0	32 100%	32
St. Johns	0	9 100%	0	9	0	18 85.7%	3 14.3%	21
Troutdale	-	-	-	0	0	6 28.6%	15 71.4%	21
Total	0 0%	9 37.5%	15 62.5%	24	1 0.3%	84 25.2%	248 74.5%	333

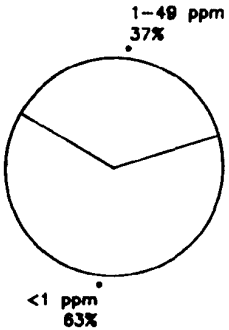


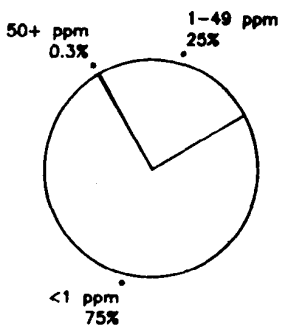


ENCLOSED CAP. HOUSES
(83 SAMPLES TOTAL)

FENCED CAP. RACKS
(133 SAMPLES TOTAL)

(FIG. 1) GENERAL SUBSTATION SURFACE SOIL SAMPLES (0"-6") IN EACH PCB CATEGORY

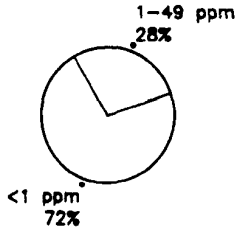




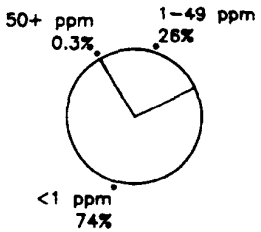
OIL FILLED EQUIP. ≤69kV
(24 SAMPLES TOTAL)

OIL FILLED EQUIP. ≥115kV
(333 SAMPLES TOTAL)

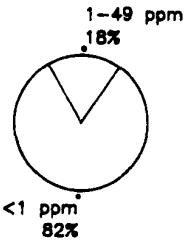
(FIG. 2) GENERAL SUBSTATION SURFACE SOIL SAMPLES (0"–6") IN EACH PCB CATEGORY



OIL STORAGE AREA
(39 SAMPLES TOTAL)



OIL FILLED EQUIP. AREA
(357 SAMPLES TOTAL)



BACKGROUND SAMPLES
(56 SAMPLES TOTAL)

(FIG. 3) GENERAL SUBSTATION SURFACE SOIL SAMPLES (0"–6") IN EACH PCB CATEGORY

PART 5:

SPILL CLEANUP

PILOT PLANT STUDIES FOR SOLVENT EXTRACTION OF POLYCHLORINATED BIPHENYL (PCB) FROM SOIL

M. B. Saunders

"Soilex" is a process for the solvent removal of PCB from soils. PCB will be transferred from the soil to the solvent phase when the two are mixed together. Kerosene and water were determined to be the solvent of choice. Kerosene can be recovered for recycle by steam-stripping. The mixing study was initiated to determine the importance of component (soil-water-kerosene) variables and mixing time. A pilot plant was operated, and results are reported.

Soil-to-water ratios of 3 to 5 and soil-to-kerosene ratios of 3 to 5 are best. No difference in extraction performance could be determined between 15 and 30 minutes mixing times. The kerosene retention in the soil was about 25 vol %. A three-stage batch pilot operating with a 6 to 1 volume ratio experienced soil feed PCB concentrations of 300 mg/L and discharge soil levels of 10-15 mg/L. Lower soil values could be obtained using additional stages.

The soil contaminated with 300-600 mg/L PCB also has a high concentration of oils and tars, resulting in a total organic carbon concentration of 10-20%. The PCB and oil was solubilized using the kerosene leaching solvent. Water was also added to the solvent mixture to help break up the soil particles. About 25-30 wt % kerosene was absorbed into the leached soil.

The PCB extraction from the soil as a function of soil-water-kerosene ratios and the mixing times were performed. The purpose of these tests was to define areas of acceptable operation. In order to minimize operation and equipment cost, the water and kerosene-to-soil ratios must be as low as possible. The data indicates that a water-to-soil less than 1.0 and/or a kerosene-to-soil ratio less than 1.0 fall into

an area which does not have enough fluid to allow for adequate mixing and, therefore, not acceptable for operation. A ratio of water-to-soil and kerosene-to-soil greater than 5.0 requires processing a high volume of material. A ratio of 3.0 to 5.0 for the water-soil ratio and kerosene-soil ratio resulted in a system having good hydraulic mixing characteristics and yielded a PCB leaching percentage of 84%.

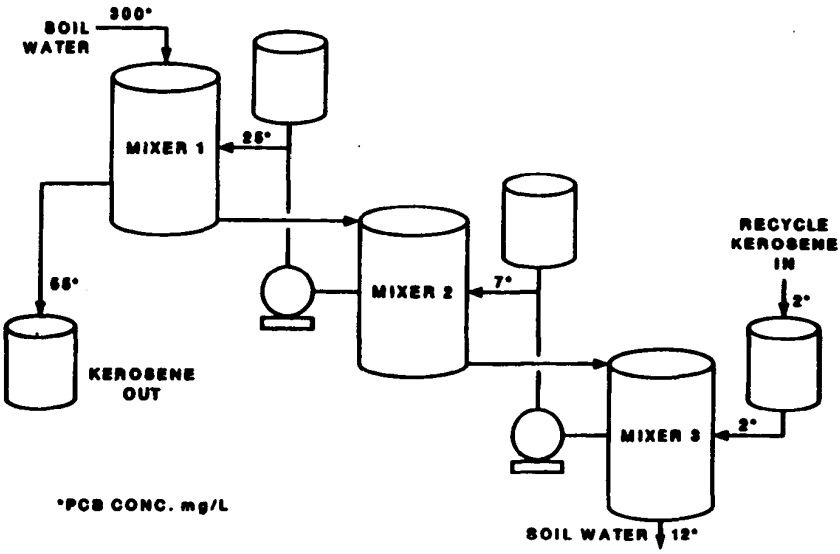
The pilot plant (Fig. 1) consists of three stages of mixing equipment. The plant is operated in a counter-current mode; soil and water are added to Stage 1 and clean kerosene to Stage 3. Each mix tank has a 200-L capacity and an air-driven mixer. An interstage solvent pump and a 120-L solvent-hold tank allows the kerosene to be transferred in a counter-current mode. The distillation-packed column system was 7.6 cm in diameter by 2.4-m long with an 18 L steam-heated reboiler and product condenser (See Fig. 2). The distillation unit was used to steam-strip the recyclable kerosene from the other oils and PCB.

The pilot plant is a one-day batch-cycle operation. Each day the solvent is pumped from each of the three mix tanks to their solvent-hold tanks. The water-soil mixed phase is transferred by gravity to the next stage, untreated soil and recycle water to Stage 1, and fully treated soil and water are discharged from Stage 3. The kerosene is then drained from the hold tanks to the next lower numbered mixer. The transfer operation takes about three hours to complete. The tanks are mixed for four hours. Samples removed from the mix tanks at 30-minute intervals indicate that tha mix tanks are at staady-state after 90 minutes. After mixing has been stopped, the mix tanks are allowed to phase-separate for 16 hours, thus consuming one day per batch.

The pilot plant was operated for 19 batch days. Successful steady operation was obtained after four days. A 25-L batch of PCB and oil from the solvent-extraction pilot plant was steam-stripped to recover the kerosene in three hours, using 500 mL/min of water feed to the boiler operating at 110°C. Twenty-two liters of kerosene were recovered at a PCB concentration less than 5 mg/L. The PCB was concentrated to 15 mg/L.

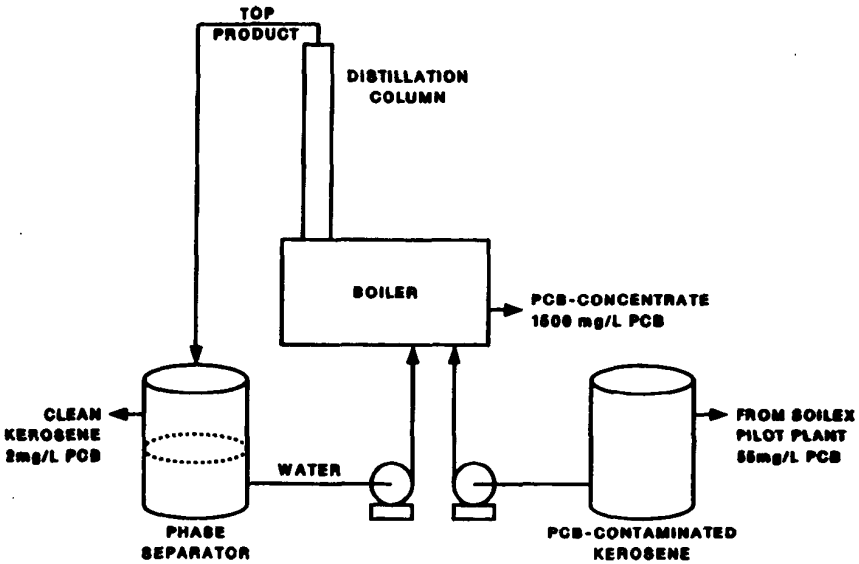
A preliminary cost estimate of the entire solvent leach and PCB removal from soil process has been completed. This cost estimate shows a very small (two to five) percentage of the total operating cost results form the loss of 25% of the kerosene to the soil phase. The cost estimate also compares cost of the solvent extraction process to direct incineration of the PCB-contaminated soil. The solvent extraction process cost was about half of the direct incineration cost.

SOILEX PILOT PLANT



MONS 018944

SOILEX STEAM DISTILLATION UNIT



POLYCHLORINATED DIBENZOFURAN CONTAMINATION OF THE STATE HIGHWAY DEPARTMENT OFFICE BUILDING IN SANTA FE, NEW MEXICO AS A RESULT OF A PCB TRANSFORMER MALFUNCTION

Fred L. DeRoos, Susan C. Watson, and Joseph A. Hatchel
Battelle Memorial Institute
Columbus, Ohio 43201 USA

INTRODUCTION

On June 17, 1985, an electrical malfunction occured in the New Mexico State Highway Department Office Building in Santa Fe, New Mexico. A transformer containing 245 gallons of Askarel consisting of Aroclor 1260 (87%) and a mixture of tri- and tetrachlorinated benzenes (13%) overheated resulting in the release of vaporized Askarel through the safety valve. The duration of the release is unknown, however it continued for at least 65 minutes after initial detection until the transformer was de-energized. Although there was no fire, charred paint on the transformer casing indicated that the casing may have reached a temperature of approximately 300 °C. Examination of the transformer and metal analyses of the coolant indicated that arcing had not occured.

The State Highway Department Office Building is a two story building of approximately 70,000 ft^2 connected to an annex building of approximately 30,000 ft^2. The Askarel vapor was distributed throughout the building by convective air currents and by mechanical transfer via the heating, ventilation, and air conditioning systems. In some areas, such as those adjacent to or above the transformer vault, the Askarel vapor condensed when it reached cooler surfaces and "rained" onto the floors and horizontal surfaces.

INITIAL CONTAMINATION LEVELS

Air and surface wipe samples, as well as coolant fluid samples, were collected within seven days of the malfunction. The airborne concentrations of PCBs in the transformer vault were approximately 42 $\mu g/m^3$. The PCB concentration ranges in the rest of the main building were:

Other Basement Areas	0.3-26 $\mu g/m^3$
First Floor Areas	1.0-19 $\mu g/m^3$
Second Floor Areas	0.7-6 $\mu g/m^3$

The total concentrations of polychlorinated dibenzofurans (PCDF) in the air ranged from approximately 10 to 500 pg/m^3 with the tetrachlorinated dibenzofurans (TCDF) ranging from approximately 1 to 55 pg/m^3. Although polychlorinated dibenzo-p-dioxins (PCDD) were detected in the range of 7 to 21 pg/m^3, no tetrachlorodibenzo-p-dioxins (TCDD) were found. The surface concentrations of PCBs were as high as 280,000 $\mu g/100\ cm^2$ in the basement areas. The highest PCB surface concentrations in the first and second floor areas were 98,000 $\mu g/100\ cm^2$ and 190 $\mu g/100\ cm^2$ respectively.

POTENTIAL PCDF INTERFERENCE

During the analyses of samples which were collected following the cleanup of the building, it was noted that the PCDF isomer elution patterns were not typical of PCB fire samples. This is illustrated by the heptachlorodibenzofuran (Hepta-CDF) elution patterns shown in Figures 1A and 1B. The heptachlorodibenzofuran chromatogram from the Santa Fe sample, Figure 1A, contains additional peaks as compared to the chromatogram from a sample from Tulsa, Oklahoma, Figure 1B. Since high levels of polychlorinated diphenylethers (PCDE) can interfere with PCDF analyses, selected extracts from the Santa Fe site were screened for PCDE. As can be seen in Figures 2A,B, 3A,B, and 4A,B, PCDE isomers account for a significant percentage of the observed PCDF response. Standard analyte enrichment procedures remove the majority of the PCDE isomers, however high levels of PCDE can result in residual concentrations in the final extract used for analysis.

Although PCDE isomers are commonly observed in biological samples, they are seldom seen in high concentrations in samples from soot producing PCB fires. The Santa Fe incident is somewhat unique in that it was a non-soot producing discharge of PCBs. It is postulated that the unique conditions of the Santa Fe incident, that is the relatively long term refluxing of the coolant, resulted in the conversion of a portion of the polychlorobenzenes to polychlorophenols. The chlorophenols then reacted with the remaining chlorobenzenes to produce the polychlorinated diphenylethers.

As a check, extracts from other PCB incidents, including Binghamton, NY, Boston, MA and Tulsa, OK were also screened for PCDE isomers. They were not detected in these samples. Several coolant fluids from in service transformers that were approximately 40 years old were found however, to contain relatively low levels of PCDE isomers. These low levels may have been produced slowly under normal in service conditions during the life of the transformer.

SUMMARY

An apparent difference in the levels of PCDE isomers in samples from soot producing and non-soot producing PCB incidents has been observed. Since the toxicity data that regulatory agencies use to select cleanup criteria are based on PCDD and PCDF levels, it is important to be certain that the detected levels do not result from interferences. It is recommeded that all PCDF analyses from non-soot producing PCB indicents include a PCDE screening to validate the PCDF identifications.

SANTA FE

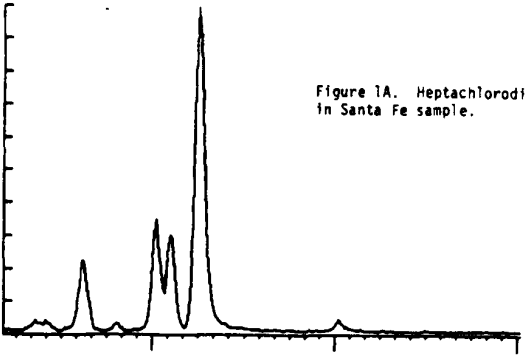


Figure 1A. Heptachlorodibensofurans in Santa Fe sample.

TULSA SAMPLE

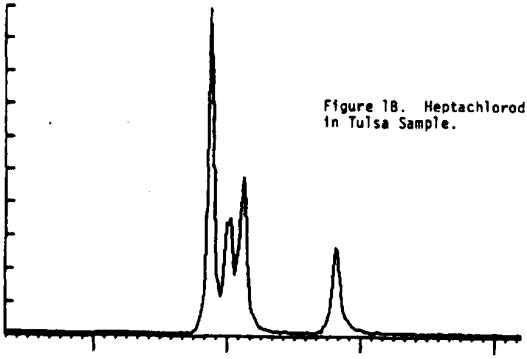


Figure 1B. Heptachlorodibensofurans in Tulsa Sample.

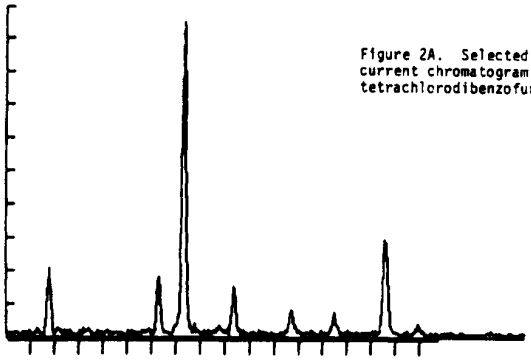


Figure 2A. Selected ion current chromatogram for tetrachlorodibenzofurans (m/z 305.899)

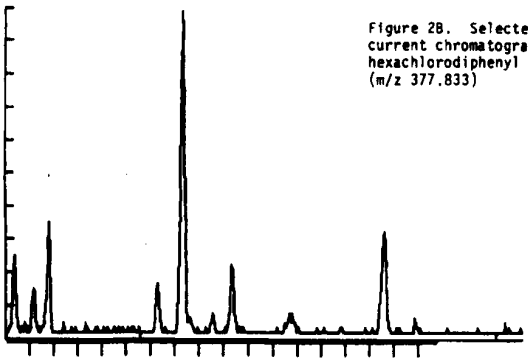


Figure 2B. Selected ion current chromatogram for hexachlorodiphenyl ethers (m/z 377.833)

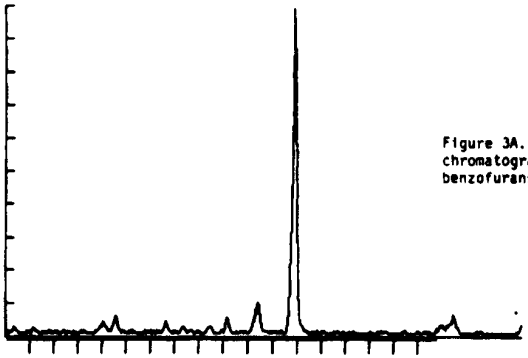


Figure 3A. Selected ion current chromatogram for pentachlorodibenzofurans (m/z 339.860)

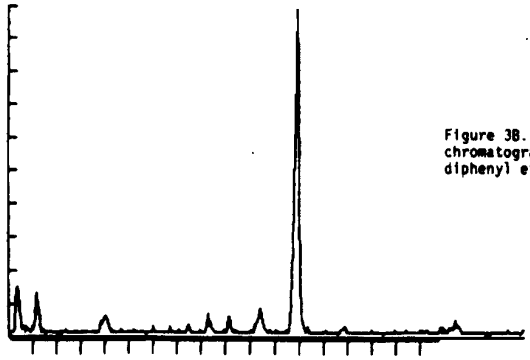


Figure 3B. Selected ion current chromatogram for heptachlorodiphenyl ethers (m/z 409.797)

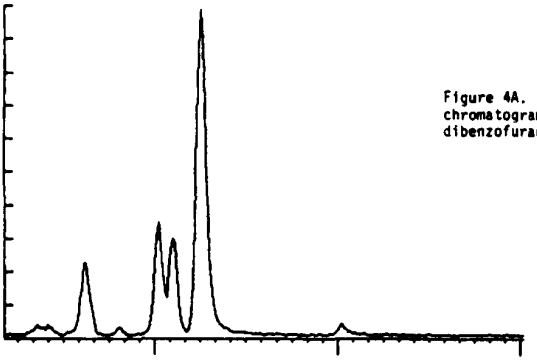


Figure 4A. Selected ion current chromatogram for heptachlorodibenzofurans (m/z 407.782)

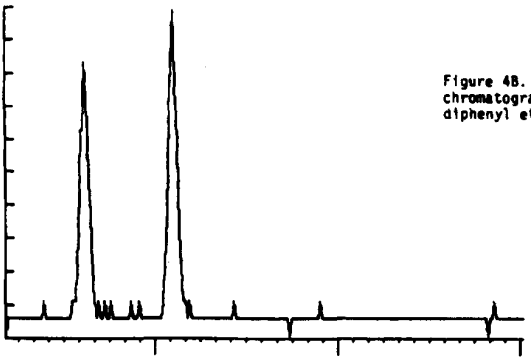


Figure 4B. Selected ion current chromatogram for nonachlorodiphenyl ethers (m/z 477.719)

DEVELOPMENT OF A SPRAY - VACUUM HEAD AND SUPPORT SYSTEM FOR THE REMOVAL OF PCB CONTAMINATION FROM WALLS, FLOORS, AND OTHER SURFACES

K. C. ASHLEY
QUADREX HPS INC.

Work is underway to develop equipment for field use by utilities to remove PCB dielectric fluid contamination from floors, walls, and related surfaces. Current techniques for such removal are both labor-intensive and time consuming and have varying degrees of effectiveness.

SURFACE CLEANING

One common approach involves scrubbing the surface with a selected detergent-water solution, followed by wiping the area with absorbent cloths. Wiping is important in this approach to thoroughly remove residual cleaning solutions (which now contain PCBs) from cracks, crevices, and other typical surface irregularities. Any residual liquid film or surface wetness of contaminated cleaning solution effectively limits the degree of surface decontamination that can be achieved. This phenomena of residual surface wetness is particularly evident with textured and porous surfaces such as unsealed concrete, cement, asphalt, etc.

A basic limitation of this static or batch-type of cleaning action is that as contaminants are removed from the surface, their concentration rises in the cleaning liquid. Alternately, a continuous flushing of the surface with uncontaminated cleaning liquid can be seen as a mechanism to significantly reduce the amount of contamination which may remain on the surface. However, a continuous flushing action necessitates some simultaneous method to remove the copious cleaning liquid. In addition, some support system is required to supply, store, and perhaps clean-up for recycle, the cleaning liquid.

TECHNOLOGY TRANSFER

The general problem of removing contaminants from surfaces challenges many industrial operations. These include semiconductor and computer manufacturing, aerospace, and nuclear materials processing.

Early engineering work by Quadrex HPS addressed the unique problem of removal of plutonium waste materials which coated the interior surfaces of a glove-box type assembly chamber. A prototype surface-decontamination system was configured which consisted of a cleaning head and support equipment.

Within the cleaning head were spray nozzles angled 30° from the surface; liquid Freon®-113 was pumped through the nozzles to provide continuous cleaning and flushing actions. The head had internal passages and a connection port for a source of vacuum. The edges of the cleaning head which contacted the contaminated surface, were designed so that the vacuum-induced in-flow of air prevented liquid leakage beyond the head. The vacuum removed contaminated cleaning liquid, flushing liquid, and dried the surface. The cleaning head was equipped with a trigger valve to control Freon® flow; the head was simply moved across the surface to achieve effective contaminant removal.

The support system (solvent storage, pumping, vacuum generation, vapor control and spent solvent handling) was specifically designed to handle radioactive materials, which meant that certain geometric and mass configurations must not occur anywhere in the system. These design restrictions do not apply to the handling of non-radioactive materials such as PCBs, thus providing the opportunity for design improvement and overall optimization.

DEVELOPMENT PROGRAM HIGHLIGHTS

The objective of this program is to develop equipment for the fast and effective removal of PCB contamination from various surfaces such as walls and floors. It is assumed that any free PCB liquids would have been removed prior to using this equipment.

The overall program has been divided into a series of fact-finding and development steps with review and assessment occurring at key stages. An initial key evaluation will be the effectiveness of the spray-vacuum head technique for surface PCB clean-up. Target clean-up levels for PCBs will be established. Surface sampling techniques will be evaluated, including the NIOSH method. Samples of various surfaces (brick, asphalt, concrete, cement, wood) which have both fresh and aged PCB liquid exposures, will be obtained. A literature search is included as well as a focused survey regarding current PCB clean-up practices, and current work by others whose results can be made available.

Two general types of cleaning liquids will be used in conjunction with the evaluation of the spray-vacuum head. These include Freon®-113 and water-detergent solutions. The effect of spray pressure for each selected cleaning liquid is being evaluated; two pressure ranges established are: 50± psi and 1000 to 2000 psi. For porous surfaces, core samples will be taken to profile cleaning effectiveness relative to substrate depth. An additional sample set will evaluate PCB leachback over time from the substrate, thus potentially recontaminating the surface.

Operator safety concerns include vapor or liquid releases, equipment control, airborne PCBs and conditions imposed by an actual application site, i.e., poor ventilation, nearby energized equipment, public exposure, etc.

The program's next development step addresses cleaning liquid recovery, processing, and possible PCB waste concentration. Three scenarios have been established for processing contaminated cleaning liquids:

1. local recovery, with purification and recycle at the site;
2. local recovery with purification occurring at some central location;
3. local recovery with disposal in lieu of purification.

EVALUATION CRITERIA

Evaluation criteria for the contaminated cleaning liquid processing (or disposal) alternatives include equipment acquisition and usage costs, overall costs, practicality, and technical feasibility.

Assuming the development program proceeds to this point, prototype equipment will be fabricated and shop tested. Suitable utility host sites will have been identified for field testing.

Field evaluation criteria include equipment portability and handling ease, surface decontamination and support system performance, and maintenance requirements.

PROGRAM GOALS

The broad goal of this program is to develop equipment and techniques of practical use to utilities. Clear user benefits of a successful prototype would include savings of clean-up labor, time, and overall costs. As this project progresses, we will be working with representatives of the user community to obtain input. We regard such input as essential for the development of equipment which would be broadly acceptable by the industry.

Sorption/Desorption of Polychlorinated Biphenyls in Soils

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Earth Sciences Department
Battelle, Pacific Northwest Laboratories

Polychlorinated biphenyls (PCBs) have found their way into a wide variety of industrial applications, a major one being coolant-insulation fluids in transformers. Because of the ubiquity and persistence of PCBs, the ability to 1) predict their long-term mobility in the soil-water environment and 2) describe their removal from contaminated soil via soil washing technologies, when remedial action is required, is of particular interest to the electric utility industry and regulatory agencies.

This paper summarizes, for both typical and low organic carbon (OC) soils, the adequacy of currently available data and estimation techniques and models for describing PCB sorption/desorption in soil-water systems. Deficiencies or gaps in available data and key unresolved issues are also discussed: 1) the reversibility of PCB sorption/desorption and 2) the extent to which sorption limits the mobility of PCBs in low OC soils. Soils for which the weight fraction of OC (f_{oc}) > 0.002 are operationally defined here as 'typical' OC soils, and soils for which f_{oc} < 0.001 are defined as 'low' OC soils. Finally, the effect of surfactants on Aroclor sorption in typical OC soils is briefly discussed.

ESTIMATION OF SORPTION PARAMETERS FROM PHYSICAL CONSTANTS

Typical OC Soils

Sorption of hydrophobic nonionizable organic compounds (HNOCs) such as PCBs at low environmental concentrations can be described by a linear isotherm model, where the amount of congener sorbed (S^i) is related to the equilibrium solution concentration (C^i) by a constant (K_p^i) termed the equilibrium partition coefficient,

$$S^i = K_p^i C^i \quad \text{or} \quad K_p^i = \frac{S^i}{C^i} \tag{1}$$

When describing the sorption of Aroclor mixtures, where the total analytical concentration of the PCBs sorbed (S_a) and in solution (C_a) are measured, the distribution ratio (K_d) is the appropriate

parameter for describing sorption and is defined as

$$K_d = \frac{S_e}{C_e} = \frac{\Sigma s^i}{C_e} = \sum_i K_p^i \left(\frac{C_e^i}{C_a}\right) \qquad (2)$$

Relatively few K_p data are available for individual PCB congeners; however, an abundance of K_d values (or its nonlinear equivalent, the Freundlich K_f) are available for various soil types [1]. This situation is unfortunate because K_d is not an appropriate parameter for describing mobility unless the K_ps for the major Aroclor congeners are known. The distribution ratio (K_d) is not appropriate for describing mobility because K_ps increase by many orders of magnitude with increasing chlorine number and thus the K_d changes as a PCB mixture moves through soil because of the chromatographic separation of congeners of differing chlorine number.

Based on extensive data for a wide variety of hydrophobic compounds (Log K_{ow} > 3 and water solubilities < 10^{-3} M) Karickhoff [2] concluded that soil organic carbon dominates observed variations in K_p for surface soils with f_{oc} > 0.001 to 0.002. Soil particle size distribution and expandable clay content (CM) in these soils are of secondary importance. Thus, to a first approximation, K_p is proportional to the weight fraction (f_{oc}) of organic carbon in the soil, i.e.,

$$K_p = K_{oc} f_{oc} \qquad (3)$$

where K_{oc} is the carbon-referenced partition coefficient; it is relatively constant over a wide range of soils.

For linear carbon-referenced sorption, regression equations of the form,

$$\text{Log } K_{oc} = a \text{ Log } K_{ow} + b \qquad (4)$$

have been extensively used in the literature, where K_{ow} is the octenol-water partition coefficient. The a and b correlation coefficient determined for various classes of hydrophobic compounds differ significantly [2-5]. It is strongly recommended that the coefficients for one class of compounds should not be used for another class [2]. These coefficients have not been explicitly derived for a series of PCB congeners; however, both Equations 3 and 4 should be applicable to PCBs.

Once the a and b coefficients and their limits of accuracy are established for a variety of soils, K_{oc} values and therefore K_p values for congeners for which no K_{oc} or K_p data exist, can be estimated from experimental [6] or calculated [7] K_{ow} values. Development of this information would represent a significant advance because K_{ow}s are far easier to measure than K_p values. It should be noted that K_p and K_{oc} are equilibrium coefficients. There is strong evidence that K_p values reported in the literature for PCB congeners and other HWOCs may not be equilibrium values and thus may be a factor of two to three lower than if equilibrium were reached. This evidence, in addition to the paucity of K_{oc} data, currently precludes determination of the a and b coefficients in Equation 4.

REVERSIBILITY AND RELEASE RATES FROM TYPICAL OC SOILS

The reversibility of PCB sorption in aqueous-soil systems is an important unresolved issue typified by conflicting information in the literature [8]. It is often reported for PCBs and HHOCs that both the sorption and desorption processes rapidly reach equilibrium, and that the overall process is reversible. Yet, others report, in addition to a rapidly released labile fraction (Q_L), the existence of a highly release-resistant 'nonlabile' or nonreversible fraction (Q_R), comprising 50% to 80% of the total sorbed PCB [9]. This resistant fraction is reported to require extended and often harsh extractions for complete removal of the sorbant from the solid phase [10,11,12]. These reports and others note that the quantity of this resistant fraction and the difficulty of its extraction usually increase with the duration of the sorption step. A key element in resolving these conflicting observations lies in the fact that for both sorption and desorption, the time required to reach equilibrium is much greater than commonly believed [2]. As a consequence, reported K_p values for PCBs may be as much as a factor of two to three too low [8].

From a practical standpoint, the question is whether this resistant fraction is truly fixed in the soil matrix, or whether a slow release of PCBs (via diffusion plus sorption/desorption) occurs over a span of months or years. For soils containing Aroclors, the questions to be addressed are 1) what are the relative quantities of sorbed PCB in the labile and resistant fractions (Q_L, Q_R); 2) what is the release rate of the labile fraction (k_L) from the soil; and 3) is the resistant fraction an artifact of not having reached equilibrium, and, if so, what is the release rate (k_L) from this fraction.

To directly address these questions, a gas stripping technique can be used on aqueous suspensions of PCB-contaminated soils. Using this technique, Q_L, Q_R, k_L, k_R, the reversibility, and the true equilibrium K_p values can be determined simultaneously for 30 to 40 of the major congeners in Aroclor mixtures that have sorbed onto soils. The gas stripping technique has been used to measure these parameters for several HHOCs from sediment [2,8,11]. The release rates, determined in this way, represent the upper limit or maximum release rates that could occur in a soil-water system. This information directly quantifies the significance of a given spill site as a PCB source term for subsequent migration in soil-water or aquifer-groundwater systems.

PCB SORPTION ON LOW ORGANIC SOILS

The quantity of OC in soils typically decreases rapidly with increasing depth. Thus, within a few meters of the surface, the weight function of OC can drop below 0.001. In addition, the OC fraction in subsurface aquifer materials often falls below this value. The sorption of HHOCs and PCBs on these low OC materials is not well understood. Few data exist in the literature for PCB sorption on low OC soils, and those available are for Aroclor sorption on pure clay minerals [1]. As a result, no bases exist for predicting the influence of sorption/desorption on the mobility of PCBs in these cases where PCBs may contact low OC soils and aquifer materials.

A well-tested predictive model equivalent to the carbon-reference model for HNOCs on typical OC soils does not exist for low OC soils. However, expandable clay minerals (e.g., smectites) are considered to be the major sorbent for HNOCs in low OC materials [3,13]. By analogy with the carbon reference model, it has been suggested [2] that K_p for low OC soils may be of the form $K_p = K_{cm} f_{cm}$ where f_{cm} is the weight fraction of expandable clay minerals in the soil, and K_{cm} is a clay-referenced partition coefficient. Whether K_{cm} is relatively constant for specific clay minerals in a wide variety of soils remains a question. Without some well-tested basis for describing PCB sorption in low OC soils, the movement of PCBs through low OC soils or aquifer materials cannot be estimated with any degree of certainty as the following hypothetical example demonstates.

Consider the retardation of hexachlorobiphenyl (2,4,5,2',4',5', $K_{oc} = 8 \times 10^5$) movement through a soil characterized by $f_{oc} = 0.0005$, 10% expandable clay, a porosity $n = 0.3$, and density $\rho = 2.6$ g/cm³. The retardation is given by

$$R = \frac{v}{v'} = \left(1 + \frac{1 - n}{n} \rho K_p\right) \qquad (5)$$

where R is the ratio of the water velocity (v) to the velocity of the advancing PCB front (v') [10]. If we make the questionable assumption that K_p can be estimated by the carbon-referenced $K_p = K_{oc} f_{oc} = 400$, then $R = 2.4 \times 10^3$. Given this R and a water velocity of 100 cm/d, we would expect PCBs to require approximately 700 years to move 100 meters. This estimate is based on the carbon reference model that we know does not apply to low OC soils [2]. Based on our current lack of information in estimating a K_p value for this low OC, 10%, clay soil, it is not unreasonable to postulate that the K_p used above could be in error by as much as a factor of ±50. In this case, the 100-meter transit time could be as low as 14 years or as high as 35,000 years. Thus, we currently have no basis with which to estimate the transport rate of PCBs in low OC soils. The point here is that additional information on HNOC/PCB sorption in low OC soils is clearly needed.

Effect of Surfactants on Aroclor Sorption/Desorption

Work by one of the authors [15] has demonstrated that Aroclor 1242 sorption from aqueous solution onto a soil containing 4% OC and 21% clay is significantly reduced in the presence of an anionic surfactant. As the concentration of this surfactant is increased, the sorption K_d steadily decreases. Surfactant concentrations examined were all well below the critical micelle concentration (cmc) at which a discrete immiscible phase (micelles) form.

In addition, the pH dependence of Aroclor 1242 sorption has been examined on an iron oxide commonly found in soils. In the absence of cationic or anionic surfactants, Aroclor 1242 sorption does not vary with pH. In the presence of either the cationic or anionic surfactant studied (below cmc), Aroclor 1242 sorption shows a strong pH dependence and is found to be completely reversible for sorption/desorption times on the order of days. The influence of surfactants on the release rates of the slowly desorbing or 'resistant' fractions of PCBs in soils has not as yet been examined.

These observations may have significant implications for aqueous-based soil-washing methodologies in which single- or mixed-biodegradable surfactants are used. Currently, work sponsored by the Electric Power Research Institute with this objective in mind is under way at Battelle Northwest to determine the influence of surfactants on PCB sorption/desorption and the release rates for soils that have been in contact with Aroclors for extended times.

SUMMARY

We have identified specific areas where additional sorption/desorption information related to the mobility of HNDCs and PCBs in soils would be useful to the electric utility industry and regulatory agencies. Specifically, these areas are 1) determination of K_p to K_{ow} correlation coefficients to enable use of extensive K_{ow} and other physical data for estimating of K_ps, 2) determination of the reversibility and release rates of Aroclors from soils in aqueous systems, 3) sorption/desorption in low OC soils, and 4) the influence of surfactants on sorption/desorption and desorption release rates of Aroclors from soils for possible application in aqueous-based soil-washing technology. Finally, it should be noted that although PCBs are important compounds to the utility industry, they also represent an ideal tool for investigating the important hydrophobic interactions that play a major role in the attenuation processes of other organic compounds that may be of current or future importance to the utility industry.

ACKNOWLEDGEMENT

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DESORPTION OF PCBs IN A SOIL-AQUEOUS SOLUTION SYSTEM

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The adsorption-desorption behavior of PCBs in soil-aqueous systems has generally only been examined using PCB concentrations well below their aqueous solubilities. The applicability of results obtained from these studies to accidental Aroclor spills from point sources such as transformers and capacitors and leaks from waste disposal sites are likely to result in localized PCB concentrations that far exceed their aqueous solubilities.

The objectives of this study were to characterize the partitioning of capacitor oil Aroclor 1242 between soil and aqueous equilibrium bathing solutions over a wide range of PCB concentrations. PCB behavior was examined as a function of homolog type and as a function of aqueous solution composition. The results obtained are expected to provide greater insight into the environmental behavior of the various PCB homologs and to provide usable data to predict the mobility of PCBs in environments exposed to accidental Aroclor spills.

Subsamples of a California soil (Linné silty clay loam, 2.4% O.M., 33.4% clay), were treated with Aroclor 1242 to impart the following Aroclor concentrations: 0, 25, 50, 100, 250, 500 or 1000 mg Aroclor-kg^{-1}. Desorption studies were performed by equilibrating 5 grams of Aroclor treated soil with 50 ml of either (1) deionized water (DW), (2) 0.01 M $CaCl_2 \cdot H_2O$, or (3) California Waste Extraction Test Solution (WET) consisting of 0.2 M citrate and 0.15 M NaCl adjusted to pH 4.5. Solutions (1) and (2) were used to characterize the behavior of PCBs in soil as a result of precipitation or irrigation with Colorado River water, respectively. The WET solution was included to determine its effectiveness in extracting PCBs. Aroclor treated Linné soil suspensions were equilibrated for 48 hours at 25°C. Following the equilibration period, the suspensions were centrifuged at 35000 x g for 35 minutes for phase separation. The supernate solution was removed and repeatedly extracted with hexane, which was then passed through Na_2SO_4 and reduced in volume by rotary evaporation. The settled Linné soil was extracted with 1:1 acetone: hexane which was passed through Na_2SO_4 and reduced in volume by rotary separation. The hexane extracts from both supernate and soil were subsampled and diluted to the appropriate Aroclor 1242 standard range for GC/ECD analysis. A gas chromatograph equipped with a ^{63}Ni electron capture detector was operated under the following conditions: injection temperature (230°C), detector temperature (340°C), column temperature 180°C. The Aroclor 1242 PCB homologs were separated by a 1.8 m x 2 mm i.d. chromatographic column packed with 3% OV-101 on 100/120 mesh Chromasorb W-HP

and with nitrogen carrier gas delivered at 20 $ml \cdot min^{-1}$. Data collection and peak area calculations were performed by an integrator.

The gas chromatograms were used to quantify PCB compositions on an Aroclor 1242 equivalent basis and on a PCB homolog basis. With respect to the latter, the chromatograms were partitioned according to data presented by Webb and McCall[1] and Hutzinger et al.[2] Aroclor 1242 was partitioned into dichlorobiphenyl (DCB), trichlorobiphenyl (TCB), and tetrachlorobiphenyl (TTCB), composing 17%, 39% and 32% (weight basis) of Aroclor 1242, respectively[1].

The distribution of PCBs between adsorbed and aqueous phases are routinely evaluated using the Freundlich adsorption isotherm model. At equilibrium the adsorbed PCB concentration, x/m (mass of adsorbed PCB/mass of adsorbent, $\mu g \cdot kg^{-1}$) is related to the aqueous PCB concentration c ($\mu g \cdot L^{-1}$) by the equation:

$$x/m = K_F C^{1/n} \qquad (1)$$

where K_F and 1/n are empirical parameters indicative of the relative adsorption capacity and adsorption intensity, respectively. The constants are evaluated via a logarithmic transformation of the x/m and C adsorption isotherm data followed by regression analysis to fit the linear form of equation (1). For PCBs, adsorption data are found to fit this model when C is approximately 60 to 70% of the aqueous PCB solubility.

Aroclor and PCB homolog desorption from the Linné soil, irrespective of PCB homolog or equilibrium solution composition, corresponded to the Freundlich model at low solution concentrations illustrating adsorption-desorption control on aqueous solution PCB content in a slightly contaminated soil. Freundlich parameters, K_F and 1/n, determined through linear regression analysis on the the three lowest system Aroclor concentrations (excluding system blank), are shown in Table 1.

Table 1. Freundlich parameters characterizing Aroclor 1242 and homolog desorption Linné soil.

	DW		$CaCl_2 \cdot 2H_2O$		WET	
	K_F	1/n	K_F	1/n	K_F	1/n
Aroclor 1242	1063.4	1.05	394.5	1.15	2570.4	0.83
1242-DCB	367.3	0.96	196.5	0.98	414.4	1.04
1242-TCB	1044.7	1.06	301.4	1.23	3022.5	0.77
1242-TTCB	3898.2	1.07	2114.2	1.05	3123.8	0.80

Aroclor 1242 homolog retention, as measured by the magnitude of K_F ($\mu g \cdot kg^{-1}$) PCB adsorbed when the equilibrium aqueous PCB concentratin is 1.0 $\mu g \cdot L^{-1}$) was found to increase in the following order: DCB < TCB < TTCB, irrespective of solution composition. This differential homolog behavior has been noted by a number of investigators through the examination of specific PCB congeners in soil-aqueous systems[3-5]. At elevated Aroclor system concentrations the adsorption data appeared to asymptotically approach a maximum equilibrium solution PCB concentration. That is, a positive change in x/m would not result in a corresponding change in C. This behavior might be indicative of solubility controlled solution PCB concentrations in highly contaminated soil. Indeed, if the full range of PCB desorption data are considered, one would find an exponential relationship between C and x/m:

$$C = \alpha[\exp(\beta x/m)] + C_s \qquad (2)$$

where x/m and C are as previously defined, α and β are empirical constants, and C_s the aqueous solubility of the species under consideration. In Table 2 are shown C_s values for Aroclor 1242, DCB, TCB and TTCB in the three aqueous systems, as determined from desorption data and Eq. (2) in comparison to published PCB (homolog and congener) data in deionized water[2,6-11].

Table 2. Aroclor and homolog solubilities.

	DW		$CaCl_2 \cdot 2H_2O$	WET
	desorption	published		
	($\mu g \cdot L^{-1}$)			
Aroclor 1242	214.6	19 - 340	325.0	480.0
1242-DCB	143.3	43 - 1941*	234.1	169.0
1242-TCB	91.6	17 - 226*	118.4	265.0
1242-TTCB	21.7	7.3 - 175*	38.1	145.0

*Includes solubility values for specific PCB congeners.

One finds the solubility values generated from desorption data are within published solubility ranges, illustrating the solubility control on aqueous solution PCB content in highly contaminated soils.

Solubilities and Freundlich parameters were affected by the composition of the equilibrating solution. The solubility of PCBs in the $CaCl_2 \cdot 2H_2O$ system were elevated with respect to those in the deionized water system. Conversely, PCB retention was greater in the deionized water system. The WET solution, developed for use in evaluating the hazardousness of waste materials, was less effective than either deionized water or $CaCl_2 \cdot 2H_2O$ solution in extracting PCBs when PCB behavior

was adsorption controlled (i.e., low system PCB contents). However, at elevated system PCB concentrations (solubility controlled) the WET solution provided a higher degree of extraction than did either deionized water or $CaCl_2 \cdot 2H_2O$. These findings indicate that under low and high system PCB concentrations, the WET solution would not provide an adequate assessment of Aroclor 1242 PCBs solubilized by either rain water or irrigation water.

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SOLVENT CLEANING OF PCB CONTAMINATED SOILS

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This paper describes a pilot-scale study of a novel system for cleaning soils that have been contaminated with PCB. The process uses solvents to extract the PCB from the soil. The PCB is then concentrated and the solvent reclaimed. Final PCB concentrations of less than 2 ppm on the soil, have been achieved.

The system was designed and built in late 1984. It was operated using non-PCB soils and shown to perform to design specifications. A permit to operate the system with PCB contaminated soil was obtained in February, 1985. Eight sets of tests were conducted and these demonstrated that soil containing up to 1,983 ppm PCB were successfully treated to less than 2 ppm. In addition to demonstrating this pilot-scale system, these tests provided design data for construction of a full-scale prototype soil washing system. The results of these tests are summarised in Table 1.

Figure 1 gives the schematic of the pilot soil washing system. It consists of a soil contactor, dirty and clean solvent storage tanks, a solvent reclamation system, steam generator and ancillary piping equipment. It also includes vent condensers and an activated carbon adsorption system for air pollution control. Operation proved very simple. One person had no difficulty operating it. Based on the results obtained with this system, a 7 cubic yard mobile soil washing system was designed and is now under construction. The following sections describe the major components of the system

The soil contactor is a semi-cylinder 4 feet in length with a radius of 2 feet. The soil washer is subdivided into two wash chambers, along its axis. The volume of each wash chamber is 11.5 cubic feet. The isolated chambers allow operation of the soil washer with two different batches of soil at a time. Access to each chamber for soil loading and removal, or to obtain soil samples for analyses, is through two hinged lids which comprise the entire flat side of the semi-cylinder. The lids are sealed with a Neoprene gasket and are clamped to the main body for operation.

Each wash chamber is subdivided by filters installed in presses isolated in slotted holders at each end of the central soil chamber. The available volume in the soil chambers is 70 cubic feet, although the chambers were not filled entirely during operation. Approximately 450 pounds of soil was cleaned during each test.

The washer is mounted to a frame by the shaft along its axis. It is rocked about its axis in order to agitate the soil/solvent mixture. It has a drive mechanism for rocking the washer which swings the contactor 90 degrees in either direction.

The system was tested on three types of soil, a (1) 50% mixture of sand and clay, (2) 70% clay mixture and (3) dark loamy top-soil. The sand/clay mixtures were obtained from the local Cincinnati area. These soils were PCB-free and were contaminated in the washer to the specified ammount of PCB. The third type of soil, dark/loamy, was obtained from a contaminated site that was being cleaned up. It contained up to 1923 ppm PCB in it.

The results of the tests were very encouraging. Table 1 shows that all of these samples were cleaned to less than 2ppm in less than 12 washes. The analytical results showed excellent closure on the ammounts of PCB removed in all but one test. In Run #5, the untreated soil was analyzed to be 548 ppm. The PCB removed, however, corresponded to 1941 ppm. It is assumed that this soil had a pocket of very high concentration PCB in it which was removed by the washing scheme but was not picked up by the sampling procedure used.

Based on these successful results, a full-scale system is now under construction.

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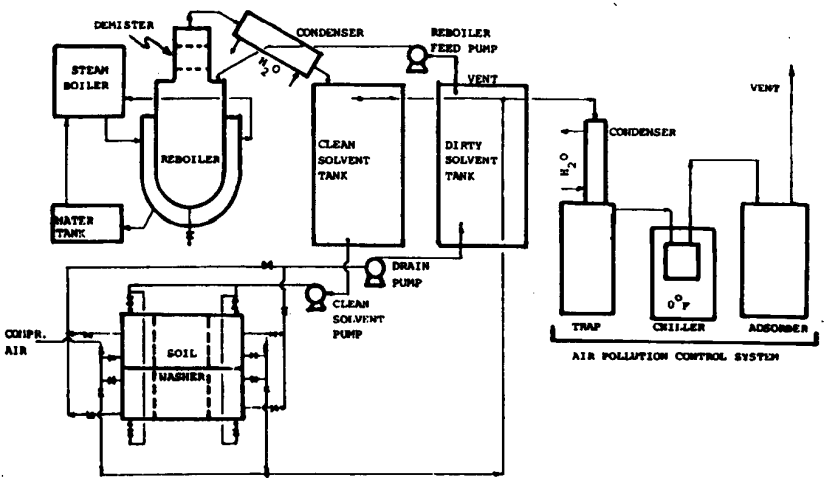

Figure 1. Schematic of Pilot Soil Washer

Table 1

RESULTS OF SOIL CLEANING TESTS

RUN #	ppm PCB			NO OF WASHES	FINAL PCB CONC. ppm
	BY AMOUNT OF PCB ADDED	BY ANALYSIS	BY AMOUNT OF PCB REMOVED		
1	37	38	38	3	<2
2	503	492	436	10	<2
3	-	67	72	6	<2
4	-	135	141	6	<2
5	-	548	1941	12	<2
6	-	832	910	12	<2
7	-	773	678	10	<2
8	-	18	16	5	<2

PART 6:

RISK ANALYSIS AND MANAGEMENT

THE INSURANCE INDUSTRY AND THE PCB EXPOSURE SITUATION

BY RICHARD G. CLARKE, CPCU

INTRODUCTION

Dramatic changes are occurring in the insurance industry regarding pollution related risks. Insurance industry experience with pollution (toxic chemical, hazardous waste, environmental) claims and loss has prompted a wave of policy exclusions for these types of exposures.

PCB is included in the insurance industry category of "pollution" exposure. The extensive loss seen with several notorious PCB incidents clearly indicates that pollution risks are two-fold. In addition to property damage claims, insurers have been faced with many liability claims (bodily injury as a result of exposure). Due to extensive clean up, EPA involvement, and the uncertainty of human exposure implications, accurate prediction of loss is nearly impossible.

It is for these reasons that insurers are excluding pollution related risks from current policies. Lack of insurance leaves PCB owners financially vulnerable, and requires that PCB managers play a more significant role in corporate risk reduction. Understanding risk management principles can help the PCB manager to be most effective.

WHAT PCB MANAGERS SHOULD KNOW ABOUT TODAY'S INSURANCE MARKETPLACE

Never has the axiom "the claim is the mother of the exclusion" had more applicability than to the general pollution liability exposure. Recent experience with pollution related claims has revealed that the actual extent of exposure for pollution related risks is uncertain. This applies to both property and liability exposure possibilities. Property exposure potential involves direct damage to insured property, as well as potential loss of income due to business interruption and associated "extra expenses". With PCB incidents requiring extensive clean up, and in one case, closure of a building for several years, it's no wonder that carriers are wary. Liability exposure potential, involving bodily injury claims, holds equal uncertainty. Widespread contamination possibilities coupled with the most environmentally conscious and knowledgeable public yet presents liability exposures of tremendous magnitude.

The distinction between property and liability exposure must be addressed by the PCB manager. PCB risk assessment must ask what damage to property is likely (including business interruption loss), as well as who and how many could be affected by a PCB incident. As previously stated, the answers are difficult to come by.

Insurance industry uncertainty regarding these questions is indicated by two significant industry developments:

- The insurance industry capacity to provide high limits of liability insurance and coverage for other than relatively routine property exposures is very strained now. The traditional source of reinsurance (insurance carrier's insurance coverage on the various coverages which it writes) eminates from London - and there is a shortage of "investors" who wish to take risks relating to large liability or property losses.

- The common, traditional source of insuring bodily injury for business or utility operations is the general liability insurance policy. Effective January 1, this particular insurance contract, considered one of the most standard, will be undergoing extensive change. Most carriers will accept the new position of not being responsible for claims or exposures which are alleged to have occurred rather than just recently and will create severe restrictions on covering pollution liability exposures. Coverage for pollution risk unless sudden or accidental (virtually impossible to purchase at this time) may become unavailable altogether as the words "sudden" and "accidental" are redefined. If available at all, such coverage would demand unrealistic premium charges.

In light of these insurance industry developments, and as PCB exposures become better known, the inevitable result will be "withdrawal" by those carriers still providing some measure of coverage.

Many electric utilities are "self-insured", reducing their dependence on carrier limitations. Self-insurance, however, does not isolate utilities from PCB expsosure problems. There is always a limit on self-insurance, even if it is the last available dollar of corporate assets (an unthinkable situation). Certainly, had various utility companies anticipated the extent of PCB caused losses, preventive measures would have been taken.

The fact that major carriers are discontinuing pollution related coverage - a business decision designed to avoid technical insolvency because of the loss involved - should be a warning signal to those who are self insuring PCB risks. If insurers won't sustain PCB losses with their tremendous reinsurance resources, how can an electric utility or major industrial facility?

THE PCB MANAGER'S ROLE IN RISK REDUCTION

Since insurance or self-insurance cannot be relied upon for total protection from PCB losses, the PCB manager becomes a more important influence on prudent protection of corporate assets. Although insurance cannot provide full coverage, the risk management principles used in that industry can be useful to the PCB manager for risk reduction plans.

The science of risk management identifies alternatives for reducing exposure to determine loss potentials. Risk management principles purport that the best possible alternative is to avoid or eliminate the loss exposure. If not viable,

the second best alternative is to control or retain (partially via deductible amounts, or totally via self-insurance) loss exposure. If this also is not a viable option, transferrence of the financial effects is then considered. (In the case of utilities and large manufacturers, there rarely are parties to whom the responsibility of loss exposures can be transferred.) Finally, if all else fails, the last option is to purchase insurance coverage.

This thought process ensures that effort (and money) is most prudently spent, i.e., when possible, $1,000 is spent once to eliminate the risk rather than $100,000 over a period of years to insure the risk.

For the PCB manager, whose job has become one of managing risk as well as electrical equipment or environmental affairs, this thought process can be a prudent guideline that is well understood by management.

The common communication gap that exists between the corporate risk manager and PCB manager must be closed. Responsibility for protecting and informing management from the same perspective is shared by both parties. Effective communication will accurately identify PCB exposures and will facilitate decisions to avoid, eliminate, control or retain these exposures.

LOOKING TO THE FUTURE

Although the insurance industry is cyclical, it is unlikely that coverage for high exposure areas such as pollution will ever be easily available.

As a result, PCB owners must become even more active in eliminating and controlling PCB risks in order to preserve financial integrity and avoid catastrophic loss situations. Options do exist for effectively reducing and eliminating PCB risk. Dyking, vaulting and closure - isolation methods can help control exposure. Reclassification technologies go even a step further toward risk elimination.

Control is mandatory because of catastrophic loss exposure. PCB elimination and the prospect of entirely non-PCB systems is the most prudent and reasonable alternative today, and the PCB manager plays perhaps the greatest role in the achievement of this corporate goal.

PREVENTIVE MEASURES FOR REDUCTION OF AIRBORNE PCB CONTAMINATION RISK

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INTRODUCTION

Electric utilities as well as other askarel equipment owners are implementing transformer fire prevention measures, either to comply with the July 17, 1985 "PCB Electrical Use Rule," or voluntarily. In recognition of the need to assist member utilities conducting airborne PCB spill risk reduction programs, EPRI sponsored development of a design manual addressing technical, economic, and environmental aspects of preventive engineering. This document (CS-4094, Design Manual for Reducing Airborne PCB Contamination) is now available through EPRI Research Reports Center.

The intent of the Design Manual is to describe a variety of cost-effective preventive measures that can be rapidly implemented. It is repeatedly emphasized that only equipment replacement (i.e., complete removal of all PCBs) will eliminate all spill risk. Other preventive measures, though less expensive, perpetuate a residual spill potential.

MANUAL DESCRIPTION

The Design Manual is organized into four Sections presented sequentially in the order of their occurrence in a risk reduction program. These are:

1. Ranking PCB installations on the basis of their potential for widespread contamination
2. Selecting the most appropriate spill reduction approach
3. Determining design requirements
4. Preparing design plans and specifications.

Each Section is self-contained, consequently users can select those elements applicable to their particular situation for integration into an overall risk reduction program.

Ranking PCB Installations on the Basis of Their Potential for Widespread Contamination

Utilities that own numerous askarel transformers may require several years to complete a system-wide risk reduction program. This section describes a methodology

for prioritizing PCB installations based on contamination potential. The results provide an objective basis for scheduling corrective action.

The risk ranking methodology utilizes a quantitative scoring format taking into account both spill probability and consequence. The major parameters affecting spill probability are:

- Equipment condition
- Electrical system design
- Operating environment.

The major factors affecting spill consequence are:

- Public safety
- Building value
- Contamination migration potential
- Cleanup complexity.

Selecting the Most Appropriate Spill Reduction Approach

Preventive measures addressed in the Design Manual include:

- Replacement
- Relocation
- Isolation
- Protection (electrical, mechanical, fire alarm, and maintenance).

Presented in this Section is a procedure for evaluating the technical, economic, environmental, and regulatory factors affecting each alternative and for comparing those factors to select the most appropriate approach.

Determining Design Requirements

Upon selection of a risk reduction approach (or combination of approaches), a site investigation to inspect design-related conditions is required. Transformer replacement and relocation are not addressed in the Design manual, as these activities are well understood by all utilities. Isolation and protective measures are included.

A predesign investigation worksheet, utilizing a checklist type format, was developed for survey use. Critical design parameters are identified to ensure thorough data gathering. Technical guidelines for each alternative are presented, principally in tabular form, for ready reference.

Preparing Design Plans and Specifications

This Section is basically technical in content. Its organization is similar to the predesign Section to facilitate cross-reference.

Those techniques, equipment, devices, and procedures determined applicable to airborne PCB spill prevention are described in detail. Recommended applications and engineering specifications are presented. References and a bibliography are included to facilitate acquisition of additional information. Key excerpts from the National Electric Code are also included.

SUMMARY

Installation of risk reduction measures can rapidly and inexpensively lower the probability of extensive airborne PCB contamination. Maximizing the cost-effectiveness of this approach requires a well-planned survey program, including on-site investigations. The Design Manual for Reducing Airborne PCB Contamination is available to assist member utilities and others conducting PCB spill risk reduction activities.

ENVIRONMENTAL FATE OF PCBS IN MINERAL OIL SPILLS

Stuart M. Brown and Artemis Antipas*

INTRODUCTION

As of 1982, approximately 21 million pieces of electrical equipment, or 88 percent of all electrical equipment, owned by the utility industry contained mineral oil (1). Some mineral oil equipment has become contaminated with low levels of PCB during either manufacturing or routine equipment maintenance. Approximately 93 percent of the mineral oil equipment contains less than 100 ppm of PCB, 70 percent contains less than 10 ppm and 44 percent contains less than 1 ppm (1).

This paper examines the environmental behavior of PCB in a contaminated mineral oil spill and shows that volatilization and leaching losses from a mineral oil spill are significantly less than those from an equivalent askarel spill. Thus, mineral oil spills pose considerably less risk. Existing and pending spill cleanup guidelines apply uniformly to both types of spills.

CONTAMINATED MINERAL OIL SPILL MODEL

The behavior of a contaminated mineral oil spill was examined by using a simple model describing the behavior of chemical spills developed by Phyper and Mackay (2). The model divides a spill event into four separate time periods:

Period A. A relatively short time period wherein the chemical penetrates into the soil.

Period B. A slightly longer time period wherein penetration continues and the chemical redistributes in the soil pores until residual saturation is achieved.

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Period C. A relatively long time period wherein dissolution of the pure phase of the chemical occurs as water percolates through the soil.

Period D. A time period of variable duration wherein the remaining chemical dissipates from the soil column through volatilization, leaching, and degradation.

The original version of the model assumes the chemical (e.g., PCB) is present as a pure liquid. In the case of a contaminated mineral oil spill, the PCB is present as a trace constituent in the oil. At the PCB concentrations typical of most contaminated mineral oil spills, it is reasonable to assume that the PCB-oil mixture behaves as an ideal solution. Given this assumption, it is possible to show that for two sparingly soluble organic compounds in the presence of water

$$P_s = x_{PCB} P_s^*$$

$$C_s = x_{PCB} C_s^*$$

where

P_s = partial pressure of PCB in the presence of mineral oil

x_{PCB} = PCB mole fraction in mineral oil

P_s^* = pure phase PCB vapor pressure

C_s = PCB solubility in water in the presence of mineral oil

C_s^* = pure phase PCB solubility in water

At a PCB concentration as high as 500 ppm of Aroclor 1242, the PCB mole fraction is only 0.0004. Thus, when a mineral oil spill occurs, the oil will substantially reduce the vapor pressure and solubility in water of the PCB, which in turn leads to reduced volatilization and leaching losses. As the spill weathers, the mineral oil will dissipate through volatilization, leaching and biodegradation producing an increase in the PCB mole fraction.

The model developed by Phyper and Mackay was modified to account for the effect of the mineral oil on PCB volatility and solubility and to estimate the change in PCB mole fraction during each time period.

MODEL RESULTS

The model was used to examine the behavior of a 10 gallon mineral oil spill contaminated with 200 ppm of either Aroclor 1242 or Aroclor 1260. The spill was assumed to cover a 100 square foot area composed of a sandy soil.

Figure 1 shows the estimated percentage of the mineral oil and PCB (as either Aroclor 1242 or 1260) remaining in the soil with time following the spill. During Period A (i.e., penetration) and Period B (i.e, redistribution) negligible mineral oil and PCB are lost from the spill site. As Figure 1 shows, both periods are relatively short in duration; combined they took less than 3 hours. During Period C (i.e., dissolution), the mineral oil begins to dissipate quite rapidly while relatively little PCB is lost. Once dissolution of the mineral oil is complete at the end of Period C, the PCB begins to dissipate. The Aroclor 1260 dissipates more slowly than the Aroclor 1242 because it is composed of more highly chlorinated PCB congeners that are less volatile, less soluble in water, and less biodegradable. The delay experienced by the PCB illustrates the impact of the mineral oil on reducing volatilization and leaching losses from a spill site.

The effect of the mineral oil is further illustrated in Table 1 which lists estimated volatilization and leaching rates of Aroclor 1242 for the spill conditions discussed above and for an equivalent spill of pure Aroclor 1242. These results show that volatilization and leaching losses for the contaminated mineral oil spill are significantly less than those for the pure Aroclor 1242 spill. Losses decrease by three orders of magnitude in the case of volatilization during the first three time periods. Once dissolution of the mineral oil is complete, the loss rates for the two spills are the same.

The model results demonstrate that PCB levels in air and groundwater around a contaminated mineral oil spill site will be orders of magnitude less than those around an equivalent askarel spill site. Thus, potential exposure levels and associated health risks will be lower.

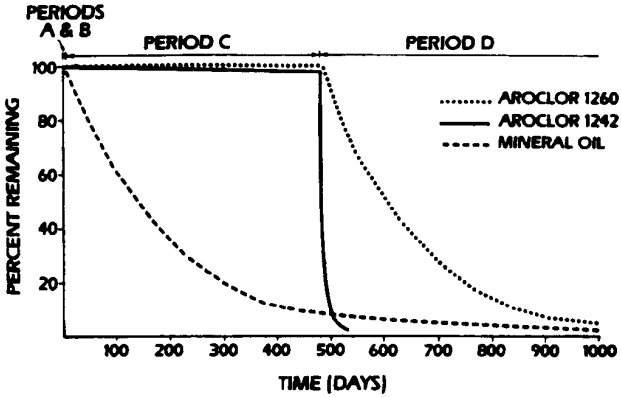

Figure 1. Percent remaining with time for a mineral oil spill containing 200 ppm of either Aroclor 1242 or Aroclor 1260.

Table 1

ESTIMATED VOLATILIZATION AND LEACHING LOSS RATES FOR A 200 PPM CONTAMINATED MINERAL OIL SPILL AND AN EQUIVALENT PURE AROCLOR 1242 SPILL (gm/day)

	Contaminated Mineral Oil		Pure Aroclor 1242	
Period	Volatilization	Leaching	Volatilization	Leaching
A	7×10^{-3}	-	38	-
B	7×10^{-3}	-	7	-
C	3×10^{-4}	5×10^{-5}	8×10^{-1}	5×10^{-3}
D	1×10^{-1}	6×10^{-4}	1×10^{-1}	6×10^{-4}

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MANAGING ECONOMIC RISKS DUE TO ELECTRICAL EQUIPMENT CONTAINING PCBS: ANALYTICAL TOOLS TO SUPPORT UTILITY DECISIONS

by

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Dean W. Boyd
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Donald S. Wilson

DECISION FOCUS INCORPORATED

The PCB Economic Risk Management Model (ASK) and the Contaminated Oil Economic Risk Management Model (COIL) are decision support tools designed to help utility personnel manage equipment containing or contaminated with PCBs. Based on the methodology of decision analysis, the models provide techniques for comparing alternative strategies in terms of equipment costs and the costs of potential incidents such as fires and spills.

INTRODUCTION

Electric utilities typically have a variety of equipment containing or contaminated with PCBs. Accidents or failures involving such equipment may lead to very large economic costs for the utility. These costs can include cleanup of the facility and the surrounding area, repair or replacement of utility and third-party equipment, and possible legal liabilities. The possibility of incurring such losses may exist even when the PCB contamination is very low. The need to weigh these highly uncertain but potentially large losses against the costs of various management alternatives prompted the development of the two decision support tools discussed in this paper. The development of ASK was motivated by the need to manage askarel transformers and PCB capacitors in the face of the potential for large financial impacts due to incidents such as fires. COIL was developed to help utilities choose management alternatives for contaminated mineral oil equipment. Both tools focus on economic risks, which include direct equipment and cleanup costs, and costs that may be incurred due to real or perceived health or environmental effects from releases of PCBs.

Management Alternatives

Utilities have a variety of options available to manage equipment containing PCBs, including replacing existing equipment with one or more alternative types of equipment, isolating the equipment or installing electrical protection devices to reduce risks, retrofilling to reduce PCB levels, or retaining the existing equipment

as is. Replacement may involve significant costs for a new unit and for installation, but may improve the operating efficiency and will eliminate the possibility of a PCB incident. Incidents involving substitute equipment may occur with greater frequency and with greater risk of conventional damage, but probably will not lead to the larger costs sometimes associated with PCB incidents.

There is often considerable uncertainty regarding the degree of PCB contamination of mineral oil transformers. Testing the equipment can help guide the choice of a management strategy and may help a utility avoid the costs associated with an incident involving PCBs. If the likelihood of severe contamination is low and incidents are rare, however, the cost of testing may exceed the value of the information gained.

Balancing Equipment Costs Against Economic Risks

Choosing the best management strategy requires careful weighing of uncertain losses against known cost and performance considerations. Is an investment in risk reduction measures or new equipment merited to remove the possibility of a potentially very expensive but relatively unlikely incident? Management questions such as these are challenging due to the large uncertainties in the likelihood, severity, and cost of incidents, as well as the complexity of the cost, performance, and financial considerations.

For example, consider the case of a utility that has a number of askarel transformers in its generating stations. There is a small chance that a fault in one of the transformers could lead to a major fire, one in which PCBs and combustion by-products would be distributed widely through the plant in the form of smoke and soot. How large would the probability of a major fire need to be, and how great would the likely costs of an incident need to be, before the company should decide to remove its askarel transformers and replace them with non-PCB equipment? The cost of installing new equipment is relatively easy to determine, but the potential incident costs are not. Utility personnel may find it difficult to estimate the costs since incidents are unlikely and the costs could be quite large. The challenges posed by decisions such as this have motivated the development of the risk management models and decision support tools described in this paper.

ASK AND COIL: AIDS TO DECISION MAKING

ASK and COIL are designed to help utility personnel make the difficult management decisions regarding PCB and contaminated mineral oil equipment. Both ASK and COIL incorporate equipment cost and performance calculations, a financial model to account for costs to ratepayers and shareholders, and explicit representation of

uncertainties in the occurrence, severity, and cost of incidents. These features are combined in interactive software packages that implement the risk management models. The software implementations have been designed to facilitate and guide analyses performed by relatively inexperienced computer users, yet remain convenient and efficient for experienced users. They provide complete capabilities for the user to enter, display, edit, save, and retrieve data, to run the models, and to display and save both summary and detailed results.

Decision Trees

The management decisions and key uncertainties are represented in ASK and COIL using decision trees. The tree for ASK, shown in Figure 1, can be used to calculate expected costs and the range of uncertainty over a large number of scenarios. The tree in this figure is a shorthand representation of the complete tree, where specific decision alternatives and uncertain events are defined, and each node is connected to every branch of the previous node. The decision tree for COIL is similar, but includes explicit representation of the sample/no sample choice prior to the equipment management alternative.

If each of five uncertainty nodes shown in the ASK decision tree had three possible outcomes, there would be a total of 243 scenarios, represented as distinct paths through the tree. The likelihood, or probability, of each scenario is simply the product of each likelihood associated with the branches along its path through the tree.

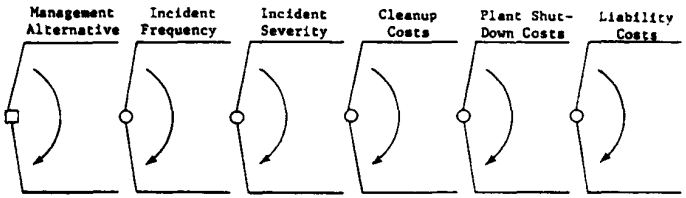

Figure 1. Key Uncertainties Are Represented as a Decision Tree in ASK

Models

For each scenario defined by the tree, the calculations in ASK and COIL are carried out using the models shown in Figure 2. The equipment model calculates all costs associated with existing and replacement equipment. It can take into account different operating and maintenance costs and efficiencies for different types of

equipment. The incident occurrence model calculates the likelihood, potential timing, and likely severity of an incident using values for the uncertain parameters, such as the rate of occurrence of incidents, from the decision tree.

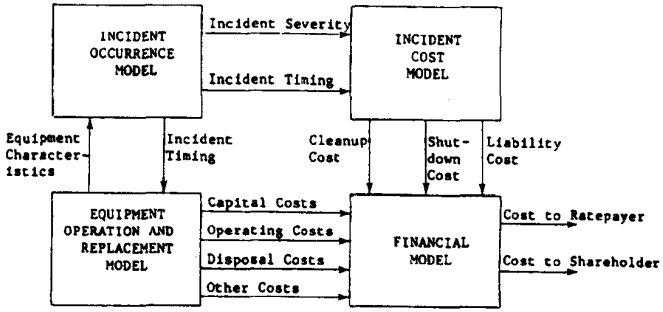

Figure 2. A Set of Models Are Used to Calculate Costs in ASK and COIL

The incident cost model calculates all costs of an incident, given that one occurs. Cost elements can include equipment replacement costs, cleanup and repair costs, costs of legal liabilities, and costs due to the shutdown of a generating plant during the cleanup and repair period. The model incorporates utility cost-of-service calculations, distinguishes between capitalized and expensed costs, and calculates costs to both ratepayers and shareholders.

SUMMARY

ASK and COIL are decision support tools that allow utility personnel to evaluate PCB equipment management options for a wide range of situations. Comprehensive analyses can be carried out quickly and efficiently, comparing different management options in terms of direct costs and costs due to incidents. Uncertainties in incident occurrence, severity, and cost may be accounted for explicitly, and a wide variety of "what if?" questions can be answered rapidly.

In addition to serving as a useful analytical aid, ASK and COIL can help utility personnel communicate with top management, regulators, and public groups about the complex nature of PCB and contaminated mineral oil problems, as well as provide key insights from the analyses. The tables produced by ASK and COIL show both the assumptions and the results clearly. The implications of alternative viewpoints and opinions can be tested and displayed quickly and easily, thus facilitating discussion and consensus building on difficult PCB management issues.

THE TRANSFORMER/CAPACITOR RISK MANAGEMENT MODEL: "TRIM"

by

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DECISION FOCUS INCORPORATED

INTRODUCTION

This paper describes the Transformer/Capacitor Risk Management (TRIM) model. TRIM has been developed to facilitate analyses of alternative utility actions and regulatory policies involving electric equipment containing PCBs (polychlorinated biphenyls). Analyses performed using TRIM can provide a basis for improved understanding and insight into the costs and benefits of alternative actions. Based on the methodology of decision analysis, TRIM includes a detailed structural model and a flexible decision tree allowing explicit representation of key uncertainties. The paper will discuss the methodology of TRIM and review example applications.

BACKGROUND

PCBs have been used extensively as dielectric fluids in transformers, capacitors, ballasts, and other electrical equipment. The use of PCBs was motivated by a combination of fire-resistant and dielectric properties. Dielectric fluid composed largely or solely of PCBs is currently used in over 30,000 large electric utility transformers and in several million capacitors. In addition, several million mineral oil transformers are potentially contaminated with small amounts of PCBs.

During the 1960s and early 1970s a small number of incidents occurred which, combined with limited scientific information, led to concerns regarding potential health effects of PCBs. Although evidence is conflicting and still far from complete, these concerns led to the regulation of PCBs by the federal government under the Toxic Substances Control Act (TSCA). The United States Congress banned the manufacture of PCBs in 1976, and the Environmental Protection Agency (EPA) has developed strict regulations concerning the continued use, phase-out, and disposal of PCB equipment.

Recently, a new set of concerns arose regarding potential by-products of combustion of PCBs that might result when equipment containing PCBs is involved in a fire. Possible by-products of PCBs include PCDFs (polychlorinated dibenzofurans), and PCDDs (polychlorinated dibenzo-p-dioxins). Some of these substances may be by-

products of other components of PCB-based dielectric fluids, such as chlorobenzenes. Both PCDDs and PCDFs are suspected of causing health effects in humans, although once again evidence is incomplete; in particular there is little direct information regarding the effects of PCDFs. As a result of these new concerns and questions, the EPA has proposed additional regulation of PCB equipment. These proposals, as well as other potential PCB-related regulatory issues, were the motivation for the development of TRIM.

METHODOLOGY AND MODEL STRUCTURE

The structure of TRIM was designed to represent the critical elements involved in PCB regulatory issues, including PCB transformer and capacitor use, releases from this equipment, human exposure, and human health effects. The model provides an integrated quantitative tool to test a variety of alternative assumptions.

TRIM includes two key components: a decision tree and a deterministic model. The decision tree, outlined in Figure 1, represents the interaction of the principal regulatory decision with critical uncertainties that can have a major impact on the ultimate outcomes. Both near-term decisions and longer-range decisions subsequent to the development of new information can be included. The model user may define the alternatives to be considered at each decision point.

The deterministic model traces the potential impacts of PCBs from their use in electrical equipment, through release due to accidents or other incidents and potential human and environmental exposure, to any ensuing health or environmental effects. The deterministic model is composed of six submodels, as shown in Figure 2, representing equipment use and replacement, spills and other incidents, human exposure, human health effects, environmental exposure, and environmental effects.

The equipment use and replacement model provides a detailed inventory of the PCB equipment in use at any time given a particular regulatory environment. This model tracks PCB equipment in use in various locations and accounts for units being taken out of service and different units being installed. TRIM also calculates the costs of phasing out and replacing equipment, and of any special risk management activities.

The spill/accident model specifies the amount of PCB material released during different types of incidents defined by the user; the frequency of occurrence of these incidents; the production of by-products during the incidents, if any; and the residual concentration of the material after cleanup. The human exposure and deposition model calculates both the number of people exposed and the average lifetime deposition for each of one or more distinct population groups possible exposed to

PCBs and by-products, for each of the saveral types of incidents in various locations. Exposure is calculated both for the short period during an incident and cleanup and for multi-year periods after cleanup is complete.

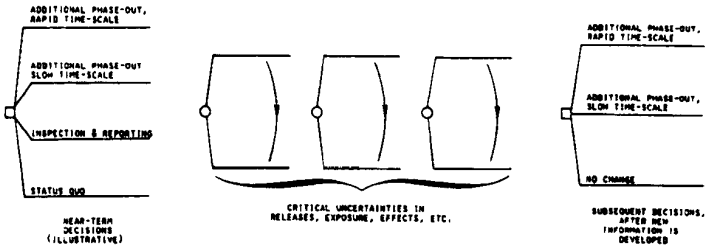

Figure 1. Outline of the TRIM Decision Tree

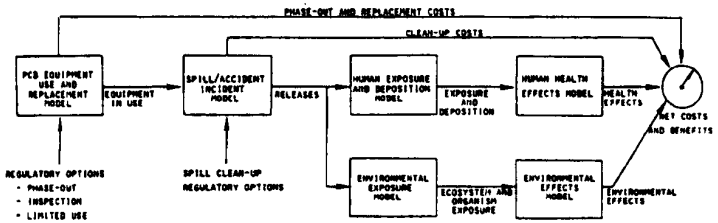

Figure 2. Outline of the TRIM Deterministic Model

In parallel with the calculations of human exposure is the environmental exposure model which calculates the total exposure to various ecological groups. The environmental effects model calculates average deposition as a surrogate measure for the impacts on exposed ecological groups. The human health effects model calculates the occurrence of potentially serious health effects due to exposure to PCBs and any by-products or contaminants, for each of the user-specified population groups.

TRIM has been implemented as an integrated, flexible computer program, incorporating both the decision tree and the deterministic model. It includes options that facilitate sensitivity and decision tree analysis. The program has been designed to run on mainframes, minicomputers, and personal computers, and is available from the Electric Power Research Institute.

APPLICATIONS OF TRIM

The primary uses envisioned for TRIM are to assist in the evaluation of regulatory policy options at the national, regional, or local levels, and to assess the possible health risks at an individual utility due to the use of PCB equipment. TRIM has been used to evaluate national regulatory options being considered by EPA. TRIM can also be used by utilities, state agencies, and other interested parties to analyze the PCB problem on a smaller scale. While much of the attention has been on askarel transformers, TRIM may be readily applied to any other types of equipment that contain PCBs or other related chemicals which may present some health hazard. Dielectric fluids that may be investigated include askarel, contaminated-oil, mineral oil, and silicone or other substitutes for PCB fluid.

AN EXAMPLE

TRIM has been used by the Utility Solid Waste Activities Group (USWAG) to carry out a detailed analysis of potential risks due to fires involving PCB transformers. The analysis assessed potential health risks associated with incidents involving utility-owned askarel transformers, and evaluated a set of alternative regulatory policy options designed to mitigate the risks. The options included maintaining a normal phase-out schedule, implementing risk reduction measures, or carrying out an accelerated phase-out of the transformers. The USWAG analysis indicated that the risks posed by fires involving utility-owned askarel transformers are very low, even with a normal phase-out schedule. Evaluation of the USWAG analysis results suggests that avoided cases of health effects would have to be valued at almost one billion dollars each before any regulatory actions beyond the status quo was merited. The analysis using TRIM served as the basis for comments USWAG submitted to the EPA regarding proposed additional rules on PCB transformers.

HUMAN HEALTH RISKS FROM PCB-CONTAMINATED MINERAL OIL TRANSFORMERS

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The objective of this study is the estimation of human health risks due to the inhalation of combustion products from accidental mineral oil transformer fires occurring outdoors. Polychlorinated dibenzofurans (PCDFs) are believed to be the principal toxic products of the pyrolysis of polychlorinated biphenyls (PCBs) sometimes found as contaminants in transformer mineral oil. This presentation highlights the different exposure levels in air risk analysis in contrast with a uniform exposure level in drinking water risk analyses. The adverse health effects addressed here are those attributable to the toxic action of PCDFs inhaled in the neighborhood of the fire. The findings are interpreted in light of accepted health guidelines for PCDFs.

A prototype scenario is based on extreme values of population density, climatology and transformer oil capacity selected from the ranges of these variables within the service areas of the Southern California Edison Company. The analysis follows three main steps: (1) Emissions characterization, (2) atmospheric dispersion estimates and (3) expectations of health hazards which could arise from downwind inhalation exposures.

In order to specify the emissions in detail we define the fire scenario, determine mass/energy balance parameters and introduce the PCB to PCDF conversion efficiency. Based on parameters of the prototype system, a subsurface vault location is chosen, and a one meter pool fire is assumed to burn 25 gallons of mineral oil contaminated by PCBs at the level of 9.9 ppm. The burning rate is derived from a correlation of observational data on many oil fires which gives 6×10^{-5} m/s for the average regression rate of the liquid surface for fires one meter and larger.

The emission rate of PCDFs is derived from the percent conversion of PCBs to PCDFs and the estimated level of PCB contamination in the mineral oil of 9.9 ppm by mass. This efficiency, based on a conservative interpretation of experimental data, is at maximum 1%. In the case of a transformer fire in Binghamton, NY, where the fluid was mostly PCB (65%) with some chlorinated benzenes (35%), the estimated conversion efficiency was only 0.1%.

We can now calculate an appropriate emissions rate to be used as a worst case estimate for our human inhalation exposure study. For a mineral oil specific gravity of 0.91 (with the derived values of pool burning rate, PCB contamination level and PCB to PCDF conversion efficiency), we calculate the PCDF emission rate from a one meter diameter pool fire to be 4.2×10^{-6} g/s. Moreover, the time required to burn all 25 gallons of mineral oil is calculated from these data to be 34 minutes.

The air dispersion calculation uses a Gaussian plume model with the urban dispersion parameters from the Industrial Source Complex formulation. An ensemble of cases for the wind speed/stability combinations for the local area were run in order to represent an appropriate range of conditions weighted by their frequencies. This procedure generates a frequency distribution of ambient concentrations at the surface in the downwind direction. Combining these statistics with the populations associated with each receptor point, we derive a likelihood parameter which shows the probability of any person exceeding some given exposure level. We have maximized the factors governing the exposure of an individual to PCDFs from inhalation of the combustion products plume ambient concentration. Combining an inhalation rate of 22 m^3/day with the fire duration and each locally calculated value of the ambient concentration, we estimate the ensemble of inhalation exposure values.

Having defined the statistics of exposure, we interpret these results in terms of health hazards. Regulatory agencies ordinarily use conservative extrapolations of animal toxicological data to humans for effects suspected of having no threshold like some forms of cancer. This conservatism is intended to allow for uncertainties in extrapolation from one species to another, from small organisms to large ones and from high doses to low doses. Each of the three prototype calculations of safe level we have selected is based on this type of analysis. We have determined the likelihood of exceeding any of the safe lifetime dose levels of PCDD/PCDF compounds as derived from three regulatory agency guidelines: (1) The California permissible level of PCDD/PCDFs in the air in a building; (2) The

California 10^{-6} risk level of PCDD/PCDFs and (3) the EPA water quality criterion level for 2, 3, 7, 8 TCDD.

The likelihood of anyone in the neighborhood of the fire receiving even the conservetive EPA safe lifetime dose level is less than one in 7,000,000, and likelihoode still lower are found for exceedance of the California State guidelines. Therefore, it would appear as if no significant health risk is posed by inhalation exposure to possibla PCDF products from mineral oil transformer fires under the system scenario employed in this analysis.

OCCUPATIONAL EXPOSURE OF ELECTRIC UTILITY PERSONNEL TO PCBS
A CASE STUDY

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A research project was developed to determine the occupational exposure to polychlorinated biphenyls (PCBs) of Southern California Edison Company (Edison) personnel. Results from this project are presented and include: identification of potentially high exposure jobs; measurement of blood PCB concentrations among Edison personnel; and evaluation of the amount of PCBs on the Edison system in electrical equipment. The data indicate that no significant occupational exposures have occurred among Edison personnel.

Personnel involved in the servicing and repair of distribution and electrical apparatus have the greatest potential for contacting dielectric fluids which may contain PCBs. Length of service in these occupations, work practices, the number of Askarel units, and the degree of contamination with PCBs in non-Askarel units will influence the actual levels of exposure for a particular work force.

To assess this exposure potential we compared levels of PCB in blood of several exposure categories of Edison personnel and measured the amount of PCB in electrical apparatus on the Edison system. This provides an historical view of exposure in a way that current industrial hygiene monitoring can not.

To establish a background blood PCB level for non-occupationally exposed individuals, blood samples from the pre-employment medical examinations of 738 new employees were analyzed for PCB. Blood PCB concentration of this group have a median of 4 ppb and a mean of 5 (SD = 4) ppb. These data are comparable to previously published values for blood PCB concentrations of non-occupationally exposed groups. Since the demographic characteristics of this pre-employment sample are similar to those of the general population, and agree with other published data, we conclude that these levels result from exposures to PCBs in the general environment.

Blood PCB levels of 1,058 current personnel have a median of 3 ppb with a mean of 4 (SD = 4) ppb. Two hundred and twenty of this group were in "high exposure potential jobs" between 1979 and 1984. This subgroup of the current personnel is considered to have the highest current exposure potential and should reflect the greatest PCB body burden if occupational exposure is occurring in this work force. Duration of exposure for these personnel averages 14 years, ranging from 1 - 37 years. Blood PCB concentrations ranges from 1 to 15 ppb with a median of 3 ppb and a mean of 4 (SD = 3) ppb. There is no significant difference in blood PCB concentrations between the pre-employment, current employment, and the the subset of high exposure potential groups. We conclude that employment at Edison has not resulted in the accumulation of PCBs different than that of the general, non-occupationally exposed population.

There is no indication that a blood concentration at these levels poses a threat to human health. Investigations of occupational groups with substantially higher blood PCB concentrations have not reported significant health or physiologic effects.

The amount of PCB on the Edison system was assessed by quantifying the gallons of PCB in capacitors, transformers, and other electrical apparatus. Capacitor fluid (entirely PCB) and Askarel-containing (predominantly PCB) transformers represent less than 1% of total dielectric fluid in electrical apparatus on the Edison transmission and distribution system. Mineral oil is the predominant dielectric used by Edison. PCB contamination of mineral oil equipment on the distribution system was 6 ppm (median less than 2 ppm) and in substation equipment the mean was 12 with a median of 2 ppm.

These data indicate that no significant occupational exposure to PCBs has occurred among personnel of this utility, and that no significant health impacts would be expected from PCBs.

PCB ENVIRONMENTAL TRANSPORT AND FATE MODELING

James W. Lingle*

INTRODUCTION

New mathematical modeling tools have recently been developed through research funded by the Electric Power Research Institute that predict the environmental transport and fate of PCBs from spills of dielectric fluid from electrical equipment such as capacitors and transformers (1). These tools can be used on mainframe or personal computers in order to examine the consequences of a particular PCB spill. They can also be used to evaluate "what if" questions regarding potential cleanup and restoration actions. The major function of the models is to predict the movement of PCBs through pathways such as air, surface water, soil cleanup, and groundwater. A model has also been developed to determine the potential exposure and dose of PCB to receptors in a given spill area. This paper briefly discusses the models used, the input data required, and the application of the models to several PCB spills. The examples include a PCB capacitor failure in a substation and a spill from a pole-mounted PCB contaminated oil filled transformer. Analytical data were available for both spills.

PREDICTION OF ENVIRONMENTAL TRANSPORT

The PCB Off-Site Spill Model (POSSM) is the main core model used to predict the partitioning of PCBs into various environmental pathways. POSSM is an adaptation of PRZM, an EPA model used to predict the fate of pesticides. It has been modified to include a pure phase component in the soil and impervious surfaces such as asphalt or concrete. The POSSM model can be used with other off-site models (shown in Figure 1) to predict the movement of PCBs to the atmosphere, rivers, lakes, and groundwater. Other models used in this analysis include PTDIS, an EPA air pollution model, and EXPOSE, a model developed to calculate the dose of PCB to receptors based on potential exposure pathways such as inhalation, dermal contact, or ingestion.

SPILL SCENARIOS

The POSSM model was used to analyze a PCB capacitor spill in a substation. About 1.5 gallons of Aroclor was spilled over an area of about 150 square feet. The input data were constructed to include a 6 inch layer of crushed stone over a Miami silt-loam soil. Soil profile data including bulk density, % organic carbon, moisture content, and soil horizon thickness were obtained from reports published by the USDA Soil Conservation Service. Daily meteorological data including wind speed, temperature, and precipitation were obtained for the area from Local Climatological Data published by the National Oceanic and Atmospheric Administration (NOAA). Other information about the spill is supplied on Table 1.

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The model input data were adjusted to include the average PCB concentration measured in the soil after the first, second, and third cleanup events. The input data were also modified to account for a new 6 inch crushed stone layer on top of the soil after restoration. PCB concentrations in the air 1,200 feet from the substation (distance to the nearest house) are shown in Figure 2. Model results for a nine-month period are as follows:

PATHWAY	PERCENT
Cleanup	97.96%
Volatilization	2.04%
Runoff	.000021%
Leached to Groundwater	None

The POSSM model was also used to analyze a spill of 100 ppm PCB contaminated mineral oil from a pole-mounted distribution transformer. Approximately 6 gallons were spilled over an area of 312 square feet. The total amount of PCB actually spilled was 2 grams or 0.07 ounces. Other conditions are provided on Table 1. Modifications discussed elsewhere were necessary to account for the difference in properties of mineral oil versus pure Aroclor 1254 (2). Soil cleanup factors were based on measured PCB levels in the soil (3.21 ppm average before cleanup, 1.18 ppm average after cleanup). The PCB levels predicted in the air 60 feet from the spill (distance to the nearest house) are illustrated on Figure 3. The total amount of PCB volatilized during the four-month modeling period was 2.75%. Volatilization was negligible after restoration.

EXPOSURE CALCULATIONS

The EXPOSE model was used to calculate the dose of PCB for persons living in homes near the spills. Input conditions included calculating the airborne concentration of PCB with PTDIS at distances corresponding to the nearest homes. Exposure was assumed to occur whenever the wind was blowing from the spill site to the house (approximately 15% of the time). No adjustments were made for differences in outdoor versus indoor concentrations. The potential health effects were estimated using the PCB dose-response function developed by the EPA Office of Toxic Substances and discussed elsewhere (3). The cumulative deposition from inhalation (in grams) was multiplied by a dose-response function of 4.0×10^{-5} to estimate the likelihood of an exposed individual incurring cancer. The results are as follows:

SPILL SCENARIO	DEPOSITION (Grams)	PROBABILITY OF A HEALTH EFFECT
Substation Spill	$.463 \times 10^{-6}$	1.9×10^{-11}
Transformer Oil	$.033 \times 10^{-6}$	1.3×10^{-12}

In these examples, both exposures are well below the 1×10^{-6} risk level which is sometimes used as a gauge of acceptability.

CONCLUSIONS

New mathematical modeling tools allow utility personnel and others to conduct more meaningful analyses of PCB spill events than in the past. These tools should help the user determine if PCBs are likely to migrate beyond the area of the spill and what the cumulative dose might be to persons exposed. The models allow the user to examine a variety of cleanup scenarios and the resultant impact on exposure potential. Additional work is necessary to field test the models to determine the accuracy of the predictions.

REFERENCES

1. Brown, S. M., and S. H. Boutwell, "PCB Spill Exposure Assessment Methodology," EPRI Report RP 1826-13, December 1984.

2. Brown, S. M., and A. Antipas, "Environmental Fate of PCBs in Mineral Oil Spills," paper presented at the EPRI PCB Seminar, Seattle, Washington, October 22-25, 1985.

3. USWAG, "Proposed Spill Cleanup Policy and Supporting Studies," submitted to EPA October 15, 1984.

Table 1

PCB SPILL MODELING INPUT DATA

	SUBSTATION SPILL	TRANSFORMER OIL SPILL
Equipment	PCB Capacitor	Pole-Mounted Transformer
Fluid Spilled	Aroclor 1016	100 ppm 1254 in Oil
Quantity Spilled	1.5 Gallons	6 Gallons
Spill Area	150 Square Feet	312 Square Feet
Soil Type	Silt Loam	Silt Loam
Surface	Crushed Stone	Grass
Event Dates		
Spill	August 3	September 11
1st Cleanup	August 4	October 3
2nd Cleanup	August 24	
3rd Cleanup	October 19	
Restoration	October 26	October 10

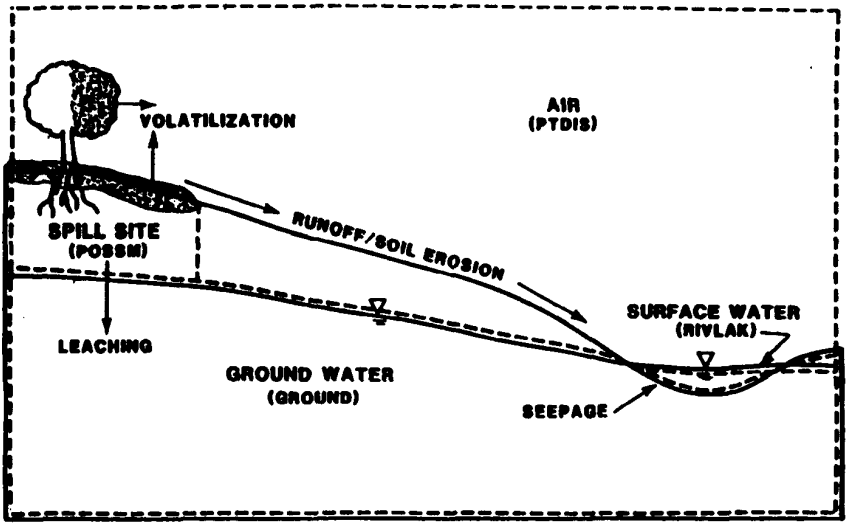
VOLATILIZATION
AIR
(PTDIS)
SPILL SITE
(POSSM)
RUNOFF/SOIL EROSION
SURFACE WATER
(RIVLAK)
LEACHING
GROUND WATER
(GROUND)
SEEPAGE

Figure 1.

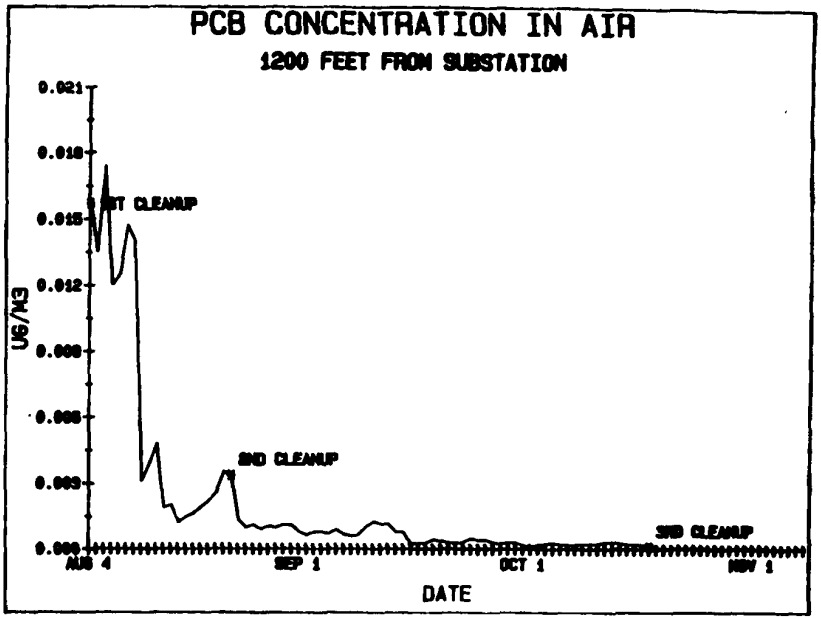
PCB CONCENTRATION IN AIR
1200 FEET FROM SUBSTATION
0.021
0.018
0.015
0.012
0.000
0.000
0.000
0.000
UG/M3
ST CLEANUP
2ND CLEANUP
3RD CLEANUP
AUG 4
SEP 1
OCT 1
NOV 1
DATE

Figure 2.

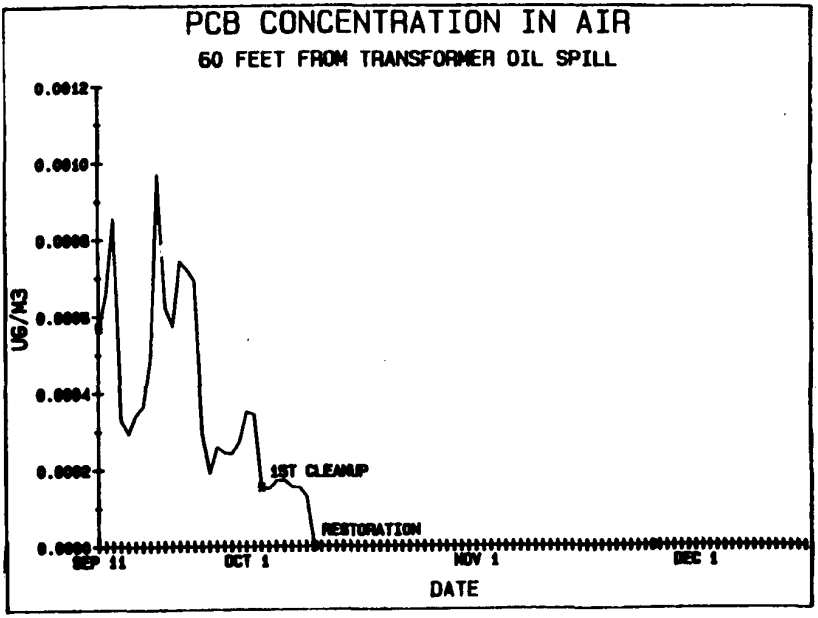
PCB CONCENTRATION IN AIR
60 FEET FROM TRANSFORMER OIL SPILL
UG/M3
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
1ST CLEANUP
RESTORATION
SEP 11
OCT 1
NOV 1
DEC 1
DATE

Figure 3.

PART 7:

PCB FIRES

Measurement of PCDF and PCDD in Utility Equiment

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Introduction

There is increasing interest in the potential for formation of polychlorinated dibenzofurans (PCDF) and polychlorinated dibenzo-p-dioxins (PCDD) from uncontrolled fires involving polychlorinated biphenyl (PCB)-containing dielectric fluids. At the temperatures that prevail in transformer fires, PCB may react to form PCDF and other toxic oxidation products. Information is sparse, however, on the distribution of PCDF and PCDD in the PCB-containing insulating fluids used by the electric utility industry. Even less is known about the effect of service time on the contaminant concentration in PCB-filled electrical equipment. There is also the possibility that abnormal operation (arcing, overheating) may create conditions that lead to the formation of PCDF and PCDD. In order to address this issue, the Electric Power Research Institute (EPRI) recently initiated a program to evaluate and develop compound-specific analytical procedures for characterizing PCDF and PCDD in PCB-containing insulating fluids.

Although the toxicological effects of PCDF and PCDD on humans is not well understood, tests using laboratory animals suggest that these compounds are much more toxic than PCB. Moreover, they generally occur at very low ambient concentrations, and toxicities can vary over a range of five orders of magnitude depending on the specific compound (i.e., degree of chlorination and location of chlorine atoms). Consequently, in order to measure specific compounds at pg/g (parts-per-trillion) levels, the EPRI-sponsored research has three basic goals:

- Improve the chemical analytical methods for individual compounds of PCDF and PCDD

- Determine the concentration of PCDF and PCDD in utility equipment that has seen varied use
- Develop a screening test that determines PCDF and PCDD concentrations rapidly in order to reduce costs and time delays before undertaking cleanup activities after PCB fires.

To this end, the program has been divided into the following tasks:

- Round-robin method evaluation
- Analysis of spiked sample matrices and in-service dielectric fluids
- Development of a rapid MS/MS screening technique.

This paper summarizes the chemical analytical methods used and some of the early results of these studies. Results of the MS/MS investigation will be reported elsewhere.

Analytical Approach

The isomer-specific analysis of trace concentrations of PCDF and PCDD in PCB-containing fluids is a challenging problem. The analytical difficulty is often compounded by the presence of interfering substances such as PCB or polychlorinated diphenyl ethers. Combined capillary column gas chromatography/mass spectrometry (GC/MS) is the method of choice for the measurement of PCDF and PCDD in trace amounts. The selectivity of high resolution GC together with the sensitivity of mass spectrometry yields detection limits of 0.5 to 2 ng/g (parts-per-billion) for these compounds.

Since GC columns cannot handle PCB-contaminated fluids (sample matrices) directly, the samples must be extracted first with a suitable solvent to separate the analytes of interest (i.e., PCB, PCDF, PCDD) from them. This is followed by an enrichment step to remove co-extracted interferences and to concentrate the PCDF and PCDD in the sample extract. Finally, GC/MS analysis of the sample extracts provides the identification and quantitative measure of the PCDF and PCDD of interest, based on the premise that GC separation of each chlorinated compound class can be achieved so that a unique set of mass spectral indicator ions can be monitored for each of the appropriate GC retention time windows. The use of high resolution GC/high resolution MS (HRGC/HRMS) improves the isolation of PCDF and PCDD from impurities and reduces the need for extensive sample cleanup.

To determine the recovery efficiency and improve quantitation, appropriate ^{13}C-labeled isotopic analogs of the "dioxins" and "furans" are added to the samples. (^{13}C-containing compounds are not present in significant quantities in naturally occurring materials and are clearly distinguishable from native compounds by mass spectrometry. Spiking samples with labeled compounds thus provides unique internal standards for accurate analysis.)

Round-Robin Method Evaluation

The round-robin method evaluation is designed to validate the analytical procedure and to determine the reliability with which specific compounds can be identified and quantified. It includes the synthesis of native and isotopically labeled standards and the analysis of spiked sample matrices using the best available in-house procedure. Five laboratories are involved in this effort: Battelle Memorial Institute, IIT Research Institute (IITRI), New York State Department of Health (NYSDH), Radian Corporation, and University of Umea. Radian synthesized the standards and prepared the spiked matrix samples. These have been analyzed by the five laboratories.

The laboratories use a variety of extraction-cleanup procedures and analytical GC/MS techniques, the main elements of which are summarized in Table 1. Five baseline samples (Aroclor 1016, Aroclor 1242, Aroclor 1260, tri- and tetrachlorobenzenes, and aged mineral oil) were spiked with the isotopically labeled internal standards ^{13}C-2,3,7,8-TCDF, ^{13}C-2,3,7,8-TCDD, ^{13}C-1,2,3,7,8-PnCDF, and ^{13}C-OCDD at concentrations of 100 ng/g each. In addition, the three Aroclors and the tri- and tetrachlorobenzene samples were spiked with the native isomers 1,2,3,4,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF at concentrations of 100 ng/g each. The aged mineral oil sample contained several additional unlabeled isomers as well as 510 µg/g Aroclor 1260 and 530 µg/g tri- and tetrachlorobenzenes. A summary of the measured average total congener class concentrations obtained by the reporting laboratories is presented in Table 2.

In general, agreement between the values obtained by the various groups was found to be within a factor of two. In the case of the tri- and tetrachlorobenzene sample, fairly good agreement was also obtained between the expected and measured amounts for the isomers spiked into the matrix, and virtually no additional PCDF and/or PCDD was detected. By contrast, the Aroclor 1260 sample contained significant amounts of a large number of PCDF compounds. Lower, but still significant, amounts were measured for the remaining Aroclors, while the aged mineral oil sample had concentrations close to that of the spiked values.

Analysis of In-Service Dielectric Fluids

A preliminary round-robin study was undertaken by three of the participating laboratories using four samples of dielectric fluids taken from in-service transformer and capacitor units. The average total congener class concentrations found for PCDF are shown in Table 3. Owing to differences in analytical procedures and variabilities in sample matrices, estimates of detection limit have not been included.

Sample ISL1O was a mineral oil contaminated with 100 µg/g PCB from a transformer that had failed in service by arcing. Sample ISL2A was an Askarel containing Aroclor 1242, which was removed from a capacitor that had bulged, but not ruptured, in service. Both samples had PCDF at concentration less than or equal to the limits of detection. Samples ISL3A and ISL4A both contained 70% Aroclor 1260 and 30% trichlorobenzene. Sample ISL3A was taken from an Askarel transformer after 20 years of service and contained 0.5 to 2.0 µg/g of PCDF. Sample ISL4A was taken from a transformer (of a different manufacturer) after 31 years of service. It had substantially higher concentrations of these partial oxidation products for all congener classes except total TCDF.

Work to date has developed improved measurement methods for compound specific PCDF and PCDD in PCB-contaminated insulating fluids. Thus far, the results do not suggest a preferred analytical technique. Analysis of the four in-service fluids indicate measurable quantities of specific PCDF compounds in 20- to 30-year old insulating fluids, however, there is insufficient information for generalization to all utility equipment.

Future work will focus on replicate analyses of another three baseline samples as well as 10 in-service samples.

Table 1. Summary of Analytical Protocols for PCDF and PCDD Measurements

Laboratory	Cleanup: Solvent Extraction	Cleanup: Column Chromatography	Analysis: Capillary Gas Chromatography*	Analysis: Mass Spectrometry**
Battelle	None	$SiO_2/Al_2O_3^{\ominus}/Al_2O_3^{\ominus}$	DB-5, CPSil-88	HRMS, EI
IITRI	None	Gel permeation/ $Al_2O_3^{\ominus}/Al_2O_3^{\oplus}$	SP-2330/CPSil-88	LRMS, EI
NYSDH	None	$Al_2O_3^{\ominus}/C/Al_2O_3$	SP-2330	HRMS, EI
Radian	CH_3CN/ hexane	$SiO_2/Al_2O_3^{\ominus}/Al_2O_3^{\oplus}$	DB-5, SP-2340	LRMS, EI
Umea	None	C-fiber/reverse elution/Florisil	SP-2330	LRMS, NCI

*Fusad-silica capillary columns

**LRMS = low resolution MS; HRMS = high resolution MS; EI = electron impact; NCI = negative ion chemical ionization (methane). (All use selected ion monitoring mode MS).

Table 2. Average Total Congener Class Concentrations of PCDF and PCDD in Spiked Baseline Samples

Congener Class	Sample, µg/g: Aroclor 1016	Aroclor 1242	Aroclor 1260	Tri- and tetra-chlorobenzenes	Aged Mineral Oil
ΣTCDD	ND	ND	ND	ND	0.03±0.02
ΣTCDF	0.01±0.01	0.94±0.78	0.55±0.39	ND	0.10±0.02
ΣPnCDF	0.01±0.02	0.33±0.24	1.15±0.68	ND	0.21±0.04
ΣHxCDF	0.18±0.12	0.10±0.03	2.73±2.08	0.34±0.44	0.44±0.44
ΣHpCDF	0.08±0.01	0.12±0.06	1.83±0.71	0.11±0.04	0.07±0.05
OCDF	0.01±0.01	0.63±1.12	2.81±1.22	ND	0.22±0.15

ND = not detected

Table 3. Average Total Congener Class Concentrations of PCDF in Four In-Service Dielectric Fluids

Congener Class	In-service Sample, µg/g			
	TSL4A	TSL3A	TSL2A	TSL1O
ΣTCDF	0.1	0.5	ND	ND
ΣPnCDF	2.6	1.6	0.01	ND
ΣHxCDF	7.6	1.6	0.01	ND
ΣHpCDF	16.3	2.0	ND	ND
OCDF	9.8	1.0	ND	ND
Total PCDF	36.4	6.7	0.02	ND

ND = not detected

FORMATION OF PCDFs AND PCDDs IN ELECTRICAL DISCHARGES

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F. L. DeRoos
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Mixtures of PCBs and TCBs (chlorinated benzenes), called "askarels", have been used as the liquid dielectric insulation and heat transfer material in transformers where fire resistance is of particular concern. There also has been an intermingling of askarels and the mineral oils more commonly used in transformers. PCDFs are products of partial oxidation of PCBs and both PCDFs and PCDDs are products of combustion of TCBs. PCDF and PCDD formation in fires is being studied widely. Their formation in the dielectric liquid in and near the vicinity of an electrical breakdown has not been examined. Electrical breakdown represents a malfunction in a transformer which is neither readily controlled nor reproduced and occasionally cannot be contained. Electrical failure of actual transformers then is not an acceptable approach to examining PCDF and PCDD formation. This report describes studies of the formation of PCDF and PCDD in controlled simulations of high energy electrical breakdown - "arcing" - in transformers. Askarels alone and mineral oil containing low concentrations of askarels have been examined.

EXPERIMENTAL

Test cells were capped, glass filament wound epoxy fuse tubes (6.8 cm ID x 40 cm L) containing 1.35 l of liquid, with a wrap of 0.23 mm thick electrical insulating Kraft paper inside the tube; both half saturated with water and fully saturated with air. The air space over the oil was 17% of the oil volume. Electrodes were radiused 1.5 cm D aluminum rods with a 1.27 cm gap, initially bridged by a small diameter low carbon steel wire to start the arc. Each cell was provided with a connection to a pressure gauge, a pressure transducer and a gas sampling container. Current, arc voltage, duration and pressure excursions were recorded; I^2*t products and arc energies were integrated automatically.

Askarels tested were electrical grade trichlorobenzene (Hooker Chemical) and Aroclors 1254 and 1260 (PCB mixtures made by Monsanto Company). TCB and a 1:1

mixture of TCB and Aroclor 1254 were each treated twice with 3% of their weight of activated Fuller's earth, a normal manufacturing practice in removing polar impurities prior to filling askarel transformers. One component usually added to askarels was 0.16% of 3,4-epoxycyclohexyl methyl-(3',4'-epoxycyclohexane) carboxylate as a scavenger for chlorine or water. The possibility of its halogenation, dehydrogenation and rearrangement to form PCDFs and PCDDs is remote and it was omitted here to simplify the testing. Oil samples were made from commercially available, Fuller's earth treated transformer oil and Aroclor 1254 [50ppm, 500ppm, 3ppt (parts per thousand), 10ppt], Aroclor 1260 (10ppt) or TCB (10ppt). PCDFs, PCDDs and some PCBs were separated from the sample matrixes using silica and activated alumina. Analysis was done by capillary column GC/MS with ^{13}C PCDF and PCDD spikes (1).

RESULTS

Two or more samples of each liquid were subjected to arcing and at least one of each pair was analyzed for PCDFs and PCDDs. Arc currents ranged from 700 to 750 amps rms and durations from 48 to 96 msec. The intent was to control the arc energy to less than 10 kJ. The pressure buildup in the cells was proportional to the arc energy, and in two cases, it pegged the pressure gauge at 60 psig. The energy dissipated in an actual transformer arc might reach 100 kJ. However, actual transformer arcs are not confined to volumes as small as that of these test cells and the test conditions are considered to be more severe. Arcing parameters are listed in Table 1.

TABLE 1

ARCING TESTS - ASKARELS AND OIL CONTAINING ASKARELS

Tube Number	Dielectric Liquid	Arc Parameters				Final Pressure (psig)
		Current (Amp)	Time (ms)	Charge (C)	Energy (kJ)	
2	TCB	745	48	36	4.3	12
	TCB/1254					
4	1:1	735	90	66	11.5	>60
5	1:1	725	55	40	3.7	13
	Oil/1254					
6	50 ppm	730	72	53	6.5	29
7	500 ppm	715	80	57	9.4	52
8	3.0 ppt	705	46	33	3.1	10
9	10.0 ppt	715	53	45	6.4	30
	Oil/1260					
10	10.0 ppt	745	48	36	3.7	14
	Oil/TCB					
11	10.0 ppt	730	88	65	15.6	>60

The concentrations of PCDFs and PCDDs in the TCB and TCB/1254 mixture before (B) and after (A) arcing are given in Table 2. A good deal of carbonaceous residue was formed in the liquids. A portion of this was filtered from a TCB sample, washed with methanol, extracted with benzene and analyzed. The results of these analyses are also given in Table 2.

TABLE 2

PCDF AND PCDD CONTENT OF ASKARELS BEFORE AND AFTER ARCING

Isomer	PCDF or PCDD Content - ng/g (ppb)			
	TCB		50:50 TCB/Aroclor 1254	
	Tube 2		Tube 4	Tube 5
	B/A	Particles	B/A	B/A
PCDF				
Tetra-	280/270	100	367/173	230/96
Penta-	2000/2500	990	1850/1740	1200/340
Hexa-	1700/2000	1500	1790/1180	1300/310
Hepta-	930/1000	1100	2960/1360	520/29
Octa-	170/150	560	217/171	100/8
Total	5820/5920	--	7184/4624	3350/783
PCDD				
Tetra-	33/29	40	21/24	20/6
Penta-	11/16	ND	ND/12	1/1
Hexa-	4/2	ND	ND/2	2/ND
Hepta-	ND/ND	ND	ND/ND	ND/ND
Octa-	ND/ND	ND	ND/ND	ND/ND
Total	48/47	--	21/38	23/7

ND - Not Detected

The results of analysis of the oil samples before and after arcing are given in Table 3 (Note - Analysis of the unarced 10ppt Aroclor 1254 in oil sample

TABLE 3

PCDF CONTENT OF OIL CONTAINING PCBS - BEFORE AND AFTER ARCING

PCDF ISOMER	PCDF Content - ng/g (ppb)				
	Aroclor - mg/g (ppt)				
	1254			1260	TCB
	Orig 1000 ppt	Tube 8 3 ppt B/A	Tube 9 10 ppt B/A	Tube 10 10 ppt B/A	Tube 11 10 ppt B/A
Tetra-	-- (180)	0.1/ND (0.5)	--/11 (2)	1/1	ND/ND
Penta-	-- (400)	3/0.5 (4)	--/4 (4)	3/2	0.4/ND
Hexa-	-- (900)	1/1 (3)	--/2 (9)	4/3	1/ND
Hepta-	-- (110)	6/ND (0.3)	--/ND (ND)	6/7	ND/ND
Octa-	-- (30)	ND/1 (0.1)	--/ND (ND)	23/15	ND/ND
Total	-- (1620)	11/2 (8)	--/7 (15)	37/29	1/ND

( ) - calculated values, see text

was not done. The concentration of PCDF in the Aroclor 1254 was estimated from the analysis of the TCB/1254 mixture and the TCB itself. The concentration in the unarced Tube 9 sample was then calculated from the dilution factor. As a check, this same procedure was followed for the 3ppt 1254 sample. The calculated and measured values are in reasonable agreement.) PCDF content of the 50 and 500ppm Aroclor 1254 samples were below the limit of detection both before and after arcing, as was the PCDD concentration in all oil samples.

DISCUSSION

The TCB and Aroclors used here were retained samples from the mid-1970's. After a laboratory treatment similar to that done on a larger scale in the manufacture of transformers, measurable PCDF and PCDD remain. It, therefore, seems probable that, if unused transformers could be found and askarel samples taken and analyzed, measurable PCDFs and PCDDs could be found. This, in turn, suggests that the interpretation of analyses of samples from functioning transformers and other sources will be complicated by the presence of an unmeasured and variable background.

It also appears that arcing TCB and PCBs under the conditions here does not result in the formation of PCDFs and PCDDs. The reliability of the analytical method is still under study, but clearly there is no major increase in the levels found. If anything, there appears to have been a reduction in the solution concentrations. This may, in part, be due to adsorption of the preexisting furans and dioxins on the carbonaceous material forming in the discharge. No attempt was made to recover all of this finely divided powder. It is a minor, but very visible, amount. Unless the extraction with benzene is very inefficient, the powder is not a sink for any major quantity of PCDFs and PCDDs which may have been formed in the discharge.

ACKNOWLEDGMENT

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(1) F. L. DeRoos, to be published in a forthcoming EPRI report.

SAFETY OF NON-PCB RECLASSIFIED TRANSFORMERS IN FIRE INCIDENTS
A BUILDING SCALE ENGINEERING STUDY

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INTRODUCTION

In July 1985 the U.S. Environmental Protection Agency promulgated new regulations that impact all electrical transformers containing greater than 500 ppm (w/w) polychlorinated biphenyl (PCB). This regulation, known as the "Fire Rule", was the result of scientific evidence that combustion of PCB containing coolants produce polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). Because of the risks posed by a fire incident, the continued use of certain PCB transformers is banned after 1990. An economic alternative to the replacement of PCB transformers is to remove PCB from the transformer cavity and refill the transformer (retrofill) with a nonhazardous coolant that does not produce PCDD or PCDF if an accidental building fire were to occur. Ideally all of the PCB would be removed by retrofilling, however due to the difficulty of extracting PCB from porous constituents of the windings, a residual amount usually remains. Current regulations consider a transformer to be non-PCB if the residual level is less that 50 ppm (w/w), following a period of 90 days normal service.

Numerous publications over the past several years have indicated that PCB can be converted directly to PCDF by intramolecular condensation reactions and that chlorinated benzenes can likewise be converted to both PCDD and PCDF by intermolecular reactions(1). In all cases, the results were obtained through small, bench-scale experiments, or sealed tube pyrolysis techniques, which did not involve combustion. Since neither the scale or the experimental conditions of previous programs simulated true fire conditions, Union Carbide and Battelle felt that it was inappropriate to extrapolate such data to assess the potential for dioxin and furan formation from building fires. Furthermore, all studies were with

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neat PCB, or neat chlorobenzenes, and no information existed on the PCDD/PCDF formation when small quantities of these materials were present, such as might exist in a transformer which had been serviced and successfully reclassified as non-PCB, i.e., less than 50 ppm.

EXPERIMENTAL

Battelle's Columbus Laboratories, under contract to Union Carbide, designed and built a pilot scale combustion apparatus which would simulate the conditions existing in an accidental building fire (see Figure 1). A panel of international experts in the area of fire research and PCDD/PCDF analysis was assembled to guide and direct this program.

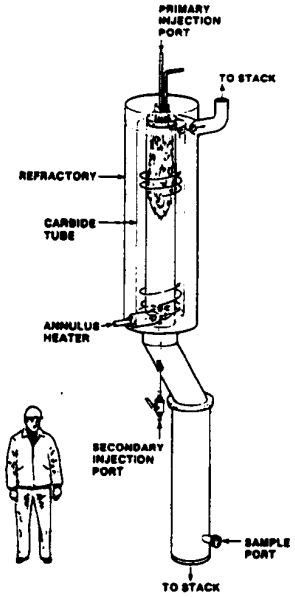

Figure 1. Schematic Diagram of the Combustion Test Apparatus

Considering the difficulty in controlling and measuring the combustion conditions, and the difficulties in collecting all by-products formed, pool fire techniques were ruled out. Instead, an enclosed furnace was built. The test unit was a 40,000 Btu/hr, vertically fired tube furnace with a combustion zone 131 cm long (4.3 ft), and having a 14 cm internal diameter (5.5 in.). The combustor was fired using kerosene containing 1% (w/w) silicone coolant. This was done to simulate organic fuel and soot conditions in a burning building fire and to provide condensation nuclei that could promote catalytic production of PCDF/PCDD.

The fluids tested in this study were introduced into the combustor at a point where the temperature profiles were approximately 800°C. The optimum temperature for PCDF (and PCDD) production is believed to lie between 450 and 650°C as a function of available oxygen. By introducing the coolants into the post flame region, the thermodynamic optimum temperatures were achieved without exposing the test liquids to flame conditions that would destroy product PCDF/PCDD.

The materials burned in this study were silicone transformer coolants containing 1.5% (w/w) Union Carbide TF-1 transformer fluid (a material used to remove PCB from inservice transformers). The five liquids tested are described in Table 1. A blank run was performed without a secondary injection liquid to test the system background. A control series was performed with TF-1 in silicone coolant as the secondary injection liquid. Three series were performed each injecting a separate Aroclor doped at 50 ppm (w/w) in silicone coolant: 1260, 1254, and 1242. Each test condition was run in triplicate and the results reported in this paper are the average of three determinations.

Table 1

COOLANT FLUIDS INJECTED INTO THE POST-FLAME REGION

Run	Fuel(1)	Coolant Injected	Dopant
1	Kerosene	Silicone	Blank
2	Kerosene	Silicone	Control(2)
3	Kerosene	Silicone	Aroclor 1260(2,3)
4	Kerosene	Silicone	Aroclor 1254(2,3)
5	Kerosene	Silicone	Aroclor 1242(2,3)

(1) The combustion fuel was kerosene doped with 1% (w/w) silicone.
(2) TF-1 at 1.5% (w/w) was doped into the silicone coolant.
(3) All Arolors were spiked into the silicone test liquid at 50 ppm (w/w).

In a building fire not all the transformer coolant will be exposed to the optimum conditions for PCDD/PCDF formation. In the center of a fire, temperatures exceed several thousand degrees farenheit, and PCDD/PCDF if formed, are probably destroyed just as quickly. At distances away from the fire, temperature profiles decrease quickly until temperatures are insufficient for conversion. Also, a fire inside an enclosed area, will not burn evenly. Rather the fire will pulse as it varies between oxygen lean and oxygen rich conditions. How much transformer coolant will be exposed to favorable conditions for PCDD/PCDF formation will vary greatly between fires and cannot be predicted. In a shakedown test, it was noted that when less than the stoichiometric amount of oxygen was used, no dioxin and lowered PCDF conversion was observed. In setting the parameters for the burn tests, several volume percent excess oxygen was maintained. Therefore, the experimental conditions in this test protocol assumed that all dielectric coolant is exposed to the flame region in a temperature profile necessary for optimum PCDD/PCDF formation, and under conditions of excess oxygen. Thus these conditions represent the worst case scenario.

Stack gas samples were collected from the pilot plant combustor using a U.S. EPA Modified Method 5 (MM5) sampling train with each train collecting a nominal 2 standard cubic meters (SCM). This sampler was previously validated by Battelle for collection of PCDD in combustion sources for the U.S. EPA (2). The MM5 train consists of a primary particulate filter section, followed by a cold water-jacketed resin trap. The trap contains 22 g of XAD-2 resin.

After combustion sampling, the filters and the XAD-2 resin modules from each train were spiked with isotopically labelled internal standards and Soxhlet extracted for 18 hours with benzene. The combined extracts were concentrated to approximately 6 mL and divided into three equal portions. These separate aliquots were blind coded and sent to three laboratories for analyte enrichment and final analysis. The Battelle analyte enrichment consisted of partitioning the extracts through two liquid chromatography columns. The first column was multilayered silica containing alternate layers of sulfuric acid treated, and sodium hydroxide treated silica gel, separated by layers of activated silica gel. The second column contained approximately 3 g of activated basic alumina. The extracts from the alumina column containing the PCDD/PCDF analytes were concentrated and solvent exchanged into n-decane.

The extracts were analyzed independently using two different gas chromatography/ mass spectrometry methods (GC/MS). Battelle and Oneida Research used capillary column GC/MS with high resolution mass spectrometry as the selective detection technique. The University of Umea used capillary GC/MS with negative chemical ionization mass spectrometry to enhance analyte sensitivity and selectivity. Each laboratory was provided standard solutions of labelled PCDD/PCDF reference compounds which were analyzed to determine response factors for quantification.

RESULTS

In the Union Carbide servicing, residual PCB are extracted from transformers with a special coolant, TF-1. When removal is complete, electrical grade silicone is placed permanently in the transformer. The liquids combusted in this study simulated the permanent silicone with small amounts of TF-1 residuals from servicing, and 50 ppm (w/w) PCB. Tri/tetrachlorobenzenes and epoxide acid scavengers were also part of Askarel formulations and were included in the silicone test liquids. Thus the materials tested in this study, duplicated the coolant from an Askarel transformer which had been serviced with TF-1 to remove PCB and subsequently retrofilled with silicone.

The results of this study revealed no measurable PCDD production and only traces of PCDF. The PCDD results are given in Table 2. In all experiments PCDD reported as total tetra and penta congeners, along with the specific concentrations of 2,3,7,8-tetrachlorodibenzo-p-dioxin(TCDD), revealed concentrations either not detectable (ND), or below the detection limit (BDL).

Furans were found at trace, but measurable levels. Results of the PCDF analyses are summarized in Table 3. It is apparent from these data that Arochlor 1260 produces the highest relative levels of PCDF which is expected due to the higher level of chlorination in Arochlor 1260 than 1254. Arochlor 1242 which has the lowest chlorine content also produced the lowest PCDF levels. In all cases the amounts of PCDF produced are below one ppb (w/w).

The conversion of Aroclor to PCDF, as measured by the tetrachlorodibenzofuran (TCDF) and pentachlorodibenzofuran (PnCDF) congeners, were extremely low under conditions of a simulated building fire. Table 4 gives the conversion factor for PCDF (total TCDF and PnCDF) based on the mass of each Aroclor burned.

Table 2

DIOXIN (PCDD) RESULTS FROM THE COOLANT FIRE STUDY
(Results in ng/kg (pptr) of Coolant Burned)

Dielectric	Dopant	Congener	Battelle	Oneida	Umea
Silicone	None	Tetra	ND(1) (ND)(2)	ND (ND)	NA (NA)
		Penta	NA(3)	ND	NA
Silicon	Aroclor 1260(4)	Tetra	ND (ND)	BDL(5) (ND)	ND (ND)
		Penta	NA	ND	ND
Silicone	Aroclor 1254(4)	Tetra	ND (ND)	ND (ND)	ND (ND)
		Penta	NA	ND	ND
Silicone	Aroclor 1242(4)	Tetra	ND (ND)	ND (ND)	ND (ND)
		Penta	NA	ND	ND

(1) ND = Not detected at the limit of detection. In all cases, the limit of detection was below 15 pg/KG collant burned.

(2) The 2, 3, 7, 8 isomer concentration is given in parenthesis.

(3) NA = Not analyzed.

(4) Aroclor dopants at 50 ppm (w/w) plus 1.5% TF-1.

(5) BDL = Below detection limit.

Table 3

FURAN (PCDF) RESULTS FROM THE COOLANT FIRE STUDY
(Results in µg/Kg (ppb) of Coolant Burned)

Dielectric	Dopant	Congener	Battelle	Oneida	Umea
Silicone	None	Tetra	0.01 (0.007)(1)	ND(2) (ND)	NA(3) (NA)
		Penta	NA(3)	ND	NA
Silicone	Aroclor 1260(4)	Tetra	0.86 (0.24)	0.39 (0.20)	0.35 (0.06)
			NA	0.50	0.24
Silicone	Aroclor 1254(4)	Tetra	0.54 (0.08)	0.19 (0.10)	0.42 (0.07)
		Penta	NA	ND	0.27
Silicone	Aroclor 1242(4)	Tetra	0.13 (0.01)	ND (ND)	0.12 (0.02)
		Penta	NA	ND	0.08

(1) The 2, 3, 7, 8 isomer concentration is given in parenthesis below TCDF value.

(2) ND = Not detected at the limit of detection. In all cases, the limit of detection was below 15 pg/Kg collant burned.

(3) NA = Not analyzed.

(4) Aroclor dopants at 50 ppm (w/w) plus 1.5% TF-1.

Table 4

PCB CONVERSION FACTORS TO PCDF TIMES 10^{-6}

	Tetra	2,3,7,8	Penta
Aroclor 1260	1 - 22	0.1 - 6	1 - 16
Aroclor 1254	5 - 15	2 - 6	7
Aroclor 1242	3 - 4	0.3 - 0.4	2

CONCLUSIONS

- No PCDD or PCDF were produced by combustion of silicon transformer coolant alone.
- TF-1 (1.5% (w/w)) representing residuals from servicing operations, produced no detectable quantities of PCDD or PCDF during combustion tests.
- Silicone coolant doped with 50 ppm (w/w) Aroclor 1260, 1254, or 1242, produced no measurable PCDD, and only trace amounts of PCDF during combustion tests. The amount of PCDF produced in any test was less that 0.001 ppm (w/w), or less than 1 ppb (w/w), based on the mass of silicone injected.
- The PCDF concentrations tended to decrease as the degree of chlorination of the doped PCB decreased; Aroclor 1242<Aroclor 1254<Aroclor 1260.
- The TCDF concentrations ranged from an average of 0.43 ppb (w/w) for Aroclor 1260, to less than 0.08 ppb (w/w) for Aroclor 1242. Likewise, PnCDF levels ranged from an average of 0.31 ppb (w/w) for Aroclor 1260 to less than 0.04 ppb (w/w) for Aroclor 1242.
- For the case of retrofilled transformers, these data indicate that worst case conversion of residual PCB to PCDD is neglegible, and to PCDF is below parts-per-billion based on the mass of dielectric consumed. This indicates that only trace amounts of PCDF would be formed during building fires that involved retrofilled transformers, and most of the PCDF would be deposited near the fire source.

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PYROLYSIS AND COMBUSTION OF PCB CONTAMINATED TRANSFORMER FLUIDS

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Various laboratory-scale experiments have demonstrated that heating PCBs at high temperatures can produce substantial concentrations of PCDFs. Real-world confirmation of this result has been produced in a variety of incidents in which PCB-containing transformers and capacitors have been involved in fires. However, much less data is available on the proclivity of dilute solutions of PCBs to form PCDFs during pyrolysis and/or combustion. Naively, it might be predicted that dilution of PCBs would result in a constant percentage conversion to PCDFs, since the process is plausibly formulated as kinetically first-order in PCB concentration. However, other possibilities exist. The diluting fluid may itself provide facile pathways for PCB decomposition into non-PCDF products, or it may be a much more effective competitor for the reactive species involved in PCDF formation, thus minimizing that process. Alternatively, it might be imagined that the diluting fluid generates a reactive species that accelerates PCDF formation, or, through a bulk solvent effort, stabilizes the transition state leading to PCDF formation. In view of these various possibilities and the potential economic importance of the question, a study was initiated to assess the PCDF-forming potential of dilute (5,000-50 ppm) solutions of Aroclor 1254 in various solvents of potential interest to the utility industry (mineral oil, tetrachloroethylene, and silicone oil).

Since transformer fires are highly complex and variable events, no simple laboratory simulation will accurately predict their outcomes. Two rather different sets of experimental conditions were investigated here; nevertheless, these experiments do not assess all the variable parameters that might influence the course of a real event. Pyrolysis, defined here as heating in the absence of a flame, was accomplished by placing 100 ul of the solution of interest in an open pyrex glass tube (6mm OD x 50 cm length): the tube was mounted vertically, and the lower 3 inches inserted into a tight fitting metal block preheated and thermostatically maintained at a specific temperature (usually 450-650°C).

Generally, a contact time of 15 minutes was used. The open end of the tube was packed in dry ice. As an additional precaution to avoid escape of any PCDFs, the end of the tube was attached to an activated carbon filter. In an effort to minimize any potential exposures to toxic mixtures and to simplify analytical procedures, preliminary experiments were performed using individual PCB congeners expected to form biological inert dibenzofurans. Since only one or a small number of dibenzofuran products was expected, it was frequently possible to approximate the "optimal conditions" (i.e., those resulting in maximum PCDF formation) using gas chromatography with electron capture or flame ionization detection rather than GC/MS. After these range finding experiments were complete, 5000 ppm Aroclor 1254-containing mixtures were pyrolyzed to confirm optimal conditions.

Finally, six samples at each concentration (5000 ppm, 500 ppm [where appropriate] and 50 ppm) were pyrolyzed and randomly combined to form two composite samples at each concentration prior to GC/MS analyses. In addition, scanning GC/MS analysis was performed on the pyrolyzed 5000 ppm solutions and on the "blank" pyrolyzed solution to allow identification of the principal non-PCDF products formed. In consideration of results obtained from these experiments, it should be remembered that the temperature regimen actually experienced by a particular congener is not well-defined, since the liquid refluxes up the tube and out of the heated region.

Combustion, defined here as heating in the presence of a flame, was conducted in an apparatus consisting of a blast burner, a combustion tube, a sample introduction unit and a sample collection unit. The quartz combustion tube (115 x 2.5 cm) has three independently heatable zones. The sample is introduced into the flame of the blast burner via a syringe drive; residence time can be varied by the introduction of make-up gas. Samples are collected in an apparatus consisting of an impinger (connected to the combustion tube), and an XAD-2 packed absorption tube. The collection apparatus is, in turn, connected through an orifice to a vacuum line. Thus, escape of any PCDF from the apparatus is unlikely. The apparatus permits determination of PCDF formation as a function of PCB concentration, residence time, wall temperature, oxygen concentration, etc.

PCB ACCIDENT IN FRANCE

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In the evening of January 14, 1985, an explosion followed by a fire ruptured a transformer in the basement of a residental building in Reims, France. Due to the low outdoor temperature the transformer was probably overloaded. The dielectric fluid in the transformer consisted of a mixture of PCB (60%) and trichlorobenzene (TCB) (40%).

Although the power was disconnected after the explosion, a "ball fire" apparently had initiated the combustion of flammable material contaminated by PCB and TCB. Soot and smoke was distributed throughout the 6-story building.

Soot and wipe samples

Two days after the accident dielectric fluid collected near the transformer and soot samples were analyzed. The results did not show the presence of polychlorinated dibenzofurans (PCDFs) or tetrachloro dioxins (TCDDs). However, other samples were collected in the building February 21 and April 2 and analyzed by us. Before extraction, the samples were fortified with ^{13}C labelled PCDFs. A Supelco fused silica column was used for the HRGC separation. The analyses were done on a Finnigan model 4500 MS instrument, the quantitative values were corrected for recovery (60-100%). A series of PCDFs have been identified with total levels up to $\mu g\text{-}mg/m^2$, see Table 1.

In three of the samples we have also found polychlorinated biphenylenes (PCBPs) at about the same levels as PCDFs but no or very low amounts of PCDDs.

Another series of samples were collected on March 15 and analyzed by a third laboratory. This laboratory could confirm the high levels of PCDFs but this laboratory did also report on a series of PCDDs at levels close to the levels of PCDFs. However, three other laboratories analyzing the same sample could not confirm the high levels of PCDDs, see Table 2.

It seems to be essential to study the chlorine cluster and the M^+ ions for the PCDDs (m/z 320, 354) to differentiate between this series and the PCBPs, which have one chlorine more and their M^+ ions at m/z 322, 356, see Figure 1.

Blood samples

Blood samples from persons exposed in this fire have been analyzed. A few Cl_5 and Cl_6 2,3,7,8-substituted PCDFs have been identified at low ppt levels.

Table 1. Levels of PCDFs and PCDDs in samples from Reims (Umeå).

	1 µg/m^2	2 µg/m^2	3 µg/m^2	4 µg/m^2	5 µg/m^2	6 µg/m^2
Tetra-CDFs	> 30	> 8	> 4.5	0.11	0.22	0.38
Penta-CDFs	960	590	37	0.89	1.5	1.40
Hexa-CDFs	760	570	36	0.70	1.2	1.90
Hepta-CDFs	530	490	27	1.2	1.9	3.3
Octa-CDF	290	220	36	NA	NA	NA
Tetra-CDDs	NA	NA	NA	NA	NA	NA
Penta-CDDs	< 1	< 1	< 0.005	< 0.005	< 0.005	< 0.005
Hexa-CDDs	< 1	< 1	< 0.005	< 0.005	< 0.005	< 0.005
Hepta-CDDs	35	32	< 0.005	0.11	0.14	0.33
Octa-CDD	16	14	< 0.005	0.18	3.45	0.33

The samples 1 and 2 were taken on the ceiling of the basement near the door of the transformer vault (February 21).

The sample 3 is a wipe sample collected externally on the door of the transformer vault (February 21).

Sample 4: Wipe sample on the second floor, near the door of an apartment (April 2).

Sample 5: Wipe sample is a bathroom, second floor (April 2).

Sample 6: Wipe sample in a kitchen, second floor (April 2).

Samples 4, 5 and 6 are collected after cleaning.

NA = Not Analyzed.

Table 2. Results from the analysis of the same sample.

	WATERLOO[*] ng/g	CERCHAR ng/g	RADIAN Corporation ng/g	RHONE-POULENC ng/g
Tetra-CDFs	35.000	500	490.0	220
Penta-CDFs	58.000	700	820.0	420
Hexa-CDF	25.000	2.000	190.0	25
Hepta-CDFs	8.000	700	3.7	110
Octa-CDF	3.000	-	14.0	160
Tetra-CDDs	56.000	< 1.000	ND[**]	45
Penta-CDDs	81.000	< 300	550.0	150
Hexa-CDDs	7.000	< 500	45.0	490
Hepta-CDDs	8.000	-	ND	210
Octa-CDD	8.000	-	ND	350

[*] Taking for the liquid 1.560 g/cm^3, the results of sample are converted in ng/g.

[**] 2,3,7,8-TCDD not measured and for other TCDD, the detection limit is 1.0 - 5.0 ng/g.

ND = Not detected.

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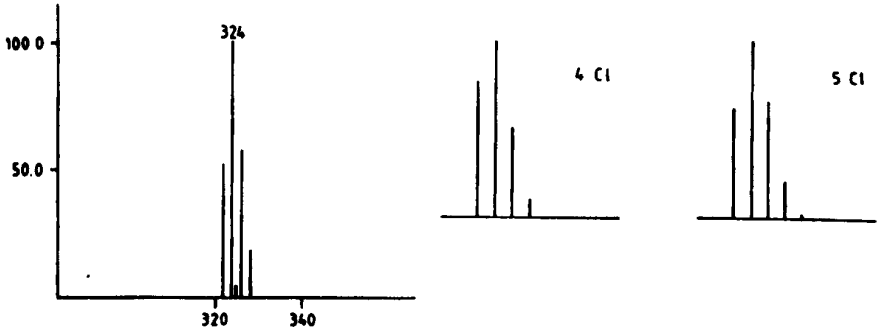

Figure 1. Pentachlorbiphenylene Identified in Soot Sample From Reims

PCBs Fires: Preliminary Correlation of Chlorobenzens and PCB Contents of the Fluid with PCDF and PCDD Contents of Soot

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PCBs, PCDDs, and PCDFs are subject to new regulations promulgated under the Toxic Substances Control Act and the Resource Conservation and Recovery Act. The finding of PCDDs and PCDFs in PCBs could restrict disposal options for PCBs. A review of major fire incidents in the United States indicates that PCDDs have been found only in the Binghamton, NY, transformer fire incident. Laboratory combustion studies further support PCDFs formation from PCBs and PCDDs from chlorobenzenes. No PCDDs were found in analyses of fluids from transformers involved in transformer fire incidents. PCDFs do not appear to increase in PCBs askarel fluids from normal usage in electrical equipment.

On July 9, 1985, the United States Environmental Protection Agency promulgated its final rule on Polychlorinated Biphenyls in Electrical Transformers, the culmination of a long fact-finding and rule-making process that developed shortly after the transformer fire at the State Office Building in Binghamton, NY, on February 5, 1981. In brief, this rule:(1)

1) Prohibits the use of higher secondary voltage (480 volts and above) network PCB Transformers in or near commercial buildings after October 1, 1990.

2) Requires, by October 1, 1990, 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.

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3) Prohibits further installation of PCB Transformers in or near commercial buildings after October 1, 1985.

4) Requires the registration, by December 1, 1985, of the exterior of all PCB Transformers with fire response personnel and building owners.

5) Requires the marking, by December 1, 1985, of the exterior of all PCB Transformer locations.

6) Requires the removal, by December 1, 1985, of stored combustibles located near PCB Transformers.

This rule does not spell the end of the issue surrounding PCB fluids in electrical equipment. Increased media attention to the problem of toxic substances generation in electrical equipment fires has prompted increased public awareness. In Washington, D.C., recently, fires or leaks involving transformers in the Smithsonian Institution, the White House, and the Department of Health and Human Services were given front-page attention in the Washington Post. Additionally, many utilities throughout the country have hundreds of thousands of gallons of PCBs in storage awaiting proper disposal. As some utilities have discovered, improper disposal can result in heavy penalties. In September 1985, the Potomac Electric Power Company (PEPCO) in Washington, D.C., signed a consent decree with the State of Maryland to clean up PCB contamination at a storage company to whom PEPCO sold 75 transformers contaminated with PCBs. The cleanup is expected to cost PEPCO from $1.5 to $3 million. Furthermore, the issue of PCBs-filled capacitors has not yet surfaced in the United States and it is not covered by the July 9 rule. However, capacitor fires in Sweden and Finland have certainly drawn attention to this area as well; moreover, the recent transformer fire in Reims, France, has not dispelled this attention.

To complicate the issue further, under the Resource Conservation and Recovery Act of 1976, EPA promulgated new rules on January 14, 1985, with regard to dioxins-contaminated wastes streams.(2) This rule defines certain waste streams as dioxins-contaminated wastes and thus, narrows waste treatment options to those approved for dioxins waste. One part of the proposed rule is intended to cover a broad variety of dioxins-contaminated wastes that are identified as EPA implements its Dioxin Strategy. In the implementation of this strategy the Agency has established seven categories or tiers of

investigation and study. Tier 4 covers: combustion sources such as municipal and hazardous waste incinerators, PCB transformer/capacitor fires, reactivation furnaces for spent granular activated carbon, boilers using PCBs and PCP-treated wood, etc.[3] Thus, this rule eventually may cover residue materials generated in a PCBs transformer fire if dioxins-contamination is shown, or, in situations where dioxins are found with "PCBs waste." A case in point is the problem encountered by a waste management company in Alabama. It accepted 40,000 gallons of "PCB waste" from the infamous Hyde Park Landfill in Niagara Falls. Since the waste contained >500 ppm PCBs, this waste was legally a PCBs waste. Unfortunately, Alabama State authorities were not informed via the forwarder's bill of lading that the nonaqueous phase leachate (NAPL) contained 20.2 ppm 2,3,7,8-TCDD along with hundreds of other halogenated organic and pesticidal residues and substantial quantities (100 to 1000 ppm) of toxic heavy metals. As a result, several of the 41 storage tanks at the waste management company's tank farm became contaminated with dioxin and 1.2 million gallons of PCB wastes are now tarmed "dioxin wastes," with no short-term solution in sight.

Regulations in the United States to date have focused on the PCDDs and PCBs. No federal regulation has been promulgated specifically for PCDFs. However, if PCDDs or PCDFs are found in PCBs, disposal options for PCBs could be further restricted.

Table 1 summarizes the analytical results of some of the major PCBs transformer and capacitor fires identified in the United States. This list represents only fire incidents where an effort was made to measure not only PCBs, but PCDDs and PCDFs as well. The list of reported PCB transformer fire incidents continues to grow in the United States and Europe.

PCDDs were clearly identified only with the Binghamton, NY, transformer fire. The finding of PCDDs at Binghamton, NY, is consistent with laboratory findings of PCDDs from pyrolysis of chlorobenzenes.[13] The Binghamton, NY, transformer contained 65% polychlorinated biphenyls (Aroclor 1254) and 35% tri- and tetrachlorinated benzenes. The intense heat of the Binghamton fire may have also created the optimal conditions for bimolecular reactions of chlorobenzenes, necessary for the formation of PCDDs.

Table 1. Some Major Fires Involving PCB's Transformers and Capacitors in the U.S.

PLACE	ANALYSES	PCDFs	PCDDs	COMMENTS	REFERENCE
Binghamton, NY State Office Building (2-15-81) (Transformer)	Soot Samples	Total PCDFs: 765-2160 ug/g 2,3,7,8-TCDF: 12-270 ug/g	Total PCDDs: 20 ug/g 2,3,7,8-TCDD: 0.6-2.8 ug/g	Transformer filled with 1060 gals. of Pyranol (65% PCBs) (Aroclor 1254) & 35% tri- and tetrachlorinated benzenes. Very hot fire, explosion & rupture of transformer with release of 180 gals. of fluid.	(4,5)
Cincinnati, OH Elementary School (12-3-80) (Capacitor)	Wipe Samples	ND	ND	Only 0.088 ml of PCBs (Aroclor 1254) was involved in the capacitor but the entire basement was contaminated at a mean level of 771 ug/100cm^2	(6)
Boston, MA Office Building (1-82) (Transformer)	Soot Samples	Total PCDFs: 165 ug/g 2,3,7,8-TCDF: 3 ug/g	ND	Transformer containing Aroclor 1254	(7)
Miami, FL Vault (4-3-82) (Transformer)	Soot Samples and Fire Residues	CDFs: 100-1000 ug/g	ND	Underground transformer vault	(8)
San Francisco, CA (Adj to High Rises) (5-15-83) (Transformer)	Wipe Samples	TCDFs - 15.6 ug/g	2,3,7,8-TCDD: approx. 0.1 of that detected in Binghamton soot[12]	3 transformers with 100% Aroclor 1242. No chlorobenzenes. 50 gals were released & smoldered for 8 hours after discovery.	(9)
Columbus, OH Office Building (3-84) (Capacitor	Wipe Samples	Total PCDFs: up to 10,000 ng 2,3,7,8-TCDF: up to 1000 ng	Total PCDDs: up to 44 ng 2,3,7,8-PCDD: up to 3.0 ng	Capacitor with Aroclor 1242	(10,11)
	Soot Samples	Total PCDFs: 10.9 ug/g	Total PCDDs: trace (tetra to octa). Trace amount of chlorobenzenes. (Detection limit at ug/g level.)		

Analysis of wipe samples from the Columbus, OH, fire also showed a very small amount of PCDDs, but the finding could not be quantified in the soot sample. No chlorobenzene was found in the soot sample from Columbus, OH. No analytical data is yet available on the capacitor oil itself, although it is known to contain Aroclor 1242; thus, it is not clear if pyrolysis of chlorobenzenes was the source of the small amount of PCDDs found. The transformer involved in the San Francisco fire was also filled with Aroclor 1242, but contained no chlorobenzenes. No PCDDs were found in the soot. In the San Francisco fire, 50 gallons of the fluid were released and allowed to smolder for 8 hours after the fire was discovered.

EPA, through a contract with the Midwest Research Institute, Kansas City, MO, has conducted several studies to evaluate thermal degradation products from dielectric fluid using a bench scale thermal destruction system.(14)

The first part of the study was to determine the optimum temperature, oxygen, and residence-time conditions for PCDF formation. The feed into the system was mineral oil spiked with three individual PCB congeners (2,3,4,6-tetrachlorobiphenyl, 3,4,5,3',4',5'-hexachlorobiphenyl, and 2,4,6,2',4',6'-hexachlorobiphenyl), which form PCDFs by the four reaction mechanisms proposed by Buser and Rappe.(13) The results indicate that the optimum values are a temperature of 675°C and an excess oxygen concentration of 8%. The residence time, in the range of 0.3 to 1.5 seconds, did not significantly affect the yield, although the observed yields of PCDFs were lower at shorter residence times.

In the next part of the study, duplicate test runs were conducted with mineral oil and silicone oil dielectric fluids containing PCBs (Aroclor 1254) at concentrations of 0, 5, 50, and 500 ppm. An askarel fluid containing 70% Aroclor 1254/30% trichlorobenzenes, and a non-PCB askarel fluid, containing mostly trichlorobenzenes with some tetrachlorobenzenes, were tested in duplicate. PCDFs were found in all samples. PCDDs were found in the samples from the trichlorobenzene runs and occasionally at low levels in some of the other samples. Up to 5,700 ng total PCDFs/ml of spiked feed oil or 4% conversion efficiency (PCBs to PCDFs) was observed for the mineral oil and silicone oil runs. Up to 19,000,000 ng total PCDFs/ml feed oil (19 mg/ml) or

3% conversion efficiency was observed for the askarel fluid. Statistical analysis showed a linear relationship for PCDFs formed versus the amount of PCBs.

PCDFs and, to a lesser extent, PCDDs were formed from the trichlorobenzene dielectric fluid under the optimum PCB-to-PCDF conversion conditions. Up to >110,000 ng total PCDFs/ml feed oil (>0.004% yield) and 1,900 ng total PCDD/ml feed oil (0.0001% yield) were observed for the trichlorobenzene runs. Tables 2 and 3 show the yields of the PCDF and PCDD homologues from the different runs.

The results indicate that the optimum conditions for PCDF formation from PCBs are near 675°C for 0.8 second or longer, with 8% excess oxygen. Under these 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 PCDDs formation.

One problem in evaluating data generated from the analysis of soot or wipe samples from a transformer or capacitor fire incident is the lack of data on the oil itself. EPA has obtained samples from transformers that were involved in fire incidents at Miami, FL, Binghamton, NY, and Chicago, IL. Total PCDFs (Table 4) in the used fluids are within the range of the PCDFs values previously reported for stock material. It does not appear that the normal use in electrical equipment generates PCDFs to any extent. PCDDs and PCDFs appear to be formed only after PCBs and diluents are released from the transformer/capacitor housing. The PCBs and diluents subsequently react under thermally stressful conditions in the presence of air or oxygen to form PCDDs and PCDFs as evidenced by: (a) detection at ug/g levels in soot samples taken from vault walls; and (b) the relative absence of PCDDs and PCDFs from the PCB fluids themselves.

Further information has been provided from European experiences[15] regarding a process used to convert lindane manufacturing wastes (α, β, δ-hexachlorocyclohexane, HCCH) to predominantly (70-75%) 1,2,4-trichloro-

Table 2. PCDF's Formed in Combustion Studies[14]

Fluid	MonoCDF (ng)	DiCDF (ng)	TriCDF (ng)	TetraCDF (ng)	PentaCDF (ng)	HexaCDF (ng)	HeptaCDF (ng)	OctaCDF (ng)	PCDFs (ng)
Mineral Oil/	-[a]	-	130	49	MQ[b]	O[c]	-	-	180
5 ppm A-1254	-	-	43	23	0	0	-	-	66
Silicone Oil/	-	-	26	0	90	0	-	-	116
5 ppm A-1254	-	-	31	9	150	0	-	-	190
Mineral Oil/	-	-	200	110	39	8.5	-	-	350
50 ppm A-1254	-	-	140	82	21	2.2	-	-	250
Silicone Oil/	-	-	290	73	62	0	0	0	420
50 ppm A-1254	-	-	530	640	83	0	0	0	1,300
Mineral Oil/	1,700	0	2,200	680	43	7	0	0	4,700
500 ppm A-1254	-	-	1,300	620	170	13	0	0	2,100
(B)	-	-	0	13	0	0	0	0	13
Silicone Oil/	-	-	2,000	740	340	45	-	-	3,100
500 ppm A-1254	50	1,300	5,000	2,100	170	12	0	0	8,600
(B)	0.4	0	0	0	0	0	0	0	0.4
70% A-1254/30% Trichlorobenzene	810	5,100	440,000	1,400,000	6,400,000	910,000	29,000	3,400	9,200,000
	1,900	7,000	220,000	1,100,000	4,700,000	660,000	19,000	1,300	6,700,000
(B)	28	190	310	1,200	17,000	3,000	-	-	22,000
Chlorobenzene Fluid	-	-	3,400	2,600	8,000	0	-	-	9,900
(tri with some tetra)	2,000	29,000	>13,000	>19,000	>22,000	5,200	0	0	>90,000
(B)	-	-	81	25	5	0	-	-	110
Lab Blank	0	0	0	0	0	0	-	-	0

[a] - = not analyzed

[b] MQ = not quantitated

[c] O = not detected

Table 3. PCD's Formed in Combustion Studies[14]

Runs	MonoCDD (ng)	DiCDD (ng)	TriCDD (ng)	TetraCDD (ng)	PentaCDD (ng)	HexaCDD (ng)	HeptaCDD (ng)	OctaCDD (ng)	PCDDs (ng)
Silicone Oil/	-	-	0	0	7.7	0	-	-	7.7
500 ppm Aroclor 1254	0	0	0	0	1.7	0	0	0	1.7
70% Aroclor 1254/	0	0	0	0	0	0	330	37	360
30% Trichlorobenzene	0	0	0	0	0	0	230	51	280
Chlorobenzene Fluids	-	-	1,100	440	0	0	-	-	1,500
(mostly tri with some tetra)	0	0	630	520	0	72	0	0	1,200

Table 4. Analysis of Fluids Involved in Transformer Fire Incidents[11]

	Miami, FL[1] (May 29, 1984) (ug/g)	Binghamton, NY[2] (February 5, 1981) (ug/g)	Chicago, IL[3] (September 28, 1983) (ug/g)
PCDDs	ND[a]	ND[a]	ND[a]
PCDFs (Total)	6.0	16.2	3.0
Tetra-CDF	0.31	0.48	<0.01
Penta-CDF	0.78	1.1	0.053
Hexa-CDF	2.2	11.0	0.47
Hepta-CDF	1.3	3.2	1.4
Octa-CDF	1.4	0.41	1.1
Chlorobenzenes (Total)	430,000	350,000	160,000
Trichlorobenzenes	260,000[b]	230,000[b]	100,000[b]
Tetrachlorobenzenes	140,000[b]	110,000[b]	51,000[b]
Pentachlorobenzenes	29,000[b]	13,000[b]	5,500[b]
Hexachlorobenzene	900[d]	45[d]	64[c]
PCBs (Total)	410,000	580,000	110,000[c]
Monochlorobiphenyls	320[c]	230[c]	<100[c]
Dichlorobiphenyls	1,100[c]	730[c]	<150
Trichlorobiphenyls	2,600[c]	3,500[d]	<200
Tetrachlorobiphenyls	2,000[c]	88,000	<400
Pentachlorobiphenyls	31,000[c]	300,000	11,000
Hexachlorobiphenyls	160,000[c]	160,000[d]	49,000[c]
Heptachlorobiphenyls	170,000[c]	24,000	45,000
Octachlorobiphenyls	32,000[c]	<800	7,300
Nonachlorobiphenyls	14,000	<1,200	<1,600
Decachlorobiphenyl	<2,800[c]	<3,500	<4,700

[a] Detection limits approximately 0.01 ug/g for PCDFs/PCDDs.
[b] Results of analysis at a dilution of 0.1 mg of oil/ml of hexane.
[c] Results of analysis at a dilution of 2.5 mg of oil/ml of hexane.
[d] Results of analysis at a dilution of 0.25 mg of oil/ml of hexane.

[1] Askarel Type A: 60% PCBs with 60% chlorine (Aroclor 1260) with 40% trichlorobenzene mixture.
[2] Askarel Type D: 70% PCBs containing 54% chlorine (Aroclor 1254) and 30% trichlorobenzene mixture.
[3] Mineral Oil with 25% PCBs (Aroclor 1260).

benzene (TCB), which, after purification, was transformed to 1,2,4,5-tetrachlorobenzene used as the feedstock for 2,4,5-trichlorophenol. The process involved the low temperature (200-240°C) pyrolysis of the lindane wastes with a carbon catalyst using indirect heating of a closed reaction mantle. The residues from both the mantle and the trichlorobenzene still were analyzed by Buser in Switzerland (see Table 5). Needless to say, the extraction procedure required for this residue was excruciatingly time-consuming and tedious.

Table 5. Dioxin Isomer Differentiation for Pyrolyzed HCCH Residues and TCB Stillbottoms (15)

Dioxin Isomer	Concentration, mg/kg (ppm)
2,3,7,8-TCDD	0.3
TCDDs	12
1,2,3,7,8-PCDD	7
PCDDs	200
1,2,3,4,7,8-HCDD	45
1,2,3,6,7,8-HCDD	150
1,2,3,7,8,9-HCDD	65
H_xCDDs	680
1,2,3,4,6,7,9-HCDD	1,400
1,2,3,4,6,7,8-HCDD	3,000
OCDD	7,600

The point here is that extreme care must be taken when pyrolyzing and/or distilling chlorinated aromatics to exclude air (oxygen) from the system.

Finally, it should be noted that EPA's Dioxin Disposal Advisory Group has been providing guidance upon request to EPA regions regarding active/inactive scrap metal reclaiming facilities, where PCB transformer and capacitor units are processed for their respective copper values. One such example in the Pittsburgh, PA, area is a 1/2-acre site in the midst of a residential community, with about 1000 persons within a 1/4-mile radius. On this site is a commercial building containing a small incinerator that was used not only to combust PCBs, but also to provide heat to the surrounding area! In August 1982, NIOSH made an inspection and detected 8 ppm OCDD in a sample of soil taken at a depth of 1 foot near the PCB liquid storage area. In April 1984, EPA Region III staff removed and analyzed dust samples from inside the building, the results of which are shown in Table 6.

Table 6. Dioxin and Furan in Dust

Homologue	Concentration, ng/g
TCDDs	17-59
2,3,7,8-TCDD	0.79-2.5
TCDFs	413-1232
2,3,7,8-TCDF	74-241

As a result, an Immediate Removal Action was initiated on May 29, 1984. An extension survey demonstrated that the dioxin/furan contamination was restricted to the interior of the incinerator building. More than 5000 tons of PCB-contaminated soil, containing $\geq$50 ppm PCBs, were excavated, loaded, and transported for disposal to the CECOS facility in Niagara Falls, NY, before the RCRA Dioxin Listing Rule went into effect (on July 15, 1985). Scrape samples from interior building surfaces showed:

TCDDs	10-94 ng/g
TCDFs	38-615 ng/g

Sixty transformer casings remain on site today. Estimated cost for the disposition of the remaining contaminated materials (i.e., PCBs, PCDDs, and PCDFs) and security of the site on a temporary or interim basis is $2.885 million -- for a 1/2-acre site! No doubt the responsible parties will be identified but, in the interim, there remain only two certified/fully permitted facilities for PCDD destruction: the EPA Mobile Incineration System, currently employed to destroy dioxins-contaminated waste liquids and soils at the Denney Farm site near McDowell, MD, and the EPA Office of Research and Development's Combustion Research Facility in Jefferson, AR. In the meantime, no new technology to relieve the capacity shortage is expected until December 1986. Meanwhile, the confusion between the applicability of the TSCA PCB regulation or the RCRA Dioxin Listing Rule to a particular site will remain.

In conclusion, the following relevant observations may be made:

1) The Binghamton, NY, fire incident is the only one where ppm levels of PCDDs have been found and quantified; 2) The formation of PCDDs from chlorobenzenes is supported by various laboratory experiments and by the Binghamton fire incident; and 3) Because of their potential for forming PCDDs and PCDFs under thermal conditions, chlorobenzenes should be used with care and disposed of properly.

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PART 8:

RETROFILL AND REPLACEMENT FLUIDS

David Slinn

FORMEL -- A NEW, SAFER, NON-FLAMMABLE DIELECTRIC AND COOLANT FOR TRANSFORMERS

ABSTRACT

A test programme is outlined describing the search for a dielectric fluid that is non-flammable under high energy arcing conditions and which, at the same time, gives an acceptable toxicity profile in the immediate vicinity of the test device during arcing. A number of fluids were studied using a combination of switching, destructive testing and analysis of fluid decomposition products as screening techniques. These studies, in conjunction with parallel examination of the fluid for other necessary properties, led to the selection of a blend of halocarbons as giving the best performance. Destructive testing of a 500 kVA transformer filled with this fluid showed that it passed the target safety criteria.

The fluid has been shown to exhibit a satisfactory performance across the spectrum of properties necessary for a transformer fluid. In particular, the combination of its low viscosity, high density and high coefficient of expansion leads to outstanding coolant characteristics. Commercialisation has taken place and the trade name Formel has been allocated.

Each component of Formel has been used widely by industry for many years and the toxicology has been studied extensively. It is considered, therefore, that the safety and environmental profile is acceptable throughout manufacture, use, maintenance and disposal scenarios.

Section 1

RESUME

Most of the work described in this report was conducted under the auspices of the Electricity Council in the U.K. Harwell Laboratories, Didcot, U.K. acted as independent consultants and I.S.C. Chemicals collaborated with regard to fluid supply and relevant technical advice.

Emphasis in the early stages was centred on the need for a non-flammable replacement for oil in switchgear. As this objective was not achieved and competitively priced alternatives, such as SF_6 equipment, were becoming available, the emphasis was changed to transformer studies and a target specification was drafted (Table 1). Most of the preliminary screening tests, under both switching and high energy arcing conditions, were conducted with typical substation switches containing about sixty litres of the fluid. During the course of this work, a variety of fluids were tested (Table 2), including commonly available "less-flammable" transformer fluids, such as esters, silicones and high-boiling oils. The latter fluids were found to give as large a conflagration as standard hydrocarbon oil, which was somewhat surprising in view of the fact that they are used on the basis of a substantially reduced fire risk. It quickly became apparent that any hydrogen containing fluid constituted a flammability risk under arcing conditions; for example, trichlorobenzene gave a small flame (Table 3). Exceptions to this finding were the cases where a highly volatile halocarbon, such as 1,1,2-trichlorotrifluoroethane mixed with a hydrocarbon (Table 3), gave a fire suppression effect. However, the vapour pressures of such mixtures were unacceptable and high concentrations of acid can be formed.

After the flammable effect of hydrogen (even in small amounts) had been established, further work centred on fully halogenated materials. Also, because of increasingly stringent environmental considerations, it was considered that only those fluids could be used that had long established uses coupled with well documented and acceptable toxicity profiles. Furthermore, all such fluids should be already commercially available, at acceptable costs.

When all the foregoing criteria were applied, the available candidate fluids narrowed to perchloroethylene and chlorofluorocarbons. Of the liquid

chlorofluorocarbons available, only difluorotetrachloroethane (CFC 112) and trifluorotrichloroethane (CFC 113) were considered as suitable liquid candidates, from vapour pressure considerations in standard transformer designs. Both perchloroethylene and CFC 113 were already being marketed as transformer fluids. High energy arcing tests were thus conducted on those materials, separately and mixed, using sixty litre capacity switches as test vessels.

In order to establish a safety target for the immediate environment during high energy arcing, the concept of the emergency exposure limit, EEL, was introduced (Table 4 and 5). This was defined as the maximum vapour concentration tenable by human beings, for a period of 5 minutes, without permanent harm. As thermal injuries from emerging hot liquid may also be a hazard, simultaneous measurement of temperature was made (Table 3).

The high energy arcing tests invariably caused violent rupture of the 60 l test vessel, usually resulting in shearing of the bolts on the lid, followed by liquid being thrown in all directions. The most significant factor emerging from tests on the remaining three candidate fluids was that the addition of chlorofluorocarbons to perchloroethylene markedly reduced the small amounts of chlorine and phosgene produced by perchloroethylene alone (Table 6) so much so that phosgene traces were well within the safety limits. However, even in the case of the optimum mixture, chlorine levels were still marginally higher than the EEL.

Having obtained the optimum mixture, and also taking the entire spectrum of properties into account (Table 1 and 17), the fluid was tested in a 500 kVA transformer, which resulted in phosgene being undetected and chlorine levels being well below the EEL (Table 7). Although the same order of energy was used for the previous switch tests, the transformer test was markedly less violent resulting in small bursts on two side welds followed by slow seepage of liquid during an hour or so. The improvement in the results obtained was considered to derive from the reduced mixing of fluid with air.

At this stage, a toxicological and environmental review (1) covering the optimised mixture (Forme l) was conducted by the independent laboratory. This resulted in a recommendation that the fluid had an acceptable safety profile, based on a considerable history of use and extensive toxicological testing. A decision was then taken to further test the electrical performance in full size transformers. This required compatibility testing in order to select suitable

materials, which showed that most conventional types were satisfactory (Table 8). Physical properties were also measured and collated (Table 17). Two 500 kVA transformers were subsequently built and installed in the London Electricity Board distribution system and two 50 kVA transformers were built to study the relative properties of Formel and transformer oil (Table 9 to 12). In parallel with these studies, a standard 500 kVA oil-type transformer was fitted with about forty thermocouples to compare the cooling properties of various transformer fluids with Formel (Tables 13 and 14). These studies showed that the liquid had similar dielectric properties to oil and that the cooling properties were superior to other available fluids. A comparison of Formel properties with several other fluids is given in Tables 18 and 19.

After one year in operation, one of the LEB transformers was disconnected and the core and windings were subjected to close visual examination, which indicated that no deterioration had occurred. Accelerated laboratory tests were in agreement with these findings (Table 15).

Following the commercial launch of Formel in February 1984, studies were made on the behaviour of Formel , if involved in a building fire. These indicated that vapours arising from Formel did not add to the smoke hazard (Table 16). Recently, attention has been directed on the formation of soots during the pyrolysis of halocarbons, following the detection of highly toxic dibenzofurans and dibenzodioxins in building fires involving PCB filled transformers. Some initial studies on Formel (2) indicate a tendency to form fully halogenated ring compounds, including chlorofluorocarbons. These species have a relatively low toxicity. However, the detection limits were only about 1 ppm and further investigation is in progress at nano gram levels.

Environmental authorities are concerned about the disposal of halogenated transformer fluids, especially in view of the problems currently being experienced with P.C.B.'s. Analysis of product from accelerated aging tests (Table 15), indicates that following its life in a transformer, the fluid can be reconstituted as Formel or can be separated into separate compounds for conventional solvent application. Current industrial requirements for the Formel-NF components are about 1.5 million tonnes in total, on a global basis.

Section 2

EXPERIMENTAL

This section contains only a summary of the work done since a full description would be beyond the scope of this paper.

HIGH ENERGY ARCING TESTS (CATASTROPHIC FAILURE)

These tests were conducted at the Switchgear Testing Company, Trafford Park, Manchester in the U.K. The majority of initial screening experiments were carried out in 60 l distribution type switches at energies of about 8 kV, 6.5 kA for 300ms. After selecting the more promising fluids, the energy was raised to a more arduous level of 12 kV, 13 kA for 300 ms.

Each test was monitored visually by high speed cine photography and thermally by an AGA Thermovision camera. After screening tests were completed, gas sampling devices were designed (Fig. 1) capable of collecting samples, from the time of arc inception to any required time afterwards. A typical arrangement of the test vessel and sampling devices is illustrated schematically in Fig. 2. Most of the analyses were conducted on site, immediately after each test, by personnel from the Physical Chemical Measuring Unit, Harwell Laboratories, Didcot, U.K. Environmental and toxicological guidance, including emergency exposure levels, was also obtained from the same laboratories (Tables 4 and 5).

SWITCHING TRIALS

In parallel with the high energy arcing test programme, switching tests were conducted both in distribution switches and in circuit breakers. Certain of the fluids exhibited promising switching properties, however, the work was not completed following the successful introduction of sulphur hexafluoride switchgear.

An overall summary of both switching and high energy arcing trials is given in Tables 2, 3, 6 and 7.

MATERIAL COMPATIBILITY WITH FORMEL

Before construction of a transformer, all cellulose and polymeric materials used were subjected to screening tests. Samples were immersed in Formel at a temperature of 100°C for a minimum period of 2 days. Assessment involved measuring dimensional change, weight change and amount of polymer extracted.

Accelerated tests were conducted in the presence of metals, since certain metals such as aluminium, zinc, magnesium and their alloys have doubtful long term stability in the presence of halocarbons. Screening was conducted by heating Formel in sealed glass tubes at a temperature of 175°C for one week. These tests indicated that copper and steel are satisfactory.

Following the selection of suitable constructional materials, two 500 kVA transformers were built and installed in the London Electricity Board. After operating for one year, one of the transformers was removed and the core and windings were inspected. Close visual examination revealed no corrosion or other compatibility problem. Chemical analysis of the Formel revealed no change. Measurement of the electrical resistance and breakdown voltage showed that the fluid was on-grade.

The results from two 50 kVA transformers, respectively filled with oil and Formel (Tables 9 to 12), are an indication of acceptable compatibility, since small quantities of dissolved materials in Formel can adversely affect the electrical properties, particularly tan δ .

ELECTRICAL PROPERTIES

The electrical resistance, tan δ and dielectric constant of Formel are routinely measured on an Olman dielectric test instrument model No CB 78 using the cell specified in BS standard 148. The breakdown strength is measured using a Foster Oil Test 90 instrument with an electrode size and gap specified in BS148. Quality control values are given in Table 17.

Capacitance, tan δ , impulse voltage and partial discharge measurements were compared for oil and Formel using two identical 50 kVA transformers (Tables 9 to 12). The capacitance between the HV winding and the transformer tank together with the loss angle (tan δ) of the total insulation was measured using a Hartman and Braun Capacitance / Tan δ measuring bridge. Impulse voltages were measured according to British Standard 923 and comprised full and chopped wave impulse voltages at 75 kV followed by a repeat at 95 kV. Negative polarity

was used throughout and the chopped wave terminated on the wave tail, 5μ seconds after inception. Partial discharge were measured with an ERA Discharge Detector Model 3 fitted with an Input Unit No. 3. Discharge inception voltage and extinction voltage were measured at 7 kV, chosen as the rounded-up voltage 10% above the nominal phase voltage of the transformer.

COOLING CHARACTERISTICS

The combined low viscosity, high density and high coefficient of expansion of Formel (Table 17) results in outstanding cooling characteristics. Hot-spot, winding gradient and overload measurements of Formel were compared with some other common transformer fluids (Tables 13 and 14). The 500 kVA transformer used was designed for use with oil and was fitted with about 40 thermocouples. Although a 50% overload performance is indicated, when Formel is compared to oil, this figure falls to about 20% in commercial Formel units, i.e. when the transformer size and number of radiators are reduced. The excellent cooling properties contribute significantly to competitively priced designs of transformers.

FIRE TESTS WITH FORMEL

In these tests Formel was compared with sulphur hexafluoride and trichlorotrifluoroethane (CFC 113) by spraying each fluid into a drum containing a blazing mixture of petrol and diesel fuel. The drum was 41 cms high, 36 cms in diameter and contained about 5 litres of fuel during each test. Samples were taken at various points downwind. Concentrations of noxious gases taken at a point near the flame edge is shown in Table 16. It was impossible for personnel to stand at this position during the burning period.

Section 3

EFFECT OF FORMEL ON TRANSFORMER DESIGN

A Formel transformer is very similar to a conventional oil design and a visual comparison is given in Fig. 3. However, the following differences apply:-

1. The transformer is significantly smaller containing about half the fluid volume of an oil-type.

2. About 40% less radiator surface is required.

3. The transformer is sealed under a partial vacuum at ambient temperature (3).

4. More stringent leak detection techniques are required during manufacture, because of viscosity and vacuum considerations.

5. Gasketing materials are limited to Viton and PTFE.

Section 4

ENVIRONMENTAL

Only general remarks are given here, a more detailed report is available (1).

Much is happening in the environmental field and many substances, including those that have been in use for many years, are coming under increasing scrutiny. Thus, common household substances such as white spirit, detergents, aerosols etc. have been found to have more associated toxicological hazards than was previously thought. However, the environmental disadvantages have to be balanced against the social inconvenience if such materials were unavailable. When authorities consider that usefulness prevails, pressure is quite rightly directed at improving modes of manufacture, handling and use. For example, products sold to domestic consumers now increasingly have detailed safety instructions prominently displayed on the package.

The foregoing considerations apply equally to the component liquids of Formel , which have been used for many years in large tonnages for metal cleaning, dry cleaning, electronics cleaning and aerospace applications. They have been used in open top tanks, continuously, in close proximity to human beings. In the case of the chlorofluorocarbon components, no rim ventilation has been considered necessary, because of their low toxicity. In recent years, for economy and environmental reasons, there has been a trend towards the use of partially or totally enclosed cleaning systems, in particular, dry cleaning machines using perchloroethylene have become totally enclosed and incorporate very efficient solvent recovery.

Loosely controlled dumping of solvent residues, both from dry cleaning and industrial sources, has led to perchloroethylene being found in water tables. Hence, this solvent is coming under increasing scrutiny and more controls are likely. However, there is no other non-flammable dry cleaning solvent likely to become available that can substitute for perchloroethylene and be free from environmental restrictions. Similar environmental disadvantages apply to chlorofluorocarbons, which are very widely used as refrigerants, solvents and aerosol propellants. Again, it is unlikely that suitable alternatives will be discovered.

Recent studies conducted on behalf of the EPA have confirmed that perchloroethylene is a hepato carcinogen to the sensitive B3C6F1 strain of mouse. However, there is no present evidence, from a considerable amount available, that this applies to other animals or to human beings. Current official thinking, in the U.K., does not consider the evidence as significant with respect to human beings. To put this finding in its context, transformer oil can be carcinogenic to humans, particularly if the oil has been pyrolysed which results in the formation of polyaromatic compounds.

Work conducted at the Mid West Research Institute, on behalf of the EPA (6), has indicated that perchloroethylene forms traces of dioxins and dibenzofurans when pyrolysed in a laboratory tube furnace in the presence of air + oxygen. By contrast, unpublished results (2) during an initial study on the behaviour of Formel pyrolysed in a tube furnace in the presence of air, indicated that the material behaved in a markedly different manner to perchloroethylene alone and, in fact, closely resembled the behaviour of chlorofluorocarbon 113. Minor concentrations of residues were formed (approx 0.1%) comprising fully halogenated ring compounds of the chloro and chlorofluoro types. These results parallel the comparative behaviour observed during high energy arcing tests, where free radicle reactions, taking place under high temperature conditions, are modified by the addition of chlorofluorocarbons to perchloroethylene (Table 6). Further tube pyrolysis studies are in progress using the conditions specified in the EPA sponsored work.

If one attempts to foresee the future in the light of current knowledge, it is likely that the long established solvent uses of the Formel components will become subject to tighter restrictions leading to increased use of semi-enclosed or fully-enclosed cleaning systems. Solvent reclamation will also become of increasing importance. Formel transformers are hermetically sealed and therefore already comply with these requirements. The fluid can also be reclaimed by distillation methods. Pressing consumer needs for the component fluids, in present applications, will ensure their availability into the foreseeable future

The safety requirements pertaining to Formel are almost identical to those required for refrigerants used in air-conditioning systems. Storage, transport and handling is simple and there are no problems in maintaining an excellent standard of industrial hygiene during manufacture, use, maintenance and disposal procedures.

Section 5

CONCLUSIONS

It is impossible to discover a transformer fluid with outstanding properties in all required aspects (Table I). Presently available "reduced flammability risk" fluids such as silicones, esters and paraffinic oils showed no reduced flammability advantage under arcing conditions. Extensive testing of a wide variety of fluids led to a blend of liquids being selected, (allocated the tradename of Formel), that passed all of the target criteria and, in addition to being totally non-flammable, exhibited outstanding coolant properties. Electrical characteristics of Formel are similar to hydrocarbon oil and thermal stability is superior. The fluid is moderately volatile and account must be taken of this in the design of transformers, however these are not markedly different from standard oil designs. Formel is classified as a low-toxicity material and can be safely used by observing simple rules of industrial hygiene. It is unlikely that severe restrictive legislation will be applied to the components of Formel in the foreseeable future.

Table 1

TARGET TRANSFORMER FLUID REQUIREMENTS

Under high energy arcs

- Total non-flammability
- Immediate environment must be tenable by human beings for 5 minutes after arc inception.

Environmental

- Toxicologically acceptable in manufacture, use, maintenance and disposal scenarios.
- Capable of being recycled.

Commercial

- Acceptable cost of finished transformer containing fluid.
- Raw materials must be readily available.
- Preferably adaptable to conventional oil-type designs.

General properties

- Effective coolant
- Thermally stable
- Acid free
- Maximum pour point of - 30°C
- Acceptable compatibility
- Good dielectric properties
- Maximum vapour press 1 atmos. at 100°C

Table 2

FAILURE MODE OF LIQUIDS TESTED UNDER BOTH SWITCHING AND HIGH ENERGY ARC CONDITIONS

Candidate Fluid	Failure mode	Candidate fluid	Failure mode
BS148 oil	2, 3, 6	Perc/CFC 112/ CFC 113 67:28:5	None
HB oil	5, 6, HO	Perc/CFP 212 80:20	3, 6, 7
HB ester	5, 6, HO	Perc/CFD 213 80:20	3, 6, 7
		Perc/CTB 80:20	1, 3, SO
Silicone	5, 6, HO	BS148 oil/Perc 50:50	2, 3, 5, 6
Perc	1, 3, 6	BS148 oil/CFC 113 50:50	3, 6
CFC 113	6 (due to volatility)	BS148 oil/Halothane 70:30	3, 6
TCB	4, 6, HO	BDO/CTB 60:40	2, 3, 4, 6
CP	4, 6, HO	BDO/TCB 60:40	2, 3, 4, 6
SF_6	3, 6	BDO/PE 60:40	2, 3, 4, 6
Fluorocarbon	7	CP/CFC 113	1, 3, SO
Perc/BDO 40:60	2, 3, 4, 6	CP/CFC 112	1, 3, SO
Perc/CFC 112 70:30	6, HO	CP/HB Ester	4, 6, HO

Notation

HB = high boiling
Perc = perchloroethylene
CFC 113 = trichlorotrifluoroethane
CFC 112 = tetrachlorodifluoroethane
CP = chlorinated paraffin
SF_6 = sulphur hexafluoride
BDO = brominated diphenyl oxide
TCB = trichlorobenzene
CFP 212 = hexachlorodifluoropropane
CFP 213 = pentachlorotrifluoropropane
CTB = trichlorobenzotrifluoride
PE = phosphate ester
SO = switching tests only conducted
HO = high energy arcing only conducted

Failure mode number

Switching
1. Poor electrical performance
2. Flammable gases
3. Unacceptable toxic/acidic products

High energy arcing
4. Small flame
5. Large conflagration
6. Unacceptable toxic/acidic products

Cost
7. Unacceptable

Table 3

FLAMMABILITY AND TEMPERATURE MEASUREMENT OF SOME OF THE FLUIDS TESTED UNDER HIGH ENERGY ARCING CONDITIONS

FLuid	Fireball	% H_2 (by weight) in Molecule	Temperature and duration of Vapour or Fireball
Formel	No	None	< 300/0.5s
BS148: 1972 Insulating Oil	Yes	14.0	> 1000°C/5s
BS148 oil + 50% Perchloroethylene	Yes	7.0	> 1000°C/10s
Trichlorobenzene (TCB)	Yes	1.6	700°C/1s
BS148 + 50% Trichlorotrifluoroethane	No	7.0	< 400°C/1s
Complex Ester	Yes	8.0	> 1000°C/7s
Phosphate Ester	Yes	5.0	> 1000°C/5s
Dichlorobenzotrifluoride (DCBTF)	Yes	3.4	700°C/1s
Silicone *	Yes	11.0	> 1000°C/6s
Paraffinic Oil *	Yes	14.0	> 1000°C/4s

NB

(i) High energy arcing conditions - prospective energy 3-phase. 12kV, 13kA 500ms.

(ii) Test equipment contained 60 litres of fluid under test.

(iii) * Energy level 1-phase, 7kV, 6.5kA, 300ms.

Table 4

RECOMMENDED EMERGENCY EXPOSURE LIMITS (EEL)
FOR SOME OF THE FLUIDS TESTED

Material	Toxicity TLV ppm	STEL ppm	EEL (ppm)
Formel	50	150	1000
Halothane	10	*	50
Trichlorotrifluoroethane (113)	1000	*	3000
Tetrachlorodifluoroethane (112)	500	*	1500
SF_6	1000	*	*
Perchloroethylene	50	150	1000
Trichlorobenzene	5	*	50

* value not known

ppm is given for w/w values (w = weight)

TLV = Threshold limit value

STEL = Short term exposure limit (15 minutes)

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Table 5

RECOMMENDED EMERGENCY EXPOSURE LIMITS (EEL) FOR POTENTIAL DECOMPOSITON PRODUCTS FROM SOME OF THE FLUIDS TESTED

Parent Compound	Potential Decomposition Products	Toxicity	TLV ppm	STEL ppm	EEL ppm
Sulphur hexafluoride	Sulphur pentafluoride	very toxic	0.025	0.075	*
	Sulphur tetrafluoride	very toxic	0.1	0.3	10
	Thionyl fluoride		*	*	*
	Sulphuryl fluoride	moderately toxic	5	100	*
	Oxygen difluoride	very toxic	0.05	0.15	1.0
	Sulphur dioxide	toxic	2	*	100
Tetrachloro-difluoroethane					
Sulphur hexafluoride	Fluorine	toxic	1	2	50
	Hydrogen fluoride	toxic	3	*	100
Trichlorotri-fluoroethane	Carbonyl fluoride	toxic	2	*	80
Halothane					
Cereclor	Chlorine	toxic	1	-	30
Tetrachloro-difluoroethane					
Tetrachloro-ethylene	Hydrogen chloride	toxic	5	*	200
Trichlorotri-fluoroethane					
Trichlorobenzene					
	Carbonyl chloride	very toxic	0.1	-	5
Brominated diphenyl oxide	Bromine	very toxic	0.1	0.3	10
	Hydrogen bromide	toxic	3	10	20
Halothane	Carbonyl bromide	very toxic	-	-	-

* values not available

TLV = Threshold limit value

STEL = Short term exposure limit

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Table 6

COMPARISON OF VAPOUR CONCENTRATIONS OF PRODUCTS FROM SEVERAL HALOCARBON FLUIDS TESTED UNDER HIGH ENERGY ARCING CONDITIONS IN 60 L. VESSELS

	FLUIDS TESTED				
Decomposition Products	P ppm	113 ppm	SF_6 ppm	Formel ppm	EEL (for 5 mins (ppm
Sulphur tetrafluoride (SF_4)	N/A	N/A	110	N/A	10
Hydrogen fluoride (HF)	N/A	ND	1000	ND	100
Fluorine (F_2)	N/A	ND	(as HF)	ND	50
Carbonyl fluoride (COF_2)	N/A	ND	ND	ND	80
Hydrogen chloride (HCl)	185	45	N/A	45	200
Carbonyl chloride ($COCl_2$)	15	5	N/A	2	5
Chlorine (Cl_2)	115	2.5	N/A	90	30
Perchloroethylene (C_2Cl_4)P	6000	N/A	N/A	1300	1000
Trichlorotrifluoroethane ($C_2Cl_3F_3$) (113)	N/A	20000	N/A	90	3000
Tetrachlorodifluoroethane ($C_2Cl_4F_2$) (112)	N/A	ND	N/A	480	1500

Notes

- ppm given in w/v for instantaneous values
- Tests carried out in switches each holding 60 litres of fluid
- Test energy for each event was 3-phase, 12 kV, 13 kA for 300 ms
- N/A = not applicable
- ND = not detected

Table 7

VAPOUR CONCENTRATIONS OF DECOMPOSITION PRODUCTS FROM A 500 kVA TRANSFORMER, FILLED WITH FORMEL, WHEN TESTED UNDER HIGH ENERGY ARCING CONDITIONS

Chemical Compound	Concentration in ppm w/v Inst	at 1 min	EEL for 5 min
Tetrachloroethylene	1100	270	1000
Tetrachlorodifluoroethane (112)	130	65	1500
Trichlorotrifluoroethane (113)	80	20	3000
Carbontetrafluoride (14)	5	5)	
Trichloromonofluoromethane (11)	60	35)	> 4000
Monochlorotrifluoroethane (13)	20	20)	
Chlorine	2	3	30
Hydrogen chloride	2.5	ND	200
Carbonyl chloride *	ND	ND	5
Carbon monoxide	ND	ND	-

ND = non detected below 1 ppm w/v

* = non detected below 0.5 ppm w/v

Inst = Instantaneous measurements - at point of emerging fluid

EEL = Emergency exposure limits

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Table 8

MATERIALS SUITABLE FOR USE WITH FORMEL

Metals	Insulation / Adhesive / Paints	Gasket / Seals
Copper	Paper	Fluorinated elastomer
Steels	Pressboard	gaskets and "O" rings
Brass	Polyvinylacetate	Polytetrafluoroethylene
Bronze	Polyester	(PTFE rope and tape).
Solders	Nomex	
	PTFE	All welded
	SRBP	construction
	Epoxy resins	
	Polyurethane	
	Adhesive Tapes - Gum arabic or Hydroxy cellulose	
	Surface Coatings - Epoxy or Urethane, both of two-pot types	

Notes

1. Aluminium and Zinc should not be used.

2. Polymeric materials can vary because of formulation compounding techniques and the degree of polymerisation, etc. If in doubt, compatibility testing should be undertaken.

Table 9

COMPARATIVE CAPACITANCE AND TAN δ FOR OIL AND FORMEL IN IDENTICAL 50 kVA TRANSFORMERS, BEFORE IMPULSE TESTING

Test Voltage kv	Oil Capacitance pF	Tan δ	Formel-NF Capacitance PF	Tan δ
.2	805	0.00264	886	0.005
1.0	805	0.00264	885	0.0053
2.0	805	0.00264	885	0.0053
3.0	805	0.00264	885	0.0053
4.0	805	0.00267	885	0.0053
5.0	805	0.0027	885	0.0053
6.0	805	0.0027	885	0.0053
7.0	805	0.00268	885	0.0053
0.2	805	0.00268	885	0.0053

Table 10

COMPARATIVE FULL WAVE AND CHOPPED WAVE IMPULSE VOLTAGE TEST RESULTS FOR OIL AND FORMEL IN IDENTICAL 50 kVA TRANSFORMERS

	TRANSFORMER					
	Oil filled Serial No. C53949			Formel filled Serial No. C53950		
75kV -ve Polarity	Phase A_2	Phase B_2	Phase C_2	Phase A_2	Phase B_2	Phase C_2
Full-Wave	///	///	///	///	///	///
Chopped-Wave	///	///	///	///	///	///
Full-Wave	///	///	///	///	///	///
95kV -ve Polarity						
Full-Wave	///	///	///	///	///	///
Chopped-Wave	///	///	///	///	///	///
Full-Wave	///	///	///	///	///	///

Notation / = voltage withstand

Table 11

COMPARATIVE PARTIAL DISCHARGE VALUES FOR OIL AND FORMEL IN IDENTICAL 50 kVA TRANSFORMERS BEFORE APPLICATION OIF IMPULSE VOLTAGE

Voltages	Oil	Formel-NF
V_i	4 kV < 5pc	4.8 kV < 5pc
V_e	3.4 kV	4.2 kV
Discharge at 7 kV	5pc	9pc

i = inception

e = extinction

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Table 12

COMPARATIVE PARTIAL DISCHARGE VALUES FOR OIL AND FORMEL IN IDENTICAL 50 kVA TRANSFORMERS AFTER APPLICATION OF IMPULSE VOLTAGE AND AC VOLTAGE WITHSTAND TEST (28 kV FOR 1 MINUTE)

	Oil	Formel
V_1	9 kV < 3pc	8.5 kV < 5 pc
V_3	8 kV	7.8 kV
Discharge at 10 kV	7pc	12pc

Table 13

COMPARATIVE TEMPERATURE RISE TEST RESULTS FOR A SELECTION OF TRANSFORMER FLUIDS

Fluid Tested	T_T	T_{AV}	$(T_T - T_{AV})$	$T_{HOT\ SPOT}$	Winding Rise (calc'd) HV	LV	Winding Gradients (calc'd) HV	LV	Estimated Viscosity (cst) at 20°C	100°C
Formel-NF	40.7	37.2	3.5	66.4	42.2	40.7	5.0	3.5	.89	.54
BS 148 Oil	47.2	39.5	7.7	86.0	50.7	54.1	11.2	14.5	20	2
Complex Esters	48.5	39.2	9.3	88.6	50.4	54.8	18.6	21.3	90	6
Silicone	48.5	38.0	10.5	93.4	51.3	59.9	20.4	27.2	50	15
Paraffinic Oil	54.7	40.5	14.5	101.2	57.9	64.0	17.7	25.8	350	16

NB

1. All test conditions remained the same for each fluid.
2. The hottest spot for each fluid was at the top of the copper coil of the low voltage winding
3. Transformer used was designed for oil.

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Table 14

OVERLOAD PERFORMANCE OF FORMEL

Parameter	Non-Flammability 100% (8.3kW)	150% (17.2kW)	175% (23.3kW)
Hot Spot Temp °C	66.6	95.5	115.0
Top Fluid Temp °C	64.5	93.0	109.0
Fluid Rise °C	41.5	69.3	83.2
Ambient Mean °C	22.5	24.0	23.5
Radiator (T_T-T_B) °C	7.5	12.5	15.5
Winding Gradient °C HV	4.9	5.6	12.2
Winding Gradient °C LV	4.5	1.6	5.7
Winding Rise °C HV	42.2	68.8	87.7
Winding Rise °C LV	41.8	64.8	81.2
Pressure psig	-3.7	3.3	12.6

Notes

1. Before temperature rise tests were conducted, a partial vacuum of 125 mm was obtained within the headspace.
2. Transformer used was designed for oil.

Table 15

TYPICAL ANALYSIS OF FORMEL BEFORE AND AFTER TREATMENT FOR ONE WEEK AT 175°C, IN A SEALED GLASS TUBE, IN THE PRESENCE OF UNCOATED COPPER AND P.V.A. COATED COPPER

Component Substances	Analysis, wt % by G.L.C. Before	After
Total chlorofluorocarbons	35.0	34.8
Perchloroethylene	65.0	65.1
Other compounds	-	0.1

Notes

1. Repeatability of analytical method ± 0.1
2. Identity of other compounds not determined.

Table 16

FIRE TESTS WITH FORMEL, CFC 113 AND SULPHUR HEXAFLUORIDE

Fluid under Test	Feed rate to burning fuel g./mm	Gas concentration at 0.5 m. distance from flames ppm					
		Chlorine	Carbonyl halides	Hydrogen chloride	Hydrogen fluoride	Perchloro-ethylene	Sulphur dioxide
Formel	810	<0.2	4.5	53	18	0.03	-
Formel	890	<0.2	2	39	-	0.02	-
CFC 113	390	<0.2	2	19	9.5	-	-
Sulphur hexa fluoride	250	-	<0.5	-	25	-	69
Emergency Exposure Limit		30	5	200	100	1000	ND
IDLH Threshold		25	2	100	20	500	100

Note : Flow rates above those values given for Formel and CFC 113 tended to extinguish the flames.

Table 17

PROPERTIES OF FORMEL FLUID

Specification	Value
Electrical Strength * kV (2.5 mm gap) r of r 2 kV(s)	50 kV min
Volume Resistivity * Ω /cm (500 V d.c.)	10^{13} min
Dielectric Dissipation Factor * (Tan δ) (2400 V a.c.)	0.01 max
Relative Permitivity * N_2 = 1 (2400 V a.c.)	2.36
Moisture Content * (p.p.m.)	20 max
Total Acidity (p.p.m.)	1 max

* Tests carried out at 20°C

Other Properties	Value
Flammability in Air	Non-flammable
Flash Point °C	None
Fire Point °C	None
Auto-ignition Temperature °C	None
Explosive Limits in Air per cent by Volume	None
Toxicity OSHA TLV p.p.m.	50
Thermal Conductivity $mWm^{-1}\,°K^{-1}$	82.8
Specific Heat $kJ\,kg^{-1}$	0.895
Coefficient of Thermal Expansion per cent $°C^{-1}$	0.107
Density * $kg\,l^{-1}$	1.63
Average Molecular Weight	178
Boiling Point °C at:-	
1 Bar	103
10 Bar	200
20 Bar	250
Pour Point °C	- 33
Surface Tension * Dynes cm^{-1}	26
Dynamic Viscosity * cP	0.884
Latent Heat of Vaporisation: $kJ\,kg^{-1}$	192
Solubility * of N_2: $ml\,l^{-1}$	162
Solubility * of O_2: $ml\,l^{-1}$	85
Vapour Pressure Bar at:	
20°C	0.04
40°C	0.10
60°C	0.24
80°C	0.48
100°C	0.90

* Values at 20°C

Table 18

HEAT TRANSFER PROPERTIES OF FORMEL COMPARED WITH OTHER COMMON TRANSFORMER FLUIDS

Property	Formel	BS148 oil (a)	Silicone oil (a)	Fluids Paraffinic Oil (a)	Complex Ester (a)	PCB (a)
Dynamic Viscosity at						
20°C	-	-	-	-	100	-
25°C	.88	25	50	350	-	15
50°C	.54	7	30	85	-	8
100°C	.47	2	16	16	6	3
Density g/ml						
25°C	1.64	.88	.96	.88	.98	1.51
100°C	1.48	-	-	-	-	1.44
Coefficient of Expansion/°C	1.07 $\times 10^{-3}$	.86 $\times 10^{-3}$	1.0 $\times 10^{-3}$	.85 $\times 10^{-3}$	.8 $\times 10^{-3}$	.75 $\times 10^{-3}$
Specific heat at 25°C Cal/gm °C	0.214	0.503	0.306	0.46	0.5	0.263
Thermal conductivity W/m °K (at 20°C)	0.10	0.14	0.10	-	0.16	0.10

Table 19

DIELECTRIC PROPERTIES OF FORMEL COMPARED WITH OTHER COMMON TRANSFOMRER FLUIDS

Property	Formel	BS148 oil (a)	Silicone oil (a)	Fluids Paraffinic Oil (a)	Complex Ester (a)	PCB (a)
Electrical strength kV/2.5mm (2kV/s.rise)	70	60	55	43	50	50
Volume restistivity cm at 25°C	10^{15}	10^{15}	10^{14}	10^{13}	10^{13}	10^{12}
Relative permitivity	2.36	2.2	2.7	2.38	3.2	4.3
Tan at 25°C	.001	.00005	.00002	.001	.001	.05
Moisture content ppm	10	20	50	35	20	70

(a) figures obtained from published data

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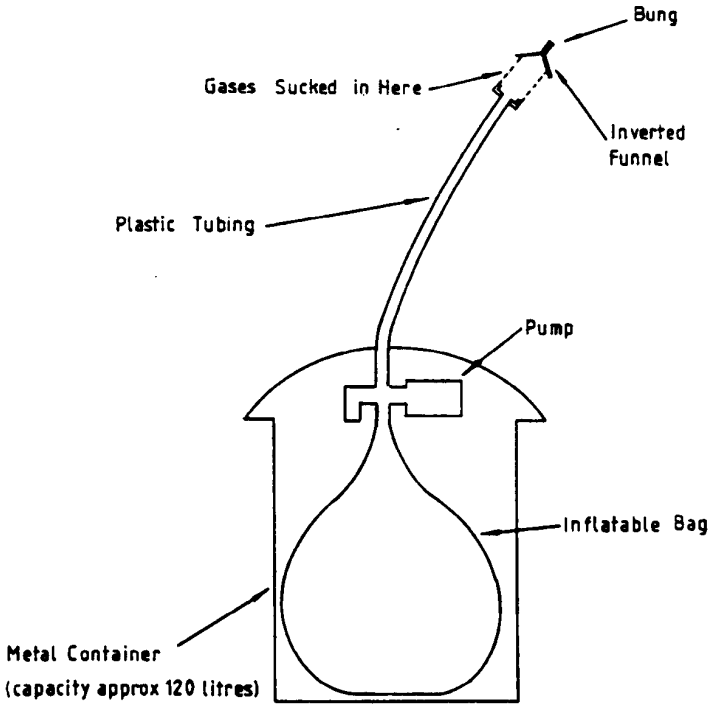
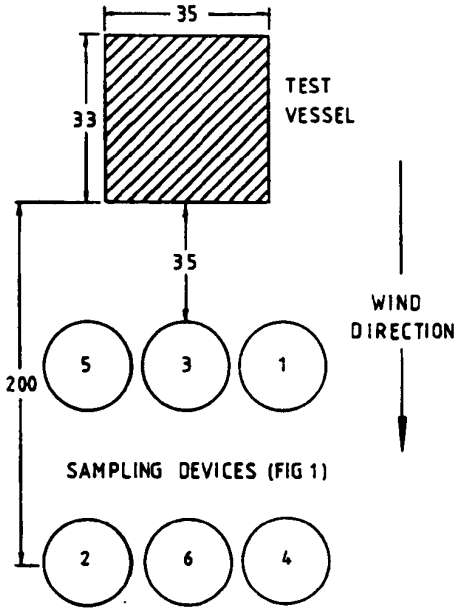


Figure 1. Schematic Diagram of Sampling Device Used During High Energy Arcing Tests



ALL DIMENSIONS IN CM

Figure 2. Typical Orientions of Test Vessel and Sampling Devices During High Energy Arcing Tests

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Figure 3. Two 11/.433 kV, 3-Phase, 500 kVA Hermetically Sealed Transformers (right) Filled with 240 Litres of Formel-NF and (left) Filled with 470 Litres of Hydrocarbon Insulating Oil

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STATE-OF-THE-ART REVIEW OF COMBUSTION/PYROLYSIS BY-PRODUCTS OF PCB SUBSTITUTES

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Since 1976, the manufacture and commercial use of polychlorinated biphenyls (PCBs) have been restricted by law. Proposals have been made to remove existing PCB-containing transformers and capacitors from service. A number of chemicals have been and are being considered for use as PCB substitutes in electrical applications. Although all have been tested for acceptable dielectric, heat transfer, and flammability properties, few have been extensively analyzed for combustion by-products.

PCBs were not restricted for problems with their dielectric properties or heat transfer capabilities, but rather for suspected toxicological properties that were not considered when PCBs were first commercially produced. These toxicological properties are attributed not only to the PCBs themselves, but also to the presence of various toxic chlorinated aromatics in the by-products of PCB/askarel fires. It is thus necessary to examine the chemical behavior of proposed PCB substitutes to identify the potential for similar problems. A state-of-the-art literature review was conducted to determine what is known regarding the chemical and toxicological nature of the combustion by-products of various PCB substitutes.

DATA ASSESSMENT

Until very recently, the major concern in any fire or explosion episode was firefighter safety. As a result, tests have focused almost exclusively on major gaseous combustion products such as carbon monoxide, hydrogen cyanide, oxides of nitrogen and sulfur, hydrogen chloride, and so forth. These are the immediate life-threatening combustion products with which one must deal, and they are generally the simplest to detect and measure.

However, it has become evident in the aftermath of several PCB incidents that the toxic trace combustion product problem is concerned more about soot deposits than the vapors formed. Trace PICs are produced in such low levels that vapor emissions dispersing in the atmosphere rapidly reach inconsequential levels. These same PICs may concentrate in soot, however, and soot provides a reservoir for

continued emissions or exposure long after a fire has been extinguished and the gases dispersed.

Furthermore, analysis of soot or even gas samples for trace PICs at the levels typically produced requires very sophisticated analytical instrumentation and highly trained specialists. Even then, complete identification of PICs in a particular sample may take years of work. As the level of sensitivity of analytical instruments increases, even more toxic PICs may become evident. For instance, continued research on PCB combustion by-products has identified not only chlorinated dioxins and dibenzofurans, but also polychlorinated chrysenes, pyrenes, xanthenes, terphenyls, quaterphenyls, and others.

This level of research has been directed at PCB because of its negative publicity and the perceived crises in regards to several PCB incidents. No such crises exist for the proposed PCB substitutes. As a result, with a very few exceptions, comparable research has not been conducted into their PICs. As noted above, existing data tend to focus on the macro combustion products present in the vapor state rather than trace PICs in the soot. Consequently, there is relatively little data on trace PICs comparable to that on dioxins or dibenzofurans. These types of by-products simply have not been identified and studied in most cases.

PROPOSED PCB SUBSTITUTES: LIQUIDS

Two types of esters, phthalate esters and benzylneocaprate, have been considered as PCB substitutes. In general, pyrolysis of esters will produce gases similar to and no more toxic than those obtained from hydrocarbons. One major decomposition product is phthalic anhydride which can react further to form naphthalene and biphenyl. In the presence of chlorobenzenes, PCB and chlorinated naphthalene may be produced.

Polydimethyl siloxane has been widely used as a retrofill fluid. During thermal decomposition, amorphous silica, several cyclic siloxanes, and a variety of simple hydrocarbons are produced. Most of these compounds are not highly toxic, and animal inhalation tests on pyrolyzed siloxanes have generally indicated a low toxicity.

Chlorobenzenes have generally not been considered PCB substitutes as much as additives to PCBs and other dielectrics. Decomposition of chlorobenzenes can produce a variety of highly toxic compounds. Pyrolysis of monochlorobenzene can

yield mono- and dichlorobiphenyls, chloronaphthalene, and vinyl chloride. In the presence of air, chlorobenzenes can produce chlorophenols which can, in turn, dimerize to PCDFs and PCDDs. Many of these combustion/pyrolysis products are very highly toxic.

Methylated diphenylethane and phenylxylylethane are used as components in dielectric fluid mixtures. No information was found on the combustion/pyrolysis products of either compound, but pyrolysis of chemically similar diphenylmethane and 1,2-diphenylethane produces a number of polynuclear aromatic hydrocarbons. Few of these are considered to be highly toxic, but several are known or suspected carcinogens.

There is no information available on the thermal decomposition products of butylated monochlorodiphenylether, another PCB substitute. However, both the unsubstituted diphenylether and polychlorinated diphenylethers have been studied. Diphenylether can break down into phenol, benzene, and dibenzofuran. Polychlorinated diphenylether can produce PCDFs and PCDDs.

There is also no information available on the thermal decomposition products of the alkyl biphenyls, specifically isopropylbiphenyl and n-propylbiphenyl.

Paraffinic hydrocarbons, such as polyalphaolefin and RTEmp, tend to decompose into a variety of short-, medium-, and long-chain saturated and unsaturated hydrocarbons. In the presence of air, organic acids, alcohols, and aldehydes are formed.

Perchloroethylene is being promoted as a transformer fluid neat, mixed with mineral oil, or mixed with fluorocarbons. Chlorine or hydrogen chloride are the principal decomposition products to be expected. Under certain conditions, phosgene or trichloroacetic acid may be produced.

PROPOSED PCB SUBSTITUTES: DIELECTRIC GASES

Chlorofluorocarbons are used as dielectrics both neat and mixed with perchloroethylene. Although generally thermally stable, at high temperatures or during arcing, decomposition is possible. Chlorine, hydrogen chloride, hydrogen fluoride, phosgene, and carbonyl fluoride are among the by-products which can be expected. Phosgene and carbonyl fluoride, in particular, are highly toxic. Sulfur hexafluoride can be used alone as a dielectric or in a mixture of gases. It

produces a number of long-lived by-products under fire and arcing conditions. The principal by-product is thionyl fluoride; other products include sulfuryl fluoride, thionyl tetrafluoride, and sulfur dioxide. Toxicity tests on sparking gases have yielded a higher toxicity than the above compounds would indicate. Thus, there are one or more unidentified trace decomposition products which contribute significantly to the toxicity of the decomposition gases.

PROPOSED PCB SUBSTITUTES: SOLIDS

Two solids were reviewed: epoxy resins and polyvinyl chloride (PVC). Complicating an assessment of their decomposition is the fact that neither is a pure compound or even a mixture of a few discrete compounds. Rather, each is a mixture of resin, hardener, filler, and various other materials, many of which may have a variable composition. Thus, the decomposition products of these solids can vary extensively, depending on the nature of the additives.

Pyrolysis of epoxy resins can produce a variety of organic compounds including benzene, methyl chloride, ethyl chloride, acetone, propylene, ethane, pentane, toluene, cresol, phenol, and others. Several of these are known or suspected carcinogens.

Decomposition of PVC can yield benzene, toluene, xylene, aliphatic hydrocarbons, __-methylnaphthalene, several chlorinated benzenes, and phosgene. Because of the production of chlorinated benzenes, the formation of PCDDs and PCDFs is a distinct possibility, although none have been identified in PVC pyrolysis gases to date.

DIFFUSIONAL MODELING DURING TRANSFORMER RETROFILL

G. R. Atwood, I. R. Moore, P. R. Dillon

INTRODUCTION

The successful operation of a retrofill type process, such as UNISON RECLASS 50[SM], for the removal of polychlorinated biphenyls (PCBs) from transformers depends upon a thorough understanding of the complex mechanisms involved, along with a recognition of the spectrum of sizes and shapes of the diversity of internal materials used. Experimental observations in the field and laboratory have been necessary for evaluating the basic concepts of the process, but mathematical modeling has been essential to develop and confirm the details of the mechanisms, as well as provide a tool for process definition and predictive control. Field data for our modeling were obtained from several Union Carbide transformers at South Charleston, WV. These were supplemented by laboratory diffusion studies, and modeling has been carried out on both the detailed aspects and the overall RECLASS 50[SM] process. Two approaches have been used. A discrete element type simulation was found valuable for understanding the phenomenological details, while a model based upon piecewise integration of Fick's second law (unsteady state diffusion) was found more useful for the overall process description. The algebraic details are too lengthy for discussion here.

THE LEACHING PROBLEM

A drained and rinsed transformer retains Askarel in a variety of ways. There is residual fluid held in gravitationally nondrainable pockets or in crevices by surface tension. More important, however, is the Askarel absorbed within the cellulosic insulation, which consists of creped paper, pressboard, adhesive laminates, and even wood. There is a spectrum of depths and tightness of such structures. No amount of scrubbing with vapor or liquid can remove this absorbed Askarel, although elaborate means have been devised and even marketed with limited success. The residual PCB always subsequently leaches out of the insulation and voids any attempt to reclassify the transformer as non-PCB. The

RECLASS 50[sm] process removes this absorbed Askarel and replaces it with an acceptable fluid, e.g., dimethylsilicone oil (1,2).

DIFFUSION

The limiting operation in the leaching of Askarel is diffusion. In order to properly evaluate the results of laboratory and field leaching, it was useful to develop a discrete elemental analysis model based upon Fick's law. The insulation matrix was mathematically treated as a flat plate divided into many layers. The incremental diffusion across the layer boundaries was simulated in a stepwise manner for those sequential layers, and repeated over as many time periods as desired. It was thus possible to determine the concentration profile changes in the matrix, as well as the rate of PCB elution from the matrix.

Diffusion is time dependent, and in transformer leaching we have no choice but to wait until the PCBs diffuse from the core of the transformer. It is essential that the leaching solvent be an acceptable transformer coolant, for we do not wish to curtail electrical operations during this diffusion period. It would seem quite logical to choose silicone oil for this purpose, as has been frequently done, though that is an unfortunate choice. There are many critical factors here, and we can discuss only a few within the scope of this paper.

Miscibility. This is crucial as was pointed out by Morgan and Osthoff (3) of General Electric Co. Even if the solubility for PCB is substantial, the lack of miscibility leads to an Askarel/leachant interface in the cellulosic matrix itself, and consequently a barrier to diffusion is set up. This barrier significantly decreases the rate of diffusion, increasing the time required to achieve reclassification. Miscibility, on the other hand removes this problem.

Viscosity The diffusion rate is an inverse function of the viscosity of the medium. The shapes of the PCB/time leaching curves and matrix concentration gradients depend upon the solute/solvent viscosity ratio. This is illustrated in Figure 1 for flat plate leaching. Viscosities of the same relative magnitude result in convex curves for classical diffusion (dotted lines), whereas if the solute (Askarel) is much more viscous, "S" shaped profiles result (solid lines), and the leach curve shows a flattened region, - misleading if not completely understood. The application of classical extraction equations would lead to extremely erroneous estimates of residual PCB. We have coined this phenomenon "ablative" diffusion, since the Askarel is effectively removed layer by layer, as the steep concentration gradient moves back into the matrix.

Temperature. This is significant principally by its effect on viscosities (see discussion above). The higher the operating temperature during diffusion, the lower the viscosity of the diffusing medium. The effect of temperature on viscosity is very pronounced in the case of Askarels, and suggesting that faster rates of diffusion occur at higher temperatures. In an operating transformer, temperature will be a function of electrical load although ambient temperatures also can be a factor. Lightly loaded transformers can be heated, and the desirability of doing so will depend upon individual circumstances.

Circulation. Bulk fluid circulation and the bulk PCB concentration level are commonly thought to be critical, - hence previous attempts at retrofill have emphasized these factors. Although relevant, they may not be critical, principally because the rate of diffusion is controlled by high concentration gradients deep within the cellulosic matrix, as in Figure 1 (b), and this rate is slow relative to the normal convective mixing of the bulk fluid. Only when the PCB removal is nearly complete can its concentration in the bulk fluid act to retard the process by "back diffusion". At this point one must act appropriately to maintain the leaching in the kinetic regime.

Silicone Oil as a Leachant. Previous attempts at retrofill have utilized silicone oil as the leechant material throughout the leaching period. We have identified the problems associated with silicone oil which made this an unfortunate choice. Silicone oil has a high viscosity and is immiscible with Askarel. Askarel is slightly soluble in silicone oil, but the oil is virtually insoluble in Askarel or any chlorinated hydrocarbon. As a consequence, the Askarel must diffuse very slowly into the oil, while the Askarel/oil interface is drawn just as slowly into the cellulosic matrix. While transformer reclassification can be achieved by this approach, the time required to attain this ultimate goal has proved to be unacceptably long, on the order of 5-6 years or more, compared with a fraction of this time for the RECLASS 50[SM] process. Additional studies, discussed below show why this is the case.

Most Askarels are mixtures of highly viscous PCB's and thinning agents such as tri- or tetrachlorobenzenes. The latter are more soluble in silicone oil than PCBs (about 3/1), and diffuse out preferentially, leaving a highly viscous, possibly solid (4), PCB residue. Figure 2 is analogous to Figure 1 (b), and profiles computed from the non-discrete elemental modeling approach show how preferential leaching leads rapidly to high PCB concentrations at the silicone oil interface, greater than the 60% initial concentration for type A Askarel, and thus much more viscous. (The upper curves are the PCB concentrations in the

Askarel phase, while the lower curves are the PCB concentrations in the silicone phase, the vertical lines representing the interfacial positions). After 1200 days, the residual Askarel is nearly pure PCB (Aroclor® 1260), and possibly solid. As a result, diffusion of PCBs into the silicone oil is greatly retarded, although the rate is high enough to void any attempt at reclassification.

Laboratory Studies. Figures 1 and 2 are mathematical simulations, but Figure 3 shows comparetive leaching studies of Askarel soaked pressboard with L-305 silicone oil and UNISON's proprietary transformer fluid, TF-1. The silicone leaches rapidly at first (though slower than TF-1), but soon slows to a crawl, due to the buildup of the highly viscous PCB layer at the interface. Similar studies have been carried out for a variety of solvents and insulating materials of different sizes. While such a study cannot disclose the actual PCB profiles as they exist in the interior of the matrix, the extraction curves themselves are consistent with those calculated from the discrete element model. The sharp reduction in the extraction rate with silicone oil, for example, is consistent with the formation of the highly concentrated and viscous PCB layer at the interface.

Figure 4 shows a device designed to study the interfacial penetration rate in the absence of the cellulosic matrix. The capillary is loaded part way with Askarel (or other fluid) and the vessel filled with silicone oil. The interfece gradually falls, and the figure gives plots of the interfacial level vs. time for type A Askarel and the proprietary TF-1 as the bottom layer. The Askarel curve not only falls more slowly, but the rate continues to decrease as the concentration of residual PCB and the viscosity builds up. The curve for TF-1 is steeper, because TF-1 is less viscous and is more soluble in silicone oil. These curves are even more linear than that in Figure 1 (a). Because of the sharp concentration gradient at the interface, interfacial diffusion can be considered an extreme form of the ablative diffusion phenomenon exhibited by miscible fluids.

RETROFILL STRATEGY

The previous data indicate that it is impractical to try to leach Askarel with silicone oil in any reasonable length of time. However, it is practical to leach with TF-1, and TF-1 can be readily leached with silicone oil. Accordingly, combined leaching by TF-1 and silicone is a preferred strategy. It was first demonstrated to be successful with our own South Charleston transformers. Four transformers were reclassified to non-PCB, and a fifth is presently undergoing

the 90 day test, with reclasification expected in the near future. A sixth transformer was initially retrofilled with silicone oil instead of TF-1, and accordingly is still leaching, but the data from this, as well as the other five, has been helpful in the process design, model, and optimization.

PROCESS MODELING

While the discrete element analysis type of model has been useful in elucidating the phenomena critical to leaching, it is rather unwieldy for field modeling. For this purpose a model based upon piecewise integration of Fick's second law proved useful. This also entailed the conception of the transformer insulation as a flat plate, with the recognition that there are in reality a spectrum of depths and matrix tortuosities to be considered. For all practical purpose, there is a process controlling effective depth, or related time constant, for the system. This represents the bulk of those structures which contain significant Askarel and are difficult to leach. The looser, shallower matrices are not controlling by virtue of being easily leached, while the very tight structures do not contain enough PCB to be significant. Fick's second law can be expressed by:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

where C is PCB concentration, t the time, x the depth in the matrix, and D the diffusivity. This equation cannot be directly integrated but can be solved in terms of a Fourier series, to give an extremely complex description, C(x,t), of the concentration profiles, and allow computation of the bulk fluid composition, $C_b(t)$, as a function of time. Discussion of these expressions and the techniques used in their derivation cannot be detailed here, but utilizing them in conjunction with actual transformer leach data has permitted optimization of the process in terms of total elapsed time and fluids used.

CONCLUSIONS

Transformers differ, and the RECLASS 50[SM] model itself incorporates three adjustable parameters which can be estimated early in the process and refined as additional data are obtained from specific customer transformers. These parameters are the fluid holdup of the internal components, the nondrainable, though free, liquid residue, and the time constant for the system (i.e., the transformer type), which reflects the effecive diffusivity and critical (i.e., process controlling) diffusion depth. From the model one can estimate the residual PCB left to leach, and hence the next optimal process step or sampling interval.

As a result, one can service the transformers in a safe, timely, and cost effective manner, and can offer in the market place a service which guarantees the attainment of non-PCB status.

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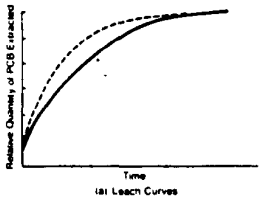


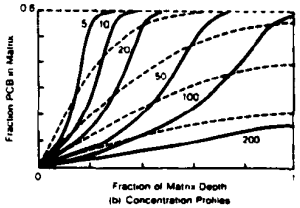


Figure 1

Ablative vs. Classical (dotted) Diffusion.
(Numbers are relative days of leach)

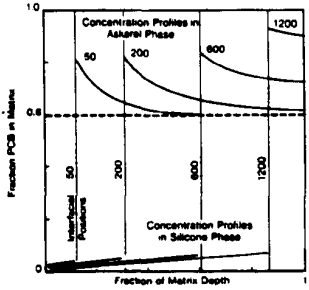


Figure 2

Interfacial Leaching of Type A Askarel with Silicone Oil.

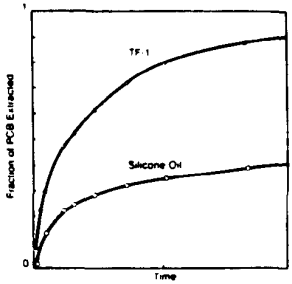
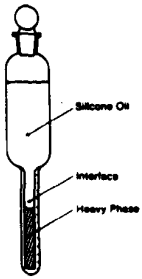


Figure 3

Laboratory Leaching Studies for Pressboard Saturated with Type A Askarel, 60°C.



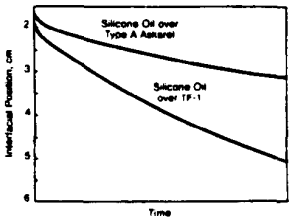


Figure 4

Interfacial Motion Studies

DECONTAMINATION OF PCB TRANSFORMERS USING ENSCO, INC.'S RETRO-1 PROCESS

J. Lee Tinney

INTRODUCTION

The electric utility industry is expected to function in an efficient, reliable, and cost effective manner. At the same time, they must adhere to federal guidelines and state regulations, face material shortages, hold rates down, and conform to rigid federal and state environmental laws, one with the greatest impact being the EPA's rules and regulations governing PCBs.

PCBs were found harmful to the environment after more than fifty years of existence. Without delay, environmentalists pushed for an immediate remedy, and consequently, the Environmental Protection Agency published rules and regulations prohibiting the manufacturing, processing, distribution in commerce, and certain other uses of PCBs.

Electric utilities have been saddled with a tremendous economic burden as they interpret the laws and formulate programs that ensure prompt and complete compliance, and as is often the case, they are the leaders in recognizing their responsibilities and developing solutions. As compliance to the PCB rules and regulations are implemented, many questions and problems have to be answered and solved. In all instances a basic choice has to be made; that is, to either leave the PCBs and adapt to the laws or find a method to remove the PCBs and not be restricted by compliance.

This paper addresses the evaluations of one method to remove PCBs for the purpose of reclassification of transformers containing PCBs.

MP&L'S PCB TRANSFORMER CONCERNS

Mississippi Power & Light Company, like other utilities has serious PCB concerns and firm management objectives for a successful and economic solution to these PCB concerns. A primary concern of MP&L is PCBs and PCB-contaminated transformers in public areas that are considered a high risk (or high liability) transformer.

To resolve this PCB concern, MP&L faced three options: 1) Do nothing and continue to comply with present rules and regulations and any future, more stringent, regulations that might come along; such as, the new "transformer rules." The problem with doing nothing is that it does not significantly reduce the liability and risk of having a transformer with PCBs. 2) Eliminate the PCB liability and risk by replacing the PCB transformer with a non-PCB transformer. The PCB-contaminated transformers would then be relocated but the PCBs would not be eliminated; consequently, these transformers would require further handling and attention at a later date as PCB regulations are tightened. 3) Leave the transformers in place and find a way to remove the PCBs. High risk transformers ideally need ALL of the PCBs removed to reduce the liability and risks. Anything less leaves the possibility of some future liability from the remaining PCBs in the transformer. Thus the analogy--No PCBs equal little or no risk, and some PCBs equal high risk.

For MP&L's PCB transformer concerns, Option 3 (Removal of the PCBs from the Transformers) seemed to be the best choice. Our objectives were simple--to find a system which could declassify a PCB transformer to extremely low PCB levels at an economical price; and the transformers must not leach back above a 2ppm PCB level to eliminate all liabilities or risk from the PCBs.

THE ENSCO, INC. RETRO-1 SYSTEM

In the spring of 1984, MP&L began talking with ENSCO, Inc. above its new transformer flushing system under development at its White Bluff, Tennessee, PCB-Transformer Decommissioning Plant. It was suspected that this system might accomplish our PCB transformer declassification objectives. After several months of talking and evaluating the development of the ENSCO system, MP&L entered into an agreement to allow field testing on four (4) PCB-contaminated mineral oil transformers. The pilot field project objectives were designed to: 1) Evaluate ENSCO's ability to accurately estimate their processing time and limits; 2) To effect changes (as necessary) in the Retro-1 equipment by field testing; 3) To accomplish MP&L's objectives of declassification of a PCB transformer to below 2ppm with only one processing of the transformer; and 4) The processing cost per transformer must be economically compatible with other options for totally eliminating PCBs at the transformer location. ENSCO called its system "The Retro-1 Transformer Recycling Process." It was designed to accomplish a thorough internal flushing of a drained transformer so that the residual PCBs remaining would be less than two-tenths of one percent (0.2%) of the original amount of PCBs in the transformer.

The proprietary Retro-1 process utilizes heated florocarbon vapors which bathe the interior of the drained transformer until the internal parts achieve the temperature of the vapor. Then this process is stopped and a refrigerated, liquid florocarbon bath is begun and the transformer is cooled down. This completes one "cycle" of processing with the florocarbon bath. These cycles are repeated for a calculated number of times according to an ENSCO formula based on the ppm level and size of transformer. The interior components are alternately heated with hot vapor and chilled with the liquid bath. The Retro-1 process permeates and penetrates all interior areas of the transformer case, including the windings, insulation, cloth, mica, bakelite, wood, and laminations. This repeated "deep cleansing" results in the maximum amount of residual PCBs being removed from the transformer.

Before beginning this field test, one of MP&L's primary concerns was the public awareness of the project since it involved PCBs.

Public Involvement:

The transformers chosen for this field project were sidewalk vault units located in a downtown Jackson network distribution system. Any work done on them would require blocking street vehicle traffic lanes, parking zones, and portions of sidewalks above each unit. The field work would be very obvious to the public and the local news media. For these reasons it was decided to hold an advance press briefing to announce plans for this project and answer any questions. The advance press briefing was a good idea because there were no further press involvements.

The general public seemed curious at times, but no complaints or concerns were ever expressed. The project was treated no differently than routine transformer maintenance work.

RETRO-1'S FIRST FIELD PROJECT

One Alternative. In January of 1985, MP&L signed an agreement with ENSCO, Inc. for the purpose of field testing the Retro-1 system on four downtown network, vault type, transformers. The transformers were high liability PCB-contaminated mineral oil units. The ppm levels were 1800ppm, 320ppm, 221ppm, and 33ppm. This range of PCB contamination levels was chosen to help develop data and determine ENSCO's ability to accurately calculate the number of cycles needed to accomplish a final declassification level of 2ppm. If the Retro-1 system were able to accomplish MP&L's objectives, then this method would be the "one alternative" we had been looking for.

Field Implementation. ENSCO brought the Retro-1 system on-site at each location and set up on the sidewalk above the vault transformer. After MP&L de-energized and cleared the transformer, the ENSCO crew connected the Retro-1 equipment and began removal of the existing PCB oils. Next, the cycling process was started and the hot and cold flushing began cleansing the residual PCB from the interior of the transformer case. After the calculated number of cycles was completed, the transformer was vacuum filled with new mineral oil immediately following the heating cycle. ENSCO removed all PCB waste from each site as it was generated for proper disposal per EPA regulations. The transformers remained de-energized for 24 hours after the processing and then were energized without load for another 24 hours before being returned to service. In each case, the transformer was successfully re-energized and the on-going testing phase, for eventual declassification, was begun.

The time required at each site varied from two to five days depending on the ppm level of PCBs in the transformers since that is what determined the number of cycles of processing. The whole project took less than three weeks.

Testing Procedures. Each transformer was tested for PCBs before processing, immediately after processing, at two weeks, and then once a month. The results are shown below:

Transformer	Before Process	After Process	2wks.	1mo.	2mo.	3mo.	4mo.	5mo.
A	33ppm	18ppm	2ppm	3ppm	INVALID	<1ppm	<1ppm	<1ppm
B	221ppm	<1	3	4		<1	<1	<1
C	320ppm	<1	<1	3		<1	<1	<1
D	1800ppm	<1	19	10		19	17	20

Our test results show that the Retro-1 process can effectively remove all PCBs from PCB and PCB-contaminated mineral oil transformers in the 2000ppm or less PCB range.

RETRO-1'S SECOND FIELD PROJECT

In May of 1985, MP&L signed a second agreement with ENSCO, Inc. for the purpose of using the Retro-1 system on two "Askarel" PCB transformers. The transformers were power plant auxiliary switchgear type, 1500KVA and 285 gallons of askarel fluid. The PCB levels were 680,000ppm and 900,000ppm.

The objectives of this project were: 1) To determine what level of reclassification or if declassification could be achieved by using the Retro-1 system on all-askarel transformers; 2) To determine what time frames were necessary to accomplish declassification; and 3) To evaluate the processing cost per askarel transformer.

It was suspected that with a combination of the 1) "Deep cleansing" ability of the Retro-1 system, 2) Refilling with silicone fluid, and 3) Carbon filtration of the silicone fluid to remove any residual askarel--would accomplish very low levels of declassification of an askarel transformer.

Transformer	Before Process	After Process*	1st Filter			
	0wk	8wks	9wks	14wks	16wks	19wks
A	680000ppm	2274ppm	Filter	305ppm	Filter	12wks
B	900000	2037	Filter	512	Filter	17

*Average of 5 tests over 8 weeks

Our tests results show that the objectives, for declassification, were obtained and in a relatively short time frame. Both transformers now have residual PCB levels of less than 50ppm and we expect to declassify them as non-PCB. Notice that in Table 2 there are two 48-hour carbon filtration periods at 9 and 16 weeks.

The savings for askarel transformers using the Retro-1 method versus replacement and disposal were approximately 40-60%.

ECONOMICS

The final decision to use the Retro-1 process rests with the economic evaluation of this process. The only other alternative method to accomplish our objective would be the expensive replacement and disposal (per EPA PCB Transformer Disposal Regulations) of each transformer. The exact cost for the Retro-1 process is dependent upon: 1) The PCB concentration level; 2) The size of the transformer; 3) The difficulty of the replacement work; and 4) The cost of the replacement non-PCB transformer.

CONCLUSION

The Retro-1 process results indicate that it should be considered as a viable alternative for declassification of PCB transformers. And depending on the individual unit, it is a cost effective method which can prevent replacement and disposal of many transformers.

MP&L plans to begin a systematic evaluation of all downtown network vault transformers to determine which units qualify for Retro-1 processing. We expect a savings of approximately 60% over any other method of removing the PCBs from these high risk, high liability, locations. MP&L also plans to evaluate future uses of the Retro-1 process for all-askarel type transformers where we expect a savings of approximately 40%.

An additional benefit of the processing is that the transformers are completely cleaned of sludge that has built up from overheating and overloading. This sludge reduces the efficiency of the transformer and they have to be filtered at least once every five years in order to remove the sludge and contamination buildup. The Retro-1 process accomplished a more thorough interior cleaning of the sludge than is possible in a normal maintenance filtering process and fulfilled a normal routine maintenance period.

This is not only an economical advantage but it also improved the operating efficiency of the transformer. We think that the removal of the PCBs, the thorough cleaning process and the improved efficiency of these transformers have extended the expected operating life of the transformers. These factors, in combination with the other economical considerations, help justify the decision to use the Retro-1 process on high risk, high liability, vault-type transformers and selected askarel transformers.

WESTINGHOUSE ELECTRIC CORPORATION
MATERIALS & MANUFACTURING TECHNOLOGY DEPARTMENT
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RP-2028-11

PRODUCTS OF PARTIAL COMBUSTION OF PCB ALTERNATIVE DIELECTRIC FLUIDS

BY

DR. C. CLAIR CLAIBORNE

INTRODUCTION

Alternative dielectric fluids which may be used in place of askarels in electrical transformers are of relatively recent origin. In 1982, the Environmental Protection Agency concluded "that adequate substitutes existed for PCB's in indoor transformer locations from the perspective of fire safety and electrical efficacy" (1).

Subsequent fire incidents involving PCB transformers focused attention on all types of transformers and their behavior in combustion situations. As a result of these incidents, EPA revised its planning and issued a request for information as a first step in promulgating a rule concerning transformer fires (2).

Although that rule was directed at transformers which may contain PCB's, at the same time, the EPA requested information on the partial and complete combustion products of several alternative transformer insulating fluids products. Although some information was available on the products of complete combustion (defined as occurring when there is an excess of oxygen present), little was available on the products of partial combustion (where insufficient oxygen is present for stoichiometric completion of the combustion) (3-5). It is generally accepted that in confined areas, such as vaults and tunnels, the nature of many fires is such that partial or incomplete combustion may be the predominant mode of combustion.

This study was initiated to investigate the partial combustion products of several of the insulating liquids used in transformers. The program was restricted to combustion situations only; decomposition products produced by an electric arc were not considered.

The primary objective of this program was to determine the chemical compounds formed during partial or incomplete combustion of liquid dielectric insulating materials used in power transformers. To attain this objective an experimental program was carried out after an extensive literature search. The literature search indicated that the information desired was generally unavailable. The references found in this search were transferred to SCS Engineers and are the subject of a separate project (RP 2028-12) and report by that organization.

EXPERIMENTAL STUDIES

Thermodynamic Equilibrium Calculations

In order to establish some indication of the types and levels of potential combustion products from the liquid dielectric materials, theoretical thermodynamic equilibrium calculations were conducted for various oxygen levels over a range of reaction temperatures from room temperature to 1500 K. Data was assembled from various sources, including the JANAF (Joint Army-Navy-Air Force) Thermochemical Tables, and input into a mainframe computer utilizing a program named "CHEMEQ", in the Westinghouse R&D laboratories. This proprietary program, similar to a computer program developed by NASA (6), but with a larger data base, has been used extensively to calculate:

1) Concentrations of chemical species in multicomponent polyphase mixtures at any specified pressure(s) and temperatures(s).

2) Concentrations and adiabatic flame temperatures of chemical products formed in the combustion process.

3) Thermodynamic and transport properties of gas mixtures at equilibrium for specified pressure(s) and temperatures(s).

Combustion Reaction Evaluations

Two separate sets of combustion experiments were conducted for each material. In one set, a thermogravimetric analyzer (TGA) was modified to conduct the combustion and reaction products were trapped in cold traps and fed to a gas chromatograph with an electron capture detector for subsequent analysis. The samples were placed in a platinum boat and heated from ambient temperatures with the oxygen level being controlled by a flow meter into the chamber.

In the other experiment set, a stainless steel reactor was employed for the combustion, and the reaction products were fed to a gas chromatograph/mass spectrometer for evaluation. The samples were injected with a syringe into the reactor and the amount of sample was varied to vary the oxygen level. In an alternative to this procedure, designed to handle viscous materials, the sample was sealed in a small aluminum capsule which was inserted into the chamber by a gas-tight piston.

In both sets of experiments, an ultimate reaction temperature of 1000° C was employed. This temperature was chosen after consultation with Dr. Richard Gann of the National Bureau of Standards as the most probable temperature for partial combustion situations (7).

Materials

One fluid of each of five types of insulating fluid was selected for this study: Chlorinated hydrocarbon--tetrachloroethylene (C_2Cl_4), WECOSOL*, Westinghouse Electric Corporation, original supplier: Diamond Shamrock Corporation; Fluorocarbon--trifluorotrichloroethane ($C_2F_3Cl_3$), Freon 113*, supplier: E.I. DuPont de Nemours; Silicone fluid--polydimethylsiloxane, Dow Corning 561 Silicone Transformer Fluid, supplier: Dow Corning Company; Mineral oil--UEMCO C*, Westinghouse Electric Corporation, original supplier: Gulf Oil Corporation; High temperature hydrocarbon--RTEmp*, supplier: RTE Corporation.

EXPERIMENTAL RESULTS

Tetrachloroethylene

With tetrachloroethylene in the thermogravimetric chamber, considerable problems were encountered when the combustion was carried out at an air level corresponding to 70% of theoretical total combustion. Detectable amounts of chlorine were generated and in addition, since the chamber was heated from ambient temperature upward, the presence of water on the interior walls of the chamber caused the production of small amounts of HCl. This in turn caused corrosion of some of the metal parts in the TGA measurement system such as the sample reference thermocouple. Since this component was not essential to the operation of the instrument for these experiments, it was omitted in the next run. However, the second run caused enough deterioration of some of the other components of the apparatus, e.g. O-rings and balance parts, to require overhaul of the instrument. As a result, the runs at 30% air were postponed and indeed were not completed during the project. Compatible materials are available which could alleviate these problems in future investigations.

Other than the expected chlorine and the normal constituents of air, only HCl was noted in small amounts in the combustion products. As was predicted in the thermodynamic equilibrium calculations, phosgene was not detected in any of the runs. Unreacted starting material was recovered in significant quantities.

The stainless steel combustion reactor was used to conduct three analytical runs with tetrachloroethylene. Two direct injection runs gave chlorine as the primary product and a low level (approximately 0.1%) of dichloroacetylene was seen in one of the direct injection runs. Unreacted tetrachloroethylene was also recovered in both of these runs. An additional sample run with the piston/capsule method gave essentially the same results with dichloroacetylene again being found. No particulates were detected on a glass fiber disk trap located at the reactor exit. With the sample quantities used in the experiment, this indicated that <3 ppm of halogenated or polycyclic particulates were formed.

Trichlorotrifluoroethane

Trichlorotrifluoroethane gave similar results to tetrachloroethylene when it was examined in the thermogravimetric chamber, except that chlorine was not observed. Again, the presence of water on the interior walls did cause production of HF which in turn caused a minor amount of etching of the chamber.

In this particular case, however, not all peaks in the chromatograph from the electron capture detector could be identified. Certain of these peaks undoubtedly could have been associated with various fluorocarbon compounds that were not readily available for confirmation of the peak identities. It was decided that the results of the other experimental arrangement would be used to qualitatively identify these other products.

Two runs were made in the stainless steel reactor using the direct injection procedure. The first run, in which the withdrawal of products was carried out after 10 seconds, showed chlorotrifluoroethylene and dichlorotetrafluoroethane. However, over 99% of recovered gaseous material was unreacted starting material. A second injection was made and the gas sample was withdrawn after 10 minutes. A little chlorine was detected but unreacted material was predominant. CF_2^+ and $CFCl^+$ was also found, which may indicate a trace of active

fluorine, although that seems unlikely. Fluorine was outside the scanning range of the GC/MS configuration for these experiments. This run did not detect the other two materials seen in the first run.

Four runs were made on trichlorotrifluoroethane with the piston/capsule technique. With this technique, products detected included tetrafluoroethane, dichlorodifluoroethylene, chlorotrifluoroethylene, trichlorofluoroethylene, tetrafluoroethylene and fluorochloroethylene. Again, no particulates of interest were detected, even in the run with the greatest variety of products, with the same detection limit as with C_2Cl_4, 3 ppm.

Many of these products may well correspond to the results of the combustion in the TGA. Since it was not possible to acquire these materials, confirmation was limited to the observation that some of these materials were predicted by the thermodynamic calculations.

Silicone

With silicone, a relatively large variety of gaseous products were detected, including CO_2, H_2, CO, methane, ethane, acetylene and other hydrocarbons. Again in this case, a large amount of unreacted material was present in the chamber and in the combustion boat at the completion of the experiment.

Above all, a significant amount of solid material was found in all tubing leading from the quartz combustion chamber. This material was white and fluffy in appearance and was most likely silicon dioxide which is known to result from combustion of polydimethylsiloxane (4).

In the experiment set utilizing the stainless steel reactor, two runs were made with the direct injection method. Since no volatiles were detected and because of the relative difficulty of transferring this rather viscous substance, the piston method was developed. However, again no volatiles were detected. The steel reactor tube contained a large amount of black, fluffy material. When this material was removed and heated in a muffle furnace with an O_2 excess at 1000o C, the substance left a white ash. This lad to the conclusion that the material was probably SiO_2 mixed with carbon. No other particulates of interest were detected on the glass fiber collector. In this case, detectability would have been on the order of <15 ppm due the different mass of starting material.

Mineral Oil

Transformer mineral oil generated significant quantities of combustible materials such as methane and ethane, which possibly resulted from cracking of the starting material, when the amount of air was limited to 30%. This indicated that the combustion was quite decidedly not complete. A surprisingly low amount of carbon dioxide was found with both the 70% and 30% air levels.

High Temperature Hydrocarbon

The quantities of combustible materials present in the products of the high temperature hydrocarbon were relatively less than for the transformer mineral oil. However, there were significant quantities of ethylene found. Again, as in the case of the silicone fluid, a large amount of unreacted material was present in the combustion chamber.

In a run made with this material in the GC/MS setup, only two products were detected in the gaseous product analysis by mass spectroscopy: benzene and toluene. In relative terms only a small proportion of the starting sample, was present as these products. No particulate material was detected.

DISCUSSION

In summation, it is important to note that none of the combustions produced detectable chlorinated or polycyclic aromatic hydrocarbon particulates. The production of chlorine (and hydrogen chloride in the presence of atmospheric humidity) from tetrachloroethylene must not be minimized, but rather should be balanced against the non-flammable nature of the material. Much the same statement may be made about trichlorotrifluoroethane and its production of hydrogen fluoride and the various fluorocarbon materials. The absence of phosgene in these experiments is also to be noted.

For the other materials, the presence of combustible materials in the product stream indicated that even in events with only partial combustion, a potentially dangerous situation may remain even after the heat source is removed.

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PCB TRANSFORMER DECONTAMINATION RATHER THAN BURIAL

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Until this year, PCB transformers required burial at a secure landfill. Since the Environmental Protection Agency is encouraging new technologies rather than burial at landfills, they have permitted a reclamation and recovery facilities for PCB transformer reclamation in Kansas City. This PCB transformer facility is under EPA control. Transformers are received, cleaned to less than 500 ppm, opened, and the internal parts processed through an assembly line operation for PCB removal and extractions. This paper includes handling, processing procedures for reclamation, to primary metal recovery for smelt.

RETROFILLING ASKAREL TRANSFORMERS - WORDS OF CAUTION

J. P. Kinney

General Electric Co.

Retrofilling transformers that were originally constructed for use with askarel is an alternative to complete changeout and disposal. In some cases where space is critical, removal is very expensive, or the installation is unique, retrofill is an approach to consider. This decision needs to be made with some key points in mind. In 1977 several papers [1, 2, 3] were published advising the industry of the potential problems involved when askarel transformers were retrofilled. Askarel composition, materials of construction and transformer designs were changed many times in the forty years they were manufactured. No overall recommendation can be made concerning all of these transformers. In each case it would be wise to include an inquiry to the manufacturer before deciding to proceed with retrofilling.

As pointed out by Morgan and Osthoff[1], the leaching out of PCB's from transformer insulation systems is a very slow process. Changing selective adsorbants or making multiple retrofills in order to maintain low PCB concentrations can become a significant factor in the economic evaluation of retrofilling.

When General Electric's Medium Transformer plant changed from building askarel filled transformers to the production of silicone filled transformers, it was necessary to make several changes in the design of the product from that previously used for askarel. Most of these changes if made today would require teardown of an existing askarel transformer, which is a violation of federal regulations[5]. If the cleanup and retrofill process followed by a minimum of three months back in service lowers the PCB content to less than 500 ppm, federal regulations would then allow teardown and modification. If the transformer is inaccessible for rework of this type, operation after retrofilling should be modified as described in the conclusion of this paper.

The key differences in properties between askarel and silicone fluid which require design changes are impulse creepage strength, heat transfer capability, thermal coefficient of expansion, material compatibility and lubricity. Some of the differences in properties are shown in Table I. This table compares silicone fluid, transformer oil and askarel. The problems and suggested modified operation are covered in the following paragraphs.

Table I

PROPERTIES OF SILICONE, MINERAL OIL, AND ASKAREL

	Silicone	Mineral Oil	Askarel
Viscosity, cs at 25°C	50	10	12.8
at 80°C	20	2.7	4.2
Flash Point, Open Cup, Min	300	145	No true f.p.
Fire Point, Open Cup, Min	340	150	None to b.p.
Oxygen Index	21.4	15.8	37.8
Specific Gravity, 25°C	0.96	0.88	1.5
Coefficient of Expansion, cc/cc/°C	.00106	.0007	.0007
Pour Point, °C	-55	-55	-40
Boiling Range, °C	None	280-370	209-381
Dielectric Constant, 25°C, 60 Hz	2.7	2.2	5.3
Dielectric Strength, kV Disk Electrode, 0.25 cm gap	35	35	35

MONS 019098

Table II

DIELECTRIC BREAKDOWN STRENGTH FOR VARIOUS CONFIGURATIONS WITH SILICONE, MINERAL OIL, AND ASKAREL

	Silicone	Mineral Oil	Askarel
Impulse Breakdown, kV			
Uniform Field, 2.54 mm (0.1 in.) gap (ASTM D1816 Electrodes)	136.4	142.0	153.3
Non-uniform Field, Rod-to-Plane 12.7 mm (0.5 in.) gap			
Negative Polarity	295.6	107.0	119.0[a]
Positive Polarity	99.6	90.9	114.0[a]
Impregnated Kraft Paper Round Edge Electrode, 51 mm (2.0 in.) diameter			
0.467 mm thickness	38.4	43.0	49.0
2.34 mm thickness	134.8	182.9	163.0
Impulse Creepage on Kraft Pressboard (2) Electrodes, 25.4 mm (1.0 in.) dia. Edge-to-Edge Spacing, 76.2 mm (3.0 in.)			
Positive Polarity	89.6	152.3	130.6
60 Hertz Breakdown, kV			
Impregnated Kraft Paper Rounded Edge Electrode 51 mm (2.0 in.) diameter			
0.467 mm thickness	19.5	22.1	28.7
2.34 mm thickness	64.3	77.0	85.5

[a] Based on limited test samples.

MONS 019099

POSITIVE POLARITY IMPULSE CREEP STRENGTH[4]

The surface impulse creepage dielectric strength of high density kraft pressboard when tested in silicone fluid is just under 70% of that experienced in askarel. Some of the more comprehensive dielectric breakdown properties are shown in Table II. When GE's then standard askarel transformer design was filled with silicone fluid and given positive polarity impulse tests, there were surface creepage breakdowns. An internal redesign to compensate for the lower impulse breakdown characteristics of the liquid achieved the full insulation levels required in the new silicone fluid transformer. If an existing askarel transformer could be satisfactorily cleaned and then retrofilled with silicone fluid, the BIL rating should be reduced and suitable surge arrestors should be applied to protect the transformer from excessive transient voltages.

HEAT TRANSFER

Industry standards for 55° or 65° temperature rise liquid filled transformers specify a guaranteed winding temperature rise over ambient. The guaranteed hot spot rises over ambient are 65°C and 80°C respectively. Heat runs conducted on prototype transformers with thermocouples embedded in the windings indicated from 5 to 25°C greater temperatures when silicone fluid was the cooling liquid as compared to askarel. Approximately 30% more surface area was added to the cooling package to meet the guaranteed winding rise of silicone fluid transformers. If an askarel transformer is retrofilled with silicone fluid, derating is required to prevent serious damage due to overheating.

THERMAL COEFFICIENT OF EXPANSION

The thermal coefficient of expansion of silicone fluid is some 40% greater than askarel. This results in tank designs with a greater gas space above the 25°C liquid level and a greater distance from this liquid level down to the highest conductor. If a retrofilled transformer is located outdoors, low ambient temperatures may cause contraction of the liquid that would expose the bus bars, bushings or other conductor. This in turn could cause dielectric and/or thermal problems. Adding external heaters or possibly an external expansion tank is recommended when a silicone fluid retrofilled transformer is located outdoors.

MATERIAL COMPATIBILITY

The gasket materials used for askarel transformers were changed many times over the years. Silicone rubber and then Viton® were found to be resistant to askarel. Silicone rubber used for approximately the last 20 years of askarel transformer manufacture is not suitable for use in silicone fluid. It is necessary to replace all gaskets when an askarel transformer is retrofilled.

Again, over the years, each design change usually introduced several new materials of construction. Some of the materials used in askarel transformers are no longer commercially available and no material compatibility testing has ever been done on them in silicone fluid or in any other transformer fluid. If a silicone depolymerization catalyst is present in any of these materials, the fire point of the liquid may be affected. Some other materials may cause viscosity increases. Frequent testing of liquid samples from retrofilled transformers should be scheduled and should include fire point and viscosity tests along with PCB concentration tests.

LUBRICITY

The "no load" (deenergized operation) tap changer of most industrial load center transformers is seldom changed from the position set before initial energization. The cap of the tap changer can be padlocked to prevent operation by unauthorized personnel. If an askarel transformer is retrofilled with silicone fluid you should label its tap changer as inoperative due to the difference in lubricating properties between the two fluids. There is a possibility of the tap changer mechanism locking up. The drive shaft may break and if the tap changer is not in the correct position the transformer may fail electrically on energization. When the manufacture of new silicone filled transformers was started a complete redesign of the tap changer was necessary to achieve satisfactory operation.

FLUSHING SOLVENTS

Some retrofill contractors have used strong solvents to attempt to remove the askarel which hasn't dripped from the core and coil after draining. This practice can seriously damage the wire enamel and other resinous materials in the transformer. One flushing solvent which shouldn't harm the insulation

system in GE industrial load center transformers is a mixture of tri- and tetrachlorobenzenes. Since this was one of the ingredients of askarel it should be compatible for a short duration of flushing. This recommendation applies only to transformers manufactured at General Electric's Medium Transformer Plant in Rome, Georgia. Information involving other GE products or products of other manufacturers should be obtained directly from the manufacturing site. Again, askarel impregnated insulation may not give up its PCB content easily in this process.

RETROFILLING WITH OTHER FLUIDS

Two other fluids used in cooling and as a dielectric in new transformers today should definitely <u>not</u> be used for retrofilling. Dielectric Grade Freon R-113 is used as a vaporization cooling fluid and askarel transformers were not designed for this cooling technique. Perchlorethylene is compatible with paper insulation but the wire enamels used in many of GE's askarel transformers will not resist the solvent action of perchloroethylene. High molecular weight hydrocarbons have not been studied from a compatibility standpoint. You should check with local building codes and your fire insurance firms before using any specific retrofill liquid.

CONCLUSION

Several years of experience have demonstrated that retrofilling of askarel transformers is still a somewhat controversial topic in the industry. If a decision is made to retrofill any Rome built G. E. transformer, the following precautions should be followed:

1. Obtain up to date Federal, State and local regulations concerning PCB's and follow them.

2. Recognize that PCB will leach out of the core and insulation with time, possibly requiring additional retrofills and more disposal costs in order to maintain acceptably low concentrations of PCB's in the fluid.

3 Change out all gaskets using appropriate replacement gaskets.

4. Set the tap changer before retrofilling, lock it, and label as inoperative.

5. Examine the load and if at or near full load - reduce it to prevent overheating. The nameplate should be modified to reflect derating and the presence of the new fluid.

MONS 019102

6. Derate the BIL of the transformer and apply suitable surge arrestors in the proper location to protect the transformer from transients.

7. If the transformer is installed outdoors take precautions such as heaters for low ambients so contraction of the fluid won't expose the bus bar or other conductor.

8. Monitor the thermal behavior of the transformer during the derated full load operation over an extended period.

9. When monitoring liquid samples for PCB decontamination progress include viscosity and fire point along with other critical properties. Continue this testing on a yearly basis.

10. Consult with your insurance carrier on the suitability of any retrofill liquid from a fire safety standpoint.

11. The manufacturers calculations and judgements on derating and material compatibility made by examining the old design drawings will be helpful but will also be an additional expense which will not have the confirmation of factory testing. In other words if you retrofill you are on your own.

We hope that the information in this paper will be of value to the owners of askarel transformers who are considering retrofilling or other alternatives that lower or eliminate PCB's.

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DECONTAMINATION OF AN ASKAREL-FILLED NETWORK TRANSFORMER

D. T. Drew Dunlop

This paper describes a pilot project undertaken to determine the feasibility and economics of decontaminating and retrofilling askarel-filled network transformers used in B. C. Hydro's underground distribution system in Victoria, B. C.

The Victoria network system consists of multiple 12 kV feeders with each feeder supplying a number of 12 kV to 120/208 V 500 kVA network transformers. The secondaries of each transformer are bussed together forming a secondary network at 120/208 V from which service leads are run to customers. The network system is completely underground with the transformers placed in vaults under sidewalks with open grills covering the vaults. When the original network system was designed in the mid-1950's, askarel-filled transformers were selected because the use of askarel-filled transformers in such locations was the standard industry practice at the time and because of the serious consequences a transformer fire could have in such close proximity to the public.

There are a total of 94 transformers in the Victoria network system. Fifty-five of the transformers are askarel-filled; the balance of the transformers were purchased subsequent to the ban on PCBs in new transformers and are filled with conventional hydrocarbon insulating oil. The Victoria network transformers are the only askarel-filled transformers exposed to the public in the B. C. Hydro system.

The transformer was thoroughly drained prior to beginning the solvent decontamination. Approximately 760 of a nominal 865 litres (87.9%) of askarel were removed from the transformer by draining.

The decontamination procedure was modified a number of times in an attempt to achieve the most efficient method for promoting the release of askarel from within the transformer components.

Initially, vapor phase degreasing was used to decontaminate the transformer. Twenty-seven vapor degreasing cycles were completed over a period of 38 days with the transformer in a vapor phase system autoclave. One degreasing cycle was completed each working day.

Shell Sol LX154, a hydrocarbon mineral spirits, was selected as the degreasing solvent. Shell Sol has a boiling point of approximately 185°C (STP); a typical askarel boils at greater than 200°C (STP). By using a solvent with a lower boiling point than askarel, the transformer components were constantly washed with clean solvent since the dissolved askarel did not volatize at the solvent boiling point.

The vapor degreasing process consisted of introducing hot solvent vapors into the transformer; these vapors condensed on the transformer winding, core and supports resulting in a washing action. The cleaning action continued for approximately five hours until the transformer components reached the temperature of the solvent vapors.

With each successive vapor degreasing cycle, the amount of askarel released from the transformer decreased. The 27 vapor degreasing cycles removed approximately 84.1 litres of askarel from the transformer.

The decontamination process was then changed from vapor phase degreasing to hot solvent soaks. The transformer was left in the autoclave and was filled with solvent. During each hot solvent soak, heat was supplied to the solvent filled transformer by flooding the autoclave with hot solvent vapors for a period of three hours. During the hot solvent soaks, the transformer winding reached an average temperature of 83°C. The hot solvent soak cycle was repeated 56 times, once each working day, over a period of 87 days. The transformer was flushed and refilled with distilled solvent every two weeks.

A decreasing amount of askarel was removed from the transformer with each successive hot solvent soak. Approximately 109.9 litres of askarel were removed from the transformer by the hot solvent soak cycles.

The decontamination process was then modified from hot solvent soaks to cold solvent soaks. Each cold solvent soak consisted of filling the transformer with distilled solvent and allowing the transformer to soak for a number of days in a static situation at room temperature. The transformer was then drained and refilled with

distilled solvent. This procedure was repeated ten times over a period of 57 days, with each soak lasting from three to eight days.

The cold solvent soaks were found to be ineffective in decontaminating the transformer. Essentially no askarel was removed from the transformer by the cold solvent soak method. It was decided, therefore, to terminate the solvent decontamination and retrofill the transformer.

The vapor degreasing cycles removed 84.1 litres of askarel which corresponds to an average of 3.1 litres of askarel per vapor washing. The hot solvent soaks removed 109.9 litres of askarel which corresponds to an average of 1.95 litres per hot solvent soak. This is in addition to the 760 litres of askarel removed by draining. The amount of askarel removed from the transformer may seem inconsistent with the assumed total quantity of transformer fluid of 865 litres. However, the quantity of fluid removed by draining is approximate and is considered to be accurate only within ±10%. In addition, the 865 litres is a nominal quantity; the exact quantity of fluid within the transformer is not known.

It was intended that the transformer be retrofilled with an environmentally acceptable synthetic insulating fluid with electrical insulating and fire resistance properties similar to askarel. However, because of the expected release of askarel into the retrofill fluid and the cost of suitable synthetic insulating fluids, it was decided to first retrofill the transformer with reclaimed conventional hydrocarbon insulating oil.

Prior to filling the transformer, the reclaimed insulating oil was tested and found to contain no measurable concentration of PCB. The next oil sample was taken one day after filling the transformer with insulating oil. The PCB concentration was found to be 118 ppm. This increased to 169 ppm with the transformer in a static situation at room temperature for 20 days.

The transformer was then insulated with fiberglass batting and energized from the low voltage side to accelerate the release of askarel into the oil. The transformer remained energized for a period of 216 days. Over this time, the PCB concentration increased to 2,063 ppm.

When it became apparent that only a minimal additional amount of askarel would be released if the transformer remained insulated and energized, it was decided to drain and then fill the transformer with a synthetic insulating fluid. The

transformer was allowed to drain for a period of 14 days in an attempt to remove as much askarel-contaminated oil as possible.

Based on synthetic insulating fluid characteristics and replacement fluid costs and availability, a decision was made to use Gulf Less Flammable Dielectric Fluid PAO+ as the retrofill fluid for the decontamination project. Gulf PAO+ is a polyalphaolefin based synthetic hydrocarbon, compatible with conventional hydrocarbon insulating oil.

An oil sample was taken one day after filling the transformer with Gulf PAO+. The PCB concentration was found to be 269 ppm. A high initial concentration of PCB was not expected and no suitable explanation for this could be found.

Because of the heat transfer characteristics of the Gulf PAO+ dielectric fluid, it was expected that the transformer would have to be de-rated. To determine the new transformer rating, temperature rise tests were performed. Based on the results of these tests and a maximum winding temperature rise of 55°C above ambient, it was determined the transformer should be de-rated by 20% to 400 kVA.

An insulating fluid sample was taken following completion of the temperature rise tests. The PCB concentration was found to be 335 ppm. To date the transformer has not been returned to service and after 18 months in storage the PCB concentration in the retrofill fluid is 830 ppm. This represents a 99.92% reduction in the amount of free PCB originally in the transformer.

The decontamination project was carried out without adverse effects to personnel, plant or the environment. There was no significant increase in blood PCB levels of employees involved in the decontamination program and no increase in PCB contamination levels within the shop facility was observed.

The decision to retrofill a transformer versus replacing the transformer involves several economic trade-offs. The cost of decontaminating and retrofilling the transformer and the remaining life of the transformer must be balanced against the cost and expected life of a new transformer. When considering the cost of a new transformer, the cost of storing and ultimately disposing of the askarel-filled transformer must also be considered.

PCB REMOVALS - OPTIONS AND IMPLEMENTATION

Francis E. Silvia, Boston Edison Company

INTRODUCTION

In June of 1983 the Boston Edison Company established a voluntary program to eliminate askarel filled secondary network and station equipment from its system by year end 1988. This program involves the disposal of some 800 pieces of equipment exclusive of EPA-mandated capacitor removals. Two years into the five-year project, we are on schedule and underbudget for this projected $32.5M program. The success of the project to date is due in large part to the research and planning efforts of project personnel prior to its implementation.

This presentation is a general description of some issues, decisions and options that must be addressed by any company considering the method of disposing of its askarel equipment. It is our intention only to suggest a framework for project setup, not to evaluate the options contained therein. Evaluation, we believe, is best left to the individual company, since it is best aware of its own particular needs.

THE CORPORATE OBJECTIVE

A primary consideration in preparing a project plan is the definition of the corporate objective. In this case, how does a particular company wish to deal with its askarel equipment? Does the company wish to be PCB "free", will it maintain some existing PCB equipment, or is some level of PCB concentration between 0 and 500 ppm satisfactory?

Establishing the objective is essential to providing an overall direction to the project and to keep it on track in its ensuing stages. It should be based not only on dollar cost, but also on potential future liabilities. Other factors that may influence the decision include the company's social obligations and responsibilities to the public, the business community and the municipalities in which it operates.

The task of establishing the corporate objective generally lies with the company's officers, since it is they who are specifically liable for compliance with existing regulations. Prerequisite to their decision is an evaluation of the alternatives available. An in-depth analysis of alternatives must be provided if an optimum decision is to be made.

OPTIONS

The project personnel, i.e., managers, coordinators and engineers, are responsible for evaluating available options and submitting recommendations to company officers. These analyses are, however, subject to re-evaluation as changes in technology and regulations come about.

Presently available options include retrofill of existing equipment with substitute insulating fluids, the addition of a filtering system to a retrofilled unit, direct replacement of askarel equipment with new equipment, and last, the "do nothing" approach which simply maintains existing equipment in accordance with applicable regulations.

At first glance the above may look simple enough since there are only four options from which to choose. But consider also that each of the four carries with it underlying considerations. For example, what types of alternate insulating media are available for retrofills or replacements? How do you deal with PCB equipment carcasses? How effective are PCB filtration systems? More specific questions include future changes in regulations, availability and lead time for services and equipment, adaptability of new equipment to existing installations, experience and licensing of hazardous waste disposal contractors, availability of disposal sites, the fire, dielectric and toxicity ratings of substitute fluids, the age, electric loss and possible de-rating of existing equipment. There may also be other ways to deal with askarel removals. For example, it may be possible to retire equipment and not replace it by shifting load to other installations, reconductoring, etc. Finally, where do you get accurate and reliable information on the above, and what about the costs?

It is easy to see that the choice of an option may not be as simple a matter as it first appears. A considerable amount of time must be spent in researching information in order to optimize the choice.

IMPLEMENTATION

After alternatives have been evaluated, the corporate objective established and options chosen, an implementation plan must be designed and executed. This plan is essentially a master schedule of when field work will be performed, but it carries with it the underlying considerations of how, who and where.

For example, there will most likely be priority locations to be dealt with. Should priorities be based on type of establishment (hospital, school, residential, etc.), voltage level of the equipment, or some other criteria? Who will perform the work? Are there sufficient in-house personnel available or should outside contractors be used? What about timing and availability of equipment and services? Can the project be interlaced and coordinated with already planned construction? Are special procedures or accounting needed to accommodate the project or are normal channels adequate? As with the evaluation of options, a number of items must be addressed in order to formulate and optimize a plan.

SUMMARY

Clearly, the execution of an askarel replacement program is not a simple task. The options are numerous and, in many cases, the time available to accomplish the task is short. It is essential that all issues be addressed if a program is to be tailored to a particular company's needs relative to the use or replacement of askarel filled equipment.

PART 9:

SPILL MANAGEMENT PANEL

AFTER A PCB FIRE - CLEANUP INSIDE BUILDINGS CONTAMINATED WITH DIOXINS AND FURANS

Kirk Blackmon

Fire involving PCB transformers at office buildings in San Francisco, California, and Binghamton, New York, resulted in the buildings being closed due to the presence of dioxins and furans. This paper presents four aspects of the subsequent clean-up of these buildings: approach, procedures, results, and costs.

My company was directly responsible for much of the decontamination in the San Francisco building (One Market Plaza), and the Binghamton State Office Building. In all these cases, not only were the buildings contaminated with PCB's after the fires, but also either dioxins or furans, or both. This means that if one of your transformers is involved in a fire, and if any of the PCB oil is subjected to high temperatures, you are going to have a serious problem. The most serious exposure you must consider is your potential liability from health related litigation. Do not let people into the building until you have had it adequately tested. But what about getting the contaminated area back in service quickly and safely. What can you do?

APPROACH

The two largest PCB-fire decontamination projects to date, One Market Plaza and Binghamton, show that decontamination can be successful and the buildings reoccupied. Our approach to both these projects was basically the same. We did not attempt to neutralize or destroy the contaminants. Instead, we cleaned all surfaces, transferring contaminants from the building and its contents to cleaning agents, cloths and sponges. The cleaning materials were then disposed of as hazardous waste. In some of our more recent projects, we have discovered that water-based cleaning agents have proven in many cases to be the most efficient methods of removing contaminants. Using these methods, a tremendous amount of waste water is generated. To handle this, we now have transportable water purification systems that are capable of reducing the contaminant levels to one part per billion.

In most cases, this is clean enough to be placed in a city sanitary sewer system.

PROCEDURES

In completing these jobs, many procedures, chemicals, and equipment have been designed, tested, and improved upon. A few of these procedures are listed below:

Medical Surveillance

Decontamination projects require the medical monitoring of all personnel entering the building until it is given a clean bill of health. This is important for the following reasons:

- It insures the exposed people are not becoming contaminated.
- Psychologically, these people feel safer because they are being monitored.
- The medical surveillance will enable you to better defend yourself if liability suits are filed.

Health and Safety Plans

The Health and Safety Plans related to these types of cleanup projects have been developed and implemented on all these previously mentioned jobs. These plans include entry and exit procedures, training procedures, protective equipment applications, respirator programs, etc.

Decontamination Facilities

Part of the health and safety plans require that all workers change clothes and shower whenever they leave a contaminated building. Our transportable decontamination facilities are equipped with dressing areas, showers, laundry facilities, and respiratory equipment maintenance areas. All of the water generated from this facility must be recaptured and processed through the water treatment plant.

Protective Gear

In many of these projects, it was found that certain areas of the buildings were lightly contaminated, some areas were moderately contaminated, and others heavily contaminated. It became quite cost effective to isolate these different areas and prescribe protective equipment specifically for each individual area. The lightly contaminated areas might require only gloves, boots, head protection, and no respirators, while the heavily contaminated areas might require self-contained breathing apparatus and impervious type suits.

Exterior Restoration

At One Market Plaza, the contaminated area included portions of the outside of the building. We had to develop a new piece of equipment specifically for this exterior cleaning, because none of the cleaning solution could be allowed to fall on the street below.

Interior Restoration

The insides of these buildings normally require everything to be cleaned. This includes elevator shafts, walls, ceilings, floors, and the entire heating and air conditioning systems. Most of the cleaning was very detailed and in many cases, special chemicals were developed to release the binders that held the contaminants to each item. Some of the most difficult interior decontamination involved the ductwork that distributes air throughout the building. At first it appeared that the entire systems at the One Market Plaza Building would have to be replaced, but we developed a new cleaning technique that worked well in cleaning all sizes of air ducts. The technique is very similar to swabbing a very large gun barrel. A machine sends a swab through the ductwork emitting the proper chemicals while mechanical agitation is taking place. After the ducts are clean, they are sealed with a resin based sealer. This technique was also used in Binghamton, where it was even more important, because in Binghamton the ductwork was sandwiched between layers of concrete. Removing the ductwork would have required extensive demolition.

Contents

In addition to decontaminating the structure elements, many times all contents must be decontaminated also. Some of the most challenging of these are computers, word processors, and other electronic equipment. Fortunately, techniques have already been developed and improved upon for removing the contaminants from such equipment. Three of the methods used to accomplish this are air brushing, ultra sound cleaning, and vapor degreasing.

RESULTS

One Market Plaza reopened to employees in March of 1984, ten months after the fire. Floors two through eighteen of the Binghamton State Office Building were vented to the outside air for the first time in four years in February, 1985. In August, 1985, these same floors were given a clean bill of health by the expert panel and released to the construction trade for refurbishing. We expect to finish the basement floors and the first floor and have it reopened soon.

COSTS

The first two major PCB decontamination projects generated awesome property damage costs, twenty-one million dollars for One Market Plaza and thirty-eight million dollars for Binghamton. Such costs may seem slightly less forbidding when compared to the cost of abandoning and demolishing the buildings, which is indeed the only other option following contamination of this type. But the cost of some of our more recent decontamination projects is significantly less. Two examples are Arnold Air Force Station in Tennessee and the State Highway Department Building in Santa Fe, New Mexico. Both were similarly contaminated but restored at much less cost. In holding cost down on these type projects, it is very important that those involved not try and reinvent the wheel. All of the preliminary research, development, testing, and experimentation that made the first two losses so expensive will help reduce costs for those that follow.

There are also services available now that did not exist at the time of the Binghamton fire. For example a process has been developed to save contaminated network protective switches when replacing PCB transformers. Many utilities are replacing these switches because they are found to be contaminated because of their proximity to the PCB transformers. The cost of replacing these switches is approximately $25,000.00 each, but because of all the research and development associated with PCB losses, it is now possible to have these switches decontaminated and restored to like-new condition for about $2,000.00 each.

PCB SPILL RESPONSE AND CLEANUP RESULTS

Author - P. J. Eisele

In mid-1982 the Detroit Edison Company was pursuing an ongoing program of gradual polychlorinated biphenyl (PCB) capacitor replacement based on equipment failure. When one distribution capacitor unit would fail, the whole bank (3-6 units) would be replaced with non-PCB equipment. In early 1983 this program was accelerated to remove some 19,000 PCB capacitors from the 7600 square miles of Company service area to meet a removal deadline of October 1, 1988 set by Toxic Substances Control Act (TSCA) regulations. The regional office of the USEPA, concerned that utilities were not moving quickly enough to beat the TSCA deadline and cognizant of general public concern about PCB spills in the Great Lakes area, met with the Company to encourage more expeditious removal. Although the agency was not aware of the progress made to date, the Company established a management team to investigate and improve corporate PCB activities. The Company management team was established under a group vice president, and included a PCB Program Manager and individual Departmental PCB Program Directors. In addition, corporate officials in Legal, Public Affairs and Environmental Affairs set policy on which response groups acted. The response program focused on five areas: improved communication with affected citizens, employes, agencies and the media; revised written spill cleanup procedures; improved training in spill clean up; revised equipment removal and replacement schedule; and escalated sampling and analysis.

The implementation of the complete program, including scheduling of replacement activities, disposal, procedure revision and training, took approximately two months. Ten thousand distribution system capacitors were removed or replaced for 1900 locations from mid-1983 to mid-1984. The program cost about 10 million dollars, including new equipment, labor and disposal.

Company cleanup procedures were rewritten to automatically include excavation of soils at least thirty cm deep, one-and-one-half meters beyond the visible spill area, and to triple-clean all solid surfaces. Afterwards, soil and wipe samples were taken using the predetermined grid found in the 1981 TSCA Inspection Manual to determine if the PCB cleanup was adequate. Laboratory analysis of PCB was done within the Company using a twenty-four hour soil drying period, soil mixing, eighteen hour soxhlet extraction, and electron capture gas chromatography. Chromatograph peaks were compared to various arochlor standards by means of linkage to a Nelson Analog to Digital Computer interface. Split samples were sent to other laboratories to be analyzed for quality control. The process from discovery of spill through initial cleanup to soil analysis results was typically about ten days. During this time period the excavated site was fenced or roped off. If the sampling results indicated the site did not meet Company standards, the process was repeated. Associated with the cleanup activity was removal and replacement of equipment with non-PCB equipment to eliminate future PCB spills. Specific line crews were dedicated to both the cleanup and replacement activities.

A major part of the program was re-inspection of current PCB capacitor spills as well as past spills dating back to 1976 for which there were records. This represented more than 200 spill sites where cleanups had been conducted based on visual extent of the spill. One of the problems in re-evaluating these sites is the variable regulatory requirements for spill cleanup over this time period.

Prior to 1978 there were no federal standards for PCB spill cleanup, although the State of Michigan required cleanup of visible traces of polluting substances under its Water Resources Commission regulations. TSCA regulations could be interpreted as setting a spill cleanup limit of 500 ppm PCB in 1978, a 50 ppm limit in 1979, and a "prevention of significant exposure" in 1982. The latter has been interpreted by some to imply any detectable level.

In the Company re-inspection process, 57 percent of the spill sites met the applicable criteria for the year in which the spill took

place. This implies that the cleanup of visible traces was sufficient over half the time. Since the Company had embarked on a recheck program and the most recent criteria was somewhat nebulous, all sites were cleaned to a newly defined operational standard. The Company set the minimum acceptable operating standard that remaining soil could contain no more than an average of 10 ppm PCB with the highest single acceptable value of 25 ppm. The goal was to remove all spilled PCB, but the operating standard would insure protection of public health. Approximately 13 percent of the sites met this operational criteria after cleanup of visible traces. The data are summarized in Table 1. Although the single highest value of the eleven soil samples taken is used to evaluate acceptability, this may be inappropriate since many times only one or two of the samples was elevated much beyond background. These elevated levels occurred at the base of the pole holding the capacitor bank. For example, using the spill recheck results for 1981 as representative for all years and applying the criteria to mean soil PCB concentrations, all twenty-six sites would meet the 1978 criteria. Only eight would require a cleanup to achieve average soil concentrations less than 50 ppm and again this would be primarily due to one or two locations with elevated levels. This is not unreasonable recognizing that less than five liters of PCB material were probably spilled. Spills did occur, however, more than once at some sites. Documentation of spills indicated that this occurred ten times thus making the actual number of spills 223.

TABLE 1

Number of Re-Analyzed Spill Sites Meeting Various Criteria Prior to Recleaning

Spill Year	Company Criteria	EPA 1979 Criteria	EPA 1978 Criteria	EPA 1977 Criteria	Total
1984	2	1	4	1	8
1983	8	3	8	9	28
1982	2	4	3	5	14
1981	3	6	12	5	26
1980	5	7	10	8	30
1979	5	6	14	12	35
1978	4	3	7	13	27
1977	3	9	6	8	26
1976	2	5	5	7	19
					Total 213

A problem associated with attempting to recheck and reclean over two hundred spill sites in a rapid fashion is the number of times recleaning is necessary. Generally two cleanups were sufficient on old sites, that is, one beyond the original visible trace cleanup when the spill occurred (Table 2). Almost sixty percent were adequately cleaned even for eight year old spills. This is not unexpected as PCB migration is usually slow depending on soil type. One excavation was not sufficient in porous soils or industrial areas where background levels would be elevated due to non-Company activities. An additional spot excavation and cleanup resulted in 81 percent of the sites meeting the operating standard. In some cases as much as seven excavations were necessary, for example, in an industrial site at an old junkyard, the excavation went down about 3m and extended about 25m in each direction. It was obvious in that case that other sources of PCB material were also being removed. Usually soil removals beyond the second excavation concentrated on one or two small areas or "hot spots". This strategy was therefore successful in meeting the goals of being effective with short term customer disruption. The time period from initial excavation through completion for 85 percent of the sites was less than one month.

TABLE 2

Number of Soil Excavations at PCB Capacitor Spill Sites Necessary to Meet Company PCB Criteria

Spill Year	Number 1	2	3	4	>4	Total
1984	2	5	0	1	0	8
1983	6	9	9	1	3	28
1982	2	8	1	3	0	14
1981	3	14	3	6	0	26
1980	3	18	6	1	2	30
1979	2	15	11	5	2	35
1978	2	12	7	3	3	27
1977	3	13	4	5	1	26
1976	2	6	6	4	1	19

Managing a PCB Fire Decontamination

by Chris Kwoka

SOS Environmental Engineering

A successful philosophy for decontaminating a building contaminated by a PCB transformer fire involves general knowledge of: 1.) the type of incident, 2.) how the contamination spread, 3.) unit operational tasks governing the clean-up.

The first two elements are quickly ascertained. The type of transformer incident, generally either soot producing or pressure venting, can be visibly determined through a simple inspection. Though it is often difficult to explain how the contamination was spread throughout the building. The source of the contamination is easily identified by locating the transformer vault. The third element, unit operations, involves the individual tasks associated with the physical decontamination of the building. This presentation focuses on these unit operational tasks specifically, tasks directly associated with decontaminating a building interior, their priority, and how they relate to an actual decontamination we discussed.

The unit operations involved in decontaminating follow a logical pattern. It is the reverse of the transmission route of the contamination. The individual tasks according to priority are:

- Removal of gross contamination
- Control of the building interior air flow patterns
- Demolition and removal of contents that cannot be decontaminated
- Decontamination of the transformer vault
- Decontamination of the HVAC system including ductwork and air

handling units

- Decontamination of structural surfaces, ductwork and piping exterior surfaces
- Content decontamination and document restoration

There are additional support tasks not directly related with the actual decontamination such as supply administration, health and safety, and sampling and analysis that play an essential role. These support tasks will not be addressed here, as they will not be addressed in this paper. The first unit operational task is the removal of gross contamination. Standing oil or heavy soot deposits not removed during the emergency response phase should be isolated and contained as quickly as possible. This involves absorbing any oil spilled on the vault or adjacent rooms and placing the saturated absorbent or any heavy soot deposits into containers for disposal.

The second and most important operation is controlling the air flow patterns within the building. This is because significant redeposition of airborne contaminants can occur when the air within the building is not controlled. It was observed at the One Market Plaza incident that decontaminated surfaces could only be cleaned to a plateau level which was above the established criteria until the contaminated air flow patterns were controlled by evacuating air through an activated carbon exhaust system. Once the negative air system was in place, two noticeable results occurred - the levels of contamination in the air started to steadily decrease and surfaces could be successfully cleaned below the criteria without being recontaminated.

This philosophy was applied to the Santa Fe decontamination project at the very start of the decontamination work. Approximately 40,000 cfm of air was evacuated from the 700,00 ft^2 Santa Fe highway Department builidng through four separate vapo-phase activated carbon treatment systems, this provided approximately

three air changes per hour through the entire structure. To accomplish this, the building was divided into zones with barriers placed in strategic locations to enhance the control of the air flow patterns. Once the systems were operational, the PCB air levels within the building were reduced from 8 to 42 ug/m3 PCBs to <0.1 to 0.4 ug/m3 within about four weeks. Surface decontamination was achieved without redeposition or recontamination.

The third task is removal of building contents which cannot be cleaned, for example, porous surfaces such as drop ceiling tile absorb PCB and Dioxin/Furan contamination. These surfaces must be physically removed and discarded. Items which are not cost effective to decontaminate such as, note pads, pencils, staplers, pencil holders, desk calendars, etc. should also be removed.

The transformer vault must also be addressed. The surfaces in the transformer vault are the most contaminated because they are the closest to the source. Generally, the only successful way to decontaminate the vault is to remove the layer of material from the wall, ceiling and floor surfaces if they are porous, metal and non-porous surfaces can then be decontaminated by similar methods as described in decontaminating ductwork.

Next, the building heating, ventilating and air-conditioning system can be divided into separate tasks - cleaning the ductwork and cleaning the air handling units. If the ductwork is large enough to physically allow a technician to enter it, the decontamination process involves initially vacuuming the ductwork followed by a detergent washing and rinsing and a detailed final cleaning. This final cleaning involves using rags on a one-wipe-throw-away basis for cleaning metal surfaces.

For ductwork with dimensions too small for a technician to enter, another strategy for decontamination must be used. One method is to cut access holes about

every four feet - close enough together to allow a technician to clean all of the ductwork by hand. A second approach is to access the ductwork at strategic locations such as elbows, turning vanes and slide dampers and running foam plugs or "pigs" repeatedly through the ductwork until it is clean. The foam plugs are used for both washing and rinsing.

Once the interior of the ductwork is decontaminated, all of the exterior surfaces must be cleaned. Decontamination starts form the ceiling and proceeds downward with all surfaces wiped with detergent and thoroughly rinsed using clean rags with each rinse.

Contents and personal effects can be inventoried and decontaminated simultaneously with the structural decontamination. Hard case items such as desks and filing cabinets are decontaminated in a manner similar to structural surfaces. Office equipment, paper, documents, and miscellaneous desk items can be effectively deocntaminated using freon based technology.

The final unit operation is decontaminating the floors. Plastic that was initially laid is removed and the floors are cleaned according to their surface type.

In summary, past experience has shown that there are a series of unit operations involved in decontaminating the interior of a building. However, one of the most important aspects of decontaminating a builidng is the necessity to control eir flow petterns of contaminated air within the building. This can be done by evacuating air from the building from strategic locations and exhausting the air through a vapor-phase activated carbon treatment system. This philosophy has a twofold benefit. The negative air treatment system effectively decontaminates the air within the building and permits the systematic decontamination of surfaces within the building without the fear of recontaminating surfaces that have already been cleaned.

Expanded Abstract for PCB Seminar

MANAGING CLEANUP OF MAJOR PCB-CONTAMINATED SITES

Authors: Nicholas A. Speed, Denny S. Parker, William E. Clister

Sites contaminated by major discharges of polychlorinated biphenyls (PCB) are usually distinguished by the magnitude of investigation and cleanup efforts required and the nature of laws, regulations, and policies applicable to them. This paper, derived from our draft guidance manual as developed for EPRI in December 1984 for remedial action at such sites, provides an overview of PCB concerns and regulatory policies applicable to major PCB-contaminated sites. It also presents an approach for managing remedial actions necessary for their cleanup.

Few classes of chemicals are subject to the degree of regulation accorded PCBs. Because of the complexity of these regulations and the extent and nature of court review and interpretation, the regulatory policies and standards applicable to PCB cleanups are uncertain and variable. Establishing acceptable criteria and cleanup levels for a specific site may involve extensive work with several agencies (including the Environmental Protection Agency (EPA)), each with differing requirements. Successfully resolving the critical question of "How clean is clean enough?" for any given project site involves detailed consideration of site-specific conditions and can be both difficult and expensive.

Managing the correction activities at a major PCB-contaminated site is discussed by addressing remedial activities as three dynamic and interrelated phases:

1. Site Investigation and Problem Definition

2. Correction Planning for Problem Resolution

3. Implementation and Verification of Corrective Work

Site investigation is a dynamic process since new information, generated as the work progresses, often alters the initial assessments which were based on earlier data. Site investigation begins with problem identification based on existing and available information and moves progressively toward problem definition. This work progression should often be stayed to ensure adequacy of the information base while minimizing overall project costs.

When the site problems and site conditions have been adequately defined, decisions must be made about the specific measures to be applied to problem resolution. Numerous options can be considered for technical application depending on the nature of the contamination problems and the objectives and requirements of the PCB cleanup. Screening of applicable measures occurs as the understanding of the problem progresses.

The screening and evaluation of alternatives for correction of specific problems and the selection of corrective measures to be implemented on a specific site involve decisions which are critical to project success. The basic criterion for selection in accordance with current EPA and judicial interpretations of the Toxic Substances Control Act (TSCA) is the achievement of the lowest level of cleanup practicably attainable through the normal use of available technology. In accordance with this criterion, the selected plan will represent a balancing of numerous costs and benefits.

After selection of a plan which the user determines to represent "best-practicable" correction of his PCB contamination problem, the plan can then be developed in a format suitable for submission to the regulatory agency(s) as the

user's Recommended Plan of Corrections for the site. This Plan is a proposal which should effect the following actions:

1. Summarize relevant site information.
2. Define existing PCB problems and site conditions.
3. Evaluate alternatives for resolving existing PCB problems.
4. Define recommended corrective actions and their impact.
5. Provide a preliminary plan for implementation.
6. Solicit regulatory agency acceptance of the Plan.

In general, the user's Plan should not depend on reference to other reports. Since the main objective of this Plan is obtaining regulatory concurrence with the user's proposed actions, all information critical to decisions by agency personnel should be included in summary form or appended.

Submission of the user's recommended plan to involved regulatory agencies can be considered the start of the implementation phase. Acceptance of the corrective action plan by the lead agency, as well as all other agencies having significant regulatory involvement in the project, is an essential milestone which must be achieved prior to any planned remedial work on the site. With few exceptions, regulatory acceptance of the correction plan will be limited to "agreement-in-principal" and conditioned upon actual achievement of stated cleanup or correction objectives, which can be demonstrated by verification sampling and monitoring both during and following site remedial work. Consequently, all project risks remain with the user and must be mitigated by careful completion of implementation planning, close management of construction work, and verification of results.

Plan finalization in preparation for construction involves completion of several elements outlined in the Recommended Plan of Corrections:

1. Confirmation of chosen contracting strategies.
2. Development of contract documents for contracted work.
3. Identification and prequalification of potential contractors.
4. Obtaining necessary permits and approvals.

Because of the inherent complexity of major site contamination problems and the usually similar complexity of the corrective measures applied to their resolution, careful management of construction activities is crucial to successful project completion. The user retains general authority over the work and must commit appropriately qualified and designated personnel to ensure that the construction work is completed by the contractor in accordance with contractual requirements.

Verification of the effectiveness of implemented corrective actions may represent the end of major construction activity on a site, but it may also extend long into the future. Where long-term monitoring is involved, successful completion of the cleanup project may be judged over a period of time in terms of quarterly or more frequent data with these data being used to interpret the degree of success of the corrective actions.

PCB CAPACITOR FIRE AT IREQ'S HIGH VOLTAGE LABORATORY AND SUBSEQUENT DECONTAMINATION

D. Train, A. Chamberland, D. Dupont, J. Castonguay

INTRODUCTION

On November 20, 1984 a large power transformer was being tested inside the Annex of IREQ's High Voltage Laboratory. Part of the test circuit consisted of a capacitor bank which was located on an upper floor inside the building. During the tests, an explosion occurred in the capacitor bank. This initial explosion started a fire and further explosions at fairly regular intervals within the capacitor bank. The fire burned for about six hours before it was eventually extinguished, but not before it had destroyed two thirds of the capacitor bank and caused some damage to the laboratory roof and part of the building structure. For the first two hours the smoke, which was very black and dense, was contained within the building but after that it escaped to the outside by means of a hole which had burned through the roof.

The capacitor bank comprised both mineral oil and askarel insulated units. The estimated volumes of oil and askarel which were burned were 2560 L and 670 L respectively.

The day after the fire, an inspection of the interior of the building showed that a fine deposit of soot had settled throughout in a nonuniform fashion. Typical analyses of soot samples indicated approximately 2500 µg/g of PCB-1242, 0.6 µg/g of 2,3,7,8 TCDF and 0.1 µg/g of total TCDD. Water samples from the basement were also analyzed and the maximum concentration of PCBs found was 1250 ppb of arocior 1242. Owing to the levels of PCDFs found, the building, representing a total volume of 500,000 m^3, and its contents were considered too contaminated to permit an immediate return to normal operation. A major clean-up, repair and de-contamination program was organized in order to resume normal activities in the shortest possible time.

CLEAN-UP AND REPAIR ORGANIZATION

Since no previous experience of building contamination on this scale existed anywhere in Canada, a clean-up and repair organization was established by drawing upon the expertise which already existed in Hydro-Québec in the field of nuclear generating station construction. A mandate for the management and execution of the

repair work and decontamination of the building and contents was given to the Engineering and Construction department of Hydro-Québec. The responsibilities of this group included: preparation of detailed work schedules and cost estimates; engagement and co-ordination of activities of the various contractors; control of costs, time and materials; engineering and quality control including the measurements of contamination levels; establishing and supervising of safety practices; overall supervision and inspection of all aspects of the work; and disposal of contaminated materials.

A Coordinating Committee was also set up with the following responsibilities: determination of priorities for the repair and decontamination work; establishment of suitable acceptance criteria for the contamination levels of surfaces and air; negotiations with unions, environmental agencies and governmental safety and health authorities; communications with the media (press, television, etc.); establishing of medical examinations and periodic checks for the clean-up crew. This Committee worked in close liaison with the Engineering and Construction team.

An Evaluation Committee was created to follow the progress of decontamination by means of regular checks and interpretation of the results of the analyses with, when necessary, recommendations concerning acceptance or rejection. Stringent sampling procedures having detection limits 10 times lower than the acceptance criteria were set up. The sampling and subsequent analyses were performed by an independent laboratory, thereby avoiding conflicts with unions, environmental agencies and governmental safety and health organisations.

Both the Construction group and the Evaluation Committee reported to the Coordinating Committee. There were regular meetings with the representatives of the unions involved to inform them of the nature of the contamination, the medical aspects, the precautions required, etc. and all communications with the media were channelled through only one person. The human and public relations aspects of the operation were considered to be of prime importance and contributed significantly to the efficient progress of the entire project.

ACCEPTANCE CRITERIA

The acceptance criteria for re-entry to the building are similar to those developed by Kim and Hawley [1]. They are based on a maximum daily intake of 2 pg/ kg-day of 2,3,7,8 TCDD or equivalent and are 10 pg/m^3 and 25 ng/m^2 for air and surface contaminations respectively. In practice, both air and surface contamination levels were measured and evaluated graphically. If the points plotted lay within

the combined acceptance limits, re-entry without protective clothing was permitted; otherwise, further decontamination was required.

The so-called "dioxin equivalent" level was established as follows:

Dioxin equivalent= (CDDs) + (CDFs) + (CPBs)
where: CDDs = (2,3,7,8 - TCDD) + (total PeCDD)/5
CDFs = (total (TCDF + PeCDF + HeCDF)/10
CBPs = (2,3,6,7 - TCBP) + (total PeCBP)/2

During the intermediate cleaning stages the dioxin equivalent level on surfaces was evaluated approximately by measuring the level of PCB 1242 and dividing by the ratio R defined as

$$R = \frac{\text{PCB 1242 concentration on surfaces}}{\text{dioxin equivalent concentration}}$$

and a value of R = 1000 was determined from the many measurements made on soot samples.

MEDICAL CONSIDERATIONS

Medical protocols were established to evaluate clinical manifestations of toxicity to PCBs and furans of personnel who either were exposed to smoke during the fire or participated in the decontamination afterwards. These protocols consisted of the determination of any previous exposure to PCBs and the extent of exposure during the fire, updating of personal clinical history and complete individual medical examination, including biological tests comprising complete blood count, liver function, cholesterol, triglycerides, blood, plasma protein electrophoresis and PCB plasma tests. No significant health problems have been attributed to workers or members of the clean-up crew exposed to PCBs and/or furans.

METHODS OF CLEANING AND DECONTAMINATION

Various cleaning methods were employed to decontaminate the building and the thousands of components and pieces of equipment. Some of the methods were: high-capacity vacuum cleaners for the soot, solvent applied with compressed air nozzle and rinsed with water, solvent alone on some electric panels, use of Freon TF for electronic instruments and documents, and removal of surface layers of porous materials such as fibreglass, gravel, etc. The effectiveness of the different techniques is indicated in Table I.

TABLE I

Contamination levels before and after cleaning
for various decontamination techniques

TECHNIQUE	PCB 1242 CONTAMINATION LEVEL	
	Before cleaning	After cleaning
Vacuum	54.0 µg/m²	3.70 µg/m²
	230.0 "	37.00 "
	160.0 "	68.00 "
	375.0 "	39.00 "
High-pressure water jet	6.0 "	
	12 x 10.0^6 "	33.00 "
	108.0 "	0.03 "
Low-pressure water jet plus solvent	37.0 "	4.40 "
	56.0 "	7.90 "
Hand wipe with cloth plus solvent	68.0 "	8.70 "
Freon TF	129.0 "	1.50 "
Layer removal (fibreglass)	9.5 µg/g	1.60 µg/g
	15.5 "	2.00 "

Items of protective clothing such as hats, masks, gloves, boots, etc. were decontaminated at the end of each shift and re-used. The cyclohexane used for this work was purified by distillation and re-cycled. All water used for cleaning was filtered and purified prior to disposal. Solvents in the water were recuperated by distillation.

WASTE DISPOSAL

All contaminated residues collected from filters and distillation systems were stored in sealed drums. Other contaminated materials were also stored in sealed drums which were then sent to a special storage site to await eventual destruction when such facilities become available in Québec.

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GUIDELINES AND ALTERNATIVES FOR PCB SOIL-SAMPLING PROGRAMS

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INTRODUCTION

During the past several years, there has been growing concern among utilities and other PCB users about the quantity of sampling that is necessary for proper management of spills onto soils. This concern was generated, in part, by closer scrutiny by regulatory agencies, the tightening of cleanup requirements, and the high cost of sample collection and testing. For small spills onto soil from single pieces of equipment, utility representatives have recommended a performance-based cleanup standard(1). This approach encourages rapid response and eliminates the need to wait for sample analytical results (sometimes as long as 3 or 4 days). However, for larger, more complex spill episodes, soil sampling, as demonstrated by industry practice, remains a significant part of the response effort. Examples of sampling include old storage areas, spills to watercourses, and transformer salvage sites. Utility concern for these types of sites is focused on the extent and intensity (and hence cost) of sample coverage, the sampling design (i.e., grid versus random grab samples), sampling methods and depth, and pre-cleanup versus post-cleanup (confirmation) sampling.

The purpose of this paper is to provide guidance to the utility representatives faced with the more complex cleanup situation. As a consultant to a group of public and private utilities involved in a voluntary cleanup, Tetra Tech, Inc., recently completed a remedial investigation and feasibility study at a transformer salvage yard in the Pacific Northwest, as called for by the utility group's consent agreement with the U.S. Environmental Protection Agency. This paper is based on the experience gained during that effort and should be useful to others who desire to retain technical and budgetary control over the management of larger spills.

Why Sample?

The most obvious reason for sampling is to determine the extent of contamination, thereby defining the general dimensions of the problem (area and depth) and permitting the proper location of barricades, fences, or other delimiters. Depending on the specific situation, discharge into storm sewers, drains, or watercourses may

need to be determined. For larger spills, sampling is valuable in defining the volume of soil that must be ultimately treated or removed. In certain instances, sampling may also be useful in identifying contaminants that may have been contributed by other sources or site users.

DEFINING THE PROGRAM'S OBJECTIVES

In addition to defining the extent of contamination, a sampling program may also include these objectives:

- Detection of related contaminants (dioxins/furans and askarel carrier solvents) if the case warrants
- Identification of "hot spots" (smaller areas of high concentration in the site's interior) requiring immediate attention or special removal/disposal procedures.

DESIGNING THE PROGRAM

The proper design of the sampling program is critical to its success and usefulness of its results over the duration of the cleanup effort. Each plan should be site-specific, and may also be influenced by regulatory agency concerns. Although the general objective is to design a program that is sufficiently representative of the site, actual experience has shown that budgetary limitations will often be a controlling factor. A typical procedure is as follows:

- Estimate the limits (area) of the site through inspection and accounts of spills and past operations
- Select a sampling technique, or combination thereof (i.e., rectangular grid, triangular grid(2), or grab sample) including sampling at depth, if necessary
- For stations on a grid system, select a "starting point" grid size and calculate the number of samples for surface soil sampling as follows:

--rectangular grid: $$N = \frac{\text{Total Area } (ft^2)}{S^2\ (ft^2)}$$

--triangular grid: $$N = 2\sqrt{3} \times \frac{\text{Total Area } (ft^2)}{T^2\ (ft^2)}$$

where: S = Distance between stations for rectangular grid
T = Distance between stations for triangular grid.

A program cost-estimate can then be developed based on a daily "production" rate and unit costs for labor, supplies, and sample analysis. An additional percentage may also be calculated for program management costs. For a two-person crew (one

sampling, one receiving and recording) surface-soil sampling daily production rates of 50-70 samples are typical. The cost of supplies should take into account the rigid requirements for equipment cleanliness, decontamination, and personnel protection.

If there is reason to suspect penetration by PCBs, sampling for PCBs at depth should be carried out. Usually, PCBs do not infiltrate any significant distance into soils, particularly if the soils have a high organic matter or clay content. At the case-study site, penetration was caused by regrading of contaminated surface soils (for erosion control) and by chronic spills of PCB fluids directly onto the soil under a storage tank valve. Air-driven split-spoon samplers proved extremely efficient for soil sampling up to a depth of 4-10 ft. A useful technique was to archive (store) the deeper samples and analyze them only when the shallower samples showed elevated PCB concentrations.

Sample Testing

Hand-in-hand with rigid quality control requirements for sampling is the need for careful analysis. When dealing with a commercial laboratory, one must accurately communicate the desired analytical technique (total PCBs or specific isomers), the necessary detection limits, and quality assurance measures (duplicate analysis, blanks, spikes). Guidelines regarding these measures have been developed by Tetra Tech(3).

Data Evaluation

Upon receiving results from the laboratory, each value should be checked to be sure it was reported at the specified degree of accuracy. Extraneous or unrealistic results should be noted and checked against site conditions and visible characteristics of the sample. Results of analyses for test standards (samples of known PCB concentration used for calibration), duplicates, blanks, and other quality-assurance samples should be assessed to determine the overall quality of the analytical effort.

Program Costs

The preparation of the feasibility study for cleanup of the salvage yard site highlighted the trade-off between sampling program costs and the actual cost of soil removal. For this large site, a rectangular grid system of surface soil sampling and subsurface borings was established with 35-ft spacing between stations. Because contaminants were discharged throughout the area and further mixed in by constant regrading, it was assumed that the result of each sample was representative of the contaminant level within the entire grid. Therefore, the goal was to structure

a grid system that minimized the required sampling/testing costs, and at the same time condemned the smallest amount of uncontaminated soil within each grid.

Within practical limits, the soil excavation process may proceed on a grid-by-grid basis. The lower grid-size limit is defined by the width of a bulldozer blade (approximately 12 ft). Assuming an upper limit of approximately 50 ft, an analysis of sampling coverage (and program costs) can be compared to the resulting amount of soil that must be removed. For the case-study site, one major goal was to accurately define the edge of contamination. The ability of a grid network to do this was based on the distance between stations and the entire area involved. For perimeter stations, this edge may lie immediately beyond the outer station showing elevated concentrations, or it may extend beyond the station's grid. In the former case, almost half the grid will be uncontaminated, yet still be condemned. This potential "worst-case" extra soil removal is converted into a cost and compared to the costs of alternate grid size programs. The calculation for an idealized (square) site using a rectangular grid system is as follows:

$$\text{sampling costs} = \$/\text{sample} \times \frac{A}{S^2}$$

versus

$$\text{perimeter soil excavation and disposal costs} = \$/\text{yd}^3 \times 0.074 \times S \times \sqrt{A} \times P$$

where:

A = site area (ft^2)
S = distance between stations (ft)
P = assumed removal depth (ft)

Tetra Tech is continuing to evaluate these cost relationships for actual sites as part of its hazardous material management services. Since sampling at the case-study site, Tetra Tech has completed a cleanup feasibility study and design drawings/specifications for site work.

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3. Tetra Tech, Inc. Quality Assurance and Quality Control Guidance for 301(h) Monitoring Programs (Draft). Prepared for U.S. EPA, Washington, DC. April, 1985.

VERIFICATION OF PCB SPILL CLEANUP BY SAMPLING AND ANALYSIS

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The U.S. Environmental Protection Agency (EPA) under the authority of the Toxic Substance Control Act (TSCA) Section 6(e) and 40 CFR Section 761.6U(d), has determined that polychlorinated biphenyls (PCB) spills must be controlled and cleaned up whenever the spill incident poses a substantial risk to human health or the environment. The Office of Toxic Substances (OTS) was requested by the Office of Compliance Monitoring (OCM) to provide written guidelines for a method to verify the cleanup of PCB spills. Emphasis was placed on the sampling design and sampling and analysis methods to be used for the verification of the spill cleanup. Three reports have been prepared. The first consists of a review and technical evaluation of the available documentation on PCB spill cleanup. Contacts were made with EPA regional offices and industry experts. This first document included the preparation of preliminary guidelines for the cleanup of PCB spills. The document was aimed at providing guidance in all aspects of spill cleanup for those organizations which do not already have working PCB spill cleanup programs.

The second report, intended primarily for EPA enforcement personnel, outlines a specific sampling design. It also makes recommendations for sampling and analysis methods to be used to determine compliance with EPA policy on the cleanup of PCB spills. The sampling and analysis methods can be used to determine the residual levels of PCBs at a spill site following the completion of cleanup activities.

Although the methodologies outlined in this document are applicable to PCB spills in general, specific indicents may require special efforts beyond the scope of this report. Future changes in EPA policy may affect some of the information presented in this document.

The third report is a field manual which provides detailed, step-by-step instructions on how to complete the field sampling for cleanup verification. This manual addresses field sampling only, and does not provide information on laboratory procedures. The types of field sampling situations covered in this manual are those typically found when a PCB spill results from a capacitor or transformer spill.

The EPA has established requirements for the spilled PCBs and materials contaminated by the spill. Under TSCA regulations [40 CFR 761.60d], PCB spills are viewed as improper disposal of PCBs. Although specific PCB cleanup requirements are not yet established in the TSCA regulations, each regional administrator is given authority by policy to enforce the adequate cleanup of PCB spills to protect human health and the environment.

Due to regional variations in PCB spill policy and the present lack of a national PCB cleanup policy, PCB cleanup activities have not been standardized. Individual companies owning PCB equipment and contract cleanup companies have developed their own procedures and policies for PCB cleanup activities keyed to satisfying the requirements of the appropriate EPA Regional Office. In addition, the EPA Regional Offices typically have provided suggestions for companies unfamiliar with PCB cleanup.

PCB spills are generally viewed as unique situations to be evaluated on a case-by-case basis by both the PCB equipment owner (or his cleanup contractor) and the EPA Regional Office. However, a general framework is often used to approach the problem. Most cleanup activities involve quick response, removal, and cleaning, of suspected contaminated material, and post-cleanup sampling to document adequate cleanup. Major considerations involved in the cleanup process include minimizing environmental dispersion, minimizing any present or future human exposure to PCBs, protecting the health and safety of the cleanup crew, and properly disposing contaminated materials.

A sampling design is proposed for use by EPA enforcement staff in detecting residual PCB contamination above an allowable limit after cleanup of a spill site is completed. The proposed design involves sampling on a hexagonal grid centered on the cleanup area and extending just beyond its boundaries. Guidance is

provided in the field Manual for centering the design on the spill site and for staking out the sampling locations, taking possible obstacles into account.

Compositing strategies in which several samples are pooled and analyzed together, are recommended for each of the proposed designs. Since an enforcement finding of noncompliance must be legally defensible, the sampling design emphasizes the control of the false positive rate, the probability of concluding that PCBs are present above the allowable limit when, in fact, they are not.

Sampling and analysis techniques are recommended for PCB-contaminated solids (soil, sediment, etc.), water, oils, surface wipes, and vegetation. A number of analytical methods are referenced; appropriate enforcement methods were selected based on reliability. Since GC/ECD is a highly reliable, widely used method, and is included in many standard methods, it is a primary recommended method for most spill situations. Secondary methods may be useful for confirmatory analyses or for special situations when the primary method is not applicable. Quality assurance (QA) must be applied throughout the entire monitoring program. Quality control (QC) measures and sample QC should be stipulated in the QA plan. They may include protocols, certification and performance checks, procedural QC, sample QC, and sample custody as appropriate.

The work was supported by the U.S. Environmental Protection Agency under Contract No. 68-02-3938 (to MRI) and subcontract to Battelle Columbus Laboratories, Subcontract No. F4138(8149)434, EPA Contract No. 68-01-6721.

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Risk Assessment Developments for PCB/PCDF Decontamination Projects

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Increased recognition of the spread of PCB's and PCDF's from transformer failures has resulted in industry and government attention to preventive measures as well as closer attention to decontamination efforts. Two critical questions which continue to surface after each of these failures which sometimes result in the spread of PCB's and sometimes PCDD's/PCDF's is the degree of exposure to individuals and the degree of contamination necessary to allow the facility to return to unrestricted use.

Two quantitive methods are now being used to help address these questions:

(1) Risk Assessment: To evaluate the degree of decontamination necessary for reoccupancy of a building or reuse of equipment. This technique can be used to generate "safe" reentry criteria. This technique has been used to set soil, air, water, surface reoccupancy guidelines by both State and Federal regulatory agencies as well as by several utilities and manufacturing corporations whom have developed site specific guideline proposals for government approval.

(2) Exposure Assessments: To quantatively evaluate potential exposures and resulting risk from people whom had opportunity for exposure to PCB's/PCDF's at the time of one of these events. This technique has been used to quantify the risk of individuals with "exposure" opportunity.

This paper will explore the most recent applications of these techniques and the state of the art in there use.

USEPA has issued generic proposed guidelines on the use of and format for both risk and exposure assessments (A), (B), (C). These guidelines are generic. Significant differences exit between assessments developed by various parties. For the purposes of discussion this paper will breakdown some of the critical assumptions made in the derivation of acceptable risk related to (PCB-PCDF potency and exposure). Today there is no scientific agreement as to what constitutes an acceptable non-effect level of exposure. Using the formula:

$P = g^{*} X$

g = potency

X = exposure

X has been determined to range from 2.0 pg/kg/day to 0.06 pg/kg/day. (see Table I).

EPA uses the 0.06 pg/kg/day 2,3,7,8- TCDD equivalents although several states have accepted 2.0 pg/kg/day.

(A) Federal Register Friday, November 23, 1984, Proposed Guideline for Carcinogen Risk Assessment.

(B) Federal Register Wednesday, January 9, 1985, Proposed Guideline for Health Risk Assessments of Chemical Mixtures.

(C) Endangerment Assessments for Superfund Enforcement Actions, Mogan et al. Support Branch Office of Waste Programs Enforcement, vs EPA 1984. Address request for information to WH-527, 401 M Street, SW, Washington, D.C. 20460.

There is also no agreement by regulatory agencies on the acceptance of risk, although EPA has accepted 1×10^{-5} risk in several risk and exposure assessments.

Toxicity Data: There has been very little change in the last 3 years - most scientist, do however, agree that 2,3,7,8- TCDD is most potent as evidenced by animal carcinogenicty testing, cell keratinization, and a enzyme inhibition bisassays. As the ring structure becomes increasingly saturated with cl atoms the acute toxicity appears to decrease. Likewise, the cl atom in the 2,3,7,8 positions appears to be a critical determinant in acute toxicities (C), (D). The exact mechanisms of acute 2,3,7,8 toxicity are still largely unknown. The dibenzofurans are considered to be significantly less toxic than the dioxins (0.1-0.33) x 2,3,7,8- TCDD.

The only two isomes of TCDD's that have undergone complete bisassay are 2,3,7,8-TCDD and two congeners of hexachlorinated dibenzo dioxins (1,2,3,6,7, and 1,2,3,7,8,9 HxCDD). These hexa isomers were on subsequent analysis found to be contaminated with 0.03% TCDD.

Inhalation Rates: In evaluating opportunity for exposures most risk and exposure assessments consider 23 m^3 of air per 24 hour day on the average. This number can however vary significantly with changes in
duration of exposure opportunity and with work practices.

Environmental Decomposition Factors: Photodegradation of 2,3,7,8- TCDD in areas of intense sunlight has been demonstrated to be significant (C). However, most risk assessments done to date place a half life from 5-10 years on PCB-PCDD-PCDF's found inside buildings or in areas on nondirect sunlight.

(C) R. J. Kociba et al - Comparative Toxicity and Biological Activity of Chlorinated Dibenzo-P-Dioxins and Chlorinated Dibenzo Furans Relative to 2,3,7,8- TCDD, Chemosphere Vol. 14, pp. 649-660 - 1985.

(D) Eve Roberts - The Ah Receptor and Dioxins Toxicity From Rodent to Human Tissues, Chemosphere Vol. 14, No. 6/7, pp. 661-674, 1985.

Table 1

ENVIRONMENTAL LEVELS OF TOTAL PCDD's/PCDF's

		Levels	Notes
(1)	Air		
	Inside	ND - 10,000+ pg/m^3	Inside building 30 days following PCB transformer failure.
	Outside	.09 - 1.3 fg/m^3	
	Water stream	1 ng/m^3 - 3 ug/m^3 (3)	After Silvex spraying (35 days).
	Incinerator Emissions	ND - 440 ng/m^3	
(2)	Water		
	Groundwater	Most studies report ND	
	Surface Runoff	0.05-0.06 ppt	42 days after Silvex application[1] (6)
(3)	Soil	(ND (<.1 ppb) - 1800+) ppb	
(4)	Surfaces	<.01 ng/m^2 - > 2000 ng/m^2	
(5)	Dust	See incinerator above	(Some buildings dust and others vapor phase contamination predominate)
(6)	Oils	PCB oils ND - 40 ppm (total PCDD/PCDF)[4]	
(7)	Plants	ND - 40 ppb[2]	Most studies shows no plants uptake from soils contaminated with low leve's of 2,3,7,8- TCDD (Possible Seveso exception)
(8)	Solid Waste Incinerator Feed Stock	ND - 440 ng/m^3 (totals PCDD/PCDF	

1. Ambient Water Quality Criteria for 2,3,7,8- TCDD - page C-2, USEPA 440/5-84-001
2. IBID #2
3. Rappe C. et al Formation of Polychlorinated Dioxins and Dibenzofuran in Municipal and Hazardous Waste Incinerators. Presented at the 103 seminar of FGU Berlisa, Dioxine.
4. IT sampling of PCB oils.
6. Kleopher R., 2,3,7,8- TCDD Contamination in Missouri, Chemosphere Vol 14, No. 6/7, pp. 739-744, 1985.
7. Tosine H.M., Levels of PCDD/PCDF and Other Chlorintated Organics in Municipal Refuse, Chemosphere Vol 14, No. 6/7, pp. 821-827, 1985.

Table 2

TISSUE LEVELS PCDD/PCDF's

	Levels	Notes
Cattle	4-40 ppt fat[1]	Cattle grazing on contaminated soils.
Bovine Milk	<40 ppt to 7.9 ppb	Seveso: Normal Silvex application rates did not result in any significant increase in milk 2,3,7,8-TCDD levels.
Human Milk	ND (<1) to 805 ppt 1	
Fish	ND - 695 ppt	(Significant variation depending on location caught).
Human Adipose Tissue	5-10 ppt Tetra Dioxins (5) (10) 600-800 ppt Octa Dioxin 17 ppt Penta Furans 17 ppt hexa 13 ppt hepta	
Mice Residing on 2,3,7,8 contaminated site		
(Soil (Surface TCDD) <20-1929 ppt)	- Sum TCDD <10-5237 ppt(9)	
(Soil (Subsurface TCDF) 1413-23,920 ppt)	- Sum TCDF ND - 13,809 ppt	

1. Water Quality Criteria Document.
2. Rappe C. Source of Identification, Especially With Respect to Dioxins and Dibenzofurans Found in the Emissions of Incinerators. Presented to Who Consultation on Organhalogen Compounds in Human Milk and Related Hazards. Belthaven, Netherlands 9-11, Januray 1985.
5. Ryan J., et al, Chlorinated Dibenzo-P-Dioxins and Chlorinated Dibenzo Furans in Canadian Adipose Tissue Chemosphere Vol 14, No. 6/7, pp. 697-706, 1985.
9. Herda H., TCDD and Chlorinated Dibenzofuran in Top Soil and Biological Samples From a Contaminated Refuse Pump, Chemosphere Vol 14, No. 6/7, pp. 919-924, 1985.
10. Similar results have been obtained by Graham et al, Background Human Exposure to 2,3,7,8- TCDD, Chemosphere Vol 14 No. 6/7, pp. 925-928, 1985, and,
Ryan John, et al, Tissue Distribution of Dioxins and Furans in Humans From the General Population, Chromosphere Vol 14, No. 6/7, pp. 929-932, 1985.

Table 3

NOEL'S USED IN RISK AND EXPOSURE ASSESSMENTS

USEPA	.06 pg/kg/day
State of Calif. Health Dept.	2 pg/kg
State of Calif. Air Resource Department	.06 pg/kg/day
New York State	2 pg/kg
State of New Mexico	.06 pg/kg/day
Canada	10 pg/kg/day
Netherlands	4 pg/kg/day
CDC	.028-1.40 ng/kg/day

GUIDELINES

Used In Various Environmental Exposure Settings for PCDD/PCDF

Fish		
	New York Health Dept.	10 ppt
	Ontario	20 ppt
	FDA	25 ppt
Soil	1 ppb - CDC	
Air		10 pg/m^3 NYS Indoors (8 hrs exp.)
		10 pg/m^3 Calif. Indoors (8 hrs exp.
		- ? - Ambient air (24 hrs exp.)
		3-28 ng/m^2 - Inside Buildings
Water		
	Michigan/outfall to river	10 pp quadrillion
	USEPA	2 part per quintrillion

Decont. Effort		Standard Accepted for Decontamination		Dose basis of Standard Development Risk Assessment
		Surface	Air	
Binghamton	PCDD/PCDF	3.3-28 ng/m^2	10 pg/m^3	2 pg/kg
	PCB's	1.0 ug/100 cm^2	1.0 ug/m^3	
San Francisco	PCDD/PCDF	3 ng/m^2 10 pg/m^3 (above backgrougd)		2 pg/kg
	PCB	1.0 u/100 cm^3	1.0 ug/m^3	
Columbus, OH	PCDD/PCDF	20 ng/m^2 *	10 pg/m^3	2 pg/kg
	PCB	1.0 ug/100cm^2	1.0 ug/m^3	
Santa Fe	PCDD/PCDF	1.0 ng/m^2	-	.06 pg/kg
	PCB	1.0 ug/100cm^2	1.0 ug/m^3	
Tulsa, OK	PCDD/PCDF	3.3-28 ng/m^2	10 pg/m^3	2 pg/kg
	PCB	1.0 ug/100cm^2	1.0 ug.m^3	

* High Contact Surfaces

Conclusions:

Development of site specific risk and exposure assessments can be expensive but the cost is decreasing as these techniques become more routine. The commonly made assumptions for such assessments are becoming more standardized, yet considerable variations still occur in the potency factors applied to individual congeners of PCDD's/PCDF's. Likewise, significant variations exists as to the potency of 2,3,7,8- TCDD (0.06 - 2.0 pg/kg/day) as acceptable intake levels.

Increased reliance is being made of the exiting risk assessment documents and the resulting standards that have been developed. Thus, future risk assessment for PCB's, PCDD's, and PCDF's likely be on hold until further toxicological evidence is developed. Advances in such risk assessment methods will likely be done as the result of critiques of the existing risk assessments.

Site specific exposure assessments, however, are powerful tools to be used to modify existing guidelines or to document quantatively evaluate risk of persons either occupationally or incidentally exposed to PCB's, PCDF, PCDD's.

A SYSTEMATIC APPROACH TO PCB CAPACITOR SPILL CLEANUP COMPLIANCE SAMPLING

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As the requirements for the cleanup of PCB fluid releases from pole-mounted capacitors have become increasingly more stringent, the need for a field sampling protocol accurate enough to demonstrate compliance with those cleanup requirements has become apparent. Regardless of the cleanup standards applied, a systematic, reproducible sampling approach which characterizes PCB levels across a spill site is the Utility's industry's best defense against possible future civil or regulatory action.

With at one time over 40,000 PCB capacitors in service, the Commonwealth Edison Company has been long familiar with PCB releases and accompanying mitigating actions. By late 1983, with increasing regulatory attention and public concern being focused on PCB spill cleanup, the need for a more accurate, reproducible method to demonstrate cleanup compliance became apparent. Thus, an effort was made to determine how to structure a PCB spill site sampling protocol to accomplish the following goals:

1. Obtain data on PCB dispersal from release events to facilitate response/cleanup activities.

2. Accurately characterize PCB levels remaining at a cleaned spill site.

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3. Provide evidence to rigorously demonstrate that a spill site has been adequately cleaned and is in compliance with appropriate cleanup standards.

The development of this protocol began with study of a data set of more than 350 soil samples collected from PCB capacitor spill events. When this data set was plotted to show PCB concentration in each sample vs. the distance of each sample collection point from the source of the release, it was obvious that PCBs were being randomly dispersed farther, and in greater concentration, than had been previously thought. Identification of soil PCB levels in excess of 100 ppm at distances over 75 feet from the source pole were not uncommon even though lower levels were measured nearer to the pole. The inadequacy of our previous low-level sampling protocol was very apparent, as was the fact that PCB dispersion could not be predicted with a high degree of certainty. The only course of action appeared to be to increase greatly both the amount of sampling and the area sampled at each spill site. The same data set was then used to develop information predicting the probability of encountering PCB concentrations of a given level at varying distances from the capacitor pole. It was hoped that such information would allow us to develop a field sampling program of appropriate intensity to ensure that an adequate cleanup would be conducted across the entire site. This probability distribution was then employed to generate a diagram depicting the distribution of discreet droplets of PCB fluid (>50 ppm) from 0 to 42 feet away from a utility pole release point. Grid sampling systems (centered on the utility pole on which the failed capacitor hung) with various spacing between sample points were then superimposed over the distribution diagram. Using this approach, it was determined that a sampling system in which samples are located 5 ft. apart could be used to adequately characterize PCB levels in lightly contaminated areas some distance from the utility pole (ie., where the PCB fluid droplets are widely scattered) as well as in those more heavily contaminated areas nearer the utility pole. Field trials of this approach have shown it to be effective.

When this grid system is deployed at a capacitor spill site, additional samples are collected from obviously-impacted areas or structures that do not fall onto the grid system, and from places where PCBs are likely to accumulate, such as cracks in pavement. Sampling is conducted such that the grid will encompass all areas of known contamination (defined by visible traces), and at least five feet beyond that area on all sides. When samples are being collected to confirm the effectiveness of a cleaning attempt, samples are collected at five-foot intervals within the cleaned area and at least five feet beyond the boundary of this area.

At each soil sampling point, soil is collected over an approximately 12-inch-by-12-inch area to a depth of about one-eighth inch. Vegetation samples are collected at each grid point over a 1 square-foot area. For hard surfaces, wipe samples are collected using the same grid system.

An artifact of this sampling approach has been to increase the number of samples collected per sampling event (there are usually between two and four sampling events per spill event) to roughly one hundred. To date, the Commonwealth Edison Company has collected nearly 20,000 environmental samples using this grid system at approximately 75 individual spill incidents.

In summary, this sampling approach has as its foundation the concept that PCB dispersion, particularly at greater distances from the pole, is a non-predictable process. Only with multiple sample collection, and the characterization of the site through the interpretation of numerous PCB analyses, can the actual PCB contamination remaining be adequately characterized and appropriate remedial action steps be determined.

Multiple sample collection increases the probability that a given area of residual PCB contamination will be detected. It does not guarantee that subsequent sampling will not find additional, previously undetected contamination. What it does do is greatly reduce the probability that additional contamination will be found. This, short of actually sampling every square foot of site surface, is an optimal approach in terms of being cost-effective, risk-minimizing and field-practical.

COMMONWEALTH EDISON COMPANY'S PCB SPILL CLEANUP PROCEDURES

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Commonwealth Edison Company has had experience with the cleanup of over 150 PCB releases from electrical equipment. These range from minor capacitor leaks to large transformer spills associated with fire. Faced with the prospect of having to take complex remedial actions at PCB release events, Commonwealth Edison Company has developed cleanup procedures to meet the following corporate and environmental goals.

1. Prevent the spread of PCB contamination.
2. Notify affected customers and the public that a spill has occurred, and restrict their access to the affected area.
3. Notify and cooperate with all regulatory agencies in whose jurisdiction the release occurs.
4. Perform the actual physical PCB removal and site cleanup in as rapid and as an effective manner as possible.
5. Confirm the effectiveness of the cleanup through well-planned sampling and analysis.
6. Restore the site to its previous condition.
7. Accomplish the above objectives in a cost-effective manner.

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While every spill event is a unique experience, adherence to the procedures discussed here, and with the above goals firmly in mind, will provide effective remedial action with the least health risk and inconvenience to the public. The cleanup procedures described here are applicable to releases from all types of PCB-containing electrical equipment, but are principally used for pole-mounted capacitor and vault or pad-mounted transformer spills. These types of spills range from simple leaks to fault-produced energetic releases. Even minor capacitor leaks, if undiscovered for some length of time, can result in large areas of contamination because of wind, precipitation and tracking. Energetic releases, especially when accompanied by high winds, can easily affect areas in excess of 185 m^2 (2000 ft^2).

The types of materials affected by the spills ranges from soil and pavement to homes, autos and animals. Depending on the physical condition and the cost of an item, it may be more expeditious to remove and replace that item rather than to clean it. Additionally, certain items are better cleaned off-site rather than in place.

The successful execution of a cleanup is dependent on the accurate assessment of the affected area, the containment of the contamination to that area, the proper methodology for removal of that contamination from the area and, of course, sufficient sampling to determine whether the area has been adequately cleaned to ensure compliance with appropriate cleanup standards. In performing these steps there are not only technical constraints, but also non-technical regulatory, legal and public perception constraints which must be taken into consideration.

For the purposes of discussion, we may divide the cleanup effort into two parallel parts. One addresses the physical removal of the contamination; the other addresses the non-technical issues. Physical removal issues include how to secure the site, techniques for soil and sod removal, techniques to clean or remove hard surface materials, how to reduce PCB dispersion during the cleanup, how to package removed materials for ultimate disposal, personnel hygiene and how to restore the site. Non-technical issues includes dealing with regulatory agency personnel, with customers and with the public.

Since Commonwealth Edison's cleanup procedures have been implemented the number of cleaning attempts required to adequately clean a site have been reduced by approximately 25%. Furthermore, cleanup performance at massive PCB spills (i.e., affecting several properties) have been particularly improved.

To facilitate the training of cleanup crews in our approach to PCB spill response, we have produced a videotape presentation which shows how all the steps of the cleanup procedure are executed and which also presents some background as to why they are necessary. A similar videotape presentation for transformer spills is being prepared.

COMMONWEALTH EDISON COMPANY'S TRANSFORMER SPILL RESPONSE PREPAREDNESS

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Because of public sensitivity, even a minor spill from a PCB-filled transformer can develop into a serious situation if the fluid contaminates customer or public property. Although the Commonwealth Edison Company has procedures which minimize this potential, releases may occur which result in the spread of contamination beyond a vault, either through human error or as a result of an uncontrollable accident. Such a release may not present an imminent danger to life or health, but, if the response is mismanaged, the time and cost of cleanup will increase. Prolonged cleanups coupled with existing public concerns regarding PCBs will increase the anxiety of customers and regulatory agencies.

Consequently, the Commonwealth Edison Company has determined that it is necessary to maintain a trained team of Company personnel to:

1. Respond as quickly as possible once a PCB release has occurred.
2. Provide on-the-scene direction to Company personnel responsible for spill containment and cleanup.
3. Collect samples to verify cleanup success and compliance with cleanup standards.
4. Interface with customers, property owners and regulatory agency personnel.

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5. Provide follow up control and coordination of PCB release response activities.

6. Restore affected customer or public property to its original condition and use as rapidly as possible.

Because of the critical nature of PCB releases, the length of time required for emergency response team personnel to reach a spill site is an important concern. A response time of 1 hour after regular working hours and 20 minutes during regular hours is possible in the Chicago area. Response is initiated by local Division personnel who use a paging system to contact a Primary Response Person. The Primary Response Person will determine, based on available information, whether an emergency response is required. If it is, he will request to be put in direct contact with the person in charge at the actual release site and will make further inquiries. He will also issue preliminary directions over the phone for containing the release and restricting access to the site. He will then dispatch one or more Technical Response Specialists to take on-site control. The Primary Response Person remains at his phone and acts as a communication center for the first few hours of the response.

The response team is specifically designed to address incidents involving PCB releases and PCB equipment failures. Because of the specialized nature of these types of environmental emergencies, it is possible to train and equip response team personnel such that each team member can fully assess a release situation and sustain response activities until additional support becomes available. Such immediate, independent response capability aids greatly in achieving an effective, timely cleanup.

This type of rapid and direct response is possible because of two factors. First, and most important, is that the individuals are not only trained and experienced in response activities, but also have been selected for their personal qualities, skills and attitudes. All personnel selected for emergency response have obtained considerable experience in PCB spill response by starting as an assistant in the cleanup and sampling of PCB capacitor spills and have built upon that experience until they are judged capable of independently directing an emergency response. In addition, appropriate training courses are provided and drills are conducted to improve skill levels and to develop a response team "spirit". Proper attitudes are developed by encouraging and testing employee resourcefulness and initiative in all aspects of the work.

Second, the emergency response equipment, although simple, is selected, periodically reviewed, and revised for maximum efficiency. Each response team member has a set of protective clothing and sampling equipment kept at home. Additional protective clothing and sampling equipment is kept packaged in a central location accessible to all team members. A team of two can bring to any spill site sufficient equipment, including sampling supplies and protective clothing, to sustain emergency response support and sampling efforts for 36 hours and, if necessary, provide some equipment to cleanup crews. This allows immediate response without waiting for the supplies to be delivered from a central storage location.

Since spill cleanups are conducted in highly visible locations, it is critical that the work progress in a professional, organized and timely manner. Usually the customer's, as well as the public's, knowledge of PCBs is limited, and best, incomplete. Therefore, it is necessary to first place the customer's concerns in proper perspective. This is done by providing clear and complete information about PCBs, explaining the response and cleanup plan and, by conducting indoor air sampling for PCBs in any situation where a building may be involved.

After the initial response to a PCB release, the work of the response team is far from over. It is at this point that the "attrition" of a protracted cleanup period, often stretching a week or more, begins. During this period, the response team is faced with having to keep the cleanup effort moving along steadily on a 24 hour a day basis, while at the same time facing increasing outside pressures from the public and regulatory agencies. Communication and control become the dominant issues in this environment.

If properly handled, particularly during the early response stage, PCB transformer release events can be handled so that negative impacts to the affected Utility are minimized.

AN ANALYSIS OF PCB CAPACITOR SPILL CLEANUP EFFECTIVENESS

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In 1984, the Commonwealth Edison Company responded to approximately 50 small volume (ie., 1.9 to 11.4 L (0.5 to 3 gal.)) PCB releases from pole-mounted electrical capacitors. Over 12,000 samples of materials (eg., soil, vegetation, gravel) and wipe samples of hard surfaces (eg., concrete, asphalt, sheet metal) have been collected at these spill sites to determine both the outer boundaries of the area affected by the spill and whether an adequate cleanup had been conducted within the affected area. A detailed analysis of the data generated at 30 of these spill incidents has been conducted to evaluate: (1) the efficiency of the procedures employed to clean various types of affected materials at individual spill sites, (2) the size of the area affected by the PCB release (ie., anywhere detectable levels of PCBs could be measured), (3) average PCB concentrations in materials and on hard surfaces at various stages of the cleanup process and, (4) the amount of residual PCB remaining on the spill site at the time of site restoration. In addition, estimates of the overall efficiency of the cleanup program at each site were also made.

The results of this analysis are noteworthy for a number of reasons. First, the surface-scrubbing techniques and soil removal procedures developed by the

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Commonwealth Edison Company effectively remove PCBs from impacted areas in a timely manner. Secondly, it appears that even the most cursory initial cleanup of visibly impacted areas (the visibly impacted area is typically less than 50%, and often less than 10%, of the affected area) will remove more than 90% of the mass of PCBs released. Subsequent cleanup efforts usually attempt to remove less than 1 kg of residual PCB contamination. To remove a proportion of this residual large enough to ensure compliance with cleanup standards of less than 50 ppm, large areas have to be cleaned. The average size of the affected area at the spill sites considered was $132 m^2$; the majority of this area will have to be cleaned to ensure compliance. Two to four cleaning attempts are usually required to meet cleanup standards over the entire site.

The effectiveness (ie., the amount of PCBs removed per cleaning) of individual cleaning attempts consistently decreases throughout the cleaning program at a given site. This loss in effectiveness is due to the fact that one is attempting to remove increasingly smaller amounts of residual PCB from the site. Once compliance with the appropriate cleanup standards had been achieved, the estimated total PCB residual at these sites ranged between 0.2 and 16.0 g ($\bar{X}$ = 4.9 g). If one assumes that a typical capacitor failure releases 7.6 L (2 gal.) of PCB fluid weighing 10.5 kg, an overall cleanup efficiency of between 99.84 and 99.998% ($\bar{X}$ = 99.95%) has been achieved at the sites considered in this analysis.

PART 10:

MISCELLANEOUS

IN SITU VITRIFICATION OF PCB-CONTAMINATED SOILS

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In situ vitrification (ISV) is a patented process (1) developed at Pacific Northwest Laboratory for the U.S. Department of Energy as an in-place stabilization technique for radioactive contaminated soils. Recent large-scale operational tests have demonstrated the vitrification of 300 MT (6600 ft^3) per setting. In addition, the process is being evaluated for potential application to soils contaminated with hazardous wastes, such as polychlorinated biphenyls (PCBs). Building upon this technology, an engineering-scale in situ vitrification test with PCB-contaminated soil has been successfully performed for the Electric Power Research Institute (EPRI) to determine the fate of PCBs and their by-products when the process is applied.

PROCESS DESCRIPTION

The in situ vitrification process as applied to contaminated soil stabilization requires the insertion of four electrodes into soil in a square array. A path for electric current is established by using a small amount of a graphite and glass frit mixture placed between the electrodes on the soil surface. Dissipation of power through the starter material creates temperatures high enough to melt a layer of soil, which establishes a molten, conductive path. This molten zone continues to grow downward encompassing the contaminated soil. At the high temperatures (>1700°C) created, organic materials pyrolyze, diffuse to the surface, and combust. Any off gases from the process are collected, monitored, and treated. Remaining ash, along with other noncombustible materials, dissolve or become encapsulated in the molten soil. Natural convective currents within the molten soil help distribute the stabilized materials uniformly. The molten soil cools to a durable glass and crystalline form resembling natural obsidian.

TEST DESCRIPTION

Maintained under vacuum by a process off-gas system, the EPRI engineering-scale test was performed in a sealed metal container on a 20 cm (8 in.) diameter by 30 cm

(1 ft) deep zone of loamy-clay type soil containing 500 ppm PCBs (8 g of Arochlor 1260). The test utilized a 23 cm (9 in.) square electrode separation with cylindrical molybdenum electrodes extending to a depth of 61 cm (24 in.). The contaminated soil was centrally located between the electrodes beginning at the 25 cm (10 in.) depth. The test was performed over a 6-hr period, achieved a depth of 81 cm (32 in.), and produced a vitrified block of 220 kg and 0.14 m^3 (480 lb and 5 ft^3). No operational problems were encountered during the test, and on-line grab sampling for chlorine and hydrogen chloride revealed less than detectable quantities (<0.33 ppm and <0.2 ppm respectively). For safety and environmental control, a dual-stage activated carbon filter (see Figure 1) was used to contain any PCBs released to the off-gas system.

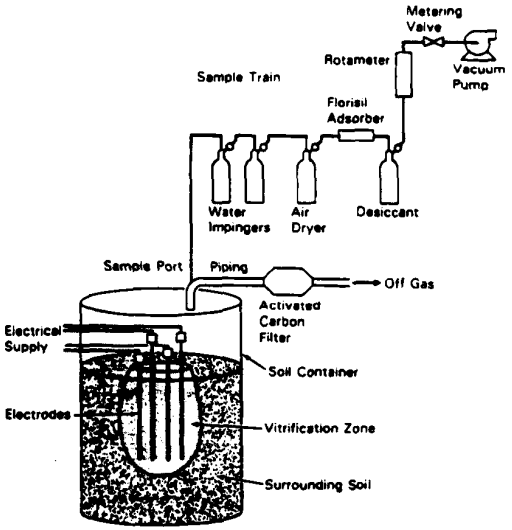

Figure 1. Engineering-Scale In Situ Vitrification System and Sample Locations

TEST RESULTS AND PERFORMANCE ANALYSIS

Samples collected to analyze ISV processing effects on PCB included: 1) off-gas emissions, 2) residues in off-gas lines and containment equipment, 3) migration to soil surrounding the block, and 4) residual level in the vitrified block. Data from off-gas release and soil container smears provided the most quantitative values on the release from the melt during and after processing. Information collected from the florisil adsorption tubes and the smear sample extractions (see Figure 1) indicated a 4.2 mg total off-gas emission, 1.1 mg of which was deposited on container surfaces. These off-gas releases account for 0.05 wt% of the initial PCB quantity, corresponding to a greater than 99.9% thermal destruction and removal efficiency (DRE) for the ISV process. Note: this does not include the removal efficiency of the off-gas system; therefore, a system DRE cannot be calculated from the available data. Activated carbon filters (2) can effectively contain any of these off-gas emissions.

The analysis of florisil also indicated a small amount furan (PCDF) and dioxin (PCDD) generated in total quantities of 0.4 μg and 0.1 μg respectively. The PCDF was detected only in the tetra and penta isomers, while the PCDD was detected only in the hepta and octa isomers. However, these small quantities are less than the reported amounts typically generated from a PCB fire (3) and do not represent a hazardous operational concern.

Sampling of the vitrified mass showed no detectable residual level of PCB, which is to be expected considering the high processing temperatures. Also, no PCB contamination was detected in the majority of soil surrounding the vitrified block, indicating that migration outside the vitrification zone was not a significant problem. A few samples directly adjacent to the block contained measurable concentrations up to 0.7 ppm, which is lower than 40 CFR 761 EPA requirements for cleanup. This initial test data indicates that the vitrification rate must be higher than the diffusion rate of volatilized PCBs in soil, thus overcoming migration away from the hot molten mass.

ECONOMIC ANALYSIS

The cost of using in situ vitrification as an in-place stabilization technique has been estimated (4). The cost estimate includes expenses from four categories: site preparation and closure activities, annual equipment charges, operational costs (labor), and consumable supplies including electrical power and molybdenum electrodes. Evaluations (4) established processing economics at between $150 to $330/$m^3$

($4 to $9/ft^3) depending on electrical power rates and soil moisture content. Soil moisture content increases the operating cost of the process by requiring more energy and time (labor) to vitrify a given volume of contaminated soil because the water in the soil must be evaporated.

CONCLUSIONS

The July 1985 in situ vitrification engineering-scale test illustrated the cleanup capabilities of ISV on soils contaminated with PCBs to meet current and anticipated EPA requirements. In addition, the test provided the following conclusions regarding performance of the in situ vitrification process:

- The small release of PCBs to the off-gas system (0.05%) can be effectively retained by appropriate design of a conventional treatment system, which utilizes a carbon filter or afterburner.
- Limited amounts of PCBs (0 to 0.7 ppm) were detected in the surrounding soil and none were found in the vitrified block, indicating that the vitrification rate is apparently greater than the PCB diffusion rate in loamy-clay soil and that migration away from the vitrification zone during processing may not be a significant concern.
- Processing of PCB-contaminated soil by in situ vitrification illustrated a processing destruction and removal efficiency of >99.9% for the process itself, exclusive of off-gas treatment.

Initial testing indicates the potential for in situ vitrification technology transfer from the nuclear to the hazardous waste arena as a potential remedial action technique. It is not a panacea, but the process holds promise for application at selected, contaminated soil sites.

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EPRI's WORK ON PCB HEALTH EFFECTS

Walter W. Weyzen

About two years ago, EPRI contracted with Clements Associates to conduct a study of occupational risks associated with exposures to PCBs. It was felt that, in view of the current uncertainties about the magnitude and nature of the hazards posed by PCBs, an objective, systematic, and technically sound assessment of occupational risk, based on available toxicological evaluation, should be made.

The study consists of three parts.

1. The collection and evaluation of toxicity information.
2. Characterization of the utility work environment, identification of potentially exposed populations, and magnitude of exposures.
3. Estimation of the health risks associated with exposures.

The first two parts of the study have now been completed. Completion of the third part is expected later this year.

Technical overview of the study is in the hands of a Scientific Advisory Committee consisting of experts in epidemiology, occupational health, industrial hygiene, toxicology and statistics, both from utilities and academia, chaired by Dr. Faeder of SCE. The results of the study will be available as a four part EPRI report in 1986.

In reviewing and evaluating the literature on PCBs, and chlorinated dioxins and dibenzofurans, approximately 3,000 titles and abstract were screened, and almost 1,600 titles were entered in the bibliography. For these, hard copies were obtained and the titles were evaluated for their relevance to risk assessment. From these, 82 papers were selected as the basis for 37 critical reviews that will form the basis for risk assessment. In addition to such factors as experimental design, significance of outcome, special attention was given to the reviews and assesment of

methods and materials used for the chemical analysis of mixtures to which humans were exposed or the materials used in animal toxicity studies. In addition, a method for weighing the results of epidemiological studies of human population was developed.

The second part of the study is an assessment of the extent, frequency, and magnitude of occupational exposure to PCBs and related chemicals in the electric utility industry. It includes a detailed review of the literature, the results of a questionnaire circulated to about 100 utilities, and site-visits and surveys of four representative utilities. Included are characterization of the PCB equipment past and present, streamflow of PCB within the utility, the workforce, and job categories with potential exposure. Sources of exposure, such as the repair and maintenance of equipment and cleanup of spills and leaks, and explosions and fires, were identified. Assessment of occupational exposures is based on the chemical composition of the fluids used, actual measurements of PCB levels in the workplaces, and measurement of PCB levels in blood or tissues of utility workers. All this information was in turn linked to the number of workers potentially exposed in each of the job categories, the frequence, magnitude and duration of exposure.

Initial findings of the study will be highlighted in the presentation.

HUMAN AND ENVIRONMENTAL BIODEGRADATION OF PCBs

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PCB PERSISTENCE: THE ETERNAL QUESTION

During the 1970's, public concern over the apparent environmental persistence of the PCBs, heightened by preliminary reports (later revised (1)) that they had produced severe human poisoning in Japan, contributed to a ban on their use in the U.S. and the initiation of remedial action projects designed to stop their further movement into the biosphere. Now, however, proposals for the excavation, transport, and reburial of PCBs are being increasingly questioned, both by local residents and national environmental organizations (2). At issue is the old question of persistence: will PCBs really remain in environmental deposits forever, or will they, like other organic chemicals, eventually biodegrade?

THE ASSESSMENT OF PERSISTENCE

Our procedures (3-5) for assessing PCB biodegradation exploit the fact that the commercially used PCB products (eg., Aroclors) are mixtures containing most of the 209 theoretically possible PCB congeners in fixed relative proportions. Each individual PCB congener differs in molecular size and shape from all the others, and hence also in its susceptibility to enzymatic attack. Each individual type of biodegradation will therefore alter the congener distribution, and hence gas chromatogram, of the Aroclor originally present in a characteristic manner. Thus, the pattern of chromatographic peak alteration can characterize the type of biotransformation that is occurring, and the degree of alteration its extent. The specific microorganism or metabolic enzyme that is responsible for an observed environmental transformation pattern may then be identified via laboratory studies with purified cultures or enzymes.

Thus far, significant degrees of biodegradation have been observed for PCBs in three very different components of aquatic ecosystems, namely, in higher animals, including man; in aerobic bacteria; and in anaerobic sediments. The three corresponding types of PCB biodegradation will be described in turn.

BIODEGRADATION AND PERSISTENCE IN MAN

In birds, mammals, and perhaps some lower animals as well, PCBs are handled like other fat-soluble xenobiotics: small amounts may be eliminated unchanged via the bile or lactation, but most elimination depends upon oxidation to more water-soluble forms. Such oxidations occur mainly in the liver, and are effected by mixed-function oxidase enzymes of the cytochrome P450 family. Rates of biodegradation vary considerably from species to species, as do also the ranges of PCB congeners that may be thereby eliminated.

Our studies of 1976-1983 clearance of PCBs from a population of heavily exposed capacitor workers (3) suggest that the individual PCB congeners may be divided into three groups as regards persistence in man: (a) non-persistent congeners, which did not accumulate; (b) moderately persistent species, which disappeared with half-times of 2-5 years; and highly persistent forms, which generally showed no significant decline. The non-persistent group was found to include virtually all congeners lacking 4-substitution on either ring, along with some of the lower 4,4'-disubstituted congeners. This group constituted 88-90% of Aroclors 1242-1016. The remaining, moderately persistent, components of such Aroclors consisted of certain 4,4'-disubstituted lower PCBs, such as the 2,4,4'-, 2,4,5,4'-, 2,4,5,2',4'-, 2,4,5,3',4', and 2,3,4,3',4'- congeners. The persistent group included all hexa-, hepta-, and octachloro's with 4,4'-substitution; such species constituted somewhat less than half of Aroclor 1254, but more than half of Aroclor 1260.

BIODEGRADATION AND PERSISTENCE IN AQUATIC ECOSYSTEMS

In aerobic aquatic ecosystems, and soils as well, most metabolism of organic matter is effected by aerobic bacteria. The complex microbial populations found in such environments include species capable of metabolizing every one of the many chemical constituents of the organic matter naturally present, and also many PCBs. To date, about two dozen pure strains of PCB-degrading bacteria have been isolated from soils and sediments and characterized as to type and range of PCB congener-degrading ability. Most of the strains belong to the 2,3-dioxygenase type (4,5); that is, they preferentially attack PCB species, such as the lower 4,4'-disubstituted congeners, which have adjacent unsubstituted carbon atoms at positions 2,3 (or 5,6) on the ring. Within this group, however, there is still a considerable range of activities, with some organisms attacking only mono- and dichlorinated PCBs and others attacking tetra's and some penta's. A few of the known strains, however, appear to belong to a 3,4-dioxygenase (4) or even monooxygenase type. These prefer to attack rings with unsubstituted 3,4- positions, but can also slowly attack 4,4'-disubstituted species, including 2,4,5,2',4',5'-hexachlorobiphenyl.

In the upper Hudson, where the reported "Aroclor 1016" level in fish has been dropping with a half-time of about 2 years, the residual PCB resembles that of Aroclor 1242 after biodegradation by 2,3-dioxygenase-type bacteria (5), which are readily isolated from the sediments. Evidently, this group of aerobes is playing a major role in PCB removal from that ecosystem.

BIODEGRADATION AND PERSISTENCE IN ANAEROBIC SEDIMENTS

In anaerobic aquatic ecosystems, metabolism of organic matter requires microbial fermentation rather than oxidation, and hence also the concommitant formation of reduction products, for example, nitrogen (from nitrates), sulfur (from sulfates), or methane (from CO_2). Recently, we discovered that PCBs could also be reduced (dechlorinated) in some anaerobic systems, notably the subsurface sediments of the upper Hudson River (5) and Silver Lake (Pittsfield, MA). At least six chromatographically distinguishable dechlorinating agents, probably corresponding to six different strains of locally prominent anaerobic bacteria, are present in the sediments examined thus far. Those present in the upper Hudson can remove most or all of the chlorines present on para (4-) positions of the biphenyl rings, and many of those in meta (3- or 5-) positions, but not those in ortho (2- or 6-) positions; their net effect has been to convert most of the Aroclor 1242 in 20-25 year old deposits to ortho-substituted mono- and dichlorobiphenyls. The Silver Lake dechlorination systems apparently remove ortho, meta, and para chlorines from the more heavily chlorinated PCB congeners rather indiscriminantly, with only a modest preference for 4-chlorine removal, but leave many tri- and tetrachlorobiphenyls unattacked. Their net effect has been to convert the Aroclor 1254 or 1260 deposits present to PCB congener mixtures having the average chlorine contents of Aroclor 1242 or 1248, but with very different congener distributions (eg, the most prominent trichlorobiphenyls are 2,5,3'- and 2,4,3'-, rather than 2,5,4'- and 2,4,4'-). It is noteworthy that the heavily chlorinated PCBs with 4,4'-disubstitution, a group which includes all the congeners found to be either persistent in man or toxic in experimental animals, are the ones most readily eliminated by dechlorination in anaerobic sediments. Thus, environmental dechlorination, while not eliminating the PCBs as legally-defined chlorinated biphenyls, can render them biodegradable in aerobic environments, and less persistent in birds, mammals, and man.

NEW ISSUES

Although PCBs are indeed undergoing both oxidative and reductive biodegradation at certain major spill sites, nature is not cooperating everywhere. A determination of whether the PCBs at any given site are biodegrading or persisting will require careful chromatographic analysis.

Selection of the appropriate response to an environmental site found to contain a biodegrading PCB may also require careful examination of the distribution of congeners present. Animal studies (6) have shown that only a few of the 209 possible PCB congeners exhibit significant toxicity. Ideally, it should be the projected levels of those suspect congeners, rather than the total level of all PCBs present, that determines the choice of response.

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COMPUTER AID FOR COMPLIANCE WITH THE RECORDKEEPING AND REPORTING REQUIREMENTS OF THE PCB REGULATIONS

Kent D. Hedrick*

INTRODUCTION

The body of information presented in this paper is directed to those individuals who are responsible for compliance with the recordkeeping and reporting requirements of the PCB regulations (40CR761). Compliance with these regulatory requirements has become more manageable for Kentucky Utilities Company since the in-house development and implementation of a computer-aided system for recordkeeping and reporting. The large volume of data that must be collected and manipulated necessitated the computerization of the entire recordkeeping and reporting process. This type of computer application results in better data management and reporting while providing more efficient allocation of resources. The data handling system used by Kentucky Utilities Company has applicability to other utility companies who likewise have access to a mainframe computer.

DATA COLLECTION

An efficient system for data collection is necessary to obtain quality data and to assure the integrity of the reports produced. The data collection system established at Kentucky Utilities consists of two forms titled, "Drum Content Report" and the "Transformer Content Report." These reports are illustrated in Figures 1 and 2. All PCB material generated for disposal is placed in drums at the site where the material is generated. The only exception is transformers. The Drum Content Report is filled out on every drum and accompanies the drum until it is transported to the Company's long-term PCB storage facility. This report is completed by the field personnel who generate the PCB waste. When the PCB item is received by the long term storage facility, an inventory number is assigned to the

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DRUM CONTENT REPORT

This report is to accompany every drum brought to the Annex III PCB Storage Facility:

Plant or Division Originating PCB Item_____ Drum No._____

District_____Date_____

Description of Contents_____

Weight_____Fill Material_____

Gasket_____Clamping Band_____

Additional Information if Contents are Capacitors:

Leaking Yes/No	Date Placed in Drum	KVAR	Serial Number	Manufacturer

Date Drum Moved to Annex III PCB Storage Facility_____

Person Responsible_____

DO NOT WRITE IN THIS SPACE; FOR GENERAL OFFICE USE ONLY.

Drum Identification # assigned when received at Annex III PCB Storage Facility

Remarks_____

Figure 1.

MONS 019171

TRANSFORMER CONTENT REPORT

Plant or Division _____ District _____

Location _____

Total Quantity of Fluid in Transformer _____ Gallons

Total Weight of Transformer _____ lbs.

Dimension of Transformer: Height _____ ft.

Length _____ ft.

Width _____ ft.

Date Removed from Service _____

Date Placed into Storage _____

Test Data:			
	Method Used	_____	_____
	Date Tested	_____	_____
	Results	_____	_____

DO NOT WRITE IN THIS SPACE; FOR GENERAL OFFICE USE ONLY.

Identification # assigned when received at Annex III Storage Facility _____

Remarks _____

_____

_____

Figure 2.

drum and recorded on the report. The drum is placed in numeric order with other drums in storage. The report is then forwarded to the Environmental Section for entry into the computer data base. All data that is needed to comply with the regulatory requirements of an Annex III storage facility is collected from this report. This includes the date removed from service if the material is capacitors or the date the waste is generated if it is debris or similar material. Other pertinent regulatory information collected includes the date received for disposal, the facility (in our case the district) that generated the material, and the weight of the item. If capacitors are contained in the drum, additional information is collected to facilitate other internal uses of the data. This information includes the KVAR, the serial number and the manufacturer of each capacitor in the drum. The information on serial number and manufacturer is presently not used, however, it could have future uses such as an aid in identifying and tracking the disposition of individual capacitors. The Transformer Content Report is used any time a PCB transformer requires disposal. It is used to collect the same pertinent information for regulatory compliance in addition to some additional data that is required by the disposal contractor.

In setting up the data collection system, a critical factor in making the program successful was the cooperation of field personnel. This was necessary because field personnel are the source of the data requiring collection and the most resource intensive part of the entire recordkeeping and reporting process turned out to be data collection. In order to obtain this cooperation, data collection had to be as simple and straightforward as possible. Also, it was necessary to minimize additional manhour requirements. People inherently do not like to complete reports, so any measure that reduced the time necessary to complete the reports was instituted. These measures included minimal changes to the existing report that was being used and to require that the reports be completed by the personnel that generate the PCB waste.

DATA ENTRY

Once the data has been collected in report form, it must be transferred to the storage file in the computer. Because of the volume of information that needed to be transferred, the process of data entry had to be efficient and the time requirement had to be minimal. Also the system needed to be simple to use.

Manual entry into the data file is possible, in fact, it was used in the old system of data entry. This type of system can be time consuming and result in an unacceptable amount of error in the data. A new system was developed to reduce the

time requirement and to minimize the number of errors to an acceptable level. The new system consists of a menu driven program that interacts with the user. The program asks the user to input specific information describing the amount of data to be entered and if the data is new information or updating previous entries. Once the program has this information, it displays the appropriate screen for the user to input the data. If the data is new, the program will check the data for completeness once the user indicates the data entry is complete. The required information for new entries consists of all the data contained on the Drum Content Report or the Transformer Content Report. The information pertaining to the actual shipment for disposal is entered after the shipment occurs as an update. The update is performed in a similar fashion. The program will ask the user to supply the number of items requiring updates. This is indicated by inputing the starting item number and the ending item number. The program will update all item numbers within the specified block. The data supplied in the update includes the date the shipment occurred, the manifest number of the shipment, and the disposal facility. After the input is complete, the program then asks the user to check the information entered for accuracy by summarizing the data on another screen that is displayed to the user. The user must confirm the accuracy by responding whether the data is correct or not. If the information isn't correct, the update is voided and must be re-entered. If the information is correct, the program writes the update to the items in the storage file. Although this may sound quite involved, the program is user friendly because its menu driven and it interacts with the user. This helps the user to understand how the program works and to figure out what information is expected to be input and in what order and form. This system of data entry forces the user to check the material being entered for accuracy and completeness, which would not always be done with manual entry. The input, update and check screens are shown in Figures 3, 4 and 5 respectfully.

DATA STORAGE

The process of storing the data in the computer had to be efficient because of the volume of data requiring storage. The previous system of recordkeeping and reporting kept both a data file and the actual report in storage. This required an enormous amount of storage space. The new system incorporated several means to reduce the necessary storage space.

One method that was used was to code as much of the data as feasible. All of the districts within the Company were assigned a numeric code unique to that district.

PCB STORAGE INPUT

ITEM NUMBER: _____
TOTAL WEIGHT: _____ lbs.
DISTRICT CODE: ___
DESCRIPTION CODE: ___

DATES:
ITEM REMOVED FROM SERVICE: / /
ITEM RECEIVED: / /

KVA/KVAR: ____ S/N: _____ MANUFACTURER CODE: ____

IF ITEM IS A TRANSFORMER, ENTER INDICATED VALUE ==) GALLONS:

Remarks: _____

"PF13" == INPUT IS COMPLETE "PF15" == ABORT INPUT SESSION

Figure 3.

PCB STORAGE UPDATE

IN ORDER TO IDENTIFY WHICH ITEMS IN STORAGE ARE TO BE UPDATED, YOU MUST INPUT ITEM NUMBERS. THE UPDATE WILL THEN BE PERFORMED ON ALL ITEMS BETWEEN (AND INCLUDING) THE TWO ITEM NUMBERS INPUT.

START UPDATE WITH ITEM NUMBER: _____
CONCLUDE UPDATE WITH ITEM NUMBER: _____
DATE TO BE SHIPPED: __/__/__
MANIFEST NUMBER: _____
DISPOSAL FACILITY CODE: ____

****

"PF13" == INDICATES YOU ENTERED THE INDICATED INFORMATION
"PF15" == INDICATES YOU DO NOT WISH TO DO THE UPDATE FUNCTION.

Figure 4.

PCB STORAGE UPDATE

IN ORDER TO IDENTIFY WHICH ITEMS IN STORAGE ARE TO BE UPDATED, YOU MUST INPUT TWO ITEM NUMBERS. THE UPDATE WILL THEN BE PERFORMED ON ALL ITEMS BETWEEN (AND INCLUDING) THE TWO ITEM NUMBERS INPUT.

START UPDATE WITH ITEM NUMBER: _____
CONCLUDE UPDATE WITH ITEM NUMBER: _____
DATE TO BE SHIPPED: __/__/__
MANIFEST NUMBER: _____
DISPOSAL FACILITY CODE: ____

THE PROPOSED UPDATE WILL INVOLVE _____ ITEMS.
ENTER AN 'X' IN FRONT OF THE APPROPRIATE RESPONSE TO THE FOLLOWING QUESTION:
IS THE NUMBER OF UPDATES PROPOSED VALID? ____ yes
____ no

IF YOUR RESPONSE IS 'NO' THEN THIS SESSION MUST BE TERMINATED.

****

"PF13" == INDICATES YOU ENTERED THE INDICATED INFORMATION.
"PF15" == INDICATES YOU DO NOT WISH TO DO THE UPDATE FUNCTION.

Figure 5.

All types of PCB waste that could be generated were also coded with a numeric code as were the equipment manufacturers and the PCB disposal facilities currently used by the Company.

Another measure that was incorporated to reduce the amount of storage space was to only store the data and not the entire report. This was the most effective measure in reducing the required storage space. A report writing program had to be developed to read the data file, interpret all codes used, and write the report all within the program itself. Once the report is complete, it is sent directly to the printer with none of the report stored in the computer. Examples of the report are shown in Figures 6 and 7. One problem this method creates is how to reproduce the report when necessary. This problem was overcome by having the program copy all the data used to write a particular report and create a separate file to temporarily store the data. Once this file is created, it is transferred to tape for permanent storage. If a specific report needs to be reproduced, the data is simply transferred back to the computer and the program is directed to write a report using this data. This method produces the same report because it uses the same data used in the initial report.

MULTIPLE USES OF DATA

One of the most beneficial uses of the new data handling system is the use of the data for inventory control. The information contained in the data file provides the means to strictly control the PCB items currently in storage at the Company's long-term PCB storage facility. A separate system was developed to keep track of the items in storage and to determine the makeup of shipments for disposal. The system can be accessed to determine the current number of items being stored and to sort the items into categories (e.g. number of drums of capacitors, of debris, etc.). This system is also used to determine the items to be shipped for disposal, based on the dates the items are received (i.e. first in, first out). The report produced by this program also provides information on the categories of material to be shipped, the date each item was received by the storage facility, and the estimated cost of the shipment. The report is shown in Figure 8. The report produced is used to schedule the shipment with the disposal contractor, to prepare the purchase requisition, and to provide the personnel at the long-term storage facility with information on which items are to be shipped so the items can be labeled with the required ORM-E shipping label.

PCB ITEM NUMBER: 1500

DESCRIPTION: CAPACITORS

TOTAL WEIGHT: 125.65 KGS. (277.00 lbs.)

DATE ITEM RECEIVED: 11/06/84

PCB SOURCE: CARROLLTON DISTRICT

DATE ITEM REMOVED FROM STORAGE: 12/17/84

DISPOSAL FACILITY: ENSCO

MANIFEST NUMBER: AR-61805

NOTE: TOTAL WEIGHT DOES NOT INCLUDE THE WEIGHT OF THE DRUM.

****

PCB ITEM NUMBER: 1501

DESCRIPTION: CAPACITORS

TOTAL WEIGHT: 146.06 KGS. (322.00 LBS.)

DATE ITEM RECEIVED: 11/05/84

PCB SOURCE: CARROLLTON DISTRICT

DATE ITEM REMOVED FROM STORAGE: 12/17/84

DISPOSAL FACILITY: ENSCO

MANIFEST NUMBER: AR-61805

NOTE: TOTAL WEIGHT DOES NOT INCLUDE THE WEIGHT OF THE DRUM.

****

PCB ITEM NUMBER: 1502

DESCRIPTION: CAPACITORS

TOTAL WEIGHT: 166.92 KGS. (368.00 LBS.)

DATE ITEM RECEIVED: 11/09/84

PCB SOURCE: HARLAN DISTRICT

DATE ITEM REMOVED FROM STORAGE: **STILL IN STORAGE - 12/31/84 **

DISPOSAL FACILITY:

MANIFEST NUMBER:

NOTE: TOTAL WEIGHT DOES NOT INCLUDE THE WEIGHT OF THE DRUM.

****

Figure 6. Annex III Annual Report on the Disposition of PCB Items. A sample page showing itemised listing of all items handled by the PCB storage facility.

SUMMARY OF PCB STORAGE FACILITY TRANSACTIONS

1. BREAKDOWN OF PCB ITEMS FOR THE CALENDAR YEAR 1984.

A. 832 WERE RECEIVED AT THE STORAGE FACILITY.
TOTAL WEIGHT: 184,770.56 KGS. (407,356.00 LBS.)

1. 399 OF THESE ITEMS CONTAINED CAPACITORS
TOTAL WEIGHT: 68,119.94 KGS. (150,179.00 LBS.)

2. 0 OF THESE ITEMS CONTAINED PCB OIL
TOTAL WEIGHT: 0.00 KGS. (0.00 LBS.)

3. 46 OF THESE ITEMS CONTAINED PCB CONTAMINATED OIL
TOTAL WEIGHT: 6,941.40 KGS. (15,303.00 LBS.)

4. 387 OF THESE CONTAINED DEBRIS
TOTAL WEIGHT: 109,709.25 KGS. (241,874.00 LBS.)

B. 577 WERE TRANSFERRED TO DISPOSAL FACILITIES.
TOTAL WEIGHT: 116,538.37 KGS. (256,921.00 LBS.)

1. 344 OF THESE ITEMS CONTAINED CAPACITORS
TOTAL WEIGHT: 57,919.98 KGS. (127,691.00 LBS.)

2. 0 OF THESE ITEMS CONTAINED PCB OIL
TOTAL WEIGHT: 0.00 KGS. (0.00 LBS.)

3. 46 OF THESE ITEMS CONTAINED PCB CONTAMINATED OIL
TOTAL WEIGHT: 6,941.40 KGS. (15,303.00 LBS.)

4. 187 OF THESE ITEMS CONTAINED DEBRIS
TOTAL WEIGHT: 51,677.01 KGS. (113,927.00 LBS.)

C. 372 WERE RETAINED AT THE STORAGE FACILITY.
TOTAL WEIGHT: 88,860.44 KGS. (195,902.00 LBS.)

1. 162 OF THESE ITEMS CONTAINED CAPACITORS
TOTAL WEIGHT: 28,855.47 KGS. (63,615.00 LBS.)

2. 0 OF THESE ITEMS CONTAINED PCB OIL
TOTAL WEIGHT: 0.00 KGS. (0.00 LBS.)

3. 0 OF THESE ITEMS CONTAINED PCB CONTAMINATED OIL
TOTAL WEIGHT: 0.00 KGS. (0.00 LBS.)

4. 209 OF THESE ITEMS CONTAINED DEBRIS
TOTAL WEIGHT: 60,005.01 KGS. (132,287.00 LBS.)

Figure 7. Annex III Annual Report on the Disposition of PCBs and PCB Items. A sample page showing summary information on all items handled by the PCB storage facility. Note that subtracting the numbers in A and B do not yield the numbers in C. This is because of items received in 1983, and shipped in 1984.

PCB ITEMS AWAITING SHIPMENT FOR DISPOSAL
FROM ANNEX III PCB STORAGE FACILITY

ID#	DATE RECEIVED	WEIGHT(LBS)
	DRUMS OF PCB OIL	
	SHIPPED UNDER MANIFEST NO. UNASSIGNED	
	**********	
2002	02/21/85	300
2365	07/22/85	380
2366	07/22/85	435
2367	07/22/85	435
2368	07/22/85	435
2369	07/22/85	420
TOTAL ITEMS TO BE SHIPPED = 6	TOTAL WEIGHT = 2405 LBS.	
SUBTOTAL = BASED ON SCHEDULE A		
	DRUMS OF PCB CONTAMINATED OIL	
	SHIPPED UNDER MANIFEST NO. UNASSIGNED	
	**********	
1943	01/18/85	450
1944	01/18/85	450
1954	01/24/85	416
2301	07/01/85	460
2314	07/03/85	225
2331	07/09/85	350
TOTAL ITEMS TO BE SHIPPED = 6	TOTAL WEIGHT = 2351 LBS.	
SUBTOTAL = BASED ON SCHEDULE A		
	DRUMS OF FILTERS	
	SHIPPED UNDER MANIFEST NO. UNASSIGNED	
	**********	
2312	07/03/85	180
2370	07/15/85	240
2371	07/29/85	260
2373	07/29/85	218
2374	07/29/85	220
2431	08/08/85	220
2482	08/18/85	225
TOTAL ITEMS TO BE SHIPPED = 7	TOTAL WEIGHT = 1563 LBS.	
SUBTOTAL = BASED ON SCHEDULE A		

==) GRAND TOTALS: TOTAL ITEMS TO BE SHIPPED = 168
TOTAL WEIGHT = 91891 LBS
TOTAL SHIPMENTS REQUIRED = 2.1 TRUCK LOAD(S)
TOTAL KVAR = 0 KVAR
TOTAL ESTIMATED COST = BASED ON SCHEDULE A

Figure 8. Inventory Control Report.
This version shows drums awaiting shipment for disposal.

The data file is also used to prepare quarterly reports on the disposition of PCB capacitors that have been removed from service as part of the Company's PCB capacitor phase-out program. The report is segregated by district (i.e. facility) and includes both the number and the total KVAR of capacitors removed from service. The report also provides information on the number of capacitors that have been shipped for disposal and those remaining in storage. This report is illustrated in Figures 9 and 10. This report has been very useful in following the progress of the phase-out program. The disposal of the capacitors is the final stage of the phase-out program and this report indicates the degree of process in this final stage.

PROGRAM STRUCTURE

Several individual programs which interact with each other make up the total computerized system of PCB recordkeeping and reporting. Each program has a specific function it performs and does so either upon command of the user or another program. The following details how the system is set up to allow this interaction to occur.

The fundamental logic behind the system is to have a master or execution program that will control the other support programs. This execution program is accessed by the user and prompts the user to input the function desired (E.G. input data, etc.). Once the user has indicated the desired function, the program runs the appropriate support program. In certain cases, the support program accesses another program to perform a specific function. This interaction can be carried out as much as needed to ultimately accomplished a desired function such as writing the annual report on the disposition of PCB items. The execution program in this system is called "Newstor Exec". Newstor is simply the program name which is short for new storage. It was named this because it is a new storage system. Exec is the program type. It is an abbreviation for execution and is actually a programming language just as Fortran is. Its primary function is to control the execution of the support programs as describe earlier. The program is accessed by the user by typing "Newstor" and entering it into the computer. This procedure causes the program to be run. It continues to run for the entire session and is under the control of the user. The user has the ability to enter new data, update existing data and initiate the writing of the annual document for the Company's Annex III PCB Storage Facility. VS Fortran is the source code used in the support programs which perform these functions.

DISTRICT OF PINEVILLE

ID#	NUMBER OF CAPACITORS CONTAINED IN DRUM	TOTAL KVAR CONTAINED IN DRUM	DATE RECEIVED FOR DISPOSAL	DATE SHIPPED FOR DISPOSAL
2429	3	300	08/08/85	IN STORAGE
2430	1	100	08/08/85	IN STORAGE

SUMMARY INFORMATION FOR THE DISTRICT OF PINEVILLE

TOTAL KVAR OF CAPACITORS RECEIVED FOR DISPOSAL = 400 KVAR

TOTAL KVAR OF CAPACITORS SHIPPED FOR DISPOSAL = 0 KVAR

TOTAL KVAR OF CAPACITORS REMAINING IN STORAGE = 400 KVAR

PERCENT OF CAPACITORS RECEIVED SHIPPED FOR DISPOSAL = 0% (BASED ON KVAR)

TOTAL NUMBER OF CAPACITORS RECEIVED FOR DISPOSAL = 4

TOTAL NUMBER OF CAPACITORS SHIPPED FOR DISPOSAL = 0

TOTAL NUMBER OF CAPACITORS REMAINING IN STORAGE = 4

PERCENT OF CAPACITORS RECEIVED SHIPPED FOR DISPOSAL = 0% (BASED ON NUMBER)

FIGURE 9. PCB Capacitor Phaseout Quarterly Report.
Sample page presenting information indicating the progress of each District (i.e. 'Facility') for the Phaseout Program.

SUMMARY INFORMATION FOR ALL DISTRICTS

==) GRAND TOTALS-YEAR TO DATE:

TOTAL KVAR OF CAPACITORS RECEIVED FOR DISPOSAL = 93050 KVAR

TOTAL KVAR OF CAPACITORS SHIPPED FOR DISPOSAL = 82900 KVAR

TOTAL KVAR OF CAPACITORS REMAINING IN STORAGE = 10150 KVAR

PERCENT OF CAPACITORS RECEIVED SHIPPED FOR DISPOSAL = 89% (BASED ON KVAR)

TOTAL NUMBER OF CAPACITORS RECEIVED FOR DISPOSAL = 1325
*** NOTE: TWO OF THESE CAPACITORS ARE SECONDARY UNITS ***

TOTAL NUMBER OF CAPACITORS SHIPPED FOR DISPOSAL = 1189

TOTAL NUMBER OF CAPACITORS REMAINING IN STORAGE = 136

PERCENT OF CAPACITORS RECEIVED SHIPPED FOR DISPOSAL = 90% (BASED ON NUMBER)

==) GRAND TOTALS-TOTAL PROGRAM:

TOTAL KVAR OF CAPACITORS RECEIVED FOR DISPOSAL = 135465 KVAR

TOTAL KVAR OF CAPACITORS SHIPPED FOR DISPOSAL = 125315 KVAR

TOTAL KVAR OF CAPACITORS REMAINING IN STORAGE = 10150 KVAR

PERCENT OF CAPACITORS RECEIVED SHIPPED FOR DISPOSAL = 93% (BASED ON KVAR)

TOTAL NUMBER OF CAPACITORS RECEIVED FOR DISPOSAL = 1863
*** NOTE: TWO OF THESE CAPACITORS ARE SECONDARY UNITS ***

TOTAL NUMBER OF CAPACITORS SHIPPED FOR DISPOSAL = 1727

TOTAL NUMBER OF CAPACITORS REMAINING IN STORAGE = 136

PERCENT OF CAPACITORS RECEIVED FOR DISPOSAL = 93% (BASED ON NUMBER)

FIGURE 10. PCB Capacitor Phaseout Quarterly Report.
Sample page presenting information indicating the progress of all Districts (i.e. 'Facilities') for the Phaseout Program.

The other program used in this system are called "PCBSHIP SAS" and "PHASEOUT SAS". As before, PCBSHIP and PHASEOUT are simply the program names. SAS is the program type. SAS is a programming software package** and is used extensively throughout the Company for load forcasting, statistical analysis, and data handling and report-writing. The PCBSHIP SAS program is the inventory control program. It is used for inventory control of the Company's Annex III PCB Storage Facility. This program can be used to write a report showing the current number and type of PCB items in storage or to write a report containing the items to be shipped for disposal. This program was described in more detail in the previous section entitled Multiple Uses of Data. The Phaseout SAS program is used to write the report on the Company's PCB Capacitor Phaseout Program. This program is also described in the previous section. These two SAS programs are run independantly from the the other programs. They are not controlled by the execution program discussed earlier, but they do utilize the same data set. A future modification to the system will allow access to these two programs from the execution program.

An IBM 4381 VM/SP Rel.4 mainframe computer is the system used at Kentucky Utilities Company. The recordkeeping and reporting programs operate under a CMS environment and are dependent on the use of CMS EXEC2 and REXX procedures, and XEDIT macros. The software that is utilized are SAS and XMENU, and VS Fortran is the program product used.

**SAS Institute Inc., Cary N.C. 27511.

RADIOACTIVE AND NON-RADIOACTIVE POLYCHLORINATED BIPHENYL (PCB) MANAGEMENT AT HANFORD

Wesley W. Leonard*
Robert F. Gretzinger*
Gary R. Cox*

RADIOACTIVE PCB'S

Equipment containing PCB's exists in both radioactive and non-radioactive areas at Hanford. For this reason, all oil samples to be shipped offsite from Hanford for PCB evaluation must be monitored for radioactivity. A scintillation count/checkup procedure for these liquid organics has been developed to accomplish this task and includes the following steps:

1. A one milliliter sample (from the sample) is collected and placed in a liquid scintillation vial which contains a standard xylene cocktail.
2. It is counted for 10 minutes, and the results are evaluated against background levels of radioactivity.
3. If the sample is above background levels, 0.1 milliliter of the sample is dissolved in 10 milliliters of iso-octaine which is then washed in ample 16 molar sulfuric acid and allowed to phase separate.
4. The sulfuric acid phase is decanted removing with it the radionuclides.
5. Repeat Step 3 three times.
6. A one milliliter sample from the acid washed solution is re-analyzed as outlined in Step 2 above, and released for PCB evaluation when levels of radioactivity are below background.

RADIONUCLIDE/PCB SEPARATION

A Sulfuric Acid Phase Separation Process has been developed, by Rockwell Hanford Operations (Rockwell), to remove the radionuclides from the liquid organic PCB. Basically, this process involves the same principles outlined above. Figure 1 illustrates a possible scaled up version of this laboratory process which might obtain a definite liter per hour throughput.

*Rockwell International, Rockwell Hanford Operations, P. O. Box 800, Richland Washington, 99352.

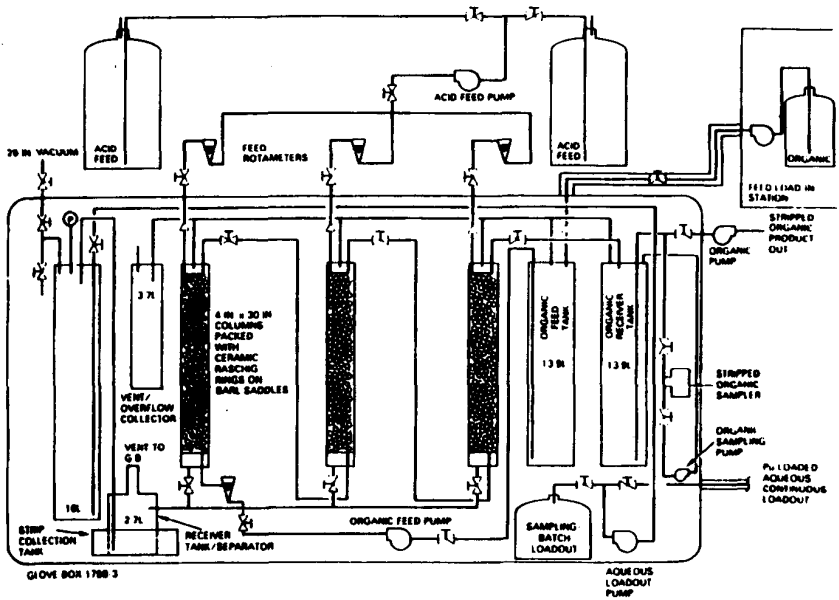

Figure 1. Sulfuric Acid Phase Separation Process

Polychlorinated biphenyl items that are found to be radioactive are sent to Rockwell's radioactive PCB management facility. Special storage and disposal difficulties have resulted because there is no Environmental Protection Agency (EPA) approved disposal site for radioactive PCB solid waste materials. Radioactive PCB fluids may be burned in an EPA approved incinerator at Los Alamos, and a request was made to the Department of Transportation (DOT) for permission to ship these liquids. This option is on hold awaiting the determination of the Hanford site's total inventory. When this inventory is known, incineration and transportation costs will be compared to the Sulfuric Acid Phase Separation process to determine the most cost effective method of disposal of the radioactive PCB fluids.

An exemption request has been submitted to the EPA asking for a waiver to allow us to bury the drained, radioactive, PCB carcasses in our solid, low level, radioactive waste disposal area, which has been modified to allow for a 20-year retrievable storage. Rockwell is awaiting EPA's clarification on this request.

TESTING

Rockwell's PCB testing program has grown from a 10 percent sampling of oil-filled electrical equipment for disposal, to 100 percent sampling of all existing oil-filled equipment in our electrical, mechanical, hydraulic, and heat transfer systems on the Hanford Site. Attempts to determine the total extent of PCB contamination on the site have developed into a major project. It has increased even further since the State of Washington has decreed that any item containing PCB's up to 50 parts per million (ppm) shall be regulated if it originates from transformers, capacitors, or the reclamation thereof.

When PCB's were discovered in the mineral oil of transformers stored for disposal, a 10 percent sampling program began of all existing transformers. Twenty-five percent contained 50 ppm or greater PCB's. At that time the 100 percent testing program was initiated for all oil-filled electrical equipment.

Other oil-filled equipment in non-electrical systems was sampled, due to the extent of PCB contamination found in the electrical systems. Polychlorinated biphenyl contamination was again found, which resulted in the 100 percent testing program of these systems. It is from these hydraulic systems which perform non-contact radioactive processing that most of the radioactive PCB's were produced.

The Clor-N-Oil screen test was used to reduce testing costs until the State of Washington enacted new regulations.*

*Department of Ecology, Hazardous Waste Regulations, Washington Administration Code (WAC) 173-303

All samples are now being sent to a lab for the determination of PCB concentration. Some false positive test results were observed in the screen tests, probably due to chlorine containing inhibitors in some of our oils. Each piece of equipment tested is dated and tagged with the test results, so that the PCB concentration is known to anyone handling it.

STORAGE AND DISPOSAL

Equipment removed from service is dispositioned to the "Storage For Disposal" facility (212-P). This facility contains:

1. A 1,500 gallon storage tank for PCB liquid.
2. A 2,000 gallon storage tank for PCB contaminated liquids.
3. An area for drum storage.
4. A controlled area for the storage of radioactive PCB liquids.

Past practices, prior to obtaining the storage tanks, included storage and disposal of equipment with the liquids inside their carcasses. The contracted disposal company would then drain the carcasses, bury them, and send the liquids to an approved disposal site for incineration. A "Certificate Of Destruction" for the oil was obtained, but ascertaining where the carcasses were buried was difficult. Presently, we are draining the carcasses, shipping the PCB carcasses separately, and storing all PCB contaminated carcasses on wooden pallets. The liquids containing PCB's are shipped to an EPA approved site for incineration. In the future, it may be possible to bury the carcasses on site, and operate an approved incinerator.

SUMMARY

Conformance to all state and federal regulations is the goal of Rockwell in the management of both radioactive and non-radioactive PCB's at Hanford. A continuing effort is being made to locate, remove, and properly dispose of all PCB's. As improved methods of management are developed, consideration will be given to them for their adaptation into the Hanford Site PCB Management Plan.