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Topics
PCBs
Chemical analysis
Transformers
Pollution control
Insulating oils
Waste disposal

EPRI EL 3581
Project 2028
Proceedings
June 1984

Proceedings: 1983 PCB Seminar

Prepared by
Electric Power Research Institute
Palo Alto, California

Proceedings: 1983 PCB Seminar

EL-3581
Research Project 2028

Proceedings, June 1984

Atlanta, Georgia
December 6-8, 1983

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NOTICE

ABSTRACT

The 1983 EPRI PCB Seminar was held in Atlanta, Georgia on December 6-8, 1983. It was sponsored by EPRI's Interdivisional PCB Task Force. It presented utility workers with existing and emerging technologies for lower cost compliance with EPA rules and PCB environmental concerns. The papers in this proceedings are divided into topics as follows: Background; Detection and Analysis of PCBs: Retrofill; Spill Cleanup and Bio-Degradation; PCB Destruction; PCB Fires and PCDF; and Decontamination of Mineral Oil.

Technology in some of these areas such as Analysis, PCB Destruction, and Decontamination of Mineral Oil, is maturing. However, other critical topics lacking information, such as polychlorinated dibenzofuran (PCDF) formation, spill clean up, and replacement fluids, have arisen to replace them. Fully 50% of the seminar attendees suggested more work on PCDF in response to a questionnaire filled out at the meeting.

The seminar must be considered a success since 50% of the more than four hundred attendees considered presentations to be too technical and 50% said "too much sales talk" and future plans must take this dichotomy into account, possibly by better separation of the subject matter and perhaps provision for attendance at specific sessions rather than the full seminar.

EPRI PERSPECTIVE

PROJECT DESCRIPTION

This EPRI PCB seminar was held in Atlanta, Georgia, December 6-8, 1983. It was the second EPRI seminar on this subject, the first having been in Dallas, Texas, in 1981 (EL-2572). The papers presented by EPRI contractors and independent speakers encompassed a broad range of PCB management subjects. The subjects covered ranged from commercial processing of contaminated mineral oil to plans for the possible use of gene splicing for biodegradation of PCBs in spills.

PROJECT OBJECTIVES

The main purpose of the seminar was to inform utility personnel of the currently available means for complying more economically with PCB regulations. In addition, research work in diverse areas was presented to delineate potential sources for future assistance.

PROJECT RESULTS

The program varied widely from practical answers to esoteric research, and the audience varied broadly in background. As a result, comments varied from "too technical" to "too much sales talk," but the overall audience reaction was overwhelmingly positive. A possible course for future seminars would be to better segregate the technical and sales talks and then provide means for daily registration, if desired by the individual.

Gil Addis, Project Manager, Electrical Systems Division
Ralph Komai, Project Manager, Coal Combustion Systems Division

PREFACE

Much of the purpose of this preface is covered in the first two papers of the proceedings. Carl Manger of Baltimore Gas and Electric thoroughly covers the background of the PCB problem in the first paper. In the second, Gil Addis and Ralph Komai, the editors of this proceedings, summarize EPRI's efforts in the PCB area and their relationship to other programs in the field.

In the last few months, new plans for EPA rule-making on PCB transformer fires have been announced. This has resulted in added pressure to develop information on PCDFs replacement fluids, and cleanup of both spills and combustion products. A workshop to encompass material of significance to the utility industry and EPA in the rulemaking is planned for late 1984.

ACKNOWLEDGMENTS

The editors received help from many sources. Narain Hingorani, chairman of EPRI's Interdivisional Task Force on PCBs gave the welcoming address and contributed in many ways to the success of the seminar. We thank Grady Baker, Jr. of Georgia Power, our keynote speaker. Additional people who assisted at the seminar or in preparation of the proceedings were:

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Barbara Cole
Brooke Eldredge
Jim Gillies (Consultant)
Jacques Guertin
Luther Kolarik
Ellen Lanum
Bill Shula
Vasu Tahiliani
Tasia Toombs
Tom York

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Harry Onishi - Commonwealth Edison
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CONTENTS

Part 1

BACKGROUND

PCB UPDATE

H. C. Manger
Baltimore Gas & Electric Company

This is a generalization of the Paper which was given as a slide presentation. It should be made clear that when I speak of Askarels, it is a generic term including both PCB's and mixtures of PCB's with tri-/tetrachlorbenzene to reduce viscosity.

Once upon a time, many years ago, PCB was heralded as a wonder fluid to be used in electrical equipment because it was:

Chemically stable
Not soluble in water and
Not volatile

Early in the 1940's, electrical equipment manufacturers, because of its non-flammable property, started to use PCB in applications where personnel and property protection were paramount.

It has acceptable heat transfer characteristics close to mineral oil and is a reasonably good dielectric.

Chemically, it is developed by starting with a biphenyl ring and substituting the hydrogen atoms with chorine atoms. There are 209 possible ways to chlorinate the biphenyl. The askarel we use is made up of only a few of these possibilities.

PCB can vary from crystalline structures to a clear viscous liquid, which is the askarel used in electrical equipment.

Before updating PCB regulations, I would like to give a little history of the regulations. The problems should be self evident. I've long since stopped thinking there is a cure. Because of growing awareness of hazardous substance storage and environmental problems, the Toxic Substance Control Act was passed in 1976.

Based on anything but firm data, environmental advocates convinced Congress to amend the Toxic Substance Control Act to specifically cover PCB. You may recall PCB was the only substance that was singled out by the Congress to be regulated. They simply outlawed PCB; its use, its manufacturer, and distribution in commerce.

Nevertheless, Congress passes TSCA in 1976 and appointed EPA the watchdog. Since then, we have been in a continuing dilemma as to how to deal with PCB's. One must realize that, with the swipe of pen, Congress legislated a fluid we had used with no obvious ill effects into a hazardous substance.

However, the Toxic Substance Control Act allows two ways for continued use of PCB's: First, and the most attractive, is if the use can be considered totally enclosed. Totally enclosed is defined as presenting insignificant exposure. The second way is use authorization. EPA can authorize a use if it can be shown that such use does not offer unreasonable risk.

These two terms are pretty important. If something is totally enclosed, it does not fall under T.S.C.A., but you may also continue to use PCB that is not considered totally enclosed by an authorization, i.e., if EPA deems that it does not offer an unreasonable risk. (EPA determines both totally enclosed and authorized use).

Exemptions are applied for by the user, who must show no unreasonable risk, indicated efforts for improvement, and reapply for the exemption every year.

On May 31, 1979, the First Final Rule was passed. You should remember that EPA looked at the use activities of PCB and deemed the capacitors and transformers as being totally enclosed. EPA felt that with what they knew of the equipment, it posed an insignificant exposure to the environment. EPA also authorized a number of uses, some of which were RR transformers, small capacitors, carbon paper, and, if I remember correctly, even servicing other people's transformers.

There were a few exemptions applied for under that May 31, 1979 First Final Rule. Another interesting side light is that electrical equipment seemed to be the major focus of EPA's interest.

Looking back to the good old days and the first set of 100 questions (by the way, there is an updated set), May 31, 1979 established 50 ppm and introduced the under 50, 50-500, over 500 concept.

It covered: marking
- record keeping
- restrictions on repairs
- disposal
- basically incineration was the recommended method
- storage inspection

It also covered improper disposal and certainly addressed violations which can be and has already been hazardous to some people's pocketbooks.

The Environment Defense Fund (EDF) challenged the May 31, 1979 Rule on three grounds (1) They felt that there was no record for EPA to establish a 50 ppm cut-off; (2) EDF felt that EPA had no data to back up the claim that capacitors and transformers were totally enclosed, and (3) the authorizations that were allowed were improper. The court ruled that transformers and capacitors were not totally enclosed and that EPA lacked substantial evidence to support a regulatory cutoff of 50 ppm for manufacture, processing, distribution in commerce, or use of PCB.

Had the court's decision gone into effect, EPA said it would have caused a major economic impact - I think we would have had to turn the lights out. However, a stay requested by EPA was granted and the famous Interim Measures were established.

As a result of this ruling, EPA published what is referred to as Rule #1 on August 25, 1982. If this infers to you that there will be more than one rule, you are right. Number 1 deals only with electrical equipment and authorizes certain uses of PCB in electrical equipment and set 50 ppm as a cutoff for electrical equipment. Some of the main points of Rule #1 are:

Prohibits the use of PCB transformers and PCB electromagnets posing a risk after October, 1985.

Authorizes the use of all other PCB transformers for the remainder of their useful lives, with inspections. Take note - it says "authorizes", where May 1979 considered a transformer totally enclosed.

There are inspection requirements of frequency, retention, and availability of records.

These inspections could be reduced if we contained 100% or retrofilled to 60,000 ppm.

Authorizes the use of large PCB capacitors located in electrical substations and indoor installations.

Prohibits the use of all other large PCB capacitors after October 1, 1988. Here we see a string tied to authorization.

Authorizes the use of all PCB-containing mineral oil-filled electrical equipment.

Presumes circuit breakers, reclosers, and cable to be less than 50 ppm.

Expands definition of electrical equipment posing an exposure risk to food or feed.

Allows storage of large PCB capacitors and PCB-contaminated equipment outside of qualified storage facilities.

Requires records of inspection and history be kept for 3 years after disposing of PCB transformers.

Defines "disposal" as including leaks and spills but does go on to say - spills, leaks or uncontrolled discharges, resulting from the unauthorized use (or storage) of electrical equipment shall not constitute a disposal violation, provided adquate cleanup measures are inititated within 48 hours after notice of the discharge.

Does not address required extent of cleanup of PCB spills.

Since Rule #1 only deals with a certain part of the PCB problem, you must use a combination of the regulations to totally comply. Again, 50 ppm is the cutoff level in this electrical equipment rule.

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Since the August 25, 1982 Rule deals with electric equipment, what about the other items and systems that have PCB in them? Since the 50 ppm cutoff was struck down by court, there are a lot of non-electrical things that now fall in the category, containing PCB (even a molecule of PCB). One of the biggest problems is the incidental generation of PCB's, a manufacturing process can create as part of the process. Although it took a lot of effort and manufacturing know-how to develop the askarel we use in electrical equipment, EPA has stated, that any time you have a carbon, chlorine and some heat, the possibility exists that you can create a polychlorinated biphenyl.

As I stated earlier, all you have to do is replace one or more of the hydrogens with a chorine and you have yourself a PCB - it is not the PCB in our transformers, but it is a PCB. Now since the possibility exists that you can incidentally generate a PCB, and the regulations say you can't, chemical manufacturers and processes fell under question by EPA. Since industrial representatives explained that there are some systems in which PCB may be created, but no PCB's are released to the environment, EPA set about to write Rule #2 dealing with closed and controlled processes, and published this #2 PCB Rule on October 21, 1982.

Late this year (August or September), a number of policy statements were released by EPA dealing with PCB Separation Methods, Residual PCB and Enforcement Liability for Violations of Disposal Deadlines.

I think this just about brings us up to date.

What's ahead? -

A proposed Rule 3 which was signed December 1, 1983, addresses by-product PCB's that are not excluded from regulation by Rule #2. The final is scheduled for July 1, 1984.

The August 25 Rule is in effect now. I have to tell you that the rule may be challenged - EDF considered appeal since they thought the regulation was not strong enough in the areas of PCB transformers. EEI, USWAG and other interests have considered appeal because they felt the rule was too strict in certain other areas.

EPA had early stated there was no need for additional electrical rules, but it appears pressures of PCB problems in Binghamton, San Francisco and possible changes within the EPA organizations have suggested additional rule making, and, in particular, PCB transformers. They have set a tentative schedule which should result in some decision in 1985.

October 1984 is an important date since any information regarding PCB transformers which could ease the regulatory burden can be presented at the hearing. Proponents of stricter rules will certainly be there. It is up to us to gather information which will help our cause.

You recall I mentioned earlier in connection with the major points of Rule #1 that it did not address required extent of cleanup of PCB spills. This must be dealt with somehow; probably with a rule - I certainly hope with more than a policy statement.

So you see out of the original May 31, 1979 Rule have come many. We're up to #3 already. No one can be sure when we will see the final - Final Rule.

To add to our burden, efforts are, at this time, afoot in Congress through a RCRA re-authorization bill, to list PCB's as hazardous waste under that act. Among other things, this could possibly add more manifesting requirements, impact on burning less than 50 ppm contaminated insulating oil, and impose shorter storage time restrictions.

The Department of Transportation is proposing to incorporate changes in its hazardous material regulations which now apply to PCB's transported in one package or container greater than 10 pounds. Under this proposal, the regulations would apply to quantities <u>greater</u> than 1 pound.

The object of this seminar, to paraphrase the invitation, is to provide us with accurate data to permit knowledgeable decisions. In looking over the program, I feel every effort has been made to do just that. But this certainly is not the end of the regulations; it's not the end of our problems, and it cartainly should not be the end of the search for data to somehow resolve this PCB dilemma.

MONS 214684

EPRI Update - Emphasis on PCDF

Gil Addis and Ralph Komai
EPRI

Much of the work included in this EPRI update will be covered in detail in individual papers presented during this meeting. It is appropriate, however, to point out the range of this activity, but since pressure for solutions to PCDF problems is becoming more intense, we will spend more time on a discussion of new contracts about to start in this area.

We do not expect to provide immediate solutions, but hopefully in one case will provide the bases for future analytical gains, and in another develop data that may provide decision guidance in the retrofill or replacement of PCB equipment.

EPRI's INVOLVEMENT

EPRI's involvement in PCB problems can be explained readily:

Why? - Tremendous potential cost to the utilities.
- Can we help lower it?

What? - Develop front-end feasibility and multiple approach funding.
- Not competition to others developing processes.

The work at EPRI is coordinated by the PCB Interdivisional Working Group of which Dr. Narain Hingorani is Chairman. Represented are three divisons, Coal Combustion Systems (CCS), Electrical Systems (ES), and Energy Analysis and Environment (EA&E). The range and scope of EPRI's program is very similar to the breakdown of sessions for the seminar.

ANALYTICAL INSTRUMENTATION

Rapid and simple analytical methods are needed for portable use in the field. The work has been divided into two areas, analysis in mineral oil and analysis in soil.

For mineral oil, a portable instrument made by Horiba was modified for screening oil samples by determining total chlorine. The instrument, based on x-ray fluorescence measurement, has been field tested by a number of utilities for over a year. More recently, a simple disposable kit for chemical analysis of mineral oil has been developed. The CLOR-N-OIL™ kit is currently being tested in the field. Nearing the field trial stage in a second generation of instruments is an infrared technique to directly read PCBs. It is anticipated that completion of these projects will bring to a close EPRI's efforts to determine PCB in oil.

For analysis in soil (askarel spills), where rapid field analysis is needed during cleanups, several analytical methods are being investigated. The leading candidate is a dedicated portable electron-capture gas chromatograph developed by S-Cubed.

A second technique that appears to be useful for spill samples is the refinement of infrared spectroscopy work by CS Associates; this work was begun at Oak Ridge National Laboratories.

DESTRUCTION OF ASKAREL FLUIDS AND CAPACITORS

In the past, EPRI had been actively involved in the early test burns of PCB fluids and capacitors, i.e., the sampling and analysis for the ENSCO test burns. Incinerstion has been proven satisfactory, and a number of incinerators, both land based and at sea, are participating in the PCB destruction business.

The preliminary design phase of a dc arc furnace (Electro-Petroleum) for destruction of capacitors has been completed. A contract is presently being negotiated for a large scale demonstration unit. Also in a current EPRI project, Chemical Treatment of Capacitors, laboratory tests to destroy PCBs from cut-up capacitors have been successful in reducing concentrations to below detectable limits. Details will be discussed in a paper by Acurex.

RETROFILLING AND REPLACEMENT OPTIONS

Retrofilling is being attempted by some utilities to substitute suitable non-flammable or low flamability fluids for PCBs. Replacement fluids considered have been:

RTEmp
Silicones
Perchloroethylene
75% Perchloroethylene, 25% mineral oil mixture
Freon 113

The same fluids plus solid insulation are being considered as replacements for PCBs in newly manufactured transformers. The decision to retrofill rather than replace must be based first on economics (in many cases the greater efficiency of new transformers significantly reduces the relative lifetime cost); followed by accessibility for replacement, public emotion and hysteria. In many cases the latter two transcend economics.

EPRI has had projects with Westinghouse to develop transformers based on perchloroethylene or a nonflammable 75% perchloroethylene, 25% oil mixture. These may be substituted directly for PCB transformers. The perchloroethylene issue has been slightly clouded by a controversy concerning long term toxicity, although it has been in common use in the dry-cleaning industry for many years. EPRI also has a project just starting to determine arc and spark by-products of two systems, perchloroethylene and the perchloroethylene/mineral oil mixture. The objective of this project is to determine whether there are harmful by-product chemicals to which a utility worker in a maintenance situation might be exposed, over and above the perchloroethylene, to which

dry cleaning workers have had relatively high daily exposures. In a project with General Electric, a two-phase Freon-cooled transformer has been developed. However, current economics of this Freon-cooled transformer make it noncompetitive.

It should be noted that for some time after even the most effective initial retrofill, there is enough PCB in the transforme. so that it is still legally classified a PCB transformer. More will be said about this when we discuss PCDF.

DECONTAMINATION OF MINERAL OIL

A number of commercial processes using a sodium reagent for removal of PCB from mineral oil are currently operating. Following an investigation of alternative processes, General Electric, under EPRI contract, has developed a solvent extraction process for separating PCB from mineral oil, reducing the disposal volume of PCB-contaminated oil by a factor of about 100. The process has been tested at 10 gallons per hour, and scale-up is being implemented.

SPILL CLEAN-UP

Spill clean-up divides into two categories. In the case of small ruptures or spills with potential public exposure, immediate cleanup is needed. The present procedure is to excavate contaminated soil and drum it for landfill disposal. Development of a poultice to remove PCBs from concrete has been attempted with erratic results by Franklin Research.

For long-term widespread clean-up in areas of limited public exposure, such as service shop areas, manufacturing facilities, or landfills, slower methods of PCB destruction can be used. An Acurex project is attempting to reduce the excavation/transportation/landfill costs by developing soil washing as an alternative disposal technique. Instead of burying 99+% dirt, the PCBs will be removed for disposal, and the soil can be replaced in the excavation. A patent is being pursued for this process, which we believe will have application to many different kinds of chemicals, such as dioxin.

Attaway and Associates has done a literature survey and interviewed commercial biotechnology firms for EPRI to evaluate biotechnological processes for PCB clean-up and disposal problems and to outline a research plan for pursuing these technologies.

RISK ASSESSMENT

Risk assessment, along with risk perception is an area of great importance in relating PCB problems to the interests and fears of the public. It is enormously difficult because each group, such as businessmen, scientists, or homeowners, perceives an entirely different risk for the same event. One obvious example is a Californian with a home straddling the San Andreas fault, oblivious to the potential earthquake dangers, but worrying about the 10 kVA PCB transformer on the pole down the street.

EPRI has initiated several projects in the risk assessment area, described below:

1. A project is in progress to establish a methodology for exposure assessment of PCBs and PCB partial oxidation products. Progress to date has been in consultation with utility experts to establish the focus for these models. Selection of problem areas will then govern the choice of models.

2. Work is about to be initiated on risk management methodologies to establish profiles of risk for PCB spills and PCB fires.

3. Decision Framework concepts for PCB are presently being explored with utility experts.

4. An occupational health risk assessment program for PCB and its oxidation products is in progress. An advisory committee from utilities has been assembled to evaluate the progress of the contractors.

PCDF/PCDD

Not covered in the present EPA regulations, but undoubtedly of highest priority in the future, are polychlorinated dibenzofuran (PCDF) and polychlorinated dibenzodioxin (PCDD). These are by-products formed under some conditions of partial oxidation from PCB and tri-tetrachlorobenzene present in askarels. Animal toxicology studies have found that certain by-product compounds are considerably more toxic than PCBs. An initial critical survey of the literature (including fires, chemistry, and toxicology) has been made for EPRI by SCS Engineers and reviewed favorably by international dioxin experts. This document is now available from EPRI's Research Report Center (CS-3308).

Because of the current intensity of interest in PCB substitutes and PCB fire hazard, EPRI has a short-term contract about to start. It is well known that when a transformer is drained for retrofilling, even under the best conditions, 2 to 5% of the original liquid in the transformer remains behind. Thus, no matter what the retrofill fluid, the immediate result is still, by regulatory definition, a PCB transformer. There are some retrofilling processes which further reduce the PCB content and permit eventual reclassification over a period of time. In this new project, laboratory tests will be made to determine the pyrolysis and combustion products of PCB at two levels of contamination in each of several potential retrofill fluids such as perchloroethylene, silicone, RTemp, and mineral oil. Information derived here may help acertain relative hazards of fires involving retrofilled transformers containing some residual PCB level. This may then be compared with the same event in an askarel transformer.

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In a second, longer term project, we are trying to determine the boundary conditions under which PCDF or PCDD might form in askarel or contaminated mineral oil equipment. It has been made obvious to us in several incidents that PCDFs/PCDDs form as a result of a fire in an askarel transformer. What happens as a result of long term overload or corona discharge in an askarel transformer? Is there any detectable PCDF formed in the case of a contaminated transformer fire? A number of these scenarios will be investigated. As a preliminary step, an attempt will be made to improve the present method of PCDF analysis. Several competent laboratories will make the preliminary analyses and assess the methodology before testing the selected field samples. Also, in the course of this project, one of the organizations will simulate a number of extreme field conditions using model transformers in the laboratory.

CONCLUSIONS

If you recall the seminar in Dallas two years ago, you will see some of the same problems and in some few difficult areas very little progress. However in general you will note that many of the problems have progressed beyond research and development and have resulted in commercially available equipment or techniques. Many new problem areas have assumed greater importance along with those that have so far resisted satisfactory solution. We expect you to find the next three days to be filled with a diversity of current and pertinent information on the various aspects of the PCB problem.

Part 2

DETECTION AND ANALYSIS OF PCBs

FIELD DETERMINATION OF PCB IN TRANSFORMER OIL -CLOR-N-OIL™ Kit-

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Askarel is a generic term for a group of non-flammable synthetic chlorinated hydrocarbons used as electrical insulating fluids in transformers and capacitors. Most contain poly-chlorinated biphenyls (PCB). PCB have been judged to be harmful in the environment and their manufacture, use and disposal have been subject to Government regulation since 1978. This regulation extends not only to askarel filled transformers containing PCB, but also to the much larger number of mineral oil-filled transformers which may have been contaminated with PCB during manufacture or service. Oils containing less than 50 ppm when taken from transformers are defined as non-PCB liquids and have no unusual limitations on their handling and disposal (except that oils contaminated with any detectable PCB may not be used in widely dispersed applications such as dust control). Oils containing 50 to 500 ppm PCB are considered "contaminated" and those containing more than 500 ppm are considered to be totally PCB. Handling and disposal of oils in these last categories requires special techniques.

Ultimately, each of the 35 million oil-filled transformers now in service in utility and industrial applications may have to be tested for PCB content to assure proper disposal. While adequate analytical methods exist for determining the PCB content of oils in the laboratory, this process is time-consuming. Samples must be packed, sent to the laboratory doing the analyses and the analysis must be performed. The aim of the work reported here has been to reduce this problem by developing techniques for the measurement of PCB in transformer mineral oils by non-chemists in the field.

A number of instrumental approaches were evaluated and the most promising for immediate field use was X-ray emission using the Horibe MESA-200 analyzer (1). This instrument determines the total amount of chlorine present in oil and, hence, gives an indirect measure of the upper limit on the PCB content. Field testing of the MESA-200 instrument firmly established the concept of using the total chlorine content in transformer oil as an indication of the PCB concentration. It appears that the chlorine screening approach can eliminate 50-70% of the transformers tested from further concern.

Initial cost of the x-ray emission analyzer is relatively high and the instrument is best transported by automobile. Recent attention in this program has focused on developing a smaller disposable means of screening PCB by determination of chlorine content of transformer oil. This has led to the CLOR-N-OIL™ PCB screening kit.

The kit developed here is based on the quantitative conversion of the chlorine atoms in PCB in transformer oil to chloride ions which in turn are extracted into an aqueous solution and measured colorimetrically. The conversion of chlorine to chloride ions is done by sodium salts formed by naphthalene together with the dimethyl ether of diethylene glycol ("diglyme") as stabilizing ligand (2). The chloride ions are extracted into an aqueous buffer solution and reected with a carefully controlled amount of dissolved mercuric nitrate. Diphenylcarbazone is added. If the mercuric ion content is greater than that taken up by the chloride ion in forming slightly dissociated mercuric chloride, a vividly blue complex is formed by the excess mercuric ion and the diphenylcarbazone. If the chloride ion contant exceeds that taken up by the available mercuric ion, the complex is not formed and the reaction mixture remains colorless to pale yellow. The reactions are carried out in soft plastic test tubes containing premeasured reagents in breakable glass ampules. Proper control of the sample size and of the quantity of mercuric nitrate allows the blue-colorless response level in the mineral transformer oil to be set at levels from a few ppm to several thousand ppm.

The test is performed in two soft sided polyethlyene tubes. The conversion of PCB to chloride ion is done in the first tube by breaking ampules containing naphthalene-diglyme and then sodium dispersion into the oil. Buffer solution is added from the second tube, the chloride ion is extracted into the aqueous phase and any excess sodium is eliminated. A minor amount of hydrogen is vented. A measured amount of the aqueous solution is returned to the second tube containing the mercuric nitrate end the indicator in separate ampulules. The color development process is done by breaking these last ampules in turn. A convenient way of transferring the aqueous phase beck and forth is provided by a flip top cap on the first tube. The tube is capped and allowed to settle after extraction of the chloride into the buffer. It is gently inverted so that the heavier aqueous phase moves to the bottom over the cap, the flip top is opened and a measured quantity of buffer is squirted back into the second tube. When done carefully, virtually all of the oil phase is retained in the first tube above a residual aqueous layer. Only the aqueous phase is returned to the tube where the indicator is finally contacted and the color observed.

The lowest retie of chlorine to PCB found in an askarel is 0.42. Therefore, an oil sample containing less than 21 ppm chlorine cannot contain more than 50 ppm PCB. A celer response level set et 21 ppm chlorine for the kit should assure that ne contaminated oil gives blue responses. The chlorine to PCB ratio fer ether askarels is as high as 1.34. Oil samples containing as little as 15.7 ppm askarel contamination can result in colorless responses as can samples containing other sources of chlorine contemination-but no PCB. Samples giving colerless responses can be checked by ges chromatography to determine whether they actually contain more than 50 ppm PCB.

The standard deviation on kits in prototypical production was found to be <2 ppm chlorine at a response level of 18.5. The kit then can be quite reliable. Actual field experience is needed to judge the overall performance of the kit. A field test is being conducted by EPRI to provide this experience.

This work was sponsored by the Electric Power Research Institute as part of Research Project 1713-1. CLOR-N-OIL is a trademark of EPRI.

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(2) J. F. Brown, M. E. Lynch, J. C. Carnahan, J. S. Singleton, Chemical Destruction Of PCB In Transformer Oil, Detoxification of Hazardous Wastes, p. 201, Ed. J. H. Exner, Ann Arbor Sci. Pub. (1982).; also T. O. Rouse, Removal Of PCB From Transformer Oil, Proc. PCB Seminar, EPRI EL-2572 (1982).

Discussion

Q1. What is the shelf life of the kits?

A. Kits have shown no sign of deterioration in the 6 months now in use. There is no reason to suspect that shelf life will not be quite long, but time is needed to establish the shelf life.

Q2. Has a national policy regarding test methods been addressed?

A. EPA does not endorse any method, but there is no reason why the method can not be accepted.

Q3. What is the effect of moisture on the test results?

A. The solubility is approximately 60 ppm. There have been no attempts to dry the oil and no problems have been experienced to that level.

Q4. What is the cost/test?

A. $4 to $6 depending upon quantitites.

Q5. Has the method been tried on hydraulic oil?

A. Some, but test results are not available. Additives could create a problem.

Q6. There was a request for a show of hands regarding interest in a test kit at the 500 ppm PCB level. 15 to 20 people indicated interest.

CLOR-N-OIL™ Field Test Program

Vasu H. Tahiliani
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Eighty-seven utilities have participated in the test program, and so far (as of the end of November 1983) we have received test results back from 40 of them. This report presents the summary of these test results.

A total of 879 oil samples have been tested both with the CLOR-N-OIL test kit as well as on a gas chromatograph. Whenever a CLOR-N-OIL kit user recognized that he erred on his test procedure, either through breaking the capsules in the wrong order or spilling some fluid, the test results were discarded for this summary report.

Of the 879 samples, 424 tested negative (with a blue color at the end of the test) indicating less than 50 ppm of PCB. The remaining 455 tested positive (turned clear). However not all of these samples were drawn randomly, since many users wanted to explore this test method in a narrow critical range of PCB contamination. This led to a larger percentage of oil samples testing clear.

If we were to choose only randomly picked samples, the test results show 372 (51%) blue and 352 (49%) clear. Of the 355 clear samples 161 (22% of the total) did contain more than 50 ppm of PCB and 194 samples (27% of the total) gave a false positive test. This in comparison to 51% of the samples being eliminated from any further tests is quite small. Of course one would like this percentage to get even smaller but in order to safeguard against contaminated samples testing negative, this is the best we can do.

A total of 18 tests showed false negatives, i.e., the CLOR-N-OIL test gave a negative (blue) test, but a subsequent PCB test indicated a contamination level greater than 50 ppm. While we continue to examine the reasons and retest many of these samples, we do have an explanation for many of the tests.

A user who reported four false negative readings in a batch of 20 tests subsequently found that the PCB tests carried out by an independent outside lab gave high PCB readings. The PCB test reported by the lab gave readings between 53 and 126 ppm, whereas the subsequent tests carried out on these same samples at General Electric tested between 2 and 11 ppm.

There were two other problems early in the test program that were rectified through appropriate changes in the instructions. One change was to show through a photograph that if a test sample has a substantial percentage of PCB (above a few hundred thousand ppm) the test sample being heavier than water will sink below the water and this test method will not work.

Another problem was eliminated through the removal of a photo showing a test resulting from a sample contaminated with 40 ppm of Askarel 1242. Here the photograph showed a slight purple ring at the top of the water layer which would look similar

to a test sample if some oil was transferred to tube #2 (in step 4 of the instructions). Since the instructions were revised only two false negatives have been reported.

Conclusions: Through the use of the CLOR-N-OIL screening test one can typically eliminate half of the oil samples from any further testing. The general experience, especially since the instructions were revised, has been exceptionally good. This test method can offer a significant cost savings to the utility industry.

Number of Utilities Participating		87
Number of Utilities that have Reported to Date		40
Total Oil Samples Tested	879	
Blue	424 (48%)	
Clear	455 (52%)	
Random Sampling		
Blue	372 (51%)	
Clear	355 (49%)	
False Positives	194 (27%)	
PCB Contaminated	161 (22%)	
False Negatives	18 (2.3%)	

MONS 214696

INTERPRETATION OF PCB FIELD TESTING KITS

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Due to the increasing number of PCB-in-oil field test kits appearing on the market, it may prove beneficial for those concerned to know the bases upon which these kits operate.

There are two major categories of test types. They are either instrumental, such as the Horiba x-ray fluorescence instrument, or a chemical based detection method, such as the Manleh, Chlor-N-oil, or Centec kits.

Regardless of the category, all these kits are based on the same assumption: that a means of detecting total chlorine can be useful in determining the presence of PCB's in oil It is important to recognize that none of these test methods, neither instrumental nor chemical, directly determine the presence of PCB's.

The PCB molecules are just a very small number of potential organochlorides. Fortunately, transformer mineral oils contain only very small (less than 1 ppm) of naturally occuring organochlorides The most probable types of such chlorinated species present in transformer fluids would be the chlorobenzenes used to dilute the arochlors.

The Horiba instrument technique is based on using x-rays to excite all the chlorine atoms and to use the resultant emissions from the chlorines as a quantitative measurement of the total chlorine content. This method is being demonstrated to be reliable and useful. However, the equipment necessary to carry out such an analysis is costly and while transportable in a station wagon, is not readily portable.

The chemical methods rely upon a chemical reaction to cleave all carbon-chlorine bonds and produce either chlorine, Cl_2, or chloride ion, Cl^-, detectable by some analytical technique less costly and more mobile than x-ray fluorescence.

The chlorine or chloride detection methods most commonly used are colorimetric, a colored solution whose appearance or intensity is dependent on the chlorine concen-

tration, or a chloride ion specific electrode system.

As previously stated, these chemical methods can only be used to "screen" for the possible presence of PCB's. You cannot use these techniques to either quantitativly determine exactly how much PCB is present, or can these techniques be used as a means to identify which particular PCB's are present.

Also contributing to the confusion on interpreting these techniques, are the presence of chlorinated benzene solvents and less than satisfactory analtyical techniques.

These PCB-in-oil tests are also designed to be most useful in samples containing only mineral oil. Scrap oil samples or soil samples may be so frequently contaminated with "other" chlorine containing materials that a direct gas chromatographic PCB analysis is frequently the most economical method for these matrices.

With this background information, it is now possible to discuss the possible types of results and how interferences will affect tha interpretation of these results.

I would first like to discuss chemical methods which utilize a colorimetric method for chlorine detection. There are two kits now available in this classification, Chlor-N-oil and Manleh. Chlor-N-oil uses sodium metal as a reagent, and Manleh uses a sodium organic salt.

As a first consideration, the Manleh reagent has a limited shelf life and is best kept as a refrigerated reagent. Both reagents, when fresh, will completely and rapidly dechlorinate all PCB's and any other organo chlorides present in transformer oils. The Manleh test sequence then uses an aqueous soluble reagent which develops an orange-red color, the intensity of which indicates the quantity of chlorine present. The operator compares the unknown oil sample with two samples of known PCB content, 10 ppm 1242, and 35 ppm 1242. Because of the small color difference involved and because the chlorine content will differ significantly from 1242 to 1260, the 35 ppm was chosen as a "safe" margin for requiring further analysis. With the Manleh kit, there are certain internal checks which should be followed to assume that neither the dechlorinating reagent nor the color reagent have lost their capacity to perform adequately.

The Chlor-N-oil kit uses a different colorimetric reagent system which is again designed to give a color dependent upon the chloride content of the aqueous extract.

As long as the sodium reagent is sealed from air and moisture, the reagent should have a long shelf life. It is possible, but improbable, that excessive moisture in the oil sample would cause incomplete dechlorination. A visual check of the sample should be made to assure that the oil sample does not contain free water along with the oil. Again, due to the inherent uncertainties of total chlorine methods, a safe limit of 30 - 40 ppm 1242 is used to interpret the result from this test.

Our studies have indicated that both these kits are unaffected by aging of the oil, sludge, or other expected transformer related contaminants. Only the presence of organic chlorides can cause errors, and these errors will always be on the conservative side.

The most serious type of situation which could occur is if the reagent does not completely dechlorinate the PCB's. A known PCB concentration should always be run when using these types of kits to check your reagent strengths. Another caution is to never use tap water to dilute or mix your samples as the chlorine from this source will radically change your results.

The other type of kit now commercially available is sold by Centec. This kit uses a chloride specific electrode to determine the chloride ion concentration. Because the dechlorinating reagent is an organo chloride salt, it too has a limited shelf life. Additionally, the data obtained on the final chloride determination is a number, rather than a color. It is important to remember that this number is just as imprecise as the results of the colorimetric tests. In fact, the final millivolt reading is subject to interference by many more factors than are the colorimetric reagents. Electrode conditions, total ionic strength of the solution, and interferring ions from hand and wipe papers are all factors which were determined to significantly affect the analytical results.

Additionally, the very accuracy of the chloride ion electrode determination can cause serious errors unless the proper PCB standards are used to calibrate the instrument.

An example of the type of error which can occur is, if one uses a curve based on Aroclor 1260 as a pass/fail criteria, then the final chloride in concentration, based on the Centec dilutions, is calculated to be 14% higher than the corresponding 1242 solution. The effect that this lower chloride ion concentration has on the meter reading is very significant and could cause the type of interpretation error which

should be avoided.

In summary, it is important that the users of these kits realize that they are designed only to screen samples. A result indicating that chlorine is present does not necessary mean that PCB's are present. A negative chlorine result means PCB's cannot be present.

There are instances where interferences could cause erroneous results, and internal checks should be done frequently.

The proper use and interpretation of these kits can result in reducing gas chromatographic testing by 50 to 60%. The net savings for such a reduction can be very significant. Additionally, these kits provide a rapid and portable means of evaluating potential problems for spills of oils in the field.

CLOR-N-OIL is an EPRI Trademark.

MONS 214700

DETECTION OF PCBs BY INFRARED SPECTROSCOPY

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Polychlorinated biphenyls (PCBs) have been used as cooling and dielectric fluids by electric power utilities in the United States since 1929. Recent concerns for PCBs in the environment have created the need for utilities to measure PCB contamination in transformer oils. Currently, the need exists to determine PCB content in the range from 50 ppm to 500 ppm in transformer oils. The standard procedure for performing these tests is the method of gas chromatography. This method is costly and relatively slow.

Attempts to reduce the complexity of analysis and to increase the number of samples which can be analyzed in a given time have led to the development of a number of specialized methods for PCB analysis. Several of these techniques are being reported in this session of the PCB seminar.

The possibility of using infrared spectroscopy for the detection of PCBs is supported by the fact that the commonly used askarels in transformers have very strong infrared absorption bands as shown in Figure 1. This makes the infrared technique an attractive method for PCB detection and analysis.

As a result of these preliminary spectra, Battelle-Columbus Division proposed to construct for EPRI a field-usable instrument for detection of PCBs in transformer oil based on infrared absorption. Operational parameters for the instrument include:

- Ability to measure PCBs in the range 50 to 500 ppm
- Measurement time of 5 to 10 minutes
- Rugged, portable operation
- Simple operation requiring no special skills of the operator

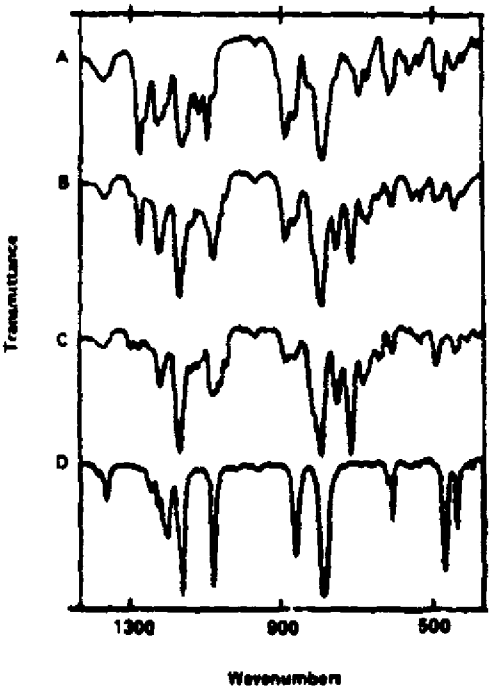

Figure 1. Spectra of various Arochlors: a) 1260, b) 1254, c) trichlorobenzene.

Before going into an analysis of these spectra and a discussion of the instrument developed, it is important to discuss the basic principles of infrared instrumentation and the methods by which data are collected. A typical infrared instrument if shown in Figure 2. Radiation from a globar source is focused into a device which cataloges the radiation intensity at each wavelength. The device could be a dispersive instrument such as a prism or grating monochromator, or it could be a Michelson interferometer. For this discussion it is not important to understand the operating principle of the device. It is only important to know that the radiation is separated into its various wavelengths.

The radiation exits the separator device and passes through the sample. Absorption of the radiation at certain wavelengths occurs in the sample. The radiation which remains is focused on the detector. The energy at each wavelength is recorded and stored for later processing.

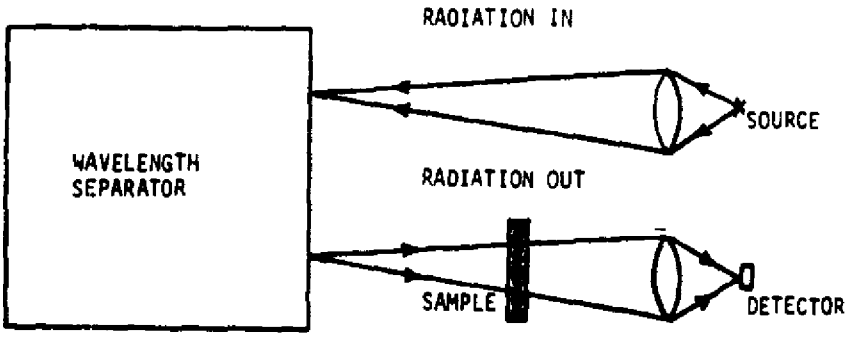

Figure 2. Components of an infrared spectrometer.

Figure 3 shows a typical spectrum recorded by an infrared spectrometer. The absorption process which occurred in the sample produces a spectral pattern which can be recognized and used to determine the components which are in the sample.

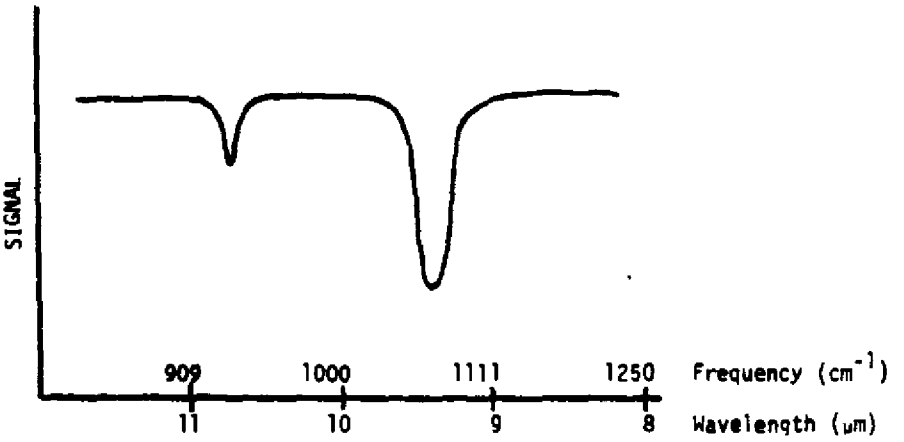

Figure 3. Form of data collected with a transmitting spectrometer.

The rules for absorption are simple. The strength of the absorption is the product of the pathlength of the radiation through the sample, the concentration of the absorbing material, and a quantity called the absorption coefficient. That is,

$$A = k \cdot c \cdot t$$

where k is the absorption coefficient, c is the concentration, and t is the pathlength.

Unfortunately, the experimentalist has control of only two of the three variables. Mother nature dictates the magnitude of the absorption coefficient for any given sample. To detect low concentrations of a given sample, the experimentalist can increase the pathlength through the sample and hope that the absorption coefficient is sufficiently strong to produce an adequate absorption to be detected.

For the specific problem of infrared detection of PCBs in transformer oil, then, the first step is to determine whether the absorption coefficients for the various Arochlor mixtures are strong enough to give good detection at low concentrations. Figure 1 shows spectra of neat samples of various Arochlors. In the spectral region from λ = 8 μm to 12 μm there are very strong absorption bands which are ideal for detection of PCBs. Not only are the absorption features very strong, but they are also unique from one Arochlor to another. This makes identification of the Arochlor possible by infrared methods. Thus, it appears that the absorption coefficients are sufficiently strong to support infrared detection of PCBs even at low concentrations.

Of course, the absorption created by the PCBs is only one part of the total problem. The other part is the absorption created by the transformer oil itself Figure 4 shows the absorption spectrum of a typical transformer oil. Unfortunately, the same spectral region where PCBs exhibited strong absorption shows strong absorption by the transformer oils. Thus, the problem of detection of the PCB absorption must be done in the presence of strong interferences.

Several methods were tried in an attempt to eliminate the problem of oil interference. The simplest of this is known as spectral subtraction. In this method, a spectrum of uncontaminated oil is used as a reference and is subtracted from the spectrum of contaminated oil. If all goes well, the resultant spectrum shows the absorption features of the PCBs only. However, it was quickly discovered that variations in transformer oils produced spectral differences which made the use of spectral subtraction impossible.

Other methods for reducing interferences were tried. They included chromatographic separation, chemical alteration of the PCBs, and chemical clean-up of the oils.

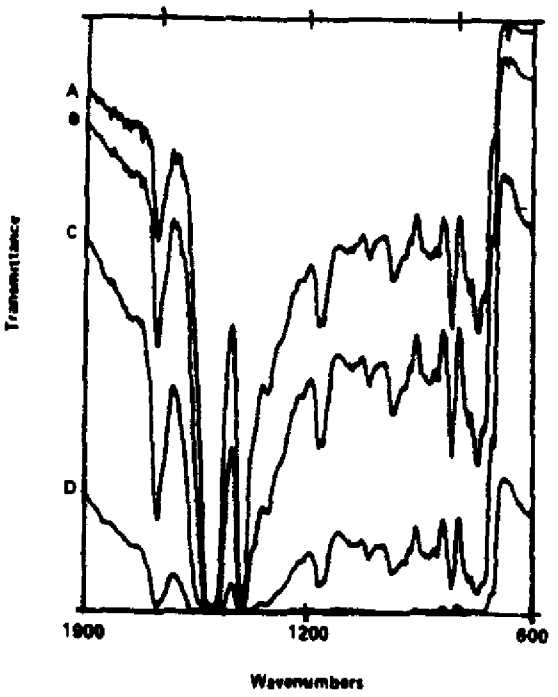

Figure 4. Transmittance spectra through various pathlengths of transformer oil: a) 100 µm path, b) 200 µm path, c) 500 µm path, d) 1000 µm path.

Of these techniques, the chemical clean-up of the oil samples held the most promise for several reasons. It was felt that the operational parameters including simplicity of operation, rapid analysis, and portability would be better served by this clean-up method than by the other methods of eliminating the interferences.

The purpose of the chemical clean-up is to eliminate the various components of the oil which cause direct interference with the PCBs and which cause the wide variations in the spectra of the oils. Since the predominant component causing spectral interference was the aromatic component of the oil, it was decided to attack that component in particular. A sulfonation process was devised which eliminated a sufficient amount of the aromatic oil to detect PCB. However, the process was difficult and required some hazardous materials. This was judged to be less acceptable for field operation than a second method.

As a result, a different chemical method was tried. This method is a modification of a process developed by Union Carbide for recovery of clean oil from PCB contaminated oil. In this process, dimethylformamide (DMF) is added to the contaminated oil to strip the PCBs from the oil. The DMF is heavier than the oil and is easily separated from the oil. After extraction, the DMF is boiled away leaving a small residue of PCB enriched oil. This residue is then analyzed for total PCB content by the infrared method.

This method satisfies all of the operational parameters required for the system. It is fast, simple, and easily transported. Thus, it was decided to design an automated system for processing the oils by this method. Figure 5 shows the design lay-out for the automated Chemistry Processing Unit (CPU). The unit automatically injects the required amounts of oil and DMF, separates the fluids, evaporates the solvent, and injects the resulting sample into the infrared sample chamber. The entire process is computer controlled.

A commercially available Fourier transform spectrometer manufactured by Nicolet Instrument Corp. is used to collect the spectra. Spectra are collected at 4 cm^{-1} resolution over the range from 400 to 4000 cm^{-1} (λ = 25 μm to 2.5 μm). After the spectrum of the sample is collected, it is analyzed by a least square method to determine the concentration of PCB. The data base contains spectral information on Arochlor 1242, 1248, 1254, and 1260. Also included are spectra of trichlorobenzene and DMF. The computer associated with the spectrometer is used to control the Chemistry Processing Unit and to perform the spectral analysis.

At the present time in the program, Battelle is evaluating the efficiency of the automated chemistry and the programs for performing the least square analysis. Analyses of system operation indicate that the 50 to 500 ppm concentration range can be achieved with an accuracy of ± 10% or better with a 10 minute processing and analysis time.

Final packaging of the system will take place during the next few months. It is expected that a prototype PCB detector will be delivered to EPRI in February of 1984.

A Syringe Sample Holder
B Solvent Measurement Chamber
C Oil/PCB Solvent Mixing Chamber
D Lower Phase Liquid Measurement Chamber
E Solvent (DMF) Evaporation Chamber
F Vacuum Valve
G Pressure Valve
H Solvent Valve
I Vent Valve
J Drain Valve
K Sample Line Valve
L To Vent
M To Drain
N To Vacuum Pump
O From Pressure
P IR Cell
Q To Solvent Pump

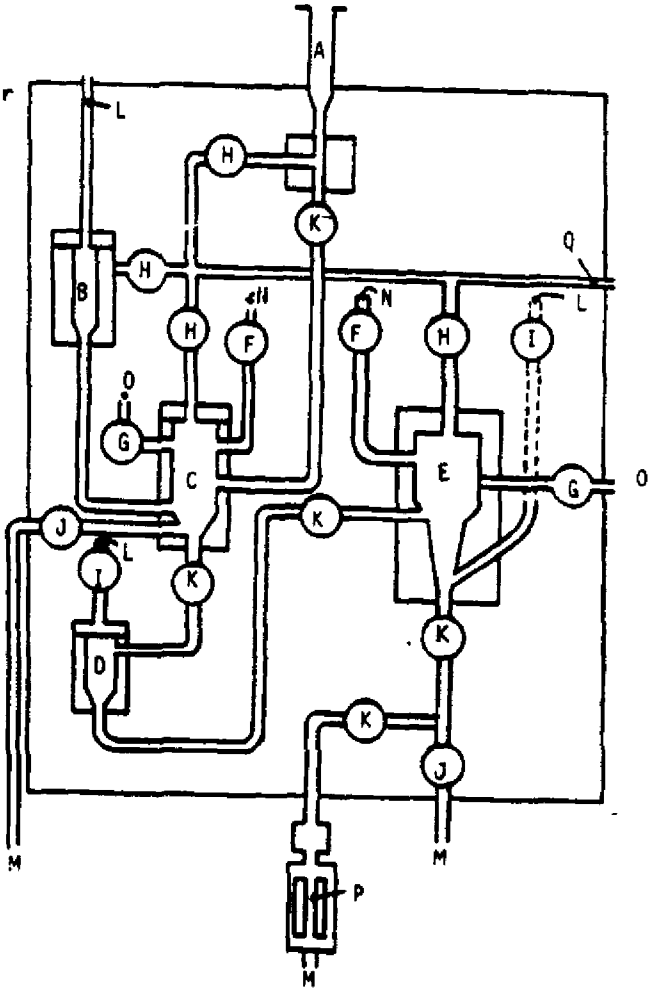

Figure 5. Design lay-out for automated Chemistry Processing Unit.

Discussion

Q1. How mobile is the instrument?

A. The instrument cannot be moved while treating a sample, but when properly prepared for shipping, there is no problem.

Q2. How about the sample thickness?

A. The cell is fixed and never dissassembled, therefore sample thickness is constant.

Q3. How does the cost compare to G.C.?

A. The author did not know the cost of G.C.

FIELD DETERMINATION OF AROCLORS USING AN AUTOMATED ELECTRON CAPTURE DETECTOR GAS CHROMATOGRAPH

J. E. Picker and B. N. Colby
S-CUBED

Owing to existing Goverment regulations concerning PCB containing materials, S-CUBED undertook a search for a reliable and portable instrument to identify and measure Aroclors. Several approaches to the problem were evaluated with respect to four major considerations; namely:

1. The instrument must be transportable in order to perform field analyses.
2. It must require only limited operator experience or training.
3. Expected regulatory procedures for the determination of Aroclors should be involved.
4. The range over which the instrument can monitor PCB concentrations should be as wide as possible.

To meet these needs, S-CUBED, with partial funding from EPRI, decided to develop a field transportable gas chromatograph with an electron capture detector called the PCBA-102. Although the concept of a transportable gas chromatograph is not novel, the PCBA-102 is unique in that it carries an onboard microcomputer to perform the data interpretation which usually requires a trained analyst. The computer monitors the output of the electron capture detector, identifies the Aroclor and determines the concentration in the sample. Little operator experience or knowledge of data interpretation is required. The operator prepares the sample using a simple sample preparation procedure and injects it into the gas chromatograph. All other functions are performed by the microcomputer. This report describes the PCBA-102, how it works and how it is used, and provides comparison data obtained using the PCBA-102 and ASTM/EPA procedures to determine PCBs in oil and soil samples.

MONS 214709

INSTRUMENT

Figure 1 shows the PCBA-102 front panel. On the left-hand side is a removable oven module which houses the injection port, the GC column and electron capture detector, as well as the necessary heating hardware. In the center of the front panel are toggle switches for carrier gas shutoff and diversion to a rotometer for flow measurement. Once flow is set, no adjustment is necessary. Also placed on the front panel are five lighted pushbuttons and one light which permit the operator to (1) supply power to the PCBA-102, (2) supply power to the oven heaters, (3) monitor the temperature, (4) select the instrument calibration mode, and (5) to begin sample introduction. Calibration is required each time the instrument is powered up and after every tenth sample has been analyzed. This provides continuing checks on instrument sensitivity and maintains accurate reported results. Also provided on the front panel is a paper tape printer for output of analysis results.

A block diagram of the instrument in shown in Figure 2. The instrument requires a small cylinder of Argon/Methane carrier gas and an oxygen trap to remove any trace of oxygen from the carrier stream. The gas and trap are connected to the rear of the instrument using standard Swagelock Quick-Connect(R) fittings. This provides a very smooth and secure connection. Carrier gas enters the rear of the instrument and flows through the oven assembly for preheating to the injector port where samples are introduced. The flow then proceeds through the column into the detector and finally through the toggle switch and rotometer. Signal from the detector is fed to the electrometer which is connected to the interface board. The interface board directs data coming from and to the electrometer, the front panel controls and the output printer, and the microcomputer.

Figure 3 shows sample chromatograms obtained in the laboratory using a gas chromatograph similar to the PCBA-102. These traces are plots of

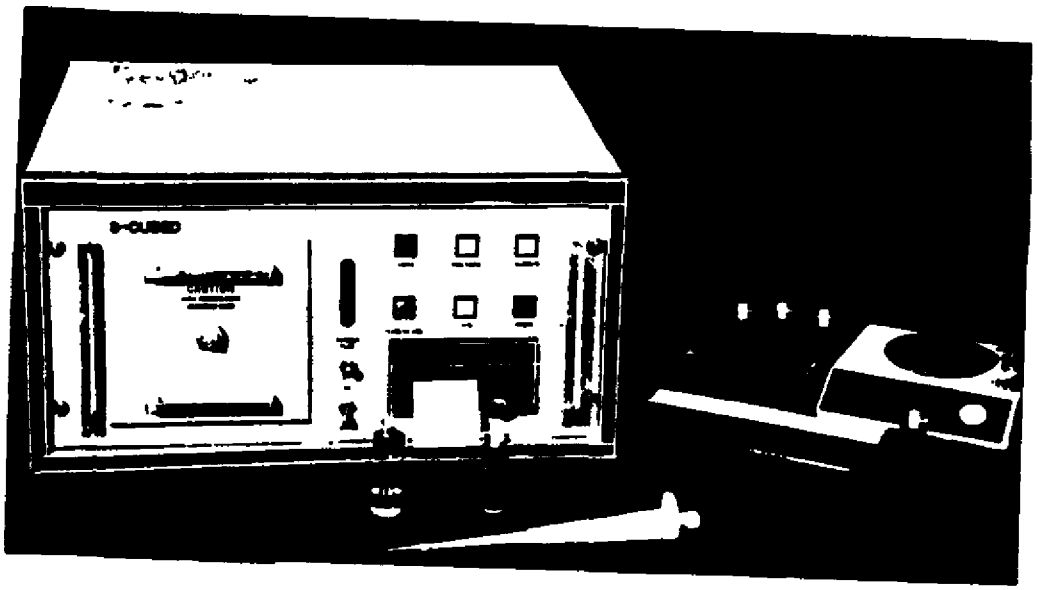

Figure 1. PCBA Front Panel

MONS 214711

GENERALIZED SCHEMATIC OF PCBA-102

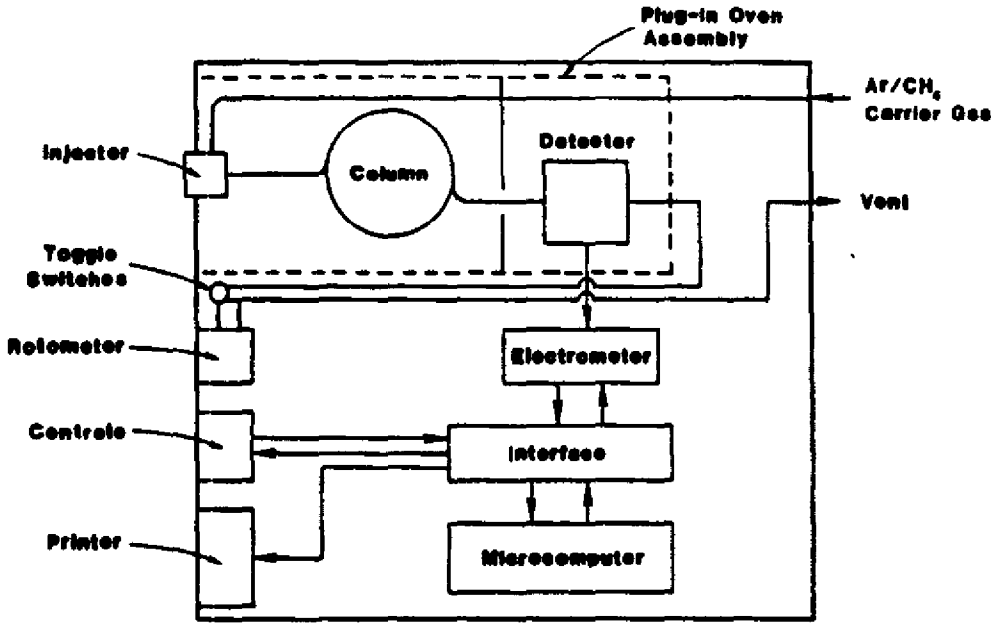

Figure 2. Block Diagram of PCBA-102

MONS 214712

CHROMATOGRAMS OF SELECTED AROCLORS

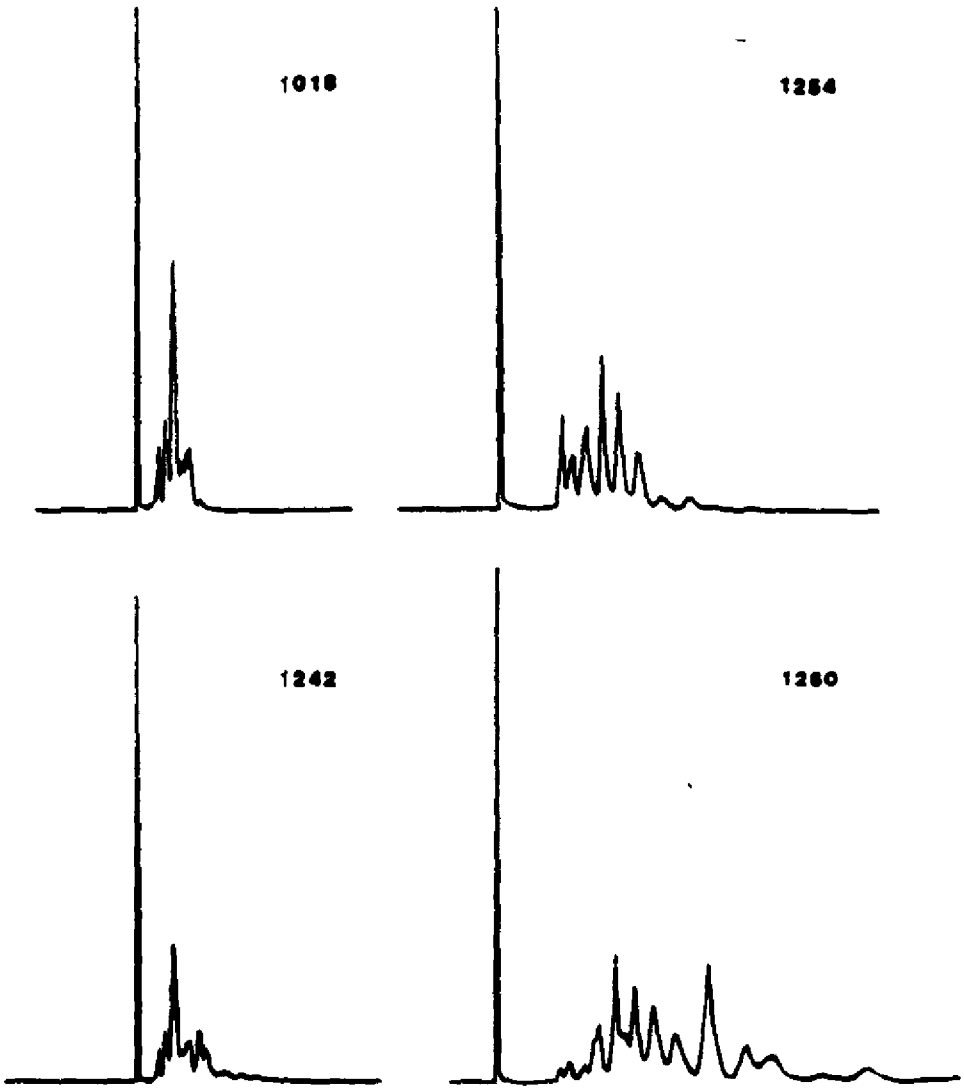

Figure 3. Chromatogram of the Four Target Aroclor Mixtures

the detector response versus time for common Aroclors (PCB mixtures). Analog pluts can be obtained from the PCBA-102 by connecting the analog signal output on the back panel to a strip chart recorder. The PCBA-102, however, "records" chromatograms in its microcomputer. Subsequent to recording the chromatogram, it performs the chromatogram pattern recognition and quantitation calculations a laboratory analyst would normally be required to do. The first of these activities is to locate and identify the peaks in the chromatogram. The PCBA-102 performs this function automatically using its peak finding program.

Once an analyst has found the peaks and has determined their retention times and areas, he would decide whether or not the "pattern" represents an Aroclor. The PCBA-102 performs this function using a pattern recognition algorithm. The algorithm uses the peaks in the chromatogram and compares their retention timas and areas to those of standard Aroclor patterns which are stored in microcomputer memory. The algorithm then determines a "MATCH" value similar to the COS e function encountered in multivariant statistics. The function is a measure of how closely the sample pattern matches that of an each Aroclor stored in computer memory. For convenience this "MATCH" number is based upon 1000 representing a perfect comparison. "MATCH" values above 800 are nigh and indicate good correlation between the sample and the reference Aroclor in memory. A comparison of "MATCH" values for the Aroclors is shown in Figure 4. The low values attained for most of the comparisons indicate that this calculation can be used reliably to differentiate among the Aroclors.

Once the Aroclor has been identified the program then proceeds to determine how much of that Aroclor is present. The program calculates concentration based on individual peaks by comparing them to corresponding peaks in the stored standard. A statistical evaluation is then carried out to reject peaks which are outliers presumebly resulting from interferences. The remaining peaks are used to report concentration on the printer.

MONS 214714

AROCLOR	DETECTED MATCH			
	1016	1242	1254	1260
1016	**999**	740	<1	<1
1242	770	**999**	8	<1
1254	<1	2	**999**	12
1260	<1	<1	18	**999**

Figure 4. Calculated "MATCH" Values for Standard Aroclor Mixtures

MONS 214715

The PCBA-102 can be readily transported into the field in a van or stationwagon. Its power requirements are such that it can be operated either from line voltage or through an invertor connected to a vehicles electrical system. It consumes about 300 watts when heating from a cold start but requires only about 200 watts once it reaches operating temperature. The PCBA-102 measures 10 x 19 x 20 inches and weighs approximately 55 pounds. The unit requires a carrier gas cylinder but can operate for several days a on small cylinder. The required gas is comprised of 5 percent methane in argon and should be of the highest quality available. A two-stage pressure regulator is used to reduce pressure from the cylinder to the unit. The second stage of the regulator should be regulated from zero to 100 psi and is used to adjust flow through the instrument. In addition to the gas requirement, an oxygen trap should be connected between the gas cylinder and the PCBA-102. One trap is provided with the instrument and it should last for several months if gas quality is good. The PCBA-102 and the trap are provided with Swagelock Quick-Connect(R) fittings for easy installation.

APPLICATIONS

The PCBA-102 is designed to measure four Aroclor mixtures in transformer fluid and/or soils sample extracts. Sample preparation is required prior to analysis to clean the sample and adjust concentration to the range required by the instrument. A kit is available in order to help perform these simple manipulations. Sample preparation is based on EPA and ASTM methods which involve partitioning with hexane and concentrated sulfuric acid.

When power is supplied to the instrument, the printer responds with the message that the power has been turned on and that the instrument ovens are heating. When the ovens have reached temperature, a second message appears indicating that the PCBA-102 is ready and that calibration is required. The front panel calibration button is lighted to remind the operator of this. At this point the operator presses the calibration button and sample button, and injects one microliter of the calibration standard. The calibration standard is a

solution containing 1 ppm of Aroclor 1254. The instrument checks to make sure that this Aroclor is found in the calibration mixture. Aroclor concentration is calculated and placed in memory. This value is used to calculate a response factor for the instrument at the present time. This factor is used in quantitation of the next ten samples. In addition, the retention times of peeks in the chromatogram are checked against stored values to make sure that the instrument is operating properly. If retention times are not correct, then a message appears asking for flow corrections. If the instrument is unable to calibrate due to improper operating conditions, no sample analyses can be performed. If the instrument was able to calibrate properly the necessary "READY" will be printed and a sample can be introduced into the PCBA.

For transfomer fluids a 100 µL aliquot is introduced into a vial containing 10 mL of hexane and 10 mL concentrated sulfuric acid using a repeating pipette. The vial is then closed and shaken vigorously. The PCBs remain in the upper hexane layer while interferences go into the acid layer. When the two layers have separated, one microliter of the hexane is injected into the PCBA-102 using a 10 µL syringe. The amount injected is a constant and does not have to be adjusted by the operator.

To analyze soils, an optional balance is provided in the sample preparation kit. The operator places a vial containing e premeasured quantity of methanol on tne balance and tares the balance to zero by pressing a button. The operator then adds 1.0 ± 0.1 grams of soil to the vial. The vial is shaken and the soil allowed to settle. One mL of the methanol solution is then introduced into e viel containing hexane and sulfuric acid using a pipete. This viel is then sheken and a 1-mL aliquot introduced into the PCBA as previously described for the oil analysis procedure. The PCBA-102 automatically acquires the resulting chromatogram, identifies the Aroclor from the peak pattern and performs quantitation based upon peak areas. This all requires approximately eleven minutes from start to finish.

The output of the PCBA-102 is a paper tape from the printer. This tape output includes the recognized Aroclor, the "MATCH" value indicating reliability of the identification measurement, the concentration of Aroclor found in parts per million and an associated error with the analysis. An example of the output tape is shown in Figure 5.

PERFORMANCE TESTS

The PCBA-102 was tested for performance in several areas. The first was a check of measurement linearity. A constant current electron capture detector should be linear over a very wide range, approximately five orders of magnitude, however, owing to software considerations and a need to limit the amount of material injected on the column, the practical range of the instrument is three orders of magnitude. Triplicate injections of Aroclor 1254 at a level equivalent to 1,000 ppm in a sample yielded an average reported concentration of 921 ppm with a standard deviation of 39 ppm. Triplicate injections at 100 ppm yielded an average reported value of 104 ppm with a standard deviation of 3 ppm. Triplicate injections at 10 ppm yielded an average reported value of 10 ppm with standard deviation of 1 ppm. Figure 6 graphically depicts these tests and shows that the instrument is linear over the range of 10 to 1000 ppm. Based on this it is clear that nonlinearity errors are small compared to errors associated with sample preparation and possible interferences in the chromatogram.

The ultimate test of any instrument is how it performs in comparison with others. To test this several oil and soil samples were prepared and analyzed using EPA/ASTM procedures and the results compared with those obtained using the PCBA-102. The results of these analyses are depicted in Table 1 for various transformer fluids. In each case the PCBA-102 correctly identified the Aroclor and quantitation was very close for all samples.

MONS 214718

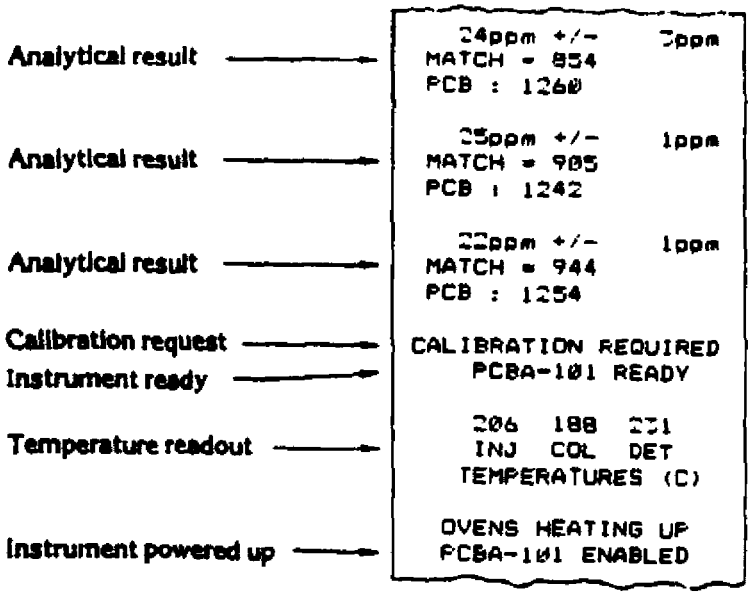

Figure 5. Printer Output Tape

MONS 214719

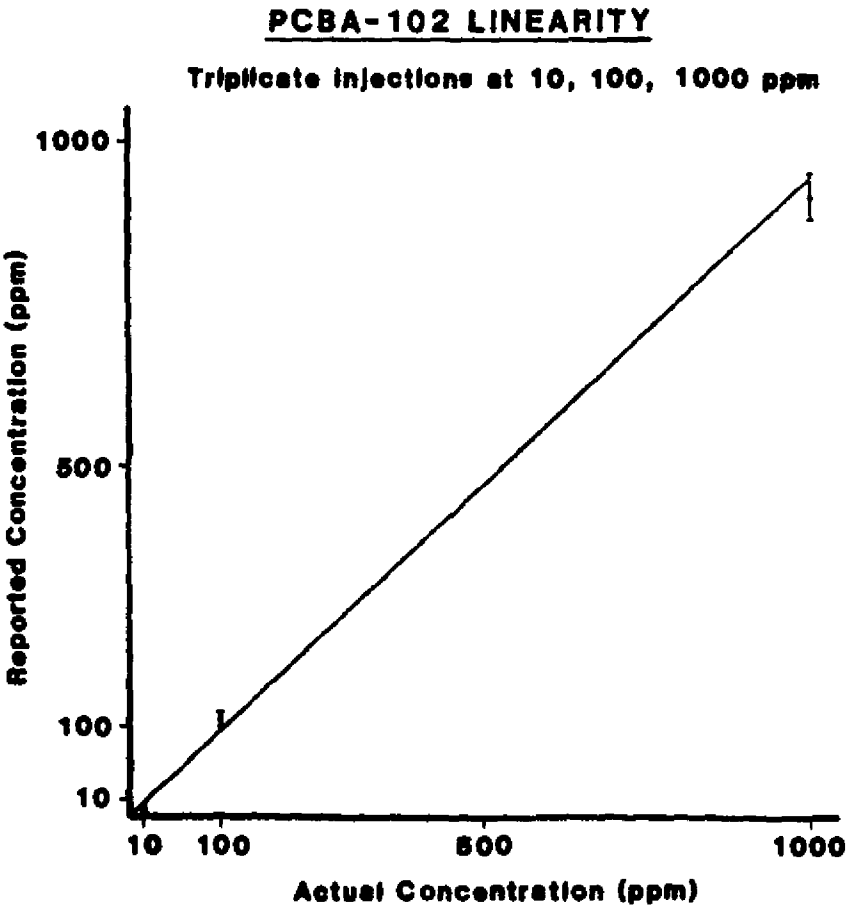

Figure 6. PCBA-102 Linearity

MONS 214720

TABLE 1

ANALYSIS OF TRANSFORMER OIL CONTAINING PCB COMPARISON OF EPA/ASTM PROCEDURE VERSUS PCBA-102
(values in parts per million)

IDENTIFICATION		QUANTITATION	
ASTM/EPA	PCBA-102	ASTM/EPA	PCBA-102
1260	1260	242	276
1260	1260	35	34
1254	1254	51	30
1254	1254	473	364
1242	1242	55	37
1242	1242	400	470
1260	1260	242	244
1260	1260	35	30

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The instrument was also tested using PCB contaminated soils in conjunction with a two-step dilution. Methanol is first used to extract PCBs from the samples. This extraction is followed by the hexane-sulfuric acid partition cleanup used for oils. The method was compared to a procedure using exhaustive hexane extraction in a soxhlet apparatus followed by exhaustive acetone extraction with the combination of the two extracts being measured. Table 2 lists the results from these tests. In all but two cases the PCBA-102 Methanol procedure correctly identified the Aroclor and quantitation agreed well. In one case the PCBA did not detect any Aroclor because the actual concentration was below the instrument's 10 ppm detection limit. The second disagreement resulted for a sample which seemed to contain both Aroclors 1242 and 1016 in a combination. The PCBA-102 chose 1016 as the closest match Aroclor and quantitated accordingly. Quantitation for this sample was very close by both methods.

Also provided in on Table 2 are results from two EPA performance evaluation samples consisting of PCB contaminated sediments. The "true value" is that provided by EPA who indicated that these samples contained interfering materials and that quantitation and identification would not be straightforward. The PCBA-102 was not able to recognize Aroclor 1242 in the first sample. Rather it selected Aroclor 1016 which has a very similar pattern. The quantitation was very close. In the second case the Aroclor was correctly identified and again the quantitation was reasonably close. It should be pointed out that the standard deviation provided by EPA for the 24 ppm sample was 11 ppm based on their analyses. Consequently the 3 ppm difference between the PCBA-102 and the "true value" is excellent.

SUMMARY

The PCBA-102 computerized gas chromatograph is able to accurately and reliably identify and quantify Aroclors in transformer fluids and soils. The instrument performs analytical chemistry functions in the field which usually require a trained analyst and complex instrumentation.

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TABLE 2

ANALYSIS OF PCB CONTAMINATED SOILS
BY PCBA-102/METHANOL PROCEDURE VERSUS
EXHAUSTIVE HEXANE SOXHLET EXTRACTION
FOLLOWED BY ACETONE EXTRACTION

IDENTIFICATION		QUANTITATION	
SOXHLET EXTRACTION	PCBA-102	SOXHLET EXTRACTION	PCBA-102
1242	ND	5	ND
1016	1016	9	5
1016	1016	34	41
1242 + 1016	1016	12	13
1016	1016	40	62
1016	1016	110	176
1016	1016	215	323
		"true value"	PCBA-102
1242	1016	24*	21
1242	1242	48*	36

ND = Not Detected.

*EPA performance evaluation samples.

MONS 214723

Discussion

Q1. How dry must the sample be?

A. Field samples taken after a heavy rain have come out well. Spiked, wet samples have also compared very well with dry samples.

Q2. How about identification of various Aroclors?

A. The instrument is designed for utility spill analysis, not for combinations of Aroclors.

MONS 214724

THE SEMIQUANTITATIVE DETECTION OF POLYCHLORINATED BIPHENYLS (PCBs) IN CONTAMINATED SOILS BY THIN-LAYER CHROMATOGRAPHY

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Section 1

INTRODUCTION

As a consequence of their persistence, their ability to accumulate, and their distribution throughout the environment, polychlorinated biphenyls (PCBs) have become a well known environmental pollutant. Bird and animal studies have shown that PCBs can induce various toxic disorders (1, 2). PCBs have also become a major concern to man because of his residence at the top of most food chains where he can concentrate substantial amounts of PCBs.

PCB-filled capacitors are potential sources for PCB release to the environment. If a pole-top capacitor ruptures, PCB released to the area beneath the pole must be collected and contaminated ground removed. However, at the present time samples must be sent to a laboratory and analyzed before the extent of contamination or the amount of PCB remaining after a clean-up operation can be determined. Off-site analyses are time consuming and can delay site restoration for many days. More important during these time delays, contaminated ground may be left exposed to the open environment where it could be washed or carried away.

Thin-Layer Chromatography (TLC) methods have previously been described (3, 4), which are capable of determining trace levels of PCBs in biological matrices. The main goals of this work were to investigate the detection of PCBs in contaminated soils using thin-layer chromatography and to evaluate its use as an aid during clean-up operations. Possible TLC interferences from chlorinated pesticides or high concentrations of mineral oil were also investigated.

Section 2

EXPERIMENTAL

APPARATUS

Baker-flex ^{R} TLC plates, type "Silicon Gel 1B", were used. Plates were 20cm x 20cm with a coating thickness of 200 microns, and were activated at 150°C for 15 minutes.

Germicidal lamp, capable of emitting strongly in the deep ultraviolet region.

Chromist ^{TM} indicator solution spray unit.

A Perkin-Elmer Model 3920B gas chromatograph equipped with a Ni^{63} electron capture detector was used. A glass column (1.8 mm x 4 mm i.d.) was packed with 3% OV-101 on 100-120 mesh "Gas Chrom Q". The column and detector were maintained at 200°C and 325°C respectively. The carrier gas was 5% methane in argon, and the flow was maintained at 80 cc/minute.

REAGENTS

"Silver Nitrate Indicator Solution." ACS Reagent Grade silver nitrate (2.0 grams) were dissolved in 225 mls of denatured alcohol and 25 mls of distilled water. The solution is stored in an amber bottle.

All acetone, acetonitrile, hexane, and methylene chloride used were Burdick & Jackson's "Distilled in Glass" grade.

Aroclor 1242, Monsanto Lot #194 was used to prepare the 25,50,100,250 and 1000 ppm (ug/ml) standards in hexane that were used to obtain the data shown in Figure 3-1. All other specifit aroclors and pesticide standards were diluted in hexane from 100 ug/g aroclor and pesticide standards obtained from the Polyscience Corp., Kit #590A.

PROCEDURE

Soil Extractions

Individual samples of contaminated soil (25 grams) are placed into separate 500 ml glass jars equipped with aluminum lined caps. (If the soil is very wet, one can add 10-20 grams of anhydrous sodium sulfate to absorb the moisture.) Approximately 25 mls of hexane are added to the jar to saturate the sample. An additional 20 mls of hexane are then added, and the soil/hexane mixture is shaken for two minutes. The extract is then decanted and suction filtered through a glass fiber filter. The same sample of soil is then extracted a second time with another 20 mls of hexane. This extract is also decanted and filtered, and then combined with the first extract. The final volume is adjusted to 50 ml in a graduated cylinder. This final solution represents 25 grams of soil in 50 ml of hexane.

TLC Determination

An activated TLC plate is marked with a pencil line 3 cm from the bottom. Each soil extract (40 microliters of sample) is placed on this line, separated by a minimum of 1-1/2 cm. Each extract is spotted, applying only a 2-4 microliter portion of the sample at a time and allowing the spot to completely dry between applications. To each plate 20 microliters of a 50 PPM aroclor 1242 standard is also spotted to ensure complete plate development.

The plate is developed in a chromatography jar in (1:4) acetone/hexane, allowing the solvent front to ascend 3/4 the length of the plate. The plate is removed, air dried, and sprayed with the silver nitrate indicator solution. It is then exposed for ten (10) minutes to the ultraviolet light of the germicidal lamp at a distance of approximately 5 cm. above the bulb. Any PCB present will develop as a dark spot with an R_f value of roughly 0.50. If the 50 PPM standard is not readily visible, the plate should be exposed to ammonia vapor, which lightens the background in preference to the TLC spots; it is then re-exposed to the ultraviolet light for ten (10) minutes.

The relative darkness and size of a developed spot is related to its PCB concentration. By using twice the volume of sample extract as standard solution, one can compare the sample spots directly to the 50 PPM standard spot. If the sample spot size (length in mm) is less than the 50 PPM spot size, or not detectable, the sample contains less than 50 PPM of PCB (on an as received basis). If the sample spot size is larger than the 50 PPM standard, then one estimates sample concentration from a standard working curve. The standard working curve can be prepared by spotting and running 20 microliters of a 25,50,100,250,500 and 1000 PPM standards.

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Section 3

RESULTS

TLC PROCEDURE - FIELD RESULTS

A standard working curve for PCBs in the concentration range of 20 to 1000 PPM for the TLC method was constructed as a semilog plot of PCB concentration (PPM) vs. spot size (length in mm). This semilog plot was found to be approximately linear over this range (see Figure 3-1).

Based upon the working curve and an experimental uncertainty of ± 1 mm for the spot size, the PCB concentrations for ten possibly contaminated soils from two sites were estimated in the field following a capacitor spill. These results were then compared to the ECD-gas chromatography results obtained in the laboratory (see Tables 3-1 and 3-2). The PCB concentrations were correctly estimated for all soil samples. Furthermore, the in-field soil extracts of samples D and E from site #1 were also analyzed using the ECD-gas chromatograph to determine the recovery efficiency of the field extraction vs. the soxhlet extraction. Field extraction recoveries for samples D and E were 91% and 101% respectively, indicating acceptable recoveries.

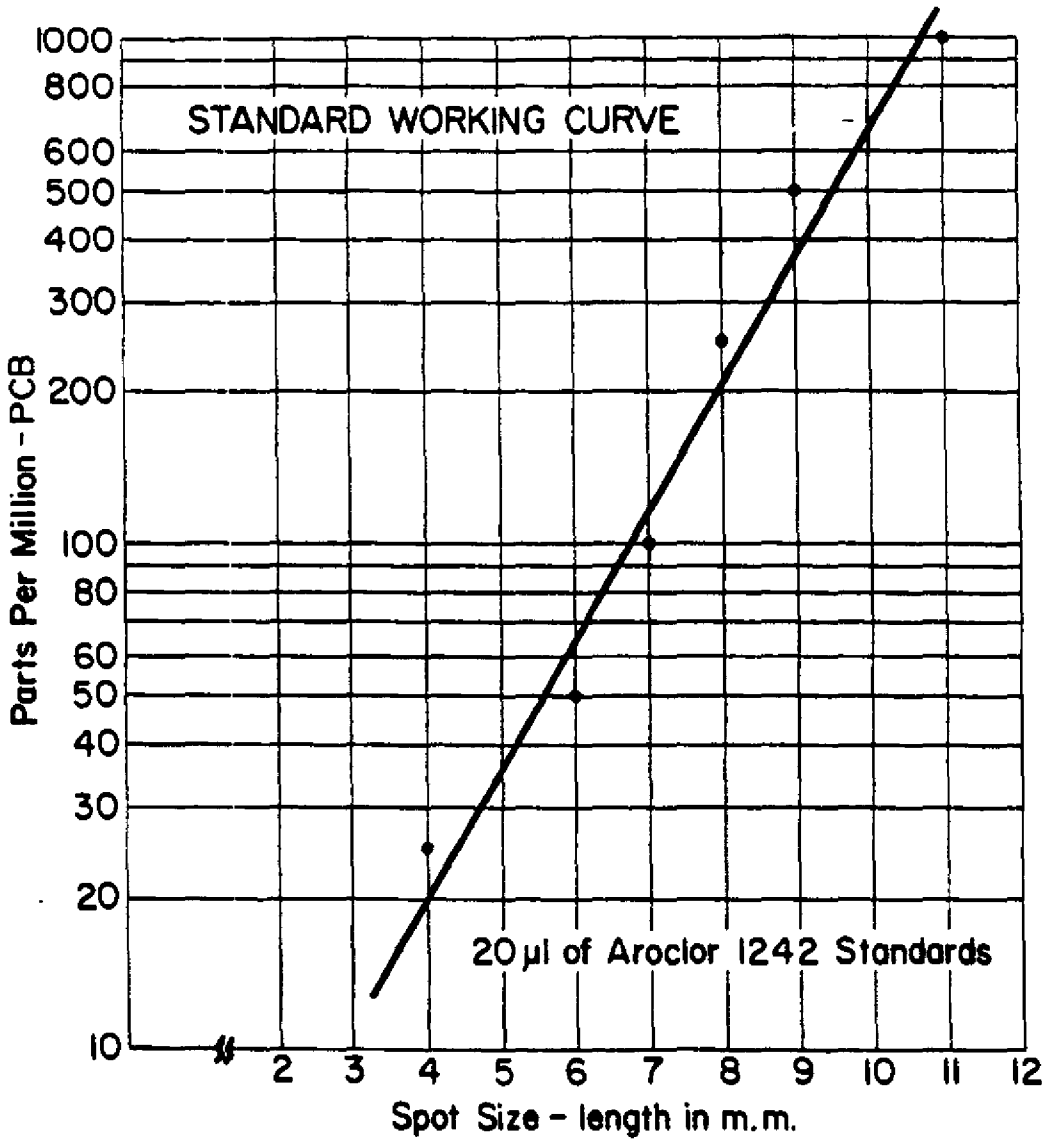

Figure 3-1. PPM PCB (µg/ml) vs. Spot Size

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TABLE 3-1

PCB CONTENT OF CONTAMINATED SOIL - SITE #1
(TLC vs. ECD - GAS CHROMATOGRAPHY RESULTS)

Sample	Thin - Layer Chromatography		ECD - Gas Chromatography
	Spot Size (mm)	PPM PCB (as rec')	PPM PCB[1] (as rec')
A	9 ± 1	200 - 600	375
B	15 ± 1	>1000	7390
C	16 ± 1	>1000	7280
D	15 ± 1	>1000	1990(2010)[2]
E	8 ± 1	100 - 350	101(92)[2]
50 PPM Standard	6 ± 1	-	-

[1]Reported as aroclor 1242. Results are based upon soxhlet extractions of sub-samples from the originally contaminated soils.

[2]The values in parentheses were obtained from the soil extracts performed in the field. They represent a 101% and 91% recovery for samples D and E respectively when compared to soxhlet extraction results.

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TABLE 3-2

PCB CONTENT OF CONTAMINATED SOIL - SITE #2
(TLC vs. ECD - GAS CHROMATOGRAPHY RESULTS)

Sample	Thin - Layer Chromatography		ECD - Gas Chromatography
	Spot Size (mm)	PPM PCB (as rec')	PPM PCB (as rec')
A	ND	< 25	< 10
B	ND	< 25	< 10
C	ND	< 25	23
D	ND	< 25	< 10
E	ND	< 25	< 10
50 PPM Standerd	6 ± 1	-	-

ND = Not Detected.

TLC PROCEDURE - INTERFERENCES

Chlorinated peeticidee have been known to interfere with the TLC determinations for PCBe (5, 6). Standerde of DDT, DDE, and Heptaclor and Aroclore 1242, 1248, and 1254 (50 PPM concentratione) were run separately uaing the TLC method. The developing eolventa were veried in an effort to reduce the interferencee from the peeticidee. Tha aolvente choeen were hexane, (1:4) acetone/hexane, methylene chloride, and eceto nitrila (hexane seturated) which resulted in a wide range of R_f veluee for the PCBe. Based upon the R_f veluee lieted in Table 3-3 for DDT, DDE. Heptaclor, and Aroclore 1242, 1248, and 1254, two concluaione were drawa: (1) Incomplete eeparetion of the chlorinated peeticidee from PCBe can be expected for all eolvente teeted. This overlep will reeult in poeitive reeulte when teeting for PCBs. However, the preeence of chlorineted peeticidee in aoile at concentratione near 50 PPM is highly unlikely. (2) Incomplete seperetion of the individual eroclore indicates that the TLC method is a non-specific teet procedure.

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Interference from high concentrations of mineral oil was also investigated in the solvents listed previously using mixtures of 1000, 10,000, and 100,000 PPM mineral oil and 50 PPM PCB in hexane. Table 3-4 lists the R_f values for various concentrations of oil and of PCBs at a 50 PPM level using different developing solvents. For mixtures containing 10,000 PPM oil the detection of the PCBs was inhibited when methylene chloride or acetonitrile was used as the developing solvent. However, even when 100,000 PPM of oil were present which resulted in extensive tailing, 50 PPM of PCBs were still detectable when the developing solvent was hexane.

TABLE 3-3

SEPARATION OF PCBs AND VARIOUS CHLORINATED PESTICIDES BY THIN-LAYER CHROMATOGRAPHY

Solvent System	R_f Values[1]					
	PCB[2]			Pesticide[3]		
	Aroclor 1242	Aroclor 1248	Aroclor 1254	DDT	DDE	Heptaclor
Hexane	0.29	0.29	0.28	0.18	0.26	0.25
(1:4) Acetone: Hexane	0.50	0.50	0.48	0.45	0.48	0.51
Methylene Chloride	0.64	0.64	0.64	0.68	0.68	0.68
Acetonitrile (Hexene Saturated)	0.89	0.87	0.85	0.89	0.87	0.85

[1]Total weight of each compound used was 1 microgram (20 microliters of a 50 PPM solution).

[2]All three aroclors tested showed approximately equal intensities at the 50 PPM level.

[3]The (o,p) and (p,p') isomers of DDT and DDE were not separated.

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TABLE 3-4

SEPARATION OF PCBs AND MINERAL OIL BY THIN-LAYER CHROMATOGRAPHY

Sample Mixture	R_f Values for Different Solvent Systems			
	Hexane	(1:4)Acetone: Hexane	Methylene Chloride	Acetonitrile (Hexane Sat.)
PCB-50 PPM[1] + Mineral Oil-1000 PPM	0.30 ND	0.49 ND	0.64 ND	0.85 ND
PCB-50 PPM + Mineral Oil-10,000 PPM	0.29 0.59±.08[3]	0.50 0.63±.08	0.66 0.71±.06	- *[4]
PCB-50 PPM + Mineral Oil-100,000 PPM	0.30 0.50±.16	0.49 0.56±.16	- *	- *

[1]Aroclor 1242.

[2]ND - Not Detectable.

[3]When developed the mineral oil appears as an off-white spot on a brown background. The "±" value is the range of R_f values with which the mineral oil overlaps.

[4]Extensive tailing.

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Section 4

SUMMARY

The thin-layer chromatography method investigated was found to be sensitive at the 50 PPM level and yielded results that are at least a good estimate of the PCB concentration of contaminated soil. The method can be easily executed in the field by a trained technician and is fairly rapid (5 samples/TLC plate/hour). Therefore, the TLC method could serve as an aid during clean-up operations of soils contaminated with PCBs following a capacitor rupture. As an aid it can be used to expedite the clean-up operations, helping to minimize the amount and length of time contaminated soil is left exposed to the environmental. Furthermore, it can help to eliminate second and third costly clean-up efforts. However, it is not intended to be used as a final clean-up confirmation. The final confirmatory samples should be analyzed using the ECD-gas chromatograph procedure which is more accurate and sensitive.

Section 5

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MONS 214736

Discussion

Q1. Why is Hexane used in view of it's toxicity?

A. Other solvents probably could be used.

Q2. What is the effect of other chlorides - particularly TCE?

A. Most of the solvents would be quite volatile and would evaporate. Unless concentration was extremely high, there should not be a problem.

MONS 214737

PORTABLE INFRARED FIELD MONITOR FOR PCBs: PHASE II

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ABSTRACT

Since the Dallas, Texas EPRI Seminar of December, 1981, a great deal of effort has been expended on developing and commercializing PCB destruction and cleanup from askarels and transformer oils. PCB-contaminated oil is still being stockpiled at an alarming rate and PCB spills continue to occur. These problems have proven to be extremely challenging ones with no widely accepted, definitive and economically feasible answers. Unfortunately, regulations have become more stringent and are more widely affecting personnel throughout the electric power industry.

It is hoped that this Phase II* study on refining and field proving an infrared (IR) portable monitor, preliminarily developed in Phase I** for PCBs in Spill conditions, will be of assistance in each of the aforementioned problem areas. The largest PCB problems occur in the form of PCB-contaminated oil in field transformers and storage containers, and pure askarel in transformers and capacitors. The most immediate need for a portable field instrument is still for use under PCB spill conditions. A simple, rugged, reproducible, and PCB-specific infrared analyzer and sampling protocol has been developed and field tested to fill this void.

Phase II has served to verify and refine significant findings of the preliminary study. All IR wavelengths have been optimized by digitization and subsequent absorbance maximization. The selection of extraction solvents has been finalized based on the application and physical properties such as volatility, toxicity, miscibility and PCB extraction efficiency. The latter two characteristics have been extensively studied utilizing a 30 x 30 miscibility matrix and distribution coefficients measured by shake out extractions and subsequent electron capture GC or radiolabeled PCB counting techniques. The emphasis has been on the development of a solvent/soil extraction procedure followed by a fixed-film application on a Horizontal Multiple Internal Reflectance (HMIR) stage coupled with a Foxboro Miran 980 IR analyzer. The refined protocol of fixed-film application using volatile, PCB-ladened solvents requires a single shake out extraction in a standard scintillation vial using relatively small amounts of sample (e.g., soil or oil) and solvent. Using such volatile extraction solvents, results in an actual preconcentration step prior to analysis and allows us to see 25-50 ug PCB/g Soil routinely, and down to 5 ug PCB/g Soil using additional sample and solvent. This technique has been aided by the development of a stainless steel "sample containment weir" which is placed over the HMIR window. Further studies have been made to minimize the effects of soil moisture on PCB extraction and potential interferences by pesticides and herbicides possibly present at spill sites. A brief instrument comparison study has been carried out with the Miran 980/HMIR (microprocessor controlled, baseline subtract, matrix calibration, etc.) and the simpler and less expensive Miran 1A/HMIR (meter read out and manual wavelength selection,

calibration, and baseline subtract). A final IR instrument selection and protocol will be made. The final stage of the study involves the analysis of actual field samples and field testing to establish the utility of the unit and sample protocol for portable or mobile use.

*Present research effort sponsored by EPRI Agreement RP1263-10 with C/S Associates, Inc. of Oak Ridge, Tennessee.

**Preliminary research sponsored by EPRI under Interagency Agreement RP12630-5; DOE No. ERD-80-061 under Union Carbide Corp. contract W-7405-eng-26 with the U.S. Department of Energy of Oak Ridge National Laboratory. EPRI CS-2628, Project 1263-5 Final Report, January 1983, "Development of a Portable Monitor for PCBs" with W.D. Bostick and S.R. Dinsmore.

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PORTABLE INFRARED FIELD MONITOR FOR PCBs: PHASE II

INTRODUCTION

Phase I Summary

The initial phase of this study essentially layed the ground work for the current instrument and protocol refinement project (1). The matrix isolation techniques currently used were preliminarily developed in this phase. These included the use of radiolabeled (^{14}C) PCB, batch adsorption studies, and extraction of PCBs from oil and soil. The feasibility studies for determining the utility of infrared spectroscopy (IR) were carried out using the techniques of Fourier Transform Infrared (FTIR) spectroscopy (Digilabs FTS-20C). All initial IR flow cell work was carried out using the Miran 1A (2, 3) while all Horizontal Multiple Internal Reflectance (HMIR) studies were performed on the Miran 980 (4) (both instruments from Foxboro Analytical).

With the initial feasibility of IR proven as a monitor for PCBs, a series of experiments was undertaken to measure PCBs and askarel in oil and soil samples. Figure 1 depicts the direct reading of pyranol in 10-C Oil (mineral oil) using a 0.2 mm pathlength BaF_2 flow cell mounted on the Miran 1A. As can be seen from the very small absorbance readings, measuring PCBs in oil or oil spills at this very critical concentration range is very difficult at best. This is due primarily to the inherently low intensity of typical IR sources and the preponderance of oil. Figure 2 again shows Pyranol in 10-C Oil. However, in this case, the oil was used to extract the askarel out of soil samples. Mineral

oil is, in fact, an ideal IR solvent for PCBs since it is IR transparent from approximately 7.5 to 12.3 microns. The extracted oil samples were again run on the Miran 1A, but using a 0.2 mm pathlength ZnSe flow cell. The calibration curves obtained in this manner were quite linear for concentrated samples.

The simplest form of PCB/Soil measurement was also attempted in Phase I. This involved the direct application of contaminated soil to the HMIR window of the Miran 980. Figure 3 illustrates the application of varying amounts of Pyranol (0 to 1 g) to 5-g soil samples. The top scan represents a soil blank. The corresponding calibration curves were again surprisingly linear. This direct application technique proved useful for concentrated askarel spills and would be useful for an initial screening of a suspected spill site. For the lower PCB concentrations that might be present in a PCB/Oil spill or after partial digging up an askarel spill, this technique had several limitations. These included inconsistent readings resulting from the soil type, soil moisture and amount of oil present.

Rather than "diluting" the PCBs with oil (or oil miscible solvent) in an extraction or dealing with the inconsistencies of direct soil application, it was decided that a preconcentration step would instead be needed. This would especially be necessary to measure contaminated (50-500 ppm) and land-fillable (50 ppm) samples. For this purpose, a fixed-film HMIR technique was developed which deposited the PCB onto the horizontal stage window as a volatile extraction solvent evaporated. Using this technique, which is the basis of the Phase II study, one can see tens of micrograms of PCB from soil. Furthermore,

the method is quite reproducible and, as can be seen in Figure 4, very linear.

Phase II Overview

As mentioned previously, the goals of the current phase of this project are to refine the necessary instrumentation and sampling protocol, as well as apply them to spill type samples. While a great deal of work has been carried out in oil matrices, the primary thrust of this second phase is to develop a rugged, portable and easy to operate instrument for use in askarel spills on land-based substances. Since the initial studies were carried out, we have had the "benefit" of further PCB information, litigation, spills and, most importantly, feedback from many potential utility users concerning actual spill conditions and possible interferences. Several excellent and extensive reviews are also available covering the general PCB situation (5, 6), PCBs in the environment (7), and portable instrumentation (8).

The scope of work for Phase II included the following tasks:

- Verification and selection of the proper wavelength(s).
- Selection of the proper solvent(s).
- Refinement of the HMIR technique and development of a protocol.
- Measurements of PCB-contaminated soil.
- Evaluation of interferences.
- Instrument selection and completion of protocol.
- Field testing of the instrument and technique.

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INSTRUMENTATION

Miran™ 1A

The simplest and most rugged of the Miran™ series of instruments from Foxboro Analytical is the single beam IR photometer called the Miran 1A. This instrument shown in Figure 5 can be equipped with either a flow cell or HMIR stage. Its portability and ruggedness for field work has been attested to in a NIOSH portable instrument evaluation (8). Wavelength selection is made with a circular interference-wedge filter, which does not give as much spectral resolution as a grating instrument but does provide higher sensitivity (due to less light loss). Figure 6 schematically illustrates the optical path of the 1A.

Miran™ 980

The majority of our work has been carried out on the Miran 980 programmable IR on loan to us from Foxboro Analytical for this study (see Figure 7). This spectrometer was equally rugged, had similar optics (and thus similar resolution and sensitivity, see Figure 8 for the 980 optical system), and could be fitted with either a flow cell or HMIR stage like the Miran 1A. What sets this instrument apart, however, is the fact that it is microcomputer controlled and is capable of on-the-fly background-corrected spectral scanning. Thus, the black body curve, 10-C Oil matrix, soil matrix, etc. can be subtracted. This feature has proven invaluable in method development. The Miran 980 also provides automatic analysis of mixtures with complete data reduction. As can be seen from Figure 7, the 980 provides (1) a keyboard for operating and data

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reduction functions, (2) a printer for "peak picking" and absorbance, transmittance or concentration readout, and (3) a cassette for parameter and baseline storage.

Multiple Internal Reflection Spectroscopy

As mentioned previously, both the Miran 1A and 980 can be adapted to a multiple internal reflection (MIR) cell. Two common configurations of MIR cells are illustrated in Figures 9-A and 9-B. The former depicts a vertical multiple internal reflection (VMIR) cell while the latter illustrates a horizontal multiple internal reflection (HMIR) window. While the sample does see twice as many reflections in a VMIR cell than in a HMIR cell, the latter configuration was used for all our MIR studies due to its convenience and simplicity in handling spill-condition samples (e.g., askarel, PCB/Oil, or PCB/Soil). It is very simple for a sample to be applied, scanned and wiped off (with an organic solvent) with no carry-over contamination or flow-cell blockage. Due to its availability, inertness (especially to water), durability and wide spectral range, a ZnSe-window HMIR was used throughout Phase I and II. Figure 9C illustrates the light path, typical angle of incidence, and typical dimensions of such a crystal. The development of a BaF_2 HMIR crystal would greatly enhance the light throughput and instrument sensitivity.

The principle of operation of MIR, also referred to as attenuated total reflection (ATR), is based on the fact that infrared energy being totally, internally reflected within a high refractive index optical material (e.g., ZnSe or BaF_2) will actually penetrate a short distance into the applied sample. If

the sample absorbs energy from specific wavelengths, this attenuation of the beam, usually expressed as an absorbance, is related to concentration. Such MIR spectra closely resemble absorption spectra using a transmission cell. Figure 10 schematically represents a MIR optical diagram from source to detector. The advantages of MIR, and in particular HMIR, for field analysis are elucidated in Table 1.

Field Sample Preparation Kit

Barring any exotic interferences from herbicides, insecticides, pesticides, etc., the routine preparation of land-based material for analysis by HMIR is quite simple and rapid. Like the method, the ancillary equipment needed for sample prep. is simple. A single small case contains the following:

- Ohaus portable digital balance for soil weighing. Precision is good to one decimal place. Powered by an AC adapter or 9V battery.
- Spatula for transferring soil to vials.
- Empty scintillation-type vials for soil (or oil) extractions.
- Vials containing the appropriate organic extraction solvent(s).
- Pipette (0-1 ml) with disposable tips for transferring solvents from vials onto the soil and extraction liquor from the extraction vial to the HMIR window.
- A stainless steel "sample containment weir" which fits down over the HMIR window. While it is open at the top to allow sample introduction and volatile carrier solvent evaporation, it corals the solvent over the window during fixed film application.

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- Disposable silica gel minicolumns for the separation of interferences such as pesticides from PCBs. Additional scintillation vials of eluting solvent can also be included. The separation/purification of PCBs is a simple and rapid procedure described in the literature (9, 10, 11).

RESULTS AND DISCUSSION

Wavelength Selection

The first task to be undertaken was that of verification and final selection of analytical and reference wavelengths. Wavelengths were roughly determined in Phase I which would minimize the effects of interferences (e.g., TCB and 10-C Oil) while maximizing the absorbance contributions of PCBs (1). See Figure 11. Selectivity and sensitivity was thus built in. These initial wavelengths were optimized by digitization and subsequent absorbance maximization. Table 2 outlines the final selection of wavelengths.

Table 2 Optimized Wavelengths for Monitoring PCBs (in microns)

Phase I	Phase II
7.2	7.169
7.5	7.447
8.5	8.551*
9.2	9.153*
12.3	12.254

*These are the wavelengths of choice for selectivity and sensitivity.

Solvent Selection

The second task of the study was the final selection of solvents for the extraction of PCBs from soil and oil. Attractive alternatives to the solvents chosen in the preliminary study are presented for use in both matrices. Solvent selection was based on toxicity, volatility, miscibility, and extraction efficiency. The toxicity and/or hazardous properties of each solvent were evaluated using a variety of sources (12, 13, 14, 15, 16). Volatilities (vapor pressure) as well as densities and molecular weights are given in Table 3 which was compiled from a wide variety of sources (1, 12, 13, 14, 17, 18, 19). Knowledge of the specific gravity of a solvent is necessary in the extraction procedure, while that of the vapor pressure is useful in designing fixed-film experiments. Solvent miscibilities were determined by the development through Phase I and II of the 30 x 30 miscibility matrix shown in Table 4. Although these are primarily common chromatographic solvents, this data is not available in any handbook to date. Table 5 below lists several additional solvent miscibilities found useful in solvent extraction development studies.

Table 5 Additional Solvent Miscibilities

	CS_2	TEP	Acetone
DMF	M	M	M
Oil	M	SR	M
H_2O	S	M	M

Finally, extraction efficiencies were determined by measuring solvent/oil distribution coefficients and percent PCB removal from soil and soil/oil

matrices. A uniformly labeled (^{14}C) PCB isomeric mixture, containing approximately 54% chlorine by weight (New England Nuclear, No. NEC-690) was used to spike samples. Such radiolabeled PCB work has also been done by Seidl and Ballschmiter (20). Counting was accomplished on a Packard Tri-Carb Spectrometer, courtesy of the ORNL Analytical Chemistry Division. A computer program was developed by W. D. Bostick in Phase I (1) which took this spectrometer data and computed counting efficiencies and net disintegrations per minute (DPM). Distribution coefficients (D) were thus determined and are summarized in Table 3 along with selected values from the work of Napier et al (17). Once such distribution coefficients are determined, PCB extraction efficiencies can be readily determined for any combination of solvents and shake out volumes and iterations as shown below:

Calculation of PCB Extraction Efficiency

$$\% \text{ PCB Remaining in Oil} = 100 \left[\frac{1}{1 + D \left(\frac{V_A}{V_B} \right)} \right]^n$$

where,

D = Distribution Coefficient $\left(\frac{\text{Conc. of Ext. Phase}}{\text{Conc. of Oil Phase}} \right)$

V_A = Volume of Extractant

V_B = Volume of Oil

n = Iterations

Sample Calculations:

1. Four extractions with acetonitrile (CH_3CN)

   where, avg. D = 0.29 $\quad \frac{V_A}{V_B} = 2$

n = 1	63% (remaining in oil)	37% (PCB extracted)
2	40%	60%
3	25%	75%
4	16%	84%

2. Four extractions with dimethylformamide (DMF)

   where, D = 1.43 $\quad \frac{V_A}{V_B} = 2$

n = 1	26% (remaining in oil)	74% (PCB extracted)
2	7%	93%
3	2%	98%
4	0.5%	99.5%

Based on the four criteria presented above, three solvents were selected for PCB extraction from soil and other land-based substances. These solvents in order of utility were carbon tetrachloride (CCl_4), methylene chloride (MC), trichlorotrifluoroethane (Freon 113) and hexane. Each of these solvents has two advantages over the previously selected solvent (1), acetonitrile (AN). These are higher volatility for rapid fixed-film vapor deposition and, very importantly, immiscibility with water. The distribution coefficient of AN in oil of 0.28 drops to 0.11 when AN is contacted with soil. The moisture in the soil mixes with the solvent and subsequently repels the PCBs rather than extracting them. Depending on the moisture content of the soil, the absorbance

measured for PCBs varies. On the other hand, PCB extraction from oil or soil/oil, N,N-dimethyl formamide (DMF) and acetonitrile (AN) are the only solvents which have proven effective and are still practical. We have not, unfortunately, found an organic solvent which is both totally immiscible with oil and water. While DMF must be handled with considerably more care then the other solvents, it does exhibit a distribution coefficient some five times that of AN.

Refinement of HMIR Technique and Sampling Protocol Development

The modest ancilliary equipment required for sample preparation has been described previously in the Instrumentation: Field Sampling Kit section. A set of calibration scans, as shown in Figure 12 can be run at the laboratory. From these scans (Miran 980) or absorbance values (Miran 1A), a calibration matrix can be stored in memory for data reduction (980) or plotted on graph paper (1A) for use in the field. The 980 is further capable of storing any number of background curves on cassette tape for subsequent baseline subtract. It will be necessary with the 1A to run backgrounds in the field. The scans in figure 12 were produced by making up PCB standard in a volatile organic (CCl_4), depositing the mixture on the HMIR window, allowing the solvent to evaporate, and scanning. An air baseline has been automatically subtracted for each. The actual Absorbance *vs* Micrograms of 1260 calibration plots are quite linear, but there are three distinct regions, low (0-100 ppm) middle (100-500 ppm) and high (>500 ppm) concentration ranges.

Upon arriving at the site, if the spill is an obvious one or if a rapid screen is desired, one can scan the potentially contaminated soil directly on the HMIR window. Instrument noise and air backgrounds can be subtracted out to produce a PCB or askarel scan. Cleaning of the window between scans is exceptionally easy using a cotton swab or tissue with an organic solvent such as hexane. No carry-over contamination has ever been observed regardless of the sample matrix. Preconcentration by multiple film depositions as proposed in Phase I proved infeasible. As subsequent layers were deposited, the initial layer would redissolve and flow. An example of the final sampling protocol developed which allowed us to see samples $\geq$ 50 ppm, 25-50 ppm and 5-25 ppm in 1260 will be given.

Actually, three slightly different sample prep. procedures were developed for soil $\geq$ 50 ppm, 25-50 ppm and 5-25 ppm in 1260. The first successful extraction and IR measurement of 50 ppm 1260 from soil was accomplished by adding 4 ml of CCl_4 to 5 g of soil containing 250 µg 1260 (i.e., 50 µg/g). Extraction is quite effectively carried out in a sealed scintillation vial with 5 minutes in a vortex mixer. One (1) ml of the 4 ml is then placed on the HMIR window. When the solvent is completely evaporated, the fixed film is scanned and a similarly extracted soil blank subtracted. It was found that a nearly identical curve (shown in Figure 13A) could be obtained by extracting the same amount of soil with only 1 ml of CCl_4 and pipetting 0.2 ml of the 0.8 ml recovered from the extracted soil onto the window. This greatly reduced the film deposition time. As mentioned, extraction of 25 ppm 1260 soil requires the former procedure of extracting with 4 ml and pipetting 1 ml of the ~3.8 ml recovered solvent onto

the window. This procedure is volume dependent (as one would expect) as shown in Figure 13B. The upper scan is a 1 ml out of 4 ml film deposited as described above. The lower scan represents 2 ml of this same solution. The absorbance doubles, again as one would expect. Finally, Figure 13C illustrates a 5 ppm scan, the lowest concentration of PCB successfully extracted from soil by this technique. A few changes are required to reach this limit, however. Five (5) ml of CCl_4 were used to extract 10 grams of soil and all of the 4.05 ml recovered after vortexing was applied to the window. It was necessary here to have a small lecture bottle of nitrogen gas to help blow down the solvent. This was carried out in the vial prior to application on the window.

Measurements of PCB-Contaminated Soil

The next step in the study was to measure actual askarel in soil samples. the interactions of and problems with PCBs or askarels in soil have been reported on numerous occasions (20, 21, 22). Some basis for the composition of askarel must be assumed since the make up in electrical equipment has purposely been varied or mixed over the years (see Table 6 (23)). All of our askarel studies were carried out on Pyranol (45% 1260).

Figure 14A represents the scan of a 50 ppm Pyranol (as 1260) in 68E Collegedale-Rock Outcrop soil. The routine method of 1 ml CCl_4 extraction of 5 g of soil (i.e., 250 µg total), 5 min. vortex, 0.2 ml applied by fixed-film to the HMIR was followed. The upper scan of Figure 14A is the soil blank, the middle scan is the 50 ppm film, and the lower scan for comparison is a 125 µg fixed-film standard deposited from CCl_4 without any extraction. Figure 14B, C and D show

this same 50 ppm Pyranol (as 1260) soil sample extracted with methylene chloride (MC), Freon 113 and hexane, respectively. Methylene chloride seems to be the most efficient extractant, while Freon and hexane produce nearly identical scans. While MC, Freon and hexane are all more volatile than CCl_4, hexane is not as good an extractant from soil and MC and Freon undergo very rapid evaporation which is difficult to control.

Figures 15A and B illustrate 25 ppm and 5 ppm Pyranol (as 1260) in soil, respectively, to show that the CCl_4 extraction and fixed-film procedure can reach these levels with askarels as well as PCBs. The two scans were the results of the special procedures developed for soils at these low levels.

Interferences

The details of our evaluation of possible interferences to this method will be given in the Final EPRI Report on this project. However, it should suffice to say that there is a very real potential for interferences from herbicides, pesticides and insecticides at spill sites. Even pole preservatives such as pentachlorophenol could be a problem. PCBs were actually added to some herbicides to extend the kill life. If these were sprayed around power poles the problem of background is further confounded. We have run scans on DDT; 2, 4-D; 2,4, 5-T; dieldrin; 2,4-dinitrophenol, pentachlorophenol; lindane, aldrin, and heptachlor. A HMIR fixed-film scan of a mixture of the latter three is shown in Figure 16.

We have eliminated the original interference of soil moisture with the current sampling protocol, however, the chlorinated, polar interferences will have to be

eliminated (or minimized) by one of two ways. Careful wavelength selection using the Miran 980 or a cleanup step using a silica gel sample prep. column will be necessary (see Field Sampling Kit section).

Final Instrument Selection

The Miran 980 with its automatic background subtract and data reduction capabilities was an absolute necessity for the methods development portion of this study. Once the protocol was developed and specific wavelengths chosen, it became clear that the much less expensive Miran 1A with a HMIR stage would possibly suffice. It is recommended that a BaF_2 HMIR crystal replace the existing ZnSe for enhanced light throughput and that the 980 be used in cases where soil might contain extreme interference by oil, herbicides, etc. A field comparison of the 980 and 1A will be presented in the Final Project Report. We have done, however, a simulated comparison by first scanning a 50 ppm 1260 in soil extractant using the 980 with a blank soil extractant background subtract. The same sample was then scanned versus air as would be the case with the 1A. The soil extractant reference was also scanned versus air and the absorbance for soil (0.0095 AU) was subtracted from that of PCB (0.0310 AU) to give 0.0215 AU. This value corresponds to 47 micrograms/gram on our low range PCB calibration curve. Since the value is very close to the expected 50 ppm and that obtained with the 980, it looks promising to use the portable Miran 1A for field work.

CONCLUSION

Inherently, IR analysis is a highly selective technique. Absorbance measurements at either 8.551 or 9.153 microns are selective for Aroclor 1260 in

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the presence of oil (an askarel substitute) or trichlorobenzene (the solvent in askarel fluids). The chief limitation of conventional IR analysis is the modest sensitivity afforded by the source. We have successfully overcome this limitation by the development of a fixed-film deposition of PCBs from a volatile organic extractant coupled with an HMIR instrument.

It has often been tempting during the study to go back to a flow cell IR technique (e.g., BaF_2) to enhance sensitivity. However, any such flow-cell work would invariably have to be carried out in oil, or perhaps CS_2, the only good windows available in this region. Since this would actually be a dilution rather than our proposed preconcentration it is not as highly recommended as the use of a volatile solvent and fixed film application. Solid particles in oil or solvent from soil would also cause light scattering problems not present in HMIR. A BaF_2 HMIR crystal is further recommended for sensitivity enhancement.

While amazingly simple and convenient, the direct application of contaminated soil on the HMIR stage is recommended for screening purposes or for obvious askarel spills only. The method gives inconsistent results and is frought with variables (e.g., uniform contact with the window, soil moisture, and oil content). The sensitivity is also limited here and those samples below 200 ppm, or certainly below 100 ppm, would be extremely difficult.

The most promising extraction solvents for PCBs in soil were found to be carbon tetrachloride, methylene chloride, Freon 113 and hexane. For PCBs in oil or soil/oil, dimethylformamide or acetonitrile are recommended. We have developed

a DMF extraction procedure similar to that developed independently by Napier et al (17) for PCB from oil cleanup on a much larger scale.

The inherent selectivity of IR analysis coupled with our fixed-film protocol and an available HMIR yield a simple, rapid, rugged, mobile (or portable) and reproducible instrumental approach for the measurement of PCBs under spill conditions in the field.

ACKNOWLEDGMENT

The authors wish to thank the Electric Power Research Institute and in particular Dr. Ralph Y. Komai, Project Manager, for their continued support and guidance in this work. This research was sponsored by EPRI under agreement RP1263-10 with C/S Associates, Inc. of Oak Ridge, Tennessee. We also wish to thank Dr. William D. Bostick, Ms. Debbie Bostick, and Mr. Stanley R. Dinsmore for their assistance in verifying Phase I work, standards selection, and radiolabeled PCB counting. Standards for many of the herbicide and insecticide scans were graciously donated by Dr. Jurgen Exner of IT Enviroscience in Knoxville, Tennessee. Finally, we greatly appreciate the support of Foxboro Analytical, a division of the Foxboro Company, in Norwalk, Connecticut. In particular, thanks to to Mr. Louis C. Franconni and Mr. Carl R. Brewer for supplying the Miran 980 and backup support during Phase II. Comparison studies using the Miran 1A were done using an instrument belonging to the Oak Ridge National Laboratory operated by Union Carbide Corp. for the U.S. Department of Energy.

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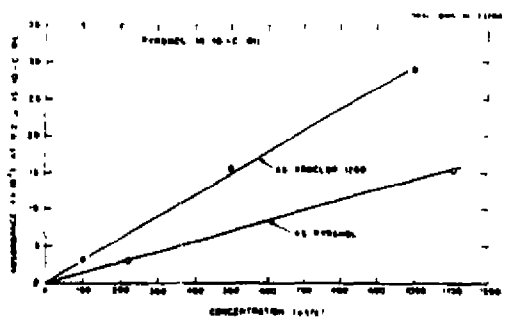


FIG. 1

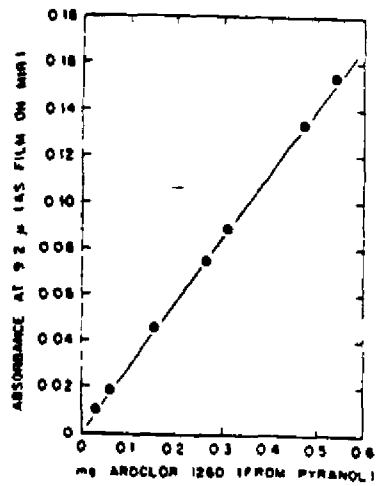


FIG. 4

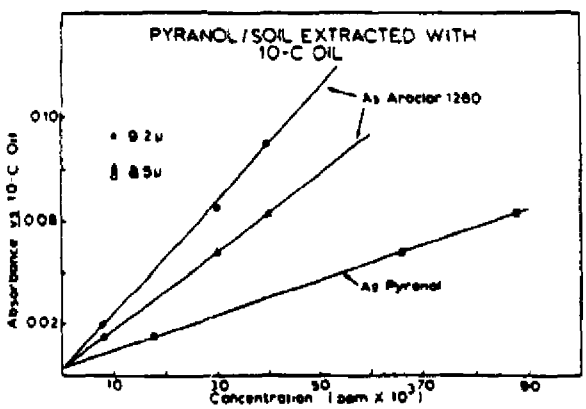


FIG. 2

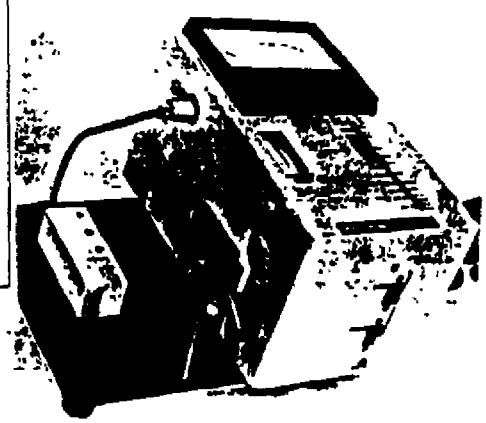


FIG. 5

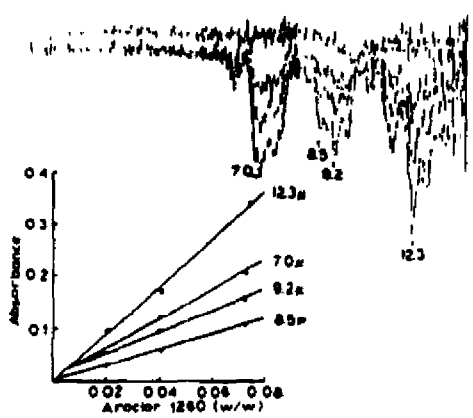
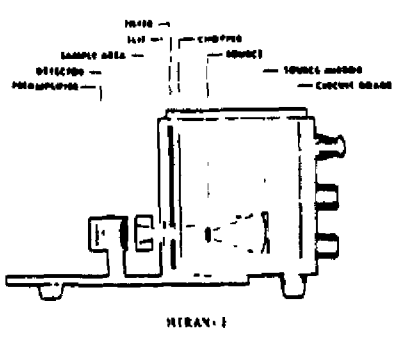


FIG. 3



Optical Schematic and Major Components

FIG. 6

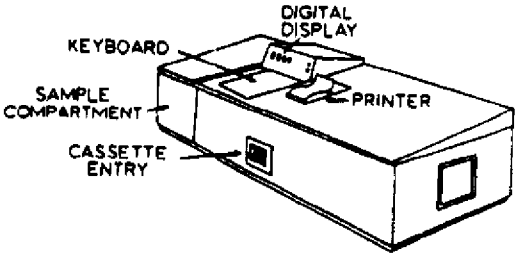


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FIG. 7

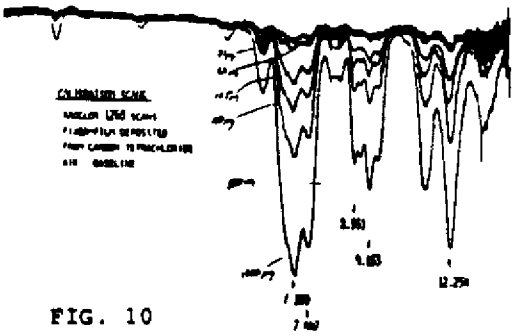
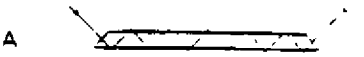


FIG. 10

FIG. 11



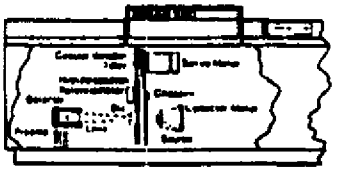
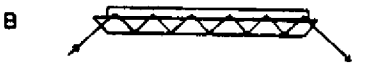


FIG. 8



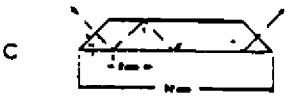


FIG. 9

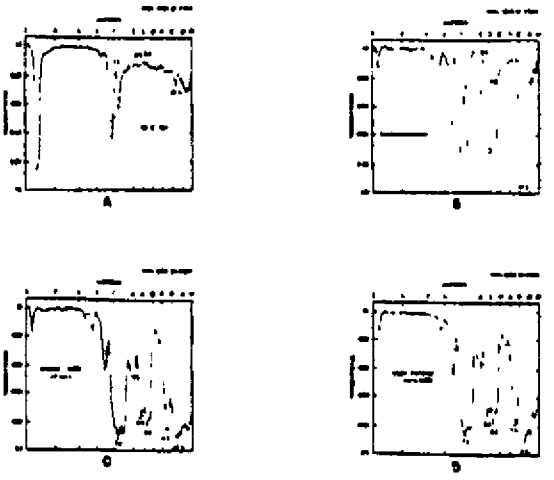
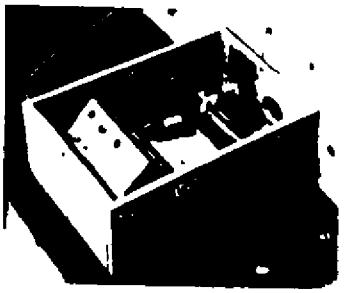
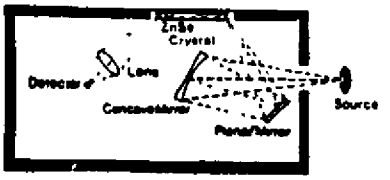


FIG. 12





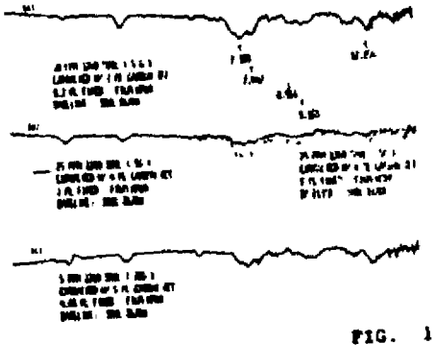


FIG. 13

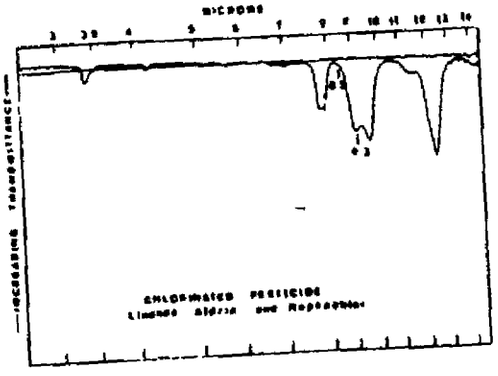


FIG. 15

FIG. 14

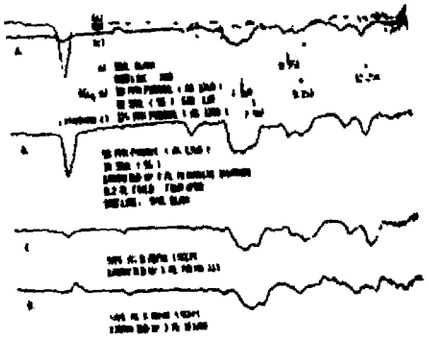
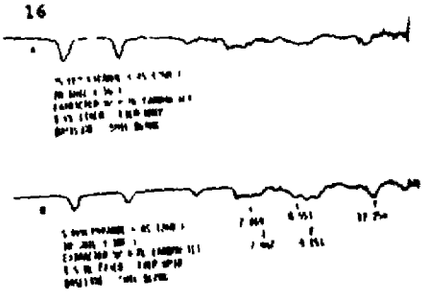


FIG. 16



Part 3

RETROFILL

THE UTILITY PCB DILEMMA - RETROFILL OR REPLACEMENT?

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DEFINING THE CRITERIA

The utility industry has been unjustifiably branded as the "bad guys" because of PCBs. Once considered a benevolent public servant, the electric utility industry is now regarded by the public as another insensitive, profit-motivated corporate giant which must be continually scrutinized by citizen action groups and heavily regulated to prevent environmental pollution and harm to the public from toxic materials. As a result, electric utilities are confronted with some important decisions about: (1) the type of electrical insulating fluids which are best suited to replace PCBs; and (2) the most effective manner in which to safely and economically replace the millions of pounds of PCBs in existing equipment.

Until recently, the process of choosing an electrical insulating fluid has never been too complicated. The proper selection of a suitable insulating fluid depended upon its ability to satisfy certain operating and engineering performance criteria such as: (1) dielectric strength, (2) viscosity, (3) flammability, and (4) compatibility.[1] Having passed these preliminary specifications, the insulating fluid would then be evaluated against more subjective criteria such as: (5) past field performance and experience, (6) availability, (7) the supplier's reputation and dependability and (8) costs.

However, to coin an old adage, "the old must make way for the new" so it goes for the process of selecting an electrical insulating fluid. The task once regarded as "business as usual" has now become more of a nightmare. To illustrate, at 5:30 a.m. on February 5, 1981, a fire broke out in the first level basement mechanical room of an 18-story office building in Binghamton, New York. The fire originated through a fault in the building's secondary (480 v) switch gear, which

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resulted in a cracked bushing on an adjacent Askarel-filled transformer providing service to the building. Approximately 180 gallons of insulating fluid spilled from the transformer. Ventilation intake ducts located adjacent to the transformer spread the oily smoke and soot throughout the building. Almost three years and more than 10 million dollars later, the building remains closed.[2] At 11:19 a.m. on May 15, 1983, in San Francisco, California, a transformer fire in an underground street vault at Steuart and Mission Streets contaminated a small area of a 28-story office tower with PCBs and forced the closure of the entire building. After 10 days of extensive testing and decontamination, floors 7 through 28 were reopened for occupancy, while floors 1 through 7 remained closed for six months. Out of these episodes have arisen more citizen action groups demanding the immediate replacement of all PCB transformers. The lesson that can be learned from these frightening experiences is that the criteria once thought sufficient to select a high quality performance insulating fluid are no longer adequate. In an ecologically sensitive culture, the public's fear of environmental contamination demands that the electric utility industry broaden the scope of its evaluation process to include the fluid's potential toxicity and effect on the environment.

SELECTING THE BEST FLUID(S)

What then are the alternatives? One concept becomes more and more apparent -- that the toxic properties of a prospective insulating fluid are equally, if not more important, in terms of an industry's public image and financial health, than the engineering qualities, and that whatever fluid is chosen must be as environmentally acceptable as it is a good electrical insulating fluid.

Once the task of identifying all the criteria necessary to properly choose an insulating fluid is completed, the next step is the selection of a suitable insulating fluid. This is the decision area which is critical and requires a thorough understanding of the importance of the toxicity and environmental criteria in making the final fluid selection. There are several non-PCB insulating fluids commercially available which have already been accepted based on their engineering qualities.[3] The question that remains to be answered is the effect that these electrical insulating fluids will have on the public and the environment.

Mineral oil (Chevron Insulating Oil and Shell DIALA Oil A) probably has the longest track record of any of the non-PCB insulating fluids. It has demonstrated satisfactory electrical insulating qualities and has never to date been associated with any harmful effects other than as a flammable liquid.[3,6] However, it may be

still too early to determine whether minsrel oil may become a problem due to the increasing interest about polynuclear aromatic hydrocarbons and their potential toxicity, and bioenvironmental implications.[3]

From all available information, polydimethylsiloxane or silicone fluid (Dow Corning 561 and General Electric SF 97(50)) appears to be not only an acceptable insulating fluid but represents the lowest potential for adverse effects to the public and the environment.[3] The only apparent problem associated with silicone fluid is its potential fire hazard.

Perchloroethylene or tetrachloroethylene (WECOSOL) is being suggested as a very good PCB substitute insulating fluid because of its electrical qualities and more important, its non-flammability.[3,6] However, perchloroethylene, like PCBs, is another chlorinated hydrocarbon which may bioaccumulate in the environment and is regarded as a toxic substance and suspected carcinogen.[3,5]

Finally, the last fluid to be considered as a substitute for PCB is a paraffin-based, high molecular weight hydrocarbon oil (RTEmp). It has good electrical properties, but it is a flammable liquid and, like mineral oil, may have some future problems due to trace amounts of polynuclear aromatic hydrocarbons.[3,6]

RETROFILL OR REPLACEMENT

As previously pointed out, the electric utility industry faces two dilemmas: (1) the selection of a suitable PCB substitute fluid; and (2) what to do with the PCBs on hand. Having discussed the relevant issues surrounding the first problem, let us now examine what alternatives are available for the disposition of the PCBs in existing equipment.

Three options are available to the electric industry to resolve the PCB dilemma: (1) a retrofill program whereby the concentration of PCBs is reduced in existing equipment; (2) a total replacement program whereby all PCB equipment is replaced; and (3) some combination of a retrofill and replacement program. However, before a commitment is made to any of these alternatives, the advantages and disadvantages of each must be carefully weighed.

Retrofill

A retrofill program allows or accommodates the implementation of a low-key PCB removal program. The three most obvious advantages of such a program include:

(1) a reduced commitment of immediate funds and manpower resources; (2) possibly less attention from the media and the general public; and (3) the costs of retrofilling existing equipment are somewhat less than a replacement program. (Estimates of the cost of retrofill have been quoted by contractors as 60-70 percent of the purchase price of the new equipment.)

Another attractive advantage of a retrofill program is the Environmental Protection Agency's recent program for recertification of PCB and PCB-contaminated equipment. This is the program whereby EPA will recertify equipment if it is shown through retrofilling that the concentration of PCBs can be reached and maintained below the legal definitions of 50 and 500 parts per million (ppm) for longer than 90 days.[4] EPA's reclassification of electrical equipment is beneficial to industries because it may facilitate employee protection and waste management programs by lessening regulatory requirements.

Finally, the removal of PCB transformers and related equipment may require the complete reconstruction of the vaults in highrise buildings or underground vaults. A successful retrofill program uses existing equipment, resulting in a more timely, more economical and more convenient PCB-removal program.

There are also some disadvantages to the retrofill program which are important and must be emphasized. One drawback to this program focused on the safety of the insulating fluids. Although some information is available on the toxic and environmental effects of these fluids, the questions of long-term toxicity, cancer-causing effects and reproductive hazards are still unanswered for some of the fluids.[3]

Another area of concern with this type of program centers on its alleged capability to reduce and more importantly, maintain the amount of PCBs below certain levels. A successful retrofill program must filter PCBs faster than they leach from the windings and paper products in the core of a transformer and maintain PCB levels below EPA defined critaria or other prescribed levels.

However, tests have shown that when the PCB-filtering and removal system is disconnected, the continued leaching of PCBs from the transformer core will, after some time, again raise the PCB concentration in the equipment.[1] Theoretical calculations indicate that the residual PCB concentration must be maintained indefinitely below 1 ppm in order to ensure that in the event of a transformer fire, PCBs and their decomposition products are not found at or above the

preliminary safe decontamination levels being proposed by an expert panel of scientists for the Binghamton fire.

Studies are under way by the Electric Power Research Institute (EPRI) and the New York State Department of Health to determine the minimum levels of PCBs necessary in silicone, perchloroethylene, mineral oil and high temperature hydrocarbon insulating fluids to prevent the type and degree of contamination demonstrated by the Binghamton and San Francisco fires. Until such time as these studies are completed in March or April 1984, it cannot be ascertained what minimum concentration of PCBs will be acceptable in a retrofilled transformer to prevent the PCB episodes seen by the Binghamton and San Francisco experiences.

Replacement

If the uncertainties of a retrofill program are too risky and unwielding, let us consider another possible alternative and discuss the advantages and disadvantages of a total PCB equipment replacement program.

Perhaps the most obvious and important attraction of a PCB equipment replacement program is that once and for all, the risks associated with PCBs would be eliminated and the utility industry might begin to breathe a bit easier in the future. Unquestionably for a utility company, the attractiveness of this course would be sufficient to pursue a PCB equipment replacement program.

However, not unlike the retrofill alternative, there is also a dark side to the PCB equipment replacement program. One disadvantage of the program is the lengthy and disruptive construction phase necessitated by enlarging the openings into existing street and building vaults to remove PCB transformers and install new equipment.

The increased costs associated with a replacement program is another drawback. In contrast to a retrofill program where the costs are derived from the purchase of new insulating fluid and any labor involved, the costs associated with a replacement program include not only the new equipment and insulating fluid, but the requisite reconstruction expenses of the program.

Furthermore, since the same insulating fluids are used in both programs, the questions of toxicity and potential environmental effects are still unresolved.

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SUMMARY

The costs, the conveniences and inconveniences, the unanswered questions about toxicity and environmental effects of the insulating fluids, and the value of retrofilling transformers for recertification purposes are some of the uncertainties which make the decision to retrofill or replace difficult. The potential risks of either alternative are high and there are no guarantees. The decision to retrofill or replace rests with each individual utility and depends on its own particular circumstances and goals. It has not been our purpose to recommend or condemn a PCB retrofill or replacement program, but to provide some insight into the type of considerations which are important and should be evaluated before a final decision is reached.

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DISCUSSION

The questions basicelly were in regard to the assumptions and limits used in the study. For example, the requirement that retrofilling should reduce and maintain 1 ppm PCB. This requirement was based on calculations of the limits of furans in soot. It was pointed out, by several discussors, that conversion to ppm furans from ppm PCB was not linear, especially in low concentretions.

Dry type transformers were not considered for replecement because of cost, size, and lower efficiency.

Questions were raised regarding trace contamination of silicone fluids with PCB and/or formaldehyde. It was reported that the silicone used was certified to contain less than 1 ppm PCB and that the formaldehyde problem had been solved.

CLEANING ASKAREL TRANSFORMERS USING SILICONE RETROFILL AND ADSORPTION TECHNIQUES TO REMOVE RESIDUAL PCBs

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BACKGROUND

Section 6(e) of the Toxic Substances Control Act (TSCA) of 1976 banned the use of PCBs after January 1, 1978. However, the statute permitted two exceptions: the Environmental Protection Agency (EPA) may allow PCBs to be used in a "totally enclosed manner" or if the use "will not present an unreasonable risk of injury to health or the environment."

In May 1979 the EPA promulgated a rule designating intact nonleaking transformers, and other electrical equipment, as "totally enclosed", thus permitting their continued use (1). This ruling was challenged in the Federal Courts by the Environmental Defense Fund (EDF). The court, ruling in the EDF's favor, found in part that EPA had not shown that transformers were indeed "totally enclosed." Thus the use of any transformer containing any amount of PCBs would constitute a violation of TSCA.

An immediate ban on the use of equipment containing PCBs would have disrupted electrical service and caused severe economic hardship. Therefore, the court granted a stay to permit the EPA to study the problem and reissue a new final rule. This "final" rule was published in the Federal Register on August 25, 1982 and became effective on September 24 of that year (2).

With respect to transformers, the 1982 rule reaffirms much of the original 1979 rule, with a few important additions. It continues the classification of transformers into three categories according to the PCB concentration of their liquid coolant. These categories are:

1. "PCB transformer", 500 ppm PCBs or more;
2. "PCB contaminated", 50 to 500 ppm PCBs;
3. "non-PCB", less than 50 ppm PCBs.

Important additions to the 1979 rule contained in the 1982 rule include:

1. after October 1, 1985 no "PCB transformer" may continue in use where there is risk of PCB contact with food and feed;

2. "PCB transformers must be inspected regularly and records kept of these inspections;

3. recognition of the possibility of reclassifying "PCB transformers" by retrofilling them with an environmentally acceptable dielectric coolant and further processing the new liquid to remove residual PCBs that leach into it from the core, windings and insulation;

4. clarification of the procedure for reclassifying "PCB transformers" as "PCB contaminated" and "non PCB".

The rules governing how a transformer may be used, serviced and disposed of depend upon its PCB classification and are summarized in Table I. Note that there is little significant difference between the rules for "PCB contaminated" and "non-PCB" transformers.

With the exception of transformers that pose an exposure risk to food or feed, a "PCB transformer" may continue in use. However, it must be labeled, inspected regularly and any service that requires the removal of the core from the tank is prohibited. When disposed of, the fluid must be burned in an approved PCB incinerator. The carcass may be disposed of in the same manner or buried intact in an approved chemical waste landfill.

A "PCB contaminated" transformer need not be labeled or inspected regularly. Any service can be performed by the owner or an exempt service company. Its liquid coolant can be disposed of in an approved chemical waste landfill or burned in a high efficiency boiler or an approved PCB incinerator. Finally, it may be used despite exposure risk to food or feed.

A "non-PCB" transformer may be used virtually without restriction. The only exception is thet fluids containing any detectable amount of PCB cannot be used "as a sealant, coating or dust control agent".

This is the situation as it stands today. However, the current rule may not be final after all. The Environmental Defense Fund petitioned the United States Court of Appeals to review EPA's August 1982 rule. And after lengthy negotiation, EPA and EDF petitioned the court to resolve their differences in the following fashion.

EPA will issue an Advance Notice of Proposed Rulemaking (ANPRM) covering PCB transformers in buildings in March 1984 (3) and has scheduled the Notice of Proposed Rulemaking (NPRM) for October 1984. The rule will be intended "to reduce the risk of future fires in PCB transformers that are located in buildings." EPA's schedule calls for completing the rule-making process in July 1985, if a final rule is deemed necessary for building transformers.

Against this backdrop of regulations and with a continuing, if not increasing, public perception that PCBs pose an unacceptable health and environmental risk, many of the owners of the 100,000 askarel-cooled transformers in the United States are looking for alternatives. Cleaning those transformers by using silicone retrofill and subsequent adsorption techniques to remove residual PCBs is one such alternative. This paper will address this cleanup technique in a generic fashion to the extent that is possible. In some instances, however, it will be necessary to refer specifically to the Dow Corning RetroSil™ System and to DOW CORNING® 561 Transformer Fluid, particularly when describing the system equipment, procedures and performance.

THE PROCESS

A silicone retrofill and adsorption approach to transformer cleanup has a number of distinct advantages. Total transformer downtime is typically less than 12 hours. Removal of residual PCB that leaches out of the transformer core (windings, paper, wood, etc.) is accomplished while the transformer is energized.

This cleanup process is also particularly well suited for transformers located in difficult-to-reach locations. Removal and replacement of these transformers is usually costly because of service interruption and because building modifications may be required to provide access.

At the heart of the cleanup process is silicone transformer liquid which is a dimethyl siloxane polymer combining the properties of low viscosity, high temperature stability, good dielectric performance, low toxicity, and low flammability. It is used primarily in small and medium-sized power transformers (4). Silicone or silicone fluid or liquid as used in this paper refers specifically to the dimethyl polymer developed for and used in transformers.

Silicone fluid is also a good dielectric (5,6,7) and has been used in more than 25,000 new transformers around the world since 1972. Its reliability and performance have been proven (8). Interestingly, the first application of DOW CORNING® 561 liquid in the United States was as a replacement fluid for an askarel-filled transformer. Hundreds of successful applications in similar transformers since that time have demonstrated convincingly that silicone fluid is a viable replacement liquid coolant for askarel.

Two final points concerning silicone liquid merit attention: low toxicity and low flammability. The liquid is chemically inert and DOW CORNING® 561 fluid contains no thermal stabilizers, pour-point depressants, or other additives. Other chemically similar silicone liquids have been used in a variety of applications including many that involve contact with people. Personal care items such as antiperspirants, hair sprays, skin-care products, and even some edible products use silicone fluids as major ingredients or additives. Extensive testing has demonstrated that silicone transformer fluid is nonirritant and not absorbed on skin, has no adverse toxic effect when inhaled, and has a very low oral toxicity (4,9,10).

Silicone transformer liquid also possesses low fire hazard characteristics. It is listed as a "less flammable" fluid with a defined heat release rate by Factory Mutual and therefore meets the requirements of the National Electric Code (11,12,13). DOW CORNING® 561 liquid's flash and fire points and heat release rates are shown in Table II (12,14).

Even though silicone fluid has a very high fire point (350°C), it will burn when ignited. However, when burned it generates relatively low quantities of heat, smoke and toxic gases. In pool fires, silicone fluid eventually self-extinguishes because a crust is formed which smothers the flame. (4)

A second important part of the askarel transformer cleanup process is the people, knowledge, and equipment committed to the program. The RetroSil™ process is usually conducted by independent service companies having expertise and a history of serving the electrical needs of the transformer owner. These companies have also been specially trained and certified by Dow Corning to perform the RetroSil™ process.

The two main RetroSil equipment components are a control station and an adsorber unit. The control station contains the system pump, control valves, pressure gauge and safety interlocks designed to shut the system down or prevent its activation in the event of problems.

The control station also houses the adsorber unit which in turn holds the activated carbon and the liquid distribution system. The adsorber unit is made from a standard 55-gallon drum that meets DOT requirements for shipping PCB wastes. Thus the adsorber unit or "filter" is first shipped to the job site as a product, used to remove PCB from the transformer, disconnected from the system, bung closures are threaded into place, a PCB label is affixed to the drum, and it is ready for shipment to a disposal site.

The adsorber units are shipped to an EPA approved incinerator where they are shredded and incinerated. This handling and disposal method minimizes employee exposure and assures that the wastes are totally destroyed. Dow Corning and the service companies also maintain a tracking system for each adsorber, thereby providing "cradle-to-grave" care.

The third important part of the cleanup system is the ability of activated carbon to selectively remove PCB from silicone liquid. Carbon is "activated" by high temperature heating to produce porous particles. Total surface area of some types of activated carbon is estimated to be 1,000 m^2/gm. In the process of adsorption, a nearly molecular layer of contaminate (PCB, in this case) binds to the carbon surface.

An "adsorptive isotherm" curve shows the constant-temperature relationship between the amount of contaminant absorbed per unit weight of absorbent and the equilibrium concentretion of the contaminant in the bulk coolant (15). Figure I shows an adsorptive isotherm curve for PCB in silicone liquid, using a typical activated carbon. Note that the capacity of the carbon to hold PCB decreases significantly as the concentration of the contaminant decreases.

RETROSIL™ PROCEDURES

The RetroSil™ program consists of many essential steps. They include:

- Preliminary testing
- Site preparation
- Fluid exchange
- Equipment installation
- Final testing

When preliminary testing is completed, the independent service company makes a recommendation as to whether or not the transformer is a suitable candidate for processing. The following tests may be performed to aid in making that judgment:

- Performance review
- Insulation resistance
- Power factor
- Turn ratio
- Liquid dielectric strength
- Leak test
- Polarization index

Site preparation is directed at assuring that proper safety (eye wash, shower, fire extinguishing equipment, protective clothing, breathing apparatus, etc.) and spill protection plans and equipment (plastic sheets, drip pans, absorbing materials, etc.) are in place including plugging or covering all sewer drains.

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Dow Corning recommends a multiple solvent (1,1,1-trichloroethane) and silicone flush to clean the transformer. The total flush volume is approximately 60% of the total transformer volume. Effective flushing with draining between flushes can lower the residual PCB content to less than 1%.

With the transformer drained, all gaskets below the liquid level are replaced and any needed transformer repairs are made. The new PCB-free silicone fluid is then introduced into the unit. Vacuum degassing can aid in removal of any entrained gas. Next the control station and adsorber are installed and connected and the silicone liquid is retested for dielectric strength and water content. The electrical tests described in the preliminary testing paragraph above are rerun before the transformer is reenergized. A sample is also taken after reenergizing to establish the residual PCB concentration.

RETROSIL PERFORMANCE

A hypothetical 1500 kVA, 300 gallon, 13.8 kV primary, 480 V secondary transformer having a residual PCB content of 1.0% after filling will follow a typical operating and adsorber changeout schedule as shown in Table II.

Four adsorber units operating 105 days plus an additional 90-day waiting period will be needed to reclassify the transformer to "PCB-contaminated." The 90-day waiting period during which time the cleanup system (control station) is not operating is required by EPA regulations to reclassify either to PCB-contaminated or non-PCB status.

Table II shows that the weight of PCB adsorbed decreases from 21 pounds on the first adsorber to four pounds on each of the subsequent three adsorbers. This decrease reflects the lowering of carbon capecity with lowering PCB concentration in the fluid consistent with a typical adsorption isotherm (Figure I). The adsorbers holding only four pounds can be reused as the first adsorbers on other transformers. This reuse technique can provide significant cost savings on jobs involving multiple transformers at a single location.

Table II also reveals important information about the nature of the residual PCB in the transformer. Adsorbers number one and two are predominantly removing PCB

that remains freely available in the fluid. That PCB can be quickly removed as evidenced by the 50 ppm PCB concentration in the fluid after only three days.

By contrast, adsorber number three and four are predominantly removing PCB that is leaching slowly out of the transformer core (wood, paper, etc.). This leaching is essentially diffusion controlled and is particularly evident in the PCB concentration gain from 40 to 450 ppm shown in the waiting period. Leaching will continue after the reclassification and additional adsorption is therefore recommended to maintain the PCB concentration in the fluid below 500 ppm.

Additional adsorbers will be required to achieve non-PCB classification. The number will depend upon the individual transformer and, more importantly, upon adsorber utilization. Based on field experience to date, plus models from lab work, non-PCB reclassification would be expected in about two years following reclassification to PCB-contaminated status. For that approximate two-year period, the PCB concentration in the fluid can be maintained below 50 ppm, or can be allowed to cycle from, for example, 500 to 50 ppm depending upon customer preference. The former method reduces any risk from spills or other accidents while the latter optimizes adsorber usage and reduces cost.

SUMMARY

Under present EPA rules, owners of askarel-filled transformers that pose an exposure risk in food or feed plants cannot continue to use these units after Oct. 1, 1985. Other owners of such PCB transformers are seeking alternatives to the outright replacement of these units, particularly where the removal of the old transformer is costly in terms of service interruption or because it is inaccessible without major changes in the structure in which it is housed.

One alternative is to clean the askarel transformer by using silicone liquid retrofill and adsorption techniques to remove residual PCBs. A typical 300-gallon 1500 kVA transformer can be retrofilled with fire-safe, environmentally safe silicone liquid with as little as 12 hours power interruption. The transformer will then contain 1/50 to 1/100 of the original amount of PCB. After about 105 days, plus a 90-day wait required by EPA regulation, this typical unit can be reclassified as "PCB-contaminated." At this point, it will contain less than 1/1000 as much PCB as the original askarel unit.

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DISCUSSION

QUESTION: Is derating of the cleaned transformer required?
ANSWER No

QUESTION: Is 1% residual PCB level after retrofill actually experienced?
ANSWER: Special techniques must be used to get to 1%. A single drain-flush will result in 5%-6%. Multiple processing is required. The flushing solvent is 60% trichloroethane.

QUESTION: How do you know when the filter unit is saturated?
ANSWER: Watch the PCB level in the fluid. When it starts to rise, the filter is saturated.

QUESTION: What control do you have to ascertain that your contractors follow procedures?
ANSWER: Dow provides training and technical assistance.

QUESTION: Previous experience did not show the success ratio now clained. Is this a new set of data?
ANSWER: Yes. To date, approximately 1/3 of the PCB transformers treated have been reclassified as PCB contaminated. The process can take up to two years to reclassify to non-PCB. To date, only one transformer has been classified non-PCB.

QUESTION: Have you examined the possibility of manifolding to speed up the process?
ANSWER: Yes we are actively looking into it now. It could increase the initial reduction. However, leaching is slow and manifolding will not speed up that process.

QUESTION: How long does complete decontamination take?
ANSWER: About two years.

QUESTION: What happens to the trichloroethane used for flushing?

ANSWER: It is drained and any remaining is absorbed during the process.

TABLE I

SUMMARY OF CURRENT EPA RULES REGARDING TRANSFORMER CLASSIFICATION

Requirement	Non-PCB	PCB-Contaminated	PCB Transformer
PCB concentration in dielectric liquid	Less than 50 ppm (1)	50 - 500 ppm (1)	500 ppm or greater (1)
PCB labeling	Not required (1)	Not required (1)	Required (1)
Inspection program and records	Not required (2)	Not required (2)	Required (2)
Service or rebuild restrictions	No restriction (1)	Any service by operator or exempt service company (1)	No service that requires coil core removal (1,2)
Carcass disposal	No restriction (1)	No restriction (1)	Approved landfill or incinerator (1)
Liquid disposal	No restriction except no fluid with detectable PCBs can be used as a "sealant, coating or dust control agent" (1)	Approved landfill, high efficiency boiler, or approved incinerator (1)	Approved incinerator (1)
Satisfies "exposure risk to food or feed" requirement	Yes (2)	Yes (2)	Yes (2)

TABLE II

FLASH AND FIRE POINT RATINGS
AND HEAT RELEASE RATES
FOR DOW CORNING 561

Flash Point	>300°C
Fire Point	>350°C

Heat Release Rates

• Radiative	25 KW/m²
• Convective	53 KW/m²

Heat release data generated by Factory Mutual Research in large-scale pool fire tests. Heat release rate values are used in the FM Loss Prevention Data Sheet 5-4S/14-8S

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TABLE III

ADSORBER UTILIZATION SCHEDULE
TO ACHIEVE PCB CONTAMINATED RECLASSIFICATION

Adsorber Number Or Event	PCB Concentration (ppm) In Liquid At		Lbs. PCB Adsorbed	Total Elapsed Time (days)
	Beginning	End		
1	10,000	1,500	21	1
2	1,500	50	4	3
3	50	50	4	13
4	50	40	3	105
Waiting Period	40	450	Note 1	195
4	450	75	4	200

Note 1: The adsorber unit is inoperable during the waiting period. The transformer is reclassified at the end of the waiting period.

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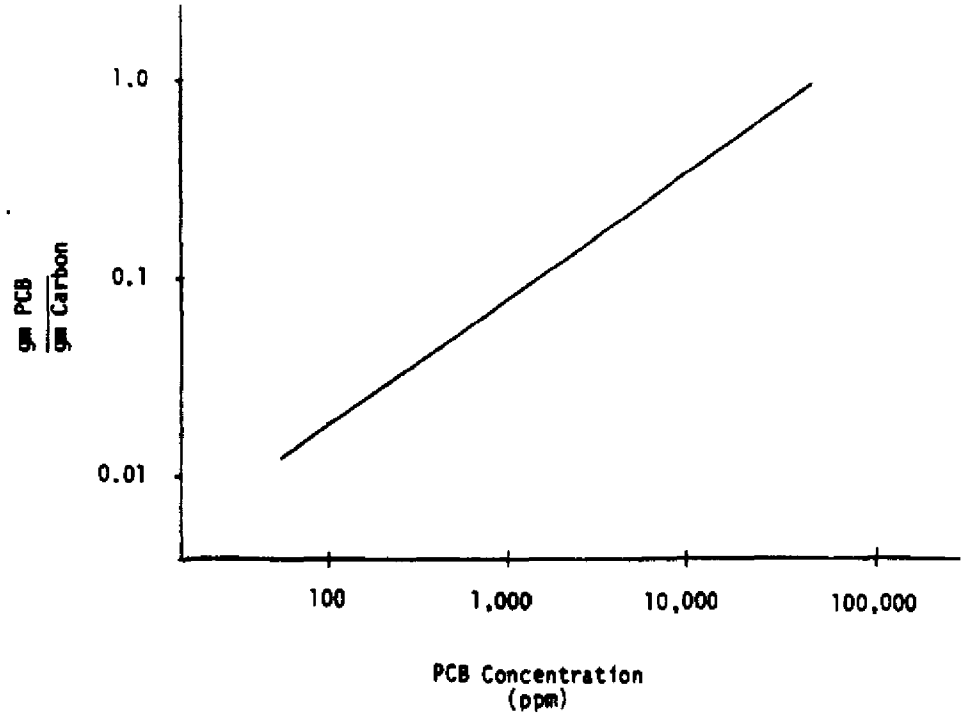
FIGURE I

REPRESENTATIVE PCB/SILICONE FLUID

ADSORPTION ISOTHERM



MONS 214784

C_2Cl_4 AS A SUBSTITUTE FOR PCBs

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When PCB's were forced out of the marketplace due to environmental concerns, there were no non-flammable replacement fluids available as a replacement. The alternatives were to use dry type transformers or to use "less flammable" fluids.

The Electric Power Research Institute, EPRI, and other utility companies initiated several projects to identify insulation systems which would be both economical and heve fire resistance equal to or better than the Arochlors.

One of these EPRI-ESSERCO projects resulted in the development of a C_2Cl_4 tetrachloroethylene based insulation system.

As part of this original EPRI-ESSERCO project, two transformers were manufactured and subsequently placed in service at host utilities. As of this date, these transformers are still operating satisfactorily. Additionally, Westinghouse hes sold, and placed in service, over five hundred C_2Cl_4 filled units since 1981.

The intent of the presentation will be to discuss some of the many variables which were considered in developing the C_2Cl_4 based insulating systems and also to briefly describe the verification testing which was used to evaluate these systems.

It will not be possible within the short time available to go into all areas in depth, but additional information can be obtained from either EPRI or Westinghouse.

Selection Of The Fluid

There were four primary criteria used in evaluating candidate fluids for use in transformers - Functionality, Economics, Flammability, and Toxicity. Each of these factors is very important, and a fluid must be capable of meeting all four requirements to be a candidate.

Non-flammable fluids come from only a few classes of chemical compounds - Inorganic polymers, phosphate esters, highly halogenated fluids, and specialty compounds such as water or liquid ammonia.

These types of fluids were examined with regard to both functional and chemical requirements. From this rather large body of potential candidates, only a few fluids met the project goals.

Flammability

The obvious choice, water, sets the criteria by which all other fluids are judged on flammability. The major problem confronted in judging fluids was what testing techniques were available for evaluation of non-flammable fluids. These were active programs at both Factory Mutual Research Corporation and National Bureau of Standards to evaluate the fire properties of dielectric fluids. FMRC efforts were directed at "less flammable fluids", and the NBS project was directed at explosion resistance of transformer fluids. The FMRC test was essentially a large pool burn where heat release and weight loss were determined. The NBS tests were basically visual comparisons of the behavior of fluids in explosive situations.

Both 100% C_2Cl_4 and 75% C_2Cl_4/25% oil were subjected to these tests. In neither test did ignition occur. In fact, in some of the tests, the fluid acted as an extinguishant for the ignition sources. Although time does not permit a more in-depth discussion of this topic, details and further information are available from either EPRI or Westinghouse.

Dielectric Functionality

THe dielectric performance of the fluid is an essential requirement. Included in this area of evaluation are not only the performance of the new fluids but also what are the aging effects and the hydrolytic effects. An actual examination of the candidate fluids based on these functional criteria, eliminated many potential candidates. Only a small number of helogenated or specialty fluids met both the flammability and functionality criteria.

Fluids were examined for dielectric and impulse performance, for hydrolytic stability, for thermal stability, for systems interactions, and for processing requirements.

As would be expected, no fluids could be used as a direct replacement for Arochlors or for oil. It was, therefore, necessary to determine what system changes would be

required to utilize each fluid. In the case of C_2Cl_4 and C_2Cl_4/oil, it was determined that there were both advantageous and disadvantageous properties. Some of the more advantageous properties were the impulse strength of C_2Cl_4/oil solutions and the greatly improved cooling and thermal properties of these C_2Cl_4 fluids. The major disadvantages were the low temperature performance of pure C_2Cl_4 and the materials capability with C_2Cl_4 based fluids. The economic ramifications of using these systems will be discussed later in this presentation.

Safety

The one area of fluid evaluation which is continually discussed but not often definitively measured is safety. Frequently, it is necessary to make a value judgment as to which type of safety hazard must be tolerated. With the fluids we are discussing here, flammability continues to be the primary concern.

In order to assume complete safety from a fire hazard, there has to be a tradeoff in some other area. C_2Cl_4 was chosen as a dielectric fluid, not because it was a totally safe liquid, but because it was a fluid which had available a tremendous amount of both toxicological and handling information.

There is a saying that "the greater the data, the greater the confusion", such is the case for C_2Cl_4 safety. In spite of all the conflicting data, there are certain bottom line observations which can be made.

1. C_2Cl_4 is not an acutely toxic material.
2. C_2Cl_4 does require certain handling and processing techniques consistant with good chemical practice.
3. The long term exposure data based on epidemiological studies are conflicting in results and may never be resolved.
4. Ditto for carcenogenic studies.
5. C_2Cl_4 should be isolated from ground water systems.
6. There is a lot of C_2Cl_4 being released to the atmosphere, and government efforts are directed at limiting this type of ammission.
7. When compared to Arochlors, C_2Cl_4 is much safer under both arcing conditions and fire conditions.

I hesitate to make this last statement because there are those who claim that C_2Cl_4, because it contains both carbon atom and chlorine atoms, should be put in the same catagory as PCB's. To a knowledgabla chemist, this statement is ridiculous. It is the tremendous chemical differences between the chemical classes of olefins and

aromatics that make C_2Cl_4 an acceptable alternative to PCB's.

Economics

Because Westinghouse is a profit making business, the economics of use and processing was a consideration for any PCB replacement fluid. Our goal was to develop a non-flammable fluid competitive with mineral oil. To achieve this goal, we had to balance the improved performance characteristics against the necessary materials and process requirements.

As the project progresses and additional information is generated, there are continued improvements being made in the cost of C_2Cl_4 based units. It is envisioned that the EPRI project goals are still possible.

The following statements summarize the current status of transformers cooled with C_2Cl_4 based fluids.

1. C_2Cl_4 based fluid insulation systems are functionally superior to PCB's in many aspects, such as fire, cooling, and toxicity.
2. C_2Cl_4 is a safe fluid if used with commonly practiced handling techniques.
3. C_2Cl_4 based fluid insulation systems are applicable over a wide range of transformer sizes.
4. Field performance over a three year period has demonstrated the superior performance of this type of unit.

DISCUSSION

QUESTION: What is the status of the National Cancer Institute study?

ANSWER: Both first and second studies have been discontinued.

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Part 4

SPILL CLEANUP AND BIO-DEGRADATION

CLEAN-UP OF SOILS CONTAMINATED WITH PCBs

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ABSTRACT

Large tracts of land across the country are contaminated with PCBs. Because of the low solubility of PCBs in water, the migration of PCBs through soils is not as rapid as observed for some other chemicals. However, as the PCBs approach property boundaries and water supplies, decontamination of the soil becomes necessary. The usual disposal method consists of physical removal of the contaminated soil to an approved landfill. Under ideal circumstances, impermeable clay barriers have also been used to stop the migration of soil contaminants. Both methods are expensive and do not remove the PCB contamination from the environment. Experiments have been performed that demonstrate the feasibility of extracting the PCBs from soil. By choosing a solvent that does not pose an environmental hazard, the soil can be returned to its original site without incurring the costs of long distance transportation required for landfilling. Once the PCBs are in the solvent, the LARC process can be used to dehalogenate the PCBs and the solvent recycled. The on-site extraction and destruction of PCBs appears very attractive when compared to alternative disposal/containment processes.

CLEAN-UP OF SOILS CONTAMINATED WITH PCBs

INTRODUCTION

Contamination of soils and sediments with PCBs has occurred as a result of transformer failure, accidental spillage and deliberate dumping. PCBs that enter the environment migrate slowly through the soil eventually contaminating surface and ground waters. Little degradation of these molecules occurs and high concentrations of PCBs can be found in the soils around spill areas 10 to 20 years after the incident. The currently accepted spill clean-up procedures involves excavation of the soil in the spill area, transport of the contaminated soil to an approved landfill and backfilling and revegetating the spill area. Landfilling of PCB contaminated soils transfers the problem to another location, it does not solve the problem of removing PCBs from the environment. For example, the State of North Carolina is currently facing the problem of what to do with a landfill containing PCB contaminated soils. North Carolina solved its immediate PCB problem by removing 42,000 cubic yards of dirt from its roadsides and placing it in a landfill. However, citizen reaction to the landfill has prompted the state to look into alternative technologies for decontamination of the PCB landfill

This paper describes the development of a process aimed at removal of PCBs from soil and their ultimate destruction. The process utilizes liquid extraction of the soil and degradation of the extracted PCBs via the LARC process. The extracted soil can be replaced in the original site and revegetated.

LARC PROCESS DESCRIPTION

LARC (Light Activated Reduction of Chemicals) is a patented photochemical process (U.S. Patent #4,144,152) which uses ultraviolet light and an optimized reducing environment to dehalogenate various chlorinated, brominated and iodinated organic compounds. Since the photochemical reaction is initiated by the absorption of light energy, the irradiation wavelength must match the absorption band associated with the bond of interest in the molecule and the solvent must not absorb significantly at the irradiation wavelength. For PCBs, low pressure mercury lamps which emit approximately 95% of their energy at 2537Å provide adequate irradiation. Solvents which meet the optical criteria include water, alcohols and hydrocarbons. However, these solvents have very different effects on the process efficiency and mechanism. In water solutions, the hydrogen gas provides the hydrogen source for the hydrodehalogenation reaction as evidenced by the incorporation of ^{1}H into kepone subjected to LARC in $NaOD/D_2O$ solution. For PCBs in heavy hydrocarbons, the preferred reaction

is the polymerization of the biphenyl radicals to yield polyphenylenes. In basic alcoholic solutions, a stepwise dechlorination occurs in the LARC reactor. This photochemical reaction occurs via the triplet state and the reaction rate is dependent on the life time of the triplet state. The hydrogen for the hydrodehalogenation initially comes from the solvent. In alcoholic solutions, the hydrogen gas increases the reaction rate by removing triplet quenchers from the solution by combination with the solvent free radicals formed. In addition to the hydrogen, small amounts of sodium hydroxide are added to the alcoholic solution as a chlorine scavenger. These photochemical conditions lead to a rapid, highly controllable reaction which yields only biphenyl and sodium chloride as the final products. No oxygenated derivatives, chlorinated dibenzofurans or chlorinated dioxins have ever been observed in the gas chromatographs or the mass spectra of the intermediates or products in the LARC degradation of PCBs.

METHODS AND MATERIALS

The application of LARC to decontamination of soil contaminated with PCBs requires that the PCBs be efficiently removed from the soil medium. Studies were performed to determine the extraction efficiency of Aroclor 1260 from soil using isopropanol as the extraction solvent. This solvent was chosen for evaluation in the laboratory because it is a good LARC solvent, the solubility of PCBs in isopropanol is greater than in methanol or ethanol and it is relatively inexpensive. For the initial extraction studies, a clay soil (2.0% organic matter; pH 5.6; Ca, Mg, P, and K levels were 660, 77, 56, and 20 mg/kg, respectively) was used. Air dried soil was spiked with Aroclor 1260 in acetone, thoroughly mixed and the acetone allowed to evaporate in a hood. Random subsamples of the soil were taken, combined and Soxhlet extracted using a mixture of 50% acetone and 50% hexane. The extract was diluted to the detector range and analyzed on an HP 5880 GC with computer controller/integrator and autosampler. Separation was affected using a 10 ft. x 2 mm I.D. glass column packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 mesh Supelcoport and nitrogen carrier gas at a flow rate of 25 mL/min. The oven temperature was held at 195°C for 2 minutes and then programmed at 10°C/min to 225°C (hold for 1 minute), then programmed at 4°C/min to 244°C (hold for 15 minutes). The injector was maintained at 270°C and the ^{63}Ni electron capture detector was maintained at 300°C. This procedure yielded an initial concentration of Aroclor 1260 in the dry soil.

Weighed amounts of dried, spiked soil (approximately 330 g) were placed in two one liter beakers. One hundred mL of distilled water were added to the soil in one of the beakers and the soil and water thoroughly mixed to yield a wet soil containing approximately 23% water. Five hundred mL of isopropanol were added to both the wet and

dry soil and the mixtures stirred on a magnetic stirrer for 10 minutes. The liquid was then decanted and the volume measured. This procedure was repeated a second time. A portion of each extract was taken, diluted and chromatographed under the above conditions to determine the amount of Aroclor 1260 removed from the soil. The soils were then air dried, a random sample taken from each, Soxhlet extracted and analyzed using the above conditions to determine the amount of Aroclor 1260 remaining in the soil.

The two extracts from the dry soil were combined, sodium hydroxide pellets added to form a 2% solution and a portion of the solution analyzed to determine the Aroclor 1260 concentration. The remainder of the solution was subjected to LARC using the single tube batch recirculation reactor shown in Figure 1. The reaction rates in this single tube reactor are significantly lower than a multiple lamp, high light density reactor, however, only 800 mL of solution are required for operation as compared to 30 gallons for our 64 lamp pilot unit. Since the scaling factors between the two reactors are known, this single tube reactor is a convenient unit for evaluating the degradation rates under differing conditions. The reaction was started by placing the solution into the reactor. The hydrogen gas was then turned on and allowed to purge the reaction mixture for 5 minutes. The ultraviolet lamp was then turned on. Samples (10 mL) were drawn from the LARC reactor after 20, 40, 60, 90, 120 and 180 minutes so that the degradation reaction could be followed and reaction rate determined. These samples were diluted to within the detector range and analyzed on a Varian 3700 gas chromatograph with autosampler. Computer controller/integrator was provided by an HP 5880 GC. The separation was performed using a 12-foot by 2 mm I.D. glass column packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 Supelcoport. The carrier gas was N_2 at a flow rate of 20 mL/min. The oven temperature was held at 180°C for 1 minute, then programmed at 10°C/min to 240°C (hold for 20 minutes).

RESULTS

The extraction data for soil contaminated with Aroclor 1260 are summarized in Table 1. Extraction of dry soil resulted in 70-75% removal in each stage with a solvent to solids ratio of 1.2/1 (wt/wt). The overall two extraction efficiency was 92% with 74% solvent recovery. The extraction efficiency for the wet soil was slightly lower, 55-60% in each stage. However, 12 mg of Aroclor 1260 or 7.5% of the initial PCB concentration in the soil were unaccounted for in this extraction. The recovered solvent (77%) also contained significant quantities of water. Overall extraction efficiency based on the PCBs remaining in the extracted soil was approximately 90%. In a real-life situation, two solid/liquid extractors would be required with each

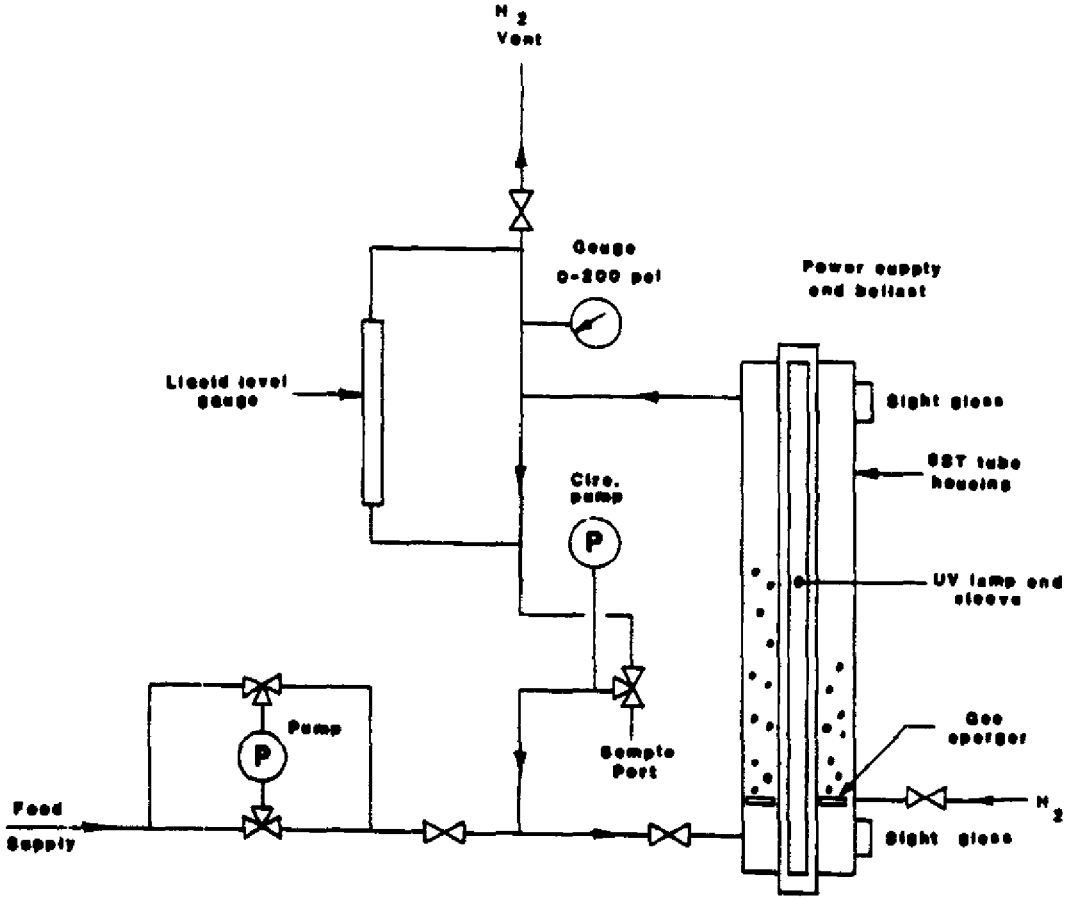

Figure 1. Schematic of Single Lamp Larc Reactor

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Table 1

EXTRACTION OF AROCLOR 1260 FROM SOIL

	Dry Soil	Wet Soil
Initial PCB Concentration (mg/Kg)*	487	486
PCB Removed From Soil in First Extraction (mg/Kg)*	337	268
Solvent Recovered From First Extraction (mL)	320	360
PCBs Removed From Soil in Second Extraction (mg/Kg)*	113	131
Solvent Recovered From Second Extraction (mL)	420	410
Final PCB Concentration in Extracted Soil (mg/Kg)*	38	50
Overall Extraction Efficiency	92%	90%

*All concentrations based on dry weight of soil.

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extractor using a solvent feed free of PCBs. Solvent/solids ratios may also have to be increased depending on the initial PCB concentration in the soil.

The results of the LARC degradation of Aroclor 1260 in the isopropanol extract of the dry soil are shown in Figures 2 and 3. Degradation proceeds rapidly even in the presence of particulates with a pseudo first order rate constant of 0.052/min. In a larger reactor with greater light density, the degradation rate can be expected to be 2 to 2.5 times that of the single tube reactor.

DISCUSSION

The laboratory data have shown that PCBs can be efficiently extracted from even a wet soil using a solvent such as isopropanol. The PCBs in the extract can be successfully degraded by the LARC process. However, in actual spill situations, the concentration of PCBs in the soils will vary considerably with lateral distance from the source and with depth. Any process must be capable of handling extremes in PCB concentration and still maintain preset criteria for removal from the soil and PCB destruction.

The data on PCB extraction from soil and degradation with LARC were combined with similar data obtained on other chlorinated organics to design a mobile unit that can clean-up spills of PCBs from soils. The process schematic is shown in Figure 4. As envisioned, this equipment will be mounted in a standard trailer and consist of two counter-current extraction units to remove the PCBs from the soil. After extraction, the soil will be vacuum stripped to remove and recover residual solvent. The soil can then be placed back into the excavated site. The extraction solvent will be sent to a still where the solvent will be recovered for reuse in the extractors and the PCBs concentrated. The extraction and concentration steps will be operated approximately 6 hours per day. The concentrated PCBs will be stored in a surge tank. The extraction/distillation step will be run to produce enough concentrated PCBs to provide feed for the LARC reactors on a continuous 24-hours basis. The concentrated PCBs will be metered into the LARC units continuously over a 24-hour period. Thus, the PCB concentration entering the LARC units can be tightly controlled even though the concentration in the soil varies dramatically. This process design provides the flexibility to treat any type of soil at varying PCB concentrations and still maintain optimum rates in the LARC reactors.

Costs for PCB removal from soil and destruction by the LARC process are dependent on the <u>average</u> PCB concentration in the soil. In most soils, high concentrations (<u>e.g.</u> 90,000 mg/Kg) will be found close to the spilled area. Once out of the immediate spill

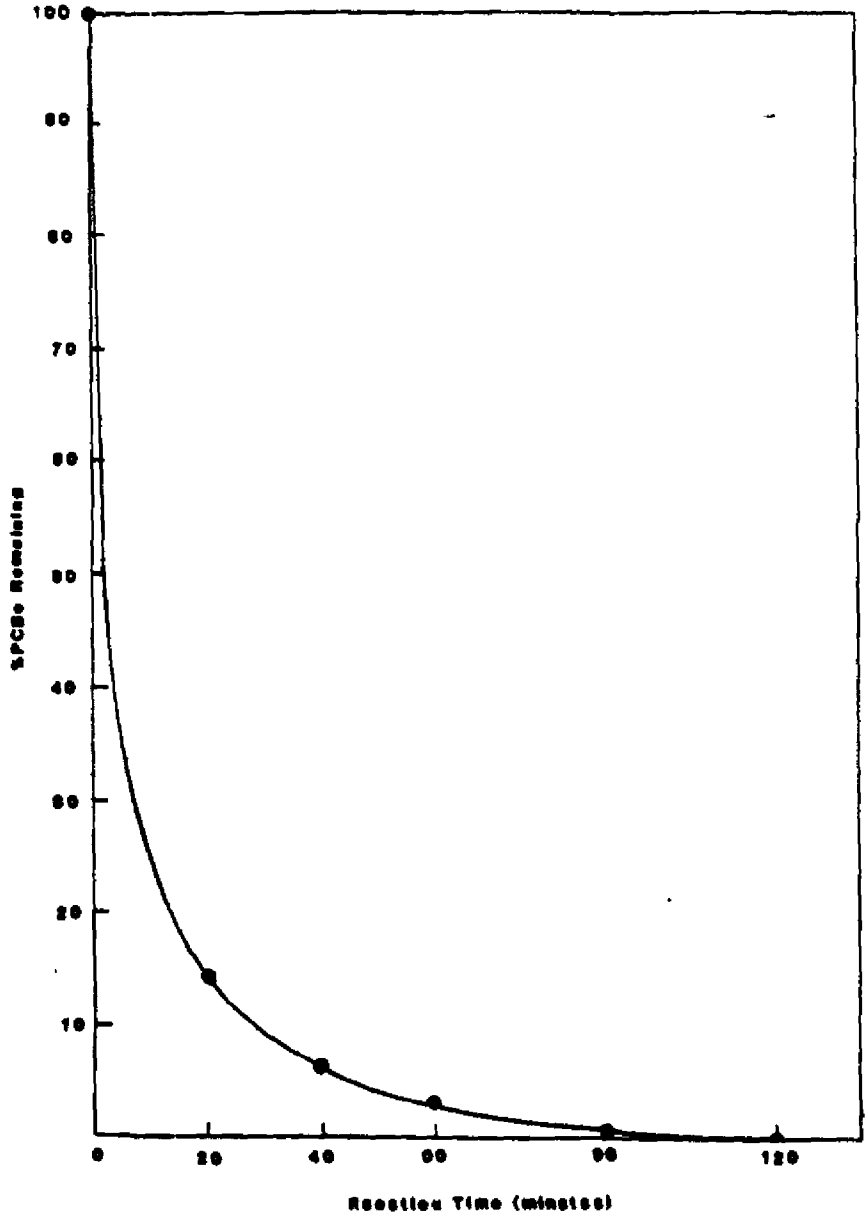

Figure 2. LARC Degradation of Aroclor 1260 in Basic Isopropanol

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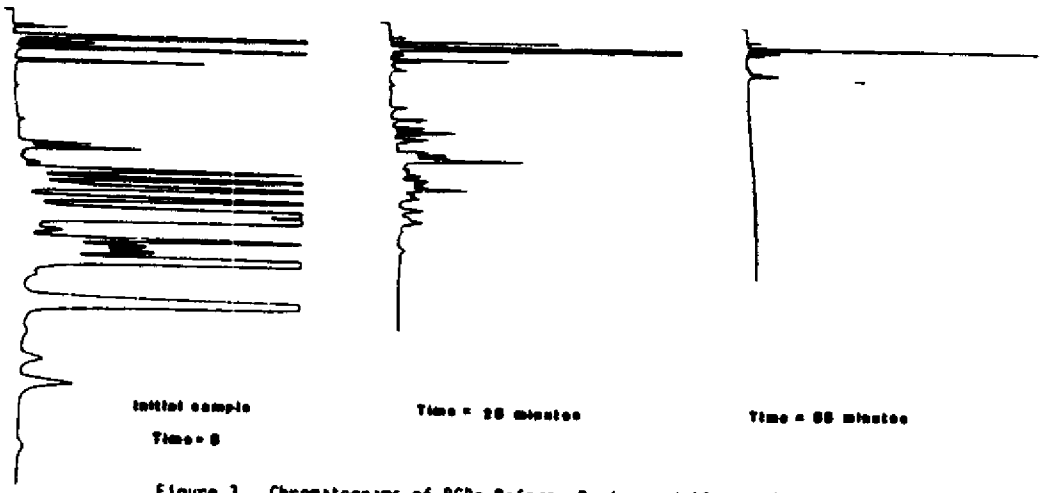

Figure 3. Chromatograms of PCBs Before, During and After LARC Treatment

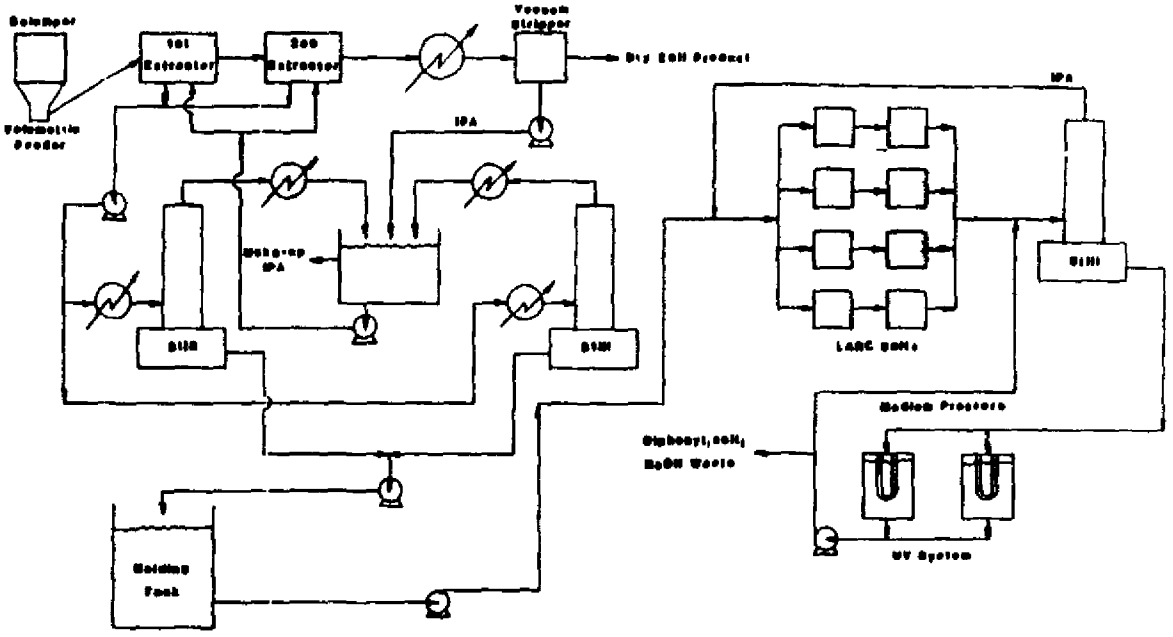

Figure 4. Schematic of LARC Mobile Unit for Destruction of PCBs in Soil

area, the PCB concentration will drop off rapidly. However, if leaching has occurred, large areas contaminated between 50 and 500 mg/Kg can be expected. In our cost calculations, we chose an average concentration of 1500 mg/Kg of PCBs. Items included in the cost estimates are capital expenses, daily operating costs, labor, analytical, travel, per diem, and profit. At an average soil concentration of 1500 mg/Kg, total costs are $84.60/ton of soil. Landfill costs for PCBs are $70/ton including tax. Transportation charges add $2.75 per loaded mile or approximately $50/ton for a 400 mile trip yielding a disposal only cost of $120/ton. Excavation costs, analytical costs and refilling costs must be added to the cost for landfilling the contaminated dirt. These costs could add an additional $50-100/ton depending on the required analyses. Thus, LARC costs for clean-up of PCB contaminated dirt range from 38 to 50% of the costs associated with landfilling the contaminated dirt, but more important it removes PCBs from the environment permanently.

Discussion

Q1. What throughput is expected?

A. LARC is designed to degrade 8500 ppm/min. It will vary, but with 1500 ppm in soil, it should be good for 15-20 tons per day. High levels of organics will slow the process down.

Q2. Have you published data on spill clean up?

A. No, and don't plan to.

Q3. Have you constructed a full scale unit?

A. No.

Q4. This work was with 2% organics. Any work with higher levels?

A. No.

Q5. What are the power requirements?

A. To provide power from internal generator. Not a great problem.

Q6. What is your estimate of cost?

A. $84/ton including excavation from site, but not including return to the excavation.

Q7. Is it a batch or continuous process?

A. Could be either.

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Q8. What % of PCB is left in the solvent?

A. Less than 2%.

Q9. Does EPA allow solvent extractions?

A. EPA currently only allows landfill, but an EPA representative present at the Seminar indicated willingness to review the process for possible approval.

CLEANING OF PCB CONTAMINATED SOILS

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The cleanup of PCB spills is a major concern to the utility industry. These occur if a capacitor, transformer, switch or other PCB-containing equipment develops a leak while in service and contaminates the surrounding area. A cleanup cost of $30,000 is not uncommon for a leaking PCB transformer or capacitor, especially if it had gone undetected for a period of time.

In addition to the cleanup of PCB leaks from field equipment, the utility industry is faced with the long-term problem of transformer yards, repair facilities, or substations that have outlived their usefulness. These older facilities can be several acres in size and because they were used at a time when PCBs were not regulated, they are often heavily contaminated.

The current method of cleaning up a small site such as a leaking transformer, involves simply removing the soil and taking it to a chemical waste landfill that has been approved for PCB disposal. The site is backfilled with clean dirt. The major expense of this process comes from trucking the dirty soil and disposing of it in a landfill.

When large areas are contaminated, hauling the soil to a disposal site becomes impractical. There is often insufficient landfill capacity available for its disposal and if it is available, it is very expensive. In these cases, the contaminated site is isolated by some form of groundwater barrier, such as a grout curtain, and then capped to reduce rainwater infiltration. Then, if necessary, groundwater is pumped from this confinement into a treatment plant. This creates a net inflow of water into the contaminated site and reduces the possible migration of the contaminant into the environment. This approach involves long-term expenses which can be formidable.

The program described here examined soil washing as an alternate PCB cleanup procedure. The technique has the potential to remove PCBs from the soil onsite and hence, eliminate both hauling, landfilling and backfilling for cleanup, thereby reducing the cost substantially. Two soil washing techniques were examined. The first, solvent washing was found applicable to most situations even where the final

PCB concentration in the soil must approach zero. The second technique, water washing proved to be an impractical procedure.

The question of "how clean is clean" will arise in any type of a cleanup operation. In some cases, any material containing less than 50 ppm PCB is considered clean. In others, no measureble PCB is allowed. After discussing this with a number of people at various Environmental Agencies, we established 2 ppm as an acceptable level of cleanliness for PCB.

THEORETICAL CONSIDERATIONS

The experimental program described in the next section sought to determine the equilibrium constant that describes the actual concentration of the PCB in the liquid after each wash.

The process of washing soil is directly analogous to that of adsorbing pollutants from a wastewater using, for example, activated carbon. In both cases, one first needs to determine the concentration of the pollutant (PCB in this case) in the liquid phase that is in equilibrium with a given concentration on the solid phase. These values over the range of concentration are commonly referred to as the adsorption isotherm for the system. In the case of soil washing, we are actually desorbing rather than adsorbing the pollutant but the process is entirely analogous from an engineering point of view.

In addition to having a favorable equilibrium, it is important that the rates at which the pollutant diffuses into the washing fluid be fast enough so that the overall process occurs in a reasonable length of time. This proved to be a problem when using pure Freon with top-soil. The equilibrium was favorable; however, it took up to 18 hours for the system to reach equilibrium. This would not result in a practical solvent washing system. With the proper choice of solvents, the time required to reach equilibrium was reduced to 30-45 minutes, a very practical value.

The design equations for the removal of PCB from solid materials was presented in greater detail in an earlier report (1). Based on that derivation, it is possible to define a constant "K" relating the PCB concentration in the liquid coming from two consecutive washes of the soil. It is defined as:

$$K = y_n / y_{n-1}$$

Where y_n and y_{n-1} are the PCB concentrations in the liquid leaving the nth and (n-1)th washes respectively. On this basis, it can be shown that after N washed, the amount of PCB residue left on the soil, S_n is:

$$S_N = L\, y_N K/(1-K)$$

Where S is weight of PCB left on the sample of soil and L is the volume of liquid used for each wash. L is constant from wash to wash.

The laboratory investigation for this system, showed that such a solvent washing system can achieve a value of approximately 0.5 for PCBs in various types of soil. This value proved to be reasonably independent of the type of soil being cleaned and the PCB concentration of the soil itself. This means that the wash liquid leaving a wash will have a PCB concentration of approximately half of the preceding wash.

The solvent used for the washing will influence the economics and safety of the system greatly. It must have the following properties.

1. Miscible with PCB to high concentrations
2. Non-flammable for safety in the field
3. Low latent heat of vaporization and low boiling point for ease of recovery
4. Low toxicity
5. Be able to "cut through" water
6. Capable of wetting the soil
7. Readily available

The study examined following solvents, representing a range of properties.

1. pure hexane
2. pure FC-113 (1, 1, 2 trichlorotrifluoroethane)
3. a proprietary solvent blend
4. FC-113/hexane blend

It was found that only the proprietary solvent was able to reduce the PCB concentration in the soil to below 2 ppm. In addition, this solvent satisfies all of the other criteria listed above.

LABORATORY EVALUATION

The first step in the laboratory evaluation was to contaminate soils with PCBs. The following types of soils were selected.

1. Pure sand
2. A high-clay soil
3. Potting soil, representing a high carbon soil

The solvent washing experiments were conducted by placing 100 grams of contaminated soil into a jar with a tight fitting lid. The soil was then covered with the solvent (100-200ml) and then the jar was placed into an ultrasonic bath. In the earlier tests of this series, samples of the solvent were withdrawn at approximately 15 minute intervals so as to determine the time required to reach equilibrium. This showed that the equilibrium is reached in essentially 15-45 minutes.

The purpose of these tests was to establish whether these soils would be cleaned to less than two ppm PCB and how many washes this would require. It is recognized that the number of washes required will be function of the volume of liquid used. The data can, however, be converted to a series of "desorption isotherms" similar to the "adsorption isotherms" commonly used to size adsorption columns for wastewater or gas cleaning.

The test were conducted by placing 100-200 grams of the soil into a jar with a tight fitting lid. Enough solvent to cover the soil with a 1-2 cm excess was then added to the jar and this volume of solvent determined.

All successive washed were conducted using this same volume of solvent. Some tests were conducted by using ultrasonic agitation to facilitate the cleaning operation. In those tests which included ultrasonics, the jar was placed into a small ultrasonic cleaning unit which was filled with water as a transfer medium. The ultrasonic cleaning was found to be a very effective aid in removing the PCB.

In order to establish how long a contact time was necessary to reach equilibrium samples were withdrawn from the jar at intervals ranging from 15 minutes to overnight. It was found that with the aid of ultrasonics and the proper choice of solvent, the PCB concentration in the liquid reached virtually a constant level within 30 minutes. This was not the case when pure FC-113 was used as a washing medium. Evaluation of the results of the potting soil tests showed as much as three-fold increase in the PCB concentration of the liquid phase when kept overnight. This is contrasted with the washes using the proprietary solvent which showed little or no change in the liquid PCB concentration even over a weekend.

Beaker tests were also conducted with combinations of these soils using water and a water/isopropanol solution. These proved very disappointing for all soils except, to a limited extent the pure sand. These liquids removed the PCB from the soil in a linear rather than in a geometric manner.

When cleaning soils down to the very low levels of PCB required here, it is essential that each successive wash remove a fraction of the PCB rather than a fixed amount. The amount of pollutant removed must be proportional to the amount on the soil resulting in a geometric reduction in the PCB concentration. The aqueous based solvents caused a linear reduction of the PCB; each wash removed anywhere from 3 to 20 ppm. Reduction of the PCB concentration from, say 1000 ppm to 100 ppm could take several hundred washes. This is inherently not impossible; however, the effluent from each wash must be treated resulting in thousands of gallons of water for each cubic yard of soil processed.

It was concluded that aqueous based solvent washing of soil does not appear to be a promising approach to achieving the low PCB concentration required.

The bulk of this experimental program investigated whether it is possible to remove PCBs from soil using washing techniques. Once the PCB is removed, however, it is still necessary to dispose of it. The overall scheme requires that the solvent be distilled off and purified after the washing of the soil and the PCB and other pollutants left behind in a reactor. The concentrated PCB can then be shipped to an incinerator or destroyed using a sodium based reagent. All of the solvent from this experimental program was treated in this manner. It was accumulated in large flasks and distilled. The PCB residue was then successfully destroyed using the Acurex PCB destruction process. Final PCB concentrations of less than 2 ppm (the limit of measure) were obtained in the liquid. This is considered to be a non-PCB material by enviromental agencies.

CONCEPTUAL DESCRIPTION

When starting this type of research program it is important to establish a design goal to work towards. This is a goal rather than a design; further reasearch will undoubtedly cause major changes in the final operating system. The initial design is, however, useful to determine the type of data that the preliminary research program must produce.

The basic soil washing system is shown in Figure 1. Please note (again) that this is a conceptual rather than an acutal design. It is recognized that because of the requirements of materials handling, structural strength and mobility, the final unit will most likely look significantly different.

Fundamentally, the unit consists of several (the drawing shows three but that is not fixed as yet) cells mounted on a trailer. The cells are set up so that soil can

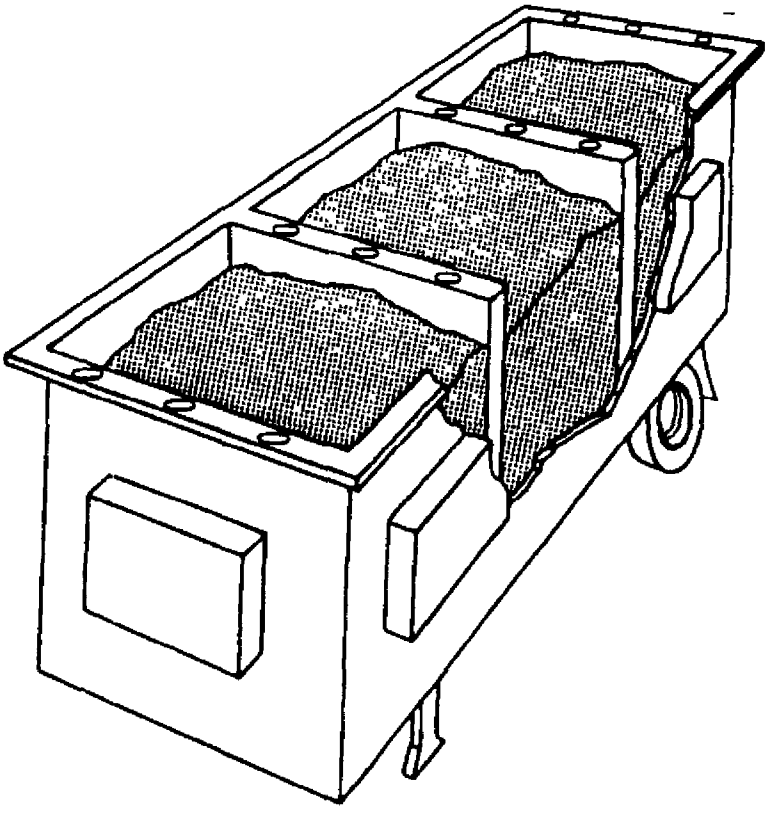

FIGURE 1

CONCEPTUAL DRAWING OF
SOIL CLEANING SYSTEM

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readily be put into them using standard earth moving equipment. The system can be tipped for ease of removing the cleaned soil. Since the solvent to be used is volatile, each cell can be sealed tightly. The multiple cells result in an even distribution of the solvent.

The laboratory test found that ultrasonic vibrations greatly enhance the efficiency of the washing cycles. The large soil washing systems have vibrators clamped to the walls to duplicate this. These are similar to vibrators used in pouring concrete and are commercially available. It is envisioned to be operated in the following manner:

1. The unit along with a portable solvent reclamation system is transported to the site of the spill or contamination and set up.

2. Soil is placed into the washing unit then it is sealed closed.

3. The solvent is pumped into the washer and recirculated for approximately 30 minutes.

4. The solvent is pumped out of the washing unit into the solvent reclamation system and clean solvent is once again added to the washing unit containing the partially cleaned soil.

5. This cleaning cycle is repeated until a sample of the solvent shows a satisfactory PCB level.

6. At that point, the residual solvent on the soil is reclaimed by applying vacuum to the washer. It may be necessary to also use a small amount of steam. After cleaning, the soil is dumped back into place, compacted and nutrients added so that it will sustain vegetation.

7. The solvent from each wash is passed through a solvent reclamation system that includes a distillation column and a secondary stripping system for concentrating the residual PCB pollutant removed from the soil.

8. The PCB concentrate from the solvent reclaimer is sent to a chemical destruction system which produces a PCB-free sludge and a PCB destruction reagent which is recycled to the process after filtration.

The system schematic is shown in Figure 2.

CONCLUSIONS

This study has shown that it is possible to wash a wide variety of soils free of PCB contamination using a solvent system that can be used in the field. It also showed that at this time the use of water as a cleaning medium does not appear to be practical in most cases. The study further showed that the proprietary solvent used for the soil cleaning satisfies all of the criteria set for it. It is relatively non-toxic, easily recovered and non-flammable. This is very important if a workable system is to designed on the basis of this work.

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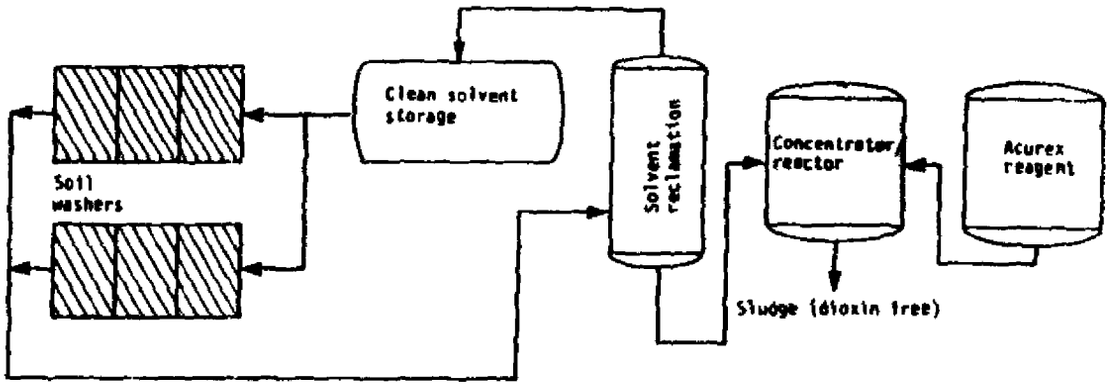

FIGURE 2
SOIL CLEANING PROCESS SCHEMATIC

quite feasible to use the Acurex PCB destruction process in the field to destroy the pollutants washed from the soil at the site. This completes the total cleanup and will make the overall process readily acceptable.

In dealing with such an operation, political acceptability is as much a factor as are the normal technical and economic considerations. The cost of getting local approvals or permits can, at times exceed the cost of doing the job itself. By making this operation totally self contained, the chances of its acceptance are optimized.

Having shown that the solvent washing of PCB contaminated soils is possible, it is now worthwhile to determine its costs. To do so, it would be useful to build a pilot scale unit, approximately 55 gallons in volume to wash soils at a greater rate. This unit could be used to answer the following questions:

1. What is the best system configuration to permit good contact between the soil and the solvent?
2. What liquid flow rates can be used so as to minimize soil entrainment in the filter medium?
3. What type of filter medium must be used commercially to effectively prevent the soil from getting out of the washing system with the solvent and yet not become clogged?
4. What is the optimum liquid to solid ratio that needs to be used for each wash?
5. What are the manpower requirements for such a commercial system?
6. What are the overall costs of operation for various size cleanups?

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Draft report on EPRI Project 1263-7

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ACKNOWLEDGMENT

The work described herein was sponsored by the Coal Combustion Systems Division of the Electric Power Research Institute. Their support and the technical assistance of the EPRI project manager, Dr. Ralph Komai is gratefully acknowledged.

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Discussion

Q1. Have you measured for solvent residuels in ground water?

A. We have not tested. However, the last step before returning the soil is to steam clean. It comes out very dry. The materials used for clean up are generally not toxic.

Q2. What reduction of dioxin can be expected?

A. Initial concentration of 450 ppb reduced to 3 in 8 washings. (It was noted in sampling, testing, and analysis at the 3 ppb level that it is very difficult).

THE COST OF PCB SPILL CLEANUP: A QUESTION OF DEGREE

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ABSTRACT

The degree of PCB spill cleanup required by regulatory agencies, or "how clean is clean", has evolved into one of the most prominent issues surrounding PCBs today. Despite the continued occurrence of PCB spills throughout the U.S., spill cleanup degree is not explicitly addressed under TSCA. The degree of cleanup required to avoid a disposal citation varies with EPA region and state, to the inconvenience and cost of industry.

This paper reviews the current state of regulation for PCB spill cleanup, and assesses the compatibility of these regulations with current practice. Several generic spill situations are presented for use in quantifying the cost of alternate cleanup procedures. Based on these situations, a cost/engineering model is presented. Results of the model are shown, including graphics to illustrate cost sensitivity to cleanup degree and spill type. Conclusions are drawn regarding degree-of-cleanup policy, its economic impact and the future regulatory climate.

Section 1

INTRODUCTION

The August 1982 PCB rulemaking allows much of the utility-owned PCB equipment to remain in service through the end of its useful life. While options for disposal of well-managed PCBs are now better defined, small PCB spills can still occur while the equipment is in service or storage. Proper spill management and emergency response planning can therefore close the perceived environmental hazard loop.

EPA has developed draft guidelines for PCB spill cleanup. The document has not yet been released for public dissemination, primarily because of the inherent difficulties associated with general guidelines geared toward site-specific problems. Regardless, some form of guidelines may ultimately be published for suggested use by the utility industry.

More importantly, there are no universal rules governing the degree to which a spill must be cleaned up. While it is generally recognized that the spilling of PCB fluid to soil or other surfaces constitutes improper disposal if not cleaned up, the question of "how clean is clean" often remains a mystery until the appropriate authority indicates that the area is clean enough. Each EPA regional office uses different cleanness criteria, some states are more stringent than EPA, and the criteria can change with time even if established by law.

The purposes of this paper are to review the stetus of PCB spill cleanup regulations, discuss the nature of PCB spills and approaches to cleanup, and to attempt to compare costs of cleaning spills to several levels of cleanness. The authors recognize the potential difficulty of modeling spill cleanup costs due to the unique nature of each event. Where appropriate, we have qualified our estimates and attempted to quantify the potential variability.

Section 2

PCB SPILL CLEANUP TECHNOLOGY

Despite the sincere efforts of scientists and engineers attempting to advance the state of the art, there are typically only two or three acceptable methods of cleaning up a given spill. For spills to soil, it is excavation and removal. For spills to solid surfaces (houses, cars, concrete, etc.), solvent washing or high pressure steam cleaning is sometimes acceptable in lieu of removal or disposal. For replaceable and/or porous surfaces, it is replacement.

For discussion purposes, three generic types of spills can be identified: transformer leaks, capacitor leaks and capacitor spraying (under pressure). With the proper training, the first respondent on the scene will attempt to visually identify the extent of the spill, seal off the area (including a buffer zone), mark the areas of expected contamination and proceed to use one of the above-mentioned cleanup techniques. Once the visible traces (and expected areas) of contamination are cleaned, sampling is performed over a predetermined grid for residual PCBs. A second cleanup is often appropriate if remaining contamination is high in some localized areas. In the absence of a concentration-based standard, cleanup might often stop there. This is not always the case.

Attempting to estimate the cost of spill cleanup under these conditions is difficult. Costs are nevertheless important to budgeting, risk assessment and bidding. It is not uncommon for project budgets to be exceeded, sometimes by a factor of two or more, due to disagreement over completion criteria.

Nevertheless, basic practice does not vary substantially between companies for a given type of spill cleanup. The practicality of an extended cleanup should therefore be a factor in determining completion, assuming an acceptable and prudent cleanup strategy is proposed and implemented.

Section 3

REGULATIONS GOVERNING PCB SPILL CLEANUP

The cleanup of PCB spills is addressed directly and indirectly throughout the 1979 and 1982 rules. The August 1983 "Question and Answer" book published by EPA* provides the most recent interpretation of its regulations. The booklet addresses three questions on the subject: spill reporting, what happens upon reporting a spill and what should be done to control or clean up a spill. The answers to these questions frame, in part, the agency's policy. It is open to interpretation, and thus explains the great variety of spill cleanup "standards" experienced today.

On the reporting of spills, the agency cites the authority under TSCA Section 8(e) to require the reporting of spills "whenever the incident poses a substantial risk to human health or environment." They note in the response that "substantial risk" cannot be precisely defined. However, they say that for any spill where people can come into direct uncontrolled contact with PCBs, or the spill is such that significant numbers of animals are exposed, the spill must be reported to the National Response Center.

The agency also cites the requirements of the CERCLA Section 103 (a) (48 CFR 23552-23605), DOT (49 CFR 171.15, 171.17), and the Clean Water Act (40 CFR 117.2). The present reportable quantity for PCBs is 10 lbs. The agency has proposed lowering that quantity to 1 lb. Similarly DOT has followed suit in an advanced notice proposing the reduction of the reporting requirement to 1 lb.

Concerning the question of spill cleanup, the EPA suggests the following steps: (1) Report spill; (2) Control the spread of spill by damming or diking the leak (a high priority should be given to spills posing a threat to water); (3) "Once contained, cleanup can be simply the removal and subsequent disposal of contaminated soil and debris." EPA further notes: "In some cases special filtration or

* The EPA Regulations Under TSCA: Over 100 Questions and Answers to Help You Meet These Requirements. Revised Edition No. 3, August 1983. Prepared by the TSCA Assistance Office and Exposure Evaluation Division, U.S. EPA.

PCB sorbents may be required"; (4) "Since the levels required for cleanup sometimes vary, depending on the region (state) in which the spill occurred, regional PCB experts should be contacted to obtain guidance on the extent of PCB spill cleanup." That is the extent of what the agency has to say about the degree of spill cleanup. They do provide a list of experts and phone numbers.

It is interesting to note that the June 1979 version of this booklet differs from the 1983 book in some of its responses. For one, as a general rule, spills involving a single capacitor do (did) not have to be reported unless PCBs threaten or enter a watercourse. However, transformer spills, other than minor leaks, should be reported.

So where does all this leave the PCB owner attempting to clean up a PCB spill? Since the promulgation of rules in 1979, many utilities have felt that cleaning up to 50 ppm would be an acceptable level of cleanup. This level could be found more from an interpretation of the 1979 regulations than an explicit statement. Many EPA regions were advising, and continue to advise, utilities that this is an acceptable cutoff. The EDF vs. EPA suit has undoubtedly had some impact on the state of the situation today, leaving a wide variety of approaches and standards, primarily because of the acceptance of the 50 ppm standard as justified and supported. The cutoff issue relates more to incidental production (and is still pending a final rulemaking), but could still be considered applicable to those grouping for a numerical rather than procedural cutoff.

Meanwhile, there have been a number of test cases with a bearing on the degree of spill cleanup. The agency has prepared an enforcement strategy and interpretation of the PCB regulations that indicates that the agency can enforce a cleanup to background standard, and is endeavoring in some regions to do this. EPA Enforcement Headquarters insists that the regulations provide them with the authority to proceed on a background standard, i.e. any exposure to PCBs is significant, however inconsistently it is applied.

Certainly, a major contributor to the confusion surrounding PCB spill cleanup is the variation in policy between EPA headquarters, regional offices and state agencies. Given the lack of a scientific basis for any "one number" cleanup cutoff, it would appear difficult to justify the background PCB concentration as a cleanup level based on these arbitrary local limits.

A straw poll of EPA regional PCB cleanup policies is summarized in Table 1. Note the variation in both cleanup level and surface treatment requirements. The most stringent of those regions polled is EPA Region 5 (Chicago); a quotation from their current internal policy memo stating the recommended practices for three types of spill locations (degrees of potential human exposure) is as follows:

(1) Limited Contact Area (i.e., Indoor Industrial Settings):

Cleanup of PCBs should be conducted down to 100 times background but not exceeding 50 ug/100 cm^2. Cleanup down to 10 ug/100 cm^2 would be preferrable. Control samples as well as post cleanup samples would be required. Air sampling following cleanup should also be a mandatory requirement to ensure that the OSHA TLV value for PCB of 1 ug/m^3 is not exceeded if unprotected individuals will be present or working in post cleanup area (NIOSH Criteria Document for PCBs, 1977).

(2) High Contact Areas (i.e., Including Industrial Settings, Food, Feed, Schools):

Cleanup should be required down to background levels. Post-cleanup samples and air sampling would also be included. Any food prepared on surfaces previously contaminated with PCB should be tested for PCBs before human or animal consumption is permitted. FDA has developed guidelines and limits for PCBs in various foods, feeds and packing materials (F.R., Vol. 44, No. 127, June 29, 1979, pp. 38330-38340).

(3) Environmental Spills:

Contaminated soils should be removed until the concentrations of PCB in surface and core samples are less than twice that of background samples. The zone plot method of sampling should be utilized (TSCA Inspection Manual, March 1981).*

*Memorandum dated November 13, 1981 from Milt Clark, Region V Health Effects Specialist, to Karl Bremer, Toxic Substances Coordinator, addressing "Interim PCB Cleanup Procedures."

This broad range of spill cleanup requirements raises an important issue: As long as no one can come to grips with a scientifically-based cleanup standard, perhaps a practical standard based on practice and performance is most appropriate (assuming that a standard will indeed be instituted). Such a standard might address sampling, a practical field approach and perhaps a minimum cleanup level standard.

The EEI Utility Solid Waste Activities Group (USWAG) PCB Committee has formed a Spill Cleanup Task Force, to address the specific degree of cleanup issue. The goal of the Task Force appears to be the EPA consideration of a procedure standard for cleanup rather than using a concentration-based performance standard, and to determine whether a procedural standard is feasible and accurate enough, in an effort to permit practicality to enter the decision process.

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Section 4

GENERIC SPILL SITUATIONS

The two principal cost components of a spill cleanup are (1) the investigation and (2) the cleanup itself. The investigation phase includes engineering support, drilling/sampling and analytical requirements. The cleanup phase includes excavation, cleaning, disposal, transportation, closure sampling and analysis. Both phases also include occupational safety and health support. The identification of these cost components is important; doubling the amount of material to be removed not only increases the excavation and disposal cost, but also adds engineering, analytical and safety costs.

In-house cost data were used to develop an empirical cost model. The model essentially simulates the cost estimating process used by an engineer or contractor to bid a spill cleanup job. The "model" is actually a cost estimating algorithm using several inputs that define the scale of the cleanup effort. Input variables include spilled fluid volume, type of spill (lead and spray), surface type, rainfall, degree of cleanup and location near obstacles. These variables, when added to several dispersion algorithms, define the vertical and horizontal extent of the spill, which in turn defines the removal/cleaning requirements. Using standard unit costs for each cleanup activity, a total cost can be computed. Varying any one or more of the input variables changes the dispersion, which changes the cost. Graphics and tables can thereby be developed showing cost sensitivity to changes in these variables.

Because of the number and variability of factors involved in cost estimating, a general model with appropriate assumptions and simplifications was developed. The model does not address regional cost variations, multimedia contamination and a variety of other factors to be discussed in more detail below. Despite this, the model provides a reasonable general cost estimate, most useful for demonstrating the effects of varying parameters on cleanup costs. In addition, contractors' unit prices are used; differences with utility costs should be negated by comparing the relative magnitude of spill cleanup costs.

The spill cleanup model is based on several parameters critical to describing the extent of the spill and contaminate migration, including the following:

- Nature of the spill.
- Volume spilled.
- Degree of cleanup required.
- Surface material type.
- Indoor/outdoor location.
- Rainfall.
- Presence or absence of structures near the spill.

The assumptions, limitations and general sensitivity levels for each variable and their relative impacts are discussed below.

Nature of the Spill

Two types of events are analyzed by the model: leaks and spray spills. For modeling purposes, spray spill is assumed to extend outward 20 feet over an angle of 20°. It is further assumed that the entire surface area beneath the spray pattern (70 sq. ft.) is contaminated with fluid. For outdoor spills, the distinction between leaks and spray spills is important only for those spill volumes that would not spread over an area of 70 sq. ft. in a flow spill. For indoor events, spray spills are assumed to contaminate walls and nearby equipment, increasing the total area to be cleaned.

Volume of Fluid Spilled

The surface area or soil volume contaminated is primarily a function of the volume of fluid spilled. Models are available to predict both the downward movement and horizontal mobility of fluids under a given driving force, given fluid volume and physical characteristics and a surface composition. These models are generally designed to deal with more sophisticated conditions than the model, and have been simplified accordingly. Using these models in their simplified forms, the volume of material contaminated can be estimated.

Surface Material

Both the downward and outward mobility of spilled fluid are dictated in part by the permeability of the surface material. As a result, the area to be cleaned or the volume to be excavated is a function of the contacted surface. Fluid will spread over a much wider area on impervious surfaces: in permeable soils, the outward spread is reduced, but the depth of soil contamination is increased. The model

addresses an impervious surface and four permeable surfaces (gravel and three soil classes). The three soil classes are as follows:

- Class 1 - Sandy gravel, less than 5 percent clay and silt.
- Class 2 - Sandy loam, less than 25 percent clay.
- Class 3 - Sandy clay, less than 35 percent clay.

These soil classes represent most naturally occurring soils.

The present model lacks the sophistication to address multi-soil spill events. Further, the model assumes a smooth surface with no slope. A leak is assumed to spread out radially from the source until it is all absorbed into the soil or further spread is retarded due to surface tension effects. In most instances, the volume of fluid lost is small enough that flow modeling is not as critical as worker exposure.

Indoor/Outdoor Location

Outdoor spills are assumed to spread radially until constrained by soil absorption or surface tension effects. Indoor spills tend to be confined to a specific area, although contamination may extend to walls and adjacent equipment.

Rainfall

The availability of rainwater is important to the mobility of a spilled PCB fluid, because the fluid head above a PCB spill provides a driving force. As a result, any liquid chemical spill in a wet environment will be more widely dispersed than a dry environment (excluding irregular geologic formations).

However, because PCBs are not highly mobile in most soils, the magnitude of the effect is not large. There will be some increase in contaminated soil volume due to rainfall, and this effect can be included in the model.

Degree of Clean Required

In the simplest sense, within a given contaminated soil volume the concentration of PCBs will be highest near the source, and will approach ambient levels at or beyond the extent of the contamination. The limits of contamination representing PCB concentrations of 50 ppm, 7 ppm and ambient levels can be most simply represented by concentric spherical surfaces, each one of larger radius. Consequently, cleanup to a lower level of contamination requires removal of more material.

Spills on concrete present a simpler picture due to the nature of the cleanup options available. Concrete (and other "impermeable" surfaces) is slightly porous, and will absorb some of the spilled fluid. Solvent scrubbing of the concrete surface will remove surface contamination and some of the absorbed material, usually sufficiently well to achieve the 50-ppm standard. However, some PCB will remain within the concrete. To obtain a 7-ppm or ambient level is assumed to require complete removal of the contaminated concrete.

Spill Investigation

Spill investigation costs are very sensitive to cleanup degree. A typical investigation of a spill on soil includes surface soil samples to determine the area extent of the spill and subsurface soil samples (obtained by drilling holes) to determine the depth of contamination. Only enough samples will be collected to delineate the extent of the spill to the cleanup level desired. With an increase in the degree of cleanup required, the area to investigate becomes larger. Consequently, more borings, surface and subsurface samples, laboratory analyses and labor will be needed to establish the bounds of the spill.

Nature of the Fluid Spilled

An important variable which could not be included in the model is the nature of the fluid spilled, i.e., the PCB concentration or mineral oil versus askarel. To include this factor would require modeling the fluid/soil concentration gradients within the soil, an exercise not practical within the scope of this model. Consequently, the SCS model is strictly applicable only to PCBs, askarels and mineral oils with at least 0.5 percent PCBs.

Section 5

COST ANALYSIS OF SPILL CLEANUP

As noted earlier, the cost of each and every spill cleanup is different due to the unique features discussed on the preceding pages. Cost estimation is nevertheless the first logical step in a comparative cost analysis.

Figure 1 shows the logic of the spill cleanup cost model, including the role of each technical factor in the analysis. Table 2 presents the unit cost assumptions used in the model. There are several mechanical assumptions inherent in the model that would tend to make the cost appear lower than experience would indicate. First, the model uses probabilities to estimate the cost of a second or third sampling and cleaning situation (that is, the cost of a second iteration (80% probable) would be 80% of the cost of the first). Second, the cost of mobilization/demobilization for a cleanup crew is not included. In most real situations, slow lab turnaround and agency approval will require removal and reactivation of the field crew, at a cost of hundreds or thousands of dollars each iteration. Third, the analytical requirements are based on a rational sampling grid system, which is usually the minimum number required. Fourth, any analysis for TCDD/TCDF in a fire cleanup will dramatically increase the analytical (and possibly the cleanup) cost, but cannot be addressed here.

The real value of the model is to vary certain parameters over a range of values, and to show the relative cleanup costs. The following set of tables and figures illustrates some of the major cost comparisons possible with the model.

Tables 3 through 8 present the costs of several example spill cleanup scenarios using the model. The costs are expressed as a percentage of the 50 ppm cleanup cost rather than as absolute dollar values.

Figure 2 shows the investigation and cleanup cost elements separately for an example situation, an askarel spill on soil Class 2 cleaned up to 7 ppm, over a range of 0 to 10 gallons spilled. The relative magnitude between the two cost components is typical of other soil classes, slab surfaces and other cleanup degrees as well. While the total cost (not shown) compares favorably with actual utility field

experience, the cost of investigation is thought to be too high for small volume spills. The stepwise nature of the investigation costs is the result of subsurface soil sampling. The costs exhibit a sudden upward rise whenever the increasing areal extent of a spill demands that another sampling hole be drilled. Soil sampling holes are drilled at discrete intervals, regardless of the size of the spill, and a larger diameter spill necessitates more holes.

Figures 3 and 4 show the relative investigation and cleanup costs at the 1 ppm and 50 ppm cleanup levels for soil Classes 1 and 3, respectively. As most PCB equipment spills are in the 0 to 3 gallon range, drilling will not be required.

Figure 5 compares the total costs for cleaning up spills in each of the soil classes to 50 ppm. Class 1 soils represent a sandy gravel with less than 5 percent clay and silt; Class 2 is a sandy topsoil with up to 25 percent clay; Class 3 is a sandy clay. The costs can be higher in the more clayey soils because of the more extensive dispersion of the material on the surface. More soil must be removed because of the greater soil volume contaminated in the more clayey soils, so excavation and disposal costs are higher.

Figure 6 compares the costs of cleaning up spills on open soil to the costs of cleaning up the same volume of spilled fluid next to a structure. Spills next to structures will migrate along the foundations and beneath the building through looser soils. There is increased difficulty in excavating beneath a structure, and this is reflected in the model by increased excavation costs.

Figure 7 shows the costs to clean up uncontained PCB leaks on impervious slabs. In general, slab cleanup to 50 ppm represents labor-intensive triple scrubbing with solvents. Cleanup to 7 ppm represents slab demolition. This figure suggests that beyond a certain volume spilled (approximately two gallons), it may be more costly to scrub the slab than to remove it entirely. However, this generalization does not apply to more common spills to concrete inside a building, where concrete removal is infeasible and scrubbing is the only option.

Figure 12 compares the costs of cleaning up leaks versus spray spills on slabs. The differences are most dramatic at the low volumes spilled, where a spray could result in greater surface area contamination than a spill. Above one to two gallons, a leak will eventually spread to contaminate an equivalent surface area as the spray spill. Thus, the lines become parallel. The difference between the two lines represents the costs of cleaning up walls, poles, nearby equipment, etc., all items

more likely to be contaminated by a spraying piece of equipment. Obviously, spraying spills of this type are the most costly per gallon, as they contaminate more surface and often result in replacement of contaminated items.

Table 1

SELECTED EPA REGIONAL PCB SPILL CLEANUP REQUIREMENTS

EPA Region	Contact (Name, Phone)	Soil	Cement/Asphalt	Other*
Headquarters	D. Hannemann (202) 383-7849			cbc*
1	T. Palermo (617) 223-5604	50 ppm+	concrete: solvent asphalt: remove	cbc
5	P. Porter (312) 353-2192	1-5 ppm	concrete: solvent (3) asphalt: remove	
6	D. Mount (214) 767-2734	50 ppm	concrete: wash asphalt: remove	cbc
9	K. Glassel	50 ppm	concrete: remove asphalt: remove	cbc

*cbc - Each instance evaluated on a case-by-case basis.

+ - Initial concentration.

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Table 2

UNIT COST ASSUMPTIONS USED IN PCB SPILL CLEANUP MODEL*

Engineering Labor	$45/hr	Labor	$35/hr
Labor	$35/hr	Bulk Disposal	$145/yd^3
Sample Analysis	$50/sample	Drum Disposal	$39/drum
Drill Rig Mobilization	$1,300	Drum Cost	$25/drum
Drilling Costs	$45/ft	Equip. Mobil./Demobil.	$1,600
Surface Sampling		Equipment	
Productivity	6 samples/man-hour	Wheeled Backhoe/Loader	$4.66/yd^3
Frequency	1 sample/6 ft	Dump Truck	$7.80/yd^3
Subsurface Sampling		Slab Cleaning	
Drill Depth	15 ft	Triple Solvent Scrub	
Productivity	2 ft/hr	Followed by Solvent	
Frequency	2 samples/ft	Absorption Materials	
		Cost	$2.70/ft^2
		Productivity	25 ft^2/man-hour
Planning & Engineering	25% of Total	6-inch slabs	
		1 Drum Disposable	
		Equipment/6 man-days	
		Slab Demolition	
		Equipment	$135/day
		Productivity	25 ft^2/man-hour
		General/Administrative	
		Costs	5% of Total

* These figures are typical of contractor costs and leased equipment.

Sources: Means Building Construction Cost Data, 1982; Richardson's Estimator; 1982 Dodge Guide to Public Works and Heavy Construction Costs.

Table 3

SPILL CLEANUP

1.5-Gallon Askarel Spill; Class 2 Soil; No Rainfall

DESCRIPTION

1.5-gallon spill from a pole-mounted Askarel capacitor to a moderately permeable soil surface. Excavation by hand with drummed material disposal.

	Relative of Costs		
	Degree of Cleanup		
Investigation	50 ppm	7 ppm	1 ppm
Sampling and Analysis	1.00	1.49	2.22
Equipment	1.00	1.00	1.00
Sample Disposal	1.00	1.35	1.81
Planning/Reporting	1.00	1.46	2.13
Total	1.00	1.45	2.13
Cleanup			
Excavation and Disposal	1.00	1.55	2.00
Equipment	1.00	1.00	1.00
General/Administrative	1.00	1.43	1.77
Total	1.00	1.43	2.09
TOTAL	1.00	1.45	2.09

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Table 4

SPILL CLEANUP

1.5-Gallon Askarel Spill; Slab Surface; No Rainfall; Flow Spill

DESCRIPTION

1.5-gallon spill from a pole-mounted Askarel capacitor to a concrete parking lot. Triple solvent scrub to 50 ppm versus slab demolition to 7 ppm (or less).

	Costs ($)	
	Degree of Cleanup	
Investigation	50 ppm	7 ppm
Sampling and Analysis	1.00	1.35
Equipment	1.00	1.00
Sample Disposal	1.00	1.00
Planning/Reporting	1.00	1.15
Total	1.00	1.15
Cleanup		
Cleanup and Disposal	1.00	1.84
Equipment	1.00	0.45
General/Administrative	1.00	1.31
Total	1.00	1.31
TOTAL	1.00	1.26

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Table 5

SPILL CLEANUP

1.5-Gallon Askarel Spill; Spray Spill; Slab Surface

DESCRIPTION

1.5-gallon spill from a spraying pole-mounted Askarel capacitor to a concrete parking lot. Triple solvent scrub to 50 ppm versus slab demolition to 7 ppm (or less).

	Costs ($)	
	Degree of Cleanup	
Investigation	50 ppm	7 ppm
Sampling and Analysis	1.00	1.37
Equipment	1.00	1.00
Sample Disposal	1.00	1.00
Planning/Reporting	1.00	1.18
Total	1.00	1.18
Cleanup		
Cleanup and Disposal	1.00	3.50
Equipment	1.00	1.17
General/Administrative	1.00	1.51
Total	1.00	2.27
TOTAL	1.00	1.93

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Table 6

SPILL CLEANUP

10-Gallon Askarel Spill; Class 2 Soil; Cleanup to 7 ppm

DESCRIPTION

10-gallon spill from Askarel transformer to a moderately permeable soil. Cleanup to 7 ppm.

	Costs ($)	
	Degree of Cleanup	
	Spill on Open Soil	Spill Next to a Building
Investigation		
Sampling and Analysis Equipment Sample Disposal Planning/Reporting		
Total	1.00	
Cleanup		
Excavation and Disposal	1.00	1.35
Equipment	1.00	1.00
General/Administrative	1.00	1.32
Total	1.00	1.32
TOTAL	1.00	1.08

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Table 7

SPILL CLEANUP

1.5-Gallon Askarel Spill; Spray Spill; Class 3 Soil; No Rainfall

DESCRIPTION

0.5-gallon spill from a spraying pole-mounted Askarel capacitor to a public park baseball field. Excavation by hand with drummed disposal.

	Relative of Costs		
	Degree of Cleanup		
Investigation	50 ppm	7 ppm	1 ppm
Sampling and Analysis	1.00	1.34	1.80
Equipment	1.00	1.00	1.00
Sample Disposal	1.00	1.08	1.08
Planning/Reporting	1.00	1.46	2.13
Total	1.00	1.08	1.19
Cleanup			
Excavation and Disposal	1.00	1.40	1.81
Equipment	1.00	1.00	1.00
General/Administrative	1.00	1.27	1.54
Total	1.00	1.27	1.55
TOTAL	1.00	1.15	1.32

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Table 8

SPILL CLEANUP

50-Gallon Spill from an Askarel Transformer Stored Outside on Compacted Soil

DESCRIPTION

50-gallon spill from an Askarel transformer stored outside on compacted soil

	Costs ($)					
	50 ppm		7 ppm		1 ppm	
	No Rainfall	After 10 Inches of Rain	No Rainfall	After 10 Inches of Rain	No Rainfall	After 10 Inches of Rain
Investigation						
Sampling and Analysis		1.00		1.49		2 20
Equipment		1 00		1.00		1.00
Sample Disposal		1.00		1.00		1.00
Planning/Reporting		1.00		1.44		2 07
Total		1.00		1.47		2.07
Cleanup						
Excavation and Disposal	1.00	1.00	1.85	1.95	2.69	2 79
Equipment	1.00	1.00	1.50	1.50	2.00	2 00
General/Administrative	1.00	1.10	1.83	1.93	2.66	2.75
Total	1.00	1.10	1.83	1.93	2.66	2 75
TOTAL	1.00	1.04	1.58	1.61	2.27	2.31

Figure 1

FLOW CHART FOR SPILL CLEANUP COST MODEL

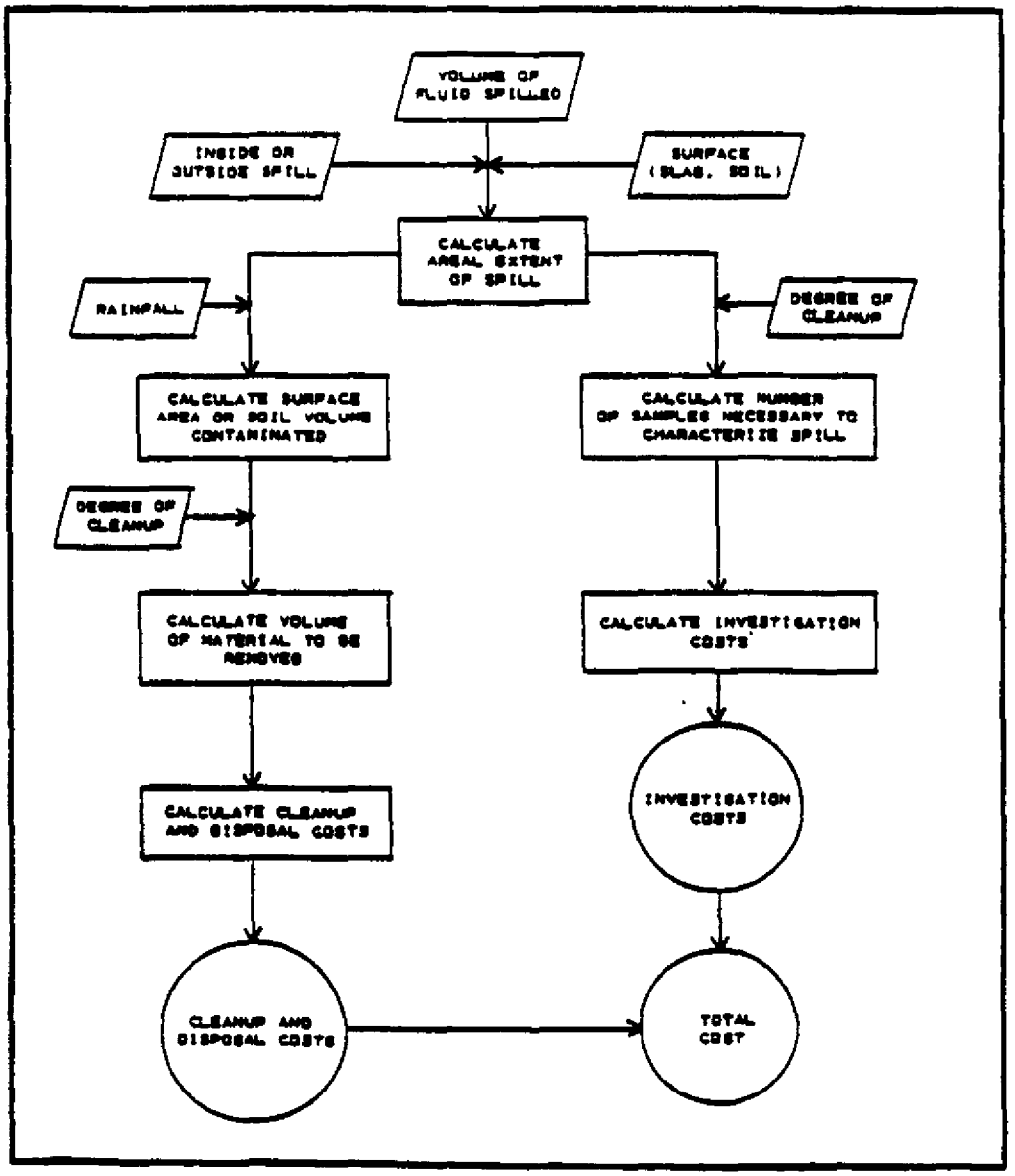

Figure 2

COST OF PCB SPILL CLEANUP TO 7 PPM, SOIL CLASS 2

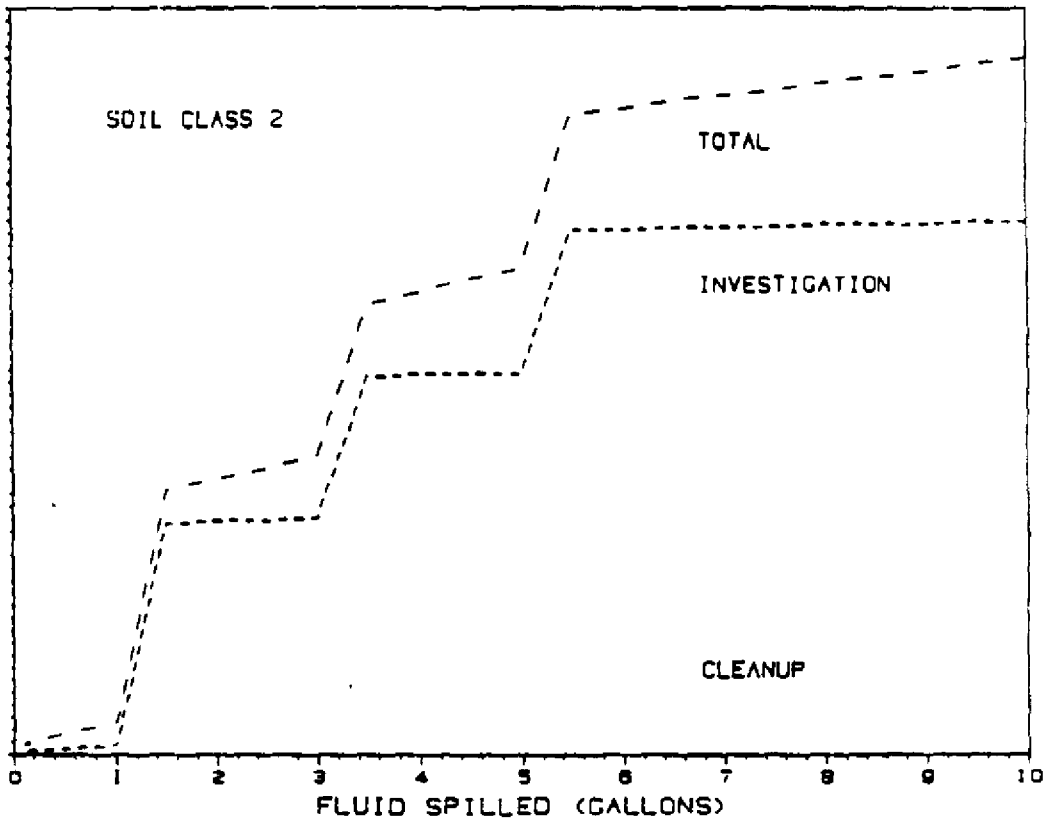

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Figure 3

COST OF PCB SPILL CLEANUP, SOIL CLASS 1

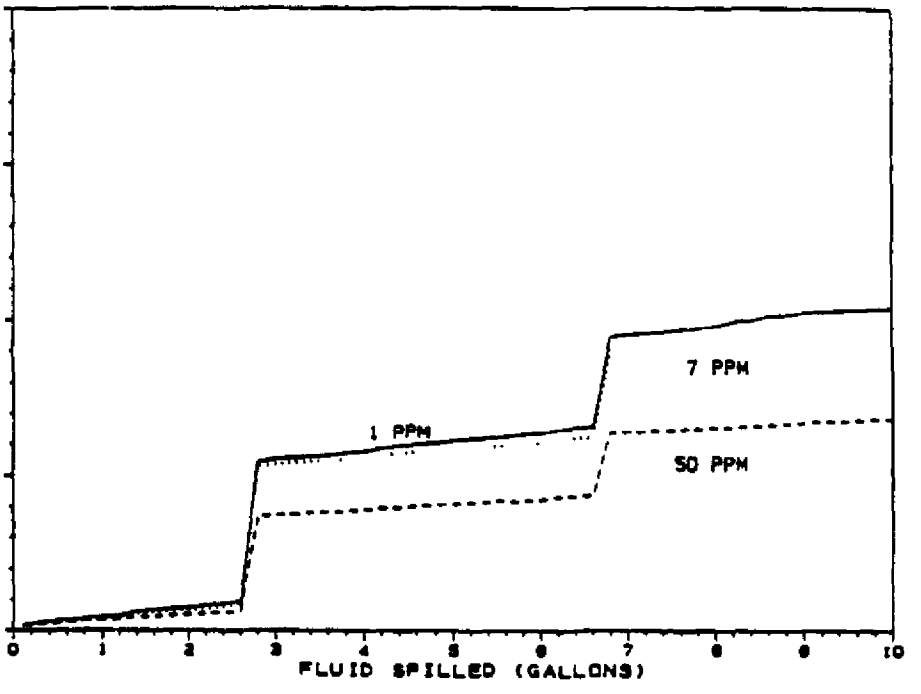

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Figure 4

COST OF PCB SPILL CLEANUP, SOIL CLASS 3

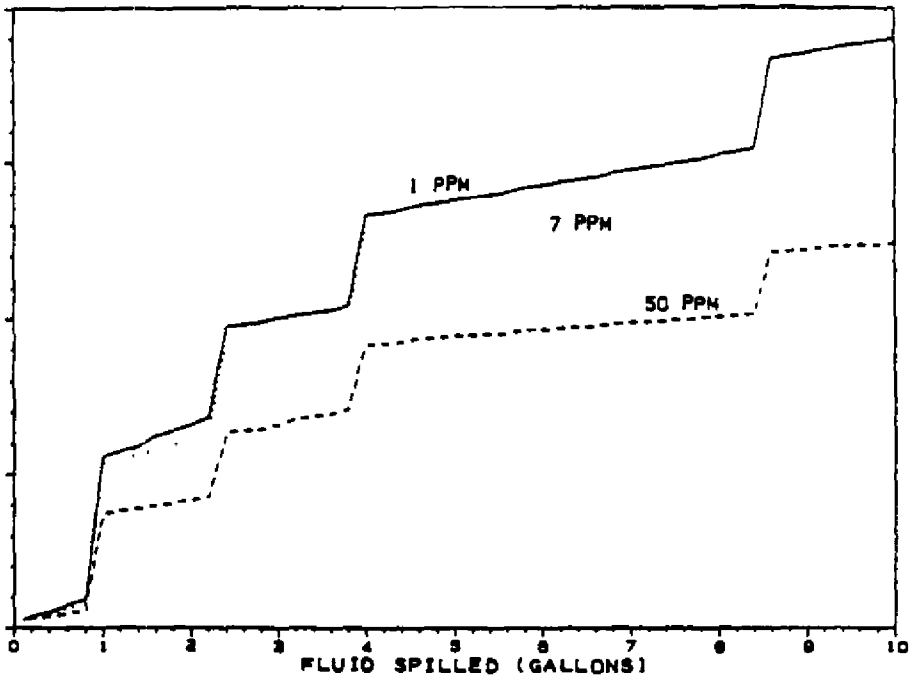

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Figure 5

COST OF PCB SPILL CLEANUP TO 50 PPM

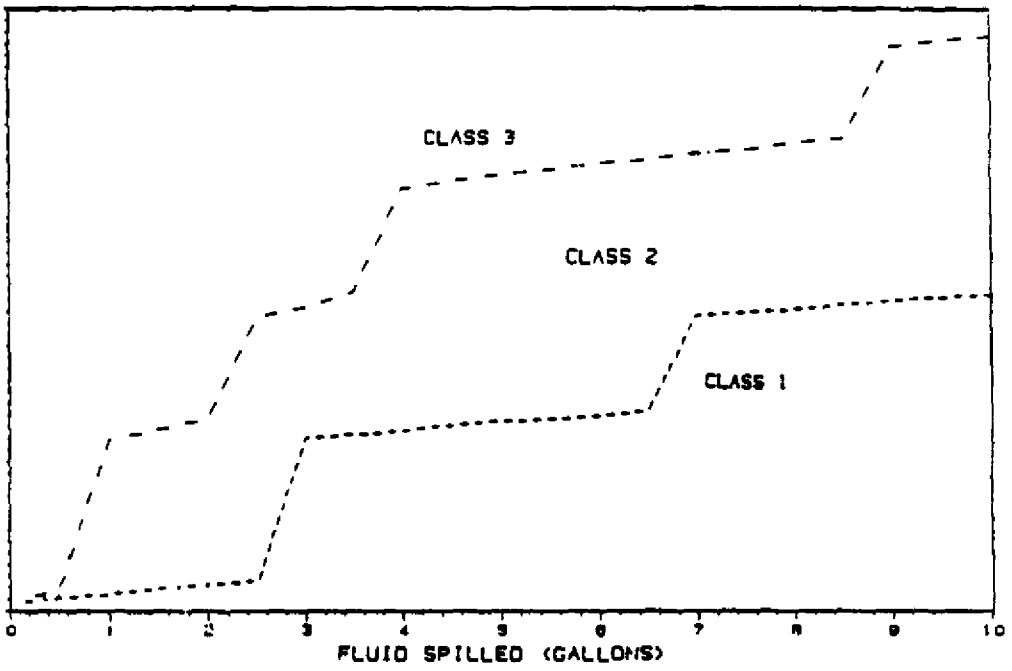

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Figure 6

COMPARISON OF CLEANUP COSTS FOR SPILLS ON OPEN SOIL AND NEXT TO STRUCTURES

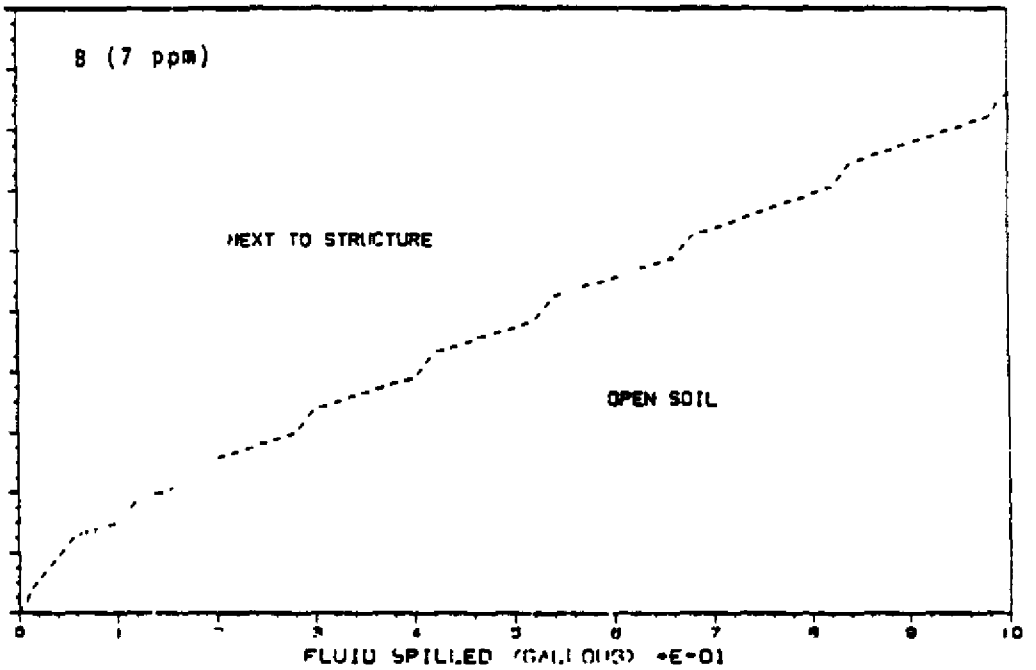

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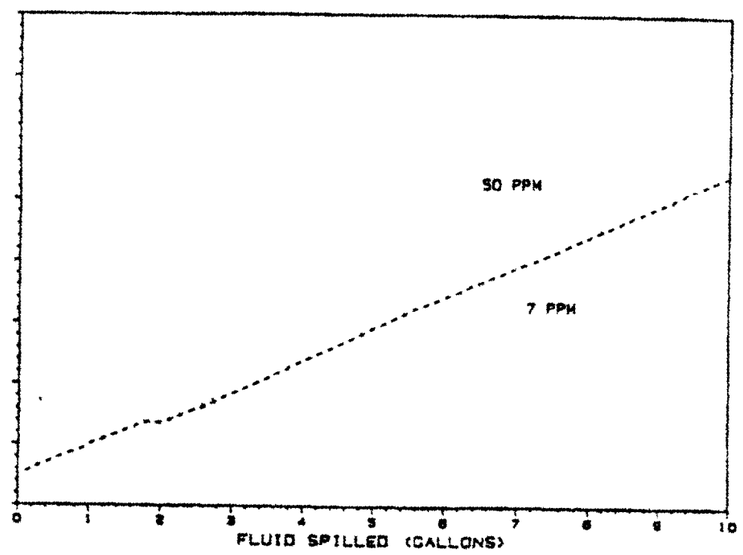
Figure 7

PCB SPILL CLEANUP COSTS, OUTDOOR SLABS



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Section 6

CONCLUSIONS AND RECOMMEDNATIONS

The preceding discussion of PCB spill cleanup costs has attempted to quantify the relative cost of cleanup to different levels of residual contamination.

Recognizing the inherent weaknesses in generic modeling of such a site-specific event, some conclusions can still be drawn regarding relative cost. First, it has been shown here that a cleanup to 7 ppm is at least twice as expensive as cleanup to 50 ppm. Cleanup to background is still more expensive, with the actual increase being a function of the background level definition and sampling protocol. Second, flow spills next to structures are up to 50 percent more expensive to remove than open flow spills. Spray spills next to structures are even more expensive and labor intensive, varying with the material contacted. Third, contained spills are less costly to cleanup than open spills to slabs or soil. The model showed that spills to impervious slabs of more than two gallons are more expensive to dispose of the slab than to clean it.

More important than the specific costs is the probabilistic nature of both the model and the actual spill cleanup exercise. Some probabilities for second and third cleanup iterations were conservatively assumed. In practice, a three-interation requirement would show an actual cost increase of 200 to 300 percent (without the probabilities applied). A four- or five-iteration exercise with demobilization would be cost-prohibitive. This is a real, practical problem, not just modeling philosophy.

Some recommendations are in order here. A standard of some type is needed. The choice appears to be between a procedural standard ("how to clean up"), a performance standard (clean up to a specified level), or a combination of the two approaches. A procedural standard must have a definable (yet non-concentration based) end point in order to be effective yet practical. A performance-based standard must be based on a practical concentration limit.

In order to set a standard of either type, more research is required, research into what is reasonably achievable by a trained, mature cleanup crew. Rather than performing laboratory research, have some crews clean up a PCB-stained area plus 6 in., 12 in. and 24 in. and check the residual concentration. Or determine what level of cross contamination is common using standard drilling and sampling equipment (hole wall collapse, for example). Then combine the two data sets to establish a practical standard to apply in all situations.

Industry has been subjected to double jeopardy in many cases, with application of both procedural and performance standards on the same spill. Those encountering PCB spillage from their equipment need to be prepared to write blank checks to their lab, cleanup contractor and attorney under the current regulatory situation. And using a standard numerical or "background" is not an improvement over the current state of affairs.

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Section 7

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INNOVATIVE DESIGN CONCEPTS FOR PREVENTION OF AIRBORNE PCB CONTAMINATION

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ABSTRACT

Within the past several years, failure of electrical equipment filled with polychlorinated biphenyl (PCB)-bearing dielectric fluids has resulted in extensive contamination of buildings in Binghamton, NY (1981); San Francisco, CA (1983) and other locations. The magnitude of these incidents was a result of "air-spills" of atomized PCBs and combustion byproducts of the dielectric fluids (furans and dioxins). Resultant cleanup costs and potential liabilities associated with these types of incidents and materials can easily run into the millions of dollars. Prior to the Binghamton incident, the potential for airborne contamination was little appreciated, with the result that the scope of other past incidents can only be estimated.

West & Hansen Engineers has recently completed surveys and design projects for seven California and Washington State agencies identifying potential sites where airborne contamination might occur and devising cost-effective methods for isolating PCB equipment. Structures surveyed included office buildings, schools, hospitals, highway bridges and tunnels. Both transformers and capacitors were involved. This paper presents some of the design techniques used to prevent widespread structure contamination. These procedures include modification of ventilation systems, partitioning of mechanical and electrical areas in utility rooms, closed heat exchangers for air-to-air equipment cooling and automatic fan shutdown devices.

Considering the amount of utility and customer-owned PCB equipment in occupied structures throughout the country, it is probable that future airborne PCB contamination will occur. Identification and isolation of high-risk equipment installations can significantly reduce potential liabilities, health effects and property impairment caused by such episodes.

INTRODUCTION

There is presently a great need to develop techniques for the prevention and control of airborne PCB contamination from electrical equipment mishaps. Although these types of incidents are infrequent, their resulting costs in terms of cleanup, liability and property loss can be enormous. Examples include the substation fire in the State of New York Building in Binghamton New York (1) and the sidewalk vault eruption adjacent to the One-Market Plaza Building in San Francisco (2). The types of airborne contaminants resulting from pressurized leaks or fires include aerosoled dielectrics such as dibenzodioxins and dibenzofurans.

Until now, spill prevention and control procedures (and regulations) for PCBs have emphasized fluid spills; i.e. dielectrics escaping from faulty valves, welds, cooling radiator fins, busnings etc. in a liquid state. Preventive and control measures for these types of spills have been developed and described previously (3,4). The Environmental Protection Agency's August 25the, 1982 Regulations on PCBs (5) describe the required response to leaks "resulting in any quantity of PCBs running off or about to run off the external surface of the transformer..." (Section 761.30 (iii)). Secondary containment (curbs, dikes or sumps) as a fluid spill control method is also suggested in Section 761.30 (v)(A). More relevant to the issue of "air-spills" is the definition of "spills, leaks, and other uncontrolled discharges of PCBs" (underlining added) as constituting a disposal of PCBs (Section 761.60 (d)(1)). However, specific methods for controlling airborne emissions from PCB equipment installations have not been well documented.

SCOPE AND OBJECTIVE

West & Hansen Engineers, Inc. and Yuen-Fenner, Inc. have been involved in a project sponsored by the California Office of the State Architect to identify and prepare risk reduction recommendations for State-owned PCB filled equipment installations. This paper presents results of those efforts as they relate to potential airborne PCB contamination. Topics include survey of inatallations to determine contamination potential, selection of a risk reduction approach, design of isolation improvements and areas requiring further research. The information contained in this paper is intended to assist member utilities contemplating or conducting similar risk reduction programs.

PROGRAM ELEMENTS

Risk Survey

The State of California is similar to many member utilities in that they own hundreds of PCB-filled transformers and capacitors spread out over a large geographic area and housed in a wide variety of structures. Unlike the State, however, utility-owned equipment is most often on non-utility owned property adding another element of risk to those facilities.

Only a small percentage of PCB installations are in what we term "sensitive" locations with respect to potential airborne contamination. A sensitive location is one where substantial structure contamination, human contact or facility disruption would occur. A comprehensive survey, conducted in part by West & Hansen Engineers and Yuen-Fenner, Inc. was undertaken by the State to identify sensitive PCB equipment sites. For each site so identified information was collected to provide a basis for selecting a risk reduction approach. Particular importance was placed on identification of pathways leading from PCB equipment locations to other portions of the structure. Typical pathways include ducting, conduits, doors, windows, drains, hallways, ventilation shafts and utility corridors. Although PCB contamination can migrate either actively, by forced ventilation or passively, via natural convection, neither appears to pose a more or less serious risk.

Risk Reduction Alternatives

Alternatives for reducing airborne PCB contamination risk fall into three categories, removal, relocation and isolation. Removal of PCB-filled equipment eliminates all spill risk entirely, however this option is expensive, and results in a PCB waste disposal problem.

Equipment relocation is generally impractical for transformer equipment, but works well in the case of capacitors. When technically feasible, relocation can provide a significant amount of risk reduction at less cost than outright replacement.

Equipment isolation offers the advantages of low cost, minimal service interruption and no generation of PCB waste. A well-engineered and constructed isolation design will provide almost total containment of aerosols and gases. However, the risk reduction afforded by equipment isolation is less than that provided by replacement or relocation.

Equipment Replacement

Some PCB equipment installations are so sensitive that the only acceptable level of contamination risk is zero. In such a situation complete removal is the only alternative. In some cases removal of the dielectric fluid only may be feasible, but generally outright replacement is the only option.

In other cases, equipment relocation or isolation may be as costly as replacement. Also, if the existing installation is aged, undersized, or has some other short coming replacement may be preferable to retention.

In some cases relocation or isolation may be technically infeasible. Where feasible, or marginally feasible, isolation may not provide an acceptable level of risk reduction. In these cases, replacement may become the preferred alternative.

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Equipment Relocation

The relative positioning of PCB equipment and ventilation structures has historically received little regard. In some cases relocation of either ventilation system components or PCB equipment can greatly reduce the contamination potential. This is particularly the case with capacitors since they can be moved so much more easily than transformer equipment. Where an acceptable alternative location is available, relocation is technically feasible, and equipment is worth retaining, relocation may be an alternative.

Equipment Isolation

Due to its technical and economic advantages equipment isolation is the preferred risk reduction alternative. Although not providing 100% complete protection from contamination, a well designed isolation job will restrict potential contamination to the electrical room vicinity, greatly facilitating structure clean up and rehabilitation.

An isolation project consists of at least one and possibly as many as three elements: 1) blocking contamination pathways 2) providing alternative cooling 3) providing safe installation discharge. Element one is a factor in every isolation job, elements two and three are factors depending upon parameters specific to each equipment location.

Blocking Contamination Pathways

Preparation of an isolation design necessitates a thorough survey of all possible contamination pathways, both active and passive. Once identified, the most efficient combination of improvements can be specified to seal the contamination routes.

Isolation designs may be broadly categorized as equipment isolations or room isolations. Equipment isolation includes those cases where a containment shell is constructed around the equipment. Room isolation refers to the sealing of the existing equipment enclosure.

Providing Alternative Cooling

Provision is usually made for some form of ventilation cooling at high voltage equipment installations. An isolation project will often result in the removal of that ventilation. The resultant higher operating temparatures reduce efficiency, shorten service life and increase probability of equipment failure. A number of alternatives are available to provide for alternative cooling e.g. heat exchangers, air conditioners, or re-directed venting with our without forced circulation. The decision to install equipment cooling is primarily based on economic considerations, i.e. capital cost of installation vs operating cost at higher temperature.

Safe Contaminant Discharge

A transformer in failure mode can evolve substantial quantities of

gases, potentially creating elevated pressures if contained within an enclosed space. Depending upon enclosure size, location and equipment type, an adequate isolation design may require provision of an emergency discharge to the outside of the structure.

It is debatable whether there exists a safe discharge for airborne PCBs from a hot ruptured transformer. If aerosoled, a mesh type mist arrestor can substantially reduce PCB concentration. Mist arrestors are inexpensive and require no maintenance. Gases will pass through such a device unaffected. Provision of a PCB gas scrubbing system is impractical except in some highly unusual situations.

DESIGN TECHNIQUES

An ideal airborne PCB spill containment design provides for effective spill control, equipment cooling, unrestricted maintenance and inspection access and ease of removal upon eventual equipment changeout. On the other hand, an ill-conceived design can significantly increase the probability of equipment failure and subsequent potential for PCB contamination.

Effective Spill Control

An effective spill control design provides for blocking every potential pathway leading to PCB contamination. Common pathways were listed previously. Techniques for pathway blocking can be broadly classified as caulking, partitioning, sealing, weather stripping, enclosing, covering, and re-directing. In most cases the most important aspect of each design will be the materials of construction. Table 1 cross references design techniques and construction materials applicable to each pathway.

The pathwaye listed in Table 1 were originally intended for ventilation, access, drainage or lighting. Once blocked, their usefulness for these purposes may very well be reduced or eliminated and alternative service may be required. Alternative lighting can easily be provided, however providing backup service for the other 3 services is usually more complicated.

Equipment Cooling and Ventilation

Oil-filled power transformers installed indoore are required to be placed in vaults with firewall isolation from the other indoor rooms. PCB transformers are exempted from codes requiring vaults because of their inherent fire resistant character. Ventilation systems from the oil-filled transformers were designed with fire isolation in mind. PCB ventilation systems were only designed to keep the ambient temperature at or below 30 degrees centigrade.

The 30 degree ambient (by the standard transformer industry design) was used as the design basis for allowing a tranaformer to be loaded to name plate rating continuously without exceeding a 95 degree centigrade insulation hot-spot temperature.

Table 1

AIRBORNE SPILL ISOLATION
DESIGN TECHNIQUES FOR
COMMON PATHWAYS

Pathway	Design Techniques	Material of Construction
Ducting	Sealing Re-directing Partitioning	Sheet Metal Gypsum board (coated)
Conduits	Caulking	Expanding silicone foam
Doors	Weather stripping Sealing Partitioning	Butyl polymer gasket tape Sheet metal Concrete block
Windows	Weather stripping Sealing Partitioning	Butyl polymer gasket tape Sheet metal Concrete block Gypsum board
Drains	Sealing Caulking Covering	Metal Concrete Expanding silicone foam Epoxy
Hallways	Partitioning Sealing	Gypsum board Concrete block
Utility corridors	Partitioning	(compatible with existing materials)
Ventilation shafts	Sealing Re-directing Partitioning	Sheet metal Concrete

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The transformer industry then designed their cooling systems around this continuous hot-spot temperature of 95 degrees and further agreed that transient excursions above this hot-spot temperature were acceptable with the understanding that the loss of life of the insulation system would double for each 8 degrees in rise in hot-spot temperature. Therefore, a transformer operating at 103 degrees centigrade (hot-spot) would last only half as long as one operating at only 95 degrees (based on the industry class A insulation system).

Sophisticated operators realize that any transformer that is not operated continuously at full load and at a constant 30 degree centigrade ambient temperature could sustain transient insulation operating temperature incursions above 95 degrees; if offset with loading conditions below 95 degrees such that the normal operating life of the transformer is unchanged.

Restricting the ventilation of the PCB transformers will limit the spread of airborne PCB compounds, but will also cause a rise in the ambient air temperature which in turn will cause a rise in the insulation hot-spot temperature. A conservative, safe operating ambient air temperature limitation is one that will not cause a transformer's normal life expectancy to be reduced.

As a rule of thumb in the transformer industry, the insulation hot-spot temperature on the average is 10 degrees centigrade higher than the transformer top oil temperature. The hot spots can not be readily measured, but the top oil temperature can be measured and often is brought out to a case-mounted temperature gauge.

A first step to closing in a PCB transformer ventilation system is to first close the system with temporary seals and then monitor the top oil temperature. If the top oil temperature on a 55-degree rise tranformer averages below 85 degrees centigrade over a typical opereting day then the seals can be made permanent and the transformer will have a normal operating life once it is closed in. If the average top oil temperature exceeds 85 degrees then heat exchangers or other cooling devices that do not have direct air-to-air contact between the traneformer room and exterior should be provided.

Consideration must be given to other equipment in the transformer area that could be adversely affected by the increase in ambient temperature created by shutting down the room ventilation system. Higher ambients will generally cause an increase in aging rates and an increase in electrical resistance with a corresponding increase in energy losses. Consideration should also be given to potential thermal loads applied to load-bearing structural members in high-rise buildings. The reduction of the risk of releasing airborne PCBs will probably override the disadvantages associated with the closing in of the ventilation system on a temporary basis. The overall advantage of auxiliary cooling should prevail over the long term.

Maintenance and Inspection Access

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Recommended transformer maintenance operations include fluid sampling, fluid filtering, and cleaning. Access is also required for switch operation and tap changing. Federal regulations require periodic inspection of PCB-filled equipment to check for fluid leaks. Additionally, it is good practice to monitor equipment temperature, pressure, and fluid level as indications of system performance.

A spill isolation design must take into account personnel and equipment access for all the above listed activities. Further, electrical codes require minimum set backs around high voltage equipment as do occupational and safety regulations.

Blocking doors, windows, hallways, or utility corridors may result in a future access problem. In all cases provision must be made for personnel entry. Consultation with the manufacturer, maintenance supervisor, or operating electrician should define equipment access requirements.

Equipment Removal

An airborne spill containment enclosure must be both permanent and durable, yet removable to facilitate eventual PCB equipment removal. Since many member utilities have instituted accelerated PCB removal problems, equipment may be replaced long before the end of its normal service life. An evaluation of the anticipated service requirements of each transformer will have a bearing on the containment design.

Drainage

Maintaining dry conditions in the vicinity of high voltage equipment prolongs service life as well as promoting worker safety. When existing drainage openings are sealed for spill control reasons provision should be made for keeping equipment dry, although if the transformer is scheduled for accelerated replacement, or if water problems are insignificant no action may be taken. Possible techniques include curbing, sump pumps, alternate drains, or sealing to exclude water from the equipment enclosure.

CONSTRUCTION METHODS AND MATERIALS

Remodeling a high voltage installation for airborne spill prevention often involves working in cramped interior rooms with poor access. As a consequence, construction methods emphasizing small, easily manipulated, modular building units are preferable.

Table 2 lists the advantages and disadvantages of four common construction methods as they apply to interior vaults. Besides indoor locations, PCB equipment installations can be outdoors, either pad or pole mounted. There are virtually no constraints on construction methods for outdoor installations.

Materials utilized in a spill isolation design must be resistant to

Table 2

ISOLATION CONSTRUCTION COMPARISONS

Construction Type	Advantage	Disadvantages
Masonry units i.e. concrete blocks, bricks, etc.	- Modular - easy to manipulate in cramped spaces. - Inexpensive - Durable - Relatively easy to remove.	- May not form a continuous unit. - Heavy
Cast in place concrete	- Durable - Continuous unit	- Expensive - Form work and pouring difficult to manipulate in tight quarters. - Difficult to remove. - Heavy
Pre-cut Assemblies	- Minimum construction activity in vault. - Easy removal - Light weight	- Skill required for good fit.
Carpentry	- Inexpensive - Easy removal - Light weight	- Combustible materials of construction.

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both chlorinated solvents and elevated temperatures. Porous or adsorbent materials are to be avoided as are flammable products. The interior faces of all isolation structures, particularly those intended to impound liquids, are usually coated with a suitable protective sealant. Caulking, weather stripping and sealing compounds compatible with these specifications are commercially available and have been successfully used in State of California isolation projects.

CASE STUDY

Vault or transformer room ventilation systems - either passive or active - are a primary cause of contaminant dispersion. In an actual transformer room inspected by West & Hansen Engineers and Yuen-Fenner, a forced ventilation system was used to cool two 643-gallon Inerteen-filled Westinghouse transformers (Figure 1). The wind tunnel was used to discharge air from the multi-story building's interior to the outside. However, fan shutdown concurrent with a substation failure would permit the tunnel and adjacent vertical ducts to act as a passive contaminant route to the building's interior.

The control program for this particular installation included recommendations that the vent ports (influent and effluent) be sealed. At the same time, the ambient and equipment operating temperatures are being monitored to determine the impact of reduced ventilation. Should the ambient temperature exceed the design temperature of 40 degrees centigrade alternatives for modified ventilation will be considered.

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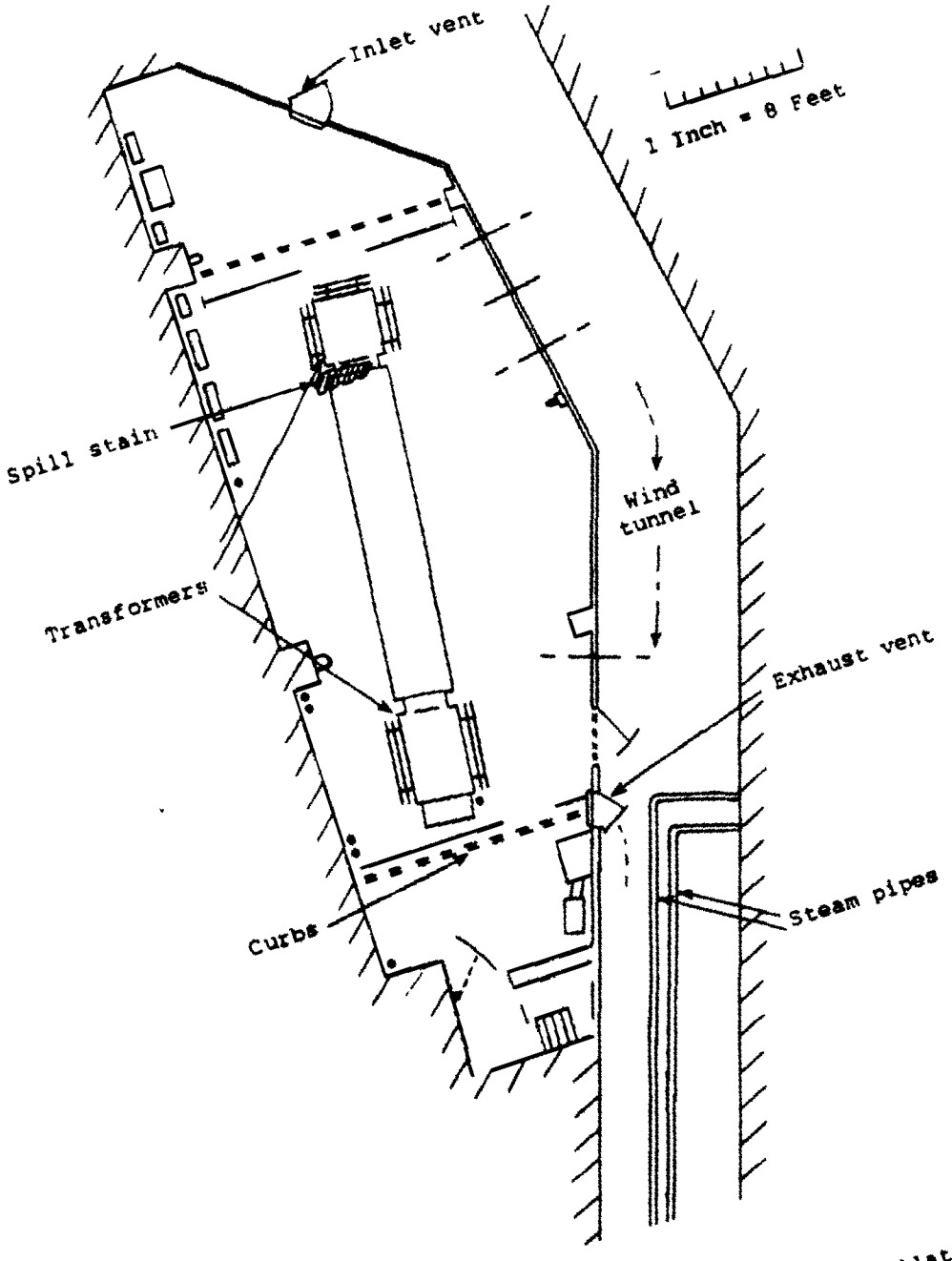

Figure 1. Case Study Installation

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BIOTECHNOLOGY POTENTIAL AS A PCB DISPOSAL OPTION
An Overview

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SUMMARY

Electric utilities must comply with EPA requirement under the Toxic Substances Control Act for the eventual disposal of about one billion (10^9) gallons of utility equipment fluids containing polychlorinated biphenyl (PCB). EPA requirements also address leaks and spills and the need for clean-up and disposal of contaminated environments under the Resource Conservation and Recovery Act and the Comprehensive Environmental Response, Compensation and Liabilities Act.

PCB in electrical equipment is composed of over 100 chlorinated biphenyl compounds all of which have been reported to be degraded by mixed cultures of natural bacteria. However, under natural conditions, the more highly chlorinated PCB compounds (those which contain a high weight percent chlorine) biodegrade far slower than compounds with less chlorine. Since the highly chlorinated congeners make up a large portion of the utility PCB inventory, rates of biodegradation must be enhanced to make biotreatment techniques competitive with other disposal means. Methods such as emulsification and genetic engineering could accomplish this enhancement.

In this paper we review electric utility's use of PCB and disposal requirements, existing evidence of PCB biodegradation, means of improving the performance of biological systems (i.e., genetic engineering), and biotreatment technologies.

We conclude that biotreatment of both spills and the planned phase-out of existing equipment inventories of PCB fluids are feasible given adequate research and development. We recommend that some of the existing data be validated, and a set of research objectives be initiated in the areas of: 1) microbiology and genetic engineering; 2) system design and testing; and 3) cost-analysis.

This biotechnology paper was prepared for the Electric Power Research Institute by American Technology Management Consultants, Lafayette, Indiana. Leland O. Attaway and Associates, San Rafael, California, provided inputs on PCB uses and characteristics.

Section I

INTRODUCTION

Polychlorinated biphenyl (PCB) has been in use in utility equipment since 1930. PCB is a major component of capacitor and transformer dielectric fluids, and is a known contaminant of mineral oil used in transformers, voltage regulators, circuit breakers, reclosers and switches. Several million such units, containing about one billion (10^9) gallons of fluid contaminated with PCB, are present in the utility power distribution network. Due to the environmental persistence and possible adverse health effects of PCB, the complete, controlled destruction of PCB waste materials is required by law. Thus, soils, and other materials contaminated by PCB spills from utility equipment, as well as fluids recovered from obsolete or recycled equipment, must be properly eliminated.

The nature of utility uses for PCB creates a diverse mixture of waste products particularly challenging to all means of disposal techniques. Inferences drawn on laboratory studies with pure PCB isomers, though meaningful for destruction of the regulatad PCB constituent, must also take into consideration the total waste matrix before an interpretation of its practical application can be drawn. Of the 209 possible PCB isomers, nearly 100 exist in commercial mixtures at concentrations ranging from 50 ppm to 100%. PCB solvents such as mineral oils predominate in transformers, and in askarel transformers, polychlorinated benzenes. (Capacitors are 100% PCB.) Trace contaminants such as polychlorinated dibenzofurans can also be present. These utility PCB mixtures combined with wash solvents and contamined environmental media pose complex problems to all waste management technologies. Nevertheless, all of the principal waste constituents are hydrocarbon derivatives and are potential sources of energy and carbon for biological growth through enzyme catalyzed degradative reactions. In fact, all of the organic waste constituents, including PCB, have been observed to undergo biodegradation by microorganisms.

In this paper we review the results of an investigation on the feasibility of using biotechnology for utility PCB disposal (1).

Section 2

UTILITY USE AND DISPOSAL REQUIREMENTS FOR PCB -

Polychlorinated biphenyl (PCB) was first synthesized in 1881 (2) and during the 1920's it was manufactured in bulk. In 1930 General Electric became a major user of PCB for capacitor fluids due to its thermal and chemical stability and electrical properties. Today it is estimated that approximately 1.1 billion gallons of PCB-laden fluids exist in the electric utility industries equipment inventory containing 82,000 tons of PCB (3). Due to PCB's potential toxicity and environmental persistence, the United States Congress mandated the Environmental Protection Agency to control the use of PCB and to prescribe methods for PCB's phaseout and disposal [Section 6 (e), Toxic Substances Control Act - PL 94-469].

PROPERTIES OF PCB MIXTURES

Biphenyl has ten possible sites of chlorination, but of the 209 theoretical isomers, only 100 are produced due to their thermodynamic properties. Aroclor is the Monsanto trade name applied to commercial mixtures of PCB, and other than Aroclor 1016, the designations 1221, 1242, 1254 and 1260 imply, in the last two digits, the weight percent of chlorine in a Aroclor's mixture. For example, Aroclor 1260 will typically contain 100 different PCB isomers, the mixture 60% chlorine. The above Aroclor mixtures are the primary types used in utility equipment (4-8). Approximately 95 percent of 1260, 80 percent of 1254, 10 percent of 1242, and 1 percent of 1221 consist of PCB with five or more chlorine atoms per biphenyl molecule. PCB with higher chlorination tend to be more environmentally persistent, thus these percent distributions are important considerations.

The stable properties of PCB that make it nearly inert and an ideal fluid for use in electrical equipment also provide the properties that cause it to persist in the environment. PCB are nearly water insoluble, non-polar, and lipid soluble. Being hydrophobic with very low aqueous solubility they are readily adsorbed to solid surfaces such as silt, clay and sand particles as well as to biological cells (9, 10). PCB are volatile, and when not sorbed onto solids will transport the air-water interface to the atmosphere (11). Being hydrophobic and lipophyllic, PCB are also transportable across biological membranes and in the absence of

enzymatic metabolism in the cell, will bioaccumulate. Often the octanol/water partition coefficient is used to estimate this bioaccumulation potential, which is large for PCB (12).

PCB USE IN UTILITY EQUIPMENT

Seven utility equipment types are typically designed to use PCB or mineral oils (13). They are:

- transformers
- capacitors
- voltage regulators
- circuit breakers
- reclosers
- switches
- underground cables

Table 2-1 gives an estimated inventory of the number of units, volume of fluid, and weight of PCB contained in utility equipment. PCB and mineral oil are used as coolants and dielectric fluids. Of the seven types of equipment listed, all but capacitors are designed to function with mineral oil. Capacitors are 100% PCB with Aroclor 1242 as the principal dielectric fluid.

PCB OISPOSAL REQUIREMENTS

Leaks and Spills

The possibility exists that leakage or rupture of utility equipment can occur, resulting in contamination of environmental media by PCB. During a recent survey of utility use of PCB (7), the Resource Planning Corporation (RPC) investigated the incidence of leaks and spills from transformers and capacitors. Table 2-2 summarizes the expected frequency and size distribution of these spills. Table 2-3 provides estimates on the geographic distribution of spills for mineral oil transformers and capacitors. In comparison to oil transformers, percentages of spills from askarel units will be lower in "rural grasslands," higher in industrial areas and public areas. The major concern for spills in each case occurs in residential neighborhoods. These spill locations reflect upon the immediacy of decontamination requirements; and the method of decontamination depends upon the general terrain, soil type, rainfall and runoff, vegetative cover, and the presence of water bodies.

Table 2-1

INVENTORY OF PCB IN UTILITY EQUIPMENT (7)

Equipment	No. Units	Gal. Fluid	Lbs. PCB
Askarel Transformers	39,640	8,525,404	74,597,283
Mineral Oil Transformers	20,227,428	958,365,880	262,230
Capacitors	2,800,000	7,547,669	87,552,460
Voltage Regulators	145,159	17,840,968	6,707
Circuit Breakers	180,939	137,335,668	12,685
Reclosers	170,158	3,403,670	410
Switches/Sectionalizers	385,768	1,415,769	329

Table 2-2

FREQUENCY AND SIZE DISTRIBUTION OF PCB SPILLS (7)

Unit	No. of Leak/Spill Incidents	Size Distribution Lbs PCB/Incident	Average Lbs PCB
Askarel Transformers	317	4.4-3500	66
Mineral Oil Transformers	161,819	0.0-19	<1
Capacitors	21,564	5.8-90	17

Table 2-3

GEOGRAPHIC DISTRIBUTION OF PCB SPILLS (7)

	Mineral Oil Transformers	Capacitors
	% of Spills	% of Spills
Waterways (lakes, reservoirs, rivers, etc.)	0.3%	<0.0006%
Rural Desert Land	<0.09	1.5
Rural Wetlands, Marshlands	0.1	1.0
Rural Grassland (farmland, ranchland)	9.2	16.7
Industrial Area	13.2	29.1
Residential Neighborhood	70.6	45.3
Public Area (shopping center, schools, etc.)	5.9	6.4
TOTAL	100.0%	100.0%

Planned Disposal

Federal regulations under TSCA and RCRA (Resource Conservation and Recovery Act) require the eventual phaseout and controlled disposal of PCB, including all PCB contained in utility equipment (14). This represents over 1 billion gallons. The data of Table 2-1 reveal that the most common form of PCB-contaminated fluid is slightly contaminated mineral oil. The identity of Aroclors which make up the contamination is not explicitly known. This low level of PCB waste will require large treatment system capacity to destroy the PCB. Fluids contained within electrical equipment must be removed by washing with an appropriate solvent (6), which further dilutes the waste.

PCB disposal capacity depends on the rate at which the units in Table 2-1 are retired. Estimates (6) have yielded the following average annual waste production rates for the highly concentrated askarel transformer and PCB capacitors:

- For Capacitors: 5.25% of inventory (approximately 140,000 units, 400,000 gallons PCB, 4.6 million pounds PCB) per year from 1984-1997.
- For Askarel Transformers: 2.63% of inventory (approximately 1000 units, 224,000 gallons, 2 million pounds PCB) per year from 1984-2017.

Therefore, a substantial portion of the inventory will remain even with a 5-10 year lead time to develop biotreatment methods.

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Section 3

BIOTECHNOLOGY AND ITS POTENTIAL APPLICATION TO PCB DISPOSAL

Biotechnology is a field of the applied sciences which encompasses those engineered industrial processes that use living organisms or their functional components (such as enzymes). For general applications to hazardous wastes, the reader is referred to a contract report to the Congressional Office of Technology Assessment (OTA) by AmTech Consultants (15) and in the proceedings of a recent symposium (16).

The basic principle behind PCB biodegradation can be simply illustrated in Figure 3-1. In biodegradation, enzymes which are coded for by DNA serve as biocatalysts to cleave the biphenyl ring and dechlorinate the substituent groups. In effect, PCB is used as a source of food to the organism, and enzymes oxidize the hydrocarbons conserving the energy liberated while ultimately producing carbon dioxide, water and chloride. In this regard, the metabolism of PCB to inorganic end products can be equated to thermal oxidation (combustion and incineration) but through naturally produced biocatalysts reacting at ambient temperatures. As illustrated in Figure 3-1, there are many factors, genetic and non-genetic, that control the production and activity of a biocatalyst as well as the host organism, usually bacteria. General texts in biochemistry, molecular biology and microbiology review these principles (17-20). Before presenting existing data on the metabolism of PCB, some of the characteristics of PCB which render it recalcitrant to biodegradation are presented.

PCB RECALCITRANCE

There are several factors that render PCB recalcitrant to biological attack. These include its innate characteristics such as hydrophobicity and molecular structure and complexity. Also possible are the presence of toxic inhibitory concentrations of chemicals and lack of a required degrading enzyme.

- PCB Hydrophobicity: PCB are hydrophobic molecules with very low solubilities in water. Thus insoluble in water, they will remain separated and form a relatively small surface area to volume interface to the aqueous phase. Because degrading microorganisms live in primarily an aqueous environment, inaccessibility of the PCB substrate is a principal physical limiting factor contributing to its biological recalcitrance and environmental persistence. This

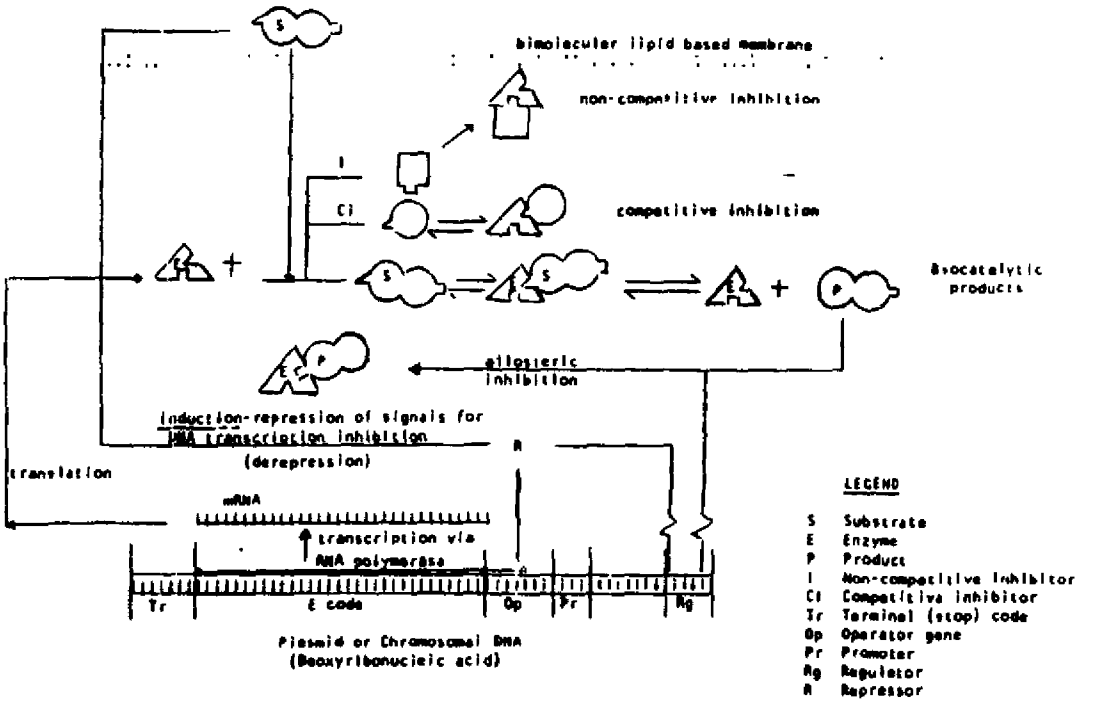

Figure 3-1. General Schematic of Enzyme Catalysis with Genetic and Non-Genetic Controls

Source: AmTech Consultants

inaccessibility, however, can be reduced by increasing PCB contact with the solution phase by forming emulsions of PCB. Enhancement of PCB degradation has been noted by several researchers using emulsifiers such as lignin sulfonate (21) and Tween 80 (22). Biologically derived emulsifiers, termed emulsans, have been found to form stable oil-in-water emulsions and though they have not been tested with PCB, could provide a means for increasing the exposed surface area of mineral oil or PCB for subsequent biological attack (23).

- Molecular structure of PCB greatly affects biological persistence. This is due to electronic and steric hindrance imparted by the number and location of chlorine substituents on the biphenyl rings.

  The electronic factors contributing to PCB recalcitrance include: a) delocalization of electrons by resonance; and b) the high energy of the aryl carbon-chlorine bond. Resonance contributes to chemical stability by making electrons less susceptible to attack. Thus, increasing the number of chlorine substituents can increase stability. Chlorine atoms are quite large, especially in comparison to the hydrogen atoms they have replaced on biphenyl rings. Their size inhibits effective nucleophilic or electrophilic attack on the carbon-chlorine bond or on nearby carbon-hydrogen or carbon-carbon bonds. Thus the location of chlorine substituents can also effect stability.

- Other chemical factors related to the recalcitrance of PCB are associated with the types of chemicals present, their concentrations and the medium in which the PCB is located. Alexander (24) has enumerated many factors which contribute to the biological recalcitrance of xenobiotics in general, and some which are applicable to PCB.

  Commercial formulations of PCB are most often found in the presence of PCB compatible solvents such as mineral oils and chlorinated aliphatics and aromatics. For biological degradation of PCB to occur, these materials must be simultaneously degraded by mixed microbial populations. Co-metabolism is frequently observed (25) and as reported by Tabak (26) and Barth (27), a wide variety of substituted chemicals, including chlorinated benzenes and phenols are relatively biodegradable. As PCB is likely to be the most persistent material in a mixture, solvents should not pose a major problem.

- Biological factors that are associated with the recalcitrance of PCB can be associated with either the absence, inhibition, or deficiency of an enzymatic activity needed to catalyze their destruction. In some cases there may not exist in nature enzymes with the properties necessary in order to efficiently degrade certain higher chlorinated isomers; however, over time processes such as plasmid evolution can be expected to develop degradative systems (28-30), and enzyme engineering may also be applied to correct catalytic deficiencies (31).

To summarize, there are innate characteristics of PCB as well as environmental factors that may cause its biological recalcitrance. The majority of these may be controllable to achieve more efficient degradation.

METABOLISM OF POLYCHLORINATED BIPHENYL

The only practical route of biological degradation of PCB is through ring cleavage and dechlorination. Many types of unicellular organisms, primarily bacteria, have been identified as being able to degrade to some extent the various PCB compounds (32-46). Both aerobic and facultative anaerobic bacteria have been isolated from various environments, including the open ocean and sediments of the Hudson River. Thus, in nature, there appears to be no particular genus or species that is the major user of PCB.

The two major chemical changes occurring in PCB metabolism are ring cleavage and dehalogenation. In no case has dehalogenation been reported to occur prior to ring cleavage. A complete pathway for the aerobic/anaerobic degradation of PCB is presented in Figure 3-2.

Ring Cleavage. Furukawa (35) presented a pathway which is quite consistent for the aerobic degradation of aromatic compounds, and provides confirmatory evidence that ring cleavage occurs prior to dehalogenation. Ring cleavage occurred on the ring with the lessor substituents at the meta position. Furukawa was unable to fully degrade the PCB metabolic product (chlorobenzoic acid) with his two cultures but other studies have demonstrated this to occur in mixed culture (47, 48). Ring cleavage of aromatic compounds is performed most efficiently in aerobic systems due to the ease of incorporation of oxygen by oxygenases, but also occurs anaerobically (49). A degradation product of PCB, dichlorobenzoic acid, has undergone anaerobic ring cleavage to yield methane and carbon dioxide (50).

Dehalogenation. Dehalogenation is obviously an important mechanism in the detoxification of PCB, but has not been specifically reported for the intact PCB molecule prior to ring cleavage. Following ring cleavage dechlorination occurs quite readily (35). Dehalogenation as an initial step would be extremely important for the more highly chlorinated compounds of Aroclor 1260 or in those structures that appear highly persistent. The enzymatic reactions which catalyze the removal of halogens from hydrocarbons have been grouped into three classes by Bollag (51): a) hydrolytic dehalogenation, in which a hydroxyl group replaces the halogen atom; b) reductive dehalogenations, where halogens are exchanged with hydrogen, and c) dehydrodehalogenation, in which both hydrogen and chlorine are removed with the formation of a double bond.

- Hydrolytic Dechlorination. Hydrolytic dechlorination is the most prevalent of the types observed. It is the method of aerobic chlorine removal from PCB alkyl chains arising after ring cleavage.

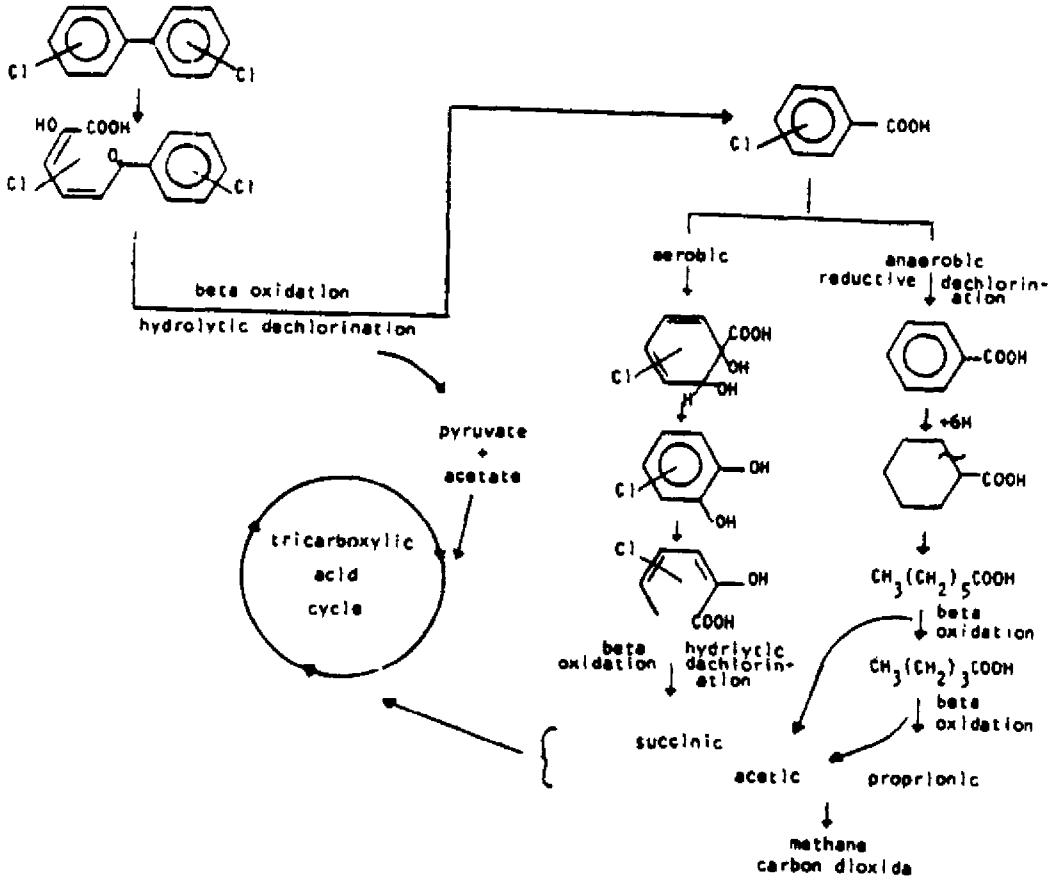

Figure 3-2. General Pathway for Total PCB Degradation.

Source: AmTech Consultants

- Reductive Dehalogenation. Reductive dehalogenation has been demonstrated for numerous microorganisms and is most effective under anaerobic conditions, with the notable exception, until recently, of chlorines attached to aromatic rings. Direct reductive dechlorination has now been observed in the laboratory with meta-substituted dichlorobenzoic acid (52,53).

Rates of PCB Degradation

Nearly all published data have indicated that the rate of PCB degradation is a direct function of the number and location of substituent groups on the biphenyl rings. As the weight percentage of chlorine increases, the rate of degradation decreases (Figure 3-3).

Table 3-1 presents a range of reported rates for PCB destruction according to the commercial Aroclor forms/compounds/percent chlorine. As indicated in the Table, there is a general trend of decreasing degradation rate up to the higher chlorinated Aroclors. Data reported for the higher Aroclors are from experiments which focused on optimizing rate, or are reports by commercial suppliers of micro organism formulations. In two of the studies where nearly 100 percent of Aroclor 1248 (22) and 1254 (21) have been reportedly degraded, measures were taken to overcome some of the physical limitation factors on PCB solubility by adding emulsifiers.

The results of converting the data in Table 3-2 to half-life form, assuming first order decay, is presented in Figure 3-4. The data indicates a biological half-life for PCB from 16 hours to one week for monochlorobiphenyls and three days to one year for hexachlorobiphenyls.

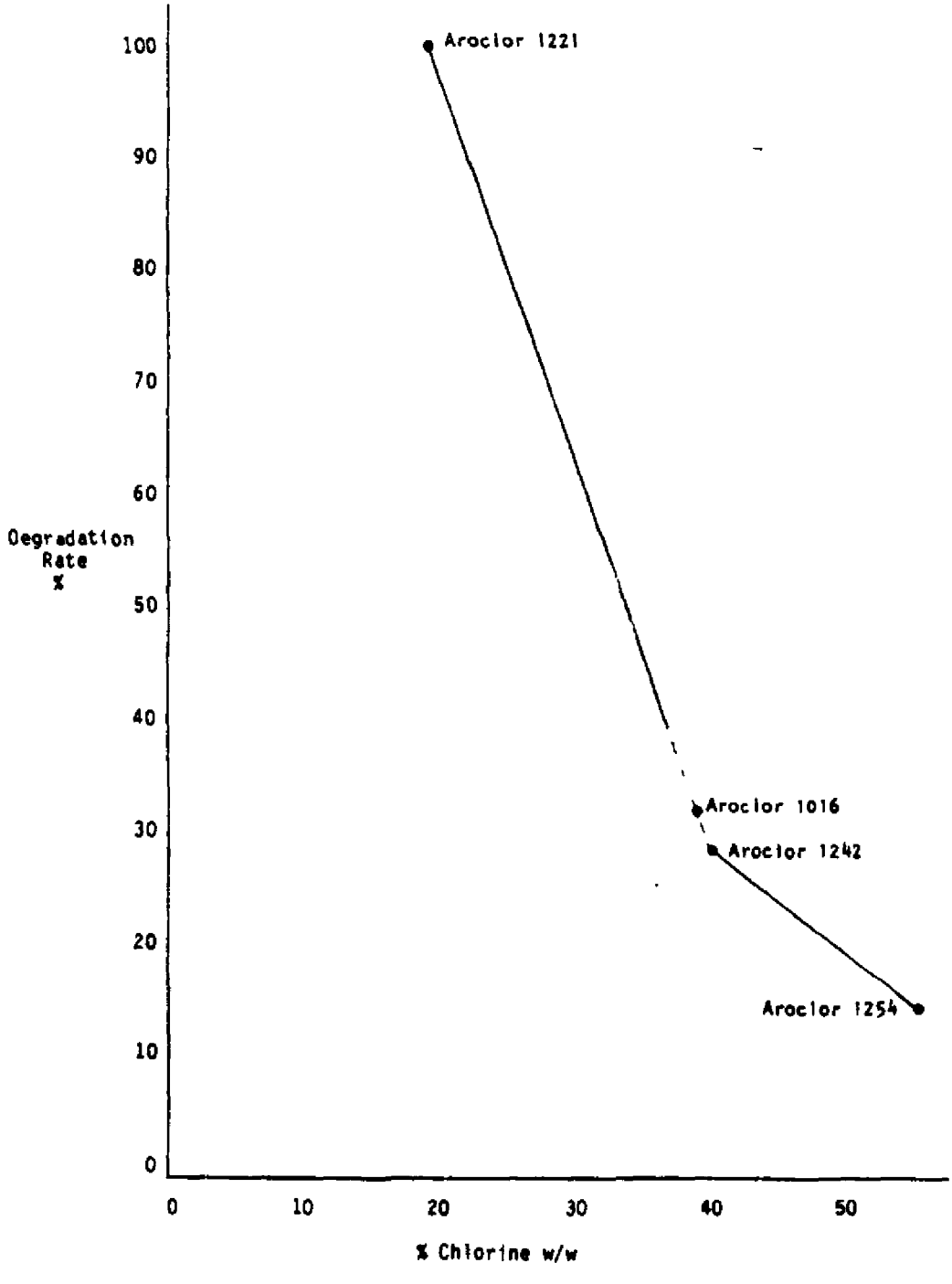

Figure 3-3. Biodegradation Rates of Various Aroclors (43).

Table 3-1

REPORTED RATES OF PCB DEGRADATION

Aroclor Mixture or Set of Isomers Studied	Reported Rate	Reference
Biphenyl	100%/2 days	43
Monochlorinated	>10 mg/l-hr	35
Monochlorinated	100%/5 days	54
Aroclor 1221	81%/2 days	43
Aroclor 1221	100%/30 days	45
Dichlorinated	1 - ≥ 10 mg/l-hr ave ≥ 7 mg/l-hr	35
Dichlorinated	50-100%/7-15 days	33
Dichlorinated	99%/5 days	54
Trichlorinated	0 - 9 mg/l hr ave= 6 mg/l hr	35
Trichlorinated	79-93%/5 days	54
Trichlorinated	30-75%/14 days	55
Trichlorinated	80-85%/28 days	55
Trichlorinated	50-70%/28 days	55
Aroclor 1016	96-98%/100 days	33
Aroclor 1242	33%/2 days	43
Aroclor 1242	88-95%/52-100 days	33
Aroclor 1242	26%/2 days	43
Tetrachlorinated	0-2 mg/l-hr	35
Tetrachlorinated	80-89%/5-15 days	54
Tetrachlorinated	0-40%/14 days	55
Tetrachlorinated	55-80%/28 days	55
Tetrachlorinated	35-60%/28 days	55
Aroclor 1248	97%/90-130 days	22
Pentachlorinated	0.1 mg/l-hr	35
Pentachlorinated	0%/14 days	55
Pentachlorinated	25-55%/28 days	55
Pentachlorinated	20-40%/28 days	55
Aroclor 1254	86-99%/4-18 days	21
Aroclor 1254	30-40%/8 weeks	56
Aroclor 1254	~ 50%/8 weeks >99%/16 weeks	57
Aroclor 1260	>99%/4 days	58
Aroclor 1260	56%/2 weeks @ 110 ppm	59
Aroclor 1260	24%/2 weeks @ 380 ppm	59
Aroclor 1260	20%/2 weeks @ 600 ppm	59
Aroclor 1260	14%/2 weeks @ 860 ppm	59

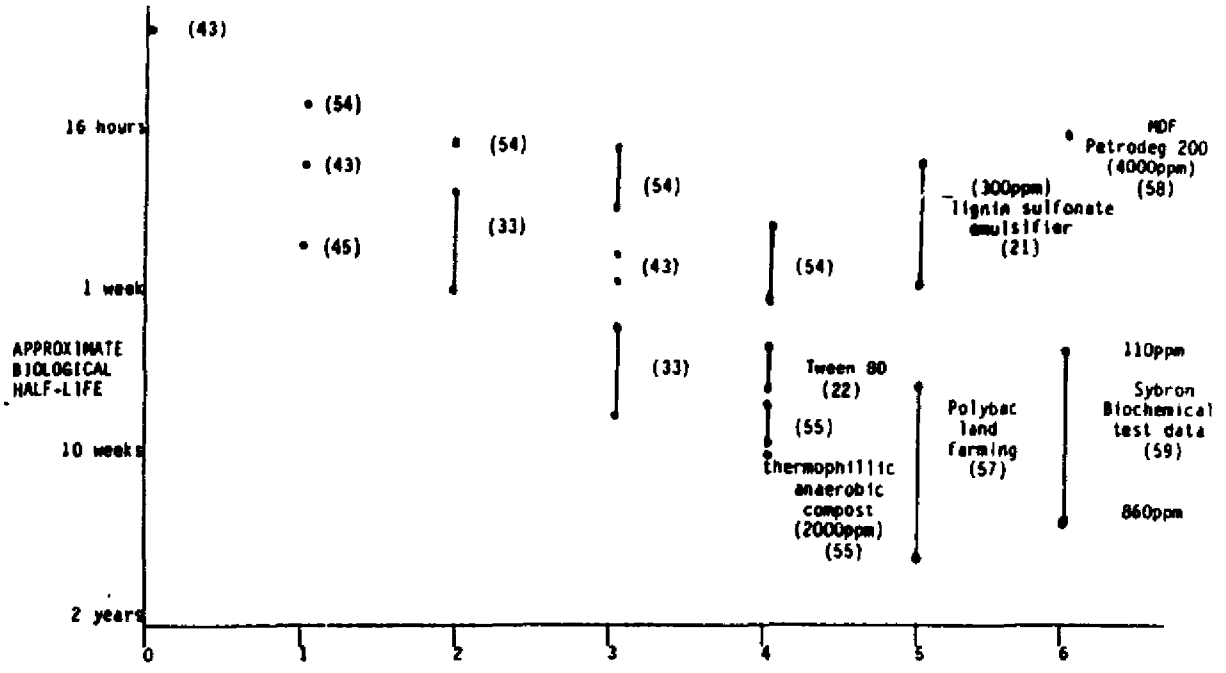

Figure 3-4. Approximate Biological Half-Life for PCB.

Source: AmTech Consultants

DATA VALIDITY AND TENTATIVE CONCLUSIONS

The scope of this study did not permit detailed review of each of the studies represented in Figure 3-4. Most of the data on the less chlorinated Aroclors were acquired from the peer-reviewed literature. However, all of the information in Figure 3-4 on Aroclors 1260 other than the lignin sulfonate emulsifier data came from proprietary field studies reported through direct communication. This does not mean that these latter data are invalid, since proprietary trade-secrets are usually protected from public scrutiny. In order to establish the validity of such field data, specific case studies must be examined in detail or a controlled demonstration must be performed. For example, there have been no reports in the peer-reviewed literature of anaerobic degradation of PCB; therefore, validation of the bench scale thermophilic, anaerobic (compost) degradation of Aroclors 1248 and 1254 is required. Similarly for the other proprietary results. Nevertheless, Figure 3-4 suggests that biotechnology application to PCB appears to hold promise as a treatment technology and the following tentative conclusions can be reached:

- Present results indicate PCB isomers at all levels of chlorination are biodegradable.
- The biodegradation rate for PCB appears to decrease with increasing molecular chlorination, all other factors being equal (e.g., absence of emulsification).
- This observed PCB biodegradation is performed by bacteria which occur naturally (i.e., have not undergone "recombinant DNA").
- The biotechnologies represented in Figure 3-4 should be amenable to considerable improvement in efficiency.
- Certain approaches represented in Figure 3-4 promise to improve PCB biodegradation significantly, i.e., emulsification and selective cell cultures.
- Although less promising than the case for planned PCB disposal, improved cell systems might actually permit rapid on-site treatment of PCB spills possibly with special cell lines. If not, it is still possible that a mixture of (e.g.) soil removal for off-site biological treatment, and in-situ biotreatment for low-level residuals would be attractive.

IMPROVING BIOLOGICAL PERFORMANCE

The overall performance of the biological component of a treatment system can be enhanced by several methods employing the relatively new techniques of applied genetics (i.e., genetic engineering). Several methods of improving biological performance are discussed below.

Genetic Engineering

"Genetic engineering" refers to deliberate manipulations of an organism's genetic code to a desired biological characteristic. The methods addressed concern: a) mutation and selection; b) recombinant DNA; c) plasmid evolution.

- Mutation and Selection. Mutations can be induced to change the chemical structure of DNA. Mutations in the genetic regions controlling promoter, operator, or regulator DNA sequences can enhance the rate of transcription of specific proteins. Ionizing radiation and certain chemicals induce mutations and have been commercially used for several decades in the pharmaceutical industry to improve yields of metabolites from production cell lines (60). It has also been applied to mutate microorganisms to preferentially degrade specific toxic pollutants (61). Selection is required to conserve a beneficial genetic trait and in the laboratory is usually conducted through enrichment subculturing and plating techniques.

- Recombinant DNA. The industrial technique termed "recombinant DNA" implies the engineered transfer of DNA from one type of organism to another. In this manner a unique gene which codes for a specific degradative enzyme could be inserted into a rapidly producing bacteria, providing for enhanced production of the desired biocatalyst. Because numerous enzymes may be involved, the utility of recombinant DNA in PCB degradation may be limited to producing whole cell lines capable of degrading many different PCB isomers on single or multiple plasmid copies in one or more bacterial strains.

- Plasmid Evolution. As in the evolution of antibiotic resistance by bacteria, evolution of specific plasmid genetic codes for toxic pollutant degradation occurs. Plasmids are not only transmissible between similar organisms but also between aerobes and anaerobes (62,63). Using techniques similar to routinely used enrichment/selection procedures for isolating cell lines, the knowledge of plasmid evolution allows for a more scientific approach in selecting the initial inocula. In this approach a wide variety of naturally selected bacteria (e.g., from contaminated dump sites) are inoculated with artificially selected bacteria harboring plasmids known to code for various sequences in a degradative pathway.

Enzyme Engineering

Enzymes are the biocatalysts responsible for PCB degradation. Enzymes can be extracellular or intracellular. Intracellular enzymes are more expensive to extract from the cell and can be unstable, though immobilization often increases their stability. There is no evidence to indicate that PCB degrading enzymes are extracellular. Because multiple isomers of PCB usually are present the range of necessary enzymes is large and the probability of using one or two enzyme systems to detoxify all PCB is extremely remote. An enzyme's catalytic activity can be

improved through various techniques using genetic engineering or by chemically synthesizing similar functional groups (31).

Bioaugmentation

The addition of biological or other materials which improve system performance is frequently termed bioaugmentation. Additives can include biological emulsifiers (emulsans), synthetic emulsifiers, nutrients, enzymes, flocculants, and microorganisms. They are used to overcome treatment difficulties in operating biotreatment systems, to maintain the population of a slow-growing organism, or in routine operations and maintenance. The main purpose of bioaugmentation is to overcome factors contributing to the persistence of chemical wastes by providing the organisms with a growth complement. Their additions are no different, for example, than the making up of spent catalysts in chemical systems.

Section 4

BIOTREATMENT PROCESS SYSTEMS

Many biological technologies used to treat industrial wastes are applicable to PCB destruction. System design depends upon waste characteristics (the waste matrix) and the degree of treatment required. The microorganisms utilized in biotreatment systems can be broadly classified as aerobic, aneerobic or facultative. Aerobic organisms require molecular oxygen for metabolism, and anaerobes function in the absence of oxygen; facultative organisms function in either the aerobic or anaerobic state. Aerobic organisms are usually considered to perform respiration, that is the use of molecular oxygen as the ultimate electron acceptor. Anaerobic organisms usually perform fermentation, which is metabolism using some other source than molecular oxygen as the ultimate electron acceptor.

The types of biological technologies applicable to PCB are identified below, along with brief descriptions of their present applications, limiting factors and environmental concerns. They include:

- conventional aerobic and anaerobic processes
- land disposal techniques
- enzyme systems
- specialized fermentation systems
- spill clean-up and remedial techniques

CONVENTIONAL AEROBIC AND ANAEROBIC TECHNOLOGIES

Most organic industrial wastes are amenable to biological treatment and the degrading populations become specifically adapted to certain compounds. Higher chlorinated PCB may, however, pose problems of recalcitrance and accumulation via adsorption onto the disposed sludge. In order to achieve maximum PCB degredation, it is necessary to base system design upon the specific PCB degradative biokinetics, or upon a mode of bioaugmentation.

Aerobic Treatments

Ring cleavage of halogenated aromatics such as PCB, is efficiently accomplished via oxygenases with molecular oxygen. Aerobic treatments of PCB are therefore very important in their biodegradation. Types of aerobic treatments include:

- activated sludge
- aerated lagoons
- aerobic digestion
- trickling filters
- rotating biological contactors

Anaerobic Treatments

Anaerobic treatments are potentially applicable to the reductive dehalogenation of PCB and degradation of oxidative products. The following are types of conventional anaerobic treatment systems:

- anaerobic digestion
- anaerobic contact
- anaerobic fixed-film treatment processes

In general, these aerobic and anaerobic systems have been designed to treat miscellaneous soluble and insoluble organic matter in the most cost effective manner reflecting minimum retention times and capital costs. As it appears that most PCB can be degraded over time -the length of time required increasing with the percent of molecular chlorination -either extended periods of treatment time, special pretreatment, or bioaugmentation would be required for existing conventional systems to degrade the more highly chlorinated isomers.

In adapting these systems as a primary means to treat PCB, aerobic processes are required because PCB is aromatic and molecular oxygen must be supplied (via oxygenase) to efficiently cleave the aromatic ring. Secondly, PCB hydrophobicity causes it to accumulate on sludges/solids, requiring an aerobic system with high solids treatment such as aerobic digestion. On the other hand, complete anaerobic degradation of PCB might eventually be possible with the development of anaerobic cell lines, but would require strict microbial control.

LAND FARMING AND COMPOSTING

Sludges and solids contaminated with PCB can be biologically treated in various land-based systems, either on the soil (land farming), or in composting systems.

- Land farming implies that microorganisms are being grown utilizing the waste as a carbon and energy source. Plant crops also can be grown. The Environmental Protection Agency includes land farming in its hazardous waste regulations as a disposal method (64). There are over 150 land farming operations in the United States ranging up to 1,500 acres in size. The petroleum refining industry uses the majority of these sites for the disposal of refinery wastes, such as API separator sludge.

  Land treating of toxic materials is highly controversial mainly because it is conducted in the open environment, but frequently it may be the only alternative in the case of low level contamination from spills. It can be conducted on a spill site as a primary treatment or as a polishing operation, or off-site for treatment of the removed contaminants. Polybac Corporation recently reported treating a quarter acre land site of PCB contaminated soils using land farming techniques (57).

- Composting is similar to land farming as it can employ a blended soil/organic matrix. Generally it is a well aerated and mixed process occurring on the soil surface or in contained systems. To some extent it resembles a dry aerobic or anaerobic treatment with the particles of cellulosic and lignin based solids serving as the support medium for biological growth. Composting involves blending dry organic material such as straw or agricultural residues with materials such as contaminated sludge or soil, and allowing the saprophytic organisms, bacteria, fungi and actinomycetes to degrade the matrix over several weeks to months depending on the process. Only one proprietary report of PCB degradation by composting has been provided to this study which was conducted on a laboratory scale (55). PCB degradation was observed in aerobic and anaerobic compost systems, but not in controls. An unusual result was a reported 25 to 40 percent degradation in anaerobic systems.

ENZYME SYSTEMS

To date, use of either cell-free extracts or in-vitro enzyme systems for PCB degradation has not been reported. Applications of enzyme systems to PCB degradation would be most appropriate as an initial detoxification step, catalyzing either aromatic ring cleavage or dehalogenation.

The use of enzymes in industry has been reported extensively. How an enzyme system is applied depends upon the characteristics of both the substrate, enzyme, and process. Maintaining enzyme stability and activity is most important as their makeup can be quite costly. Enzymes can be applied in a free or immobilized state, the latter on carriers in either a fixed or fluidized reactor configuration. In

their free state the enzymes become part of the substrate matrix and are wasted with the catalyzed substrate solution. Thus, immobilization is preferred in order to conserve the enzyme and allow it to be used many times over. However, for water insoluble substrates (such as PCB), free enzyme systems would be required unless emulsifying could place PCB into aqueous suspension.

SPECIALIZED FERMENTATION SYSTEMS

Specialized fermentation systems are developed for use on a specific substrate and are either aerobic or anaerobic processes with pure or mixed cultures. They usually take on an intensive approach to process control. Specialized fermentation systems employ specific cell lines which metabolize well-defined substrate streams and are optimized on scales much smaller than for conventional systems.

Specialized fermentations use cell systems in either immobilized or in suspended states. The main difference between immobilization and suspension fermenters is in the method for contacting the bacteria with the substrate. Fermenters usually employ a high rate of mixing to force the biomass into suspension. Thus, care must be taken to avoid shearing and damage to the cells. Instead of mixing, immobilized systems use an array of support media packed as columns or beds in the reactor.

SPILL CLEANUP SYSTEMS

Biological technologies can be used to clean up toxic commercial materials that contaminate either land or water. The principles involved in land application also apply to accidents involving spillage of organic compounds. The major difference is that very high loading rates are often associated with spills, but tha affected area is normally small in size.

Section 5

PROMISING APPROACHES

BIOTREATMENT OF PCB SPILLS

Biotreatment of PCB-contaminated spill sites would be preferable to the commonly used technique of excavating and landfilling contaminated materials. A large demand exists for a rapid, easily applied treatment method for PCB spills, and biotreatment may eventually be used in this manner. An ideal biodegradative system would include an organism and/or its associated enzymes in a packaged form which could be reconstituted in the field and applied as needed to contaminated solids. In the near term, in-place treatment appears feasible for particular contamination situations where time is available and a health threat is not imminent. Polybac demonstrated its ability to treat on land Aroclor 1254 contamination of 230 ppm over a 5-6 month time period, but required the use of a proprietary reducing agent to dechlorinate the higher chlorinated Aroclor forms. With additional research and improvement in cell lines and additives, it is likely that soil cleanup techniques could be considerably improved. On-site treatment with mobile composting facilities or centralized off-site treatment on land farms may also be applicable.

BIOTREATMENT FOR UTILITY PCB FLUIDS

Systems for planned disposal of bulk PCB-contaminated fluids must be capable of treating PCB, mineral oils, polychlorinated benzenes, and solvents used to wash out utility equipment. Although these wastes will be diluted to PCB concentrations amenable to biological treatment, high organic loading will occur. Continuous or batch flow systems could be used. Emulsification would play a significant role in all systems as well as bioaugmentation with genetically engineered cell lines. Types of concepts include:

- coupled high-mix aerobic bioreactors
- sequential anaerobic-aerobic-anaerobic
- immobilized cell aerobic treatment with high pressure oxygen saturation
- complete anaerobic treatment

Section 6

CONCLUSIONS AND RECOMMENDATIONS

Biotechnology appears to hold considerable promise for the treatment of PCB for the electric utility industry. However, studies to date have been conducted mostly on laboratory scales. Some have not been validated, and most have not considered the complex problems associated with actual waste matrices and practical treatment approaches. Thus, efforts are required to substantiate findings reported herein and to advance technology development.

CONCLUSIONS

From the review and analysis of available published and private data we conclude:

1. Efficient treatment of electric utility PCB wastes will become feasible and should be available in 5 to 10 years given adequate research and development.

2. Promising biotechnologies include:

   --Improved PCB degrading species through genetic engineering.

   --Specialized bioreactors for aerobic and anaerobic PCB treatments.

   --Possible enzyme systems for select PCB decontaminations.

   --Systems for growing and harvesting cells for bioaugmentation, as well as in enzyme production processes.

RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT

If biotechnology is to achieve its potential to treat electric utility PCB wastes, a well-designed research and development strategy should be developed and implemented. Such a strategy should include validation of existing data as a first step to confirm and advance the state-of-the-art. Research and development should focus on three areas: microbiology and genetic engineering; system design and testing; and cost analysis. These recommendations are briefly listed below.

Microbiology and Genetic Engineering

- Inventory and collect PCB degrading cultures and isolate new strains
- Identify degradative pathways, enzymology and genetics
- Improve degradative performance through genetic engineering techniques on collected strains
- Characterize and test emulsifiers, and transfer PCB degradative genetics to bioemulsifying strains
- Test cell extracts for PCB degradative potential

System Design and Testing

- Process development systems are required based upon the performance of pure or mixed PCB degrading cultures above
- Promising cell-free enzyme systems will require development of production reactors and application techniques
- All characterized waste matrices require laboratory and field test development
- Successful systems require scale-up and pilot plant operations

Cost Analysis

- Conceptual design cost analysis should be conducted for candidate systems to screen for cost-effectiveness
- Sensitivity and financial risk analysis should be performed in comparison with approaches alternative to biotechnology for those selected as serious candidates

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Discussion

Q1. Wouldn't many enzymes be needed to complete the destruction of complex PCBs?

A. Yes, it would need a lot of development work. Use of whole cells can produce many enzymes.

Q2. In pretreating spills, isn't there a risk of groundwater contamination?

A. Bugs are not poison and they are in soil anyway. However, if these processes were commercialized, it might be necessary to use some containment to prevent possible spreading.

BACTERIAL DEGRADATION OF PCBs: EVIDENCE OF DISTINCT PATHWAYS IN *CORYNEBACTERIUM* SP. MB1 AND *ALCALIGENES EUTROPHUS* H850

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INTRODUCTION

More than 100 forms (congeners) of polychlorinated biphenyls (PCBs), differing in the number and position of chlorines, were commonly used over the last half century. The same properties which formed the basis for their use (thermal stability, chemical stability) have also contributed to their accumulation in the environment. Furthermore, PCBs are highly insoluble in water and are only slightly mobilized by aqueous systems. Thus, PCBs have accumulated in soil and lake and river sediment at sites of their production, use, storage, or disposal.

Microorganisms are generally responsible for the breakdown of complex organic materials into simpler forms that can be recycled. However, synthetic compounds, especially those which are chlorinated, frequently resist microbial degradation (1). This has been true of PCBs; congeners containing more than three chlorines have been markedly recalcitrant to biodegradation. On the other hand, evidence is accumulating that bacteria may be adapting by evolving enzymes capable of degrading chlorinated aromatics including PCBs. It has been well documented that many different genera of bacteria are capable of degrading mono-, di-, or trichlorobiphenyls when presented as single compounds (2-9) or in a commercial mixture such as Aroclor 1242 (10-14). However, there have been few reports of degradation of the more highly chlorinated PCBs in Aroclor 1254 (7,14,15). Furthermore, in these cases no details have been published of either the organisms, the enzymatic mechanisms, or the specificity of degradation.

On the other hand, Furukawa and colleagues have convincingly demonstrated the ability of two pure bacterial cultures, *Alcaligenes* Y42 and *Acinetobacter* P6, to

degrade pure PCB congeners containing up to five chlorine atoms (16,17,18). The ability of these cultures to degrade a broad range of PCB congeners has prompted questions about the origin of PCB degradative competence in bacteria and the enzymatic pathways involved. In response, we have undertaken an in-depth study of the biochemistry and genetics of bacterial PCB degradation aimed at providing a sound basis for understanding what is happening in the environment.

A number of key questions provided the framework for our studies: Could other bacteria be readily found with a degradative competence equal or superior to that of Acinetobacter P6? How rapidly can microorganisms degrade PCBs? What are the degradation products? What structural factors limit the degradation of PCB congeners (position, number of chlorine atoms)? Is there more than one pathway for degradation of PCBs? Is there any relationship among genes which specify PCB degradative enzymes in different organisms? Can these genes be exchanged among bacterial species or genera? We describe here some of our recent findings with two bacterial species capable of degrading a broad range of PCB congeners including pentachlorobiphenyls. Ultimately, it is our intention to characterize the biochemistry and genetics of PCB degradation in these organisms by studying the products of PCB degradation, elucidating the pathway(s) of degradation, and isolating and studying the genes responsible for this biotransformation.

METHODS AND MATERIALS

Isolation and Culture Methods

All cultures were grown and maintained aerobically at 30°C in a gyratory shaker on a mineral salts medium containing 1 mg/ml of biphenyl and supplemented with 0.005% yeast extract.

Strain H850 was isolated from a landfill containing PCB contaminated dredge spoils. Approximately 5 g of soil was incubated in 50 ml of the culture medium described above. After approximately 12 transfers individual colonies were isolated and characterized. Four strains of Alcaligenes eutrophus, exhibiting only slight differences, were isolated from the enrichment culture and it is one of these, strain H850, that we describe herein. Two strains of Alcaligenes eutrophus were purchased from the American Type Culture Collection (Rockville, MD). The type strain, ATCC 17697, has been extensively characterized for dissimilation of aromatic compounds. (19) while the second strain, ATCC 29597, is characterized only by its ability to grow autotrophically.

Preparation of Resting Cells

Cells were grown overnight on biphenyl, then the crystals of biphenyl were removed by filtration through glass wool. The cells were harvested by centrifugation (5000 rpm) for 15 minutes in a Sorvall (Model RC-2B) using an SS34 rotor. The cells were washed twice in 0.05 M sodium phosphate buffer, pH 7.5, and resuspended in the same buffer to give an optical density of 1.0 at 615 nm.

PCB Degradation Assays

Three different substrates were employed in degradation assays: individual PCB congeners, a synthetic mixture of seven PCB congeners, or Aroclor 1248. A 100X stock of the synthetic mixture was prepared in acetone from 2,4,4' and 3,4,2' trichlorobiphenyls (1.28 µg/ml each), and 2,3,5,6; 2,5,2',5'; 2,3,2',3'; 2,5,3',4'; and 3,4,3',4' tetrachlorobiphenyls (1,46 µg/ml each). The PCB stock solution in acetone was mixed with the cell suspension to yield a final PCB concentration of approximately 10 ppm.

The Aroclor 1248 substrate was added in 60 µl of acetone to a 30 ml cell suspension, to give a final concentration of approximately 10 ppm. After thorough mixing, a 10 ml aliquot was removed and transferred to a tube containing 0.1 ml of 70% perchloric acid. This time zero (T_0) control sample was mixed thoroughly and frozen for later analysis. Alternatively, suitable controls were prepared by heat inactivation (70°C, 20 minutes) of the cell suspension prior to incubation with PCBs. Both heat and acid pretreatment of cell suspensions destroyed activity against all Aroclor 1248 PCB congeners. The remainder of the cell suspension was incubated for 3 days at 30°C with shaking, then acidified and frozen until analysis.

When individual PCB congeners or the synthetic mixture of PCB congeners were used as a substrate, the above procedure was used except that incubation was limited to 24 hours.

PCB Extraction

A C_{18}-Sep-Pak cartridge (Waters Associates, Milford, MA) was activated with methanol and the acidified cultures applied to the cartridge by gravity filtration. The aqueous filtrate was discarded and the PCBs were eluted from the cartridge with methanol. When Aroclor 1248 was used as a substrate, the methanol extract was used for gas chromatographic analysis directly without further extraction. When the synthetic congener mixture was used, water was added to the methanol (final concentration 25%), and the PCBs were reextracted with hexane.

PCB Metabolites

The cultures were adjusted to pH 1-2 with perchloric acid and extracted twice with one half volume each of anhydrous ethyl ether. The extract was dried, resuspended in 0.8 ml of tetrahydrofuran, and derivitized with 0.4 ml of N,O-bis-(trimethylsilyl) acetamide (BSA, Pierce Chemical Company, Rockford, IL) for 30 minutes at 65°C. The PCBs and the silyl esters of the PCB degradation products were detected using gas chromatographic analysis.

Gas Chromatographic Analysis

Samples containing the synthetic PCB mixture were analyzed on a Hewlett Packard Gas Chromatograph (Model 5830IA or 5880A) fitted with an automatic sampler and an electron capture detector. A glass column (6 ft x 4 mm) packed with 1.5% SP-2250/1.9% SP-2401, on 100/120 Supelcoport (Supelco, Inc., Bellefonte, PA) was used. The carrier gas was 10.4% methane in argon at a flow rate of 60 ml/min. Chromatography was run isothermally at 192°C for analysis of PCBs alone. For analysis of PCBs and metabolites, the temperature was increased from 160°C to 240°C at 5°C/minute and held at 240°C for 10 minutes.

Aroclor 1248 samples were analyzed on a Varian 4600 gas chromatograph using a fused silica capillary column (J and W, 30 m x 0.25 mm id; ID #10967). The liquid phase was DB-1 and the film thickness was 0.25 μm. The carrier gas was helium at a flow rate of 30 cm/s. The make-up gas was nitrogen at a flow rate of 25 ml/min. Grob type injection was employed (2 μl injection size). The column was run at 40°C for 2 minutes, then the temperature was increased to 80°C at a rate of 10°C/min and finally to 225°C at a rate of 6°/min. The temperature was held at 225°C for 10 minutes.

The data were stored on disc using a Varian Vista 401 Series Data System and replotted to give a direct comparison of each experimental sample (T_f) with the corresponding control (T_o). The control to experimental ratio was calculated for each of the 33 PCB peaks. The assignments for the Aroclor 1248 peaks were determined by R.E. Wagner and J.C. Carnahan (Manuscript in Preparation) based on published identifications (20) using gas chromatographic columns with comparable specifications.

Plasmid Purification and Analysis

Plasmids were demonstrated in H850 and MB1 using the protocol described by Hansen and Olsen (21). Cells were grown on biphenyl to an optical density of 0.4-0.6 at 615 nm, filtered to remove the biphenyl and harvested by centrifugation. Follow-

ing a brief digestion with lysozyme, the cells were lysed with 2.5% sodium dodecyl sulfate during a series of heat pulses at 55°C. Chromosomal DNA and RNA were partially removed by alkaline denaturation. Chromosomal DNA was removed by sodium dodecyl sulfate precipitation, and the plasmid DNA in the supernatant was concentrated by precipitation with polyethylene glycol.

Plasmid DNA was analyzed by electrophoresis in 0.75% agarose on a horizontal slab gel apparatus. The buffer used was 89 mM Tris, pH 8.3, 89 mM boric acid, 2.5 mM disodium EDTA. After staining with ethidium bromide, plasmids and DNA fragments were visualized by a UV transilluminator. Hind III fragments of phage lambda DNA were used as molecular weight markers.

Chemicals

For growth studies, biphenyl was purchased from Aldrich Chemical Co. (Milwaukee, WI) and monochlorobiphenyls were purchased from Pfaltz and Bauer, Inc. (Stamford, CT). For degradation studies, analytical grade PCBs were purchased from Analabs, Inc. (North Haven, CT). Omnisolv grade hexane, methanol, and acetone were purchased from MCB Manufacturing Chemicals, Inc., (Cincinnati, OH). Nanograde hexane was purchased from the Aldrich Chemical Co.

Restriction endonucleases were purchased from New England Biolabs (Beverly , MA) and used as per the manufacturer's instructions. Electrophoresis grade agarose (Standard Low M_r) was purchased from Bio-Rad Laboratories (Richmond, CA).

RESULTS AND DISCUSSION

Isolation and Taxonomic Characterization of Bacterial Strains

Strain B850 was isolated by biphenyl enrichment from a landfill containing PCB contaminated dredge spoils and sent to the American Type Culture Collection (ATCC) (Rockville, MD) for characterization. It has been identified as Alcaligenes eutrophus according to Bergey's Manual of Determinative Bacteriology (22). The cells were gram negative coccal rods occurring singly, in pairs, and in chains, and motile by peritrichous flagellation. The tests for oxidase and catalase were positive, whereas tests for hydrolysis of casein and gelatin were negative. The organism is capable of growth between 25 and 37°C but not at 41°C and metabolism is respiratory, never fermentative. A wide variety of organic compounds can be utilized as substrates by strain B850 including fatty acids, dicarboxylic acids, hydroxy acids, non-nitrogenous aromatic compounds, and aliphatic and aromatic amino acids. However, few carbohydrates and no pentoses or disaccharides are utilized. Fructose, but not glucose can support growth of these

cells. This unusual pattern is characteristic of Alcaligenes eutrophus. This is the first report of growth on biphenyl or degradation of PCBs by this species although there have been several reports of members of the genus Alcaligenes with these characteristics (12,13,16-18).

Strain MB1 was isolated from a stock of Acinetobacter sp. P6 (22) and subsequently characterized by the American Type Culture Collection. It has been classified as belonging to the genus Corynebacterium based on the following criteria: The cells are nonmotile, gram positive pleiomorphic rods and are catalase positive but oxidase negative. Tests for indole production, casein and gelatin hydrolysis, citrate utilization, methyl red reaction, and Voges-Proskauer reaction were all negative. Whole cell hydrolysis demonstrated the presence of meso-diaminopimelic acid, a characteristic typical of this genus. Only two other gram positive organisms have been shown to degrade PCBs. The first, Nocardia sp. NCIB 10603, was reported by Baxter et al. (3). The second was isolated as a contaminant of Acinetobacter sp. P6 and was identified as Arthrobacter sp. MS (23). The characteristics of Arthrobacter and Corynebacterium are very similar, but these genera can be distinguished by cell wall analysis. We cannot rule out the possibility that the MS strain of Furukawa and Chakraborty (23) is identical to Corynebacterium sp MB1.

Growth on Monochlorobiphenyls

Both MB1 and H850 grew readily on biphenyl. Corynebacterium sp. MB1 grew moderately well on 4-chlorobiphenyl but not on 2- or 3-chlorobiphenyl. Alcaligenes eutrophus H850 utilized all three monochlorobiphenyls as a growth substrate but to differing degrees. Growth was best on 2-chlorobiphenyl, moderate on 3-chlorobiphenyl, and poor on 4-chlorobiphenyl. We did not test the ability of either of these strains to utilize higher chlorinated PCB congeners as growth substrates.

Degradation of Aroclor 1248

Each culture was incubated with commercial grade Aroclor 1248 to determine its ability to degrade PCBs. Figure 1 shows gas chromatographs (G.C.) of Aroclor 1248 before (control) and after a three-day incubation with H850 or MB1. The 49 congeners in the mixture range from di- to hexachlorobiphenyls and are resolved into 33 peaks. The extensive changes in the PCB profile demonstrated by this assay are indicative of degradation and not selective adsorption for the following reasons: [1] In all cases both the cell mass and the aqueous phase were extracted. [2] The Aroclor 1248 profile recovered by extraction of the PCBs

DEGRADATION OF AROCLOR 1248 BY RESTING CELLS

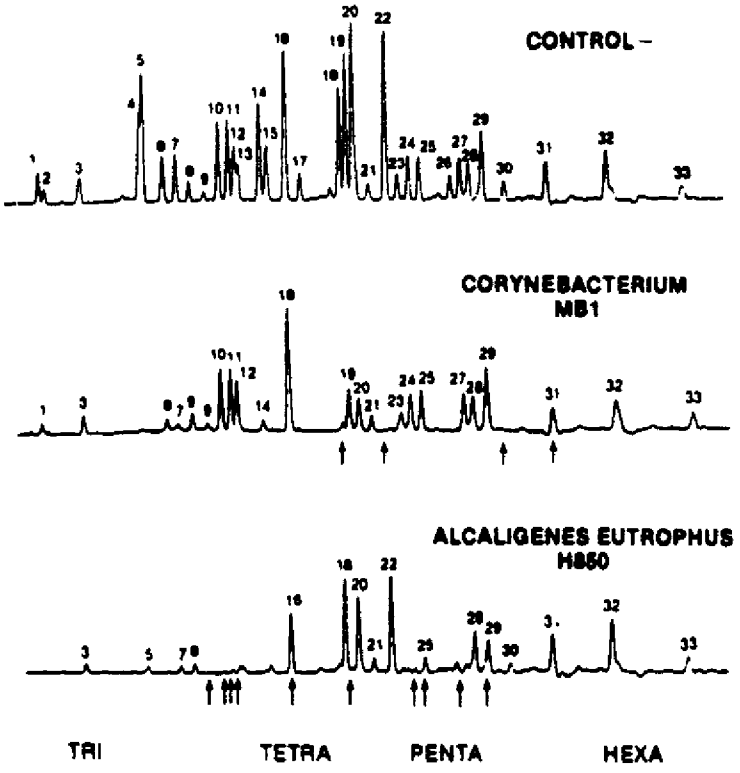

Figure 1. Degradation of Aroclor 1248 by Resting Cells. Cells were grown on biphenyl, washed, and resuspended in phosphate buffer. Aroclor 1248 was added to a final concentration of 10 ppm. The control shows a capillary gas chromatograph of the PCBs extracted from an aliquot of cells acidified immediately after addition of the PCBs. The middle and lower panels show the PCBs extracted from the MB1 and H850 cell suspensions after 3 days incubation.

from cells acidified at T_0, or from heat-inactivated cells at T_0, or after 3 days incubation, is identical to the profile of an Aroclor 1248 standard. [3] A mutant strain of MB1 which has lost the ability to grow on biphenyl does not alter Aroclor 1248. Similarly, two strains of Alcaligenes eutrophus which do not grow on biphenyl (ATCC strains 17697 and 29597) have no effect on Aroclor 1248. [4] A yellow color which is generally taken to be indicative of PCB metabolism

Table 1

DEGRADATION OF AROCLOR 1248 BY RESTING CELLS

Peak Number	PCB Congener Tentative Assignment	MB1	KB50
1	2,5,2'	P	+
2	2,4,2' and 4,4'	+	+
3	2,3,2' and 2,6,4'		P
4	2,5,4'	+	+
5	2,4,4'	+	+
6	2,3,3'	P	+
7	2,3,4' and 2,4,2',6'	P	+
8	Tetra		P
9	3,5,3'		+
10	2,5,2',5'		+
11	2,4,2',5' and 2,4,6,3'		+
12	2,3,4,6		+
13	2,4,2',4'	+	+
14	2,3,2',5' and 2,3,2',4'	+	+
15	3,4,4'	+	+
16	2,3,4,2' and 2,3,6,4'		P
17	2,3,2',3'	+	+
18	2,4,5,4'	+	
19	2,5,3',4'	P	+
20	2,4,3',4' and 2,3,6,2',4' and 2,3,6,2',5'	P	P
21	2,4,5,2',6'		
22	2,3,4,4' and 2,3,4,2',6'	+	P
23	2,3,6,2',3' and 2,3,5,2',5' and 2,3,5,2',4'		P
24	3,4,3',5' and 2,4,5,2',5'		P
25	2,4,5,2',4'		P
26	2,4,5,2',3'	P	P
27	2,3,4,2',5'		P
28	2,3,4,2',4'		
29	3,4,3',4' and Penta		P
30	2,4,5,3',5'	+	
31	2,4,5,3',4' and 2,3,6,2',4',5' and 2,3,4,5,3' and 2,3,4,6,2',5'	P	
32	Penta		
33	2,5,4,2',4',5'		

This table represents an individual analysis of the data shown in Figure 1. Most of the congeners in Aroclor 1248 have been identified and tentatively assigned to peaks in the chromatograph profile (J.C. Carnahan and R.R. Wagner, Manuscript in Preparation) Each experimental sample was compared to its own (T_o) control and the reduction in each peak height was used to assess degradation as either partial (50-80%; P) or complete (> 80%, +) on the basis of the ratio of the peak areas. In some cases this conservative scoring method may have underestimated the extent of degradation, particularly where a single peak represents several PCB congeners.

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(2,7,9,11,16-18) appears in viable cultures but not in the controls. Therefore, these changes cannot be explained by selective adsorption to the cells or the glassware. Finally, the fact that only cells which can utilize biphenyl alter the PCB profile is fairly strong evidence that the changes are due to microbial degradation.

Two other points are immediately apparent: [1] Both MB1 and B850 degrade the commercial PCB mixture extensively: MB1 attacks approximately 49% of the PCB congeners and B850 degrades approximately 69%. In each case PCBs chlorinated at up to five positions are degraded. [2] The degradative competence of the two cultures is quite different. Although MB1 and B850 degrade many of the same PCB congeners, each strain is superior to the other in its ability to degrade certain congeners. These differences are indicated by arrows on Figure 1 and are even more apparent when the data are tabulated (Table 1).

Degradation of Synthetic Mixture of PCB Congeners

Encouraged by the above results, we devised an assay using a synthetic mixture of seven pure PCB congeners to focus more closely on the differences in the degradative competence of MB1 and B850. The results, shown in Table 2, were striking.

Table 2

DEGRADATION OF A SYNTHETIC MIXTURE OF PCB CONGENERS

PCB Congener	MB1	B850
2,4,4'	95%	53%
3,4,2'	98	98
2,5,2',5'	-	100
2,3,5,6	-	-
2,3,2',3'	92	96
2,5,3',4'	-	91
3,4,3',4'	-	-

This table shows the percent degradation of each of seven PCB congeners of a synthetic mixture following incubation for 24 h with resting cells of MB1 or B850. Each congener was present at 5 nmol/ml (approximately 1.5 ppm). Percent degradation was calculated by comparing the area of each G.C. peak in the control (T_0) and experimental (T_f) samples. The values given represent the mean of two separate experiments.

Again, the two cultures demonstrated identical competence for some PCB congeners; two were not degraded by either strain and two were readily degraded by both cultures. However, H850 completely degraded two tetrachlorobiphenyls which were not metabolized by MB1. In contrast, MB1 degraded 2,4,4' trichlorobiphenyl more readily than H850. It is clear that both the position and the number of chlorines are critical in determining whether a particular PCB congener can be degraded.

These data led us to question whether the position of the initial enzymatic attack on the aromatic ring might differ in MB1 and H850. A number of laboratories have postulated pathways for PCB (2,13,16) or biphenyl (24-26) degradation. In each case, the initial enzyme is thought to be a 2,3-dioxygenase. Subsequently, meta-cleavage occurs between carbon atoms 1 and 2 (Figure 2) (2,16,26)

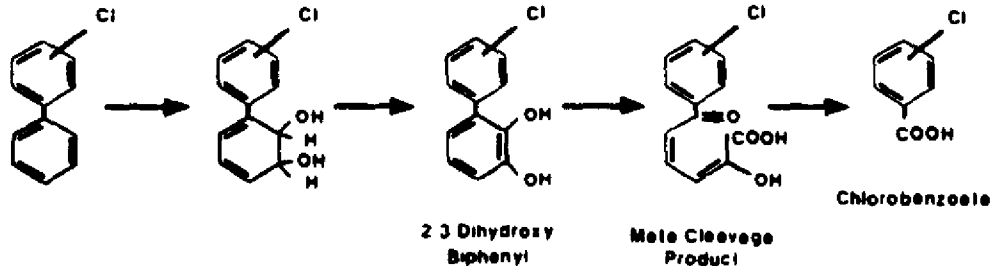

Figure 2. Proposed pathway for degradation of PCBs by a 2,3 dioxygenase (2, 17)

or between carbon atoms 3 and 4 (24,25). In theory, a dioxygenase could also attack at positions 1,2 or 3,4 (Figure 3A). As depicted in Figure 3, the position of the chlorine atoms in 2,5,2',5' tetrachlorobiphenyl would most likely hinder the approach of either a 2,3 or 1,2 dioxygenase, but each of these enzymes could readily attack 2,4,4' trichlorobiphenyl. The converse is true for a 3,4 dioxygenase. Substitution in both para positions would clearly impair the approach of a 3,4 dioxygenase, but 2,5,2',5' tetrachlorobiphenyl would be readily accessible to this enzyme. The differences in degradative competence of these two organisms demonstrated in the 1248 assay support this model. Generally MB1 shows more extensive degradation of peaks which include congeners substituted in the 2,4,4' configuration (Table 1, Peaks 18,22,31) whereas many of the peaks which are degraded more readily by H850 include congeners substituted in

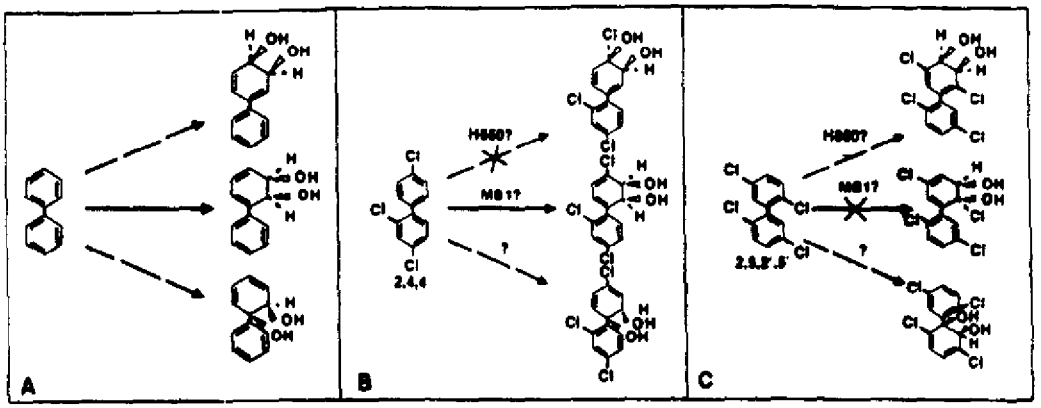

Figure 3. Allowed positions of attack of initial dioxygenase. Panel A shows the dihydrodiol biphenyl intermediates that would result from enzymatic attack of a dioxygenase at carbon positions 3,4 (top), 2,3 (middle) or 1,2 (bottom). Panels B and C show the corresponding intermediates for 2,4,4' trichlorobiphenyl and 2,5,2',5' tetrachlorobipenyl. Dotted lines indicate pathways that are theoretically possible but which have not been demonstrated.

the 2,5,2' configuration (Table 1, peaks 10,11,23,24,25, and 27). Based on these observations, we propose that the initial degradative enzyme in Alcaligenes eutrophus is a 3,4 dioxygenase or possibly a 1,2 dioxygenase.

Degradation Products of Selected PCB Congeners

We have recently begun to study the metabolites of selected PCB congeners with the ultimate goal of elucidating the PCB degradative pathway in each of these bacteria. Our preliminary findings are consistant with the model we have proposed. Two PCB congeners which are substituted in both para positions, 4,4' dichlorobiphenyl and 2,4,4' trichlorobiphenyl, were extensively metabolized by MB1 yielding a low molecular weight metabolite with the same G.C. retention time as 4-chlorobenzoic acid in the first case, and large amounts of four different high molecular weight intermediates in the latter. In contrast, we could find no evidence that H850 metabolized 4,4' dichlorobiphenyl and we detected only small amounts of metabolites from the trichlorobiphenyl. Conversely, H850 produced extensive metabolites from PCB congeners substituted at positions 2,5,2' or 2,3,2',5' while MB1 produced only small amounts of degradation products from these congeners. Furthermore, although some of the metabolites generated were common to both organisms, in many cases the major metabolites produced by H850

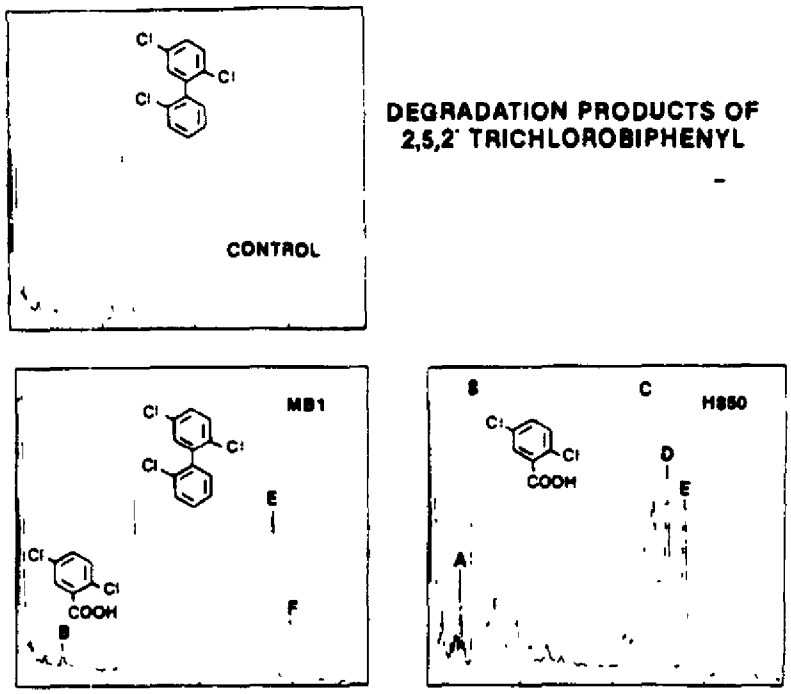

Figure 4. Degradation products of 2,5,2' trichlorobiphenyl. Resting cells were incubated with 2,5,2' trichlorobiphenyl (50 ppm) for 21 h; metabolites and PCBs were extracted and analyzed by gas chromatography as described. The upper panel shows the extraction of heat-inactivated cells which were incubated under the same conditions as MB1 and H850. The only peak seen is the PCB. The lower panels show the PCB and metabolites extracted from MB1 (left) and H850 (right). In MB1 the amount of PCB has decreased and three metabolites B,E, and F have appeared. Metabolite B is most likely 2,5 dichlorobenzoate. In H850 the PCB has been completely metabolized, apparently to 2,5 dichlorobenzoate. At least five metabolites identified as A-E, have been produced. Metabolites B and E have the same retention time for both bacterial strains.

were unique. An example of this is shown for 2,5,2' trichlorobiphenyl in Figure 4. Two of the metabolites, B (which has the same retention time as 2,5-dichlorobenzoate) and E, were produced by both MB1 and H850. However, MB1 produced a small amount of metabolite F which was not seen in H850, and H850 produced large amounts of the metabolites labelled C and D and a low molecular weight metabolite identified as Peak A. Moreover, the 2,5,2' congener was com-

pletely metabolized by H850, apparently to 2,5 dichlorobenzoate. Thus the data support the hypothesis that the major route of PCB metabolism differs in MB1 and H850 and are consistent with an initial attack by a 2,3 dioxygenase in Corynebacterium sp. MB1 and a 3,4 dioxygenase in Alcaligenes eutrophus H850. We are in the process of identifying these metabolites by gas chromatography combined with mass spectrometry in an effort to elucidate the major PCB degradative pathways operative in H850 and MB1.

Plasmid Analysis

We have also begun to investigate the genetics of PCB biodegradation in MB1 and H850. Most genetic information in bacteria resides on the chromosome, but frequently a significant amount of genetic information is associated with an extrachromosomal piece of DNA called a plasmid. In fact, plasmids are the primary means of genetic exchange in bacteria. Typically, plasmids harbor genes which carry nonessential but useful information such as antibiotic or metal resistance. More importantly, the degradation of various aromatic hydrocarbons (toluene, salicylate, naphthalene) (27,28) and even chlorinated aromatics (chlorophenols, chlorobenzoates, chlorinated phenoxyherbicides) (29,30,31) is often associated with plasmids. Finally, evidence is accumulating that the genes responsible for PCB degradation may reside on plasmids (31).

Therefore, we were anxious to learn if MB1 and H850 harbored plasmids. As shown in Figure 5, there is a single large plasmid in each organism. We immediately asked whether these plasmids were identical. By using specific enzymes called restriction endonucleases to cut plasmid DNA at specific points, one can generate a specific fragmentation pattern which is unique to that plasmid. If two plasmids are identical, their restriction patterns will be identical. Restriction enzymes were used to analyse the plasmids from both H850 and MB1 (M. Brennan, data not shown, and J.R. Yates, personal communication). The results clearly show that the plasmids are not identical in the two organisms. However, it is also possible that the two plasmids are not completely different, but have some common genetic information. Our preliminary findings using hybridization analysis indicate that the plasmids in these two bacteria do not share any common genes (M. Brennan, data not shown).

We do not as yet have any firm evidence that the PCB degradative pathway is associated with a plasmid in either MB1 or H850. We do know, however, that for H850 the ability to grow on biphenyl (and presumably also the ability to degrade PCBs) is readily lost if the culture is not maintained on selective medium with

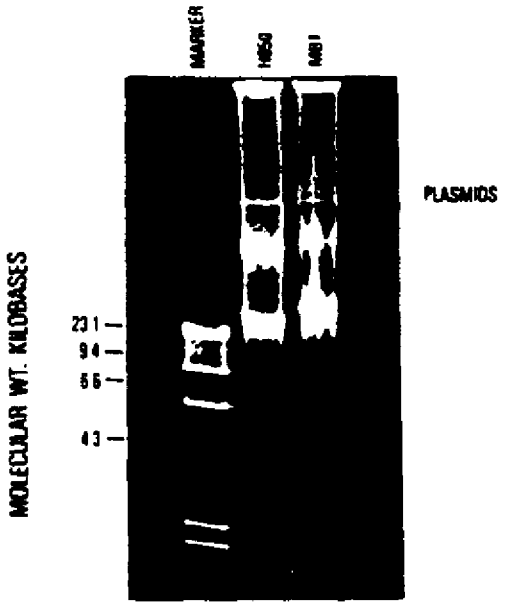

Figure 5. Large plasmids in H850 and MB1. Plasmid DNA was isolated as described and analyzed by agarose gel electrophoresis. The direction of electrophoresis is from top to bottom. The first lane shows Hind III fragments of phage lambda DNA used as molecular weight markers. The position of the plasmid DNA is indicated. The diffuse band of DNA which migrates slightly behind the largest lambda DNA fragment is chromosomal DNA. The large band of DNA which migrates between the chromosomal and plasmid DNA most likely contains plasmid DNA in a different physical form.

biphenyl as the sole carbon source. This type of genetic instability is most frequently associated with plasmid encoded functions.

In the future we plan to transfer the plasmid from Alcaligenes eutrophus H850 to other Alcaligenes eutrophus strains as well as to other bacterial species which are not capable of growth on biphenyl or degradation of PCBs. If the recipients acquire the ability to degrade PCBs as a result of the plasmid transfer, we will have established that PCB degradation is controlled by a plasmid in Alcaligenes eutrophus H850.

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Finally, we are currently using recombinant DNA techniques to clone fragments of H850 DNA as a first step toward identifying and characterizing the gene(s) specifying the enzymes of the PCB degradative pathway in this strain. This will allow us to develop an understanding of both the structure and regulation of these enzymes.

SUMMARY

We have isolated and characterized two distinct organisms, Alcaligenes eutrophus H850 and Corynebacterium sp. MB1, which extensively degrade Aroclor 1248, but which exhibit clear differences in the particular congeners which are degraded. In general, PCB congeners with the 2,4,4' substitution pattern are metabolized rapidly by MB1, but poorly by H850. In contrast, many congeners substituted at positions 2,5,2' are rapidly degraded by H850, but not by MB1. The production of metabolites unequivocally establishes that this is indeed degradation. Some degradation products, including chlorobenzoates, are common to both organisms, but in many cases the major metabolites produced by H850 are unique. These data are most readily explained by postulating that the major pathway of PCB metabolism in H850 utilizes a dioxygenase which preferentially attacks at carbon positions 3,4. If this is the case, it will be the first demonstration of involvement of a 3,4 dioxygenase in the biodegradation of biphenyl or PCBs. In contrast, MB1 probably employs a more common 2,3 dioxygenase mechanism. Finally, the two organisms harbor distinct plasmids which may be involved in PCB degradation. We are now in an excellent position to begin realizing our long-term goals, namely, understanding the biochemistry and genetics of bacterial PCB degradation.

ACKNOWLEDGMENTS

We thank J. C. Cornahan, R.H. Wagner, J. Smith, and R. Rohling for gas chromatographic analysis, T.J. Toffimire and R.E. Brooks for help in collecting PCB contaminated environmental samples, K. Furukawa and A.M. Chakrabarty for a stock of Acinetobacter sp. P6, H.L. Finkbeiner, and T.M. Su for helpful discussions, and B. Moreen for typing this manuscript.

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Discussion

Q1. Isn't this process limited to a specific Aroclors?

A. Yes, the study so far has been limited to site-contaminated with 1242. Would need to isolate microbacteria from other sites to study other Aroclors.

MONS 214904

COMPOSTING FOR DEGRADATION OF PCBs IN SOIL

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ABSTRACT

This study evaluated aerobic and anaerobic composting of PCB contaminated soil on a laboratory scale. Composts were composed of alfalfa hay, horsefeed and Lakeland soil spiked to contain 2000 mg/Kg of Aroclor 1242 (dry weight basis). Warm humidified air was drawn through aerobic compost materials. Anaerobic composts were flushed with nitrogen. All composts were incubated at 55°C.

After two and four weeks of incubation, compost materials were oven dried, ground, subsampled and Soxhlet extracted for GC analysis. The aerobic composts showed the greatest destruction of PCBs with 41.6 and 48.1% destruction in two weeks and 55.7 to 67.6% destruction in four weeks. PCB destruction in anaerobic composts was 18.4 to 28.0% after two weeks and 27.9 to 46.9% after four weeks of composting. Individual peek areas from the GC chromatograms of control and test compost extracts were compared to determine the decrease of different PCB isomers. A significant decrease in the trichlorobiphenyls and one of the tetrachlorobiphenyls was observed in extracts from the two week aerobic composts. After four weeks of aerobic composting, significant decreeses in all of the chlorinated biphenyls were observed. Anaerobic composting showed significant reduction of all chlorinated biphenyls after four weeks of composting. The mechanism of degradation appears to be rapid dechlorination of biphenyls containing three chlorines or less since no build-up of the mono- or dichlorinated compounds was observed. Dechlorination of the penta- and tetra-chlorinated molecules is slower but does occur at a useful rate. No chlorinated dibenzo-p-dioxins or dibenzofurans were found in the chromatograms or in the GC-mass spectra run on the composted sample extracts.

COMPOSTING FOR DEGRADATION OF PCBs IN SOIL

INTRODUCTION

Polychlorinated biphenyls (PCBs) are complex mixtures of various chlorinated biphenyls which were widely used because of their physical, chemical and biological stability as well as their high dielectric constant. PCBs have entered the environment through spills and losses during manufacture, vaporization or leaching from PCB-containing formulations, leaks from sealed or partially sealed systems and disposal of waste PCB (1). PCBs have been found in ocean sediments, the atmosphere and in many terrestrial and aquatic locations including both polar ice caps (2). Because of their physical and chemical stability, these compounds are persistent environmental pollutants.

Weathering and microbial processes degrade PCBs only to a limited extent in the environment (3). Evidence indicates that PCBs may be biotransformed as well as metabolized by some microorganisms (4,5,6). Several investigators have reported biotransformation of the lesser chlorinated biphenyls (mono- and dichlorobiphenyls) to chlorobenzoic acid (7,4,8,9,10). Tucker et al. (6) showed that mono- and dichlorobiphenyls were readily biodegraded by activated sludge but as concentrations of the higher chlorinated biphenyls increased, degradation rates decreased. Kong and Sayler (9) simulated natural river conditions to demonstrate the degradation and mineralization of monohalogenated biphenyls by mixed microbial cultures from PCB contaminated river sediments. Furukawa and Chakrabarty (11) demonstrated total degradation of mono- and dichlorinated biphenyls using Acinetobacter or Arthrobacter sp. containing a plasmid specifying conversion of chlorobiphenyls to chlorobenzoic acids and a genetically constructed psaudomonad capable of metabolizing mono- or dichlorobenzoates.

This paper describes a study in which composting was evaluated for decontamination of soil containing PCBs. This study is part of a series of experiments to determine the applicability of composting techniques for the destruction of persistent hazardous materials contained in a soil or sediment matrix.

EXPERIMENTAL MATERIALS AND METHODS

This study evaluated composting of PCB contaminated soil on a laboratory scale. Both aerobic and anaerobic composting were studied to compare PCB biodegradation in the two systems. The experiments were carried out with soil that was intentionally spiked with PCBs (Aroclor 1242).

The experimental apparatus used in the laboratory studies is shown in Figure 1. Mason jars were used to contain the compost materials. A ring of plastic tubing with holes drilled at 1/4 inch intervals was located beneath the compost in each jar. The ring was connected to a glass tube which extended through the stopper in the top of the Mason jar. For the aerobic composts, the tube was attached to two traps in series, one containing sodium hydroxide and the other water. A second tube inserted through the stopper was attached to a series of traps containing sodium hydroxide, sulfuric acid and activated carbon as shown in Figure 1. These traps were connected to a vacuum pump. Warmed air was first drawn through a sodium hydroxide trap to remove any CO_2 and then through a water trap to humidify the air and remove any caustic material. The scrubbed air was then drawn through the compost materials. The atmosphere above the compost was continually drawn out through sulfuric acid, sodium hydroxide and activated carbon traps to remove any gaseous biodegradation products. The dead traps prevent contamination of the composts or individual gas traps in case of vacuum failure. For the anaerobic composts, the initial NaOH scrubbing trap was eliminated. The anaerobic composts were initially flushed with nitrogen to remove oxygen from the system and were flushed every 3-4 days thereafter to change the atmosphere in the composting vessels.

Each compost was made up of 23.7 g of alfalfa hay, 24.7 g Purina Sweetena Horsefeed and 5 g of Lakeland soil (a total of 50 g dry weight). The soil was spiked to yield 2000 mg/Kg of Aroclor 1242 in the total compost (dry weight basis). The compost materials were thoroughly mixed and the composting process initiated by addition of sufficient water (containing primary effluent and horse manure) to give the composts a 60% moisture content. The composting apparatus was then placed in a 55°C incubator and attached to the vacuum system. The experimental matrix for the composts is presented in Table 1. The temperature of each compost was monitored daily by means of a thermocouple placed within the compost materials.

The composts were sacrificed as specified in Table 1. At the time of sacrifice, each compost was examined for its appearance and smell. A sample (approximately 1 gram) was taken from the center of each compost and dispersed in distilled water (1:9 solids to water ratio) to determine the pH of the compost. The remainder of the compost material was dried in an oven at 60°C for 24 hours. The dried compost materials were ground with a hammer pulverizer to 18 mesh (1 mm) and the ground powder thoroughly mixed. Two subsamples from each compost (approximately 3 to 4 grams) were taken, weighed and Soxhlet extracted with a mixture of 40% benzene, 40% acetone, 10% hexanes and 10% methanol. Extraction efficiency of Aroclor 1242 from uncomposted material (positive controls) was 77%. Extraction efficiency from composted materials ranged

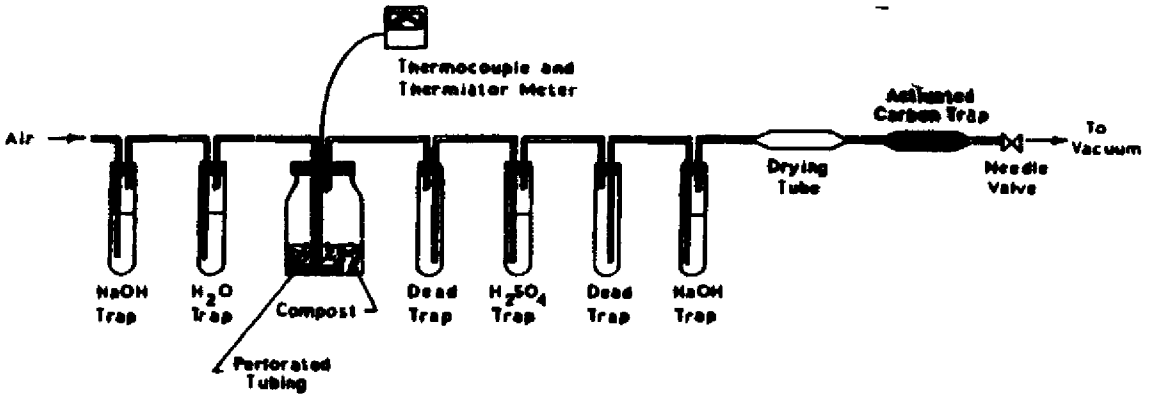

Figure 1. Laboratory Compost Aeration Apparatus

Table 1

EXPERIMENTAL MATRIX FOR COMPOSTS

Type of Compost	Number	Time Sacrificed
SPIKED LAKELAND SAND		
A. Positive Controls	2	0 week
B. Negative Aerobic Controls (no Aroclor 1242)	2 2	2 weeks 4 weeks
C. Experimental Aerobic Composts	2 2	2 weeks 4 weeks
D. Negative Anaerobic Controls (no Aroclor 1242)	2 2	2 weeks 4 weeks
E. Experimental Anaerobic Composts	2 2	2 weeks 4 weeks

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from 83 - 89%. The extract was analyzed on a Varian 3700 gas chromatograph with autosampler and electron capture detector. A Hewlett-Packard 5880 controller/integrator was used to control the Varian gas chromatograph. The GC parameters were: injection port - 280°C; oven - 170 to 230°C @ 15°C/min; detector - 300°C. Separation of the PCBs was accomplished with a 2 mm I.D. by 10 ft. glass column packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 mesh Supelcoport using nitrogen carrier gas at a flow rate of 24 mL/min.

RESULTS

Results of the laboratory-scale PCB composting studies are summarized in Tables 2 and 3. The aerobic composts showed the greatest reduction in PCB concentration with a 41.6 to 48.1% decrease in 2 weeks and 55.7 to 67.6% decrease in 4 weeks. PCB concentrations were not reduced as rapidly in anaerobic composts. A decrease of only 18.4 to 28.0% in the PCB concentrations of the anaerobic composts was observed after 2 weeks of anaerobic composting and 27.9 to 46.9% after 4 weeks.

Aroclor 1242 is a mixture of chlorinated biphenyls composed of approximately 1% monochlorobiphenyl, 16% dichlorobiphenyl, 49% trichlorobiphenyl, 25% tetrachlorobiphenyl, 8% pentachlorobiphenyl and 1% hexachlorobiphenyl (12). The normal method for GC quantitation compares the total integrated area from all of the peaks in the sample to that of standards of similar chlorination. The methodology yields a comparison of PCB concentrations in the experimental samples with the positive controls but gives no information on the effects of treatment on the individual chlorinated biphenyl isomers. To evaluate the effects of composting on the individual isomers, areas of selected chromatogram peaks of the experimental samples were normalized and compared to corresponding chromatogram peaks of the positive controls. These comparisons for the 2 and 4-week aerobic and 4-week anaerobic composts versus the positive control (100%) are shown graphically in Figure 2. Typical chromatograms are presented in Figures 3 and 4. After two weeks of aerobic composting, a significant decrease in the trichlorobiphenyls and one of the tetrachlorobiphenyls was observed. No decrease in the higher chlorinated biphenyls was observed. However, after 4 weeks of aerobic composting, significant decreases in all of the chlorinated biphenyls occurred with less than 25% of the trichlorinated biphenyls remaining. Anaerobic composting at four weeks also showed significant decreases in all of the chlorinated biphenyls.

Table 2

AEROBIC COMPOSTING OF PCB CONTAMINATED SOIL

Sample	Time[1]	pH	PCB Concentration[2] µg/g	% PCB Decrease[3]	Comments
Positive Control	0	N.D.	1591		
Positive Control	0	N.D.	1517		—
Negative Control	2 weeks	5.0	17		Wet hay smell. Not well composted.
Negative Control	2 weeks	6.2	31		Moderately damp, brown, composted.
Experimental A	2 weeks	5.6	908	41.6	Wet hay, moderately damp, yellow.
Experimental B	2 weeks	6.0	807	48.1	Moderately damp, brown, composted.
Negative Control	4 weeks	5.0	17		Not very damp, not well composted.
Negative Control	4 weeks	5.4	35		Old shoe smell, fungal growth.
Experimental C	4 weeks	5.0	504	67.6	Less than 60% moisture. Wet hay smell
Experimental D	4 weeks	5.0	688	55.7	Sweet smell, <60% moisture, yellow.

[1]Time of sacrifice with respect to compost set-up.

[2]PCB concentration at time of sacrifice

[3]Decrease in PCB concentration based on the average control value of 1554 µg/g

N.D. = not determined.

Table 3

ANAEROBIC COMPOSTING OF PCB CONTAMINATED SOIL

Sample	Time[1] (weeks)	pH	PCB Concentration[2] µg/g	% PCB Decrease[3]	Comments
Positive Control	0	N.D.	1591		
Positive Control	0	N.D.	1517		
Negative Control	2	5.2	6		Mildew smell, light yellow.
Negative Control	2	4.8	8		Mildew smell, composted.
Experimental A	2	5.0	1268	18.4	Mildew smell, yellow.
Experimental B	2	4.7	1119	28.0	Musty smell, moderately composted
Negative Control	4	6.0	10		Wet hay smell, moderately composted.
Negative Control	4	7.0	12		Wet hay smell, moderately composted.
Experimental C	4	5.5	825	46.9	Sweet smell, fungal growth, brown.
Experimental D	4	6.5	1120	27.9	Sweet smell, dark color.

[1]Time of sacrifice with respect to compost set-up.

[2]PCB concentration at time of sacrifice.

[3]Decrease in PCB concentration based on the average control value of 1554 µg/g.

[4]N.D. = not determined.

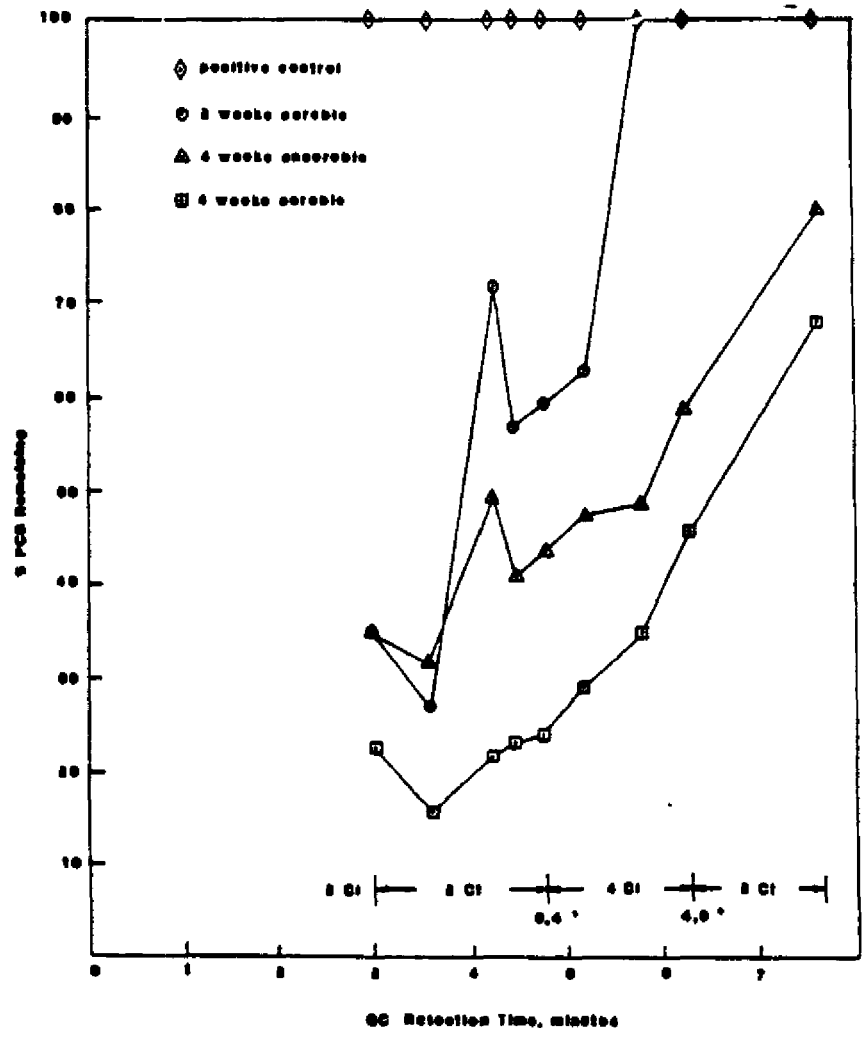

Figure 2. Comparison of Normalized Peak Areas with Positive Controls

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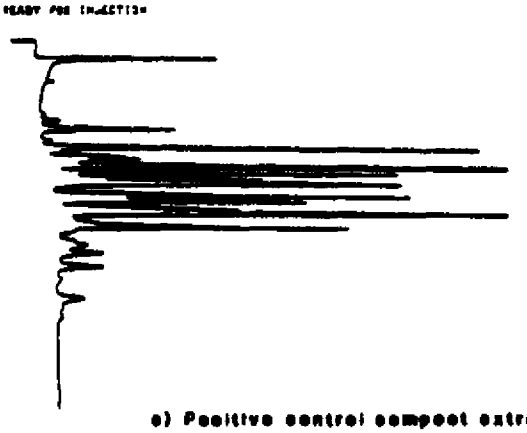

a) Positive control compost extract

b) 4-week aerobic compost extract

Figure 3. Chromatograms of Aerobic PCB Compost Extracts (1/20 dilution)

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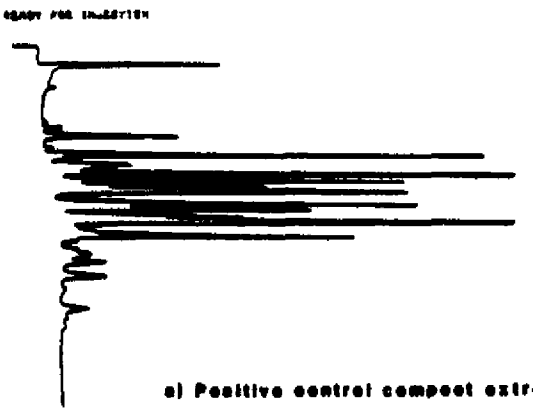
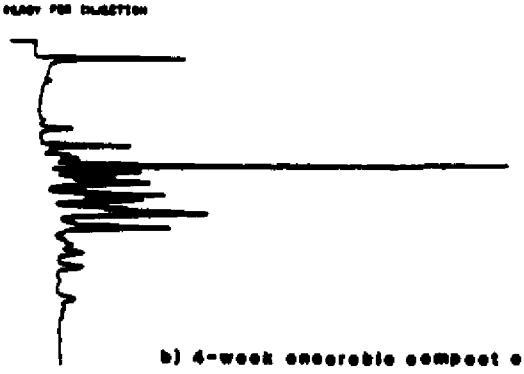


a) Positive control compost extract



b) 4-week anaerobic compost extract

Figure 4. Chromatograms of Anaerobic PCB Compost Extracts (1/20 dilution)

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DISCUSSION

The mechanism of PCB degradation in compost appears to be rapid dechlorination of biphenyls containing three chlorines or less since no build-up of the mono- or dichlorinated compounds was observed. Dechlorination of the tetra- and penta-chlorinated molecules is slower but does occur at a useful rate. No chlorinated dibenzo-p-dioxins or dibenzofurans were found in the chromatograms or in GC-mass spectra of the composted sample extracts.

These preliminary laboratory-scale composting studies indicate that composting may have potential as a method for on-site decontamination of soils or sediments contaminated with PCBs. Aroclor 1242 concentrations of 2000 mg/Kg in the compost materials (soil contaminated at 20,000 mg/Kg) were tolerated by the microbial populations present in the composts and significant decreases in PCB concentrations were observed.

Composting for decontamination of soil or sediment is relatively simple, requiring only that the soil or sediment is thoroughly mixed with the compost materials. Composting can be carried out in various ways. The most popular methods currently in use are the windrow and forced aeration systems. In the windrow method, a pile or windrow of waste material is periodically turned by a machine to mix and aerate the organic matter. Anaerobic and aerobic decomposition occur in this system with aerobic decomposition resuming each time the material is turned. Generally composting temperatures are lower in this system than in other systems and non-uniform biodegradation of organic materials may result. A second method, enclosed systems, requires a complex mechanical system which gives more rapid composting than the windrow system. These bioreactors are designed to provide operational control over environmental conditions such as air flow, temperature and mixing and to isolate the composting material from the surrounding environment. A third method, the Beltsville Aerated Pile Method was developed at the Beltsville Agricultural Research Center for composting of undigested sludges. In this forced aeration system, compost materials are mixed and bulking materials are added as needed. The compost pile is placed on a base of woodchips covering perforated plastic pipe. Air is drawn through the pile via the perforated pipe in the base of the pile. The major advantages of this system are the production of a stable humus-like organic material, low capital investment and low energy requirements.

Composting for degradation of PCBs in soil or sediment should be further evaluated to answer the following questions:

- What is the maximum PCB concentration tolerated by the compost organisms?
- What is the effect of the PCB chlorine content on composting?
- What is the mechanism of PCB degradation in compost and what are the byproducts?
- What effects will different soils have on PCB degradation in composts?
- What type of compost system is best suited for degradation of PCBs in soil?
- What are the rates of PCB degradation for the different chlorinated biphenyls?
- What is the optimal composting time to achieve maximal PCB degradation?
- Can the microbial populations responsible for PCB degradation in composts be improved?

Degradation rates as determined by laboratory-scale studies will provide a conservative estimate of rates in large-scale systems. Degradation rates observed in larger systems may be twice as rapid as those observed in the laboratory scale studies. The major advantages of composting include on-site decontamiantion, production of a potentially useful organic material as a plant nutrient or soil conditioner, low capital investment and low energy requirements.

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Discussion

Q1. Have you looked at pH - buffering?

A. Not in this study.

Q2. Did you look at a carbon trap to see if temperature was actually driving the PCB out?

A. No - we did not analyze traps.

BACTERIAL DEGRADATION OF POLYCHLORINATED BIPHENYLS IN SLUDGE FROM AN INDUSTRIAL SEWER LAGOON

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ABSTRACT

A laboratory experiment was conducted to determine if polychlorinated biphenyls (PCB's) found in an industrial sewer sludge can be effectively degraded by mutant bacteria. The aerated sludge was inoculated daily with mutant bacteria in order to augment the existing bacteria with bacteria that were considered to be capable of degrading PCB's. The pH, nitrogen, and phosphorus levels were monitored daily to maintain an optimum growing medium for the bacteria. A gas chromatographic method was used to determine the PCB concentrations of the sludge initially and also throughout the experiment. Results and discussion of the bacterial treatment of polychlorinated biphenyls are presented in this paper.

SUMMARY

A 90-day laboratory sized experiment was conducted to determine the viability of using mutant bacteria to decontaminate an industrial type sludge that was contaminated with polychlorinated biphenyls (PCB's). The contaminated sludge samples were obtained from an industrial waste sewer lagoon system which is an integral part of a water pollution control facility. Four representative samples of sludge were selected for treatment with mutant bacteria. The samples originally contained the PCB Aroclor 1260 in concentrations ranging from 135 to 232 parts per million (ppm). In addition to the four samples, a fifth sludge containing only three ppm of Aroclor 1260 was spiked with nearly 1000 ppm of Aroclor 1260. This spiked sample was used to determine whether high concentrations of PCB's in sludge would be affectd by the bacteria.

The five samples were inoculated daily with mutant Pseudomonas aeruginosa bacteria that had a potential for degrading PCB's. The nitrogen, phosphorus, and pH levels were monitored daily to maintain a growing medium for the bacteria. At the completion of the 90-day augmentation period, the concentrations of the PCB's in the sludge samples were found to be higher than the original concentrations. The cause of the apparent increase in concentrations has not been fully understood. One possibility is the biodegradation of the sludge in which the sludge is metabolized and broken down into lighter molecules. The lighter sludge increases the concentration of PCB on a weight-to-weight basis.

The apparent lower PCB concentration found around 20 days after inoculation suggests that the PCB was absorbed by the bacteria, thereby causing the apparent decrease in the PCB concentration of the sludge. After 20 days, the bacteria began to die, perhaps caused by the build up of toxic metabolic wastes, and subsequently released PCB back into the sludge without having metabolized the PCB molecules. Thus, the experiment can be summarized as that the PCB in the sludge was absorbed by the mutant Pseudomonas aeruginosa bacteria for 20 days. After 20 days, the bacteria began to release the absorbed PCB's back into the sludge which by now has been degraded into lighter molecules. Thus, the PCB concentration appeared to decrease at around 20 days, then increase after 20 days. Under the constraints of this experiment, the PCB was absorbed by the bacteria, but was not degraded.

Section 1

INTRODUCTION

Polychlorinated biphenyls (PCB's) are chlorinated aromatic organic compounds that are commonly used as dielectric fluids in capacitors and transformers. Their physical and chemical properties are such that they are chemically and thermally stable, fire resistant, essentially non-conductive, and have a low solubility in water.

Because of their chemical and physical stability, they are virtually indestructible when spilled into the environment, whether accidently or discarded for disposal purposes. High temperature combustion processes and special chemical treatment methods are evolving which are used to destroy the PCB's or to degrade the components into non-toxic materials. The U.S. Environmental Protection Agency has established a level of 50 parts-per-million above which materials must be disposed of in a Federally approved landfill or incinerator. Other treatment and cleanup methods are under investigation, and one of the most appealing concepts is biological treatment in which bacteria is used to degrade PCB's in situ.

Early studies in the use of bacteria for the degradation of specific chemicals reported in 1970, have shown that biphenyl can be degraded by gram-negative bacteria isolated from soil (Ref. 1). In that study, biphenyl was converted to phenylpyruvate in a salt medium. Other studies of biphenyl degradation involved bacteria such as Pseudomonas putida, Beijerinckia species, and a strain of Mucor. For the metabolism of pure chlorinated biphenyl (not PCB), Rhizopus japonicus was used to convert 4-chlorobiphenyl to 4-chloro-4-hydroxybiphenyl. Two species of Achromobacter, isolated from sewage effluent, degraded biphenyl to benzoic acid, and 4-chlorobiphenyl to 4-chlorobenzoic acid. However, no natural bacteria was found to successfully degrade polychlorinated biphenyls, which are mixtures of many chlorinated biphenyls.

If bacteria that can degrade PCB's are found, they most likely will be developed through genetic engineering. The use of such mutant bacteria would be particularly effective in the treatment of soils, sludges, and waste water for the decontamination of PCB's in those environments. Contaminated waste water lagoons would not

require the subsequent draining and physical removal of PCB contaminated soil and sludge. The lagoon could be conveniently treated by adding a mutant bacteria in situ and effect a clean up process at a relatively low cost and with little effort.

To determine the feasibility and effectiveness of bacterial augmentation, a laboratory experiment was conducted using PCB contaminated sludge samples from an industrial sewer lagoon. By using the actual sludge samples from the lagoon, this experiment was to provide insight as to whether the lagoon can be decontaminated by mutant bacteria. This paper describes the experiment and discusses the results of using mutant Psuedomonas aeruginosa bacteria with PCB contaminated sludge samples.

Section 2

EXPERIMENT

The industrial sewer lagoon used for this study is part of a six-lagoon water pollution control facility which receives decante waters generated from waste tanks that process rinse waters and liquid wastes generated by metal plating and tube cleaning facilities. This lagoon serves as an equalization pond holding about 3.5 million gallons of waste water. An earlier investigation indicated widespread, low-level PCB contamination in the lagoon. Few sites were found to be contaminated with PCB's in excess of 50 parts-per-million (ppm) of Aroclor 1260. The EPA regulated concentration is 50 ppm.

In order to fully determine the magnitude and extent of PCB contamination in the lagoon, an extensive sampling program was conducted. Sampling equipment was loaded in a boat and towed to the selected sampling points. Core samples of sludge and the sediment were collected. Average depth of the sediment was about six inches with the base material of clay. These samples were analyzed for PCB concentrations which ranged up to the highest concentration of 467 ppm. A definite water flow pattern was observed in which the inlet of the lagoon contained the highest concentrations and toward the discharge outlet the concentrations gradually declined.

After contamination levels were determined, many alternatives and possibilities were considered for decontamination of the sewer lagoon. The alternatives ranged from closing the lagoon; permanently fixing the sediment into concrete-like material; biological and physiochemical methods; to physically dredging the sediment for disposal, treatment, or incineration. Many other possibilities were also considered, but one of the most attractive alternatives was the in-place degradation of PCB by microorganisms. If this microbiological method proved valid, draining of the lagoon water and physically removing the sludge would not be required. Using the sludge samples that had been analyzed for PCB, a small laboratory experiment was carried out to determine whether biological degradation of PCB's would be feasible for the industrial waste lagoon. Glass dessicators with approximately 2-liter capacities were used as experimental tanks. Five such sludge tanks were charged with the first tank containing about 450 grams of sludge with

205 ppm concentration of PCB. Water was added to bring the aqueous level up to one liter. The second tank contained 50 grams of sludge with 222 ppm PCB diluted to one liter. The third tank was two liter tank containing 100 grams of sludge in which 980 ppm of Aroclor 1260 was added to the sludge originally containing 3 ppm. This tank was started to determine whether high concentration of PCB in the sludge would be affected by the bacteria, and to roughly determine the degradation rate to see how long the treatment would be needed to bring the concentration below the 50 ppm level. The fourth tank contained 50 grams of sludge with 135 ppm, and the fifth tank had 50 grams of sludge with 232 ppm diluted to one liter.

These experimental sludge tanks were inocculated with the mutant Pseudomonas aeruginosa bacteria obtained through a biochemical firm that has considerable experience and expertise in genetic engineering. The bacteria culture which was contained in a bran base was prepared for augmentation by soaking the culture in water for six to nine hours with a pinch of sodium bicarbonate. The initial dosage rate was 0.1 grams of the culture per one liter, then the dosage rate was gradually decreased over 20 days to a maintenance level of 20 milligrams per liter. Along with daily supplementation of bacteria, a nutritional balance for biological activity was maintained each day. The dissolved oxygen was kept at about 7 ppm level by aeration of the tank and agitation of the slurry. The pH level was maintained at 7.5, and nitrogen as ammonia determined by the Nesslerization method was over 5 ppm level. The phosphorus as ortho-phosphate was determined by the molybdate method and maintained at 1 ppm. The temperature of the tanks was kept at about 75° F.

Section 3

RESULTS AND DISCUSSION

In monitoring the sludge tanks daily, the general trend has been the drop in the pH and nitrogen, while phosphorus concentration remained above 1 ppm level. No particular pattern was observed other than a need for almost daily addition of sodium bicarbonate to bring the pH up and an ammonium compound to supplement the nitrogen level. To compensate for nitrogen loss, ammonium hydroxide was used if the pH dropped to about 6.8, and ammonium nitrate was used if the pH was near 7.5 level.

During the augmentation period, biological activity in the tanks was monitored biweekly. An ordinary microscope at 100 magnification and a phase contrast microscope at 400 magnification were used to insure the presence of active organisms in the tanks. As activated sludge is formed and ages, there is a successive predominance of protozoans and rotifers which correlates with the bacterial population (2). In general, as the bacteria population increases, flagellates become predominant. When the bacteria population is at the maximum, free swimming ciliates are the predominant organisms. As the bacteria population declines, rotifers become predominant. In the sludge tanks, the protozoans and rotifers were observed with the flagellates and free swimming ciliates as the predominant organisms. At about the middle of the augmentation period, the number of the higher organisms appeared to have sharply declined. Toward the end of the augmentation period, the higher organisms were almost absent.

In the last 12 days of augmentation, a large amount of bacteria was added to each tank along with supplemental food to provide an additional carbon source. The population of microorganisms correlates with the sludge conditions, in that the sludge starts to age and breaks down when the population of microorganisms is at the maximum. The sludge becomes digested and the food source for the bacteria becomes diminished. With further digestion of sludge, the organisms eventually utilize the internal material through endogeneous process, resulting in the diminished population. Near 12 days toward the end of the augmentation period, the sludge appeared emulsion-like and the higher organisms were almost absent.

This indicated that the microorganism population had severely declined due to lack of an external food source. Although a large amount of bacteria was added along with supplemental food, no improvement was observed.

The results of bacterial augmentation over a 90-day period are presented in the Table. These results were obtained by analyzing the sludge samples by a gas chromatographic method. A sample of sludge was weighed, then PCB was extracted with 1:1 acetone and hexane mixture using an ultrasonic bath. Extracted PCB was analyzed by a gas chromatograph equipped with an electron capture detector. This analytical instrument was fitted with a two-metar glass column packed with 3% OV-1 on 80-100 mesh Chromosorb W-HP and maintained at 200° C. The carrier gas was ultrapure nitrogen at a flow rate of 25 milliliters per minute. The injection port was kept at 250° C. and the detector was maintained at 300° C. The output of the gas chromatograph was recorded on a 1 mv strip chart recorder. The PCB chromatogram of the sample was quantitated from the standard chromatograms.

As shown in the Table, PCB in the industrial sewer sludge appears not to have been degraded by the bacteria over 90 days period. In these sludge tanks, the final concentrations of PCB at the end of 90 days are higher than the starting concentrations, although in Tank 2 the concentration is decreased slightly. This small decrease in Tank 2 cannot be regarded as an indication of bacterial degradation of PCB, since the fluctuation between the anlysis dates and the precision of sampling and analytical method could cause this small difference.

An interesting observation from the results is the apparent dip in the concentration around 20 days from the beginning of the experiment. After this 20-day period, the concentration rises and remains at an elevated level. Although it is possible that the sampling and the analysis may be in error, this initial dip in the PCB concentration of the sludge might indicate an effective biological activity in the first 20 days, after which the biological activity appears to have ceased. The apparent lower concentration suggests that the PCB was degraded or absorbed by the organisms present in the tanks. Since the PCB concentration increases after 20 days, the absorbed PCB may be subsequently released back into the sludge.

Perhaps, after about 20 days, the sludge tanks become saturated with materials such as the bacterial metabolites that may attack or cause the bacteria to decompose and release the absorbed PCB back into the environment. This is difficult to substantiate because limited data is available. With so many variables that can adversely affect the microorganism population, it is conceivable that the

organisms have decomposed since the microorganism population declined as the augmentation period progressed. Another supportive factor is that the experimental sludge tanks are essentially batch reactors in which no water flows in or out of the tanks on a continuous basis. All added materials and metabolic wastes are accumulated in the tanks. If PCB was metabolized or degraded by the bacteria in order to gain energy and ennance growth, the PCB peaks in the gas chromategram may show an indication. Possibly, one or more gas chromatographic peaks may be decreasing faster than the other peaks since PCB contains a mixture of chlorinated biphenyls. This hypothesis could not be fully tested because of apparent rise in all PCB peaks after the 20-day period.

The apparent rise in the PCB level cannot be explained at this point, but one possible explanation is that the organisms may be preferentially attacking the abundant carbon source of the sludge before attacking the PCB. This may have the effect of increasing the PCB concentration, on a weight-to-weight basis, in the biodegraded sludge. Therefore, when a sample of sludge is weighed out and analyzed, the concentration of PCB would appear to be higher as shown in the results.

Section 4

CONCLUDING REMARKS

In each of the five experimental sludge tanks, the bacterial augmentation over a 90-day period resulted in an apparent increase in the PCB concentration. At the end of 90 days, the final concentrations of PCB in the industrial sewer sludges were higher than the original concentrations. These results may be due to the sludge being degraded prior to PCB and due to the sludge tanks becoming toxic to the bacteria by the bacterial metabolites that cause the bacteria to decompose and release absorbed PCB back into the sludge.

It appears that around 20 days after the augmentation, microorganisms released the absorbed PCB back to the sludge without metabolizing or breaking down the molecules. In this case, if a continuous water system was used to allow a flow of water in and out of the augmentation system, the PCB concentration in the sludge would be decreased by the organisms with absorbed PCB being carried away with the water flow.

At any rate, the mutant bacteria of Pseudomonas aeruginosa used in this experiment did not degrade the PCB's found in the sludge from an industrial sewer lagoon. It is important to test each PCB contaminated material to determine the feasibility and effectiveness of bacterial augmentation prior to an actual field demonstration.

Section 5

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TABLE: RESULTS OF PCB CONCENTRATIONS
IN BACTERIA AUGMENTED SLUDGE, ppm

No. Days	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5
0	205	222	983	135	232
21	94	65	821	---	---
24	---	---	---	110	210
30	145	206	962	---	---
36	---	---	---	131	258
42	195	154	1449	---	---
50	---	---	---	165	275
57	255	162	1160	---	---
75	230	174	1443	---	---
82	253	157	1225	---	---
90	262	181	1476	---	---
91	---	---	---	163	287

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Discussion

Q1. How or why did the increase in ppm occur?

A. The emulsion sludge is a much lower density and it contains both live and dead organisms.

Q2. Why was that particular strain of Pseudomonas aeruginosa used?

A. That strain had been used in jet fuel tanks, we so decided to use the same on the sludge.

Q3. Is 90 days enough time?

A. That was the alloweble test period.

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Part 5

PCB DESTRUCTION

DESTRUCTION OF HIGH CONCENTRATION PCBs IN A UTILITY BOILER

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INTRODUCTION

As with most electric utilities and other industrial concerns, Union Electric Company produces significant quantities of waste oil and other combustible products during the course of normal business activity. The greatest majority of these wastes come from two primary sources; 1) dielectric fluids used in electrical equipment, and 2) lubricating oils used in motor vehicles and large power plant machinary. Because of previous manufecturing and servicing procedures, some mineral oil dialectric fluids will inadvertantly contain the chemical compound polychlorinated biphenyl or PCB in varying but generally low concantrations. Other dielectric fluids, known generically as askarel, intentionally contain about 60 percent PCBs for a specific purpose and use. In comparison to many other organic chemicals the sciantific information available would seem to indicate that PCBs are relatively low in toxicity. However, because of their extreme stability and bioaccumulative nature and the inexact natura of the science in this area, prudent action requires that special care be taken to see that these fluids are disposed of properly.

On May 31, 1979 the U.S. Environmental Protection Agency promulgated regulations (44 FR 31514) rigidly governing the handling of PCBs. A key feature of this regulation is the grouping of PCB waste liquids into three categories with differing disposal options for each group. The classifications and their disposal options are:

1) For those liquids containing 500 ppm PCBs or greater, disposal must take place in an incinerator which complies with the provisions of 40 CFR 761.70 ("PCB incinerator" requirements).

2) For those liquids containing between 50 and 500 ppm PCBs there are three disposal options: burning in a PCB incinerator; placement in a landfill which complies with the provisions of 40 CFR 761.75 ("chemical waste landfill" requirements), or incineration in a high efficiency boiler meeting specific requirements.

3) Finally for those liquids containing less than 50 ppm PCBs, no direct restrictions are placed on their disposal except that they cannot be used as sealants, coatings or dust control agents.

With the promulgation of this regulation Union Electric began to examine which options best met the Company's disposal needs and objectives. Continuing and substantial liabilities for these wastes even after proper disposal in accordance with regulations made landfilling undesirable. However, PCB liquid incineration costs were high. Therefore, Union Electric decided to pursue the high efficiency boiler disposal option for contaminated oil. This alternative was attractive because it allowed Union Electric to maintain control of the substance through its ultimate disposal. As well, the resource was not wasted in that the energy value of the oil was recovered through generation of electricity.

On July 7, 1980 Union Electric requested approval to dispose of 50 to 500 ppm PCB liquids in their Labadie Plant Unit #4 located near Labadie, Missouri. During November 1980 public meetings were held and in early January, 1981 a series of trial burns were conducted while the stack effluent, ash, and ambient air in the surrounding area were carefully monitored. No PCBs were detected in any of these samples.

On May 26, 1981 the Missouri Department of Natural Resources certified the boiler as a resource recovery facility and on the following day approval under the PCB rule was granted by EPA Region VII.

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With this approval Union Electric solved its PCB contaminated oil disposal problem. However, it did not solve the problem of disposing of those liquids greater than 500 ppm and especially askarel. For dielectric fluids containing greater than 500 ppm PCBs, the regulations disallow the high efficiency boiler method of disposal, and dilution to lower PCB concentrations is also deemed illegal. As previously noted, disposal of these fluids must take place in an incinerator which meets stringent standards established in the regulations. However, this requirement is not absolute. The Regional Administrator has the authority under 40 CFR 761.10(a) to approve alternative disposal methods if they can be shown equivalent to a PCB incinerator and if they will not present an unreasonable risk of injury to health or the environment. Union Electric carefully examined the design and operational features of the Labadie Unit #4 and determined that such a demonstration could be made for this facility while burning an oil/askarel blend containing 5 percent PCBs in conjunction with pulverized coal as the primary fuel source. Therefore in December, 1981 Union Electric initiated formal discussions with EPA Region VII which ultimately resulted in approval of the system presented herein.

This paper describes the engineering analysis of the design features and operational parameters which lead to the conclusion that the boiler can essentially destroy all PCBs introduced and the results of a carefully planned test burn which was conducted to confirm these conclusions.

BOILER DESCRIPTION

Labadie Unit #4 is the newest of four 600 megawatt (MW) coal fired generating units located on the south bank of the Missouri River in Franklin County near Labadie, Missouri.

The boiler (Figure 1), which is essentially identical to the other three boilers at the site, is a tangentially fired unit manufactured by Combustion Engineering Inc. and was placed in commercial operation in August of 1973. The boiler has a maximum continuous rated (MCR) heat input of 5387 million BTU per hour which corresponds to a burn rate of about 240 tons per hour of pulverized coal. The

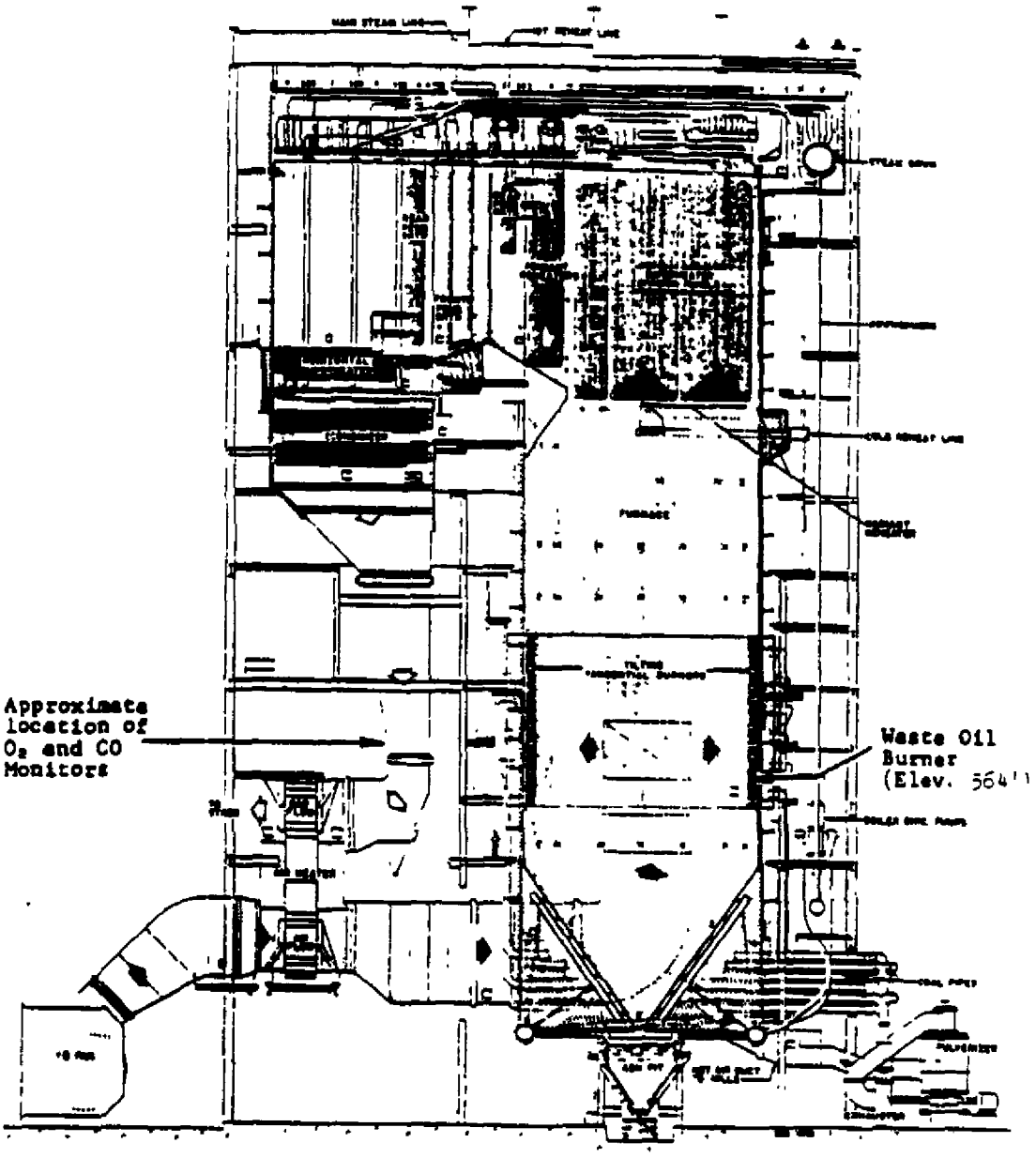

Figure 1. Sectional View, Labedie Unit #4 Boiler

SOURCE: COMBUSTION ENGINEERING

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pulverized coal is transported in air suspension from the coal mills to six levels of burners located at each of four corners of the boiler (Figure 2). The coal is injected into the furnace through the burners in such a manner as to intimately mix with the secondary air and to form a large vortex about the boiler's vertical axis thereby creating a huge, rotating ball of flame. Oil-fired warm-up guns are provided between the bottom two coal burner levels for boiler warm-up and to assist in stable coal ignition during start-up. One gun is located in each corner of the boiler. At full load the flame temperature within the fireball is about 3000°F and gas temperatures at the superheater division panels approach 2400°F.

SYSTEM DESIGN

In preparing to burn PCBs at Labadie significant modifications were made to the boiler and plant at considerable expense prior to the initial test burn of contaminated oil. The purpose in making these changes was to provide a well-designed system solely for PCB waste oil which minimizes the exposure of this oil to the environment and insures its proper disposal. After approval to burn up to 5% PCBs it was decided to further modify the system to include additional storage capacity and blending facilities. The following is a more detailed description of the various components of this system (see Figure 3).

Waste-Oil Storage and Blending

In order to store PCB contaminated oil at the plant until sufficient quantities for blending and incineration have been generated, an existing tank located above ground and immediately south of the plant has been designated and prepared for this purpose. In addition an adjacent tank has been designated for blending 5% PCB batches for incineration. Both tanks were previously used to store No. 2 fuel oil, were built to conform to the American Petroleum Institute (API) Standard 650 and meet all applicable OSHA requirements.

The oil tanks are surrounded by a 5 foot high concrete block dike designed to contain the entire volume of both tanks. In addition, the areas between the

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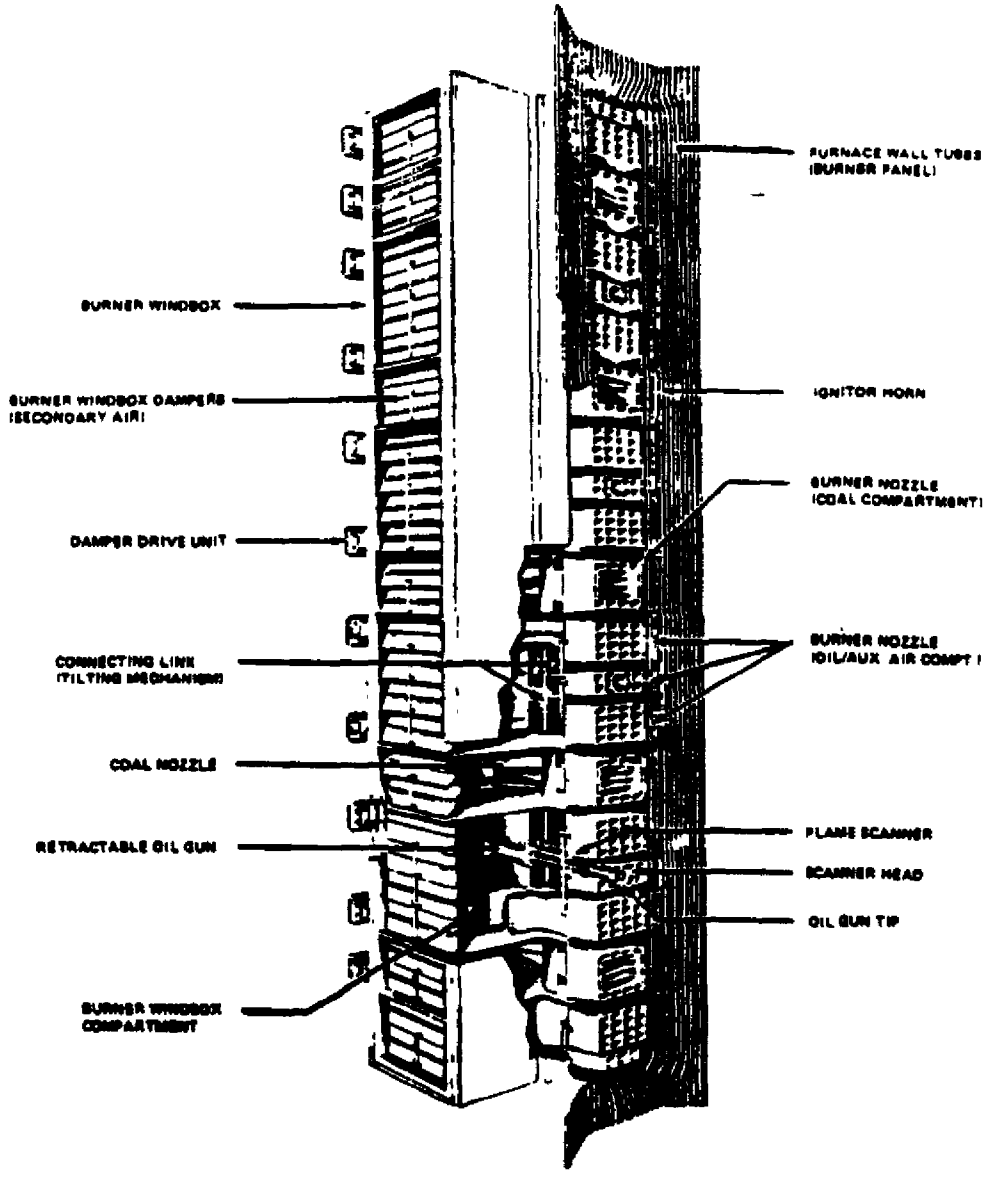

Figure 2. Cutaway View, Typical C-E Tilting Tangential Burner Assembly

SOURCE: COMBUSTION ENGINEERING

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Finally, we are currently using recombinant DNA techniques to clone fragments of H850 DNA as a first step toward identifying and characterizing the gene(s) specifying the enzymes of the PCB degradative pathway in this strain. This will allow us to develop an understanding of both the structure and regulation of these enzymes.

SUMMARY

We have isolated and characterized two distinct organisms, Alcaligenes eutrophus H850 and Corynebacterium sp. MB1, which extensively degrade Aroclor 1248, but which exhibit clear differences in the particular congeners which are degraded. In general, PCB congeners with the 2,4,4' substitution pattern are metabolized rapidly by MB1, but poorly by H850. In contrast, many congeners substituted at positions 2,3,2' are rapidly degraded by H850, but not by MB1. The production of metabolites unequivocally establishes that this is indeed degradation. Some degradation products, including chlorobenzoates, are common to both organisms, but in many cases the major metabolites produced by H850 are unique. These data are most readily explained by postulating that the major pathway of PCB metabolism in H850 utilizes a dioxygenase which preferentially attacks at carbon positions 3,4. If this is the case, it will be the first demonstration of involvement of a 3,4 dioxygenase in the biodegradation of biphenyl or PCBs. In contrast, MB1 probably employs a more common 2,3 dioxygenase mechanism. Finally, the two organisms harbor distinct plasmids which may be involved in PCB degradation. We are now in an excellent position to begin realizing our long-term goals, namely, understanding the biochemistry and genetics of bacterial PCB degradation.

ACKNOWLEDGMENTS

We thank J. C. Carnahan, R.E. Wagner, J. Smith, and R. Rohling for gas chromatographic analysis, T.J. Tofflemire and R.E. Brooks for help in collecting PCB contaminated environmental samples, K. Furukawa and A.M. Chakrabarty for a stock of Acinetobacter sp. P6, E.L. Finkbeiner, and T.M. Su for helpful discussions, and B. Moreen for typing this manuscript.

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Discussion

Q1. Isn't this process limited to a specific Aroclors?

A. Yes, the study so far has been limited to site-contaminated with 1242. Would need to isolate microbacteria from other sites to study other Aroclors.

COMPOSTING FOR DEGRADATION OF PCBs IN SOIL

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ABSTRACT

This study evaluated aerobic and anaerobic composting of PCB contaminated soil on a laboratory scale. Composts were composed of alfalfa hay, horsefeed and Lakeland soil spiked to contain 2000 mg/Kg of Aroclor 1242 (dry weight basis). Warm humidified air was drawn through aerobic compost materials. Anaerobic composts were flushed with nitrogen. All composts were incubated at 55°C.

After two and four weeks of incubation, compost materials were oven dried, ground, subsampled and Soxhlet extracted for GC analysis. The aerobic composts showed the greatest destruction of PCBs with 41.6 and 48.1% destruction in two weeks and 55.7 to 67.6% destruction in four weeks. PCB destruction in anaerobic composts was 18.4 to 28.0% after two weeks and 27.9 to 46.9% after four weeks of composting. Individual peak areas from the GC chromatograms of control and test compost extracts were compared to determine the decrease of different PCB isomers. A significant decrease in the trichlorobiphenyls and one of the tetrachlorobiphenyls was observed in extracts from the two week aerobic composts. After four weeks of aerobic composting, significant decreases in all of the chlorinated biphenyls were observed. Anaerobic composting showed significant reduction of all chlorinated biphenyls after four weeks of composting. The mechanism of degradation appears to be rapid dechlorination of biphenyls containing three chlorines or less since no build-up of the mono- or dichlorinated compounds was observed. Dechlorination of the penta- and tetra-chlorinated molecules is slower but does occur at a useful rate. No chlorinated dibenzo-p-dioxins or dibenzofurans were found in the chromatograms or in the GC-mass spectra run on the composted sample extracts.

COMPOSTING FOR DEGRADATION OF PCBs IN SOIL

INTRODUCTION

Polychlorinated biphenyls (PCBs) are complex mixtures of various chlorinated biphenyls which were widely used because of their physical, chemical and biological stability as well as their high dielectric constant. PCBs have entered the environment through spills and losses during manufacture, vaporization or leaching from PCB-containing formulations, leaks from sealed or partially sealed systems and disposal of waste PCB (1). PCBs have been found in ocean sediments, the atmosphere and in many terrestrial and aquatic locations including both polar ice caps (2). Because of their physical and chemical stability, these compounds are persistent environmental pollutants.

Weathering and microbial processes degrade PCBs only to a limited extent in the environment (3). Evidence indicates that PCBs may be biotransformed as well as metabolized by some microorganisms (4,5,6). Several investigators have reported biotransformation of the lesser chlorinated biphenyls (mono- and dichlorobiphenyls) to chlorobenzoic acid (7,4,8,9,10). Tucker et al. (6) showed that mono- and dichlorobiphenyls were readily biodegraded by activated sludge but as concentrations of the higher chlorinated biphenyls increased, degradation rates decreased. Kong and Sayler (9) simulated natural river conditions to demonstrate the degradation and mineralization of monohalogenated biphenyls by mixed microbial cultures from PCB contaminated river sediments. Furukawa and Chakrabarty (11) demonstrated total degradation of mono- and dichlorinated biphenyls using Acinetobacter or Arthrobacter sp. containing a plasmid specifying conversion of chlorobiphenyls to chlorobenzoic acids and a genetically constructed pseudomonad capable of metabolizing mono- or dichlorobenzoates.

This paper describes a study in which composting was evaluated for decontamination of soil containing PCBs. This study is part of a series of experiments to determine the applicability of composting techniques for the destruction of persistent hazardous materials contained in a soil or sediment matrix.

EXPERIMENTAL MATERIALS AND METHODS

This study evaluated composting of PCB contaminated soil on a laboratory scale. Both aerobic and anaerobic composting were studied to compare PCB biodegradation in the two systems. The experiments were carried out with soil that was intentionally spiked with PCBs (Aroclor 1242).

The experimental apparatus used in the laboratory studies is shown in Figure 1. Mason jars were used to contain the compost materials. A ring of plastic tubing with holes drilled at 1/4 inch intervals was located beneath the compost in each jar. The ring was connected to a glass tube which extended through the stopper in the top of the Mason jar. For the aerobic composts, the tube was attached to two traps in series, one containing sodium hydroxide and the other water. A second tube inserted through the stopper was attached to a series of traps containing sodium hydroxide, sulfuric acid and activated carbon as shown in Figure 1. These traps were connected to a vacuum pump. Warmed air was first drawn through a sodium hydroxide trap to remove any CO_2 and then through a water trap to humidify the air and remove any caustic material. The scrubbed air was then drawn through the compost materials. The atmosphere above the compost was continually drawn out through sulfuric acid, sodium hydroxide and activated carbon traps to remove any gaseous biodegradation products. The dead traps prevent contamination of the composts or individual gas traps in case of vacuum failure. For the anaerobic composts, the initial NaOH scrubbing trap was eliminated. The anaerobic composts were initially flushed with nitrogen to remove oxygen from the system and were flushed every 3-4 days thereafter to change the atmosphere in the composting vessels.

Each compost was made up of 23.7 g of alfalfa hay, 24.7 g Purina Sweetena Horsefeed and 5 g of Lakeland soil (a total of 50 g dry weight). The soil was spiked to yield 2000 mg/Kg of Aroclor 1242 in the total compost (dry weight basis). The compost materials were thoroughly mixed and the composting process initiated by addition of sufficient water (containing primary effluent and horse manure) to give the composts a 60% moisture content. The composting apparatus was then placed in a 55°C incubator and attached to the vacuum system. The experimental matrix for the composts is presented in Table 1. The temperature of each compost was monitored daily by means of a thermocouple placed within the compost materials.

The composts were sacrificed as specified in Table 1. At the time of sacrifice, each compost was examined for its appearance and smell. A sample (approximately 1 gram) was taken from the center of each compost and dispersed in distilled water (1:9 solids to water ratio) to determine the pH of the compost. The remainder of the compost material was dried in an oven at 60°C for 24 hours. The dried compost materials were ground with a hammer pulverizer to 18 mesh (1 mm) and the ground powder thoroughly mixed. Two subsamples from each compost (approximately 3 to 4 grams) were taken, weighed and Soxhlet extracted with a mixture of 40% benzene, 40% acetone, 10% hexanes and 10% methanol. Extraction efficiency of Aroclor 1242 from uncomposted material (positive controls) was 77%. Extraction efficiency from composted materials ranged

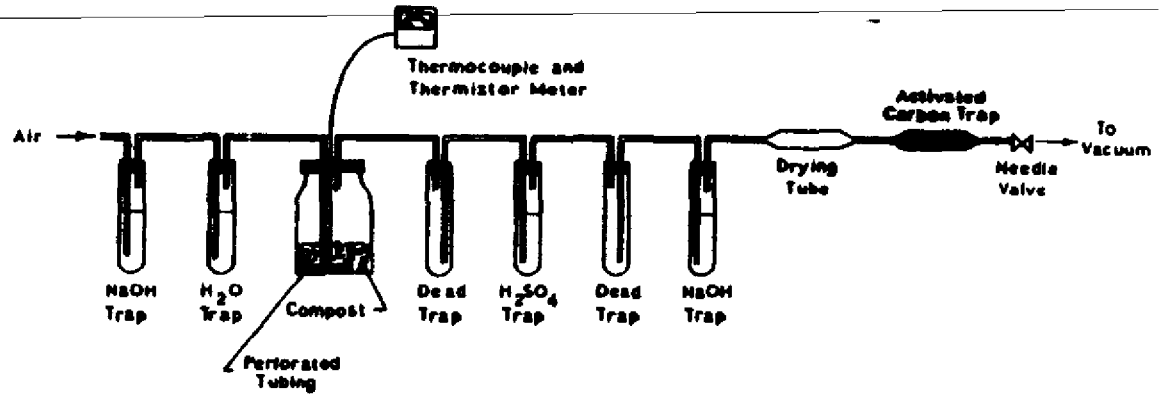

Figure 1. Laboratory Compost Aeration Apparatus

Table 1

EXPERIMENTAL MATRIX FOR COMPOSTS

	Type of Compost	Number	Time Sacrificed
SPIKED LAKELAND SAND			
A.	Positive Controls	2	0 week
B.	Negative Aerobic Controls (no Aroclor 1242)	2 2	2 weeks 4 weeks
C.	Experimental Aerobic Composts	2 2	2 weeks 4 weeks
D.	Negative Anaerobic Controls (no Aroclor 1242)	2 2	2 weeks 4 weeks
E.	Experimental Anaerobic Composts	2 2	2 weeks 4 weeks

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from 83 - 89%. The extract was analyzed on a Varian 3700 gas chromatograph with autosampler and electron capture detector. A Hewlett-Packard 5880 controller/ integrator was used to control the Varian gas chromatograph. The GC parameters were: injection port - 280°C; oven - 170 to 230°C @ 15°C/min; detector - 300°C. Separation of the PCBs was accomplished with a 2 mm I.D. by 10 ft. glass column packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 mesh Supelcoport using nitrogen carrier gas at a flow rate of 24 mL/min.

RESULTS

Results of the laboratory-scale PCB composting studies are summarized in Tables 2 and 3. The aerobic composts showed the greatest reduction in PCB concentration with a 41.6 to 48.1% decrease in 2 weeks and 55.7 to 67.6% decrease in 4 weeks. PCB concentrations were not reduced as rapidly in anaerobic composts. A decrease of only 18.4 to 28.0% in the PCB concentrations of the anaerobic composts was observed after 2 weeks of anaerobic composting and 27.9 to 46.9% after 4 weeks.

Aroclor 1242 is a mixture of chlorinated biphenyls composed of approximately 1% monochlorobiphenyl, 16% dichlorobiphenyl, 49% trichlorobiphenyl, 25% tetrachlorobiphenyl, 8% pentachlorobiphenyl and 1% hexachlorobiphenyl (12). The normal method for GC quantitation compares the total integrated area from all of the peaks in the sample to that of standards of similar chlorination. The methodology yields a comparison of PCB concentrations in the experimental samples with the positive controls but gives no information on the effects of treatment on the individual chlorinated biphenyl isomers. To evaluate the effects of composting on the individual isomers, areas of selected chromatogram peaks of the experimental samples were normalized and compared to corresponding chromatogram peaks of the positive controls. These comparisons for the 2 and 4-week aerobic and 4-week anaerobic composts versus the positive control (100%) are shown graphically in Figure 2. Typical chromatograms are presented in Figures 3 and 4. After two weeks of aerobic composting, a significant decrease in the trichlorobiphenyls and one of the tetrachlorobiphenyls was observed. No decrease in the higher chlorinated biphenyls was observed. However, after 4 weeks of aerobic composting, significant decreases in all of the chlorinated biphenyls occurred with less than 25% of the trichlorinated biphenyls remaining. Anaerobic composting at four weeks also showed significant decreases in all of the chlorinated biphenyls.

Table 2

AEROBIC COMPOSTING OF PCB CONTAMINATED SOIL

Sample	Time[1]	pH	PCB Concentration[2] µg/g	% PCB Decrease[3]	Comments
Positive Control	0	N.D.	1591		
Positive Control	0	N.D.	1517		
Negative Control	2 weeks	5.0	17		Wet hay smell. Not well composted.
Negative Control	2 weeks	6.2	31		Moderately damp, brown, composted.
Experimental A	2 weeks	5.6	908	41.6	Wet hay, moderately damp, yellow.
Experimental B	2 weeks	6.0	807	48.1	Moderately damp, brown, composted.
Negative Control	4 weeks	5.0	17		Not very damp, not well composted.
Negative Control	4 weeks	5.4	35		Old shoe smell, fungal growth.
Experimental C	4 weeks	5.0	504	67.6	Less than 60% moisture. Wet hay smell.
Experimental D	4 weeks	5.0	688	55.7	Sweet smell, <60% moisture, yellow.

[1]Time of sacrifice with respect to compost set-up.

[2]PCB concentration at time of sacrifice

[3]Decrease in PCB concentration based on the average control value of 1554 µg/g

N.D. = not determined.

Table 3

ANAEROBIC COMPOSTING OF PCB CONTAMINATED SOIL

Sample	Time[1] (weeks)	pH	PCB Concentration[2] µg/g	% PCB Decrease[3]	Comments
Positive Control	0	N.D.	1591		
Positive Control	0	N.D.	1517		
Negative Control	2	5.2	6		Mildew smell, light yellow.
Negative Control	2	4.8	8		Mildew smell, composted.
Experimental A	2	5.0	1268	18.4	Mildew smell, yellow.
Experimental B	2	4.7	1119	28.0	Musty smell, moderately composted.
Negative Control	4	6.0	10		Wet hay smell, moderately composted
Negative Control	4	7.0	12		Wet hay smell, moderately composted.
Experimental C	4	5.5	825	46.9	Sweet smell, fungal growth, brown.
Experimental D	4	6.5	1120	27.9	Sweet smell, dark color.

[1]Time of sacrifice with respect to compost set-up.

[2]PCB concentration at time of sacrifice.

[3]Decrease in PCB concentration based on the average control value of 1554 µg/g.

[4]N.D. = not determined.

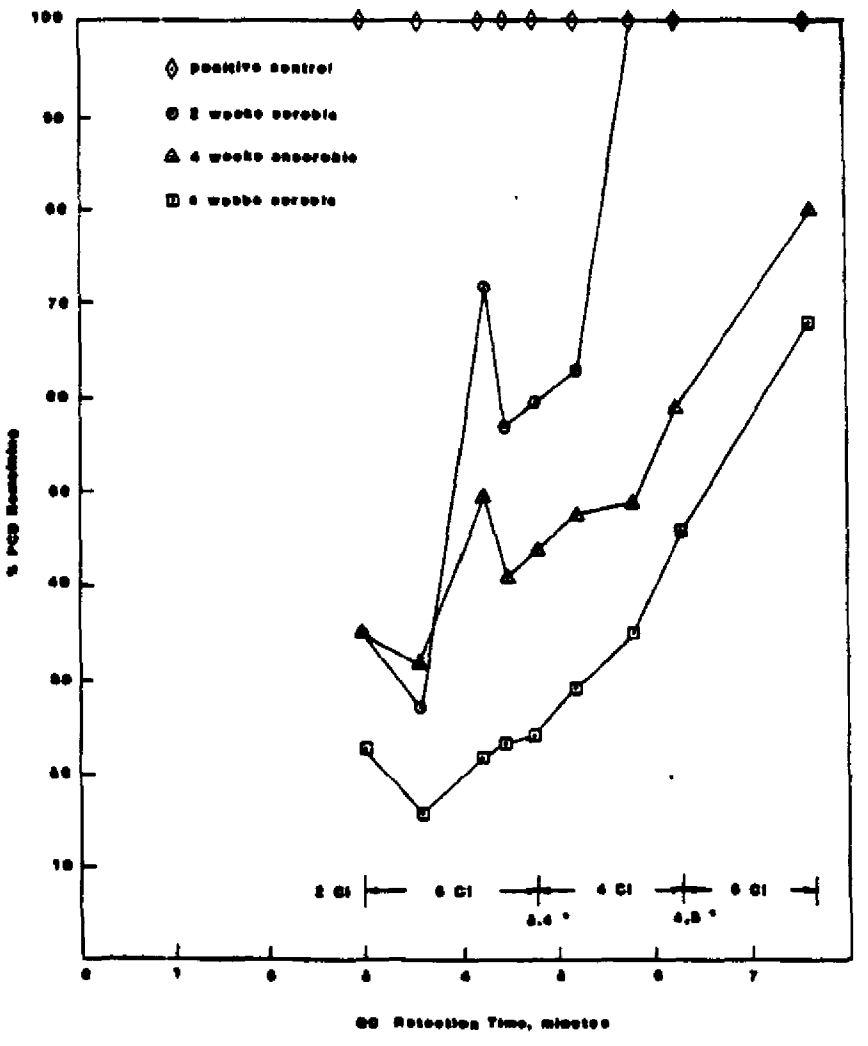

Figure 2. Comparison of Normalized Peak Areas with Positive Controls

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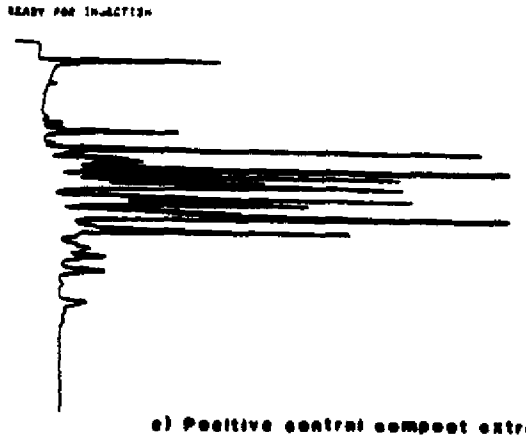
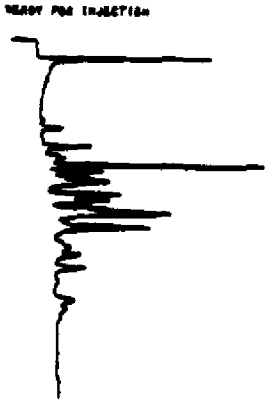


a) Positive control compost extract



b) 4-week aerobic compost extract

Figure 3. Chromatograms of Aerobic PCB Compost Extracts (1/20 dilution)

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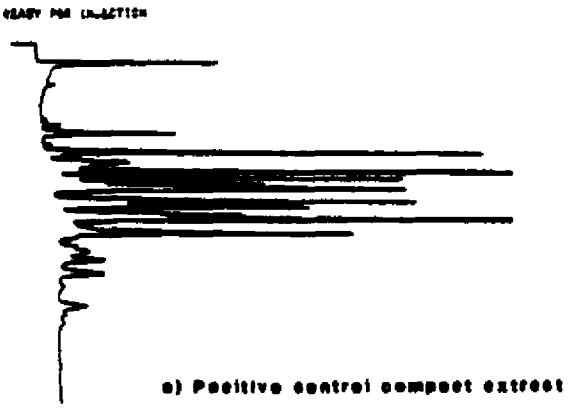
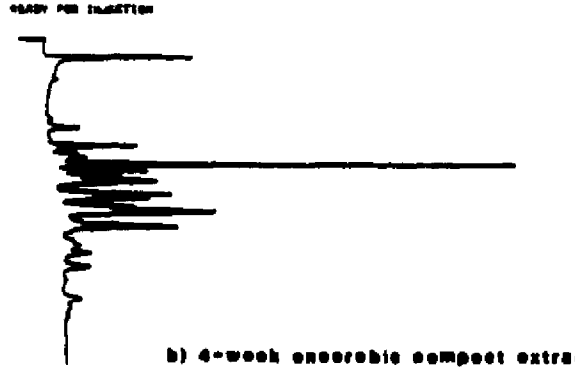


a) Positive control compost extract



b) 4-week anaerobic compost extract

Figure 4. Chromatograms of Anaerobic PCB Compost Extracts (1/20 dilution)

DISCUSSION

The mechanism of PCB degradation in compost appears to be rapid dechlorination of biphenyls containing three chlorines or less since no build-up of the mono- or dichlorinated compounds was observed. Dechlorination of the tetra- and penta-chlorinated molecules is slower but does occur at a useful rate. No chlorinated dibenzo-p-dioxins or dibenzofurans were found in the chromatograms or in GC-mass spectra of the composted sample extracts.

These preliminary laboratory-scale composting studies indicate that composting may have potential as a method for on-site decontamination of soils or sediments contaminated with PCBs. Aroclor 1242 concentrations of 2000 mg/Kg in the compost materials (soil contaminated at 20,000 mg/Kg) were tolerated by the microbial populations present in the composts and significant decreases in PCB concentrations were observed.

Composting for decontamination of soil or sediment is relatively simple, requiring only that the soil or sediment is thoroughly mixed with the compost materials. Composting can be carried out in various ways. The most popular methods currently in use are the windrow and forced aeration systems. In the windrow method, a pile or windrow of waste material is periodically turned by a machine to mix and aerate the organic matter. Anaerobic and aerobic decomposition occur in this system with aerobic decomposition resuming each time the material is turned. Generally composting temperatures are lower in this system than in other systems and non-uniform biodegradation of organic materials may result. A second method, enclosed systems, requires a complex mechanical system which gives more rapid composting than the windrow system. These bioreactors are designed to provide operational control over environmental conditions such as air flow, temperature and mixing and to isolate the composting material from the surrounding environment. A third method, the Beltsville Aerated Pile Method was developed at the Beltsville Agricultural Research Center for composting of undigested sludges. In this forced aeration system, compost materials are mixed and bulking materials are added as needed. The compost pile is placed on a base of woodchips covering perforated plastic pipe. Air is drawn through the pile via the perforated pipe in the base of the pile. The major advantages of this system are the production of a stable humus-like organic material, low capital investment and low energy requirements.

Composting for degradation of PCBs in soil or sediment should be further evaluated to answer the following questions:

- What is the maximum PCB concentration tolerated by the compost organisms?
- What is the effect of the PCB chlorine content on composting?
- What is the mechanism of PCB degradation in compost and what are the byproducts?
- What effects will different soils have on PCB degradation in composts?
- What type of compost system is best suited for degradation of PCBs in soil?
- What are the rates of PCB degradation for the different chlorinated biphenyls?
- What is the optimal composting time to achieve maximal PCB degradation?
- Can the microbial populations responsible for PCB degradation in composts be improved?

Degradation rates as determined by laboratory-scale studies will provide a conservative estimate of rates in large-scale systems. Degradation rates observed in larger systems may be twice as rapid as those observed in the laboratory scale studies. The major advantages of composting include on-site decontamiantion, production of a potentially useful organic material as a plant nutrient or soil conditioner, low capital investment and low energy requirements.

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Discussion

Q1. Have you looked at pH - buffering?

A. Not in this study.

Q2. Did you look at a carbon trap to see if temperature was actually driving the PCB out?

A. No - we did not analyze traps.

BACTERIAL DEGRADATION OF POLYCHLORINATED BIPHENYLS IN SLUDGE FROM AN INDUSTRIAL SEWER LAGOON

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ABSTRACT

A laboratory experiment was conducted to determine if polychlorinated biphenyls (PCB's) found in an industrial sewer sludge can be effectively degraded by mutant bacteria. The aereted sludge was inoculated daily with mutant bacteria in order to augment the existing bacteria with bacteria that were considered to be capable of degrading PCB's. The pH, nitrogen, and phosphorus levels were monitored daily to maintain an optimum growing medium for the bacteria. A gas chromatographic method was used to determine the PCB concentrations of the sludge initially and also throughout the experiment. Results and discussion of the bacterial treatment of polychlorinated biphenyls are presented in this paper.

SUMMARY

A 90-day laboratory sized experiment was conducted to determine the viability of using mutant bacteria to decontaminate an industrial type sludge that was contaminated with polychlorinated biphenyls (PCB's). The contaminated sludge samples were obtained from an industrial waste sewer lagoon system which is an integral part of a water pollution control facility. Four representative samples of sludge were selected for treatment with mutant bacteria. The samples originally contained the PCB Aroclor 1260 in concentrations ranging from 135 to 232 parts per million (ppm). In addition to the four samples, a fifth sludge containing only three ppm of Aroclor 1260 was spiked with nearly 1000 ppm of Aroclor 1260. This spiked sample was used to determine whether high concentrations of PCB's in sludge would be affectd by the bacteria.

The five samples were inoculated daily with mutant Pseudomonas aeruginosa bacteria that had a potential for degrading PCB's. The nitrogen, phosphorus, and pH levels were monitored daily to maintain a growing medium for the bacteria.
At the completion of the 90-day augmentation period, the concentrations of the PCB's in the sludge samples were found to be higher than the original concentrations. The cause of the apparent increase in concentrations has not been fully understood. One possibility is the biodegradation of the sludge in which the sludge is metabolized and broken down into lighter molecules. The lighter sludge increases the concentration of PCB on a weight-to-weight basis.

The apparent lower PCB concentration found around 20 days after inoculation suggests that the PCB was absorbed by the bacteria, thereby causing the apparent decrease in the PCB concentration of the sludge. After 20 days, the bacteria began to die, perhaps caused by the build up of toxic metabolic wastes, and subsequently released PCB back into the sludge without having metabolized the PCB molecules. Thus, the experiment can be summarized as that the PCB in the sludge was absorbed by the mutant Pseudomonas aeruginosa bacteria for 20 days. After 20 days, the bacteria began to release the absorbed PCB's back into the sludge which by now has been degraded into lighter molecules. Thus, the PCB concentration appeared to decrease at around 20 days, then increase after 20 days. Under the constraints of this experiment, the PCB was absorbed by the bacteria, but was not degraded.

Section 1

INTRODUCTION

Polychlorinated biphenyls (PCB's) are chlorinated aromatic organic compounds that are commonly used as dielectric fluids in capacitors and transformers. Their physical and chemical properties are such that they are chemically and thermally stable, fire resistant, essentially non-conductive, and have a low solubility in water.

Because of their chemical and physical stability, they are virtually indestructible when spilled into the environment, whether accidently or discarded for disposal purposes. High temperature combustion processes and special chemical treatment methods are evolving which are used to destroy the PCB's or to degrade the components into non-toxic materials. The U.S. Environmental Protection Agency has established a level of 50 parts-per-million above which materials must be disposed of in a Federally approved landfill or incinerator. Other treatment and cleanup methods are under investigation, and one of the most appealing concepts is biological treatment in which bacteria is used to degrade PCB's in situ.

Early studies in the use of bacteria for the degradation of specific chemicals reported in 1970, have shown that biphenyl can be degraded by gram-negative bacteria isolated from soil (Ref. 1). In that study, biphenyl was converted to phenylpyruvate in a salt medium. Other studies of biphenyl degradation involved bacteria such as Pseudomonas putida, Beijerinckia species, and a strain of Mucor. For the metabolism of pure chlorinated biphenyl (not PCB), Rhizopus japonicus was used to convert 4-chlorobiphenyl to 4-chloro-4-hydroxybiphenyl. Two species of Achromobacter, isolated from sewage effluent, degraded biphenyl to benzoic acid, and 4-chlorobiphenyl to 4-chlorobenzoic acid. However, no natural bacteria was found to successfully degrade polychlorinated biphenyls, which are mixtures of many chlorinated biphenyls.

If bacterie that can degrade PCB's are found, they most likely will be developed through genetic engineering. The use of such mutant bacteria would be particularly effective in the treatment of soils, sludges, and waste water for the decontamination of PCB's in those environments. Contaminated waste water lagoons would not

require the subsequent draining and physical removal of PCB contaminated soil and sludge. The lagoon could be conveniently treated by adding a mutant bacteria in situ and effect a clean up process at a relatively low cost and with little effort.

To determine the feasibility and effectiveness of bacterial augmentation, a laboratory experiment was conducted using PCB contaminated sludge samples from an industrial sewer lagoon. By using the actual sludge samples from the lagoon, this experiment was to provide insight as to whether the lagoon can be decontaminated by mutant bacteria. This paper describes the experiment and discusses the results of using mutant Psuedomonas aeruginosa bacteria with PCB contaminated sludge samples.

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Section 2

EXPERIMENT

The industrial sewer lagoon used for this study is part of a six-lagoon water pollution control facility which receives decante waters generated from waste tanks that process rinse waters and liquid wastes generated by metal plating and tube cleaning facilities. This lagoon serves as an equalization pond holding about 3.5 million gallons of waste water. An earlier investigation indicated widespread, low-level PCB contamination in the lagoon. Few sites were found to be contaminated with PCB's in excess of 50 parts-per-million (ppm) of Aroclor 1260. The EPA regulated concentration is 50 ppm.

In order to fully determine the magnitude and extent of PCB contamination in the lagoon, an extensiva sampling program was conducted. Sampling equipment was loaded in a boat and towed to the selected sampling points. Core samples of sludge and the sediment were collected. Average depth of the sediment was about six inches with the base material of clay. These samples were analyzed for PCB concentrations which ranged up to the highest concentration of 467 ppm. A definite water flow pattern was observed in which the inlet of the lagoon contained the highest concentrations and toward the discharge outlet the concentrations gradually declined.

After contamination levels were determined, many alternatives and possibilities were considered for decontamination of the sewer lagoon. The alternatives ranged from closing tha lagoon; permanently fixing the sediment into concrete-like material; biological and physiochemical methods; to physically dredging the sediment for disposal, treatment, or incineration. Many other possibilities were also considered, but one of the most attractive alternatives was the in-place degradation of PCB by microorganisms. If this microbiological method proved valid, draining of the lagoon water and physically removing the sludge would not be required. Using the sludge samples that had been analyzed for PCB, a small laboratory experiment was carried out to determine whether biological degradation of PCB's would be feasible for the industrial waste lagoon. Glass dessicators with approximately 2-liter capacities were used as experimental tanks. Five such sludge tanks were charged with the first tank containing about 450 grams of sludge with

205 ppm concentration of PCB. Water was added to bring the aqueous level up to one liter. The second tank contained 50 grams of sludge with 222 ppm PCB diluted to one liter. The third tank was two liter tank containing 100 grams of sludge in which 980 ppm of Aroclor 1260 was added to the sludge originally containing 3 ppm. This tank was started to determine whether high concentration of PCB in the sludge would be affected by the bacteria, and to roughly determine the degradation rate to see how long the treatment would be needed to bring the concentration below the 50 ppm level. The fourth tank contained 50 grams of sludge with 135 ppm, and the fifth tank had 50 grams of sludge with 232 ppm diluted to one liter.

These experimental sludge tanks were inocculated with the mutant Pseudomonas aeruginosa bacteria obtained through a biochemical firm that has considerable experience and expertise in genetic engineering. The bacteria culture which was contained in a bran base was prepared for augmentation by soaking the culture in water for six to nine hours with a pinch of sodium bicarbonate. The initial dosage rate was 0.1 grams of the culture per one liter, then the dosage rate was gradually decreased over 20 days to a maintenance level of 20 milligrams per liter. Along with daily supplementation of bacteria, a nutritional balance for biological activity was maintained each day. The dissolved oxygen was kept at about 7 ppm level by aeration of the tank and agitation of the slurry. The pH level was maintained at 7.5, and nitrogen as ammonia determined by the Nesslerization method was over 5 ppm level. The phosphorus as ortho-phosphate was determined by the molybdate method and maintained at 1 ppm. The temperature of the tanks was kept at about 75° F.

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Section 3

RESULTS AND DISCUSSION

In monitoring the sludge tanks daily, the general trend has been the drop in the pH and nitrogen, while phosphorus concentration remained above 1 ppm level. No particular pattern was observed other than a need for almost daily addition of sodium bicarbonate to bring the pH up and an ammonium compound to supplement the nitrogen level. To compensate for nitrogen loss, ammonium hydroxide was used if the pH dropped to about 6.8, and ammonium nitrate was used if the pH was near 7.5 level.

During the augmentation period, biological activity in the tanks was monitored biweekly. An ordinary microscope at 100 magnification and a phase contrast microscope at 400 magnification were used to insure the presence of active organisms in the tanks. As activated sludge is formed and ages, there is a successive predominance of protozoans and rotifers which correlates with the bacterial population (2). In general, as the bacteria population increases, flagellates become predominant. When the bacteria population is at the maximum, free swimming ciliates are the predominant organisms. As the bacteria population declines, rotifers become predominant. In the sludge tanks, the protozoans and rotifers were observed with the flagellates and free swimming ciliates as the predominant organisms. At about the middle of the augmentation period, the number of the higher organisms appeared to have sharply declined. Toward the end of the augmentation period, the higher organisms were almost absent.

In the last 12 days of augmentation, a large amount of bacteria was added to each tank along with supplemental food to provide an additional carbon source. The population of microorganisms correlates with the sludge conditions, in that the sludge starts to age and breaks down when the population of microorganisms is at the maximum. The sludge becomes digested and the food source for the bacteria becomes diminished. With further digestion of sludge, the organisms eventually utilize the internal material through endogeneous process, resulting in the diminished population. Near 12 days toward the end of the augmentation period, the sludge appeared emulsion-like and the higher organisms were almost absent.

This indicated that the microorganism population had severely declined due to lack of an external food source. Although a large amount of bacteria was added along with supplemental food, no improvement was observed.

The results of bacterial augmentation over a 90-day period are presented in the Table. These results were obtained by analyzing the sludge samples by a gas chromatographic method. A sample of sludge was weighed, then PCB was extracted with 1:1 acetone and hexane mixture using an ultrasonic bath. Extracted PCB was analyzed by a gas chromatograph equipped with an electron capture detector. This analytical instrument was fitted with a two-meter glass column packed with 3% OV-1 on 80-100 mesh Chromosorb W-HP and maintained at 200° C. The carrier gas was ultrapure nitrogen at a flow rate of 25 milliliters per minute. The injection port was kept at 250° C. and the detector was maintained at 300° C. The output of the gas chromatograph was recorded on a 1 mv strip chart recorder. The PCB chromatogram of the sample was quantitated from the standard chromatograms.

As shown in the Table, PCB in the industrial sewer sludge appears not to have been degraded by the bacteria over 90 days period. In these sludge tanks, the final concentrations of PCB at the end of 90 days are higher than the starting concentrations, although in Tank 2 the concentration is decreased slightly. This small decrease in Tank 2 cannot be regarded as an indication of bacterial degradation of PCB, since the fluctuation between the anlysis dates and the precision of sampling and analytical method could cause this small difference.

An interesting observation from the results is the apparent dip in the concentration around 20 days from the beginning of the experiment. After this 20-day period, the concentration rises and remains at an elevated level. Although it is possible that the sampling and the analysis may be in error, this initial dip in the PCB concentration of the sludge might indicate an effective biological activity in the first 20 days, after which the biological activity appears to have ceased. The apparent lower concentration suggests that the PCB was degraded or absorbed by the organisms present in the tanks. Since the PCB concentration increases after 20 days, the absorbed PCB may be subsequently released back into the sludge.

Perhaps, after about 20 days, the sludge tanks become saturated with materials such as the bacterial metabolites that may attack or cause the bacteria to decompose and release the absorbed PCB back into the environment. This is difficult to substantiate because limited data is available. With so many variables that can adversely affect the microorganism population, it is conceivable that the

organisms have decomposed since the microorganism population declined as the augmentation period progressed. Another supportive factor is that the experimental sludge tanks are essentially batch reactors in which no water flows in or out of the tanks on a continuous basis. All added materials and metabolic wastes are accumulated in the tanks. If PCB was metabolized or degraded by the bacteria in order to gain energy and enhance growth, the PCB peaks in the gas chromatogram may show an indication. Possibly, one or more gas chromatographic peaks may be decreasing faster than the other peaks since PCB contains a mixture of chlorinated biphenyls. This hypothesis could not be fully tested because of apparent rise in all PCB peaks after the 20-day period.

The apparent rise in the PCB level cannot be explained at this point, but one possible explanation is that the organisms may be preferentially attacking the abundant carbon source of the sludge before attacking the PCB. This may have the effect of increasing the PCB concentration, on a weight-to-weight basis, in the biodegraded sludge. Therefore, when a sample of sludge is weighed out and analyzed, the concentration of PCB would appear to be higher as shown in the results.

Section 4

CONCLUDING REMARKS

In each of the five experimental sludge tanks, the bacterial augmentation over a 90-day period resulted in an apparent increase in the PCB concentration. At the end of 90 days, the final concentrations of PCB in the industrial sewer sludges were higher than the original concentrations. These results may be due to the sludge being degraded prior to PCB and due to the sludge tanks becoming toxic to the bacteria by the bacterial metabolites that cause the bacteria to decompose and release absorbed PCB back into the sludge.

It appears that around 20 days after the augmentation, microorganisms released the absorbed PCB back to the sludge without metabolizing or breaking down the molecules. In this case, if a continuous water system was used to allow a flow of water in and out of the augmentation system, the PCB concentration in the sludge would be decreased by the organisms with absorbed PCB being carried away with the water flow.

At any rate, the mutant bacteria of Pseudomonas aeruginosa used in this experiment did not degrade the PCB's found in the sludge from an industrial sewer lagoon. It is important to test each PCB contaminated material to determine the feasibility and effectiveness of bacterial augmentation prior to an actual field demonstration.

Section 5

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TABLE: RESULTS OF PCB CONCENTRATIONS
IN BACTERIA AUGMENTED SLUDGE, ppm

No. Days	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5
0	205	222	983	135	232
21	94	65	821	---	---
24	---	---	---	110	210
30	145	206	962	---	---
36	---	---	---	131	258
42	195	154	1449	---	---
50	---	---	---	165	275
57	255	162	1160	---	---
75	230	174	1443	---	---
82	253	157	1225	---	---
90	262	181	1476	---	---
91	---	---	---	163	287

Discussion

Q1. How or why did the increase in ppm occur?

A. The emulsion sludge is a much lower density and it contains both live and dead organisms.

Q2. Why was that particular strain of Pseudomonas aeruginosa used?

A. That strain had been used in jet fuel tanks, we so decided to use the same on the sludge.

Q3. Is 90 days enough time?

A. That was the allowable test period.

Part 5

PCB DESTRUCTION

DESTRUCTION OF HIGH CONCENTRATION PCBs IN A UTILITY BOILER

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Union Electric Company

INTRODUCTION

As with most electric utilities and other industrial concerns, Union Electric Company produces significant quantities of waste oil and other combustible products during the course of normal business activity. The greatest majority of these wastes come from two primary sources; 1) dielectric fluids used in electrical equipment, and 2) lubricating oils used in motor vehicles and large power plant machinery. Because of previous manufacturing and servicing procedures, some mineral oil dielectric fluids will inadvertently contain the chemical compound polychlorinated biphenyl or PCB in varying but generally low concentrations. Other dielectric fluids, known generically as askarel, intentionally contain about 60 percent PCBs for a specific purpose and use. In comparison to many other organic chemicals the scientific information available would seem to indicate that PCBs are relatively low in toxicity. However, because of their extreme stability and bioaccumulative nature and the inexact nature of the science in this area, prudent action requires that special care be taken to see that these fluids are disposed of properly.

On May 31, 1979 the U.S. Environmental Protection Agency promulgated regulations (44 FR 31514) rigidly governing the handling of PCBs. A key feature of this regulation is the grouping of PCB waste liquids into three categories with differing disposal options for each group. The classifications and their disposal options are:

1) For those liquids containing 500 ppm PCBs or greater, disposal must take place in an incinerator which complies with the provisions of 40 CFR 761.70 ("PCB incinerator" requirements).

2) For those liquids containing between 50 and 500 ppm PCBs there are three disposal options; burning in a PCB incinerator; placement in a landfill which complies with the provisions of 40 CFR 761.75 ("chemical waste landfill" requirements), or incineration in a high efficiency boiler meeting specific requirements.

3) Finally for those liquids containing less than 50 ppm PCBs, no direct restrictions are placed on their disposal except that they cannot be used as sealants, coatings or dust control agents.

With the promulgation of this regulation Union Electric began to examine which options best met the Company's disposal needs and objectives. Continuing and substantial liabilities for these wastes even after proper disposal in accordance with regulations made landfilling undesirable. However, PCB liquid incineration costs were high. Therefore, Union Electric decided to pursue the high efficiency boiler disposal option for contaminated oil. This alternative was attractive because it allowed Union Electric to maintain control of the substance through its ultimate disposal. As well, the resource was not wasted in that the energy value of the oil was recovered through generation of electricity.

On July 7, 1980 Union Electric requested approval to dispose of 50 to 500 ppm PCB liquids in their Labadie Plant Unit #4 located near Labadie, Missouri. During November 1980 public meetings were held and in early January, 1981 a series of trial burns were conducted while the stack effluent, ash, and ambient air in the surrounding area were carefully monitored. No PCBs were detected in any of these samples.

On May 26, 1981 the Missouri Department of Natural Resources certified the boiler as a resource recovery facility and on the following day approval under the PCB rule was granted by EPA Region VII.

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With this approval Union Electric solved its PCB contaminated oil disposal problem. However, it did not solve the problem of disposing of those liquids greater than 500 ppm and especially askarel. For dielectric fluids containing greater than 500 ppm PCBs, the regulations disallow the high efficiency boiler method of disposal, and dilution to lower PCB concentrations is also deemed illegal. As previously noted, disposal of these fluids must take place in an incinerator which meets stringent standards established in the regulations. However, this requirement is not absolute. The Regional Administrator has the authority under 40 CFR 761.10(a) to approve alternative disposal methods if they can be shown equivalent to a PCB incinerator and if they will not present an unreasonable risk of injury to health or the environment. Union Electric carefully examined the design and operational features of the Labadie Unit #4 and determined that such a demonstration could be made for this facility while burning an oil/askarel blend containing 5 percent PCBs in conjunction with pulverized coal as the primary fuel source. Therefore in December, 1981 Union Electric initiated formal discussions with EPA Region VII which ultimately resulted in approval of the system presented herein.

This paper describes the engineering analysis of the design features and operational parameters which lead to the conclusion that the boiler can essentially destroy all PCBs introduced and the results of a carefully planned test burn which was conducted to confirm these conclusions.

BOILER DESCRIPTION

Labadie Unit #4 is the newest of four 600 megawatt (MW) coal fired generating units located on the south bank of the Missouri River in Franklin County near Labadie, Missouri.

The boiler (Figure 1), which is essentially identical to the other three boilers at the site, is a tangentially fired unit manufactured by Combustion Engineering Inc. and was placed in commercial operation in August of 1973. The boiler has a maximum continuous rated (MCR) heat input of 5387 million BTU per hour which corresponds to a burn rate of about 240 tons per hour of pulverized coal. The

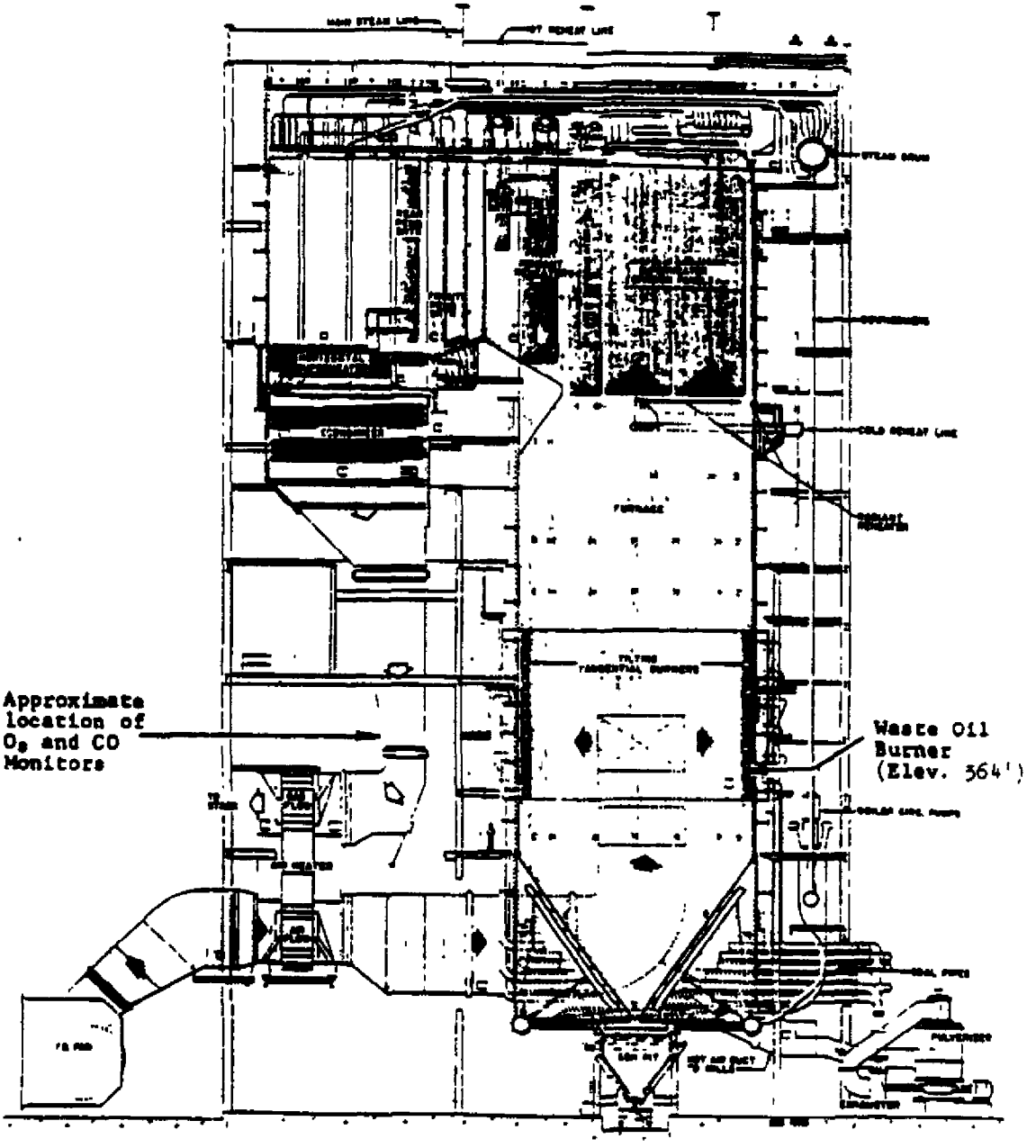

Figure 1. Sectional View, Labadie Unit #4 Boiler

SOURCE: COMBUSTION ENGINEERING

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pulverized coal is transported in air suspension from the coal mills to six levels of burners located at each of four corners of the boiler (Figure 2). The coal is injected into the furnace through the burners in such a manner as to intimately mix with the secondary air and to form a large vortex about the boiler's vertical axis thereby creating a huge, rotating ball of flame. Oil-fired warm-up guns are provided between the bottom two coal burner levels for boiler warm-up and to assist in stable coal ignition during start-up. One gun is located in each corner of the boiler. At full load the flame temperature within the fireball is about 3000°F and gas temperatures at the superheater division panels approach 2400°F.

SYSTEM DESIGN

In preparing to burn PCBs at Labadie significant modifications were made to the boiler and plant at considerable expense prior to the initial test burn of contaminated oil. The purpose in making these changes was to provide a well-designed system solely for PCB waste oil which minimizes the exposure of this oil to the environment and insures its proper disposal. After approval to burn up to 5% PCBs it was decided to further modify the system to include additional storage capacity and blending facilities. The following is a more detailed description of the various components of this system (see Figure 3).

Waste-Oil Storage and Blending

In order to store PCB contaminated oil at the plant until sufficient quantities for blending and incineration have been generated, an existing tank located above ground and immediately south of the plant has been designated and prepared for this purpose. In addition an adjacent tank has been designated for blending 5% PCB batches for incineration. Both tanks were previously used to store No. 2 fuel oil, were built to conform to the American Petroleum Institute (API) Standard 650 and meet all applicable OSHA requirements.

The oil tanks are surrounded by a 5 foot high concrete block dike designed to contain the entire volume of both tanks. In addition, the areas between the

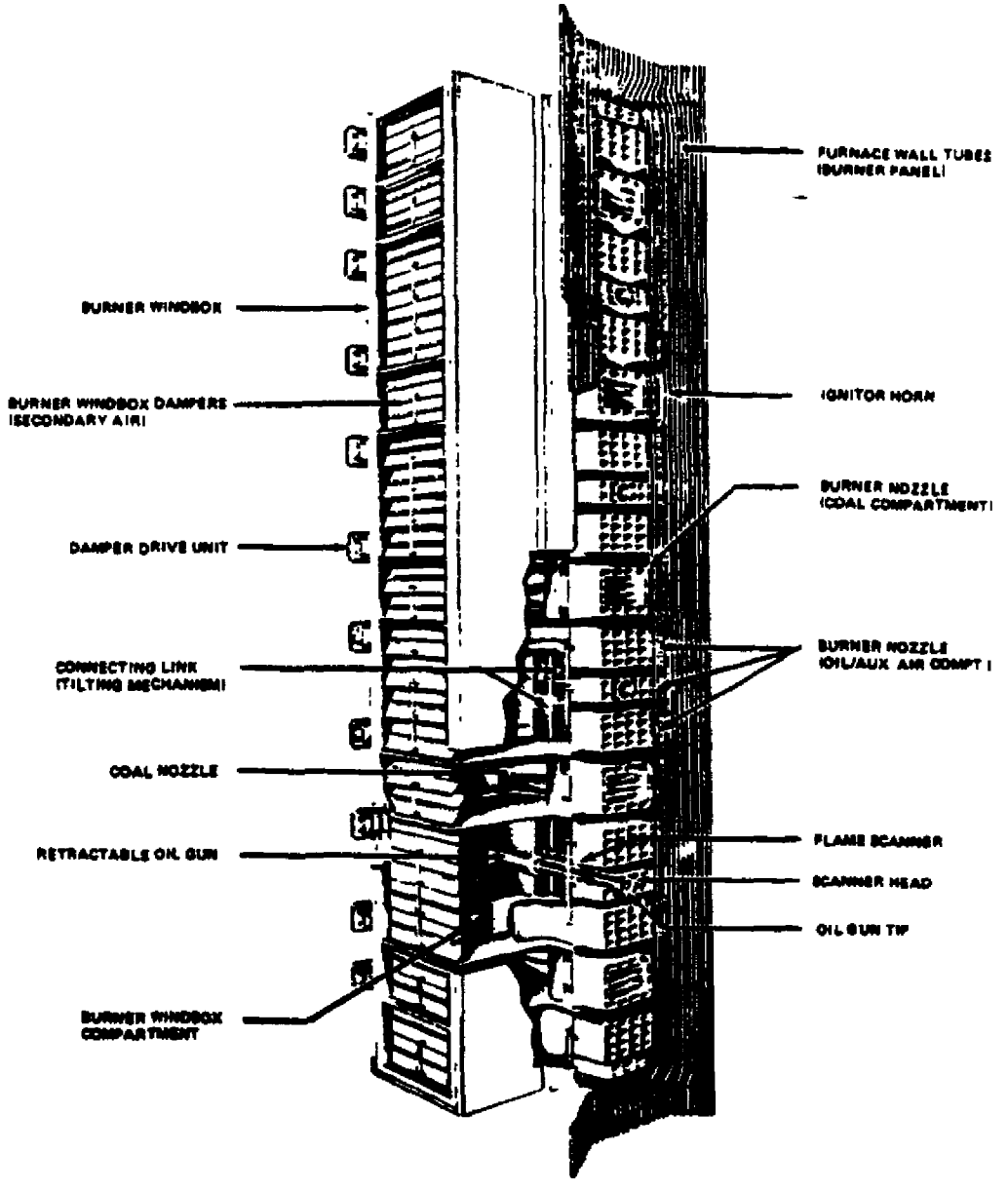

Figure 2. Cutaway View, Typical C-E Tilting Tangential Burner Assembly

SOURCE: COMBUSTION ENGINEERING

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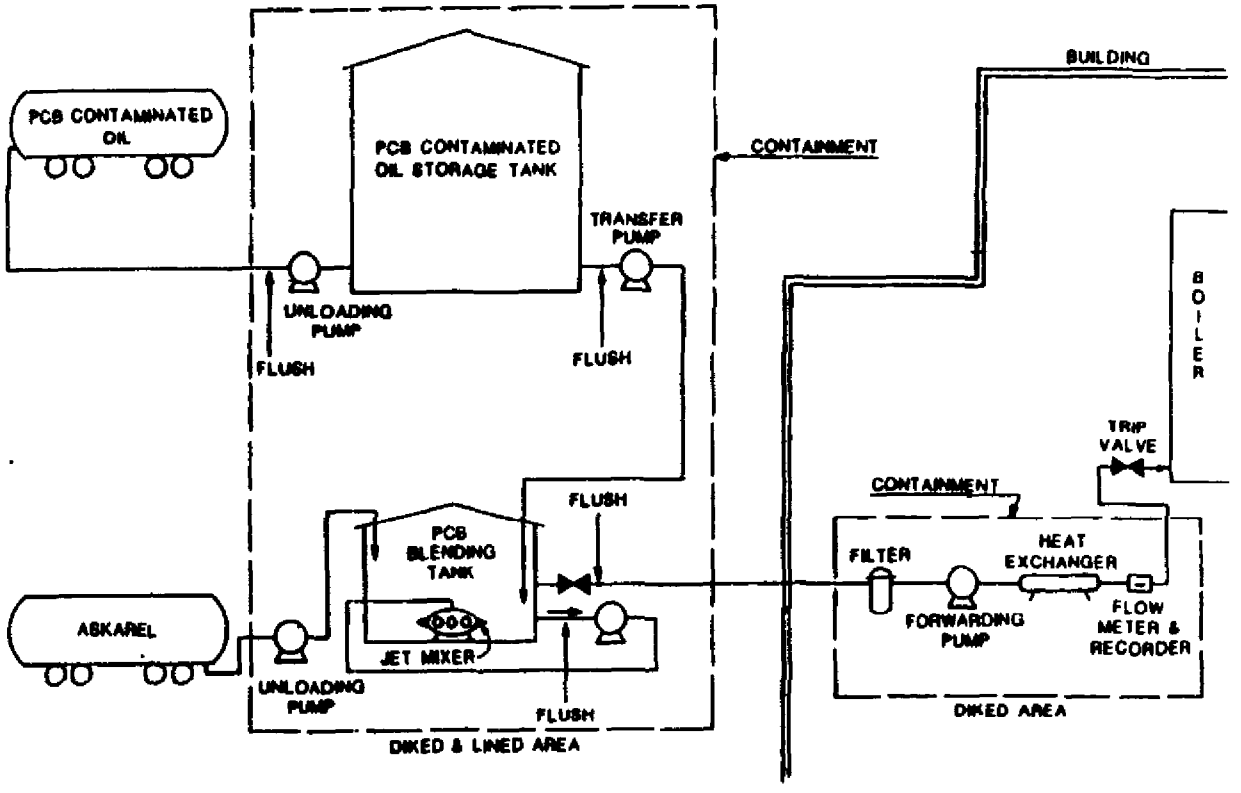

Figure 3. Labadie PCB Blending and Incineration Facilities

SOURCE: UNION ELECTRIC

tanks and wells, including the internal sides of the dike have been lined with a 30 mil dacron reinforced chlorinated polyethylene liner. The liner is covered with six inches of smooth stone to protect it from damage.

When plant personnel are ready to conduct a burn, contaminated oil is transferred from the PCB contaminated oil storage tank to the blending tank using a permanently installed transfer pump and meter located within the containment. Mounted in the center and free standing on the bottom of the blending tank is an eddy jet mixer with a series of twelve double acting jet nozzles. A positive displacement circulation pump adjacent to the tank removes fluids from the tank and discharges them back through the jet mixer.

When the selected quantity of PCB contaminated oil is pumped to the blending tank, the pump is energized and circulation is established. A carefully calculated quantity of askarel sufficient to produce a 5% PCB/oil blend is then introduced. After all the askarel is introduced, circulation and mixing are continued until the fluids are fully blended. Upon completion, samples are collected at various depths to insure uniform mixing and proper PCB concentration. Heating value, percent chlorine and flash point are also measured. When proper conditions have been confirmed the batch is then ready for incineration.

Waste Oil Forwarding

The waste oil forwarding equipment is that equipment necessary to transport the oil from the blending tank to the boiler during the incineration process and includes the waste oil pump, totalizing flow meter, strainers, a temperature regulating valve, heat exchanger, and all associated piping, valves, gauges and controls.

Piping is routed from the tank to just inside the plant building where the oil flows through a duplex basket strainer for solids removal to protect downstream equipment from damage and enhance atomization. The oil then flows through a positive displacement pump nominally rated at 750 gallons per hour. After discharging from the pump, the oil flows through a heat exchanger to maintain a

consistent oil viscosity regardless of ambient temperature extremes. The heat exchanger is present to insure optimum atomization and combustion at the burner. However, under normal conditions, the viscosity of the PCB/oil blend is totally acceptable and the heat exchanger is not currently used. The final piece of equipment is the totalizing flow meter to record the volume of waste oil being incinerated. This entire equipment package is surrounded by 12 inch high curbing to contain any oil which might leak or otherwise escape. A special emergency response and spill cleanup station is located nearby. A written SPCC plan which includes provisions for the incineration system has also been prepared and implemented.

Waste Oil Burner

The oil is then transported through color coded piping up to the southeast corner of the boiler where it passes through a trip valve and on to the waste oil burner. The primary element of the burner is the oil gun. The waste oil and atomizing air pass through the gun and are mixed at the burner tip as they are injected into the boiler. For the waste oil system, a special Combustion Engineering WRTE type oil gun equipped with a "J" style nozzle has been purchased from the boiler manufacturer. The gun utilizes an outside mix arrangement wherein the oil and air travel down the gun in parallel, non-concentric passages and only mix at the spray nozzle. Contrary to standard gun design the atomizing air is placed at the outside of the mixing plate which promotes better mixing. The manufacturer believes this gun will atomize the fuel to a finer droplet size, will achieve greater flame penetration and is more tolerant of flame and fuel fluctuations. This gun is maintained as a separate device which must be installed in place of the normal warm-up oil gun whenever incineration of waste oil is required. A second special emergency response and spill clean-up station is located near the burner as an additional precaution.

Waste Oil System Controls

In order to integrate the waste oil burner into the boiler system, appropriate controls have been added and necessary interconnections have been made. A trip

valve, identical to that used on the warm-up oil supply line, is installed in the waste oil piping at the point where it connects into the existing warm-up oil line near the burner. It is controlled by a selector switch in the control room. This switch is used to select the normal warm-up oil burning mode or the special waste oil burning mode. In either position, the switch locks the trip valve which was not selected in the closed position. All start and trip signals effect only the valve selected. The system will operate as it presently does in the normal mode. In the waste oil burning mode, the southeast corner burner operates independently of the other guns and does not hinder their operation.

Controls must confirm that certain operating conditions exist before they will allow the operator to enter the waste oil burning mode. The existing trip signals are used to close the waste oil trip valve if any of in the following events occur.

1) air/fuel differential pressure less than 5.5 psid
2) oil pressure less than 40 psig
3) emergency shutdown command due to boiler trip caused by:
   a. air flow less than 25 percent
   b. loss of both I.D. or F.D. fans
   c. inadequate water wall circulation for more than 3 seconds
   d. high furnace pressure
   e. turbine trip
   f. loss of AC power for more than 2 seconds
   g. loss of all fuel
   h. flame failure
   i. manual emergency trip

Additional trip signals are provided to trip the waste oil valve when:

1) the exhaust gas CO concentration is greater than or equal to 100 ppm; or
2) the exhaust gas O_2 concentration falls below 3 percent; or
3) the unit's generation falls below 300 MW.

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The latter trip signal is provided to indirectly control the gas temperature and residence time to well within limits established for complete destruction.

The atomizing air supply during waste oil incineration uses a separate pressure regulating valve (PRV) for the southeast burner rather than the common PRV used for burning warm-up oil. The new PRV is set to control the air pressure at 15 psi higher than the oil pressure. The atomizing air piping has a trip valve identical to that in the oil piping, which closes under all of the same trip conditions, thus, stopping the flow of air to the gun.

Combustion Monitoring Equipment

In order to monitor and record the indicators of high combustion efficiency during batch PCB/oil incineration, several different analyzers and associated support instrumentation are used.

Oxygen

Oxygen levels are normally required as a boiler control input for maintaining proper fuel to air ratios. Therefore, as part of the boiler control design a Westinghouse Hagen Model 218 oxygen analyzer system is installed in the boiler backpass downstream of the economizer, but prior to the air heaters. The percent oxygen signal is returned to the control room where it is indicated on a continuous strip chart recorder.

Carbon Dioxide

Continuous CO_2 analyzer results from the two test burns demonstrated that CO_2 levels in the boiler are consistently in the range of 14 to 16 percent as would be anticipated. Because of the high predictability and low variability of the CO_2 levels and their insensitivity as a combustion indicator, continuous monitoring of this parameter on a routine basis is not required.

Carbon Monoxide

In order to monitor CO concentrations, a representative sample is extracted from a location adjacent to the oxygen analyzer probe. This extractive sample first passes through a sample conditioner where particulates are filtered and moisture is removed. The conditioned sample then passes through a sample line to a Horiba Model PIR-2000 luft-type nondispersive infrared (NDIR) CO analyzer. The signal from the analyzer is sent to the control room for strip chart recording.

Since carbon dioxide is an exhaust gas constituent which is consistently in the range of 14 to 16 percent, and since this gas acts as a low level interference for NDIR analyzers, the calibration gas used with the system has a carbon dioxide level of 15 percent to effectively eliminate this interference.

Temperature and Residence Time

It is well documented that the right combination of combustion temperature and retention time will insure complete destruction of PCBs. For this reason the PCB incinerator standards require continuous measurement of the gas temperature.

Because of the very high temperatures and the abrasive and corrosive nature of the stack gas environment it would be very difficult to install a continuous temperature measuring device in a utility boiler. Metal probes alone cannot withstand the elevated temperatures. Ceramic probes cannot consistently withstand large temperature cycles and eventually become brittle and break. Because the boiler tubes are designed to structurally act as the boiler wall and since they always have a flow of water or steam through them, a metal implanted thermocouple in the tube wall would read metal temperature which is lower than gas temperature. Optical pyrometers need a target from which to measure emissivity and require some interpretive judgement in their reading. If boiler slag is not present, which is usually the case at lower loads, the only surfaces available are boiler tubes. As noted above, the tube metal temperature does not accurately represent gas temperature but is generally lower. Therefore, the only

technology available is water cooled thermocouple probes which would be very expensive to install and very maintenance intensive.

Later discussion in this paper clearly reveals that at normal loads both temperature and residence time minimum requirements are exceeded. Therefore, it logically follows that a reliable alternative to continuous temperature measurement is to establish a minimum load below which no PCB incineration would take place. Based upon temperature and residence time data, a load limit of 300 MW will insure boiler conditions at all times in excess of established minimum requirements. This conclusion is confirmed by the test burn results.

Waste Oil Feed Rate

While not a PCB incinerator requirement, an additional precaution to insure complete PCB destruction is to limit the feed rate of PCBs to a level much smaller than the total fuel input. High efficiency boiler requirements for PCB contaminated oil incineration establish this level at 10 percent of the total fuel. Considering the maximum capacity of the waste oil pump and the amount of fuel required to achieve the minimum load of 300 MW, it is estimated that the highest ratio of actual PCBs to total fuel input would be approximately 0.1 percent.

Operating Design and Procedures

In addition to the physical modifications described for proper PCB disposal, well thought out operating procedures must be established to insure proper coordination and understanding of the equipment by the operating personnel. To insure this consistent operation, written procedures have been prepared and are strictly adhered to during the incineration process.

In order to minimize exposure of personnel to residual concentrations of PCBs during operation and maintenance a flushing system is provided beginning at the tank and flowing through the entire system and into the boiler. Whenever the system is shut down it is flushed with No. 2 fuel oil for sufficient time to insure at least three equivalent volumes of the system have been pumped and burned.

During startup the system is initially operated on fuel oil. A complete walk down inspection is made to check for incorrect valving or leaks and the waste oil system is not valved in until the system completely checks out. Periodic inspections are also made during the incineration process. As well, various important operating parameters are audibly and visually alarmed in the central control room. If an alarm occurs, operating personnel are immediately dispatched to inspect and correct any malfunction.

COMBUSTION EVALUATION

During the initial evaluation of the boilers' ability to combust PCB compounds a number of factors affecting this combustion were carefully evaluated.

On a purely intuitive basis the basic design would suggest the Labadie boiler as an excellent PCB incinerator. The boiler itself is approximately the height of an eighteen story building (183 ft.) and has a total furnace volume of 422,000 cubic feet. The flame ball that spans the burner elevations is approximately 36 feet in height with a cross-sectional area of 2765 square feet. The injection of the PCB/oil blend occurs at an oil gun level which is located between the lower two coal burners in one corner of the boiler. The oil must pass through the highly turbulent flame area and spiral up through nearly the entire furnace volume. Under worst case conditions the relative feed rate of the waste oil to coal is very low and on a weight basis the fraction of PCBs to the total fuel input is only 0.001.

Because of the very large quantities of coal burned in utility boilers, it is essential that they be designed with high combustion efficiencies for economic reasons. Minor reductions in combustion efficiency on a boiler the size of Labadie Unit #4 can easily add up to hundreds of thousands of dollars per year in additional fual costs. Obviously then, there is a strong motivation to design and operate the unit at its maximum efficiency. Carbon monoxide and carbon dioxide data from the previous test burns clearly demonstrate this fact. The tests showed that the combustion efficiency of Labadie Unit #4 averages 99.99 percent.

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In order to make a more technical evaluation of the potential for PCB destruction, the details of the various combustion mechanisms must be examined.

The Combustion Process

Combustion is an exothermic reaction in which fuel is rapidly oxidized thereby releasing potential chemical energy in the form of heat. There are three basic components of the combustion process; fuel, oxidant and diluent. A fuel is a compound containing energy rich bonds such as carbon-carbon or carbon-hydrogen bonds. When an oxidant, such as molecular oxygen, is present under the right temperature conditions, the combustion reaction occurs, releasing significant amounts of energy. Since air is the most common source of oxygen and since it contains other elements in its molecular composition, (the most notable of which is nitrogen), these other elements are present during the combustion process. Impurities in the fuel are also present. These additional substances are considered diluents and do not participate chemically in the reaction but rather influence it by heat absorption thereby acting as a thermal sink. In addition to nitrogen, other commonly present diluents include excess amounts of oxygen beyond stoichiometric requirements and fuel contaminants such as sulfur, chlorine and ash. The presence of these diluents are a practical reality to any commercial fuel-burning process, and they are not considered a limitation to highly efficient combustion.

Coal and waste oil combustion in a utility boiler is an oxidation reaction which must have oxygen present in order to occur. High temperature reactions occurring within the fuel itself when there is no oxygen present are known as pyrolysis. Pyrolytic conditions must be avoided since they have potential to convert PCBs and other organics into more toxic organic compounds. Because of the intimate mix of fuel and air in the highly turbulent combustion zone of a utility boiler, the addition of sufficient excess air and the fact that these potential byproducts are destroyed at much lower temperatures, their potential for emission from the Labadie boiler is essentially non-existent.

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On a macroscopic scale there are five parameters which effect combustion; appropriate physical and chemical properties, availability of combustion air, high gas temperature, long residence time and adequate mixing.

Physical and Chemical Properties

There are two basic physical properties which affect combustion of liquids such as waste oil; viscosity and the size and concentration of suspended solids. The lower the viscosity the easier it is to achieve fine atomization. The finer the drops of oil the greater the surface area exposed to the heat of combustion. This, in turn, allows for rapid vaporization giving more time for molecular contact with the oxidant and driving the reaction towards maximum completion. The viscosity of the PCB/oil blend is similar to No. 2 fuel oil. In addition a heat exchanger has been installed in line in order to maintain proper viscosity prior to the oil reaching the boiler. Finally, a special gun which provides finer atomization and which is more tolerant of changes in viscosity has been purchased for this purpose.

It has been shown that suspended solids in the fuel can impair atomization and cause plugging and buildup on the burner tip. Experience shows that the blended oil has negligible suspended solids. In addition, a duplex filter has been installed ahead of the pump to further protect against such occurences.

Important chemical properties to be considered are elemental composition, moisture and heating value. Typical contaminants for the waste oil and askarel were characterized. It was clear from this examination that no contaminants or moisture are present at levels of significant concern.

The heating value of the PCB/oil mixture is on the order of 19000 Btu/lb from which it is apparent that self-sustaining combustion can be easily accomplished. However, by system design, a coal supported flame of much greater magnitude will always be present.

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Combustion Air

As noted earlier, although considered a diluent to the process, excess oxygen above ideal stoichiometric levels is a necessity in the real world. This is the case because of the physical limitations in accomplishing complete and instantaneous mixing of fuel and oxidant at a molecular level. The additional oxygen is present in order to insure that the oxidation reaction is maximized. However, a diluent acts as a thermal sink to the process and if present in quantities too great, it will limit the reaction temperature and increase the mass flow through the boiler, thereby reducing the residence time. Therefore, an optimized balance must be struck wherein sufficient temperatures, residance times, and oxygen levels are all maintained.

The requirements for this balance in a PCB incinerator are a minimum 3 percent excess oxygen level while maintaining a gas temperature of at least 2192°F (1200°C ± 100°C) at a residence time of at least 2 seconds. Normal oxygen level for the Labadie boiler is between 3.5 an 4.5 percent. The controls are arranged to trip the waste oil feed should the oxygen levels fall below 3 percent. Therefore, it can be safely assumed that sufficient oxygen will always be present.

Temperature and Residence Time

Because residence time is so dependant upon temperature, they are discussed together.

As noted above, the minimum acceptable regulatory levels of temperature and residance time for complete PCB destruction are 2192°F and 2 seconds respectively. Scientifically a temperature of 2000°F and 2 seconds residence time are considered adequate.

Heat transfer, mass flow and reaction rates all increase with temperature. Therefore, all other factors being equal, the higher the temperature the more

complete the combustion. Obviously then, it is highly desireable to characterize the temperature regimes within the boiler as thoroughly as possible.

Elsewhere in this paper the difficulty in obtaining accurate measurements within the combustion environment of a utility steam-generating boiler is described. However, a research project designed to investigate boiler slagging problems was conducted on Labadie Unit #4 during 1977. The project was conducted by Battelle Laboratories under contract to the Electric Power Research Institute (EPRI) and included an entire series of temperature traverses at various points in the boiler. The temperature measurements were made using a shielded, high velocity thermocouple probe which was water cooled. During this same period optical pyrometer measurements were taken and correlation between the two was shown to be excellent. All measurements were taken between 540 and 560 MW with excess oxygen ranging between 4.8 and 5.2 percent. Over 120 individual observations were made. Later, additional optical pyrometer measurements were made on several Labadie boilers at four different loads ranging from 300 to 565 MW. Although the measurements were taken on various Labadie units, the boilers are essentially identical and the data should be representative of Unit #4 conditions. It should also be noted that any inaccuracy in these measurements is conservative in that the error introduced is generally considered to be on the low side because of the possibility of experiencing the cooling effect phenomenon due to water and steam flow through the boiler tubes.

Based upon this temperature data and knowledge of the boiler elevations at which these temperatures were taken, calculations were performed to determine residence time at various points within the boiler. Gas flow at standard conditions and 4 percent excess oxygen was determined using stoichiometric calculations based upon "as burned" ultimate coal analyses. Finally, using boiler dimensions and starting from the waste oil burner level, a temperature and residence time profile was determined at four different loads. Figure 4 summarizes the results of these calculations.

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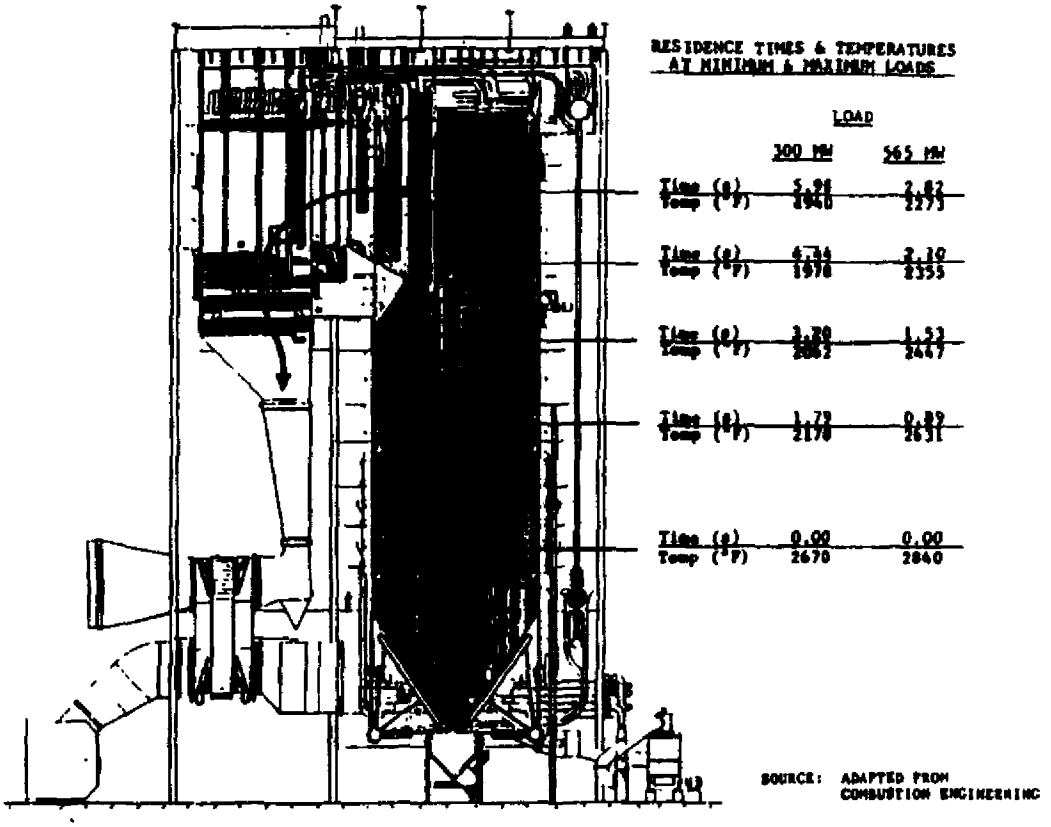

Figure 4. Side Elevation of Controlled Circulation Steam Generator for Labadie Units

Table 1 below shows the temperature of the gas after a two second residence time and the average temperature of the gas during this two second period. This information demonstrates that temperature and residence time requirements for complete PCB destruction are exceeded in this boiler even at lower loads. As previously described, a minimum load level of 300 MW has been established which insures that proper destruction conditions will always exist within the boiler when incineration takes place.

TABLE 1

GAS TEMPERATURES (°F)

AT A TWO SECOND RESIDENCE TIME

Unit	Unit Load	Gas Temperature @ 2 Sec. Residence Time	Average Temperature During 2 Sec. Time
1	300	2154	2412
4	375	2251	2484
3	400	2255	2493
2	460	2183	2480
3	565	2371	2606
4	580	2351	2634

Mixing

The final parameter which is key to complete destruction of PCBs is mixing. As previously noted, in order for the combustion reaction to occur, the fuel and oxidant must mix at a molecular level. This mixing is achieved by the creation of turbulent flow. An inherent feature of the tangential firing mechanism of the Labadie boiler is the turbulence which occurs when the coal/air mixture is blown into the boiler at high velocity. The vortex established results in a large swirling ball of flame. Action of adjacent fuel streams on each other augments the highly turbulent condition and this turbulence as well as oxidation, is further encouraged by the introduction of jets of secondary air around each burner.

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The PCB/oil blend is injected at a low point in the flame bell and therefore is exposed to the maximum mixing possible.

TEST BURN

In the early stages of the project EPA Region VII requested a formal test plan be submitted for review and approval. Recognizing the need to show equivalency to a PCB incinerator and the inherent dangers in pushing laboratory analyses to their absolute sensitivity limits it was decided that the sampling method selected must collect sufficient sample to demonstrate appropriate destruction levels and minimize potential for false positives. After extensive study and evaluation and in conjunction with Environmental Science and Engineering, the stack testing consultant, a comprehensive test plan was prepared for submittal to EPA.

Test Plan

The basic scope of the test program consisted of conducting four test burns with the first test being conducted without burning the PCB/oil blend to serve as a baseline. The next three tests would be while burning 5% PCBs in oil with boiler loads at or near 300 MW (i.e. worst case conditions). During each test burn, samples of stack emissions, fly ash, and bottom ash were collected as well as various support samples such as waste oil, coal and river water used for eluicing ash. Oxygen, carbon dioxide, and carbon monoxide were continuously and independently monitored in the boiler backpass by the stack testing consultant. All samples except the coal samples were analyzed for PCB content. Stack gas, fly ash, bottom ash, and river water were also analyzed for polychlorinated dibenzo-P-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Two separate sampling trains were used for collection of stack gas samples. Both trains were identical with the exception that the organic traps in the PCB train were packed with Florisil whereas the traps in the PCDD/PCDF train were packed with XAD-2 resin. Backup traps were provided to check for possible breakthrough.

The approach selected for collection of stack gas samples consisted of employing a high volume source sampling (HVSS) version of the EPA Method 5 train

appropriately modified to collect PCBs and other chlorinated organics at high sampling rates. The train design (Figure 5) was essentially based upon the methodology described by Beard & Scheum in EPA's interim policy guideline document "Sampling Methods and Analytical Procedures Manual for PCB Disposal: Interim Report, USEPA office of Solid Waste, February 1978." However the method was modified by scaling up the design to collect samples at a nominal 5 cfm flow rate as opposed to the more standard 1 cfm.

Collected stack samples were extracted with hexane using a Soxhlet extractor followed by concentration and sulfuric acid cleanup. Quantitative analysis for PCBs was performed using gas chromatography with electron capture detection (GC/ECD) with confirmation as necessary by gas chromatography mass spectrometry (GC/MS) in the selective ion monitoring (SIM) mode. GC/MS-SIM was also used for determination of PCDDs and PCDFs.

Extensive quality assurance was established both in the field and in the laboratory. For example elaborate glassware cleanup was conducted prior to each test. A third sampling train was placed on the stack during each burn to provide a direct check for contamination. All equipment was calibrated to NBS traceable standards immediately prior to the test burn. In the lab selected samples were analyzed in duplicate. Spikes and blanks were analyzed as were EPA Quality Control Samples at three levels of detection. For a more complete discussion of the sampling and analysis protocol, see a paper by A. J. Polcyn, et al titled "PCB Waste Destruction Study: High Efficiency Boiler" presented at the APCA Specialty Conference on Measurement and Monitoring of Non-Criteria (Toxic) Contaminants in Air, (March, 1983).

TEST RESULTS

The test burns were conducted on May 19-24, 1982. Four test burn runs were originally planned. However, failure of one of the stack sampling trains to meet EPA Method 5 criteria for a post-test leak check voided the fourth run requiring that a fifth run be conducted.

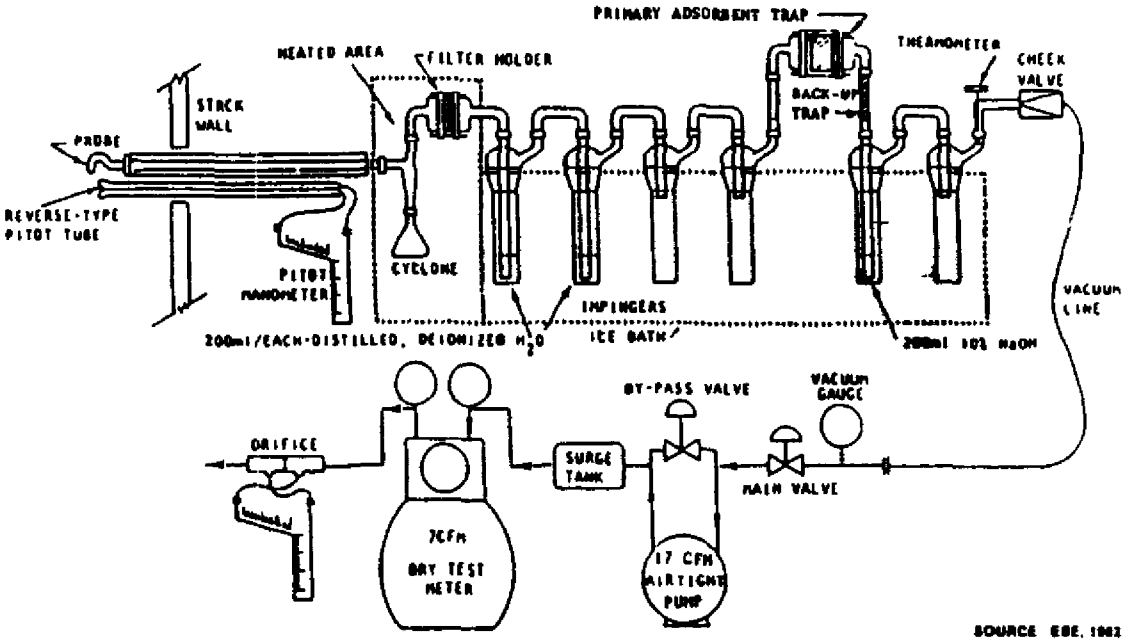

Figure 5. Modified Method 5 for PCB Sampling

PCB test results are presented in Table 2. PCDD and PCDF test results are presented in Table 3. In summary, the test results show that no PCBs, PCDDs or PCDFs were detected in any of the emission samples nor in any of the bottom ash or fly ash samples collected during each of the test burns. Based upon this information it can be stated that the Labadie Unit #4 boiler demonstrated a PCB destruction efficiency of greater than 99.99999 percent.

All of the results given for the PCBs leaving the boiler are presented as less than the stated value for the respective collected sample. This presentation of results indicates that the detection limit of the analytical method for the given sample was reached or that detection below the stated value was limited by interference from other organics that could not be removed without also stripping the organics of interest (PCBs). Where the latter situation was true, every effort was made to clean the sample extracts by successive acid rinses until no reasonable further improvement was observed. This may be noted in the case of the PCBs reported in the stack gas samples collected during runs 1, 3, and 5 which are reported as less than 600, 250, and 150 nanograms, respectively. Note that although Run #1 was the background run, this sample was observed to have a higher level of interfering organics than those samples collected during the PCB burn runs. Although the oil burned during the background run was off spec No. 2 fuel oil which when analyzed was found to contain a low level of PCBs (20 ppm) it is unlikely that the quality of this oil could have contributed significantly to the total level of organics in the sample. However, a large change in load was initiated during the latter portion of the background run which could explain the higher level of interferring organics.

All of the control train extracts were found to be below the method detection limit and therefore demonstrate that sample train preparation, sample recovery, extraction and analytical procedures did not introduce any errant contamination or other interfering bias. As well, seperate analyses of each Florisil backup trap, which were also found to be below the method detection limit, suggest that no breakthrough of PCBs occurred.

TABLE 2

Parameters	Units	Run #1 (Baseline)	Run #2	Run #3	Run #4*	Run #5
Average Generating Load	MW (Gross)	400	357	363	315	308
Sampling Period	Minutes	300	240	300	300	300
Average Stack Gas Flow Rate	ACFM DSCFM	1,478,000 901,000	1,353,000 800,000	1,322,000 869,000	1,285,000 815,000	1,247,000 781,000
Total Sample Gas Volume	DCF (metered) DSCF	838.9 803.3	587.9 566.0	830.0 797.9	N/A N/A	743.8 725.1
Total Quantity of Waste Oil Burned	Gallons	3,738	2,611	3,200	3,484	3,048
PCBs in Waste Oil	ppm (ug/gm)	20	47,000	50,700	N/A	51,400
Total PCBs Into Boiler	kg	0.25	408.6	540.2	N/A	521.6
PCBs in Stack Gas Samples	ng	<600	<50	<250	N/A	<150
PCBs in Back-up Traps	ng	<50	<50	<50	N/A	<50
Total PCBs Exiting Stack	ng	<202	<14	<83	N/A	<49
Destruction Efficiency	Percent	N/D	>99.999997	>99.999985	N/A	>99.999991
PCBs in Blank (Control) Train	ng	<50	<50	<50	N/A	<50
PCBs in Fly Ash	ng/gm	<6	<8	<6	<5	**
PCBs in Bottom Ash	ng/gm	<0.4	<0.5	<0.6	N/A	<0.3
PCBs in River Water	ng/ml	<0.02	<0.03	<0.02	N/A	<0.02

* Run #4 had to be voided due to an unacceptable post-test leak check on the Florisil (PCB) train.

**The fly ash sample for Run #5 was lost due to breakage in transit, therefore, the Run #4 fly ash sample was analyzed. Note that test conditions during Runs #4 and #5 are similar.

Source: RSE, 1982.

TABLE 3

SUMMARY OF POLYCHLORINATED DIBENZO-P-DIOXIN (PCDD) AND

POLYCHLORINATED DIBENZOFURAN (PCDF) TEST RESULTS

Parameter	Units	Analysis Results			
		Run #1	Run #2	Run #3	Run #5
PCDD Compounds in XAD Train Extract	ng	<800	<800	<800	<800
PCDF Compounds in XAD Train Extract	ng	<800	<800	<800	<800
PCDD Compounds in Fly Ash Extract	ng/gm	<42.5	<34.2	<18.0	<16.7
PCDF Compounds in Fly Ash Extract	ng/gm	<42.5	<34.2	<18.0	<16.7
PCDD Compounds in Bottom Ash Extract	ng/gm	<9.4	<10.1	<10.5	<10.4
PCDF Compounds in Bottom Ash Extract	ng/gm	<9.4	<10.1	<10.5	<10.4
PCDD Compounds in River Water	ng/ml	<0.4	<0.4	<0.4	<0.4
PCDF Compounds in River Water	ng/ml	<0.4	<0.4	<0.4	<0.4

Source: ESE, 1982.

CONCLUSION

Based upon the design modifications, technical analyses and trial burn results, the EPA Regional Administrator authorized the use of Labadie Unit # 4 for destruction of PCBs at a level of 5% in mineral oil dielectric on January 20, 1983. It was the Agency's conclusion that the system described "does not present risks of injury to health or the environment" and that the "disposal has been demonstrated to provide PCB destruction equivalent to an incinerator meeting the requirements of 40 CFR 761.70." As well it is the conclusion of Union Electric that this means of disposal of PCBs provides a sensible and cost effective means of solving a sensitive environmental problem while at the same time conserving a valuable energy resource.

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Discussion

Q1. What was the burn rate use?

A. 750 gph.

Q2. What was the local public reaction?

A. Union Electric conducted several public meetings and special press briefings, which resulted in quite balanced reporting and general public acceptance.

Q3. Have you done at cost-benefit analysis?

A. Strictly speaking, the process is marginally beneficial economically.

Q4. What is the plant worker attitude?

A. The plant manager met with the crews to discuss procedures used to minimize exposure. It has been accepted by the crews.

Q5. How much time have you actually been on line?

A. There have been 5-40,000 gallon test burns and 5 at the 5% level.

MONS 214998

ARC PYROLYSIS OF PCBs

ELECTRO-PETROLEUM, INC.

J. K. WITTLE EPI
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Program Summary

Electro-Petroleum, Inc., in cooperation with Pacific Gas & Electric, has undertaken a three-year program to design, construct, demonstrate and commercialize a high temperature DC arc furnace for the destruction of PCBs and PCB contaminated wastes. The technology is based upon the utilization of a direct current arc impinging upon a molten metal bath. The system is designed so that initial decomposition takes place in the molten bath and the resultant gaseous products are passed in the vicinity of the high temperature arc. The system reduces the PCBs to HCL, CO, H_2, and carbon by thermal pyrolysis. When solids are added to the system, they will melt and slag in the molten pool.

The arc furnace system is made up of three major subsystems. They are, the electrical system (power supply), arc furnace, and gas handling equipment. Major effort is underway to site the prototype system, provide for adequate environmental protection and develop analytical procedures for evaluating the process, as well as obtaining appropriate permits.

Program Objective

The objective of this project is to develop a mobile alternative technology to conventional incineration which can destroy PCB solids with an efficiency acceptable to regulatory agencies, at an acceptable cost for construction, operation and maintenance, and with environmentally acceptable solid waste and waste streams.

Discussion

PCBs have high thermal stability and Federal legislation requires combustion temperatures in the order of 1600° C. for total destruction. Conventional combustion systems have several major problems which are: difficulty in maintaining 1600° C. temperature, generation of large gas volumes to be scrubbed, and difficulty in handling solids.

MONS 214999

A viable and highly desirable alternative method for the total and final disposal of all types of PCB waste is by use of the Electro-Petroleum DC arc pyrolysis technique. This technique, based on arc furnace technology and originally developed for municipal trash disposal, was issued as U.S. Patent 3,812,620. This technology can be expanded to handle PCBs by designing a sealed system utilizing materials compatible with environment in the arc furnace.

Basically, the process is one in which the PCB will be initially decomposed in a molten metal bath. In the region above the molten bath the gases, including PCB vapor, will be subjected to intense UV radiation and heat from the arc plasma. The decomposition products will then be directed in the vicinity of the high current DC arc which will have a temperature in excess of 6000° C. There is considerable evidence that PCBs are totally destroyed at 1600° C. and are converted to biologically acceptable gases. Analysis of the products created in electric arcs in PCBs have substantiated these claims. Our direct current arc pyrolysis approach decomposes liquid PCBs to CO, CO_2; H_2, CH_4, and HCL. The conversion of the inorganic materials in capacitors and other utility wastes will produce a harmless residue from which the metals may be recovered. Organic materials, such as paper and plastics, will also be totally destroyed along with the PCBs.

This progam is intended to be completed within a three-year period from start of engineering effort to final commercialization. In order to commercialize the process in the shortest amount of time, a Joint Venture Company is being formed with a waste management company to manage the project, and offer to utilities a commercial service for PCB capacitor destruction. It is the intent of the Joint Venture to provide the number of units to meet market demands for capacitor disposal services.

System Design

A mobile arc furnace was sized to dispose of the largest PCB capacitors currently being removed from utility service and will be treated at a rate of 1.5 tons per hour.

A novel feed system will permit the introduction of sealed capacitors to the system and minimize contact of workers to the PCB. This approach was selected after evaluating a number of alternative feed devices. A lining has been selected which is resistant to the environment of the furance. The bottom electrode is designed to be an integrated portion of the furnace shell. The top electrode will utilize available arc furnace technology for positioning, moving and sealing techniques

in its construction. This electrode will be hollow so that gases generated inside the furnace will be forced into the vicinity of the arc plasma, thereby insuring total destruction of the PCB materials. Existing technology will be utilized for the removal of metal and slag from the furnace.

Gases exiting from the furnace will be treated in a fume handling scrubber system designed to meet the most stringent air emissions regulations as specified by California Bay Area and Southcoast Area Air Quality Management Boards.

Power will be supplied by a DC power supply which was selected from seven potential candidates. The selected power supply proved to be small and more cost effective than other supplies while providing controlled power to the arc furnace and minimizing harmonics feedback to the utility power system.

Three potential sites have been selected in the PG&E power distribution area. They are located at three remote sites near Kettleman, California.

Permitting agencies have been identified with contact having been made with those having regulatory control for PCB facilities.

A public information program is also being developed.

Cost analyses have indicated that this is an economically viable process, which will be environmentally more acceptable than current technology .

The system offers several other significant advantages over existing technology:

1. Pyrolysis produces significantly less gaseous byproducts to be treated.
2. Total decomposition is assured at the ultrahigh temperatures in the furnace.
3. The molten metal pool in the arc furnace solves the hearth problems of conventional furnaces.
4. Passage of exit gases in the vicinity of the high current arc exposes the gas to at least 6000^{0} C.
5. The gas in the furnace will be subjected to intense ultraviolet radiation from the arc.
6. The system generally uses developed technology.
7. Capital equipment costs are projected to be substantially less than conventional incinerators of comparable capacity.
8. The small size of the equipment suggests that it will be possible to move it from site to site.
9. The process handles sealed containers which need not be opened or shredded prior to introduction into the furnace.
10. The process has the potential to recycle the metals from the capacitor cans.
11. Produces environmentally safe byproducts.

MONS 215001

CHEMICAL CLEANING OF PCB CAPACITORS

Leo Weitzman. PhD

Acurex Corporation
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INTRODUCTION

The disposal of capacitors containing polychlorinated biphenyl (PCB) dielectric fluids is a major problem for the electric utility industry. Before March 1, 1981, the Environmental Protection Agency (EPA) had allowed their disposal in chemical waste landfills; however, with the start of operation of the Energy Systems Corporation (ENSCo) incinerator in El Dorado, Arkansas, EPA ruled that sufficient capacity was available and landfilling would no longer be permitted. This prompted an effort by the EPRI to identify other technologies with which to destroy them. This paper describes a series of studies performed by Acurex Waste Technologies which evaluated the chemical destruction of PCBs in capacitors and designed a system to do this.

One of the major difficulties in establishing new PCB disposal facilities is the objections voiced by its neighbors. There is no need to elaborate on the "not in my back yard" arguments voiced in opposition to such facilities. Chemical processing of capacitors sidesteps this issue by allowing the operation to be made mobile. Mobile liquid PCB destruction systems have run into no such opposition in the past. As a result, the number of processes built can be governed by the requirements of the market rather than availability of potential sites. In addition, chemical processing systems do not require site-specific air permits as they are not considered air pollution sources. Because of these considerations, chemical destruction of PCBs was investigated through this multi-phase study.

The study consisted of the following phases:

1. Phase 1, published in June, 1982 (1), was a literature search and theoretical evaluation of the concept. In addition, the EPA permits and approvals needed for Phase 2 were obtained.

2. Phase 2, completed in November, 1982, was a laboratory study which resulted in:
   - design data for a full-scale system
   - a medium size pilot unit
   - costs for the process, both capital and operating
   - conceptual design of the full scale operation

3. Phase 3, now in progress, is a design of the pilot system.

The bulk of the work was performed under Phase 2 and this paper will deal mainly with these results. The other work will, however, be included as appropriate.

CHEMISTRY OF PCB DESTRUCTION

It is known that sodium can, in the presence of naphthalene and tetrahydrofuran, dechlorinate organic molecules such as PCB's. Work has been done in this area by several investigators since 1936, (1, 3, and 4). The procedure works as follows:

- Prepare a sodium reagent by mixing sodium metal with the proper amounts of naphthalene and tetrahydrofuran. This must be done under nitrogen as air and water will react rapidly with sodium and deactivate the reagent. The reagent is referred to as sodium naphthalide and is represented in this report by the symbol Na*.
- The reagent is added to the PCB-contaminated material and the PCB destruction reaction is permitted to occur.
- After the reaction has taken place, the excess sodium is quenched with water, converting it to sodium hydroxide.

PCBs are destroyed via a reaction of the sodium naphthalide radical anion (Na*) with the organic chlorine. The reaction proceeds in steps, one chlorine removed at a time. The products are sodium chloride and a complex mixture of nonchlorinated polyphenyls, as well as the sodium hydroxide formed during the quenching of the excess sodium with water. The chemical reactions are illustrated in simplified form below:

$$Cl_4H_6(BP) + 2Na^* \rightarrow Cl_3H_6(BP)Na^* + NaCl$$

$$Cl_3H_6(BP)Na^* + H_2O \rightarrow Cl_3H_7(BP) + NaOH \text{ or}$$

$$2\ Cl_3H_6(BP)Na^* \rightarrow Cl_3H_6(BP) - (BP)Cl_3H_6 + 2\ Na^*$$

These reactions illustrate what happens to a tetrachlorobiphenyl, identified as $Cl_4H_6(BP)$. The term (BP) refers to the biphenyl structure. As shown, the product is either a trichlorobiphenyl or an undefined polymer that includes the chlorobiphenyls. The sodium will continue to remove chlorine from these compounds until the nonchlorinated form is reached. At this point, the PCB molecule ceases to exist from both a legal and technical point of view. With proper design of the system, it is possible to achieve essentially complete destruction of the PCB at least to the limit of measurement.

The basic process described above suffers from a number of drawbacks. The most significant is that naphthalene is classified as a "priority pollutant". Its presence in any residue formed by the process could subject the residue to disposal

limitations under the Resource Conservation and Recovery Act (RCRA). There are a number of chemicals available to replace naphthalene in this process. Since these variations are, however, considered proprietary, the subsequent discussion will focus on the use of naphthalene.

In addition to the choices available for replacing naphthalene, there is no reason why only tetrahydrofuran (THF) needs to be used. The THF can be replaced by any one of a number of ethers such as dimethyl or diethyl ether, ethylene glycol dimethyl ether and diethylene glycol dimethyl ether, to name a few. THF was chosen for this purpose because when treating capacitors the ether acts as both a component in the formation of the sodium reagent and a solvent to carry the reagent to the solid material. The volume of ether required to cover the solid material in the reactor is more than required by the reagent. The THF on a per gallon (or per liter) basis is cheaper than the ethylene glycol ethers and safer to use than the dimethyl or diethyl ethers. Furthermore, the laboratory tests found it to be satisfactory from the point of view of reagent preparation and PCB destruction.

CAPACITOR DESCRIPTION

The laboratory experiments were conducted on a 15KVA Westinghouse capacitor of the FP Inerteen type. The unit was obtained from the Cincinnati Gas and Electric Company with the approval of EPA Region 5. The capacitor had the following Nameplate Specifications:

Manufacturer: Westinghouse Electric
Type: FP Inerteen
Normal Voltage: 2400
Maximum Voltage: 2640
KVA: 15
Phase: 1
Cycles: 60
Style: 1176665A
Test Number: 44K 2974
Capacitor contains 1.1 gal. of inflammable fluid (inerteen)

The unit's external dimensions were 4¼" deep by 13½" wide by 13⅜" high. The electrical connectors are 7½" high. It consisted of a steel case, approximately 1/8" thick. A cardboard shell inside the case shielded it from contact with the electrical packs. The capacitor packs were tightly wedged into the shell. A ceramic insulating plate was on top of the packs. I cannot be cut with a saw, A few important observations are worth noting. First of all, the material is wedged into the capacitor so tightly that it is impossible to inject reagent or solvent into the intact capacitor. Secondly the surface tension and viscosity of the liquid is so high that any flat surfaces that touch each other will tend to stick together. This prevents the solvent or PCB destruction reagent from reaching

all the surface areas. It is thus essential that the capacitor be properly cut up prior to treatment.

The unit was opened, drained, cut up and the components weighed and analyzed for PCB. The results were:

Total weight of the capacitor	29.8 kg
Weight of core material after draining	13.38 kg
Weight of shell material after draining	12.81 kg
Weight of PCB liquid drained	3.58 kg
PCB content of drained shell material	.67%
PCB content of drained core material	22 %
Total weight of PCB in the capacitor	6.72 kg
PCB content of total capacitor	22.6 %
Total volume of PCB liquid in capacitor, Identified as Askarel 1254 (density = 1.5)	4.48 l (1.18 gallons)

TECHNICAL APPROACH

The following two methods of treating capacitors were examined:

1. Solvent extract the PCB from the cut-up capacitor and concentrate the PCB for subsequent chemical destruction or incineration
2. Treat the cut-up capacitor material, solid and liquid directly with the PCB destruction chemicals.

It is recognized that several commercial processors have attempted to treat capacitors by extracting the PCBs liquid and sending it to incineration; however, we had understood that the cleaning of the core material had met with varying degrees of success in the past and further work in this area appeared warranted. More importantly, it quickly became apparent that the chemical destruction method worked very well; if the PCB destruction chemicals could be made to properly penetrate the solid material, they would destroy the PCB. The solvent leaching tests, therefore, served as surrogates to help determine the best ways of getting the chemicals into the mass of the solid material.

Tests of the direct chemical destruction of the PCB with the capacitor solids were conducted to determine the following:

1. chemicals usage
2. capability of reusing components of the chemicals
3. temperature changes during the process
4. intensity of the reaction
5. rate of reaction

The successful end-point for all cases was considered to be a PCB concentration of less than 2 ppm (mg/kg) on the solid material and in the liquid phase.

Solids were analyzed for PCBs by extracting overnight using a Soxhlet extractor with hexane and analysing the resultant liquid with a GC/EC. The analytical method used was cross-checked with other standard methods, including extraction with methylene chloride and found to give consistent results.

The most important result from this set of experiments is that there does not appear to be any material inside the capacitor which inhibits the chemical destruction of the PCBs; that it is possible to destroy the PCBs without separating them from the capacitor solids. What is more, the destruction is almost completely stoichiometric in sodium. The sodium reagent is added to the shredded core material and then additional sodium is added to the slurry until all of the PCBs have been destroyed. The PCB destruction can be followed both by analysis of samples of the liquid and colorimetrically; the reagent itself is a dark blue-green in color. If the sodium is consumed by the PCB (or any other reactive material) it turns brown or gray. Addition of more sodium returns the blue-green color.

The economics of chemical treatment depend on the reusability of the other components of the reagent -- other than sodium which is consumed by the chemical reaction. The laboratory tests showed that 93-97% of the reagent is recovered when a reactor is drained after the PCB is destroyed. Higher recovery rates can readily be achieved in a properly designed system. This means that any excess sodium used, along with the tetrahydrofuran and naphthalene (or replacement chemicals for these) is largely recovered.

The reaction occurs very rapidly. The PCBs are destroyed in the liquid phase almost instantaneously; however, in order to allow the sodium reagent to penetrate into the pores of the core material, it is necessary to keep it covered with reagent for at least two hours. In addition, it is important that the solution be kept circulating to prevent the formation of pockets of sodium depletion where no reaction would occur.

The polyphenyl residue as well as the sodium chloride formed remains with the solid material rather than carrying over to the next batch with the liquid. This is important as no filtration of the liquid is required prior to reuse. Based on these results, it is possible to describe a conceptual chemical treatment system.

The first step in processing capacitors is opening them to expose the core material. The capacitor packs are typically about 4-6 inches in width. In order to assure that they become properly loose, it is necessary to shred them into pieces that are less than four inches. While a hammer mill can be used to achieve this size reduction, it is very dusty and would require a large dust suppression system to be used in this application. There are shredders available that would fit this application nicely. They are commonly used to shred a variety of materials ranging from scrap metal to tires and solid waste. They shred the material by squeezing it

between hardened disks that contain cutting teeth on them. Such a shredder would be more than adequate for achieving the needed size reduction.

An alternative method of cutting up the capacitors at a lower initial investment is an industrial saw. This would require an additional operator but its cost would be in the $10-20,000 range depending on the degree of automation required. A saw would be able to cut up approximately 500 to 1000 pounds of capacitor per hour; this is much closer to the design capacity of the rest of the treatment system and is probably more suitable for a demonstration system.

No matter which type of shredding system is used, it will be necessary to enclose it to prevent the release of fumes and dust. In addition, to minimize PCB fume formation, it will be necessary to cool the cutting system. A recirculating stream of transformer oil (PCB contaminated is acceptable) would be a good cooling fluid. In addition, at least a portion of the system would have to be enclosed to prevent the release of dust.

The shredded material along with the resultant free liquid is transferred to a reactor for processing. The reactor must have facilities for discharging solid material as well as for addition and removal of liquids. In additinn, it must have provisions for the circulation of the liquid through the mass of solid. It is very important that the reactor be air-tight, be nitrogen blanketed and have provisions for safe pressure relief such as a rupture disk or equivalent.

After being filled with the shredded material, the reactor is sealed and flooded with nitrogen to eliminate air. It is then filled with sodium reagent and the circulation started. Then sodium metal (either as a dispersion or as activated metal) is added slowly to the reactor until approximately 1.2X stoichiometric sodium has been added. A sample of the liquid is withdrawn. If it is the proper color, the system is allowed to recirculate for at least two hours with samples of reagent taken periodically. If the reagent changes color, more sodium should be added. After two hours, a sample of the solid material is removed from the reactor through an access port and quenched thoroughly with water. A sample of the soft core material is then macerated and mixed with a measured volume of a solvent such as hexane with rapid agitation. The hexane is then analyzed for PCBs. If it contains less than the required amount of PCBs, the reagent is drained from the reactor to a holding tank. The reactor is then flooded with water (slowly) to quench the excess sodium; quenching should take at least 30 minutes with good water recirculation. The water is then drained into a second holding tank. The now-treated solid mass of capacitor material is then dumped for disposal. It is no longer a PCB material and (if no naphthalene is used) it is a nonhazardous waste.

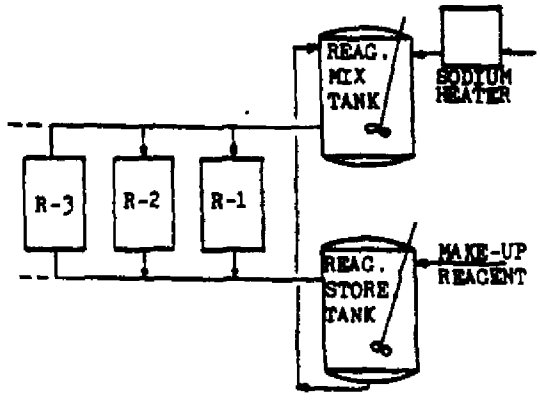


FIGURE 1
REACTION SYSTEM SCHEMATIC

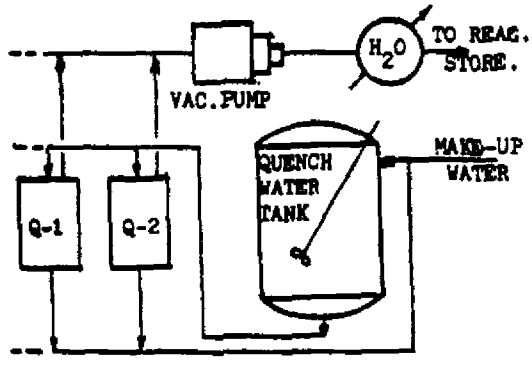
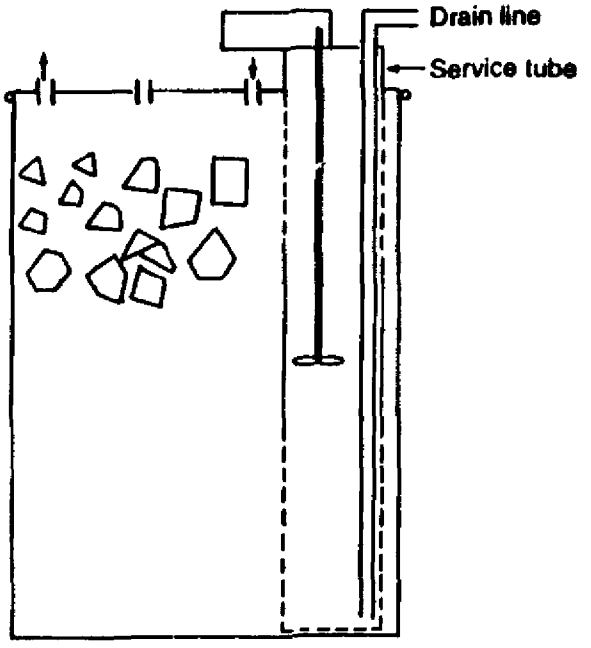


FIGURE 2
QUENCH SYSTEM SCHEMATIC

MONS 215008



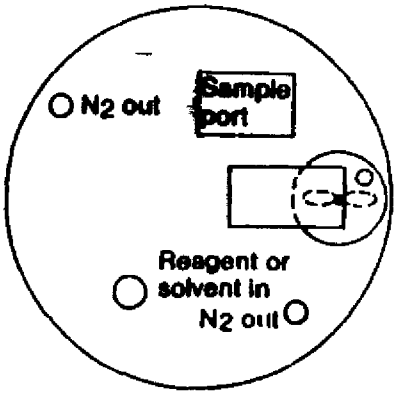


FIGURE 3
PROCESSING MODULE

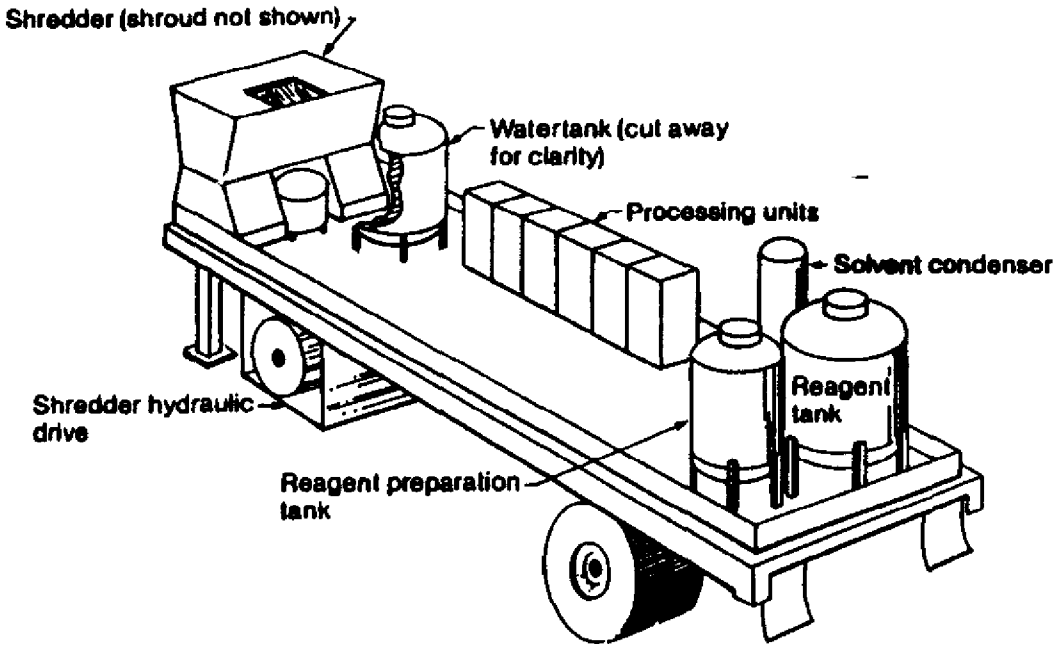


FIGURE 4
DEMONSTRATION SYSTEM

It is possible to change the through-put of a system very easily. The throughput of the design is limited by the number of modules that can be kept on the truck while the analyses for PCB are being performed. A cycle only takes about two to three hours. If provisions are made to remove the drained, but chemically still active, drums from the struck and storing them prior to quenching, until the analyses are complete, it should be possible to readily increase the amount of capacitor material decontaminated by as much as 50%. Conversely, by not installing or not using all of the modules on the system it is possible to reduce the capacity. In fact, for the purposes of a demonstration, it is only necessary to install as few as two modules on the system.

SOLVENT WASHING SYSTEM DESCRIPTION

The solvent washing system bears a strong physical resemblance to the chemical treatment system. This is because the physical layout and the large pieces of equipment are all governed by the type of solid material that is being processed. Both systems have a shredder or some form of capacitor cutting system and in both cases, the capacitors are treated in 55-gallon modules or drums. Furthermore, each module sits in a cell that is of the same configuration. While the process looks similar, the operation is very different. In the case of the capacitor washing system, each module is exposed to about 20 seperate cycles of washing with solvent. Since the time per cycle is about two hours, it is expected that the system will be able to process, at best, about 400 lbs of capacitors per hour.

The simplest method of washing the capacitors is to simply run fresh solvent from the reboiler into the processing module for each wash and then run the solvent wtih PCB back to the reboiler. This requires an approximate 200,000BTU per hour (about 60 KW) reboiler system which is difficult to heat electrically in a field location. It is possible to reduce this load in half or even lower by using the solvent 2 or 3 times before reclaiming it.

To illustrate, consider Table 1. This table shows the (somewhat hypothetical but adequate) values of the PCB content of the solids in a given wash and the liquids leaving it. If one were to match the liquid compositions of washes 1 with 11, 2 with 12, and so on, it becomes evident that if the liquid leaving wash (for example) 11 were directly pumped into a module containing material about to begin its first wash (#1), there is little or no loss in cleaning efficiency. The same is true of each of the washes paired in Table 1. In this way, the pure solvent enters only the washes going through the final stages of cleaning. It then goes directly into the modules containing material going through the first stages of cleaning. The load on the solvent reclamation system is thereby halved. These pairs of modules are referred to as "mates".

Table 1

ESTIMATED PCB CONTENT IN SOLIDS AND LIQUIDS
LEAVING SUCCESSIVE WASHES WITH PURE LIQUID

WASH NO.	SOLIDS PCB(mg/kg)	LIQUID PCB(mg/l)	WASH NO.	SOLIDS PCB(mg/kg)	LIQUIDS PCB(mg/l)
1	287,000	100,000	11	300	170
2	143,500	80,000	12	150	85
3	73,500	40,000	13	75	43
4	37,000	20,000	14	38	19
5	19,000	10,000	15	19	10
6	9,500	5,000	16	10	5
7	4,800	2,500	17	5	3
8	2,400	1,300	18	3	2
9	1,200	650	19	1.5	1
10	600	330	20	.8	0.5

Note: Liquid PCB in mg/liter

Solid PCB in mg/kg

NONS 215012

It is possible to further subdivide the washings into three or even four mates by cascading up in concentration; however, in practice the logistics of this becomes too complex. As it is, it will be necessary to provide the operators with some form of computer assistance to run the system. The system can work in the following manner:

1. Capacitors are shredded or cut apart and passed over a simple screen where the free PCB liquid is allowed to drain from them into a receiving drum.
2. The drained capacitor solids are packed into processing modules about 200 pounds (75kg) per module and placed into a processing cell where the system is connected.
3. Relatively clean solvent from the "mate" to this particular processing module then enters the module and it is agitated for about one hour.
4. The module is drained and the cycle repeated for an additional nine times.
5. After the tenth wash, the module becomes the first one of the two in the pair that are "mated". The "mate" to the module in question has completed the wash cycle, it has been drained, and the excess solvent has been vacuum stripped off from it. It is removed and a new module containing untreated solid is placed into it.
6. Now fresh solvent enters the module under consideration and at the conclusion of the wash, it is pumped into the mate.

As can be seen, multiplying this procedure by ten mates gets to be very complicated. In addition, it is necessary to go through a moderately elaborate startup procedure so as to establish the schedule. Clearly, computer assistance is required.

ECONOMIC EVALUATION

As was stated in the preliminary report on this subject, there appears to be no scientific or technical reason why PCB capacitors cannot be detoxified chemically. The question is rather, is it feasible to do so. This section explores the costs of alternative routes for the removal or destruction of PCB in capacitors. The following schemes are evaluated:

1. Shredding followed by chemical treatment of the total capacitor material.
2. Shredding followed by draining of the free PCB liquid followed by Freon washes to separate the PCB from the capacitor material. The liquid PCB is sent to an incinerator for disposal.

On the basis of the following evaluation, the costs of processing the capacitors and the capital investment involved are shown in Table 2. As can be seen, the capital investment for the capacitor washing scheme is higher than that required for chemical treatment. This is partially balanced by the lower chemical costs but the cost per pound of capacitor treated is still slightly higher. The difference is well within the bounds of the error of this analysis so it appears

that the cost per pound of capacitor treated is essentially the same whichever route is chosen. While the washing method does require an added investment, the level of technical expertise of the operators can be lower, since they do not have to work with sodium. This may be desirable for some conditions. The washing route should, therefore, not be eliminated as a visble option at this point.

This study was only intended to develop a conceptual design for the two types of capacitor cleaning systems. As a result, the costs can only be approximate at this time. The laboratory work gave reasonable values for the chemical costs and these are believed to be reliable. The capital costs are adequate for determining whether the basic process appears to be economical but because no detailed designs have been developed as yet, they can be as much as 30% on the high side. The costs of the various pieces of equipment, were generally estimated very conservatively. It was felt that a feasibility study such as this would be better served by using worst-case rather than optimisitc cost estimating techniques. Even when vendors of equipment provided reliable costs, 10-20% contingency factors were added for this study.

The operating costs were figured using the best estimate for travel expenses, hauling, etc. that were available. While they do incorporate a fair amount of judgement, they are based on the Author's experience in operating field systems.

As shown in Figure 2, on-site chemical treatment of capacitors appears to be cost competitive with incineration. The highly conservative cost estimate for the chemical treatment is approximately 50¢ per pound delivered to the incinerator. The cost of shipping capacitors varies from about 3¢ to 10¢ per pound depending on the distance they must be shipped. The cost of chemical treatment has been estimated using highly conservative methods. Further process refinements can reduce it significantly.

The solvent washing system, if operated by a crew who travels all over the country is estimated to cost 58.2¢ per pound of capacitor treated to operate. This makes it economically unattractive if a crew comes in from a distance; however, if the purpose of the system is to treat a utility's in-house waste capacitors, then the differential between chemical processing and solvent washing becomes only 4.3¢ per pound of capacitor treated. This is well within the limits of accuracy of this analysis and for all intents, the two methods are of equivalent cost. It is felt that the solvent washing system can readily be operated (if properly designed) by a utility's own personnel.

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Table 2

COMPARATIVE COSTS OF TREATMENT
FOR DIFFERENT SYSTEMS

	CHEMICAL TREATMENT	SOLVENT WASHING
Capacity (lb/hr)	900	400
(kg/hr)	400	180
Capital Cost (4)	220,000	300,000
Operating Cost		
Labor	8.0	9.0
Chemicals	12.8	9.4
Utilities	1.0	2.0
Waste Disposal	10.0	13.4
Maintenance	4.0	5.2
Field Costs	5.7	9.8 (0.9)
Depreciation (¢/lb)	8.3	9.4
Total Cost (¢/lb)	49.8	58.2 (49.3)

Note: ¢/lb, cents/lb of capacitor treated
The fitura in parentheses for the solvent washing system assumes that the system is operated by the utility for its own use, hence, no field costs for the crew is required.

MONS 215015

CONCLUSION

Chemical treatment appears to be a reliable, cost-effective method for the disposal of PCB capacitors. It has a number of advantages over other methods of disposal, including:

1. can be made mobile so there are no difficulties siting it
2. low capital investment
3. easy to build more capacity to meet market demand
4. environmentally acceptable

The process has been shown to be effective in the laboratory and, indirectly, on a pilot scale. It is now necessary to build a full-size module to test the system and then build a demonstration system so as to obtain the necessary cost data and permits for it.

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ACKNOWLEDGEMENT

The work described here was sponsored by the Coal Combustion Systems Division of the Electric Power Research Institute. Their support and the technical assistance of the EPRI project manager, Dr. Ralph Komai, is gratefully acknowledged.

MONS 215016

MOBILE PLASMA PYROLYSIS

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ABSTRACT

A thermal plasma, properly applied to toxic waste destruction, provides a pyrolytic environment with distinct advantages over other competing technologies. Complete atomization of organic fluids has been demonstrated to occur in less than one third of a millisecond. Kinetic recombinations of atomic entities are predictable. Chlorinated wastes produce a hydrogen chloride byproduct which is completely converted to salt in a caustic scrubber. Destruction efficiencies in excess of 99.9999999 percent have been corroborated by external monitoring agencies for the destruction of Askarel fluids with chlorine contents up to 58 percent.

Since this process is pyrolytic, the scale of the equipment is small for high throughput rates. Energy requirements for the destruction of Askarels are typically less than one kilowatt-hour per kilogram of waste. A mobile prototype unit is being constructed for the Department of Environmental Conservation of the State of New York for a throughput rate of one gallon per minute of liquid waste. The mobility and efficiency of such systems limit the controversy associated with siting fixed facilities.

MOBILE PLASMA PYROLYSIS

INTRODUCTION

The disposal of toxic and hazardous wastes continues to be a controversial matter. In North America, more than thirty five mega-tonnes of such waste requires disposal annually. More than ninety percent of this waste receives inadequate attention and is returned to the environment through leaking landfills and lagoons. In North America, approximately fourteen thousand landfills have been identified as contaminated with toxic materials, and one hundred and eighty thousand lagoons are perceived by the public as posing significant threat to health and environmental quality.

Imposing regulations which demand proper disposal of toxic and hazardous materials does little for the environment unless cost effective disposal alternatives are available to industry. All too often, public reaction to siting suitable technology thwarts such development efforts. Similarly, the costs associated with permitting appropriate technology create financially unattractive business ventures for large industries or are prohibitive for new growth industries. It must also be recognized that the regulations required for permitting some new technologies have yet to be written. The and result in such a scenario is that midnight dumpers prosper at the expense of the environment. It has been stated that we do not own this earth but we have merely borrowed it from our children. This attitude is profound when it is realized that 2,3,7,8 TCDD released to the environment requires about two billion years to thermally degrade to show a destruction and removal efficiency (DRE) of 99.99 percent at ambient temperatures. PCB and PCDF compounds require longer and have thus earned their reputations for persistence in the environment. Better procedures are required to favour the development and application of new technology if environmental quality is to improve.

First, let's consider the issues associated with the siting and operating of a new technology. Generally, three interest groups are involved and can be identified as either regulatory, enterprise or citizens. The regulatory representatives are concerned with the maintenance of the environmental quality. Ideally they would

like to see technology which destroys compounds such as PCB's and produces an effluent with zero residual toxic materials. However, technology has not as yet provided a mechanism of measuring zero residuals and thus regulatory standards are established. Initial standards of ppm were replaced with ppb and subsequently ppt levels, and before long we will be measuring femto-grams and atto-grams in the inevitable pursuit of zero. Enterprise representatives are concerned with profit and loss potentials which surround a waste disposal concept such as a high temperature incinerator. The concept must be able to compete with alternative disposal techniques on both cost and performance scales. However, as regulatory standards become more severe, monitoring and safeguard costs escalate to the point where a mega-scale complex is required to take advantage of economy of scale. It is recognized that it is difficult for any appropriate waste disposal technology to compete with often employed non-appropriate means of disposal and the question of corporate conscience is brought into play along with the third interest group, the citizens.

The citizens' representatives are the guardians of the heritage of our children. They demand a safe environment and are reluctant to see a mega-scale complex sited in their neighborhood. Such a complex will attract a continuous fleet of tankers which pour pollutants from abroad into their vested domain. The dangers of transport accidents represents one type of isolated threat. In contrast, what goes into the complex must come out as a detoxified effluent to the degree that the regulatory standards can be met. This means that a continuous threat is posed by the effluent stream which, albeit dilute in residual toxic material, is perceived to contaminate the neighborhood with wastes from abroad. Using today's standards for many regulated wastes, of a DRE of 99.99 percent, it can be readily shown that the processing of a mega-tonne of such waste will contribute one hundred tonnes of dispersed effluents to the neighborhood, a most unappealing proposition.

If the new facility can be demonstrated to give a higher DRE, than the effluents would have a smaller impact on the surrounding community. Similarly, if the facility could operate cost effectively at lower throughput rates, then the rate of buildup of effluents in the community would be proportionally reduced. In addition, if the citizens' representatives could be assured that minimum effluents would only stem from processing local wastes rather than transported regional wastes, then a better political environment would be created to deal responsibly with the annual production of toxic and hazardous wastes. Plasma pyrolysis offers high DRE in a mobile configuration which is cost effective with low

throughput rates.

THE TECHNOLOGY

The heart of this technology centres around the plasma arc device. A co-linear electrode arrangement is used to create an electric arc. Low pressure air is used as the medium through which an electric current is passed. In passing through the air, the electrical energy is converted to thermal energy by absorption by the air molecules which are activated into ionized atomic states, losing electrons in the process. A recirculation vortex dynamically produced inside the co-linear electrode arrangement ensures a stable plasma core with predictable performance. Ultraviolet radiation is emitted when molecules or atoms relax from the highly activated states to lower levels.

Waste fluids can be injected into the co-linear electrode space where they interact with decaying plasma species to become rapidly atomized prior to exiting the electrode space. An integral part of this process technology is the pyrolytic simulation computer model. New compounds which are created from the recombination of atomic species is predictable based on kinetic equilibrium. The minimization of Gibb's free energy is used to determine the equilibrium concentrations of product species over a wide range of selected temperatures and pressures. Thus appropriate operating conditions can be predicted for any organic waste fluid prior to its destruction, and undesirable products can be minimized or eliminated through altering the character of the fluid or the operating conditions. Changes in enthalpy between feedstock and output products are used to predict the plasma energy required adiabatically for the pyrolysis of the waste being treated.

At the Royal Military College of Canada, a pilot unit has been operating since 1979. Preliminary testing on that initial Canadian unit was conducted with Askarel which contained twenty percent each of aroclor 1254 and 1260 as well as sixty percent of trichlorobenzene. The results of the initial testing showed a DRE of 99.9999 percent. In 1982, the system was modified to include the co-linear electrode arrangement as shown in Figure 1-1, as well as increase the throughput capacity. The co-linear plasma device was mounted on top of a refractory lined, stainless steel vessel with a volume of approximately 0.5 cubic metres. A caustic soda liquid scrubbing system followed the vessel and an induction fan draws product gases through the system. Acid gas and graphitic carbon residues are trapped by the scrubber while fuel gas products are burned on the flare stack. Figure 1-2 illustrates the system in operation, destroying Askarel, and the flare stack flame can be noticed through the window of the laboratory. The scrubbing system

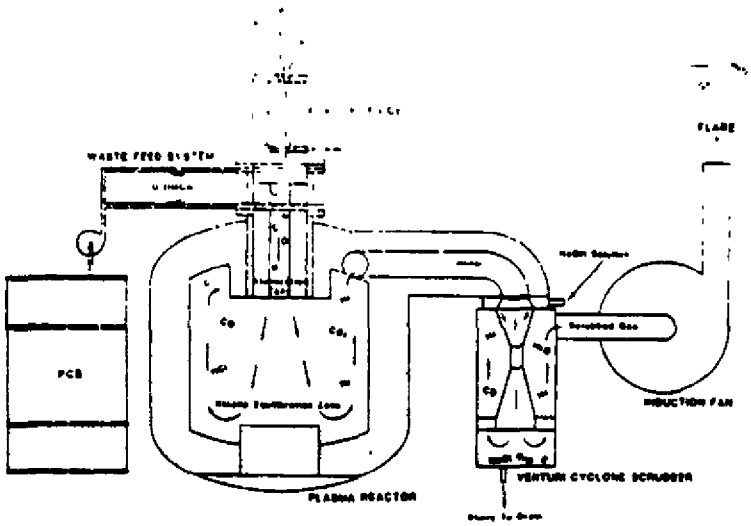

Figure 1-1. Pilot Scale Schematic

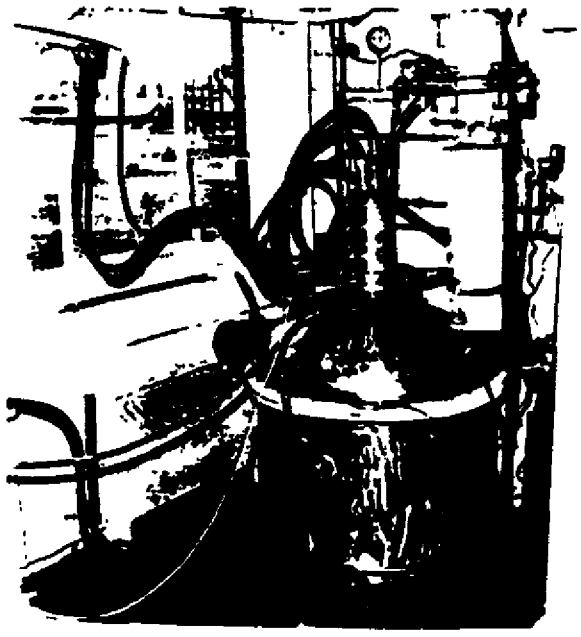

Figure 1-2. Pilot Unit in Operation

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had been calibrated and shown to recover approximately 96 percent of insoluble low volatile compounds. Measurements of PCB residual in the scrubber water were externally corroborated to be less than 0.17 ppt, giving a destruction efficiency in excess of 99.9999999 percent. It should be noted that the scrubbing unit employs a water and liquid caustic soda atomizing system which creates micron sized droplets that have a high trapping efficiency for acid gas and particulates. The amount of caustic soda injection is controlled by pH monitoring to ensure slightly basic scrubber effluent fluids.

An assessment of approximately forty emerging technologies was conducted by the Environmental Protection Agency (EPA). Five were selected for demonstration since they showed a high potential for successful application to toxic and hazardous wastes. Under a co-operative agreement between the EPA and the New York State Department of Environmental Conservation (NYSDEC) a demonstration program was established to further investigate plasma pyrolysis. A contract was awarded to Pyrolysis Systems Incorporated in Welland, Ontario in 1983 by NYSDEC for the fabrication and demonstration of a mobile prototype.

THE MOBILE PROTOTYPE

The mobile prototype unit is being constructed in Niagara Falls, Canada and is composed of nine major sub-assemblies which are completely contained inside a closed forty-five foot moving van type drop-bed trailer. These nine sub-systems link together to form the plasma pyrolysis system. In addition, a fully instrumented control room complete with on-line, close to real time monitoring is also located inside the trailer space. The unit is being sized for a nominal throughput rate of one gallon per minute, yet has surplus power and capacity to that nominally required. Each sub-system is briefly described along with the monitoring and failsafe considerations associated with the design of this unit.

Plasma Sub-System

The plasma sub-system is comprised of a power supply and a plasma device. The power supply is a six pulse thyristor water cooled unit rated at 500 kW and is located in the forward area of the trailer. Primary 480 volt, three phase power feeds the power supply from a commercial service line. The direct current power from the power supply is delivered to the plasma device to provide variable plasma output from 200 to 500 kW. The plasma device is horizontally mounted onto a refractory lined pyrolysis chamber which has an internal volume of approximately two cubic metres. While the co-linear electrodes serve as a plug flow atomisation zone for organic fluids, the pyrolysis chamber serves as a completely mixed

recombination zone. Residence times in the atomization zone and the recombination zone are approximately five hundred micro-seconds and one second respectively. The recombination zone is equilibrated at a temperature of 900-1000°C.

Domestic Water Sub-Systems

A two inch water connection is required to feed domestic water to the trailer unit. In the trailer, a header is used to vector domestic water to four separate user sections. Water is fed from the header through an air gap into a reservoir from which water is drawn for the scrubber. A second line feeds water through a deionization unit and subsequently through an air gap into a second conditioned water reservoir which provides cooling to the plasma device. A third water line vectors water to a heat exchanger which is used to cool the conditioned water loop. A fourth line takes water to the onboard laboratory sink and hot water tank system.

Conditioned Water Sub-System

The conditioned water system is designed to provide adequate cooling to the plasma system with water of suitable quality. This system includes a 130 gallon tank, a high pressure, high flow circulation pump, a heat exchanger and sufficient temperature, pressure, flow and quality measuring devices to ensure the adequacy of the system. Provisions are made to automatically dump portions of the conditioned water and add fresh deionized water to maintain the desired resistivity within this water circuit. In the event of a total power failure, the system is designed to be pneumatically charged, thus forcing the contents of the water storage tank through the plasma device and provide sufficient cooling.

Scrubber Water Sub-System

A variable speed pump is used to pump water from the scrubber water reservoir. A portion of this water is branched off the main flow to pass through the thyristor cooling loop prior to rejoining the main flow. Water used in the scrubber experiences a once through criteria and a flow rate of approximately 20-40 litres per minute is anticipated. Additional temperature, pressure and flow instrumentation are used to verify the operation of this sub-system. Provisions for pneumatic charging of the scrubber water reservoir to provide cooling and cleaning of the product gas is also included in the design of the system.

Caustic Soda Sub-System

The caustic soda sub-system is designed to meter sufficient sodium hydroxide into the scrubber water stream to ensure complete neutralization of acid gas and recovery of hydrogen chloride. Caustic soda reserves may be contained in either a separate tank truck or an external reservoir. Provision for onboard storage of approximately 55 gallons of caustic soda is made. A pH sensor is used to verify the condition of the spent scrubber water and provide operator signals for variation in speed of the caustic soda pump.

Gas Cleaning Sub-System

A three stage spray ring is located at the producer gas outlet from the plasma recombination zone. Water and caustic soda are fed into this ring where an atomizing spray creates micron sized droplets. These tiny droplets impinge on particulate matter in the product gas stream as well as react with the hydrogen chloride to form salt water. The temperature of the producer gas is reduced from the 900-1000^{o}C to less than 80^{o}C in this ring. The scrubber solution and quenched product gas are drawn into a cyclone system where particulate laden salt water is extracted. A pump on the sump of the fluid extraction cyclone vectors the fluid to a sanitary sewer drain. Provision is made for collection of a composite sample of this fluid which is then subjected to analyses. The quenched product gas is drawn off the cyclone by the induction fan sub-system.

Induction Fan Sub-System

The induction fan sub-system continuously draws on the reactor and scrubber units to maintain atmospheric to slightly negative pressure in the system. Producer gas from the induction fan passes through a three-way valve. During normal operation, this gas is vectored to the flare stack where it is electrically ignited. Since the gas is mainly hydrogen, carbon monoxide and nitrogen, it burns with a clean flame at a temperature of 1800-2100^{o}C. This flare stack serves as an air pollution control device to prevent the release of fuel gas to the environment. The potential to vector this fuel gas back into industrial furnaces will be considered later for site specific applications. In the event of a power failure, the three-way valve vectors the product gas through an activated carbon filter to block the potential release of undestroyed toxic material to the environment. Provision is made to sample the product gas prior to the flare.

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Compressed Air Sub-System

The compressed air sub-system supplies plasma air to the plasma arc device as well as compressed air for operating air valves, pressurizing the two previously described water reservoirs and blowing down the system for maintenance. A series of temperature, pressure and flow sensors are used to ensure adequate air supplies for each requirement. In the event of a total power failure, the air compressor is designed to have a reservoir of sufficient capacity to meet all pressurization and flow requirements.

Waste Feed Sub-System

The waste feed sub-system contains two process reservoirs, a variable speed pump and a series of automatic features which prevent selection of waste feed until appropriate reactor operating conditions are achieved. One process reservoir contains organic fluid such as ethanol and is used during a startup sequence as a precursor feed and during a shutdown sequence to flush the waste feed system. The second reservoir would normally be a storage reservoir at an industrial site. A flexible connection would normally be used to deliver the contents of that reservoir through the waste feeding system to the reactor. Provision is made for a 55 gallon onboard process reservoir into which waste materials can be pumped.

Failsafe Considerations

During normal operation, the plasma pyrolysis reactor requires approximately three minutes of warmup prior to commencing injection of toxic or hazardous wastes. Similarly, approximately twenty minutes are required for the cooling of key components prior to conducting post-run maintenance. These short cycle times make this unit basically an on/off system which can respond rapidly to adverse conditions. The system hardware is arranged to provide failsafe operation even in the event of a total power failure. Normal scheduled maintenance of pre-engineered components such as motors, fans, valves, meters and sensors should safeguard against unforeseen malfunctions. Thus, consideration for failsafe is limited to monitoring essential conditions and providing protection in the event of the development of an adverse situation. Three scenarios must be considered which include controlled operations, loss of plasma and total loss of power.

A MACSYM 350 process control computer is used to control the total operation of the system. Thus, under conditions which preclude total loss of power, the computer is programmed to provide operator warnings as well as take positive action in the event of adverse conditions developing. Under total loss of power,

the arrangement of the hardware takes over this function. Waste feed shutdown signals are generated under the following conditions:

- loss of plasma arc
- detection of unacceptable products
- loss of induction sub-system
- loss of cooling water sub-systems

The plasma arc may be lost as a result of electrode burnout. Calculations have shown that under this condition, as little as five micro-grams of undestroyed waste may pass through the pyrolysis system. This material would be trapped on the activated carbon filter which forms one of the failsafe features. Unacceptable products may include trace level detection of principle organic hazardous constituents (POHC's) or excessive release of hydrogen chloride from the scrubber.

In addition to generating waste feed shutdown signals and taking appropriate action, the computer system also provides operator warning signals, which if not rectified in a preset period will automatically shut the system down. Operator warning signals stem from monitoring the following conditions which are compared to computer programmed limit ranges:

- reactor temperatures
- scrubbed gas temperature
- scrubber water temperature
- scrubber water pH
- plasma cooling water temperatures
- plasma air flow
- water pressure
- caustic fluid quantity
- toxic waste fluid quantity
- flare ignition

Failsafe criteria are instituted to safeguard the environment. Obviously, the degree to which the environment is protected will bear directly on the accuracy of monitoring activities.

MONS 215026

Monitoring Techniques

While we may intuitively accept the theoretical conclusions, that the conditions evolving from the plasma arc will dissociate all organic compounds into their components, there are other factors to be considered under actual working conditions. The main ones are whether the feed stock is totally or only partially destroyed or dissociated, or whether re-combinations following dissociation will create more toxic compounds. These concerns can be addressed through accurate and precise monitoring and analysis of product gas, its scrubbing medium and minute quantities of deposits expected within the plasma pyrolysis system.

The prime objectives of the emission monitoring are to insure that the plasma reactor is achieving the required degree of destruction efficiency and that no new hazardous chemicals are being created in the process. These objectives can best be met by analyzing the product gas before it is flared. Detection of trace chemicals is assisted by their being at their highest molar concentration at that point, where they have yet to be altered through combustion. Sampling at this point should preclude the need for trace analysis of effluents further downstream.

In the mobile unit, trace analysis will be performed by a Hewlett-Packard 5792A gas chromatograph coupled to a Hewlett-Packard 5970A mass selective detector (MSD). The MSD has a detection level of one nano-gram while in the spectral scan mode and 10 pico-grams while in the selected ion mode. It is proposed to use this equipment in a manner which will provide an analysis in less than ten minutes, as close to real time monitoring for such trace analysis as technically possible. The physical nature of the product gas and the low concentration of chemicals being monitored require a carefully designed sampling system. A suggested analytical protocol would be that developed by the National Research Council of Canada for a study of pesticides in ambient air at concentrations ranging down to three pico-grams per litre.

A one hundred litre sample of product gas will pass through a heat traced line to a particulate filter to remove residual carbon. The cleaned gas then passes through an absorber with a capture efficiency of 99 percent. The adsorber is then rapidly heated to release trapped organics. A nitrogen stream carries the organics to the GC-MSD for analysis. The mass detector in its selected ion mode should provide a detection level of one pico-gram of POHC per gram of waste feed. The MSD in the specific ion mode will provide information on residual masses for six selected ions whose presence either indicates the degree of toxic waste destruction or the formation of new toxic compounds. If the concentrations of

these chemicals exceed the predetermined limits, automatic feed shutdown procedures will be initiated. If the concentration limits are not exceeded, the analysis cycle will then be automatically repeated.

The possibility of the formation of chemicals not specifically scanned for, by the above procedure, must also be considered. To determine whether such chemicals are being produced, the mass spectrometer will scan from ten to six hundred atomic mass units at appropriate time intervals. The detection of a significant concentration of an unknown compound whose mass is equivalent to that of a hazardous chemical will invoke a standard shutdown procedure.

Bulk gas analysis of the scrubbed product gas will also be performed at this sampling point located downstream of the induction fan. A Hewlett-Packard 5880A gas chromatographic system will provide on-line analysis of hydrogen, water, nitrogen, methane, carbon monoxide, carbon dioxide, ethylene, ethane, acetylene, propane, propylene, 1-butene and hydrogen chloride. The monitoring of water will assist in completing a water balance for the system. The analysis for hydrogen chloride will provide a means to monitor the removal efficiency of the hydrogen chloride by the scrubber. The operator will be alerted upon the detection of concentrations in excess of 200 ppm. In this way, removal efficiencies in excess of the required 99 percent will be ensured for a waste feed containing thirty-five weight percent of chlorine. The detection concentration to signal the operator can be adjusted in accordance with the chlorine content of the waste being destroyed.

SUMMARY

Production of the mobile plasma pyrolysis unit is well underway in Canada. The first unit should be ready for preliminary testing early in 1984. In that the pilot unit has shown unprecedented destruction efficiencies for PCB compounds as well as a high destruction efficiency for refractory compounds such as carbon tetrachloride, the mobile prototype should be equally effective in dealing with toxic and hazardous wastes.

No permit to construct has been applied for on this project since the unit is being built in Canada. However, other permit applications will be required prior to this unit operating in the United States. Permitting may be required under the Clean Air Act, the Toxic Substance Control Act (TSCA) and the Resource Conservation and Recovery Act (RCRA). Preliminary discussions indicate that the unit will be exempt by virtue of scale and stack size (four inch diameter) under

the Clean Air Act. Under TSCA, a permit for destruction of PCB compounds will be required and the technology will be regulated as alternative technology in contrast to combustion technology. However, waste PCB compounds do not exist as pure substrates. Commercial preparations normally contain solvents such as trichlorobenzene and thus this technology requires a permit under RCRA for wastes other than PCB. However, while RCRA recognizes thermal processes such as pyrolysis as distinct from incineration processes, regulations governing that permit application (RCRA part B sub-part X) have yet to be written.

Technology is taking an extremely serious approach to curb the irresponsible disposal of toxic and hazardous waste. It would be most unfortunate if demonstrated technology had to sit idle until the present program of developing permitting regulations is completed. Perhaps it would be more appropriate to reconsidar a more efficient alternative. That is, rather than write regulations which attempt to encompass all technologies, it would be more appropriate to review each specific technology and provide responsible guidelines under which it can operate. It is unlikely that all encompassing regulations will be effective and could conceivably restrict the commercial application of new technology to the global pollution problem.

The mobile concept which is represented in this report is highly effective in destroying wastes. It can operate cost effectively at small throughput rates. The performance of the pilot unit indicates that it could operate in a community without any environmental impact and thus destroy toxic wastes at industrial sites where they were created. The attitude of citizens' groups in Canada indicates that such groups are prepared to allow the destruction of their local hazardous and toxic wastes provided transportation of such wastes is minimized and importation of such wastes to their community is eliminated. Conceivably, this approach could reverse the trend favouring midnight dumpers and the development of new Love Canals.

MONS 215029

ENERGY AND BYPRODUCT RECOVERY FROM CHLORINATED HYOROCARBONS: CHLOE-CHIMIE'S VRC® INCINERATION PROCESS FOR POLYCHLORINATED BIPHENYLS

by

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ABSTRACT

Chloe-Chimie, a subsidiary of the French Groupe Elf Aquitaine, has developed and successfully marketed a heat and byproduct recovery process using waste chlorinated hydrocarbon residues. The prototype, full-scale incineration unit, termed the VRC® process, has been in operation in Saint-Auban, France since 1974 and has a capacity of 16,000 tonnes of waste materials per year. It can accept 2,000 kgs/hr of chlorinated waste, is designed to operate at 1200°C at a retention time of 5 seconds, and can produce 4,300 kgs/hr of clear 33% HCl. Tests with waste PCBs were conducted in October 1979 and May 1981 and showed no discernable PCBs, PCDFs, and PCDDs in effluents at detection limits of 0.1 ppb (100 ppt) for each entity. Borden Chemical is currently operating a larger Chloe-Chimie VRC® unit at its Geismar, Louisiana chlorinated solvents plant.

INTRODUCTION

Chloe-Chimie, as a leading European producer of chlorinated hydrocarbons, historically has faced the problem of disposal of highly chlorinated, refractory wastes. The research undertaken in the early 1960's led to the development of a series of incineration units, culminating in the fabrication of the VRC-2 unit. The latter "VRC-2" (from Valorisation des Residus Chlores, Type 2) is designed to burn more than 2 tonnes per hour of residues. The plant has an outstanding operational flexibility and recovers high quality hydrochloric acid solution of 33% w/w or gaseous hydrogen chloride, which can be either marketed or captive.

The plant has been licensed seven times as follows:

Spain	1976	Perchloroethylene residues
Morocco	1977	VCM wastes
USSR	1976/1981	Four plants
USA	1982	VCM residues

In order to demonstrate the high efficiency of this type of incinerator, tests were conducted on October 16, 1979 and from May 10-14, 1981, employing as feedstock used commercial PCBs returned from customers. The tests were carefully monitored to determine the possible presence of unburned PCBs and/or other oxidized harzardous compounds such as PCDFs and PCDDs in the effluents from the unit. EPA sampling and analytical methods were utilized (see Modified Method 5 Train, Appendix).

CONCLUSIONS

The incineration tests performed in the Saint-Auban plant on commercial, spent PCBs show clearly that this technology is able to achieve essentially complete combustion of commercial PCBs without fuel addition with HCl recovery as muriatic acid and comply with the recommendations of the EPA published in the Federal Register of May 31, 1979: that is to say, PCBs in emission gases were not detected at 0.1 ppb with a resultant destruction efficiency in the range 99.99997-99.99999%.

Oxidized byproducts of the PCBs combustion, such as PCDFs (polychlorinated dibenzofurans) and PCDDs (polychlorinated dibenzo-p-dioxins) were not found at a detection limit of 0.1 ppb (100 ppt).

More than 99% of the chlorine contained in the wastes can be recovered as 33% w/w HCl solution or as 100% HCl gas.

The VRC® unit can burn waste with a caloric value as low as 2,200 kcal/kg (3,700 BTU/lb) without additional fuel.

O&M costs for this technology range between 2.5-3.5% of capital investment. This is partly due to the minimal/almost lack of corrosion, but also to uninterrupted performance of the equipment over very long periods of trouble-free operation.

VRC® INCINERATOR AT SAINT-AUBAN

*. Historical

Built in 1915 to produce chlorine, the Saint-Auban facilities continue to be specialized in chlorinated hydrocarbons (600 tonnes of chlorine per day). The heavy and light end byproducts must be disposed in an enviromentally proper way and, since 1968, this has been accomplished by land-based incineration in an incinerator designed and constructed at the Saint-Auban facility. This unit produces and recovers HCl and steam without corrosion problems.

Recognizing its outstanding performance as an environmentally sound technique, the French authorities sponsored the construction of this plant and certified the tradename of: "Valorisation des Residus Chlores".

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- Description (see Chart 1)

The incinerator comprises:

- Furnace (F.101)

  A vertical, cylindrical furnace is designed to satisfy the previously defined temperature and residence time conditions (i.e., 1200°C and 5 seconds). It is lined with a refractory material specially selected for its corrosion resistance and durability.

- Burner (B.101)

  The furnace-burner has been developed and patented by Chloe-Chimie. This burner can handle liquids, as well as viscous fluids, containing solid particles and gases. This system requires no liquid pressure (gravity feed) and has a maximum air pressure requirement of about 0.4 bar (58.8 psig).

- Quench and Washing Tower (D.810)

  The quench (Chloe-Chimie's patent), a solid section made of graphite, was developed in cooperation with the French firm Vicarb-Grenoble. This very light, extremely reliable piece of equipment (more than 5 years of practically uninterrupted service at the Saint-Auban plant) reduces the temperature of the combustion gases from 1200°C to 60°C. The temperature of the quench is controlled by recycling cooled HCl solution. The same solution is also sprayed directly into the washing tower.

  The cooling loop, connected to the washing tower, is designed to operate in such a way that no HCl absorption occurs. A purge withdrawn from the loop eliminates ashes, metallic impurities, and/or other materials. This purge (approximately 25% w/w HCl solution), can be led from the washing tower to a tank where it decomposes the hypochlorites resulting from the neutralization of effluent gases. The decomposition gases (chlorine plus inerts) can be recycled to the furnace, and the resulting brine sent directly to the wastewater treatment system.

- Absorption Equipment (R.815)

  These units ensure the gas circulation and maintain a slight negative pressure in the furnace (venturi system). The increase in the solution's concentration is systematically accomplished through countercurrent mixing with the combustion gases. One, two, or three units are necessary, depending upon such factors as:

  - the chemical composition of the residues
  - the temperature of the available cooling water
  - the desired concentration of the final HCl solution

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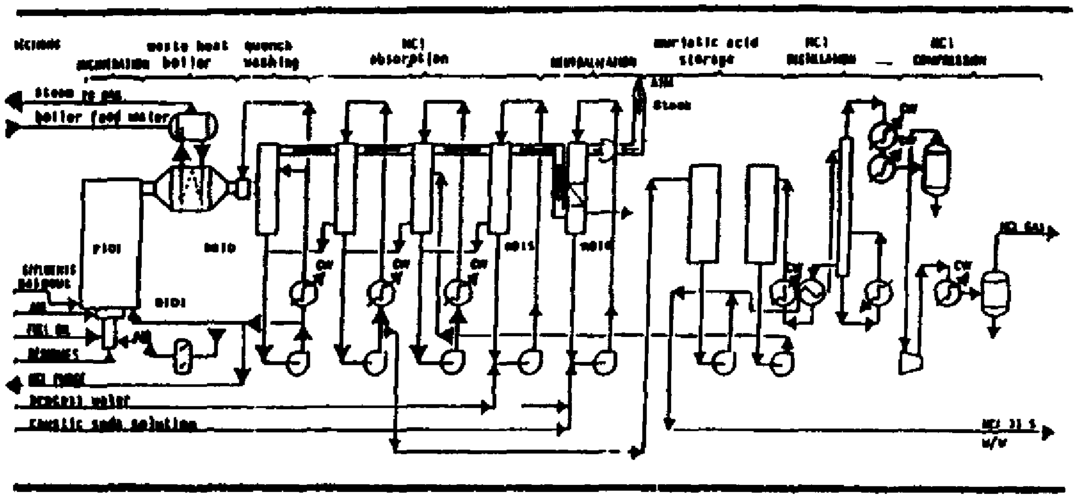
FLOW-SHEET OF VRC SYSTEM - CHART 1



PROCESS DIAGRAM

CHLOÉ Chimie

- Final Processing of Tail Gases (R.818)

  Without causing major changes in the pH and output conditions, a predetermined amount of caustic soda is injected into the neutralization stage to react with any chlorine and HCl that escapes absorption in the previous stages. Neither phosgene nor nitrogen oxides were observed in previous operations over the last six years at the Saint-Auban VRC® unit.

- Gas Effluent, Stack (F.101)

  After the caustic soda treatment section, the gas is practically chlorine- and HCl-free (i.e., less than 30 ppm), and easily meets the environmental protection requirements. Consequently, scrubbed gas is discharged directly to the atmosphere.

- Range of Residues Processed

  The VRC® unit was designed to incinerate waste byproducts from the following organic chemical manufacture:

  Vinyl Chloride Monomer (VCM)
  Trichloroethylene (Tri)
  Perchloroethylene (Perc)
  Carbon Tetrachloride (Tetra)
  1,1,1-Trichloroethane

  Some residues (from VCM for instance) are mainly composed of light ends and have a chlorine content less than 60% w/w. Other residues (from Tetra/Perc) containing 70% or more chlorine, are very viscous with a melting point over 160°C, and resemble tars. Residues with up to 74% chlorine maximum, i.e., 2,200 kcal/kg, may be incinerated without additional fuel, whereas other types of incinerators can only accept residues with 3,500 kcal/kg caloric value, and require fuel addition.

- HCl and Steam Recovery

  The present Saint-Auban plant, built before the 1973 oil crisis, recovers only HCl. Should this plant be designed today, a heat recovery waste heat boiler (WHB) must be added. Such a WHB, used in another plant of the group since 1974, has been licensed several times for use with waste incineration units.

  Recovered HCl is a marketable 33% w/w muriatic acid and the steam generated in the WHB is of average pressure in the range of 16 bars (230 psig).

INCINERATION OF PCBs

- Types of PCBs Incinerated

  The average composition of the spent PCBs trademarked PYRALENE T1® comprised a mixture of:

  - 60% DP chlorobiphenyl, which in turn, consisted of:

    50% hexachlorobiphenyl and

    50% heptachlorobiphenyl

  - 40% Tri- and tetrachlorobenzenes

  Fifteen tonnes of this product, liquid at room temperature, were charged to the VRC® incinerator in Saint-Auban and totally incinerated.

- Operating Conditions

  - Preparation of the Plant

    No modification whatsoever was made to the plant for the incineration tests using PCBs. The absorbers were emptied and rinsed with fresh water. Consequently, due to the relatively small quantity of PCBs burned, the concentration of the HCl produced was low: 20% solution at the termination of the test.

  - Technical Data for October 1979 Test

Duration of the test	15 hours
PCBs feedrate	0.8 tonne/hr
Gas temperature at furnace outlet	1,160°C
Retention time in the furnace	5 seconds

    The 3 tonnes balance, retained from the daily storage, was burned together with a new supply of aliphatic chlorinated hydrocarbons.

    Note: The furnace was formerly heated by ordinary wastes incinerated at the Saint-Auban facility (i.e., from VCM and chlorinated hydrocarbon production), so the startup with PCBs caused no problems as the caloric value of the PCBs was sufficiently high to allow burning without additional fuel.

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SAMPLING

Four samples were taken:

- Acid solution in the washing tower just after the quench, D.810 (see Chart 1).
- Muriatic acid production, R.815.
- Neutralized solution, R.818.
- Gas effluent in the stack, according to EPA Modified Method 5 (see Appendix).

RESULTS

Results of the tests are delineated in Tables 1 and 2. No PCBs, PCDFs, or PCDDs were found at detection limits of 0.1 ppb (100 ppt), respectively. Destruction efficiencies for PCBs of 99.99997-99.99999% were realized both for liquid and gaseous effluents.

ANALYTICAL METHODOLOGY

- Scope

  The methodology used to establish the amount of PCBs in the samples taken during the incineration tests was developed in the Rhone-Poulenc Research Center of Decines near Lyon as part of the Rhone-Poulenc research program concerning PCBs produced in its manufacturing facilities since 1946.

  This analytical protocol is a modification of the German "DAPA 1976 - Analytical zeitung 280-9-13-1976" and the method published by Drs. Han Rudolf Buser and Hans Paul Bosshard.

- Principle

  The PCBs present in the neutralized samples (aqueous) are extracted with a non-miscible solvent (hexane). The solvent phase is dried and concentrated and the PCBs present are analyzed by gas chromography, coupled with mass spectrometry and mass fragmentography (GC/MS/MF).

  The discrimination among PCBs, PCDFs, and PCDDs is accomplished using both differences in retention times on GC columns and molecular weights and the isotropic ratios of chlorine content per each type. Quantitetion is achieved by comparing the peak areas to well-known standards. The linearity of the responses in the working range of quantities is routinely checked.

Table 1. Liquids - Results

Component	HCl	Cl2	NaCl	NaOCl	Na_2CO_3	$NaHCO_3$	PCBs	PCBs out per hour	PCBs out / PCBs in (2)	PCBs Destruction Efficiency	PCDF	PCDD
Units	g/l	mg/l	g/l	g/l	g/l	g/l	ppb (weight)	mg/hr	ppm	%	ppb	ppb
Purge Acid from D.010	From 75.0 to 14.24 (1)	From 1.3 to 1.0 (1)	-	-	-	-	2.0	47	0.06	99.99999	(5)	(5)
Muriatic Acid from R.015	From 7.3 to 7.66 (1)	1.5	-	-	-	-	2.0	47	0.07	99.99999	(5)	(5)
Neutralized Solution from R.016	-	-	1.2	1.4	From 24.4 to 26.5	From 10.5 to 21.0	37.4	150	0.20	99.99997	(5)	(5)

(1) Variation observed during the test. It takes a certain time, the plant being washed and emptied at the beginning of the test to reach the equilibrium of concentration in the series of absorbers.

(2) Feed rate of PCBs : commercial 750 kg/hr
pure 525 kg/hr

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Table 2. Gaseous Effluents - Results

Component	CO	CO_2	O_2	Excess air	NOx	$COCl_2$	Ashes	Unburnt Particles	HCl	Cl_2	PCBs	PCBs out per hour	PCBs out(2) / PCBs in	PCBs Destruction Efficiency	PCDF	PCDD
Unit	ppm	%	%	% calculated	ppm	ppm		ppm	ppm	ppm	ppb	mg/hr	ppm		ppb	ppb
Sample trapped in the stack	≤ 150	from 6.6 to 13.5(1)	from 4.0 to [illegible](1)	from 20 to 90(1)	from 20 to 60(1)	(3) ≤0.5	non detectable	from 0 to 2(4)	≤ 30	≤ 1.5	13	61	0.12	99.9999	(5)	(6)
TOTAL EFFLUENTS												305	0.50	99.99999		

(3) Detection limit = 0.5 ppm
(4) Detection limit = 2 ppm
(6) Below detection limit of 0.1 ppb

- Miscellaneous

  In solution, chlorine content, unburned particles, ashes, phosgene, NO_x, CO, CO_2, and excess oxygen have been determined following standard methods.

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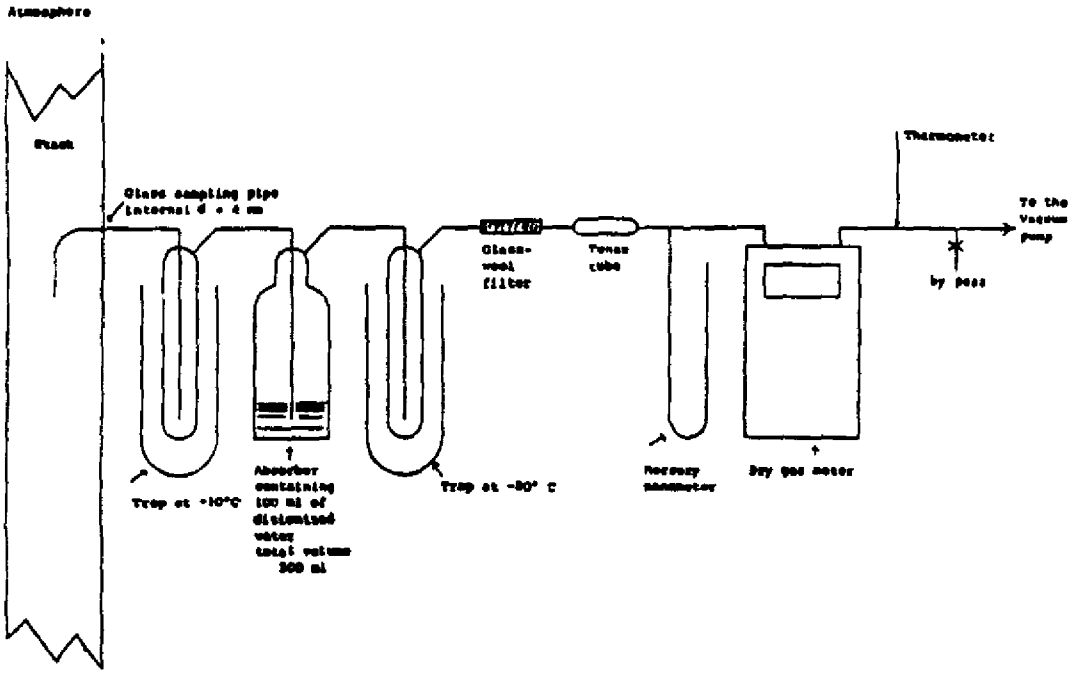
APPENDIX

Modified Method 5 Sampling Train

Sampling train, modified following the EPA recommendations concerning isokinetic sampling, pressure drop across system, and position of sampling line in a stack (different position of two diameters in the linear part of the stack). The total volume taken was more than one standard cubic meter for each sample.



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Part 6

PCB FIRES AND PCDF

PCBs, PCDFs, and PCDDs Resulting from Transformer/Capacitor Fires: An Overview

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Abstract

The purpose of this paper is to give an overview of what the author considers to be current information concerning PCB transformer/capacitor fires in the U.S. On December 15, 1983, the Environmental Protection Agency issued a national dioxin strategy for investigating, identifying, and cleaning up sites contaminated by dioxin. Within the framework of this strategy is a plan that calls for research to be conducted on PCB transformer/capacitor fires. This research will entail an investigation into the characterization of sources of PCDFs and PCDDs, that is, the chemistry of PCB fires and theoretical products of thermal stress based on composition of askarel used; emergency response protocols for firemen, including protective clothing; and practical remedial measures for building cleanup.

The author also feels that only through the sharing of information and full cooperation among electrical utilities, chemical manufacturers, firemen, insurers, EPRI, EPA, and NIOSH can "preventive maintenance" be performed to minimize or preclude future impacts of PCB transformer/capacitor fires.

PREFACE

On January 10, 1979, a railroad tank car carrying 75,000 liters of crude o-chlorophenol ruptured near Sturgeon, Missouri. Forty-seven workers from the Norfolk & Western Railway Company were employed to clean up the spill and in the process were exposed to a variety of toxic chemicals, including chlorinated phenols, phenol, and the toxic artifact, 2,3,7,8-TCDD (1). In fact, the concentration of this dioxin isomer amounted to only 22 ug/kg (ppb) (2). As a result of alleged exposure and the manifestation of certain perceived health effects and physiological symptoms, e.g., rashes, dizziness, loss of memory, extreme fatigue, impotence, upper respiratory difficulties, and in one case, cancer of the testicles and the skin, the workers brought suit in an Illinois court against the railroad company and the manufacturers of the tank car and the faulty coupling, including Monsanto, the manufacturer of the orthochlorophenol. On August 26, 1982, the Edwardsville, Illinois jury awarded the highest monetary judgments ever made as a result of a

single tankcar spill - $57.95 million (1). Prior to the commencement of the April 5 trial, Monsanto, General American Transportation, and Dresser Industries settled out of court for an estimated $8 million. This court decision represents the first time a jury has concluded that dioxin caused permanent harm to humans and thus has highlighted the more than 30 waste disposal sites within the State of Missouri that contain polychlorinated dibenzo-p-dioxins (PCDDs)(3).

Recently, in November and December of 1983, three separate suits (4)(5) were filed in St. Louis Circuit Court: in one case, by 57 persons who contend they suffered general systemic effects from dioxin-tainted soils at six sites in eastern and central Missouri - for $684 million; in a second case, by 25 dockworkers and a widow of a former dockworker of a trucking firm in St. Louis - for $620 million; and finally, by 183 people at Times Beach and Castlewood who assert that they suffered serious health deficiencies as a result of dioxin exposure - for $1.8 billion.

Therefore, this situation has catalyzed an acute public and governmental awareness of the potential severity and explosiveness of the PCDD problem. PCB transformer fires, accidental spills, and inappropriate disposal have compounded the problem particularly in regards to PCDFs (furans) and to some extent PCBPs (biphenylenes).

INTRODUCTION

The most toxic and extensively studied polychlorinated dibenzo-p-dioxin (PCDD) and -furan (PCDF) isomers are 2,3,7,8-tetrachloro-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF), respectively. There are pronounced differences in biological and toxicological effects between different PCDD and PCDF isomers. Those isomers with the highest acute toxicity are 2,3,7,8-TCDD, 1,2,3,7,8-PCDD, 1,2,3,4,7,8-HCDD, 1,2,3,6,7,8-HCDD, 1,2,3,7,8,9-HCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PCDF, 2,3,4,7,8-PCDF, and 2,3,4,6,7,8-HCDF (See Figure 1).

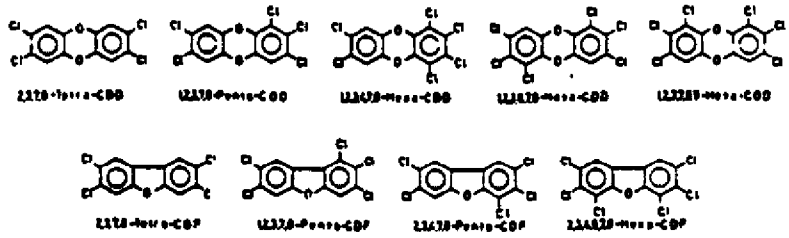

Figure 1. The most toxic PCDD and PCDF isomers (6).

Each of these isomers has its respective four lateral positions substituted for chlorine and each has LD_{50} values in the range of 1-100 ug/kg for the most sensitive animal species (generally the male guinea pig). There exist 75 PCDD isomers and 135 PCDF isomers. Acute toxicity among the isomers can vary up to 100,000 times (See Table 1). In comparison, the most acutely toxic PCB isomer is only about one-fourth as toxic as 2,3,7,8-TCDD (8).

Table 1. Acute oral toxicity of polychlorinated dibenzo-p-dioxins as dose expected to cause death of 50% of the animals within 30 days (7).

	Acute Oral LD_{50}, ug/kg Body Weight		
PCDD	Guinea Pig	Rat	Mouse
Di 2,7		>1,000,000	>2,000,000
2,8	>300,000		
Tri 2,3,7	30,000		>3,000
Tetra 1,3,6,8 mixed		>100,000	
1,3,7,9			
2,3,7,8	0.6	22 (M)	
	2.1	45 (F)	
	2		280
Penta 1,2,3,7,8	3		340
1,2,4,7,8	1,100		>5,000
Hexa 1,2,3,4,7,8	73		825
1,2,3,6,7,8	70-100		1,250
1,2,3,7,8,9	60-100		>1,440
Mixed Isomers		100,000	
Hepta 1,2,3,4,6,7,8	>600		
Octa 1,2,3,4,6,7,8,9		>1,000,000	>4,000,000

Recent information arising from a 1983 National Cancer Institute carcinogenicity study of a mixture of 1,2,3,6,7,8- and 1,2,3,7,8,9-HCDD in female rats led to the preliminary conclusion that this mixture of hexachlorodioxins was carcinogenic. Because public comment criticized the manner in which the experiments were conducted, the National Institute of Environmental Health Sciences/National Toxicological Program (NIEHS/NTP) was asked to reexamine the results of the study. It is therefore the opinion of NIEHS/NTP that the hexachlorodioxin mixture was indeed carcinogenic under the conditions of the test (9).

Analyses of Commercial PCB Mixtures

PCBs contain a complex mixture of PCDFs with up to 40 isomers being present. Rappe and Buser (6) have analyzed a number of commercial PCBs and their findings are shown in Table 2. The highest concentration of PCDFs, found in a Mitsubishi PCB fluid used for over two years, amounted to 10 ug/g (ppm), with 1.25 ug/g being the 2,3,7,8-TCDF isomer. When commercial mixtures or well defined isomers are heated in air in a sealed glass container or ampoule, yields of PCDFs have been observed in the 1-5% range and this technique has been successfully employed to prepare PCDF standards (10). Using the synthetic standards currently available, the major PCDF isomers present in commercial PCBs have been identified (See Figure 2).

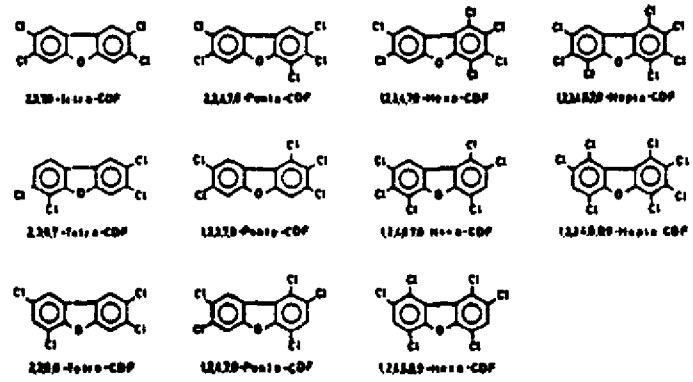

Figure 2. PCDF isomers identified in commercial PCBs (6).

Table 2. Concentrations of PCDFs in commercial PCBs, ug/g (6).

Sample	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	Total PCDF
Aroclor 1248 (1969)	-	0.5	1.2	0.3	-	2.0
Aroclor 1254 (1969)	-	0.1	0.2	1.4	-	1.7
Aroclor 1254 (1970)	-	0.2	0.4	0.9	-	1.5
Aroclor 1254	0.10	0.25	0.70	0.81	-	1.9
Aroclor 1254 (lot KK 602)	-	0.05	0.10	0.02	-	0.2
Aroclor 1260 (1969)	-	0.1	0.4	0.5	-	1.0
Aroclor (Lot AK 3)	-	0.2	0.3	0.3	-	0.8
Aroclor 1260	0.06	0.30	1.0	1.10	1.35	3.8
Aroclor 1016 (1972)	-	<0.001	<0.001	<0.001	-	-
Clophen A 60	-	1.4	5.0	2.2	-	8.4
Clophen T 64	0.10	0.30	1.73	2.45	0.82	5.4
Phenoclor DP-6	-	0.7	10.0	2.9	-	13.6
Prodelec 3010	0.41	1.00[a]	0.35	0.07	-	2.0
Mitsubishi (used)	2.13	4.00[b]	3.30	0.53	-	10.0

[a] Major isomer 2,3,7,8-TCDF
[b] Contains 1.25 ug/g 2,3,7,8-TCDF

Discussion of Various PCB Fires

* Binghamton, New York

On February 5, 1981 at approximately 5:30 a.m., an electrical panel in the basement of a 22 story office building located in a governmental complex was involved in an incident described as an explosion. A nearby electrical transformer containing about 1100 gallons of Aroclor 1254 (65%) and tri- and tetrachlorinated benzenes (35%) was involved. Leakage occurred and about 180 to 200 gallons of fluid leaked from the transformer. Due to the ventilation system of the building, smoke contaminated with soot-containing chemicals, was spread in a non-uniform fashion to most work areas of the building as well as to interstices within air conditioning ducts, false ceiling arees, elevator shafts, and within desks and file cabinets. This appears to have been facilitated by air ducts or simply open shafts running from the basement area, up to the top of the building, with openings into the men's and women's bathrooms on each floor. These bathrooms hed only metal gratings separating them from the open shaft area. In addition to this architectural arrangement, fire or smoke safety doors, which were designed to open in the presence of smoke as a health measure, did just that during the series of explosions that occurred at the time of the incident. Because the outside air temperature was below freezing at the time, the opening of safety doors on the roof, which were located above the building's two stairways, caused a small vacuum that sucked air containing smoke, soot, and as was later found, toxic chemicals from the bathroom areas on each floor and deposited the residue in a non-uniform fashion into most areas of the office building later tested.

Chemical analyses were performed at: Galson Laboratory in Syracuse, New York and at General Electric Laboratory in Schenectady, New York and revealed PCBs in soot and air, which was strongly suggestive of PCDFs present in substantial amounts; The National Fish and Wildlife Laboratory in Columbia, Missouri, which established the presence of many of the dioxin isomers; and by the New York State Health Department's Division of Laboratories and Research, which established the presence of 2,3,7,8-TCDD. A later examination of material from the underground garage that was contaminated and washed (twice with steam and detergent) was found still to have trace amounts (nanograms per square meter) of PCDFs and PCDDs in some areas by Wright State University. Total PCDF isomers in the soot were initially found to be as high as 2160 ug/g, PCDDs 10-20 ug/g, and PCBs 100,000-200,000 ug/g (See Table 3). It is noteworthy that the most toxic isomers are the major components within each group, viz., 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PCDD, 1,2,3,7,8-PCDF, and 2,3,4,7,8-PCDF (See Figure 1). Since the tri- and tetrachlorinated benzenes comprise 35% of the dielectric fluid, it is not unreasonable to assume that this diluent mixture represents the precursor to the PCDDs produced as a result of the fire.

Nearby Binghamton City Hall, which was used as a staging area during the initial cleanup efforts in February 1981, was also contaminated. The County Building also next door to the Binghamton State Office Building was contaminated to a lesser extent.

There have been $12 million allocated so far by the State of New York for the cleanup. The building is self-insured so no insurance funds are available. It has been closed since February 5, 1981. Over $1 billion in lawsuits have been threatened by some of the more than 500 persons who were, or believe they were, exposed to toxic chemicals, and who are themselves concerned with physical or psychological/medical damages.

* Stockholm, Sweden

In August 1981, a fire broke out in a 10 KV capacitor battery in an electrical power station in Stockholm, which was probably caused by a malfunctioning electrical system. Wipe tests were taken about one meter from the capacitor (13). Inspection of the chromatograms revealed several peaks, in addition to PCBs, with molecular weights corresponding to di-, tri-, tetra-, and pentachlorobiphenylenes (PCBPs). It is probable that these PCBPs were formed by a direct cyclization of PCBs present. The level of PCDFs was found to be 1375 ng/m^2 (See Table 4), whereas a rough estimate for PCBPs gave levels of 25,000-30,000 ng/m^2. Polychlorinated pyrenes (PCPYs) were also detected, but not quantified.

Table 3. Levels of PCDFs (ug/g) from accidental burning of PCB-containing electrical equipment.

Isomers	Capacitor Skövde, Sweden(10) 0.5m*	Capacitor Skövde, Sweden(10) 3m**	Transformer Binghamton(10)	Transformer Miami (11)#	Transformer Boston (12)¢
Total PCDFs	0.8	0.2	2160	n.d.-1.79	165
Total Tri-CDFs				n.d.-0.18	50
Total Tetra-CDFs	0.6	0.1	28	n.d.-0.53	60
2,3,7,8-Tetra-CDF	0.1	0.02	12	n.d.	3
Other isomers	0.5	0.06	16		
Total Penta-CDFs	0.1	0.04	670	n.d.-1.0	35
1,3,4,7,8-Penta-CDF			65		
1,2,4,7,8- "			25		
1,2,4,7,9- "			22		
1,2,3,7,8- "			310		
1,2,3,6,7- "			60		
1,2,6,7,8- "			25		
2,3,4,7,8- "			48		
2,3,4,6,7- "			12		
Other isomers			110		
Total Hexa-CDFs	0.04	0.04	965	n.d.-0.18	15
1,2,3,4,6,8-Hexa-CDF			50		
1,3,4,6,7,8- "			125		
1,2,4,6,7,8- "			50		
1,2,3,4,7,8- "			510		
1,2,3,6,7,8- "			150		
1,2,3,6,8,9- "			58		
2,3,4,6,7,8- "			10		
Other isomers			250		
Total Hepta-CDFs	0.01	0.01	460	n.d.	2
1,2,3,4,6,7,8-Hepta-CDF			230		
1,2,3,4,6,7,9- "			120		
1,2,3,4,6,8,9- "			55		
1,2,3,4,7,8,9- "			55		
Octa-CDF	0.005	0.005	40	n.d.	n.d

* soot sample taken 0.5m from capacitor on the floor
** soot sample taken 3m above capacitor on the wall
\# Detection limit: 10 ng/g
¢ Detection limit: 100 ng/g

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Table 3. Levels of PCDDs (ug/g) from accidental burning of PCB-containing electrical equipment. (cont'd)

Isomers	Capacitor Skövde, Sweden(10) 0.5m*	Capacitor Skövde, Sweden(10) 3m**	Transformer Binghamton(10)	Transformer Miami (11)#	Transformer Boston (12)£
Total PCDDs	-	-	20	n.d.	n.d.
Total Tri-CDDs				n.d.	n.d.
Total Tetra-CDDs	-	-	1.2	n.d.	n.d.
2,3,7,8-Tetra-CDFs	-	-	0.6	n.d.	n.d.
Other isomers	-	-	0.6		
Total Penta-CDDs	-	-	5.0	n.d.	n.d.
1,2,3,7,8-Penta-CDDs	-	-	2.5		
Other isomers	-	-	2.5		
Total Hexa-CDDs	-	-	4.7	n.d.	n.d.
1,2,3,4,6,8-Hexa-CDD	-	-	1.2		
1,2,4,6,8,9 "	-	-	1.2		
1,2,3,4,7,8 "	-	-	0.7		
1,2,3,6,8,9 "	-	-	0.6		
1,2,3,7,8,9 "	-	-	0.4		
1,2,3,4,6,7 "	-	-	0.5		
1,2,3,4,6,7,9-Hepta-CDD	-	-	4	n.d.	n.d.
1,2,3,4,6,7,8- "	-	-	3	n.d.	n.d.
Octa-CDD	-	-	2	n.d.	n.d.

* soot sample taken 0.5m from capacitor on the floor
** soot sample taken 3m above capacitor on the wall
# Detection limit: 10 ng/g
£ Detection limit: 100 ng/g

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Table 4. Analyses of wipe samples from various PCB fires.

Isomers	Skövde(14) ng/m^2	Stockholm(14) ng/m^2	Cincinnati(13) ng/m^2
Total PCDFs	n.d.-873	1375	n.d.
2,3,7,8-Tetra-CDF	n.d.-100	150	n.d.
1,2,7,8-Tetra-CDF		150	
2,3,6,8-Tetra-CDF		125	
1,4,6,9-Tetra-CDF		75	
2,4,6,7-Tetra-CDF		37	
3,4,6,7-Tetra-CDF		7.5	
1,3,6,7-/1,3,6,9-Tetra-CDF		300	
Other Tetra-CDFs		750	
Total Tetra-CDFs	<1-600	1200	n.d.
2,3,4,7,8-Penta-CDF		45	
1,2,4,7,8-Penta-CDF		38	
1,2,3,6,7-Penta-CDF		15	
1,3,4,7,8-Penta-CDF		11	
2,3,4,6,7-Penta-CDF		7.5	
1,2,4,6,8-Penta-CDF		3.8	
1,2,4,7,8-Penta-CDF		3.8	
1,2,3,6,7-Penta-CDF		3.8	
1,2,4,8,9-Penta-CDF		3.8	
2,3,4,6,8-Penta-CDF		2	
1,2,3,7,8-/1,2,3,4,8-Penta-CDF		15	
Other Penta-CDFs		19	
Total Penta-CDFs	n.d.-100	175	
Total Hexa-CDFs	n.d.-60	<0.5	
Total Hepta-CDFs	n.d.-8		
Octa-CDF	n.d.-5		
Total PCDDs	n.d.		n.d.
Total Tetra-CDDs	n.d.		n.d.
2,3,7,8-Tetra-CDDs	n.d.		n.d.

MONS 215050

* Skövde, Sweden

In March 1982, a 400 volt capacity battery, serving a high frequency oven in a casting line of a foundry in Skövde, experienced an electrical malfunction leading to a fire (13)(14). The dielectric fluid employed comprised either mineral oil or PCBs. The fire started in a mineral oil capacitor and burned for about two hours before being extinguished. Temperatures exceeding 1100°C were realized because copper electrical wiring melted. The smoke spread from the basement into the building above, an area of 60 x 30 meters. The capacitor battery contained 21 capacitors filled with 5 kgs of PCBs each. Post-fire inspection showed leakage from 12 of these capacitors. Both wipe tests and soot samples were taken. Results are tabulated in Tables 3 and 4. These show that high levels of PCDFs (>100 ng/m^2 and <800 ng/g) could only be found in an area near the fire. Concentrations of PCDFs dropped off dramatically with distance from the fire. The highly toxic 2,3,7,8-TCDF was one of the major tetra-CDF isomers present. Other chlorinated compounds that may be present are the PCPYs, but verification could not be obtained due to lack of standards. No PCDDs were identified in samples taken from this fire (there were no chlorinated benzenes used as diluents). No PCBPs were observed.

* Miami, Florida

On April 13, 1982, an underground electrical fire occurred in a transformer vault in Miami. City of Miami firemen were called in to extinguish the blaze. They also voiced their concerns about the possible contamination of fire equipment and protective clothing used during the performance of their duties. As a result, the International Association of Fire Fighters in Washington, DC, contacted the NIOSH Region IV representative and the latter agency conducted a thorough investigation. Table 5 contains the results of the analyses of surface samples taken during the investigation. As expected, samples removed from inside the vault indicate the heaviest contamination levels (up to 27,400 ug/100 cm^2 PCBs). Results of prior NIOSH investigations indicate that normal background levels of PCBs on uncontaminated surfaces should be less than 0.5 ug/100 cm^2. As indicated by the sampling results, turnout coats, boots, helmets, and other personal protective equipment were not found to be contaminated from the fire. This is probably due to the decision to allow the fire to self-extinguish, thus minimizing exposures to the smoke and soot. The only contaminated piece of equipment found at the station was the smoke ejector fan, which contained greater than 31 ug/100 cm^2 PCBs because the area wiped for this particular sample was estimated to be less than the standard 100 cm^2. The fan blade guard was found to be heavily coated with soot and dirt from the smoke exhausted from the vault fire.

Results of PCDD and PCDF analyses are shown in Table 3. No PCDDs were detected, but tri-, tetra-, penta-, and hexa-CDFs were found, ranging from non-detectable (n.d.) to 1790 ng/g. No 2,3,7,8-TCDF was detected in any of the samples. However, the samples did exhibit high levels of PCBs through Cl_{10} and polychlorinated diphenylethers (PCDPEs) through Cl_8.

Table 5. PCB residue from Miami transformer vault fire (11).

Sample Location	Type Sample#	PCBs* (ug/100 cm²)
Inside transformer vault		
Wall behind transformer	(soot) wipe	434**
Top of primary cable above fire	(soot) wipe	389
Primary cable support bracket	(soot) wipe	704
Floor near isolating switch	(dirt) wipe	27,400
Ceiling near fire location	(soot) wipe	860
Secondary bus near vault ceiling	(dirt) wipe	195
Wall next to exit ladder	(dust) smear tab--dry	2
Rung of exit ladder	(dust) smear tab--dry	79
Above transformer vault:		
Sidewalk grating	smear tab--dry	2
Water at curb near vault	wipe	3
Firemen's clothing/equipment:		
Miscellaneous clothing	smear tab--dry	<0.1
Smoke ejector fan	smear tab--dry	>31
Normal PCB Background***	wipe	<0.5

* As Aroclor 1260 (used as standard for quantifying samples).

** As mixture of Aroclor 1254 (231 ug) + Aroclor 1260 (203 ug).

*** As determined by previous NIOSH Health Hazard Evaluation.

\# Wipe samples were collected on sterile cotton pads soaked in n-hexane.

* Cincinnati, Ohio

On December 3, 1980, a capacitor containing PCBs for a 1/2 HP electric motor overheated in a basement storage room of a private elementary school. This capacitor contained 22 ml of dielectric fluid comprised of 21.9 ml of a biodegradable fluid and 0.1 ml of PCBs. Approximately one-half of the fifth-grade students using three classrooms in the basement area complained of itchiness of the skin. Power to the electric motor was shut off and the exterior door was opened to allow ventilation of the smoke from the room. Since air is locally recirculated, central distribution via a mechanical system throughout the school did not occur.

PCBs were not detected in any air sample at a limit of detection of 0.05 ug/sample, which is equivalent to an airborne concentration of approximately 1 ug/m^3.

Table 6 summarizes the results of 63 wipe samples collected by NIOSH. Fifty-one of the 63 samples were taken from surfaces within the school including books, desks, walls, floors, ceilings, and other surfaces. Two were taken from surfaces within a mobile classroom and ten were obtained from surfaces at three locations in eastern, central, and western Cincinnati to establish background levels of PCBs for this area. The 20 samples obtained from Room 27, which contained the overheated capacitor, ranged from non-detectable to 7200 $ug/100\ cm^2$ PCBs. The remaining rooms ranged from non-detectable to 0.45 $ug/100\ cm^2$.

The two wipe samples with the highest PCB concentrations were also analyzed for PCDDs and PCDFs, with particular emphasis on the 2,3,7,8-tetra-isomers. Neither PCDDs nor PCDFs (See Table 4) were detected in either of the samples. The detection limits employed were 0.10 and 0.09 ug/sample, respectively.

* Boston, Massachusetts

In January 1982, there was an electrical fire involving PCBs in a Boston office building. One bulk soot sample was analyzed for PCDDs and PCDFs. Table 3 shows that high concentrations of the tri- through the hepta-CDFs were found in the soot sample, ranging from 2 - 60 ug/g (detection limit = 0.1 ug/g). No PCDDs were found. A considerable amount of the highly toxic 2,3,7,8-TCDF was detected--3 ug/g. Levels of PCBs were also found at 10 - 100 times that of the PCDFs.

Table 6. Summary of PCBs wipe sample results, Our Lady of Visitation School, Cincinnati, OH (capacitor fire) (15).

Sample Location	Mean PCB level, ug/100 cm^2 *
Room 27 (capacitor location)	n.d. - 7200**
Room 25	n.d. - 0.14
Room 24	n.d. - 0.06
Room 26	n.d.
Hallway	n.d. - 0.07
Room 8	n.d. - 0.08
Room 22	n.d. - 0.29
Room 10	n.d. - 0.20
Room 11	0.07 - 0.11
Room 12	0.06 - 0.09
A.V. Room	n.d.
Principal's Office	0.05 - 0.45
Mobile Classroom	0.06
Background Levels (3 Cincinnati locations)	n.d. - 0.13

* Detection limit: 0.05 ug/sample (sample = quantity wiped per 100 cm^2).

** Two wipe samples with highest concentrations of PCBs were found to contain no detectable PCDFs or PCDDs.

* St. Paul, Minnesota

On June 22, 1982, a transformer fire occurred in a public high school in St. Paul. NIOSH took both surface wipe and air samples on June 23 (the day after the fire) and on July 7 (after the area was decontaminated). Table 7 contains measurements of air contamination, pre- and post-cleanup, by PCBs, trichlorobenzenes, and tetrachlorobenzenes. The NIOSH recommended permissable limit of 0.001 mg/m^3 (8-hr TWA) for PCBs was exceeded in all areas sampled except for two locations. The tri- and tetrachlorobenzenes found did not exceed any existing limits.

Table 8 shows the effect of the decontamination methods employed. The transformer vault room PCBs (wipes) were reduced from a high of 4,000 ug/100 cm^2 to 120 ug/100 cm^2 or less. No PCDDs or PCDFs were found in the liquid sample of Askarel provided (detection limit = 40 ng/g (40 ppb)). However, it is interesting to note that NIOSH did not analyze for PCDDs or PCDFs in the soot. The results may have shown significant concentrations of these isomers, given the areal concentrations of tri- and tetrachlorobenzenes detected.

Table 7. Areal concentration of PCBs and chlorinated benzenes, Hill-Murray High School, St. Paul, MN (transformer)(16).

Sample Site	Airborne Concentration, mg/m^3					
	PCBs*#		T_3CBs		T_4CBs	
	A	B	A	B	A	B
Transformer vault, 5 ft above floor	0.05	0.007[c]	22.6	0.331	18.2	0.651
Transformer vault, 1 ft above floor	0.09	-	17.6	-	25.7	-
Outside of transformer vault doors	0.02	n.d.	10.2	0.048	11.7	0.229
Woodshop	0.004	n.d.	0.73	0.020	1.21	0.089
Head of stairs	n.d.	n.d.	0.12	0.011	0.26	0.037
Cafeteria	n.d.	n.d.	0.35	0.010	0.27	0.032
8-hr time-weighted average exposure criteria	0.001[a]		40[b]		none	

A = June 23, 1982; B = July 7, 1982

* = Detection limit : 0.001 mg/m^3

= as Aroclor 1260

a NIOSH recommended permissable exposure limit. OSHA permissable exposure limit is 0.001 mg/m^3 8-hour time weighted average.

b ACGIH threshold limit value. Neither NIOSH nor OSHA has exposure criteria.

c sample taken 3 ft above floor

Table 8. Analyzed PCBs# in wipe samples,
Hill-Murray High School, St. Paul, MN (transformer) ¢(16).

Sample Site	PCBs#, ug/100 cm^2	
	A	B
Vault room	n.d. - 4000	2 - 120
Ventilation dust	n.d.	-
Corridor outside vault room	n.d.	-
Cafeteria	0.22 - 0.24	n.d.
Gymnasium	0.29	
Rooms 106, 109, 138	0.26 - 2.1	n.d. - 0.8
Outside Room 106	5.8	0.8
Woodshop	n.d.	-

Detection Limit : 5 ug/sample

A = June 23, 1982; B = July 7, 1982

¢ = no analyses conducted for PCDFs or PCDDs.

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DISCUSSION

The previous PCB transformer/capacitor incidents are but a representative sampling of cases where data are readily available. Other electrical equipment episodes include: Toronto, Ontario, Canada in 1977; and Norrtälje and Surahammar, Sweden and Imatra, Finland in 1982 (17). More recently, in the U.S., three such episodes have occurred:

Date	Location	PCB Fluid
5/15/83	San Francisco, CA	1242 only
9/28/83	Chicago, IL	65% Aroclor/35% Chlorobenzenes
12/21/83	Syracuse, NY	87% 1254

Because of the continuance of such incidents, the Environmental Defense Fund and the Natural Resources Defense Council challenged the August 25, 1982 PCB Electrical Use Rule issued by EPA. As a result, a Start Action Request has been initiated by the EPA Office of Pesticides and Toxic Chemicals, which includes the following court-ordered schedule for the issuance of an Advanced Notice of Proposed Rulemaking (ANPR) regarding PCB transformer fires (18):

ANPR: March 1984
Proposed Rule: October 1984
Final Rule: July 1985

The objective of an ANPR is to present data that indicate a reason for concern and, more importantly, to solicit data for the Proposed Rule. The major elements of the ANPR include:

- Description of risks associated with PCB transformer fires through analyses of Binghamton, San Francisco, Chicago, Syracuse, etc. events.
- Description of number and distribution of PCB transformers.
- Solicitation of data on number and location of such electrical equipment.
- Presentation of information on other lesser-known fires.
- Presentation of estimates of frequency of fires.
- Solicitation of data on other fires and frequency of other fires.
- Discussion of PCDF/PCDD formation (and PCBP, PCCY (crysenes), PCDPE, PCPY, etc. where data are available on these compounds).
- Solicitation of data on mechanisms of formation.
- Presentation of possible regulatory options.
  - Substitutes
  - Retrofilling
  - Fire hazard inspections
  - Costs/benefits of various mechanisms to reduce spread of PCBs, PCDFs, PCDDs, etc. from fires - use of early warning protection devices

Currently, the EPA Office of Research and Development (ORD), in support of the Agency's Dioxin Strategy (18), released publicly on December 15, 1983, is planning to conduct research on PCB fires, which will cover three areas: (a) the chemistry of PCB fires and a theoretical discussion of products of thermal stress based on composition of askarel used; (b) emergency response protocols for firemen, including protective clothing (this research will be conducted in cooperation with NIOSH); and (c) practical remedial measures for building cleanup.

As a result of my participation in the preparation of the Dioxin Strategy document and in several Agency dioxin workgroups, including the Dioxin Disposal Advisory Group and the PCB Transformer Fires Workgroup and based upon my expertise concerning the subject matter (20), I believe that I enjoy a perspective that few EPA technical staff have. Because of this, I can relate to you the following facts: Given that chemical production facilities in the U.S. no longer produce 2,4,5-trichlorophenol (the most significant historical source of 2,3,7,8-TCDD), I can state that soot produced as a result of PCB transformer/capacitor fires contains the highest concentrations of PCDFs and PCDDs (the latter only if chlorobenzene diluents are present in the askarel mixture) found in the U.S. today; on a weight basis, however, municipal combustion devices account for the largest quantity of PCDFs and PCDDs produced currently. The soot from the Binghamton fire was evaluated by the New York State Department of Health in tests using chick embryos in 1981 (21). Results were positive. In other words, the PCDDs and PCDFs in the soot were not inactivated (as in the case of fly ash from an incinerator or by activated carbon) as demonstrated by the chick embryo fetotoxicity and teratogenicity tests performed. The soot can therefore be considered toxic and may contribute to "environmentally induced or promoted cancers, reproductive abnormalities, immunologic deficiency, and possibly premature death from infection, neurologic and gastrointestinal system pathology and possibly, by elevating serum triglyceride and cholesterol levels, excess or avoidable cardiovascular and cerebrovascular pathology" (22, p. 678).

I thus stand firmly behind the convictions that firemen responding to such incidents must have the most up-to-date information at their disposal and that remedial methods employed must be practical, sound, and effective. As a result, EPA-ORD is in the process of securing PCB samples from Binghamton, NY, Chicago, IL, San Francisco, CA, and Syracuse, NY. The EPA analytical laboratory in Cincinnati, OH will conduct a chlorobenzene isomer screen on the samples together with homologue analyses for PCBs, the purpose being an attempt to correlate PCDDs and PCDFs content of soot and wipe samples (in the vaults) with chlorobenzene and PCB content in the transformer fluid. The information gathered will be shared among the electrical utilities, insurers, firemen associations, EPRI and NIOSH.

In closing, I wish to share some recent and quite pertinent information. The NIEHS/NTP has concluded two animal studies involving bioaccumulation of 2,3,7,8-TCDD from contaminated soils and has submitted these papers (23) to Science for publication. These papers conclude that 2,3,7,8-TCDD in soil from two sites in Missouri, namely, Times Beach and Minker-Stout, is absorbed in a highly efficient manner (>50%) and that 2,3,7,8-TCDD

-contaminated soil presents a hazard to humans if ingested. Thus, further laboratory evidence has been amassed regarding potential risk to humans for 2,3,7,8-TCDD. I believe that this audience is sufficiently astute to comprehend the long-term implications of these investigations.

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QUESTIONS AND ANSWERS

QUESTION: What can EPRI do to help solve the problem?

ANSWER: Identifying the actual risk from transformers would be helpful.

Several discussions questioned the source of PCDD and PCDF from fires, pointing out that, generally, materials other than from transformers are involved.

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POLYCHLORINATED DIBENZOFURANS AND PCB-TRANSFORMER FIRES: TOXIC HAZARDS AND DETERMINATION OF DECONTAMINATION GUIDELINES

Thomas H. Milby, M.D.*

Thomas L. Forrester**

In 1970, Vos and his colleagues (1) identified polychlorinated dibenzofurans (PCDFs) as toxic impurities in European PCBs at the ppm-level. Rappe and Buser (2) have extended this work (Table 1). Formation of PCDFs from the pyrolysis of PCBs has been accomplished in the laboratory (3). On February 5, 1981, a transformer fire in a state office building in Binghamton, New York demonstrated that conversion of PCBs to PCDFs and other toxic substances can occur under "real world" conditions and create a very serious problem of environmental contamination. The Binghamton state office building transformer fire was extensively studied and may be considered the model for the understanding of similar events. The transformer fire which occurred in May, 1983 in San Francisco confirmed the Binghamton finding that, under conditions of current usage as transformer dielectric fluids, PCBs can be converted to PCDFs in the event of a fire. Although it is my intention to cite certain data reported from the Binghamton fire in this presentation, to my knowledge very little data from this event have been published in scientific journals. Accordingly, I would refer those interested to the innovative and pioneering work of researchers from the Center for Laboratories and Research, New York State Department of Health, Albany,

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New York 12201 for detailed information. At the time of this presentation, to my knowledge, no technical data on the San Francisco, California transformer fire have been published, although a draft document recommending clean-up levels has been released (4). I would emphasize, however, that there were very substantial quantitative and qualitative differences between the PCB-derived combustion products created by the two transformer fires. Therefore, it is important to understand that although clean-up goals may be similar where PCB-transformer fires occur, efforts required to meet these goals will vary considerably.

At the time of the Binghamton fire, very little information on the toxicology of PCDFs was available. Information that was available was based primarily on experimental animal studies. However, because animal studies indicate that the toxic effects of PCDFs and polychlorinated dibenzodioxins (PCDDs) are qualitatively similar, and because substantially more information is available on the toxicity of PCDDs, the Binghamton investigators were able to make certain very useful assumptions about the toxicity of PCDFs. At the time of this presentation, we find ourselves in about the same situation. The significance of this state of affairs becomes extremely relevant to those facing the task of determining safe exposure levels to PCDFs present as residues in the air and on the surface of structures contaminated by smoke from PCDF-containing transformer fires.

To my own personal knowledge, two methods have been used for establishing standards for acceptable clean-up levels following transformer fires. One method assumes the major hazard to human health represented by the PCB-PCDF contaminant is carcinogenesis. In this case, a common approach is to extrapolate to low level exposure

in humans, using high dose carcinogenic bioassay data from studies in experimental animals. This procedure calculates a dose which corresponds to a given lifetime cancer risk. A second approach, which does not consider the potential carcinoganic properties of the contaminant mixture to be the major issue, is based on the establishment of an acceptable daily intake (ADI), most often based on a no-observed effect level (NOEL) from animal study data. In connection with PCDFs, the decision on which approach to use, that is to base the standard on carcinogenesis or on an established NOEL, is one which does not enjoy a unanimity of opinion among those who consider the matter.

The PCDF or PCDD for which the most toxicological data are available for risk assessment computation is 2,3,7,8-TCDD. Although this compound is carcinogenic in laboratory animals, it does not appear to be genotoxic. Thus, some would argue that it is more appropriate to establish a safe standard based on the NOEL for this compound rather than on its carcinogenic potential. According to the latest information of which I am aware, Kim and Hawley, of the New York State Department of Health, acting with the approval of the Binghamton State Office Building Expert Advisory Panel, have selected the NOEL approach to calculation of risk assessment (5). It is beyond the scope of this presentation to go into detail on the Kim and Hawley calculation, however, it is of interest that the basis for the calculation is the reported no-observed effect level for 2,3,7,8-TCDD of 1 nanogram/kg-day in rats reported in both a three generation reproduction study (6) and a two-year oncologic study (7). An uncertainty factor of 500 was recommended by the Binghamton Expert Advisory Panel and included in the Kim-Hawley calculation. Accordingly, the acceptable daily intake (ADI) for humans was

calculated to be 2 picograms/kg-day. Assuming a 50 kg individual, the ADI would be 100 pg/day for 2,3,7,8-TCDD. Further assuming a breathing volume of 10 m^3 for an average 10-hour day, the calculated air guideline for 2,3,7,8-TCDD would be 10 pg/m^3 of 2,3,7,8-TCDD. Based on acute toxicity studies of transformer fire-generated soot from the Binghamton state office building, and adding a correction factor which takes into consideration the ratio of 2,3,7,8-TCDF and 2,3,7,8-TCDD concentration in the soot, an acceptable air concentration guideline of 8.4 pg/m^3 of 2,3,7,8-TCDF was reached. Other assumptions included in this final acceptable air concentration were that a worker would be exposed for 30 years, 250 days per year as a maximum possible exposure duration. Also included was the assumption that the contaminant concentration would remain constant during the 30-year period. Kim and Hawley included an alternate calculation of acceptable air concentration which included the assumption that over a 30-year period, contamination levels would drop to 1% of the value found on the day the building is reoccupied. With this assumption, an acceptable air concentration of 39 pg/m^3 of 2,3,7,8-TCDF was calculated.

The Kim and Hawley calculation also included provisions for ingestion/dermal exposure. This calculation made certain assumptions about surface area of the body of a 50 kg female which might make contact with contaminated surfaces, dermal absorption, and amount of contaminant on the surface area of the hands assumed to be ingested daily. Depending upon which set of assumptions on ingestion/dermal exposure is selected, the range of acceptable surface contamination calculated was from 2.5 to 110 nanograms/m^2 of 2,3,7,8-TCDF.

Should a decision be made to establish an acceptable risk level based on carcinogenesis, several mathematical models are available

for performing cancer risk calculations. Mantel-Bryan in 1961 (8), defined a virtually safe risk for a lifetime as 1×10^{-8}. Since then, regulatory agencies have used risks in the 1×10^{-7} tc 1×10^{-5} range for setting standards for acceptable exposure to carcinogenic agents. The Carcinogen Risk Assessment Group of EPA performed a risk assessment for 2,3,7,8-TCDD using a carcinogenic extrapolation procedure in which a 1×10^{-6} risk was found to correspond to a dose level of 0.00236 pg/kg-day (9)

As might be expected, available statistics have been utilized to examine the risk of death in the United States from a number of causes which help put into perspective the acceptable risk standards used by regulatory agencies. Table 2 shows results of some of these risk assessment calculations.

Calculation of a NOEL from Yusho data. As mentioned above, Kim and Hawley (5) calculated a no-observable effect level for 2,3,7,8-TCDF for application to human exposures based on studies in rats. An uncertainty factor of 500 was incorporated at least in part to account for differences between rodent and man. It occurred to me that as another way of looking at the exposure-effect relationships it would be interesting to examine the published Japanese Yusho data to determine whether information existed with which to calculate a NOEL for PCDFs based on observations in humans rather than in rodents.

It is to be recalled that "Yusho", Japanese for "oil disease" occurred as an epidemic in Southwestern Japan in 1968. The cause of this problem was traced to accidental contamination of rice oil by PCBs and PCB-derived materials, including PCDFs and polychlorinated quaterphenyls (PCQs). Yusho was characterized by an abrupt appearance of severe dermatitis (chloracne), often combined with

other skin, gastroenteric, and neurological manifestations. Kuratsune and his colleagues have received world-wide acclaim for their excellent initial and continuing work on the clinical, epidemiologic, and toxicologic studies of Yusho (10). As it turns out, there is sufficient information available to make such a calculation if we define "effect" as absence of skin lesions based on clinical examination as did Japanese Yusho investigators (11). In view of the observation that skin lesions constitute the most common positive clinical finding associated with overexposure to halogenated cyclic compounds such as PCBs, PCDDs and probably PCDFs- indeed, Reggiani (12) calls chloracne "the most sensitive indicator of overexposure to TCDD we have in the human subject"- there is some support for this definition. However, since subclinical effecs are likely to be more significant than chloracne, I offer these calculations as an interesting exercise only. I do not suggest that a NOEL based on the absence of chloracne be considered as a human health standard for this class of compounds. Rather, I present these calculations because I found them to be of interest.

Having dismissed the importance of these calculations as of personal interest only, I will not dwell further on their weaknesses here. Rather, I offer the four following points which drew my attention to the Yusho incident as the equivalent of a 135-day "feeding study" involving humans:

a) The comparison is man to man, not rodent to man;

b) PCBs, PCDDs and PCDFs share many basic toxic effects, the major differences are quantitative rather than qualitative; and

c) The clinical severity of Yusho disease was found to correlate fairly well with the total amount of oil consumed over a 1-6 month "latent" period, with the latent period defined as the period during which oil was ingested before symptoms appeared. In sense, this corresponds to a "dose-response" relationship.

Clinical severity of Yusho correlated with the total amount of oil consumed during the latent period but not with the amount of oil consumed per kg of body weight per day. Clinical severity of the Yusho response was graded from 0 to 4, with grade 0 designating a condition with physical complaints but without skin lesions, and grade 4, a condition with extensive distribution of acneform eruptions. In a table entitled "Data For The Six Yusho Patients Consuming The Smallest Daily Dose Of Oil During The Latent Period", Hayabushi, et al (11) included two patients graded 0 for severity of clinical response who ingested a total of 314 and 353 ml contaminated rice oil, respectively, during a 135-dey latent period. Assuming, as stated by Hayabushi et al, (11) that the Yusho oil contained 633 ppm PCBs, 596 ppm PCQs, and 3.4 ppm PCDFs, and assuming further that all observed signs and symptoms were due to PCDFs only, none to PCBs and PCQs:

314 ml x 0.9 g/ml (Sp gravity) x 3.4 mg/kg x 1 kg/1000g =

0.96 mg PCDF;

or, for a latent period of 135 days, 0.96 mg/135 = 7.12

ug/day NOEL.

Of course, this NOEL specifically refers to clinical grade 0 Yusho as defined by Japanese investigators. However, I believe that we can safely assume that a dose at or around this level did not result in a "epidemic" of birth defects or abortions in the Yusho population.

Another way to examine this NOEL for comparison to animal-derived data is to consider the 0.96 mg PCDF total dose over the 135-day period as a maximum lifetime allowable dose. Thus, spreading this 0.96 mg total dose over 30 years, assuming 250 days per year as the Binghamton investigators did (5) , one divides 0.96 mg by 7500 (30 years x 250 days), for a value of 128 ng/day. (These data refer to two Japanese women, 19 and 46 years of age; it is unlikely that either weighed in excess of 50 kilograms.) In the case of TCDF, the advisory group at Binghamton argued that 50% of a NOEL dose is inhaled and 50% absorbed through skin contact (5). Therefore, for air, 50% of 128 ng = 64 ng. Assuming, as is usually done, that on inhales 10 m^3 of air in an 8-hour work day, we can calculate a NOEL air concentration from the Yusho data to be of 6.4 ng/m^3.

Recall that the Kim-Hawley (5) calculation, based on a NOEL for 2,3,7,8-TCDD in rats, applying the same basic assumptions, reached a recommended acceptable air level of 8.4 pg/m^3 for 2,3,7,8-TCDF, a value approximately 1000 times lower than the calculated Yusho-based NOEL, but containing a 500-fold "uncertainty" factor. In view of the extensive list of assumptions applied to both the 1 ng/kg-day rodent NOEL for 2,3,7,8-TCDD based on chronic studies and the 0.96 mg human "clinical" NOEL for PCDFs based on 135 days of ingestion, the calculated "acceptable" air levels are, in my opinion, suprisingly consistent.

SUMMARY

When exposed to high temperatures, PCBs form PCDFs. This phenomenon has been demonstrated in the laboratory as well as in the "real-world" in connection with PCB-containing transformer fires. One such fire, the February 5, 1981 Binghamton New York State Office Building fire has been well described in terms of environmental contamination by PCB-darived materials, especially PCDFs. At least two methods have been used for establishing standards for acceptable levels of clean-up following such fires. One method assumes that the major hazard to human health represented by the PCB-PCDF contaminant mixture is carcinogenisis. Here, a common approach is to extrapolate to low-level exposure in humans from high dose carcinogenic bioassay data from studies in experimental animals. This procedure calculates a dose which corresponds to a given life-time cancer risk. A second approach which does not consider the carcinogenic properties of the contaminant mixture to be the major issue, is based on the establishment of an acceptable daily intake (ADI), most often based on a no-observed effect level (NOEL) from animal study data. There is no consensus among those who consider this matter on which of the two methods to use in calculating an acceptable level to PCDF following a transformer fire. Based on data reported by Japanese Yusho investigators, an alternative method of calculating a NOEL for human exposure to PCDFs based on the absence of chloracne as an effect is examined. Considering the myriad of assumptions included in these acceptable exposure calculations, the Yusho-based NOEL for PCDF is surprisingly close to the NOEL based on experimental animal studies. Nonetheless, the Yusho-based method is not recommended for serious consideration because sub-clinical effects, as opposed to clinical

effects such as chloracne, may be more important and occur at dose levels lower than those required to cause clinical dermatitis.

TABLE 1

ppm Levels of PCDFs in Commercial PCBs

Sample	3-CL	4-CL	5-CL	6-CL	7-CL	Total
Aroclor 1248,1969	-	0.5	1.2	0.3	-	2.0
Aroclor 1254	0.10	0.25	0.70	0.81	-	1.9
Aroclor 1260,1969	-	0.1	0.4	0.5	-	1.0
Aroclor 1260	0.06	0.30	1.0	1.10	1.35	3.8
Aroclor 1016,1972	-	0.001	0.001	0.001	-	-
Clophen A 60	-	1.4	5.0	2.2	-	8.4
Clophen T 64	0.10	0.30	1.73	2.45	0.82	5.4
Phenoclor DP-6	-	0.7	10.0	2.9	-	13.6
Prodelec 3010	0.41	1.08	0.35	0.07	-	2.0
Mitsubishi (used)	2.13	4.00	3.30	0.53	-	10.0

Modified from Rappe & Buser (2)

* FRG

** France

*** Japan

TABLE 2

Risk Assesment By Cause of Death

CAUSE OF DEATH	Risk of Death per Person Per Year
Car racing	1.2×10^{-3}
Smoking 20 cig./day	5×10^{-3}
Car driving	1.7×10^{-4}
Industrial	2×10^{-4}
Air travel	1.0×10^{-5}
Drowning	3.4×10^{-5}
** Coffee, 1 cup/day	4×10^{-5}
Drinking 1 bottle/day	7.7×10^{-5}
*** 2,3,7,8,-TCDD (0.00236 pg/kg-day)	1.0×10^{-6}
Earthquake (California)	1.7×10^{-6}
* Dietary PCBs (3.3 ug/d.)	3×10^{-7}
Hurricanes	4.0×10^{-7}
Lightning	7.7×10^{-7}
Meteorites	6×10^{-11}

Source: no asterisk (13)

* (4)

** (14)

*** (9)

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DISCUSSION

QUESTION: Since other synthetic materials were involved in these fires, couldn't the contamination come from something other than the liquid?

ANSWER: It's possible, however, a large source of other materials would have to be required.

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THE SEARCH FOR PCB HEALTH EFFECTS

Paper presented at EPRI PCB Seminar, December 6-8, 1983, Atlanta, Georgia.

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INTRODUCTION

Research on the chemical, physical, environmental, biological, and medical properties of PCBs has grown to a level sufficient to produce 1200 published scientific papers last year. Those of us who do research on PCB health effects keep getting some questions I'd like to address here: What's going on? What's being learned? And how does it impact on those national and international controversies regarding the risks of PCB exposure?

HISTORICAL BACKGROUND

As most people in this audience are aware, the polychlorinated biphenyls, or PCBs, were widely used in this country for nearly fifty years, within the period 1929-1978, primarily in capacitors and fire-resistant transformers. During this period, about 1.3 billion pounds of PCB were used, and much of that PCB is still in equipment that is in service today. Thus, the opportunities for human exposure remain.

Most of that PCB usage occurred after several toxicological studies at the Harvard School of Public Health, and a fair bit of practical industrial experience, had indicated that PCBs were of sufficiently low acute and chronic toxicity to permit handling without danger to the health of those involved. This longstanding perception was seemingly contradicted in 1968 by an outbreak of chloracne and related illness in southwestern Japan. Chloracne is a skin disease, first described in the 1890's, that is characterized by eruptions resembling adolescent acne, often accompanied by hyperpigmentation, a general feeling of malaise, and a variety of less frequent symptoms. It can be caused by chlorinated coal tar; by the polychlorinated naphthalenes, or Halowaxes, that were once used in electrical cables; by certain polychlorinated dioxins; and by several other natural and synthetic chemicals. The 1968 Japanese outbreak was traced to ingestion of rice oil (or "yusho") that had been contaminated with heat transfer fluid from a direct-fired heat exchanger that had originally been filled with a Japanese PCB, Kanechlor 400. By 1981, the toxic agents responsible for the yusho disease outbreak were generally believed to be 2,3,4,7,8-pentachlorodibenzofuran

and other polychlorinated dibenzofurans, or PCDFs, which may be formed from certain PCBs by heating in air to temperatures around or above 300 C. However, the initial Japanese reports implicated the PCBs themselves as the toxic agents. These reports appeared at a time when the PCBs were already of concern because of their environmental persistence, and were of major importance in stimulating the regulatory attack on PCBs that culminated in the 1979 ban, and the intensive search for biological effects that might have been overlooked during the previous 40 years of widespread use.

BIOLOGICAL FINDINGS

The studies of PCB bioeffects have resulted in literally thousands of published scientific papers on PCB uptake by, persistence in, and effects on many life forms, including plants, algae, bacteria, tissue culture cells, invertebrates, fish, birds, mammals, and man. I will not attempt to summarize this body of literature in its entirety, but I would like to note certain general findings that relate to the question of human health hazards.

The first of these is that all PCBs are essentially water-insoluble, fat-soluble materials that are readily taken up from the food eaten or the air breathed. They can also be taken up by absorption through the skin, but the rates and importance of such processes are unknown. Once inside the body, they rapidly distribute themselves, localizing in each tissue in proportion to its fat content. Thus, the route of entry into the body has little effect on either the internal distribution or the pharmacological effects produced.

The second general finding is that the individual PCB isomers differ enormously in both persistence and biological activity. There are 209 theoretically possible ways of attaching between 1 and 10 chlorine atoms to a biphenyl nucleus, and about 100 of these possible isomers have actually been detected in the commercial PCB mixtures, generally in proportions that vary systematically with the mean degree of chlorination, or boiling range, of the particular PCB grade. Generally speaking, the more volatile, less highly chlorinated isomers, such as those that predominated in the capacitor-type PCBs, Aroclors 1221, 1016, and 1242, are more easily metabolized and eliminated by mammals, and their pharmacological effects are limited to the induction of drug-metabolizing enzymes that include P450 cytochromes; that is, the same enzyme group as is induced by phenobarbital. Conversely, the less volatile, more highly chlorinated isomers, such as those that predominated in the transformer-type PCBs, Aroclors 1254 and 1260, are usually only slowly eliminated. Most of these "higher PCBs" also induce the P450 family of drug metabolizing enzymes; however, a few of them are also weakly active at inducing the P448-type enzymes, whose induction in animals appears to be correlated with manifestations of a chloracnegenic toxic response.

The third general finding is that in sensitive animal species the manifestations of P448-correlated, or chloracne-like, toxicity are independent of the type of chloracnegen used: a minute dose of an active PCDF or a huge dose of PCB may produce the same symptoms. However, the relative sensitivities of different species to any of the chloracnegenic agents vary enormously, and with little regard for genetic relationships. Thus, chickens, guinea pigs, and rhesus monkeys are very sensitive to chloracnegens in general, while quail, rodents, and humans are orders of magnitude less so, so that with weakly active agents, such as the commercial PCB mixtures, this type of toxic response may no longer be demonstrable. Until the biochemical bases for these large interspecies differences are understood, it will be difficult to predict human risk from animal data on such substances.

A different problem in risk extrapolation is presented by the tumorigenicity testing data. The production of tumors by PCBs has required use of a species, such as the rat, which is pretty insensitive to chloracnegens, and then feeding it a non-metabolizable PCB such as Aroclor 1260 to a cumulative dose around 2.5 g/kg. Since such PCBs are mostly retained in the rat, simple calculations show that the PCB concentration in body fats must rise to levels between 1 and 2%. At such levels, purely physical effects, such as membrane disruption, would be anticipated. Consistent with this is the recent finding that the PCB loading is indeed acting upon the rat as a tumor promoter rather than a tumor initiator. What all this means is that the usual rationale for linear dose extrapolation is lacking, and one has no basis for presuming that a low level of carcinogenesis might also occur at less extraordinary PCB levels.

In short, for the PCBs there exist some unusual barriers to the prediction of human health hazards from the usual sorts of animal toxicological data. At the same time, there exist some unusual opportunities to make meaningful clinical and epidemiological observations on humans themselves: there was extensive exposure in the past; the degree of exposure can be determined by measurement of the levels of persistent PCB isomers in the body; and there has been a sufficient lapse of time for the manifestation of any delayed health effects.

RECENT CLINICAL FINDINGS

Our own studies were initiated because of access to a 194-person group of capacitor workers that had direct exposure to Aroclors 1254, 1242, and 1016 liquids and vapors over the period 1946-1977. We've had these people under medical surveillance since 1976; have collected enormous volumes of clinical data on them; and have run literally thousands of regressions on our computer in order to identify the statistical associations between their PCB levels

and clinical measurements. In addition, we've been working closely with federal, state, and academic researchers who've been running other studies on the GE capacitor worker population, and also keeping in touch with investigators looking at other PCB-exposed groups around the country. At present there is substantial agreement among scientists working in this field as to what happens to PCB-exposed people, and I shall attempt to summarize that consensus in my remarks.

The first thing we've all learned is that considerable quantities of PCB can be picked up, particularly by people like capacitor workers who were exposed to the more volatile PCBs. In our own study population, we estimated the mean minimal uptake up through early 1976 as 15 g, and there were undoubtedly some members of the group who absorbed several times that much. That 15 g mean minimal uptake, incidentally, represents 20 times the mean PCB uptake ingested by the Japanese yusho victims. Nevertheless, neither in our study population, nor in any of the others reported in the recent literature, have there been any confirmed findings of chloracne or other PCB-related disease in workers exposed to ordinary, unpyrolysed, American-made PCBs. This probably should come as no surprise. Experience with other chemicals indicates that a chloracne outbreak in a working group is a pretty unmistakeable event, and if there'd been any tendency for ordinary PCB to produce chloracne, that fact should have been well known by the mid-1930's, at the latest.

The second thing that I believe most investigators in the field would agree on, although the observational evidence is mostly indirect, is that a weak induction of drug-metabolizing enzymes of the P450 family may occur. In workers with high levels of the lower PCBs, one can see some PCB-correlated elevations in the level of serum gamma glutamyl transpeptidase (GGTP); some decrease in antipyrine clearance times, implying increases in microsomal oxidases; and some decrease also in bilirubin levels, implying increases in microsomal glucuronyl transferase. The implied changes in microsomal enzyme levels were, however, smaller than those seen in comparably dosed rats; the affected clinical parameters all remained within the normal ranges of clinical variation, and the apparent effects all disappeared after discontinuance of direct exposure.

A very recent finding is that despite earlier reports to the contrary, PCBs in humans do not cause elevations of the serum lipids, that is, the serum triglycerides and cholesterol, nor of the associated serum enzymes, alkaline phosphatase and serum glutamate pyruvate transpeptidase, all of which had been interpreted as indicators of deranged liver function. The earlier reports had been based upon observation of statistical associations between the serum levels of these substances and those of the PCBs. It is now apparent that that particular statistical association is perfectly real, but that it has a trivial explanation: because of the tendency of PCBs to distribute between body tissues and fluids in proportion

to their lipid content, any elevation in serum lipid, from whatever cause, will automatically result in PCB redistribution, and hence an increase in serum PCB. Two other research groups have now confirmed our discovery that when one avoids this pitfall by comparing the serum lipid levels with those of the PCBs in body lipids, no correlations are seen.

Finally, the mortality studies that have been performed by NIOSH on the entire exposed GE capacitor worker population, where the PCB exposures went back to 1946, and on a similar group at Aerovox, where the exposures went back to 1938, have shown no increases in standard mortality ratios for deaths due to cancer, cardiovascular disease, nervous system diseases, nor for all causes combined, nor any significant increases in any individual type of cancer.

Nevertheless, it must be pointed out that the total numbers of deaths involved in the mortality studies were still small enough so that a modest increase in a rare type of fatal disease could not have been detected. Similarly, the total populations involved in all clinical studies to date may not have been large enough for the reproducible observation of a rare type health effect.

In summary, although scientific studies can never exclude the possibility of unobservable phenomena, it does seem established that PCB exposures at the high levels provided by prolonged, direct occupational contact had no reproducibly observed effects upon the health of the vast majority of the exposed individuals. These individuals had exposures that were approximately a thousand-fold higher than those provided by the kinds of PCB-contaminated environments being encountered today. Accordingly, there seems little basis for concern over the health risks presented by environmental exposure to residual PCBs at today's levels.

CHEMISTRY OF PCDDs/PCDFs

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Since 1979, research has shown a potental concern resulting from the presence of some chlorinated aromatic hydrocarbons associated with PCBs, predominantly polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Traces of similar compounds, such as polychlorinated biphenylenes (PCBPs), polychlorinated pyrenes (PCPYs), and polychlorinated chrysenes (PCCYs), have also been reported in some samples. These compounds occur in extremely low concentrations in PCB liquids. However, some PCDD, PCDF, and PCBP isomers are acutely toxic as determined by laboratory tests on animals and demonstrated in industrial incidents. Toxicities of some of these isomers are orders of magnitude higher than PCBs.

PCDD and PCDF compounds have been found in the original PCB fluids manufactured in the United States, Europe, and Japan. Several PCB accidents in which PCDDs and PCDFs were prominent have also been documented, including the Yusho incident in Japan involving ingestion of PCDF-contamianted rice oil, and a similar subsequent incident in Taiwan. More recently, a fire involving electrical equipment containing PCB fluids in a Binghamton, New York, office building produced soot which was found to contain PCDFs and PCDDs. These findings indicate the possibility that PCDDs, PCDFs, and other related chlorinated aromatic compounds can form from askarel fluids at high temperatures.

Polychlorinated Dibenzo-p-dioxins (PCDDs)

There are a limited number of direct precursors and reactions by which PCDDs can be formed. In order to be a dioxin precursor, a compound must meet two conditions:

- The compound must be an ortho-substituted benzene ring in which one of the substituents includes an oxygen atom directly attached to tha ring.
- It must be possible for the two substituents, excluding the oxygen, to react with each other to form an independent compound.

An example of the ideal dioxin precursor is shown in Figure 1. A reaction between two of these molecules could yield a dioxin and 2 XY molecules, as shown in Figure 2.

Although the number of direct dioxin precursors is relatively small because of the conditions set forth above, there are many indirect precursors, i.e., compounds which do not fit the model, but which can degrade or be transformed into direct precursors. This will be discussed in more detail later.

Buser (1) and Rappe, et al. (2), have identified the following basic reaction for chlorinated dioxin formation:

- Dimerization of chlorophenols and phenoxy acids (pyrolytic and photochemical) - A bimolecular reaction in which the relative ratio of isomers formed depends on the concentration of the chlorophanates; yields decrease in more dilute systems, such as contaminated mineral oils.
- Cyclization of predioxins (pyrolytic and photochemical) - Unimolecular, and thus concentration-independent.
- Dechlorination of higher chlorinated PCDDs - Unimolecular, and thus concentration-independent.
- Direct chlorination of dibenzo-p-dioxins.

The dimerization reaction basically follows a two-step mechanism (Figure 3).

The intermediate diphenyl ether compound is called a predioxin. Typically, a predioxin will either cyclize to dioxin or break down to the precursors. For example, in one test, when Irgasan DP300, a compound with a predioxin configuration (Figure 4) was heated to 980°C, the reaction yielded both dioxins and precursors (3). Because of such compating reactions, dioxins are seldom found in more than trace quantities. It has been shown that the higher chlorinated pradioxins are amenable to self-condensation, while the lower chlorinated predioxins apparently do not readily cyclize further (4). For instance, in one test, irradiation of 2,4-dichlorophenol yielded a predioxin, but no further reaction (5).

Temperatures for dioxin formation by dimerization/cyclization have been reported at values from 180° to 620°C. Dioxin formation from pentachlorophenols has generally been reported in the 300° to 400°C range, whereas using tri- and tetrachlorophenols as precursors requires temperatures from 400° to 600°C

However, the formation of dioxins from chlorophenols is exothermic, although there are no published data on the amount of heat released (6, 7). This fact, combined with the need for heating to initiate the reaction, suggests that one or more of the reaction steps in the dioxin formation sequence has a high activation energy. The

high activation energy contributes directly to the low yields. In addition, the boiling points of many dioxin precursors are lower than the reaction temperature range. Thus, there is a loss of precursor molecules before reactions can occur (8). Most laboratory syntheses of dioxins rely on closed reaction vessels or pressure to keep precursors in the liquid state.

Another major source of penta- and tetra-CDD isomers is photochemical dechlorination of higher isomers, mainly OCDD (9). The principal toxic isomers, 1,2,3,7,8-pentachloro and 2,3,7,8-tetrachloro, are not as readily formed as other penta- and tetrachloro isomers. The major hepta-CDD formed is the 1,2,3,4,6,7,9-substituted isomer, indicating a preferential loss of lateral (2,3,7-, or 8-) chlorine atoms (10, 11). The major hexa-CDD formed is either 1,2,4,6,7,9- or 1,2,4,6,8,9-hexa-CDD (10). The major penta-CDD is expected to be the 1,2,4,6,9-substituted isomer, and the major tetra-CDD is 1,4,6,9-tetra-CDD (10). These reaction products show a preferential removal of the lateral chlorine atoms. Lower isomers (di- and trichloro) may be formed by irradiation, but they decompose via the same route, and thus do not accumulate (12).

Pyrolysis of chlorobenzenes at approximately 620°C in the presence of air also yields PCDDs. Since chlorobenzenes do not fit the conditions set down earlier for dioxin precursors, Buser (1, 13) has postulated that the alkaline hydrolysis of chlorobenzene to PCDD involves a two-step condensation process from ortho-chlorinated phenoxy anions via a polychlorinated 2-phenoxy phenate (Figure 5).

This dimerization is exothermic. Below approximately 180°C, usually very minor amounts of PCDDs are formed (<1 ppm), but significant quantities (1 to 10 percent yields) result at temperatures over 180°C (1).

Dioxins have also been detected in residues from a variety of combustion processes, including municipal incineration, the burning of fossil fuels, wood in wood stoves, and cigarettes (14). Precursors of dibenzo-p-dioxins are also known to be formed after simply adding hydrogen chloride to the flame of a Bunsen burner (14). Combustion research has been centered on municipal incinerators and industrial heating plants. PCDD isomers have been detected in municipal incineration fly ash in Switzerland, Italy, and the Netherlands in concentrations over 2000 ng/g (ppb). The major isomers detected in Switzerland were the same as those formed in the pyrolytic dimerization of 2,4-di-, 2,4,6-tri-, 2,3,4,6-tetra-, and pentachlorophenates.

The mechanism(s) of PCDD formation in fly ash is presently unknown. Two suggested sources are:

- Condensation of chlorophenols.
- Thermal synthesis from any organic materials and inorganic chloride (the "trace chemistries of fire" hypothesis) (15).

Even ideal PCDD precursors, such as polychlorophenols, show very low PCDD conversion efficiencies. Thus, although every chlorinated organic compound or organic compound/inorganic chlorine mix might be regarded as a potential precursor, the range of likely precursors for formation of detectable quantities of PCDDs is probably not that broad. It seems more likely that those compounds which can be pyrolyzed to benzene, chlorobenzene, phenols, catechols, and/or inorganic chlorine are more probable indirect precursors. The mechanism(s) by which PCDDs are formed during combustion is still not well understood; thus, the effects of combustion temperature, fuel characteristics, catalysis, and other parameters have not been determined.

There has been some question regarding the role of PCBs in PCDD formation. In 1981, an electrical fire in the State Office Building in Binghamton, New York, resulted in the pyrolysis of PCB fluid from a transformer (16, 17, 18). Soot from this fire contained PCDFs and PCDDs. PCBs do not fit the precursor model discussed earlier, and PCDDs would not be expected to form readily in a mixture of biphenyl compounds (19). Conceivably, PCBs could be oxidized to polychlorinated hydroxybiphenyls which could, in turn, cyclize to form dioxins (20). Another reaction that has been suggested is degradation to a chlorinated benzene, followed by oxidation to a chlorophenol and dimerization to PCDD (21).

However, neither mechanism quite fits the thermal decomposition pattern for PCBs. The PCB fluid at Binghamton was a mixture of 65 percent Arocior 1254 and 35 percent chlorobenzenes. Rappe, et al. (22), have suggested that pyrolysis of the chlorobenzenes is a more likely source of the PCDDs than PCBs.

Polychlorinated Dibenzofurans (PCDFs)

While PCDFs and PCDDs can share some of the same precursors, PCBs are the most common source of PCDFs. Buser and Rappe (23) have identified four basic mechanisms of PCDF formation from PCBs (Figure 6).

Reaction 1 involves the loss of the ortho-Cl. Reaction 2 is a loss of HCl involving a 2,3-chlorine shift. Reaction 3 has a loss of ortho-HCl. Reaction 4 involves a loss of ortho-H.

PCDFs have been identified as trace contaminants at the ppm level in a number of American, European, and Japanese commercial PCB mixtures (24, 25, 26, 27). Concentrations and isomer ratios vary with the type of PCB and the country of origin, probably as a result of differences in manufacturing conditions (Table 1). For instance, Bowes, et al. (27), detected PCDFs in American-manufactured Aroclor 1260 and 1248 at total concentrations of 0.8 and 2.0 ppm, respectively; none were detected in a single sample of Aroclor 1016. The total quantities of PCDFs in German Clophen A-60 and French Phenoclor DP-6 were estimated to be 8.4 and 13.6 ppm, respectively (26). PCDFs have also been detected in several Japanese-made PCBs at concentrations from 1 to 20 ppm, with the highest concentration in a sample of Kanechlor KC-400 (32, 33).

PCDFs may also form during PCB use. The best known example of this is the "Yusho" incident in Japan. The PCBs, which had leaked from a heat exchanger, had PCDF/PCB ratios 200 to 250 times higher than that of the original Kanechlor KC-400 (32, 30). Furthermore, the PCDFs in the Yusho oil contained the same isomers as a sample of used PCBs (34). This suggested that most of the PCDFs had been formed in service (26). Similar PCDF isomer ratios have been detected in other used Japanese PCBs (9).

Other sources of PCDF include condensation of chlorophenates and chlorobenzenes, photochemical degradation of higher chlorinated isomers, cyclization of polychlorinated diphenylethers and polychlorobenzenes, and direct chlorination of dibenzofurans (11). Chlorophenols and chlorobenzenes can form PCDFs via an intermediate polychlorinated diphenylether (PCDPE) (1, 5) (Figure 7).

PCDPEs usually occur as contaminants in chlorophenols, and are known to form PCDFs by thermal, photochemical, or metal-catalyzed reaction (35). PCDPEs and PCDFs probably form early in the reaction when large concentrations of chlorobenzenes are still present, whereas PCDDs are formed toward the end of the reaction (35).

Fires in electrical equipment containing PCBs have resulted in PCDF formation. Jansson and Sundstrom (36) investigated the aftermath of a 1978 capacitor fire in

Sweden. Whereas the original PCB contained 1.1 to 1.3 ug PCDF/g (amounts of mono-, di-, tri-, and tetra- isomers about equal), PCB samples from inside the exploded capacitors averaged 81 ug PCDF/g PCB (approximately one-half of PCDF di- isomer, one-third mono-, and the rest tri-, with a trace of tetra-), and samples from the inside surfaces contained 45 to 107 ug PCDF/g PCB (predominantly di- and mono- isomers with some tri- and a trace of tetra-). Soot from a 1977 transformer fire in Toronto contained 5 ug PCDF/g, while the original PCB contained 0.05 ug PCDF/g (36). Similar results have been obtained in the aftermath of other PCB fires.

PCDFs have also been detected in fly ash samples from municipal incinerators and industrial heating facilities. Incinerator fly ash from the Netherlands averaged 1309 ng PCDF/g (37). Incinerator fly ash from Italy averaged about 1300 ppb of combined PCDD and PCDF (38). Fly ash from an industrial heating facility and municipal incinerator in Switzerland contained 0.3 and 0.1 ppm PCDF, respectively (25). Thus far, the exact source of the PCDFs in fly ash is unknown.

TRANSFORMER/CAPACITOR CHEMISTRY

Most PCB-filled electrical equipment is designed to operate at temperatures of 100° to 130°C, and transformer "hot spots" are typically no greater than 135°C (31). All units may contain air, but most newer ones have an inert atmosphere, usually nitrogen. Askarel units are sealed, but some seals can deteriorate with time, permitting the entry of air and water. Hydrochloric acid can be generated, leading to internal corrosion. Water can cause arcing. Internal transformer malfunctions can cause bushings and winding connections to become white hot. During these occasional short-circuit episodes, temperatures reach 200° to 250°C for a few minutes. In cases of an arc where the transformer fails, maximum temperatures may reach 1000°C; these failures occur within fractions of a second (31). Capacitors typically operate below 100°C. In those capacitor failures resulting in rupture, heating and internal arcing may have occurred prior to rupture.

Samples of used askarels from capacitors and transformers have been analyzed for PCDF with mixed results. One researcher concluded that concentrations will increase with time in service, although concentrations detected never exceeded 5 ppm. Other tests on 40-year-old askarels showed PCDF concentrations comparable to those in unused askarels. In general, PCB conversion to PCDF or chlorobenzene conversion to PCDD and PCDF might be possible in a malfunctioning transformer or capacitor, provided that there is sufficient time at optimum temperature and/or oxygen conditions

for their formation. Ordinary working conditions do not appear conducive to PCDD/PCDF formation (31).

Finally, it should also be noted that most of the research on PCB/askarel conversion to PCDD, PCDF, and other chlorinated species has been performed using pure PCBs or askarel formulations containing at least 50 percent PCBs. Very little research has been conducted on dilute PCB systems, such as contaminated mineral oils. Consequently, there is little data available on the effects of dilution on PCB chemistry.

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DISCUSSION

QUESTION: How about furans generated in household cooking?

ANSWER: FDA has gone through risk assessment. Risk is negligible.

Table 1

LEVELS (ug/g) OF PCDFs IN COMMERCIAL PCBs

Sample	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Total	Reference
Aroclor 1248 (1969)	-	0.5	1.2	0.3	-	2.0	27
Aroclor 1242	-	0.07	0.03	0.003	-	0.15	28
Aroclor 1242	-	2.3	2.2	N.D.*	-	4.5	29
Aroclor 1243	0.1	0.25	0.7	0.81	-	1.9	30
Aroclor 1254 (1969)	-	0.1	0.2	1.4	-	1.7	27
Aroclor 1254 (1970)	-	0.2	0.4	0.9	-	1.5	27
Aroclor 1254	-	0.02	0.2	0.4-0.6	-	0.8	31
Aroclor 1254 (KK 602)	-	0.05	0.1	0.02	-	0.2	30
Aroclor 1254	-	0.1	3.6	1.9	-	5.6	29
Aroclor 1260	0.06	0.3	1.0	1.10	1.35	3.8	30
Aroclor 1260 (1969)	-	0.1	0.4	0.5	-	1.0	27
Aroclor 1260	-	0.8	0.9	0.5	-	2.2	29
Aroclor 1260 (AK 3)	-	0.2	0.3	0.3	-	0.8	27
Aroclor 1016 (1972)	-	N.D.	N.D.	N.D.	-	-	27
Clophen A60	-	1.4	5.0	2.2	-	8.4	27
Clophen T64	0.1	0.3	1.73	2.45	0.82	5.4	30
Phenoclor DP-6	-	0.7	10.0	2.9	-	13.6	27
Prodelec 3010	0.41	1.08**	0.35	0.07	-	2.0	30
Kanechlor 400	-	-	-	-	-	ca. 20.0	31
Mitsubishi (used)	2.13	4.00	3.30	0.53	-	10.0	30

* N.D. = None Detected.
** Major isomer 2,3,7,8-tetra-CDF.

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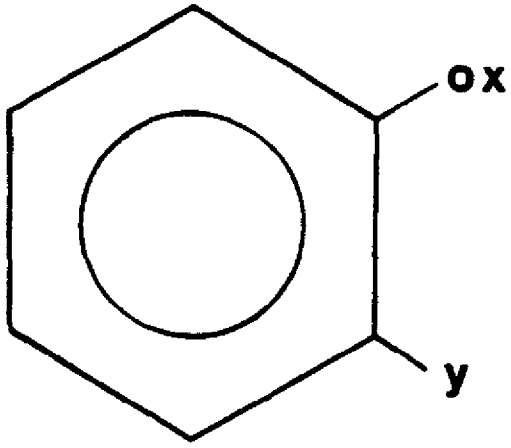

Figure 1. Ideal Dioxin Precursor Molecule

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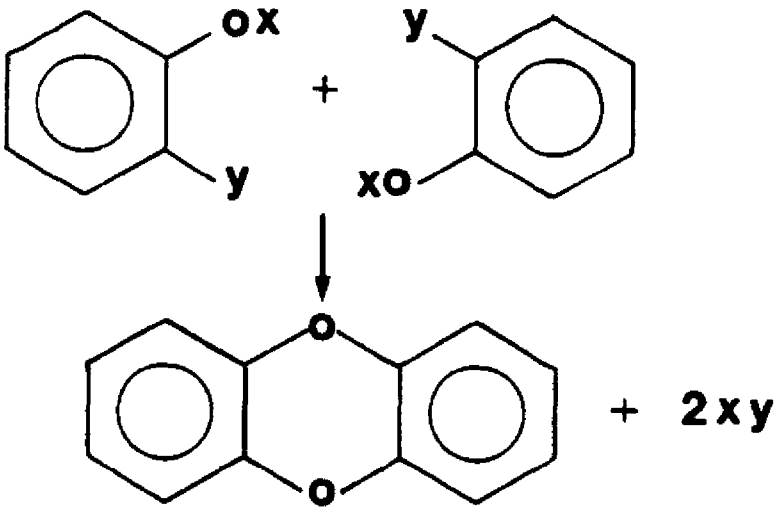

Figure 2. Simple Dimerization Reaction to Form Dioxin

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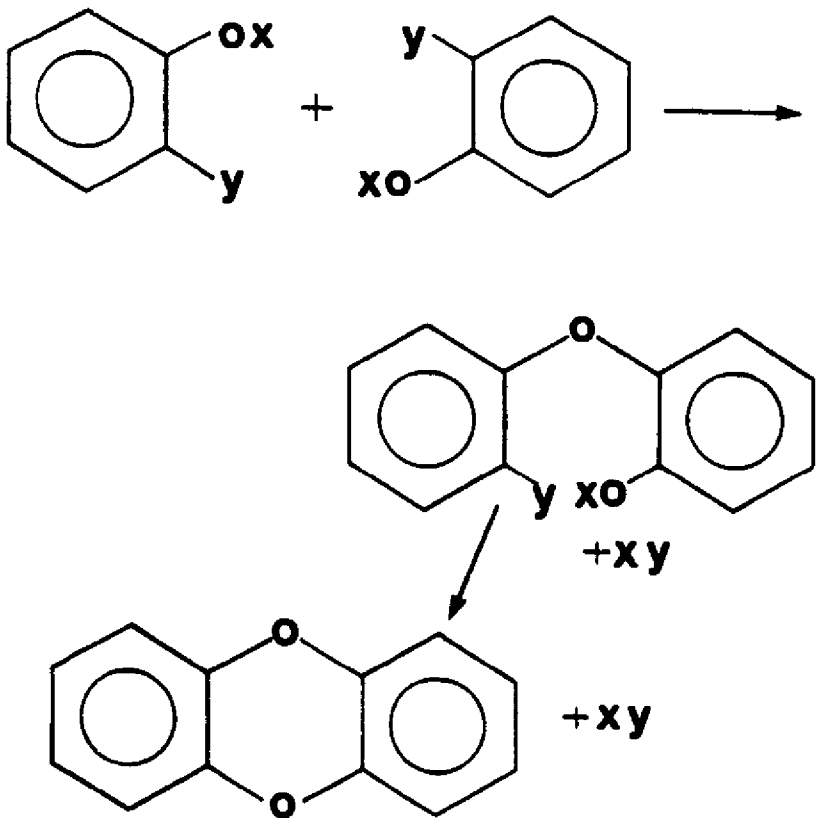

Figure 3. Dimerization Reaction Mechanism

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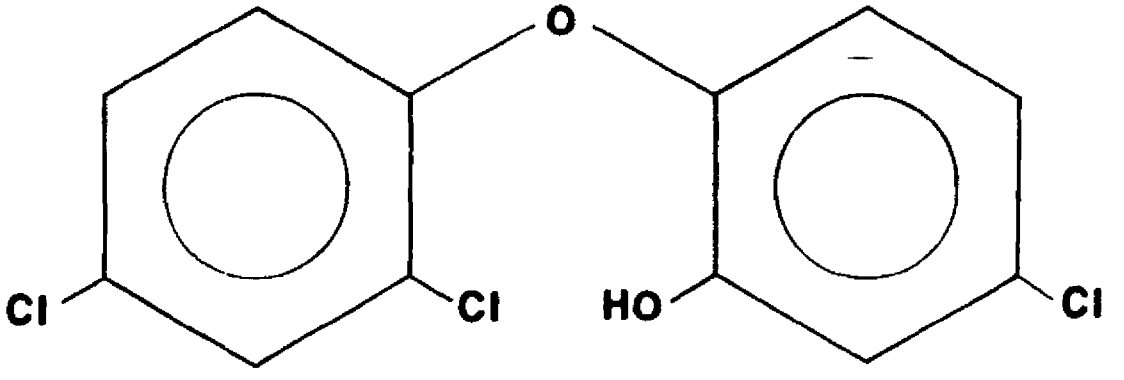

Figure 4. Irgasan DP300, A Typical Prodioxin

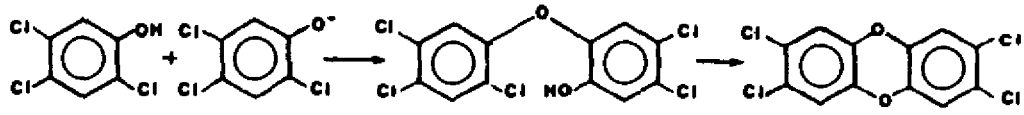

Figure 5. Formation of Dioxin from Chlorinated Phenoxy Anions

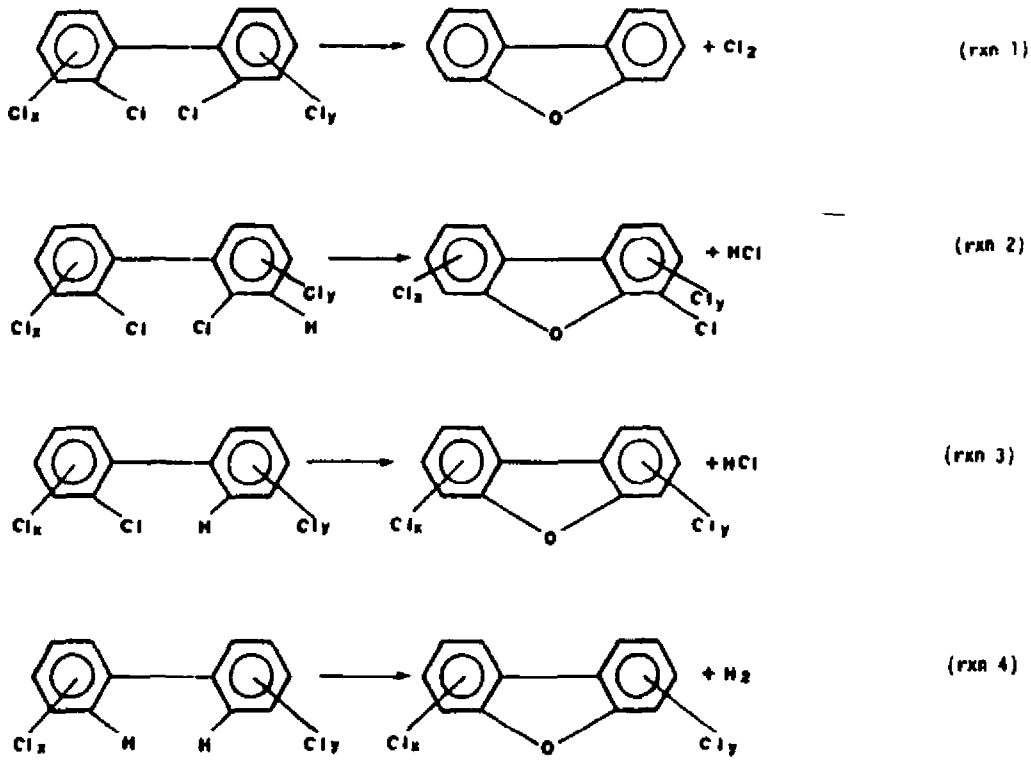

Figure 6. Basic PCDF Formation Reactions

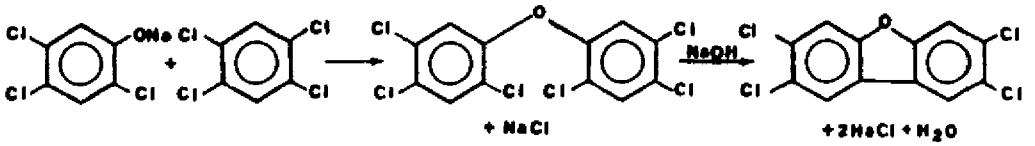

Figure 7. PCDF Formation

AN UPDATE ON ANALYTICAL METHODS FOR POLYCHLORINATED BIPHENYLS (PCB), POLYCHLORINATED DIBENZOFURANS (PCDF), AND POLYCHLORINATED DIBENZO-p-DIOXINS (PCDD)

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DISCUSSION

Evidence supporting the widespread distribution of polychlorinated biphenyls (PCB) in the environment has been documented as early as 1966, when PCB were found to interfere with the environmental determination of pesticide residues. Due to the persistence and widespread geographic distribution of PCB, animal and human toxicological studies were performed which subsequently led to the regulation of these compounds by the Toxic Substances Control Act in 1976.

Until regulation was enacted, commercial mixtures of PCB, named Aroclors, were widely used in the electric power industry as dielectric fluids in capacitors and transformers. During fires involving transformers, incomplete combustion of Aroclor containing oil produced chlorinated furan and dioxin compounds.(1)

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are relatively stable under normal environmental conditions and tend to concentrate in biological matrices due to their lipophilic nature. Although limited data are available which demonstrate the effects of PCDD and PCDF on humans, significant data have shown the toxic, carcinogenic, and mutagenic effects of these compounds in mammalian systems. Toxicities for the specific isomers vary by a factor of approximately 10,000. The chemical structures of two of the most toxic isomers in this class of compounds, having four chlorine atoms in the 2, 3, 7 and 8 positions on the furan and dioxin molecular skeletons, are shown in Figures 1 and 2.

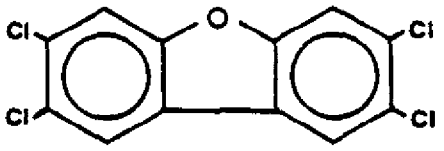

Figure 1. 2,3,7,8-Tetrachlorodibenzofuran [2,3,7,8-TCDF]

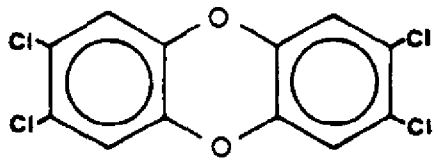

Figure 2. 2,3,7,8-Tetrachlorodibenzo-p-dioxin [2,3,7,8-TCDD]

As a result of the persistent and hazardous nature of PCB, PCDF, and PCDD, considerable emphasis has been placed on controlling the distribution of these compounds into the environment. A key issue in the control of PCB, PCDF, and PCDD is the analytical methodology. Although PCB have historically been quantified as commercial Aroclors, analysis of these compounds is complicated when mixtures of Aroclors or compositional alterations through weathering occur. Accurate PCDF and PCDD determinations are hindered by the large number of positional isomers that may exist. In total, there are 210 PCDD and PCDF positional isomers as shown in Table 1.

Table 1

PCDD AND PCDF POSITIONAL ISOMERS

Chlorine Substitution	Number of PCDD Positional Isomers	Number of PCDF Positional Isomers
Mono-	2	4
Di-	10	16
Tri-	14	28
Tetra-	22	38
Penta	14	28
Hexa-	10	16
Hepte-	2	4
Octa-	1	1

Despite the difficulties in PCB, PCDD, and PCDF analysis presented by matrix complexity and isomer configurations, reliable analytical methods are available for determination of these compounds.

Various screening methods have been reported for PCB. For quantification, the method of choice continues to be gas chromatography coupled to an electron capture (EC) detector. This technique, however, is subject to interferences from other chlorinated species which have the potential of indicating elevated levels of PCB. As a result, most samples are subjected to some form of cleanup to remove interferences prior to analysis. The cleanup procedure usually involves liquid column chromatography using silica gel, alumina, or Florisil. Complex environmental samples, however, may require a more extensive cleanup prior to analysis.

Most PCB analyses are performed using packed column gas chromatography which is adequate for many applications. Recent advances in column technology making fused silica capillary columns widely available, have made the separation of complex mixtures easier for the average laboratory. The higher resolution of capillary columns and the relative convenience of fused silica capillary columns compared to glass capillary columns has led to increased use of capillary columns in PCB analysis. Separation of an Aroclor standard using a packed GC column is shown in Figure 3. The same Aroclor separated on a capillary GC column is shown in Figure 4.

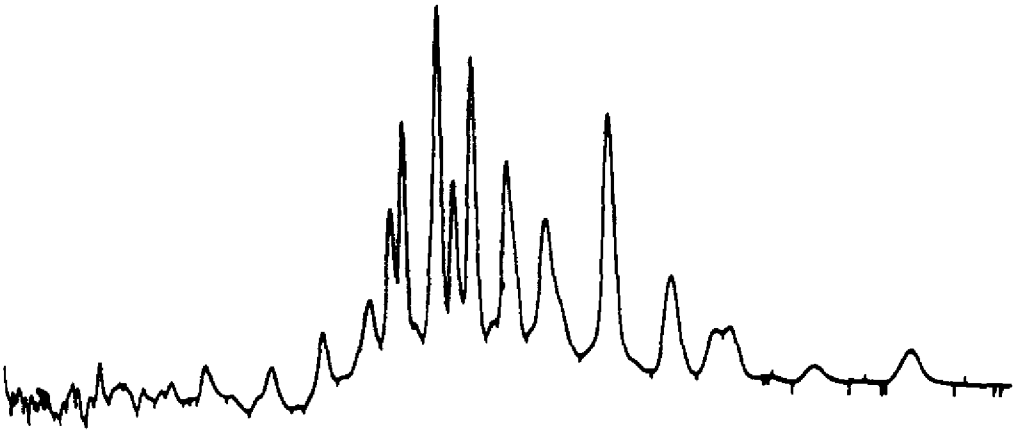

Figure 3. Packed Column GC Chromatogram of Aroclor Standard

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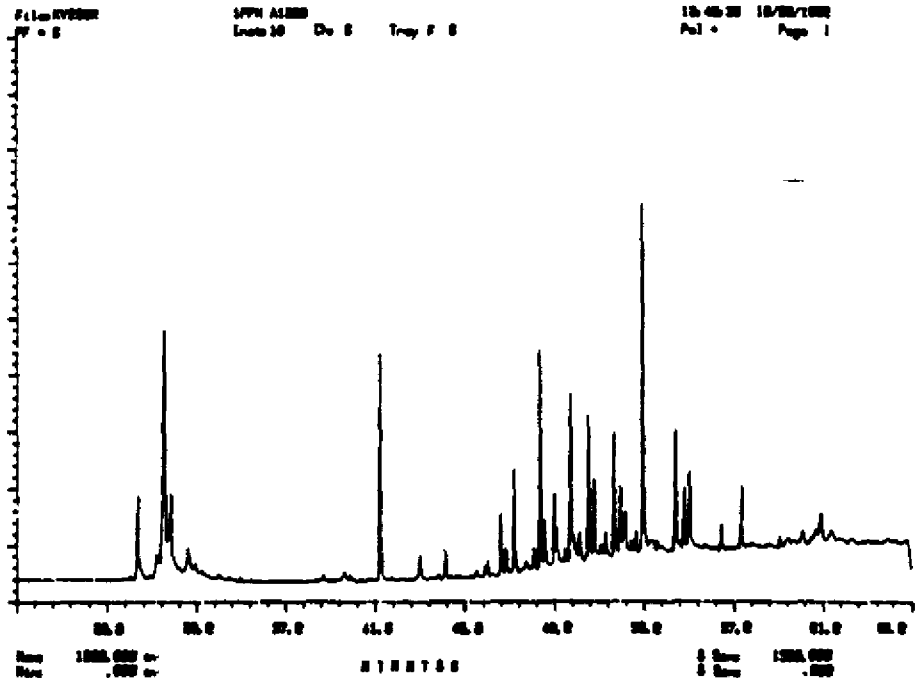

Figure 4. Capillary Column GC Chromatogram of Aroclor Standard

Emphasis in PCB analysis is now shifting toward electron impact gas chromatography/ mass spectrometry (GC/MS) and, in particular, capillary column GC/MS as the technique to provide the most selective and unambigous determination of PCB, regardless of whether they are of incidental origin or commercial Aroclors. Earlier efforts to quantify PCB using electron impact GS/MS generally resulted in identification of specific Aroclor petterns and quantification of these commercial products. A composite mass chromatogram resulting from the GC/MS analysis of an Aroclor 1254 standard is shown in Figure 5. The extracted ion current profiles represent the molecular ion of PCB having one to eight chlorines. A similar GC/MS analysis of a sediment sample containing a mixture of Aroclors as well as other chlorinated species is shown in Figure 6. The elution pattern of isomers having 5, 6, and 7 chlorines (m/z 326, 360, 394) in the unknown and standard clearly establishes Aroclor 1254 as a major constituent in the sediment sample, and provides a mechanism for quantification that is relatively free of inteferences.

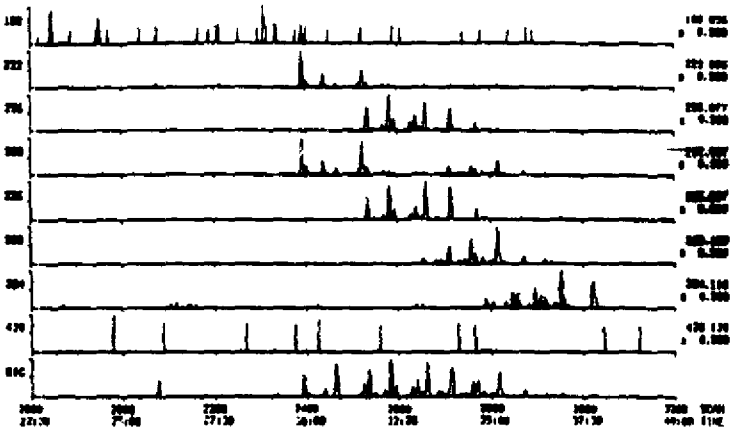

Figure 5. Mass Chromatogram of Aroclor 1254 Standard

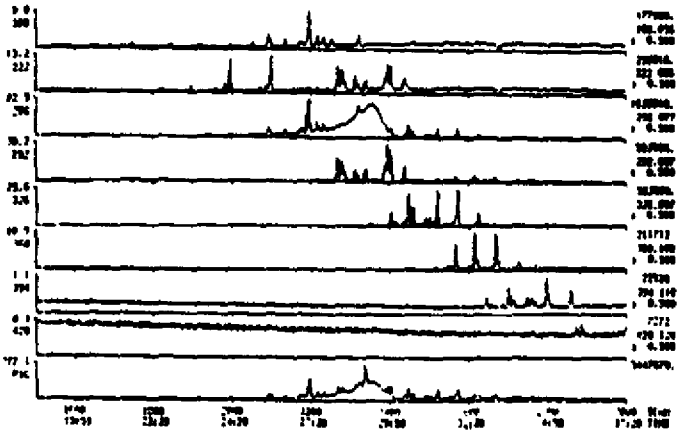

Figure 6. Mass Chromatogram of Sediment Sample

For PCDD and PCDF analyses, extremely high selectivity and sensitivity are needed to unambiguously determine these compounds at ultra-trace levels in environmental samples. These characteristics are achieved by high resolution gas chromatography/ high resolution mass spectrometry (HRGC/HRMS). A chromatogram from an HRGC/HRMS analysis of a ten liter water sample spiked with two TCDD isomers is shown in Figure 7. In this chrometogram, specific isomer determination is made for 5 parts-per-quadrillion (W/W) 1,2,3,6,8-TCDD and 8 parts-per-quadrillion (W/W) 2,3,7,8-TCDD. This represents an analytical sensitivity of approximately 8 x 10^{-12} grams.

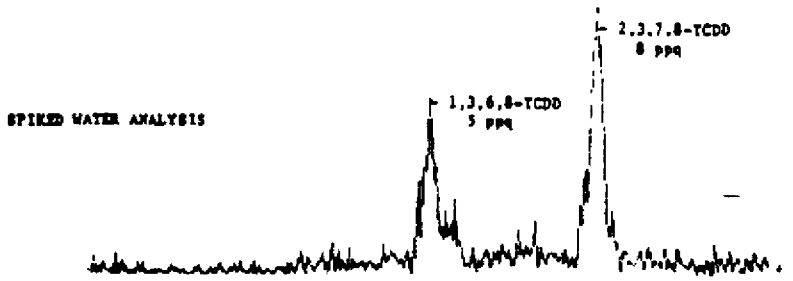

Figure 7. HRGC/HRMS Chromatogram From Spiked Water Analysis

The high selectivity of HRGC/HRMS allows the analyst to distinguish close eluting interferences as shown in the chromatogram given in Figure 8. This chromatogram was produced from a spiked fish tissue sample which was extracted, extensively partitioned by column chromatography, and then analyzed by HRGC/HRMS for 1,3,6,8-TCDD, 1,3,7,9,-TCDD and 2,3,7,8-TCDD. Detection and quantification of 3 parts-per-trillion (W/W) of 1,3,7,9-TCDD was achieved in this complex biological matrix.

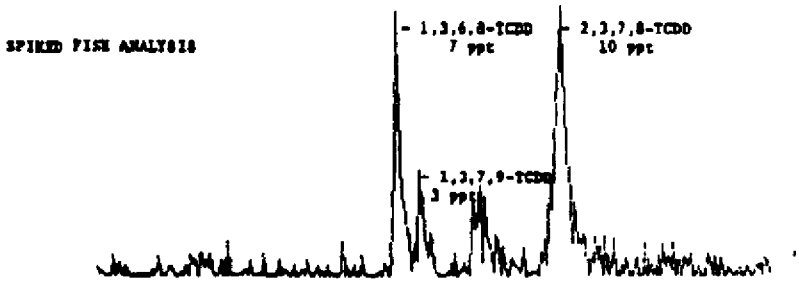

Figure 8. HRGC/HRMS Chromatogram From Spiked Fish Analysis

The highest selectivity and sensitivity for PCDD and PCDF analyses is provided by combining HRGC/HRMS with a technique called multiple ion detection. With this

procedure, the mass spectrometer is repetitively jumped between the peaks of interest. Since time is not required to scan between peaks, the ultimate sensitivity is achieved. Unlike low resolution mass spectrometry that monitors a one atomic mass unit wide window, high resolution mass spectrometry monitors a much narrower window. Thus interferences with nominal masses that are the same as PCDD/PCDF are often resolved. The high resolution mass spectrometer is typically operated at a resolution of 10,000. Resolution is defined by the ratio M/ΔM where M is the nominal mass and ΔM the difference between two adjacent peaks of equal height which have a valley of 10% between them. The exact masses that are monitored for selected PCDD/PCDF isomers are listed in Table II.

Table II

SELECTED DATA FOR THE POLYCHLORINATED DIBENZOFURANS AND POLYCHLORINATED DIBENZO-p-DIOXINS OF INTEREST

Compounds	Accurate Mass		Theoretical Isotope Ratio
	Low Mass	High Mass	
Tetrachlorodibenzofuran	303.9016	305.8987*	.77
Tetrachlorodibenzo-p-dioxin	319.8965	321.8936*	.77
Pentachlorodibenzofuran	339.8597*	341.8567	1.54
Pentachlorodibenzo-p-dioxin	355.8546*	357.8517	1.54
Hexachlorodibenzofuran	373.8207*	375.8178	1.23
Hexachlorodibenzo-p-dioxin	389.8156*	391.8127	1.23
Heptachlorodibenzofuran	407.7817*	409.7788	1.03
Heptachlorodibenzo-p-dioxin	423.7766*	425.7737	1.03
Octachlorodibenzofuran	441.7428	443.7398*	0.88
Octachlorodibenzo-p-dioxin	457.7377	459.7347*	0.88

* Quantitation Mass

For each isomer class, two of the molecular ion peaks are monitored, thus increasing the selectivity of the method. By requiring that isotope ratios are correct, false positive identifications are greatly reduced.

CONCLUSIONS

The large number of isomeric forms and the complex nature of environmental matrices pose a difficult problem for the chemists and biochemists struggling to determine the existence, distribution, and toxicity of PCB, PCDD, and PCDF in the environment. This problem can be met by the resolution and sensitivity capabilities offered by glass capillary gas chromatography, combined high resolution gas chromatography/high resolution mass spectrometry, and other sophisticated analytical methods.

REFERENCES

[1] O. G. Barnes, "Dioxin" Production from Combustion of Biomass and Wastes," presented at the 1983 Energy from Biomass & Wastes VII Conference (Institute of Gas Technology) Lake Buena Vista, Florida, January 24-28, 1983.

DISCUSSION

There were a number of comments regarding the developing "standards" and the measuring techniques.

DETECTION OF POLYCHLORINATED DIBENZOFURANS AND OTHER CHLORINATED PYROLYSIS PRODUCTS IN THE SOOT FORMED IN PCB FIRES

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ABSTRACT

Uncontrolled electrical fires involving transformer oils containing PCBs are found to form a complex and potentially toxic mixture of chlorinated products in the soot, including the chlorinated dibenzofurans (CDFs), with degrees of chlorination from Cl_1 to Cl_6. Concentration levels vary widely, depending on the specific conditions of the fire, but levels of 2,3,7,8-tetrachloro dibenzofuran (2,3,7,8-TCDF) in the range of 1-10 ug/g of soot were measured in some samples. In the same samples, no chlorinated dibenzodioxins (CDDs) were detected, but several other classes of chlorinated products were found in greater abundance than the CDFs. These included the chlorinated biphenylenes (Cl_1-Cl_6) and chlorinated PNAs, such as the chlorinated pyrenes (Cl_1-Cl_5), as well as residual PCBs. Unchlorinated PNAs from anthracene to the benzopyrene (5 ring) group were also detected at levels comparable to the PCBs.

INTRODUCTION

The purpose of this work was a comprehensive characterization of the organic products found in the soot formed in PCB electrical fires. The samples, both bulk soot and surface wipes, were collected by NIOSH industrial hygienists at the site of several fires involving PCB-askarels. Radian was directed to identify and quantify any CDFs or CDDs in these samples, as well as the other major organic species, chlorinated or not. The analytical method was based on Soxhlet extraction followed by high resolution gas chromatography (HRGC) coupled to a mass spectrometer (MS) operated in either a limited scanning (SCAN) or selected ion monitoring (SIM) mode, using only electron impact ionization. The results of these analyses are summarized here. A more complete report of this work is being published in Chlorinated Dioxins and Dibenzofurans in the Total Environment, Volume 2, Butterworth, 1984.

EXPERIMENTAL METHOD

Bulk soot in quantities from 0.1 to 1g and surface wipe samples on filter paper (100 cm^2) were collected by NIOSH industrial hygienists at the site of several PCB fires. The samples were analyzed by Radian Corporation using the experimental method shown in Figure 1. Both sample media were Soxhlet extracted with benzene or toluene for 8-12 hours and analyzed without cleanup in order to characterize the complete sample. Samples were spiked before extraction with internal standards of $^{13}C_{12}$-2,3,7,8-TCDD, d_6-3,3',4,4'-TCB (d_6-TCB) and d_{12}-chrysene. Sample extracts were concentrated to final volumes of 100-500 uL by low temperature (25-50°C)

solvent evaporation. The concentrated extract was spiked with another internal standard, d_{12}-anthracene, just prior to analysis.

Samples underwent two successive HRGC-MS analyses: a screening analysis with the MS in a limited mass scan (150-500 amu) mode, and a confirmation analysis with the MS in a SIM mode, simultaneously measuring four characteristic ions. Both these analyses were carried out on a Hewlett Packard Model 5985A quadrupole GC-MS system. The screening analyses were accomplished using a 50m WCOT capillary column with a bonded, neutral stationary phase, e.g., DB-5 or OV-1. Isomer-specific confirmation of the TCDFs was accomplished on a 60m silica capillary column coated with a more polar phase, Supelco 2340. Figure 2 shows an HRGC-SIM-MS chromatogram of a Radian standard containing all 22 of the TCDD isomers, plus the internal standard $^{13}C_{12}$-2,3,7,8-TCDD, analyzed on the Supelco 2340 column.

RESULTS AND CONCLUSIONS

Some of the bulk soot samples collected at the site of PCB fires show a very complex pattern of occurrence of the PCDFs. Figure 3 shows the HRGC-SIM-MS chromatogram of a bulk soot sample analyzed for the PCDFs. At least 21 peaks were identified as PCDFs and as many as 26 of the 38 possible isomers could have been present. It can be seen that one of the major TCDF peaks is identified as the 2,3,7,8 isomers (28.8 min). Three large peaks coeluting with the TCDFs were identified as trichloropyrenes. Figure 4 shows the characteristic mass spectrum of 2,3,7,8-TCDF in which the loss of the CDCl to produce the fragment ion at mass 241 is apparent. Figure 5 shows the mass spectrum of one of the trichloropyrenes which has the same molecular weight but a different chlorine isotope pattern and a different fragment ion (234) due to the loss of Cl_2.

The occurrence of the most significant chlorinated products formed in the pyrolysis/combustion of the PCBs in accidental fires is indicated in Figure 6. It seems clear that the mechanism of formation of these major products may involve both pyrolysis and combustion and may depend on other organic materials present in the fire in addition to the PCBs.

Figure 7 gives a pattern of occurrence for the major pyrolysis/combustion products that were detected in this study of soot and wipe samples from PCB fires. The ordinate in Figure 7 is given without units since the actual concentrations found will depend on the specific circumstances of each fire and the sites where samples are collected. However, in this study, maximum concentrations of the PCDFs in the soot were measured in the range 1-10 ug/g (ppm w/w), with corresponding levels on surface wipes falling in the range of 100-1000 ng/100 cm^2.

The most significant findings in this work are summarized as follows:

- high concentrations of TCDFs and other CDFs can be found in the soot formed in accidental PCB fires;
- the acutely toxic 2,3,7,8-TCDF is one of the most abundant isomers in the complex pattern of TCDF homologues extracted from the soot;
- other potentially toxic chlorinated products and PNAs are found in even higher concentrations than the CDFs in the soot from PCB fires; and
- no dioxins (CDDs) were found in this study above a detection limit of 1-10 ng/sample, i.e., 1-10 ng/g for soot and 1-10 ng/100 cm^2 for wipes.

DISCUSSION

QUESTION: Has the soot been tested for toxicity?

ANSWER: Yes. At Binghamton they did toxicity tests with the soot. It was toxic to animals

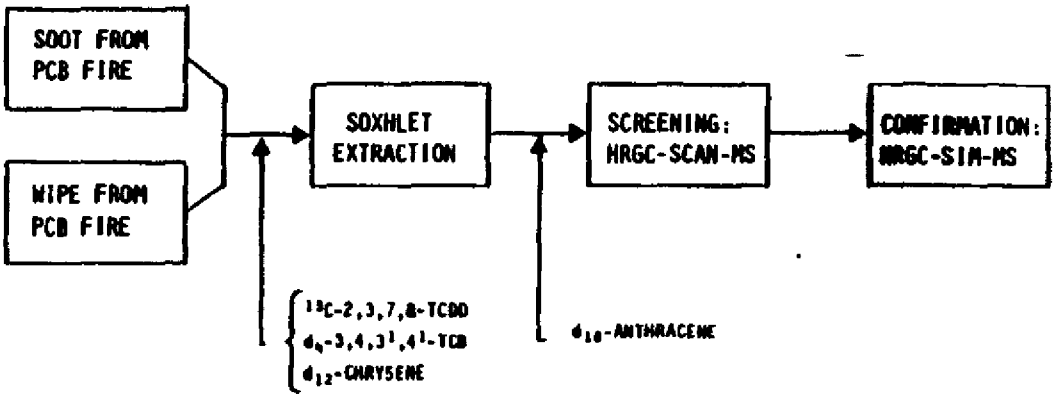

Figure 1. Block Diagram of the Analytical Method

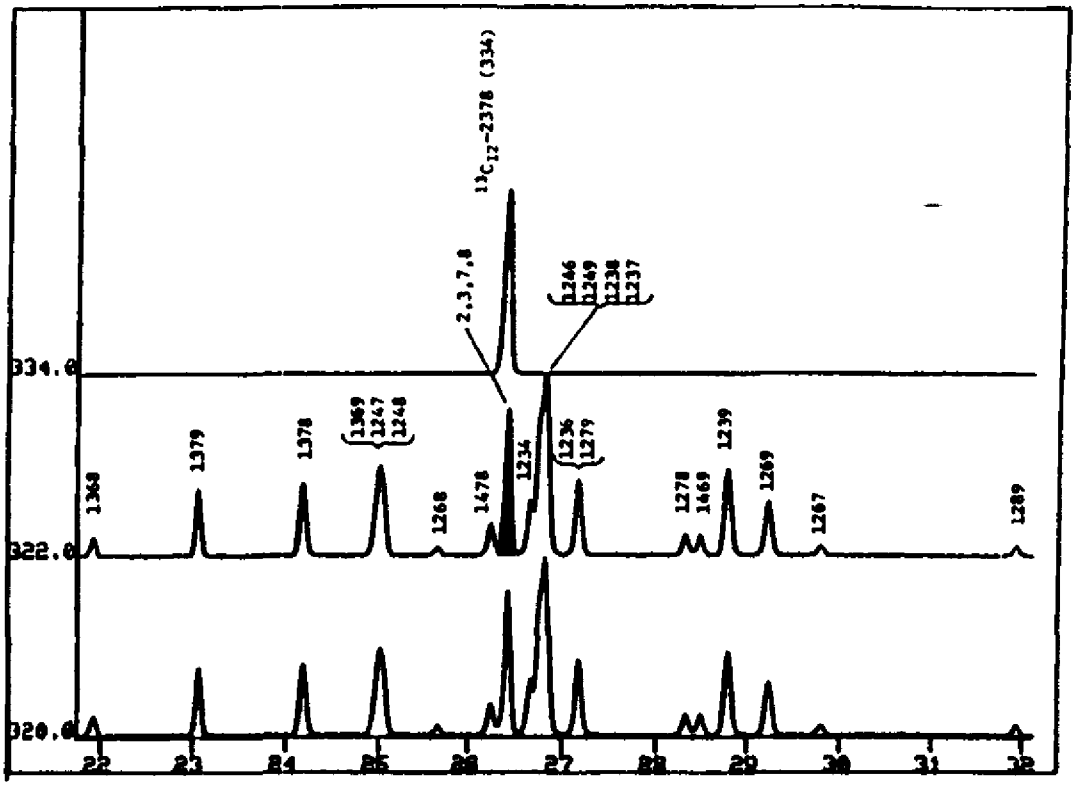

Figure 2 HRGC-MS Chromatogram of Radian Standard of all 22 TCDD Isomers plus the Internal Standard $^{13}C_{12}$-2,3,7,8-TCDD

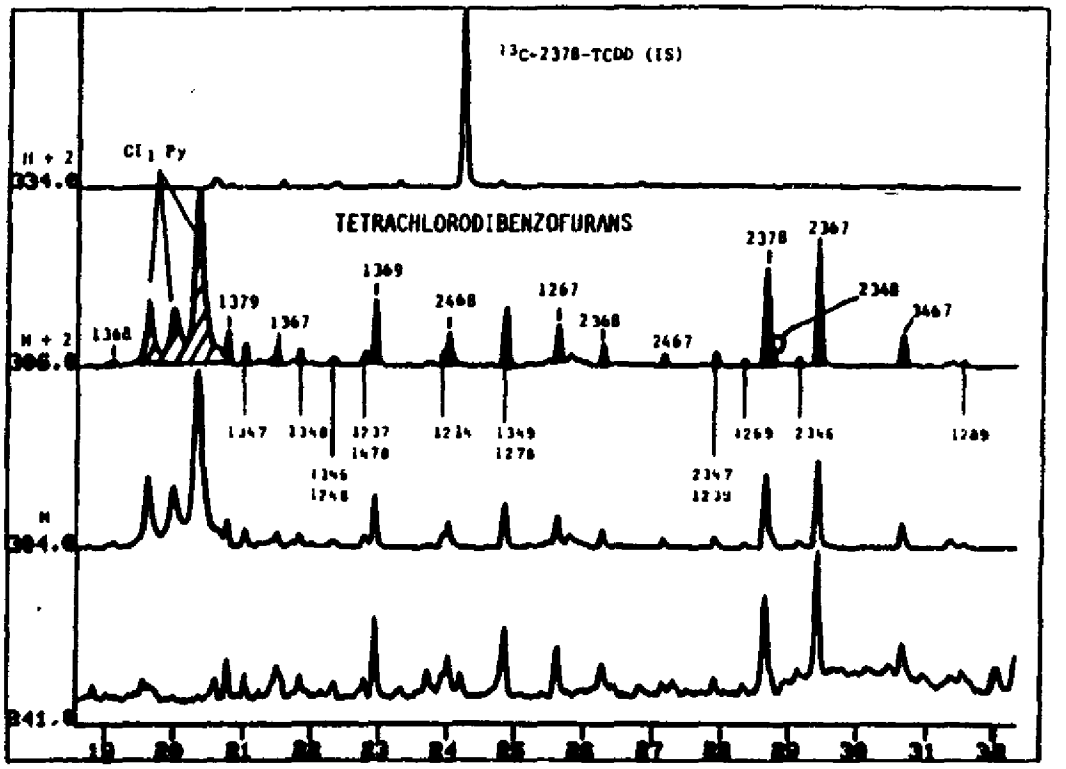

Figure 3. HRGC-SIM-MS Chromatogram of Bulk Soot Sample from a PCB Fire Analyzed for the TCDFs

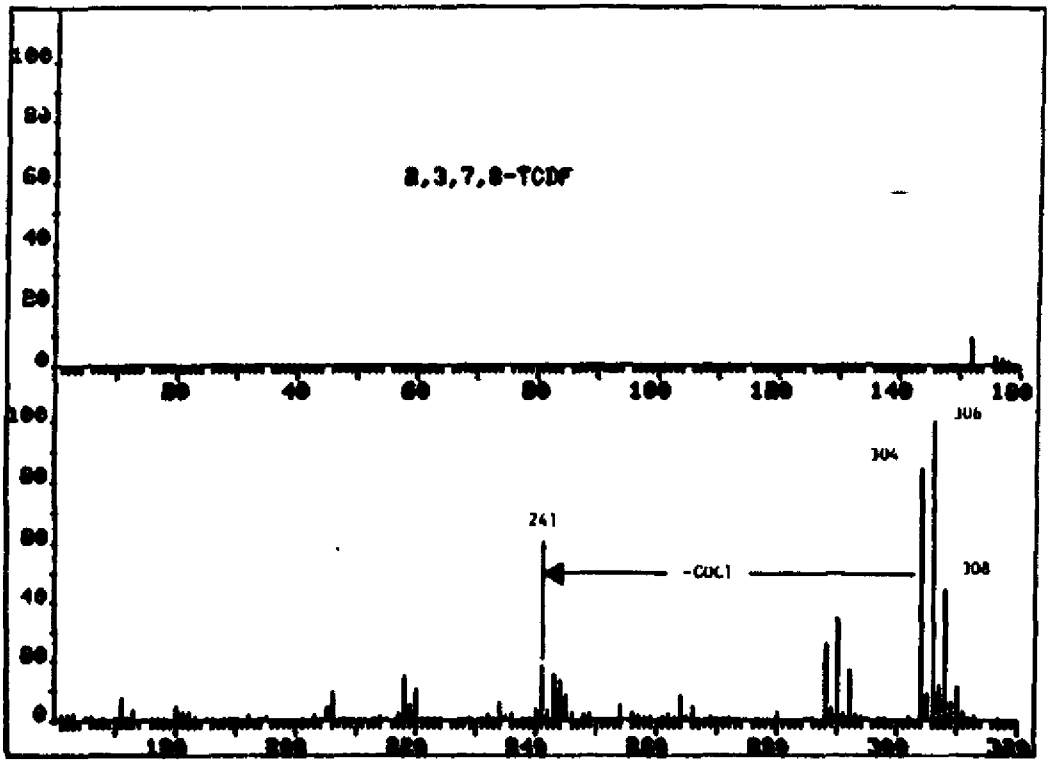

Figure 4. Mass Spectrum of 2,3,7,8-TCDF from the Peak in the Chromatogram of Figure 3

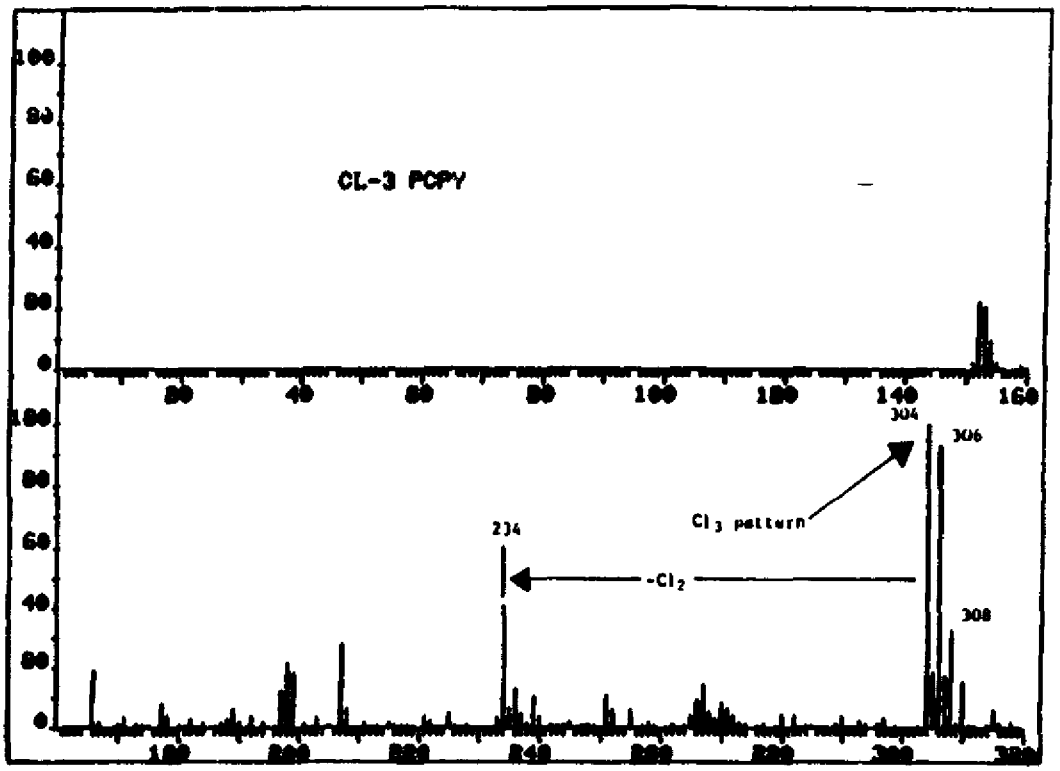

Figure 5. Mass Spectrum of a Trichloropyrene from the Peak at 20 3 minutes in the Chromatogram of Figure 3

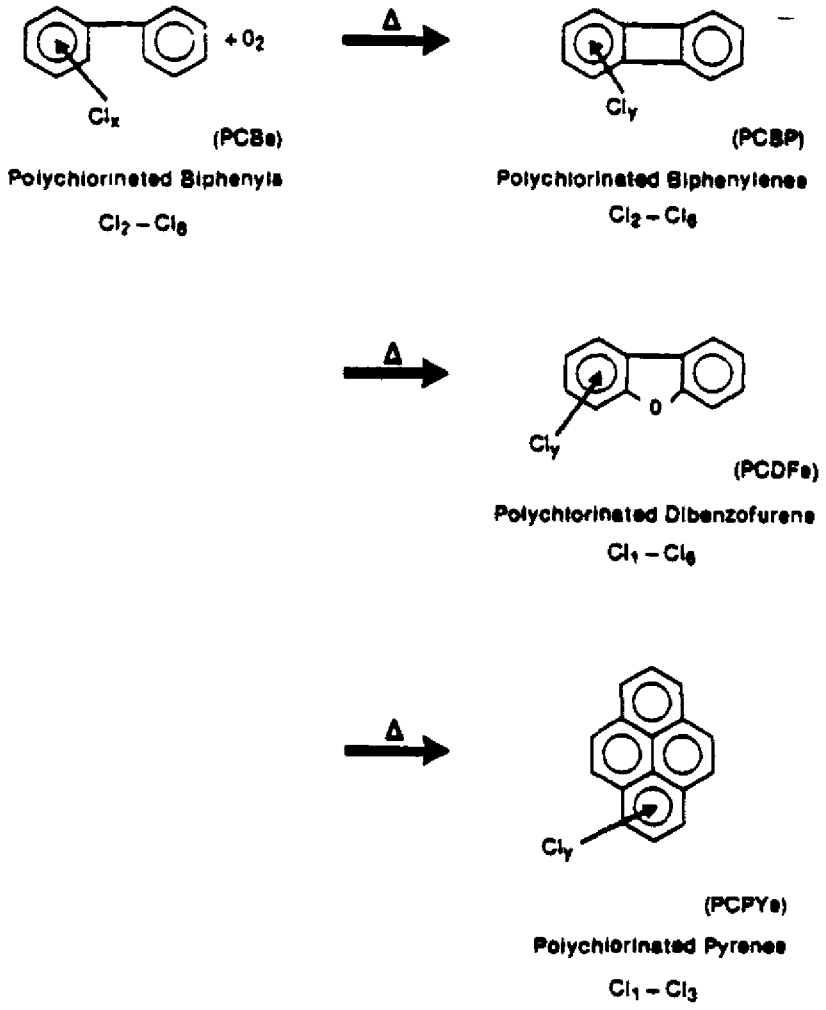

Figure 6. Representation of the Structures of the Principal Chlorinated Pyrolysis/Combustion Products Found in the Soot from PCB-Askarel Fires.

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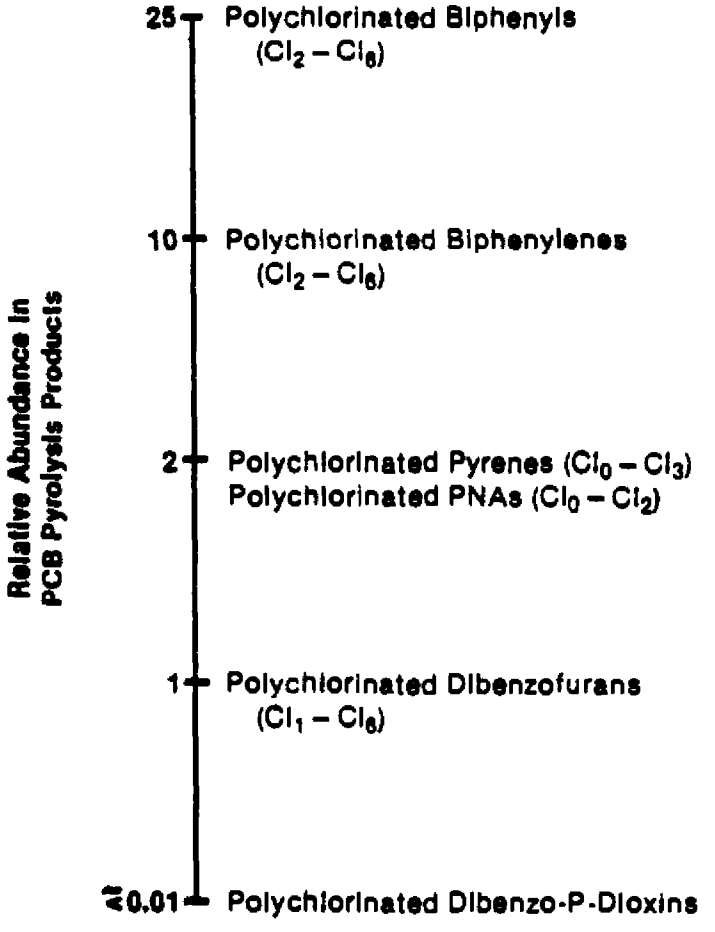

Figure 7. Relative Abundance of Pyrolysis/Combustion Products Formed in PCB-Askarel Fires.

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Part 7

DECONTAMINATION OF MINERAL OIL

SOLVENT EXTRACTION OF PCB FROM TRANSFORMER MINERAL OIL

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PCB (polychlorinated biphenyls) can be removed from a transformer mineral oil by mixing the oil with an immiscible liquid in which PCB are soluble. PCB will be removed from the oil into the extraction liquid until equilibrium is established. If the partition coefficient is one, one-half of the PCB in the oil will be dissolved into an equal volume of extraction liquid initially containing no PCB. Ninety percent of the PCB will be extracted on mixing the oil with nine volumes of the second liquid - and so on. Oil-liquid systems with higher partition coefficients require less extraction liquid to reduce the PCB content of oil by a given amount. Unfortunately, large partition coefficients for PCB-oil systems are unlikely on thermodynamic grounds and the amount of extraction solvent needed to remove PCB will be large. Any practical process will require reuse of the solvent after removal of the previously extracted PCB. This can be done by using an extraction liquid which has a boiling point well below that of PCB (~275°C and up). The solvent can be recovered by distillation, leaving the accumulated PCB in the distillation column bottoms for removal to final incineration (1).

The work reported here is based on extraction of PCB by the monomethyl ether of diethylene glycol - methyl Cerbitol™ ("MeC"). The boiling point of MeC is 193°C and its density is greater than that of oil (1.03 g/ml versus 0.9 g/ml @ 25°C). MeC was selected from half a dozen candidates on the basis of preliminary testing at ambient temperature in the laboratory. The PCB partition coefficient is approximately one, its solubility in oil is ~4% and the solubility of oil in MeC is ~8%. The interfacial tension between MeC and either unused or aged transformer oil is rather low (<1 dyne/cm). The choice of MeC represents a compromise. The partition coefficient for dimethyl acetamide, for example, is two to three times higher but so also is its solubility for oil. The solubility of oil in methanol is much lower, but the partition coefficient for PCB is also substantially lower.

A small scale demonstration plant was designed and put in place to establish the technical feasibility of the extraction process and to evaluate the relation between controllable process parameters and efficiency in a continuous operation in order to estimate the magnitude of the process costs. A commercially available (York Process Equipment Company) agitated multi-stage countercurrent extractor was used. Oil containing PCB was fed into the column near the bottom and the extracted product was removed at the top of the column. PCB-free MeC

was introduced into the column near its top and removed near the bottom. The extract was fed to a vacumm distillation column where the MeC was distilled from the dissolved PCB end oil The MeC was recycled to the extraction column and a PCB enriched oil fraction accumulated in the distillation column bottoms.

Two unusual modifications were made to this process. If, for example, the flow rates of MeC and oil were equal in an extraction column of given design operating at ~25°C, a certain efficiency of PCB removal (PCB concentration in the feed stream minus concentration in the product streem/concentration in tha feed) would be achieved. Without modification, the process would lose 8% of the oil feed to the PCB residue and hence to incineretion. Either e larger column or a higher solvent-to-oil retio can increase the efficiency. The first adds to the capital cost of the equipment; the second edds to the oil lost and the incineration cost. However, if the oil is recycled from the distillation column bottoms back into the bottom of the extrection column as extractor reflux, it contributes to maintaining the oil saturation in the extract streem. This reflux extraction reduces the oil loss to that deliberately removed for incineration when the PCB concantration reaches some predetermined level. Loss of no more than 1% of the oil was set as a goal in this study. This would result in a PCB concentration in the distillation column bottoms one hundred times that of the reduction in concentration between the feed and product oil. An extractor reflux concentration and residue concentration as high as 5% PCB could be reached.

It also is desirable not to overheat the oil in the still bottom in order to reduce degradation of oil in the reflux stream, some of which mixes back into the product oil flow. To minimize the bottom temperature without requiring an extremely low vacuum, the solvent separation is carried out in two steps, a partial separation by distillation, and then a final purification by phase separation. In the partial separation, enough solvent is allowed to remain in the distillation column bottoms to permit operation of the column under economical vacuum conditions and acceptable temperatures. This may correspond to a distillation column bottoms composition of between 20 and 80 percent solvent. In the second separation, this bottom product is cooled to a temperature below the limits of complete mutual solubility so as to form a PCB-oil phase end a solvent phase. After separating these two phases by decanting, the solvent phase is returned to the distillation column, while the PCB-oil phase is returned, for the most part, to the extractor as reflux.

The pilot plant was operated with oil feed rates up to 10 gallons per hour and extraction reflux rates to 2 gallons per hour (the reflux rate cannot exceed the limit of the fractional solubility of oil in the solvent flow). A reflux retio in the distillation of one to four was used and the PCB content of the returning MeC remained less than 1 ppm. Ratios (weight/weight) of solvent-to-oil (feed + reflux) rates ranged from 1.7 to 4. Unused oils with initial concentrations between 300 and 1400 ppm of Aroclor 1254 and aged oils with initial concentrations between 150 and 500 ppm of Aroclor 1260 were tested.

The results were evaluated using the standard model for countercurrent solvent extraction:

$$E(\%) = 100 \times [(mL/V)^{n+1} - (mL/V)]/[(mL/V)^{n+1} - 1]$$

where E is the efficiency of extraction; m, the partition coefficient; n, the number of theoretical stages in the extractor; L, the internal mass flow rate of solvent and V, the internal mass flow rate of oil (in this case, the combined feed and reflux flows) in the column. The data is an excellent fit for a value of n of 3.3 and values of m of 1.0 and 0.6 for Aroclors 1254 and 1260 respectively.

Aroclor 1260, the more heavily chlorinated PCB mixture, is less effectively extracted because of its lower "avarage" partition coefficient. The chromatography of the feed and product streams shows that the partition coefficients decrease for the more heavily chlorinated isomers. Aroclor 1242, the least chlorinatad of the PCB mixtures used in askarels, should be the most effectively removed.

Variation of extractor temperature between 20 and 40°C had no effect. The column efficiency was not affected by agitator speed between 195 and 260 vpm. Above this foaming occurred, the phases failed to separate and the extractor column flooded. The rather low interfacial tension is presumably the cause.The case of ninety percent removal efficiency is of interest in that feed streams containing up to 500 ppm PCB could be reduced to below 50 ppm (At 1% oil incineration, the bottoms concentration would be less than 4.50%). The case of 98% efficiency is also of interest in that feed streams containing up to 100 ppm PCB could be reduced to less than 2 ppm. For estimating purposes, it is assumed that three quarters of the PCB in a typical feed stream will be from Aroclor 1260 and the remainder will be due to a mixture of Aroclors 1242 and 1254; i.e., m~0.7. With an extractor of the present design, solvent to oil flow rate ratios of 2.2 and 4.1 would be required to achieve 90 and 98% extraction efficiency respectively. If the number of stages is increased by fifty percent, the same result can be reached with solvent to oil ratios of 1.7 and 3.0.

The lower solvent-to-oil ratio and more efficient extractor design appears to be a more cost-effective approach. The costs resulting from several possible operating scenarios have been estimated using this approach. Costs were estimated for operation at oil processing rates of 60 to 480 gal/hr and for one, two or three shifts per day. Annual production then ranged from 100,000 to slightly less than three million gallons. In the base case, it was assumed that a fixed installation site would be adjacent to an existing facility for treating, handling or burning oil. Labor and supervision were expected to be shared with that of the existing facility. Available indoor space for installation of control and instrument panels was assumed. Steam generation and cooling water facilities were expected to be in place. The costs for these scenarios are summarized on Table 1. The estimates include transportation and the incineration cost for 2% of the oil.

The added costs for operation in a second siting situation also have been estimated. It was assumed that steam generation and cooling water facilities must be installed together with housing for the weather sensitive equipment and, further, that isolated installation would be made where full manpower requirements must be met and that oil handling facilities would have to be added. The additional costs of these scenarios are listed in Table 1.

It was assumed in the base case that transformer oil reconditioning facilities were available. Additional costs are listed for a situation where this is not the case and filtering, degassing and claytreat equipment must be put in place.

It must be reiterated that these are estimates based on the usual engineering basis and using typical costs for utilities, interest rates and so forth. They are intended merely to define the general range of costs and may not reflect the real cost. An estimate has been made, however, on a comparable basis for a process described elsewhere (1,2) using sodium metal, naphthalene and diglyme to destroy the PCB in situ in transformer oil. The results are similar. Cost of PCB removel by high energy electron treatment or by critical fluid extraction (1) are estimated to be higher.

The results of these preliminary tests indicate that reflux extraction of PCB from transformer oils can be done with high efficiency. Preliminary estimates suggest that it is potentially cost competitive with other processes.

This work was sponsored by the Electric Power Research Institute as a part of Research Project 2028-1.

(1) T. O. Rouse, Removal Of PCB From Transformer Oil, Proc. PCB Seminar, EPRI EL-2572 (1982); also, Removal Of PCB From Transformer Oil-Final Report, EPRI RP 2028-1 (in preparation).

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TABLE 1

SUMMARY

COST ESTIMATES

PCB - SEP PROCESS

PRODUCTION RATE (Gal/Hr)	60		480	
Shift/Day	1	3	1	3
ANNUAL PRODUCTION (KGal)	105	360	840	2880
STATIONARY INSTALLATION				
98% REMOVAL EFFICIENCY				
CAPITAL INVESTMENT ($K)	470		1260	
PROCESS COST ($/Gal)	2.66	1.25	1.03	0.60
90% REMOVAL EFFICIENCY				
CAPITAL INVESTMENT ($K)	410		1015	
PROCESS COST ($/Gal)	2.37	1.12	0.84	0.49
ADDITIONAL PROCESSING (ADD TO BASE COST ABOVE)				
REMOTE LOCATION - ADD STEAM BOILER, COOLING TOWER, BUILDING, OIL TANKAGE & FULL MANPOWER				
ADDED INVESTMENT ($K)	215		402	
ADDED COST ($/Gal)	1.42	0.91	0.26	0.14
CLAY TREAT & DEGASSING				
ADDED INVESTMENT ($K)	55		130	
ADDED COST ($/Gal)	0.21	0.07	0.07	0.03

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Pilot Plant Studies for Solvent Extraction of Polychlorinated Biphenyl (PCB)

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Nuclear Materials Processing and
Waste Management Technology Department
Development Division

Operated by

UNION CARBIDE CORPORATION
for the
U. S. DEPARTMENT OF ENERGY
under Contract No. W-7405-eng-26

ACKNOWLEDGMENTS

The authors would like to acknowledge the professional services of P. F. (Paul) Meredith and F. L. (Lynn) Yearwood for laboratory operating and construction advice; and K. R. (Kelly) Hopson, N. G. (Nell) Cannon, and R. J. (Ron) McElhaney for analytical chemistry assistance.

SUMMARY

The polychlorinated biphenyl (PCB) concentration system performed very satisfactorily while using dimethylformamide (DMF) as a solvent. The pilot-plant extraction system processed oil with a PCB concentration as high as 300 ppm at a rate of 0.8 L/min using two columns which were each 10 cm in diameter and 4.6 m high. Higher volume flows and lower PCB removal should be obtainable if larger extraction columns were used. The PCB removed from the DMF is 16 to 20 times more concentrated than the PCB present in the original oil. The recovery of dry DMF (less than 1.5 vol % water) was accomplished using distillation at a rate of 0.38 kg/h-cm^2 (based on distillation column cross section).

Section 1

INTRODUCTION

A large quantity of mineral oils (used as transformer, machine cutting, cooling, and lubricating oils) in the Oak Ridge Y-12 Plant* contain low concentrations (50-300 ppm) of polychlorinated biphenyls (PCB). Because the Plant does not have a burial ground, these oils must either be stored or incinerated. Also, as some of the oils are contaminated with uranium, they cannot be shipped off-site for incineration or burial because commercial PCB disposal facilities cannot accept uranium-contaminated wastes.

Long-term storage is an option but, because of space and labor requirements, is expensive. To reduce storage or disposal costs, the PCB must be concentrated before off-site incineration or on-site storage.

The developed extraction process contacts N,N-dimethylformamide (DMF) with PCB-contaminated oil and transfers the PCB to the DMF phase. Water is then added to the PCB-loaded DMF to destroy the polar bonding of the PCB and to transfer the PCB to a smaller volume of oil.

*Operated by the Union Carbide Corporation's Nuclear Division for the Department of Energy.

Section 2

PILOT-PLANT EXTRACTION SYSTEM FOR PCB

PROCESS

The DMF-PCB extraction process removes PCB from oil into a DMF phase using a counter-current, liquid-liquid packed column (Figure 1). The DMF must be relatively water-free (less than 1.5 wt %) to ensure satisfactory extraction. The PCB is later released from the DMF phase into a receiving oil phase by the addition of water, which is soluble in the DMF. The water renders the PCB insoluble in the DMF by reducing the polar bonding of the PCB. The resulting oil phase has a PCB concentration factor of 16- to 20-fold, based on the PCB concentration in the original oil. The DMF-water can then be separated by distillation for recycling the DMF to the extraction columns.

PROCESS CHEMISTRY

Under ordinary circumstances, all PCB compounds are highly stable and unreactive due, in part, to the resonance stabilization offered by the chlorine substituents. Only extreme reagents and reaction conditions form new compounds. It would be expected that, because of the chlorine atoms, the resultant dipole would render PCB soluble in polar solvents. However, experimental results revealed that the mineral oil, although nonpolar, was one of the best solvents. Furthermore, dipole moments measured for PCB showed them to be considerably less than the analogous allyl chlorides. An explanation for this is that chlorine, although highly electronegative, is releasing electrons to the ring by double bonding rather than attracting the electrons. This situation would allow the chlorine to increase the resonance stabilization of the molecule and reduce the expected negative charge. The electron release by the chlorine would also make the carbon ring more negative. Thus, the intramolecular bonding in PCB is less polar and more van der Waals in nature; therefore, high solubility in nonpolar organics would be expected. The PCB compounds also show high solubility in polar organic solvents but low solubility in water. The solubility in polar solvents appears to be the result of a positively induced carbon in the solvent that attracts the negative charge on the biphenyl ring structure. The insolubility of water is possibly due to resonance inhibition caused by hydrogen bonding to the chlorine.

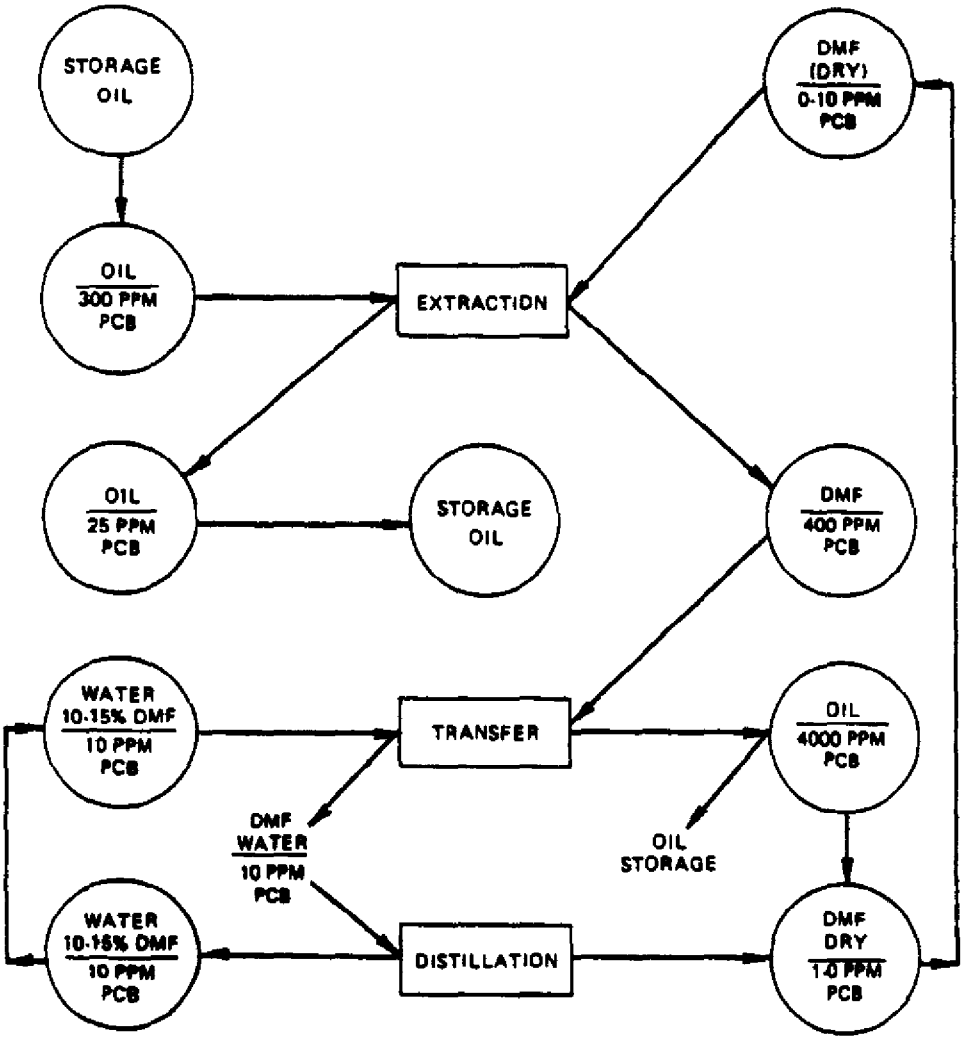

Figure 1 PCB RECOVERY FLOWSHEET

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PROCESS EQUIPMENT

The pilot-plant process equipment flowsheets (Figures 2 and 3) consist of three parts: (1) extraction, (2) transfer, and (3) distillation. The extraction consists of two 55-gal feed tanks and two 55-gal PCB-contaminated oil feed tanks. Two packed extraction columns are each 10 cm (4 in.) in diameter X 4.6 m (15 ft) high, with a 91-cm (36-in.) unpacked phase separation zone at each end of the columns. Two 55-gal stripped oil product tanks, a DMF interstage tank with a pump level controller, and a tank to hold PCB-loaded DMF were also part of the pilot plant. Each column had a bottom control valve actuated by a bubbler differential pressure (DP) cell, liquid-level control system to maintain a DMF continuous phase. The DMF transfer tank was a cone-bottom, 55-gal drum with a mixer. The columns were packed to a 4.6 m (15 ft) depth with 2.5-cm (1-in.) ceramic saddles.

The distillation equipment consisted of the following items:

1. A packed column 7.62 cm (3 in.) in diameter X 2.4 m (8 ft) high packed with perforated stainless steel packing.

2. A reboiler with a volume of 18 L and heated by a 0.46-m^2 (5-ft^2) steam coil heat exchanger connected to 120 psig-regulated steam service.

3. A top condenser with a cooling area of 0.46 m^2 (5 ft^2), including a reflux splitter.

4. Two 55-gal feed tanks, two 55-gal water product tanks, and two 55-gal DMF product tanks.

COLUMN EXTRACTION TESTS

Using one or both of the columns, tests have been performed using recycled DMF from the distallation column and clean oil to which concentrated PCB was addedto a concentration of 200 to 400 ppm in oil (Table 1). The recycled DMF had a water content of 0.7 to 1.5 wt % water. About 2 wt % water is the permissible maximum allowable for satisfactory PCB extraction. The oil feed must also be water-free (i.e., less than 1.5 wt %). The mutual solubility of DMF and oil in each other is about 5%.

The extraction tests were performed using both DMF and oil-PCB as a continuous phase. There was no apparent differece in extraction performance using the

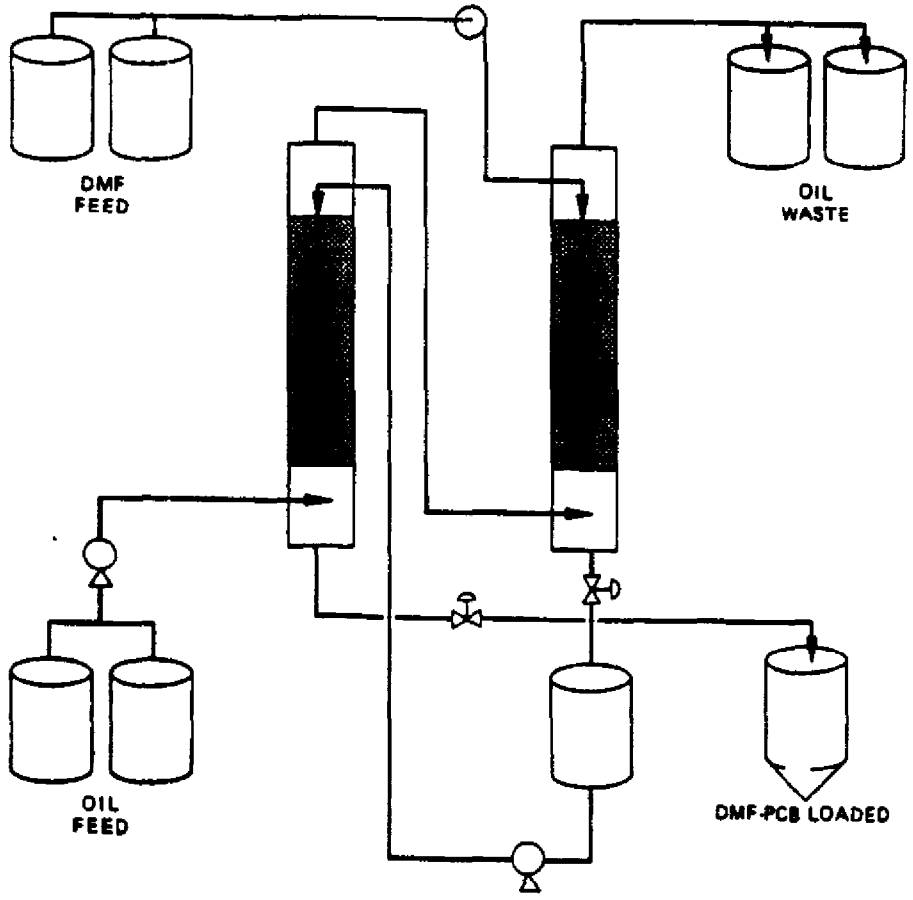

Figure 2. PCB RECOVERY EQUIPMENT FLOWSHEET
EXTRACTION SECTION

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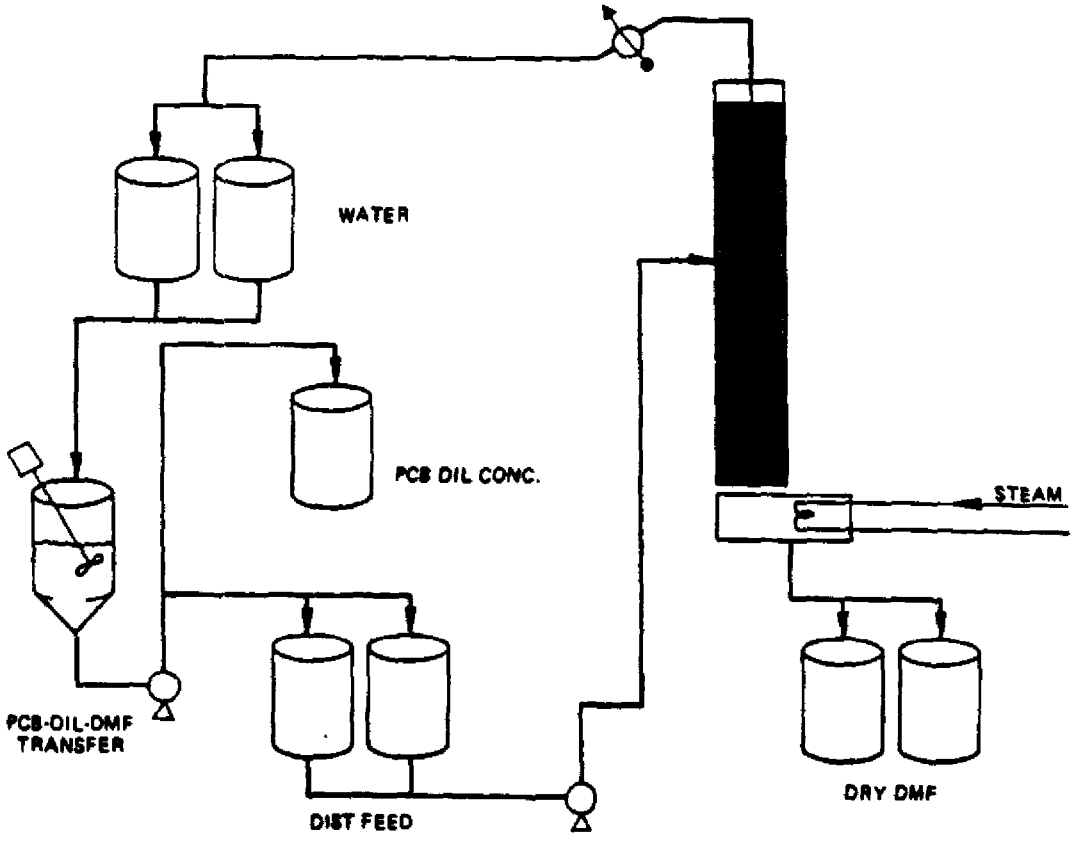

Figure 3. PCB RECOVERY EQUIPMENT FLOWSHEET
TRANSFER AND DISTILLATION SECTION

MONS 215129

Table 2-1

SOLVENT EXTRACTION TESTS

Test Number	DMF Flow (mL/min)	Oil Flow (mL/min)	Column Length (m)	DMF In (ppm)	DMF Out (ppm)	Oil In (ppm)	Oil Out (ppm)	DMF/Oil Distribution Coefficient Top	DMF/Oil Distribution Coefficient Bottom
1	550	440	4.6	120	200	270	110	-	-
2	370	430	4.6	5	150	160	50	1.6	1.4
3	230	1200	4.6	25	420	300	200	-	-
4	660	750	9.2	2	220	380	94	1.6	1.5

different continuous phases. Therefore, a DMF continuous operation was selected because the phase interface was at the top of the column, which was better for the interface control instruments.

The flow rates were varied from 0.3-1.2 L/m for both phases to determine maximum operation rates. The phase separation capability at the top of the extraction column was the limiting operation. The continuous DMF-phase can be operated slower than the loaded oil phase. A typical set of flow rates are 0.60 L/m (7.7 cm^3/cm^2 min) for DMF and 0.80 L/m (10.3 cm^3/cm^2 min) for oil, based on empty extraction columns. Table 2 contains details of the extraction column tests.

The phase distribution coefficient (DMF-oil) was determined using equal volumes entering and exiting each end of the extraction column (i.e., loaded DMF and loaded oil for one pair and clean DMF and clean oil for the other pair). The two phases were shaken for 1 min, allowed to separate, and then analyzed for PCB content and compared. The calculated value, using laboratory analytical data of 1.5 for the phase distribution coefficient, confirms earlier batch shake-out data.[1]

DMF-WATER, PCB-OIL TRANSFER

The PCB can be released by the addition of water, which is soluble in the DMF phase, reducing the polar bonding of the PCB to the DMF and allowing the PCB to be transferred to a receiving oil phase. Tests were performed (Table 3) to determine optimum water volume percent, oil volume percent, and mix time parameters for maximum PCB transfer. Using 22 vol % water and 4 and 10 vol % oil respectively,

Table 2-2

SOLVENT EXTRACTION DATA

	Feed	Flow (L/min)	PCB (ppm)	011 (%)
DMF	0.5 - 0.8	0 - 10	1	Continuous Phase
011	0.8 - 1.0	200 - 300	-	Discontinuous Phase

		PCB (ppm)	011 (%)	DMF (%)
Product	Loaded DMF	400 - 600	5	-
	Stripped 011	50	-	5

Equipment: 2 - Columns, 10 cm diam (4 in.) X 4.6 m (15 ft)
Filled - 1.9 cm (3/4 in.) Ceramic Saddles

Phase: Equilibrium Data (distribution coefficient)

$$PCB\ \frac{DMF}{011} = 1.4 - 1.6$$

Table 2-3

PCB TRANSFER

Feed	PCB (ppm)	011 (%)	DMF (%)	Volume Percent
Loaded DMF	400 - 600	5	-	67
Water (recycle)	5	2	2	25
Receiving 011	25 - 200	-	5	8

Mix - 30 min

Discharge	Total Volume Percent	PCB (ppm)	DMF (%)	011 (%)
011	7	4000 - 8000	5	95
DMF-Water	93	10 - 30	95	5

Batch Size - 40 gal
Settling Time - 4 h

MONS 215131

the 10 vol % oil test removed the PCB from the DMF 120% better than the 4 vol % oil test. Tests using 15, 21, and 28 vol % water showed that the 28 vol % water tests phases separated better, and a better PCB removal was obtained. A test with 72 vol % DMF, 28 vol % water, and 15 vol % oil was mixed for 5, 10, 20, and 40 min and sampled after each time period. The PCB concentration in the DMF was 6 ppm in each time period sample, indicating very fast equilibrium transfer time. Although 5 min should be sufficient, 30 min was selected because extra time was available.

DISTILLATION

The distillation unit is a "high efficiency" unit 7.62 cm (3 in.) in diameter. The maximum water boil-up rate at 100 psig steam is 1200 mL/min. The normal DMF-water feed is 72 vol % DMF and 28 vol % water (Table 4). Controlling the reboiler at 151-153°C, the water overhead distillate has a DMF concentration of 5-10 vol % DMF. DMF in the water phase is not serious because it is recycled to the transfer tank along with the water used for polar bond breaking. The bottom DMF reboiler product has a water concentration of 0.5-1.0 vol %.

Table 2-4

DISTILLATION

	DMF-Water (vol %)	PCB (ppm)	Oil (vol %)	Rate (L/min)
Feed	67 - 26	10 - 30	7	0.5 - 0.9

Product	PCB (ppm)	Oil (vol %)	DMF (vol %)	Water (vol %)	Temperature (°C)	Rate (L/min)
Top-Water	15	5	10.0	85.0	103 - 105	0.2 - 0.4
Bottom-DMF	20 - 40	1	98.5	0.5	151	0.3 - 0.5

Equipment: Steam Heated - 105 psig Sat. at 180°C
Boiler - 5 gal and 5 ft^2 Heat Transfer
Column - 4 in. diam - 5 ft

PROCESS ECONOMICS

The evaluation of the economic factors strongly favor concentration of the PCB in oil before incineration or other final disposal operation. The resulting processed

oil with less than 50 ppm PCB can incinerate in a furnace with heat recovery and off-gas control. The ten- to twentyfold PCB-oil concentrate can be shipped to a licensed disposal center. The cost of final disposal is usually based on volume, not on PCB concentration.

The container, shipping, and disposal costs will be decreased by a factor of two or more by the PCB concentration process. The DMF-PCB-solvent extraction process will provide the needed PCB concentration to be cost effective. Table 5 lists the cost factors compared to incineration of the original PCB-oil mixture. An attempt to concentrate the PCB more than twentyfold is economically unsound because of base solvent extraction cost of $4/gal.

Table 2-5

COMPARISON OF COST FOR DISPOSAL OF PCB CONTAMINATED OIL
(Basis = $/Gal of Original Oil)

	As Received	Solvent Extraction 1/10	Conc. 1/20
Solvent Extraction	--.--	4.00	4.00
Drums	1.00	0.10	0.05
Shipping	0.50	0.05	0.03
Incineration	11.00	1.10	0.55
Total Cost	12.50	5.20	4.63

CONCLUSIONS

PCB can be removed from waste oils and concentrated for disposal of a concentration of about 300 ppm. PCB in oil has been removed from oil in pilot-plant equipment (i.e., two extraction columns having a 10 cm diam), reducing the concentration to below 50 ppm. The DMF extraction system consists of two 2.7-m (15-ft) columns with an oil feed rate of 0.8 L/min (approximately 300 gal per day), which is equivalent to a PCB rate of 0.2 g/min. The PCB was water-transferred to a disposal oil phase with a PCB concentration up to 400 ppm. The DMF was separated from the water and added to the DMF in the PCB transfer-to-oil storage step by simple distillation at

a reboiler temperature of 151-153°C. The distillation rate is about 0.35 L/min, and the water content in the DMF was reduced to less than 1.5 vol %.

REFERENCES

1. Napier, J. M., Travaglini, M. A., Laggis, E. G., Makarewicz, M. A., Evaluation and Development of Polychlorinated Biphenyl Removal Process, Y-OZ-1, February 5, 1982.

DISCUSSION

QUESTION: Do you see any problem with DMF in contact with steel materials?

ANSWER. No.

QUESTION: How much DMF is in the oil?

ANSWER: 1%-2% which can be water scrubbed out, so essentially, none.

QUESTION· Can the process get below 2 ppm?

ANSWER: Pilot plant was based on getting below 50 ppm, but it can get below 2, if needed.

STATISTICAL SURVEY OF PCB CONTAMINATION IN SUBSTATION AND DISTRIBUTION SYSTEM EQUIPMENT CONTAINING MINERAL OIL

Mark D. Saperstein* and Edward J. Feeder**

ABSTRACT

Electric utility substation and distribution equipment containing mineral oil can be contaminated with polychlorinated biphenyls (PCB). This contamination may occur during the manufacturing of the equipment, or during service and repair if PCB contaminated materials and equipment are used. Three sampling programs have been conducted to examine the extent of PCB contamination in a large electric utility company's substation and distribution system equipment. The specific goals of each survey and the sampling techniques used were somewhat different. Due to these differences, the extrapolation of sample results to estimate contamination on the entire system is limited in some respects. However, all three surveys give consistent results indicating that only about three to six percent of mineral oil equipment is contaminated with PCB above the 50 ppm level. The mean PCB concentration in distribution system transformers was approximately 8 ppm and the median level of contamination was less than 2 ppm. The mean PCB concentration in substation equipment was approximately 12 ppm with a median level of contamination of 2 ppm.

INTRODUCTION

Electric utilities have previously had the choice of purchasing substation and distribution equipment containing either Askarel (a mixture of PCB and chlorinated benzenes) or mineral oil as an insulation or heat exchange fluid. In 1979, a regulatory ban was imposed on the manufacture and use of PCBs in commerce, and utilities are now phasing out the use of certain PCB-containing equipment. There is concern over the extent of PCB contamination of mineral oil-filled equipment

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manufactured before the ban of PCBs and equipment serviced in the same facilities with PCB-containing equipment. Under current federal regulations, liquids contaminated with ≥ 50 ppm of PCB are considered PCB contaminated liquids and, if disposed, must be handled as hazardous waste. Furthermore, all mineral oil equipment must be assumed to contain ≥ 50 ppm of PCB unless otherwise verified.

It is therefore of great interest for utilities and regulatory agencies to determine the extent of PCB contamination in mineral oil equipment since this will influence waste disposal methods, spill cleanup practices and equipment handling procedures. The extent of PCB contamination will, in part, determine the financial impact of any future changes in the regulatory definition of PCB contaminated liquids.

The Southern California Edison Company has 741,851 pieces of equipment on its system which contain mineral oil or Askarel as heat exchange or dielectric fluid. The great majority of this equipment contains mineral oil. It is estimated that the total amount of fluid in mineral oil equipment is approximately 36 million gallons with most of this being in mineral oil transformers (29 M gal) and mineral oil circuit breakers (5 M gal). The remaining oil is contained in switches, sectionalizers, voltage regulators, reclosers and other equipment. Table 1 shows the amount of PCB and mineral oil contained in various types of equipment.

Over the past two years, three surveys have been conducted to determine the extent of PCB contamination in mineral oil-filled equipment. The three surveys were designed with different objectives in mind, and therefore, the sampling techniques used in each survey are somewhat different. The results of each survey are subject to certain limitations with respect to extrapolation of sample statistics for describing the entire population of transformers or other mineral oil equipment. Since each survey was conducted in a different manner, combining the data into one large sample for analysis was considered inadvisable. Each survey will be described separately and then the results will be compared and contrasted.

SAMPLE SELECTION

Sample 1: Distribution Transformers at a Storage and Test Facility

The methods and results of this survey have been described in a previous paper (1) and so they will only be briefly summarized here. The objective of this sur-

Table 1

ASKAREL, PCB AND MINERAL OIL ON THE SOUTHERN
CALIFORNIA EDISON TRANSMISSION AND DISTRIBUTION SYSTEM

Type of Equipment	Gallons of Fluid
Askarel Transformers	16,044
PCB Capacitors	331,684
Total Fluid in Askarel Equipment	347,728 gal.
Mineral Oil Transformers	29,285,381
Mineral Oil Voltage Regulators	419,368
Mineral Oil Circuit Breakers	5,224,324
Mineral Oil Reclosers	37,600
Mineral Oil Switches & Sectionalizers	1,300,900
Total Fluid in Mineral Oil Eqpt.	36,267,573 gal.
Total Askarel & Mineral Oil	36,615,301 gal

vey was to sample a small portion of the 537,000 distribution transformers on the system in such a way so that an accurate estimate of PCB contamination in the entire distribution transformer population could be made.

Distribution transformers vary with respect to manufacturer, size, design and age. The first system survey was designed to obtain a sample which was representative of the whole distribution transformer population. One method of obtaining such a sample is to conduct stratified random sampling in which the population of transformers are classified into strata with similar values of known characteristics. Units are then sampled within each stratum in a random manner, using tables of random numbers.

Developing a stratified sample with more than one stratifier can become cumbersome and it is simpler to stratify by one factor which is expected to account for the greatest amount of variability within the sample. With regards to PCB contamination in mineral oil transformers, it was felt that production source of the unit (manufacturer) was the key variable. The sample was therefore stratified on manufacturer. The number of units sampled from a given manufacturer was proportional to the percent of that manufacturer's units in the distribution transformer population. Age, size, or some other factor may have also helped to predict PCB concentration, but it was not possible to tabulate how the population varied with respect to these factors, and therefore, they could not be used in

stratification. Sample sizes were developed for each manufacturer and an initial training sample of 185 units was obtained.

Although it would be desirable to sample transformers which are on-line and in service, this type of sampling is quite expensive because of the time and manpower involved in de-energizing segments of the distribution system. As an alternative, samples were taken from transformers at a storage and test facility. Only transformers which had not been serviced were sampled. The sampling of these transformers was not truly random in that the sampling personnel selected the transformers from each manufacturer as they wished. (They may have chosen those units which were easiest to sample.) It is also possible that transformers at the shop and test facility were not representative of the population of transformers with respect to age or some other factor.

After the initial sample was obtained and analyzed, a second sample was obtained using an optimum allocation strategy in which the number of units sampled from each manufacturer was a function of the internal variability in each strata (number of contaminated units) as well as the size of the stratum (2). This technique was used to minimize the variance of the final estimate of the percent contaminated.

The total number of units sampled in this survey was 260. Two values which were obtained from sludge residues rather than oil were discarded.

Sample 2: Interim Measures Regulations

The second survey was performed in response to EPA's Interim Measures Regulations for the management of PCBs. The regulations mandated that mineral oil-filled transformers located in areas where leakage could cause contamination of food or animal feed, must either be inspected weekly for leaks or be tested to determine the PCB content of the oil. There were 619 SCE distribution transformers which fall into the "food and feed facility" category and all were tested for PCB content. Unlike the previous storage yard sample, these transformers were in use and sampled on-site. Though the sample was not stratified with respect to manufacturer, the resultant composition was similar to the population in this respect. This sample was also reported to be similar to the population with respect to overall size and age; however, these were only the subjective reports of the personnel who sampled the equipment, and cannot be verified via documentation.

For Samples #1 and #2, the same laboratory was used to determine PCB concentrations. Methods previously have been described (3). Samples were periodically resubmitted to the laboratory for retesting to verify the laboratory's accuracy No inconsistancies were found.

Sample 3: Substation Equipment

The third sample consists of 1070 samples of mineral oil from substation equipment including transformers (85 percent), circuit breakers (10 percent) and small amounts of other equipment including reactors, regulators, load tap changers and oil storage tanks.

The basic approach in this survey is to sample all large pieces of equipment until the entire population of substation equipment has been sampled. Approximately 15 percent of the large power transformers are represented in this sample.

Substation personnel have routinely sampled mineral oil and tested for carbon contamination and dissolved gases which indicate that malfunctions may be occurring. Initially, PCB analysis was added to these maintenance tests to determine if the equipment should be labeled as containing PCBs at levels $\geq$ 50 or $\geq$ 500 ppm. Currently, equipment is sampled for the specific purpose of determining PCB concentration.

While this sample is larger than the first two combined, it has several shortcomings which limit its usefulness. There was no summary information available to describe the substation population with respect to composition by various manufacturers, age and size of the equipment. It is therefore difficult to determine how well the sample represents the population.

The types of equipment sampled were not recorded in a systematic manner and in a small percentage of cases, it is not clear precisely what type of equipment was sampled (e.g., the oil in a circuit breaker or the current transformer associated with the circuit breaker). There may have been some mixing of oils from different equipment through the use of mobil oil treatment equipment and storage tanks.

The PCB analyses were conducted at a different laboratory than the one used in the first two surveys. In order to cut analyses costs, PCB concentrations below 1.0 ppm were not accurately measured but were merely reported as 1 ppm.

ANALYSIS

Analysis of data from these three surveys was designed to answer three basic questions:

1) Is mineral oil found in electrical equipment contaminated with PCBs, and, if so, to what extent?

2) What is the best estimate of the proportion of units contaminated at levels of $\geq$ 50 ppm?

3) Are one or more manufacturers solely responsible for the PCB contamination?

Levels of PCB Contamination[1]

Results from Sample #1 indicate that PCB contamination in mineral oil-filled transformers was a common event, although levels of contamination were very low. Subsequent samples of mineral oil-filled equipment were in agreement with these findings. Figure 1 shows the frequency distribution of contaminated units by concentration of PCB for Samples #1 and #2 combined. Sample #3 exhibits a similar pattern. The frequency of contamination drops dramatically between the concentrations of 0 and 25 ppm with only 3 to 4 percent of the units contaminated at levels above 50 ppm in each survey. This same pattern was observed within each of the individual manufacturers which constitute Sample #1 and Sample #2.

Figure 2 shows the cumulative frequency distribution for Samples #1 and #2 combined. Sample #3 exhibits a similar pattern. This figure also demonstrates that the great majority of contamination occurs at low concentrations.

Mean PCB concentrations were calculated for each sample. Since the composition of the distribution transformer population was well known with respect to manufacturers, the means for Samples #1 and #2 were corrected to adjust for differences between the sample stratification and the population.

[1]Although federal regulations currently define PCB contaminated fluids as those containing at least 50 but less than 500 ppm PCBs, in this study, PCB contamination will refer to the presence of any concentration of PCBs measured in mineral oil.

MONS 215140

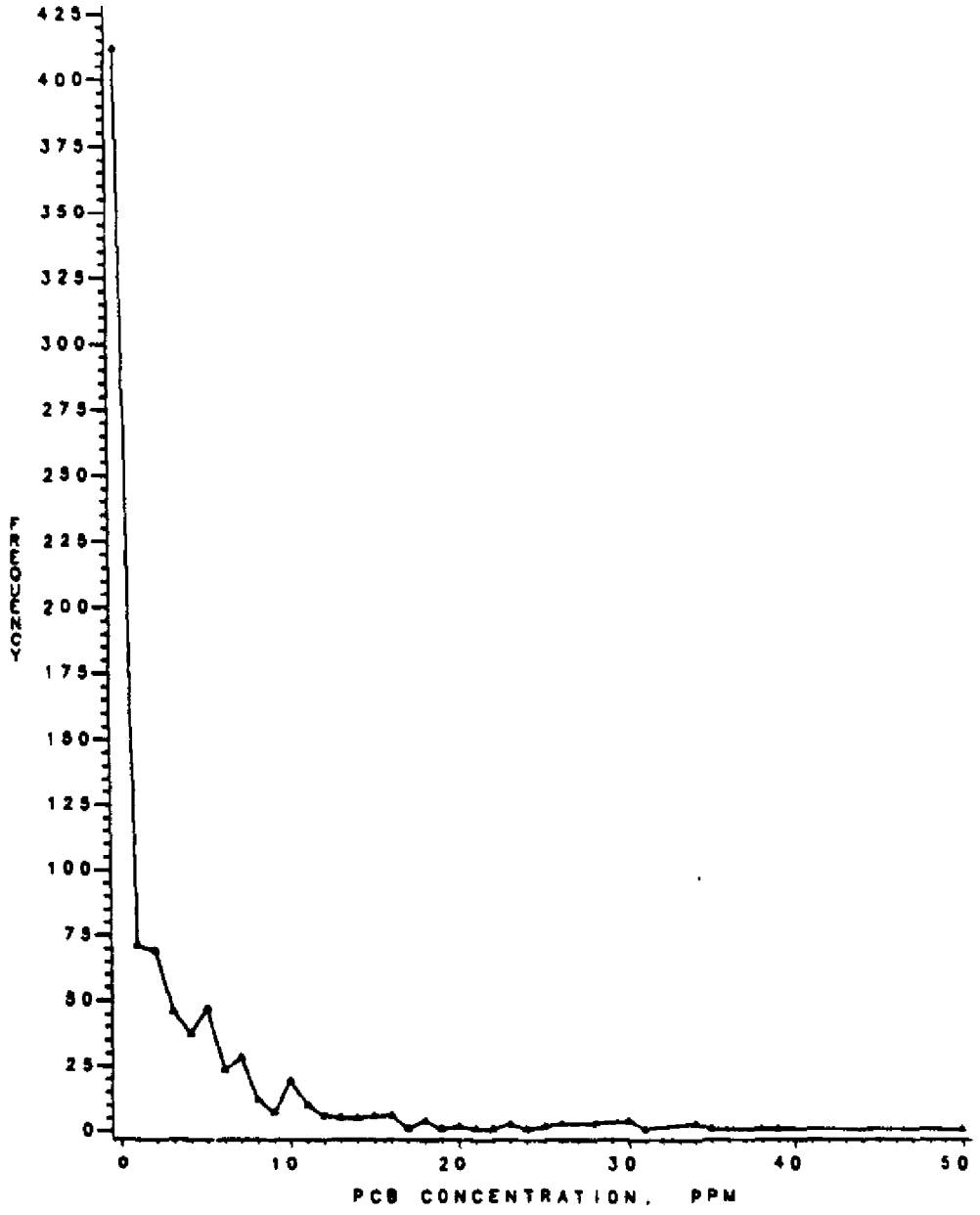

Figure 1. Frequency distribution of PCB contamination in mineral oil filled equipment. Data from Sample #1 and Sample #2 combined.

MONS 215141

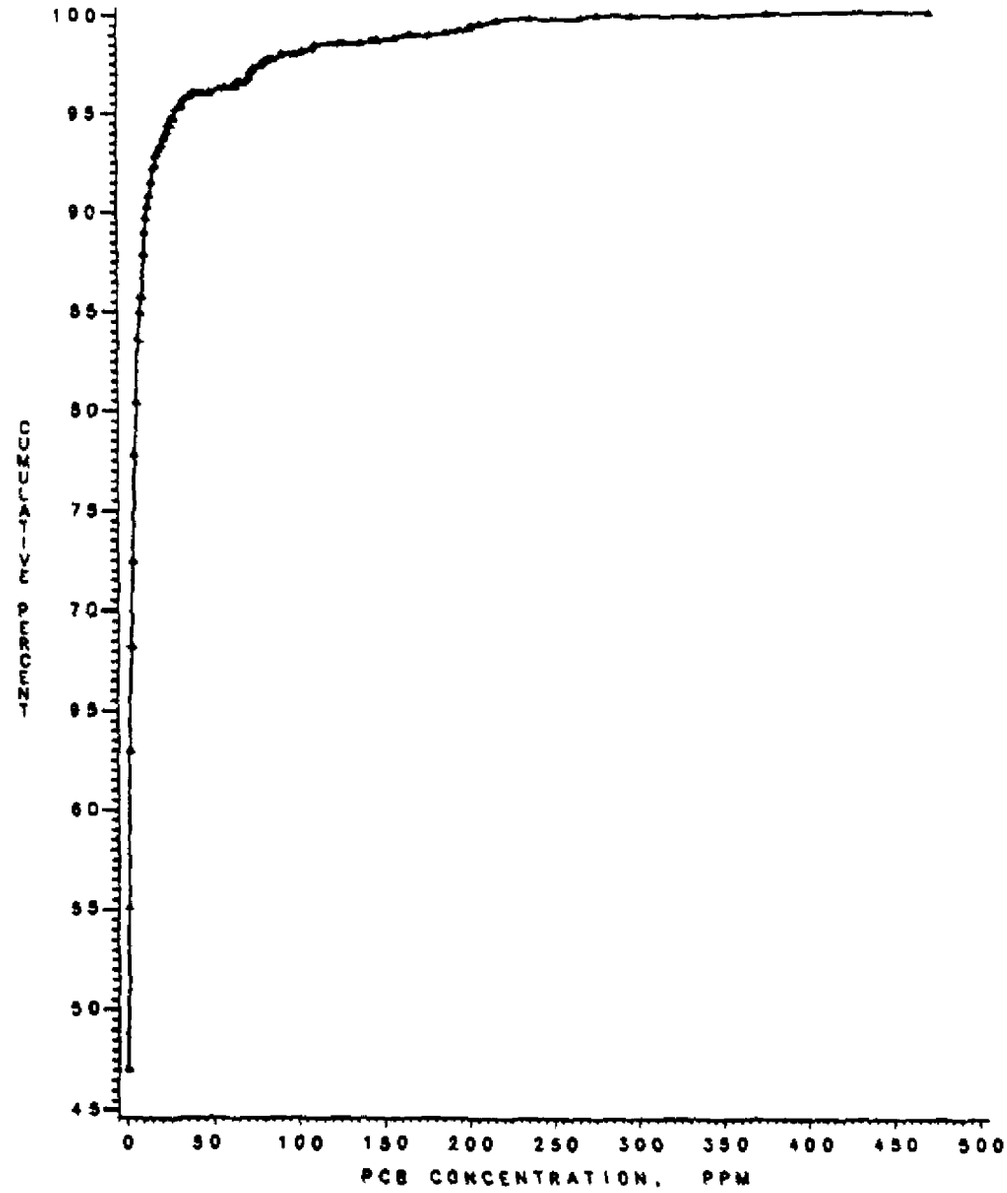

Figure 2. Cumulative percentage of PCB contaminated distribution transformers. Data from Sample #1 and Sample #2 combined.

MONS 215142

The composition of the population of substation equipment was not known and the mean for Sample #3 was calculated by grouping all samples together without regard to manufacturer or type of equipment.

Mean PCB concentrations calculated for Samples #1 and #3 are somewhat conservative. Laboratory results for some samples in Sample #1 were reported as "less than" a given concentration. These values were decreased by 0.1 ppm for ease in calculations (e.g., < 2 ppm becomes 1.9 ppm). For Sample #3 concentrations below 1 ppm were reported as 1 ppm.

Given the skewness of the distribution the mean is not a good indicator of the central tendency of the data. Although the mean for Sample #2 is 9.9 ppm, one is much more likely to find a sample below this level than above it. Medians and modes were also calculated for each sample to more completely describe the data (see Table 2). If the data from the distribution transformers samples are combined, the mean level of contamination is 8.5 ppm and the median is 0.8 ppm.

To investigate differences in PCB contamination in different types of substation equipment, Sample #3 was divided into 4 general categories of equipment;

1) Transformers including power transformers, tap changers, current transformers and a few reactors.

2) Circuit breakers and associated current transformers.

3) Regulators

4) Oil Storage Tanks

A few miscellaneous pieces of equipment could not be placed into any of these categories and were left out of this analysis. Summary statistics for each group were calculated and are shown in Table 3. Regulators may be more often contaminated with higher levels of PCB than other substation equipment. More samples are currently being collected to determine the extent of contamination in this type of equipment.

Table 2

SUMMARY STATISTICS FOR THE THREE PCB SAMPLES

Description	Sample #1 Distribution Transformers	Sample #2 Distribution Transformers	Sample #3 Substation Equipment
Sample Size	258	619	1,070
Mean PCB	6.4	9.7	12.1
Adjusted Mean	6.1	9.9	--
Standard Deviation	15.6	38.2	52.2
Skewness	4.4	7.2	12.8
Median	1.9	0.5	2.0
Mode	0.0	0.0	1.0
Proportion ≥ 50 ppm PCB	3.5%	4.2%	3.6%
95% Confidence Interval for Adjusted Proportion ≥ 50 ppm PCB	3.3% ± 2.1%	4.3% ± 1.6%	3.6% ± 1.1%

Table 3

PCB CONTAMINATION IN SUBSTATION EQUIPMENT

	Transformers	Circuit Breakers	Regulators	Storage Tanks
Number Sampled	910	106	34	16
Mean PCB	11.3	10.1	42.8	8.4
Standard Deviation	54	15.1	77.5	10.2
Skewness	13	2.7	2.3	1.3
Median	2	5	5.5	3.5
Proportion ≥ 50 ppm PCB	3.0%	3.8%	24.0%	0.0%

MONS 215144

Differences Between Manufacturers

A comparison of sample statistics and a chi-square analysis indicated that there were significant differences between manufacturers.

A chi-square analysis was performed on distribution transformer data to examine the differences in the number of contaminated units between manufacturers. Cell frequencies were sparse when contamination was defined as $\geq$ 50 ppm, rendering the results of the test unreliable. However, as the cut point used to define contamination was lowered (e.g., to 25 or 10 ppm), the analysis indicated significant differences in contamination between manufacturers.

Proportion Contaminated at Concentrations Over 50 ppm

Contamination of materials with PCBs at levels greater than or equal to 50 ppm is of regulatory significance. It was therefore of interest to attempt to estimate the proportion of the company's total inventory of mineral oil-filled equipment which was contaminated at this level. The accuracy of these estimates is dependent upon the sampling methods which were used in each of the three surveys. Samples #1 and #2 provide the best estimates of contamination in the distribution transformers since the composition of both the population and samples by manufacturer could be described accurately. To calculate this estimate the proportion of units which were contaminated at levels greater than or equal to 50 ppm were tabulated for each manufacturer. An adjusted estimate of the proportion of the population contaminated at this level and a standard deviation were calculated using the methods described by Cochran for stratified samples (2). These estimates for Samples #1 and #2 are 3.3 $\pm$ 2.1% and 4.3$\pm$ 1.6%, respectively (95 percent confidence limits).

Sample #3 provides the only available data for estimating contamination in the substation equipment population. However, these estimates must be made with caution because of the methods by which the sample was collected. One can calculate a proportional estimate of contamination over 50 ppm and then estimate the uncertainty around this estimate using a binomial distribution. The estimate of contamination is 3.6 percent which is in very close agreement with the estimates from the other two samples. These estimates of contamination are shown in Table 2.

MONS 215145

DISCUSSION

Although the three sets of mineral oil samples were collected using widely different techniques, the results of the analyses are in general agreement with respect to the shape of the frequency distribution of PCB contamination and the proportion of units contaminated at levels above 50 ppm. Caution must be exercised when attempting to use the data in these three samples to extrapolate to the Company's entire inventory of mineral oil-filled equipment or to equipment used by other utilities.

When extrapolating to the total inventory of equipment within the company, the potential sampling bias in each sample must be considered. In Sample #1, there may be some reason why transformers in the storage and service facility are not representative of the population with regard to PCB contamination. Sample #2 may have similar problems because all of the transformers surveyed were used in similar types of facilities (food and feed faailities). However, interviews with distribution system engineers did not uncover any reasons why such biases should exist. If these potential sampling biases can be ignored, we estimate the median level of contamination to be in the range of 0.5 to 1.9 ppm and the proportion of units contaminated over 50 ppm to range from 1.2 percent to 5.9 percent (95 percent confidence limits).

The potential for bias in the substation equipment sample is large due to the sample selection methods. However, lack of information on the characteristics of the substation equipment population precludes us from verifying or analyzing these potential biases. A comparison of the results of this sample with the results of the first two indicates a good deal of consistency.

It is uncertain whether these results are applicable to other utilities. Since there appear to be significant differences among manufacturers, other utilities with a different mix of equipment from various manufacturers would not be comparable. Perhaps the most important problem in extrapolating these results to other utilities is that of different maintenance procedures and the probability for cross contamination between Askarel and mineral oil equipment. According to SCE maintenance procedures, mineral oil transformers have never had Askarel added to them to replace fluid losses. In addition, fluids from Askarel equipment and mineral oil equipment are not stored in the same storage tanks. The proportion of Askarel-filled equipment is very small at SCE and the possibility of accidental contamination is therefore reduced. Other utilities with a larger percentage of PCB equipment or which use different maintenance procedures may have a

greater degree of PCB contamination in transmission and distribution equipment.

It should be noted that although the substation sample was the largest, it provided the least information for extrapolation because of the manner in which the samples were obtained. Each large piece of substation equipment is sampled until the entire population (or most of it) has been measured. Little attention has been given to the order in which the equipment has been sampled or the representativeness of the sample at any point in time. Since the potential for selection bias is large, any estimates derived from this sample must be used with caution until the sampling has been completed.

This type of information has been useful to SCE in interactions with State regulatory agencies responsible for hazardous waste disposal and spill cleanup procedures It has also proved useful in predicting potential regulatory impacts resulting from the lowering of the definition of PCB contamination below the current federal level of 50 ppm.

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1. M. D. Seperstein, R. J. Gordon and E. J. Faeder. "PCB Contamination in Distribution Transformers." Journal of Environmental Science and Health A17(2), 241-251 (1982).

2. W. G. Cochran Sampling Techniques, third edition, 1977, John Wiley and Sons.

3. R. J. Gordon, J. Szita and E. J. Faeder. "Determination of Polychlorinated Biphenyls in Transformer Oils by Capillary Gas Chromatography." Analytical Chemistry Volume 54, pp. 478-481 (1982).

DISCUSSION

QUESTION 1. Do any other utilities have statistical data on their equipment?

ANSWER: Several company representatives indicated approximately the same, i.e., 4% greater than 50 ppm (The statistics quoted were generally accepted).

QUESTION 2. How did you find test accuracy from different labs?

ANSWER: Below 100 ppm, very good agreement but not above.

QUESTION 3. Any special procedure used for sampling the tank?

ANSWER: No.

MONS 215147

TRANSFORMER RISK ASSESSMENT AND OPTION ANALYSIS

Patrick R. Herbert
High Voltage Maintenance Corp.

A Transformer Risk Assessment and Option Analysis Program is the first step in developing an action plan to cope with the potential problems involved with the ownership and operation of PCB or PCB contaminated transformers.

Implementation of an inspection program utilizing the check list approach as outlined in this paper will provide an objective viewpoint as to the relative degree of risk with each individual transformer in your Electrical Distribution System. Action priorities can then be developed to expediently implement a practical and economical approach to minimize PCB transformer liabilities.

The inspection check list should be completed by only one person on all units within a plant or corporation so that a standardization of recommendations will result. The procedure of checking each applicable comment under all topics and the substitution of the numerical values of each comment into the equation at the bottom of page three will provide a risk value that can then be evaluated by comparing it with the numerical parameters on page one. The values assigned in this section have been developed through the comprehensive analysis of several thousand transformers in various locations throughout the United States.

MONS 215148

The option analysis on page four will point out the significant characteristics of the inspected unit that will assist with the decision to retain, replace, or retrofill the transformer. The Cost Estimate Outline on this page will strongly influence this decision.

MONS 215149

PROJECT#_____INSPECTION#_____DATE_____

TRANSFORMER: PCB RISK ASSESSMENT

Client_____

Address _____

Transformer Identification_____

Transformer Location_____

Transformer Manufacturer_____KVA_____Phase_____

Serial No._____Class_____Type_____Voltage_____

Fluid Volume_____/gallons Fluid Type_____Fluid Weight_____

Transformer Total Weight_____Length_____Width____Weight___

Bottom Valve___P/V Gauge___Temp. Gauge___Level Gauge_____

Top Valve___Pressure Release___Tap Changer Top___Side_____

Bushings Top___Side___Throat___Transition Compartment_____

Bushings Gasketed_____Welded Membrane_____

Top Welded_____Bolted_____Inspection Cover_____

Fans Yes__ No___ Automatic Control Yes___No_____

NUMERICAL RISK EVALUATION

__0- 400____Good - Inspect and maintain periodically

_401- 800____Minimal Risk - Inspect Weekly_____Otly._____

_801-1500____Potential Hazard - Inspect Weekly ___Otly._____

1501-3400____Major Risk - Corrective maintenance required

__>3400_____Immediate Problem - Repair Immediately

Analysis Comments:

Inspection by:_____Analysis by:_____

MONS 215150

TRANSFORMER CLASSIFICATION

(0) Non PCB (determined by analysis)
A (1) PCB Contaminated (50 to 500 ppm) by analysis or nameplate
(2) PCB Filled (greater than 500 ppm) by analysis or nameplate

TRANSFORMER PAD INTEGRITY

(1) Pad has no drains, cracks or conduit openings
(5) Pad has drain, cracks or conduit openings
B (2) Pad complexity would be difficult to decontaminate
(3) Porous concrete block or wood floor
(5) Underground pad with sump pump

LIQUID LEVEL

(1) Full (as indicated on liquid level gauge)
C (2) Slightly low
(3) Very low

PCB LIQUID QUANTITY

(1) Less than ten (10) gallons
D (4) More than ten (10) gallons but less than one hundred (100) gallons
(8) More than one hundred (100) gallons but less than five hundred (500) gallons
(10) More than five hundred (500) gallons

FACILITY TYPE

(1) Non-food processing facility
E (5) Food processing facility non-critical area
(20) Food processing facility critical area

TRANSFORMER LOCATION

(10) Indoor vault or isolated area (minimal leak hazard)
(20) Indoor people frequented area
(20) Indoor upper floor, balcony or roof
F (2) Outdoor in locked vault
(5) Outdoor on open pad
(8) Outdoor in underground vault
(10) Outdoor on pole
(15) Outdoor rooftop location

HOUSEKEEPING

(1) Transformer location free of debris and storage
G (2) Transformer location adjacent to debris or storage
(3) Transformer adjacent to potentially damaging machinery

SAFETY

(1) Proper fire extinguisher available at transformer
(1) Automatic Fire Extinguishing System on Transformer
H (2) Fire extinguisher unavailable at transformer
(1) Protective clothing and breathing equipment available
(2) Protective clothing and breathing equipment unavailable

CONTAINMENT

(1) Transformer diked to contain total liquid
J (3) Dike will not contain total liquid
(6) Dike deteriorated or damaged but functional
(10) No dike or containment

SPILL RESPONSE

K (1) Spill clean up drums, rags, absorbent available at transformer
(5) No spill clean up material available

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DAMAGE SUSCEPTIBILITY

	(1)	Non susceptible to damage (vault or elevated platform)
L	(3)	Minor - some protection provided (fence or curb)
	(6)	Moderate - vehicular traffic damage possible
	(8)	Highly susceptible - accidental damage risk

TRANSFORMER VENT SYSTEM

	(1)	Vents - fumes outside away from windows, food, people, water
M	(3)	Vents - fumes outside to possible critical areas
	(5)	Vents into occupied buildings

SPILL CONSEQUENCE

If major spill occurred, the liquid would

	(1)	be totally confined or contained
	(3)	contaminate pad and transformer only
	(5)	contaminate soil, gravel or other material
	(10)	contaminate processing or manufacturing area
N	(20)	contaminate floor below
	(20)	contaminate occupied areas
	(20)	contaminate water drains, ditches, sewers, etc.
	(20)	contaminate bodies of water

TRANSFORMER LEAK STATUS

( )	Transformer not leaking
( )	Transformer fins or tubes rusting
( )	No active leak but old stains on pad or casing
( )	New small stains noted under valves
( )	New small stains noted under bushings
( )	Large leak residual requiring immediate action
( )	Moderate leak requiring drip pan or absorbent
( )	Active spill contaminating pad and area

TSCA REGULATION COMPLIANCE

( )	Not required
( )	Labelled properly
( )	Labelling required but absent
( )	Leak inspection required (weekly) (quarterly) (not required)
( )	Inspection required (weekly) (quarterly) (not required)

HEAT RELEASE INFORMATION

Transformer to wall distance F_____B_____R_____L_____
Wall Material_____
Transformer to ceiling distance_____
Ceiling Material_____
Transformer Length_____Width_____
Dike Dimensions Length_____Width_____Height_____

RISK ASSESSMENT FORMULA

$$A(B+G+H+L+M)+D(B+L)+G+F(G+H)+(A+D+F)(J+K+M^2+N)$$

RETAIN VS. REPLACEMENT VS. RETROFILL

	RETAIN	REPLACE	RETROFILL
Condition (Damaged) (Rusted) (Extremely Dirty) (Average) (Clean)			
Is unit now leaking? (Yes) (No) (Possibly)			
Does location require high fire point liquid transformer (Yes) (No)			
Is location a potential environmental pollution risk? (Minor) (Major)			
Is location a potential risk to personnel? (No) (Minor) (Major)			
Is location (Wet) (Extremely Hot) (Corrosive) (Extremely Dirty) (Dry)			
Is spill retention dike now in place? (Yes) (No) (Inadequate)			
Ease of physical replacement: (Easy) (Complicated) (Difficult)			
Transformer characteristics: (Standard) (Unusual) (One of a Kind)			
Is transformer in food product sensitive location? (Yes) (No)			
Client sensitive to adverse PCB publicity: (Low) (Average) (None)			
Transformer bushing type: (Gasketed) (Non-Gasketed)			
Transformer bushing location: (Top) (Sidewall)			
Age of transformer (5) (10) (20) (30) (40+)			
History (No Problems) (Unit Rebuilt) (Existing Unexplained Problem)			
Allowable downtime: (None) (8 hours) (24 hours) (Unlimited)			
Is a spare replacement available? (Yes) (Possibly) (No)			
Is transformer compatible with future requirements? (Yes) (No)			
Anticipated or desired remaining life: (5 years) (10 years) (20+ years)			
Transformer owned by: (Client) (Utility) (Other)			
Transformer avarage temperature: (Normal) (Overheating) (Extremely Hot)			
Electrical testing program: (Yearly) (2+ Years) (None)			
Recent electrical test evaluation: (Poor) (Deteriorated) (Average) (Good)			
Leak inspection program: (Weekly) (Monthly) (Quarterly)			

RECOMMENDATIONS:

COST ESTIMATE TO:

Retain (Fincial liability - Minor - Major - Excessive)

Remove. disposal and replacement_____

Retrofill with_____Fluid_____

Recommendation Analysis By_____Date_____

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SUNOHIO PCB DETOXIFICATION EXPERIENCE
BY M. JAMES KOZAK, V. P. OPERATIONS
EPRI CONFERENCE, DECEMBER 8, 1983

I want to focus it on what we consider four key areas - quality, operational efficiency, environmental compatibility and reclassification capabilities.

Quality is the heart of the Sunohio process. We sell a unique service and that service is the decontamination of PCB's in transformer mineral oil. However, if all we did was decontaminate PCB's, we would be tha same as all the rest of the boys on the block. Our primary difference is that we produce a decontaminated mineral oil of such impeccable quality that it can instantly be reused in high voltage power equipment. We have come a long way in establishing a reputation as being a quality leader. We have now completed over 300 contracts and have treated over three million gallons of dielectric fluids. Part of our quality control program is rigid specifications and intensive and accurate testing. Our field specifications are written into and warranted by each and every contract.

We have had our share of bumps and bruises while developing a sound quality assurance program. With five PCBX rigs and up to three shifts on each rig, it's easy to understand why it would be difficult to obtain consistent field testing results. When we first started, we had our share of oil quality problems, especially in the area of high moisture content and low interfacial tension. These were due to extended use of the earth beds and improper operation of the vacuum degasser.

Our problems were complicated because we were getting inaccurate testing. Our field technicians were analyzing the oil as good quality; but when the samples came back to the home office, the quality was unacceptable. With a little bit of a diagnostic effort we soon resolved that the problems were related to sampling techniques and improper operation of the field testing equipment. With proper field information we were then able to zero in and correct our operational procedures.

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We took two steps to resolve the problems. First, we bit the bullet and told the customers involved that there was a quality problem and returned at our own expense to reprocess the oil and make good on our contractual obligations. Our commitment to our contractual guarantee is ironclad. Secondly, we re-evaluated our quality assurance program and took the proper steps to improve field testing and to implement a system which would tolerate a degree of test error in the field.

Under our present quality assurance program, we utilize a fully equipped mobile laboratory for each PCBX rig. We monitor each and every transformer for both PCB level and electrical properties throughout the detoxification cycle and when we are satisfied, we have achieved completion, we draw a final set of samples, one of which we analyze in the field, a second of which we send for backup verification at our in-house laboratory in Navarre, Ohio and a third set which we will provide to the customer if he so desires. We utilize our in-house laboratory as our standard in evaluating our performance on a contract. To insure that field operations meet contract specifications, we utilize a two tiered set of standards. (Exhibit 1 - comparison of oil quality specifications). By setting the field standards significantly higher than the contract specifications, we allow ourselves a margin of test error when comparing field results with the final evaluation of the home office laboratory. In evaluating PCB content, we use a similar duplicate testing structure. PCB standards are purchased from nationally known reputable sources and samples are analyzed on two different gas chromatographs. Field operations utilize a Varian 3700 Electron Capture Gas Chromatograph and these results are verified using a different set of standards with a different laboratory technician on a Hewlett Packard 5880 Electron Capture Gas Chromatograph in our Naverre laboratory.

Our technique of employing a higher-than-required standard for field testing and a duplicate sample analysis is both time consuming and expensive and it has resulted in our returning to a few job sites to do warranty work, but overall it has resulted in an extremely impressive record of high quality performance.

We have come a long way in our detoxification capabilities and in the number of EPA regions and states in which we have been licensed to operate. When we first began commercial operations in the fall of 1981, we had EPA approval in only two of the ten regions and we were limited to decontaminate oils with a maximum of 500 PPM of PCB's. By May of 1982, we had obtained approval in all ten EPA regions and by August of 1982 we had increased our detoxification license limit to 2500 PPM. While we technically have the capability to decontaminate in excess of 10,000 PPM ... a 2500 PPM level is in concert with competitive economics.

We have experienced occasional difficulties with detoxifications. In the early days, we had some significant problems with various aroclors and with various properties within the oil. I can recall a job in early 1982 in which we were processing on a rather large transformer contaminated to a level of about 3000 PPM. I believe it was Aroclor 1242. It took us about 12 hours to make a pass on this transformer and in the first pass we reduced the contamination level to about 2000 PPM. For the next five days, we continued to process while the transformer remained at the 2000 PPM level. We made a variety of process changes and modifications and tried alternate detoxification and filtration steps and slowly we began to reduce the contamination level. In all total, it took us over two weeks to fully decontaminate this transformer. Over the two plus years that we have been in operation, we have learned how to handle these types of problems. We have learned which adjustments to make for various aroclors and we have learned which adjustments to make for differing oil quality specifications. Today that transformer would have been completed in two to three days.

Lately there has been a governmental policy shift to give the states more authority and responsibility in handling their own environmental affairs. Each state has or is now developing, its own permitting regulations. Each state now requires a separate application ranging from a simple submission of an EPA license to a complete engineering and environmental impact study.

Managing field operations in 50 states is a rather interesting process. To complicate matters, California, for instance, has 26 air pollution control districts which operate rather autonomously from the State Air Pollution Board. Even though it's not 1984 yet, the big brother is always watching us. Our business is like life in a goldfish bowl.

The exhaust stream from the vacuum degasser was of major concern to several states which have ective air pollution boards. Our first trip to California was rather interesting. At that time, we had no control devices on the emission stream and the exhaust from the vacuum degasser looked very similar to the exhaust from a car on a cold day.

A young engineer from the air pollution district came to visit the job site with some rather unsophisticated testing equipment. He got very excited when he saw this exhaust stream and he took his hydrocarbon analyzer and stuck it up the exhaust pipe and said ... "Gee, you've got a lot of hydrocarbons here." I think it pegged his meter. Then he took his Opacity Meter out and tested it and said ... "It's more than 20% on the opacity scale and since it has hydrocarbons in it, you are in total violation of our standards and you must shutdown

immediately." Well, we quickly called the director of the district who recognized this was a demonstration run and since the exhaust stream was less than 1/10 of one pound per hour, determined that we could continue operations. He did, however, inform us that we may be subject to a fine. The young engineer returned the next day wanting to collect some grab samples so that he could have those analyzed. He came armed with what appeared to be two Hefty trash bags and he proceeded to wrap these around our exhaust pipe until they blew up like a big balloon. He sealed these and carted them off to his laboratory. A month later we were told that if we wanted to come back into that district, we would have to do something about the vinyl chloride which we were producing in our exhaust stream. If you have any familiarity with organic chemistry, you know it's pretty damn difficult to produce a vinyl chloride from a PCB contaminated mineral oil stream. However, it's not too difficult to pick up trace amounts of it from a vinyl trash bag.

The next time we came into California, we were armed with demisters and charcoal filters on our vacuum degasser exhaust stream. We invited the Los Angeles District Air Pollution Board, the California Air Pollution Board and an independent testing organization to evaluate the air emissions from this vacuum exhaust. Of particular concern were emissions of PCB's, dioxins, dibenzofurans and, of course, to satisfy the young engineer in another district, vinyl chloride.

This second testing was considerably more formal than the early adventure. Each of the testing groups had a specific protocol and each team used the latest scientific sampling devices and were manned by trained engineers and laboratory technicians. They took sampling probes and monitored the exhaust both before and after the demisters and charcoal filters. These samples were then analyzed by three different laboratories. The independent tests proved conclusively that the PCBX process emits no PCB's, no dioxins, no dibenzofurans and no vinyl chloride. This information was critical in allowing us to meet the permitting requirements of several states including California, Texas and Michigan.

We've stated that we can produce an oil of excellent quality, that we can legally and economically detoxify PCB's up to the 2500 PPM level, that we have no negative environmental impact and that we have been accepted in 48 of the 50 states; but what about our ability to reclassify transformers? That's really the height of the matter isn't it?

Well, just like the rest of the things we've talked about today, this has been a learning and maturing process for us. At the onset, we had great speculation about leach rates. We talked about reclassifying transformers in the 5000 PPM range.

But we learned our lessons quickly. We have now developed a strong track record of enabling transformers to be reclassified.

We guarantee that by using the PCBX process on a transformer of 1000 PPM or less, we will certify that the oil in the transformer will be less than 50 PPM after the EPA required operating time and temperature and that the owner of the transformer will then be able to reclassify it. Sometimes, when one of our salesman wants to sell a job very badly, we will stretch the limit of that guarantee and we have even been successful in doing that.

How do we do it? We carefully circulate on the transformer at a flow rate designed to provide maximum washing of the core and coil with an absolute minimum of turbulence. We control the leach back by setting a PPM level for the oil leaving the bottom of the transformer and entering the PCBX unit. Although the oil leaving our unit has to be below 2 PPM, it is critical to set an incoming standard. The standard used is dependent upon the original contamination, the type, size and age of the transformer. Normally, the standard is the 6 to 10 PPM range and then we further insure costification by continuing to process for an additional specified number of gallons before finally signing off on the transformer.

The only way you can guarantee the customer's ability to reclassify a transformer at 1000 PPM is to have a leach back rate that is less than 5%. That's about half the usual rate for retrofill. During the past two years we have reclassified over 400 transformers and have demonstrated an average leach back of less than 2%. I want to make one point very clear. We define leach back rate as the increase contamination level that has occurred after PCBXing versus the initial contamination level. (Exhibit II). Assume you have a transformer with an initial contamination level of 1000 PPM. Upon completion of the PCBX process, this transformer has been decontaminated to a level of 8 PPM. Upon resampling it after 90 days, the transformer shows a contamination level of 33 PPM. The increase in contamination level has been 25 PPM, therefore, the leach back rate is 25 PPM divided by the initial concentration of 1000 PPM ... or 2.5%.

I'd like to share with you the experience that we've gained over the past 2½ years in estimating leach beck characteristics. (Exhibit III) This chart represents the leach back rates for all of the transformers that we have processed from January 1, 1981 through the first quarter of 1983 ... 344 transformers in total.

I've divided the transformers into four groups based upon their initial contamination level. As you can see, the mean leach back rate for each group of transformers is approximately 2%. Extending this data into a probability distribution we see that for transformers under an initial contamination level of 250 PPM, 98%

of these have leach back rates of less than 10%. In the more critical groups, our performance is more dramatic. 98% of the transformers in the 250 to 1000 PPM group have leach back rates of less than 5%; while 98% of those above 1000 PPM yielded rates of less than 3%.

Let me close by emphasizing that Sunohio is in the restoration business, we restore the oil to a completely reusable condition and we restore the transformer to a non-PCB status, assuming it was originally in the 1000 PPM range. Restoring askarel transformers to a non-PCB status is a formidable task, but when a working system is announced, you just may find Sunohio involved. Thank you.

Exhibit I

OIL QUALITY SPECIFICATIONS

	SUNOHIO FIELD SPECIFICATIONS	NORMAL SUNOHIO CONTRACT SPECIFICATIONS
NEUT. NUMBER ASTM D-974	.02 MAX	.04 MAX
I.F.T. ASTM D-971	37 MIN	33 MIN
DIELECTRIC STRENGTH ASTM D-877	35 MIN	30 MIN
POWER FACTOR ASTM D-924 @ 25°C	.08% MAX	.10% MAX

Exhibit II

LEACH BACK RATE COMPUTATION

Initial Contamination Level	1000 ppm
Immediately After PCBX	8 ppm
Retest at 90 Days	33 ppm
Increase Since PCBX	25 ppm
Percent Leach Back 25 ÷ 1000 =	2.5%

Exhibit III

LEACH BACK STATISTICS

	50 - 249 PPM	250 - 499 PPM	500 - 999 PPM	1000 - 1500 PPM	TOTAL
No. of Units	182	66	70	26	344
Mean Rate	2.2%	1.7%	1.4%	1.0%	1.8%
90% Probability	6.9%	2.7%	3.1%	1.9%	5.8%
98% Probability	10.5%	4.7%	4.2%	2.6%	9.0%

DESIGN OF A FIXED PCB STORAGE FACILITY TO PRODUCE THE MOST VALUE FOR CLEANED OIL

Dr. Louis Centofanti
PPM, Inc.

PPM, Inc. is a waste management firm specializing in PCB handling, chemical destruction and testing. PPM has offices and facilities in Kansas City, Missouri; Atlanta, Georgia; and Canada. PPM's laboratory, located in Atlanta, is equipped with the most modern equipment available to measure PCBs and other hazardous contaminants in oil, air and water.

PPM, Inc. has incorporated its chemical destruction process into a mobile decontamination unit that can destroy PCBs on the generator's site, thereby avoiding transportation liabilities. Mobile units are operating both in the U.S. and Canada.

During several of our utility clean-ups, we have worked with utilities to evaluate, design and site treatment facilities. This work has involved initial planning and evaluation of all disposal options and the optimum facility for such. A decision on the type of disposal used has a significant impact on the design of the utility's storage facility.

Disposal options available to utilities include both on-site and off-site treatment or destruction. On-site treatment includes chemical destruction or the use of utility high-efficiency boilers. Off-site options include chemical destruction, incinerators or landfilling. In evaluating disposal options and facilities, general consideretions should include:

1. Short- and long-term liability
2. Reuse of the decontaminated oil
3. Reliability of the disposal firm
4. Economics.

Both short- and long-term liabilities must be considered when reviewing options.

The most serious long-term liability exists with non-destruction options, especially landfills. PPM, Inc. views landfills as nothing more than long-term storage. Although it is legal to use landfills for the disposal of PCB contaminated wastes, we recommend to our clients that only destruction options be used, since the generator may be required in the future to pay to have the landfill cleaned.

Short-term liabilities exist for all options. The most serious off-site liability exists with transportation of the hazardous material to the disposal facilities. Leaky tankers, spills and accidents during transit can produce a significant risk to the generator. This liability does not exist for on-site treatment.

Liabilities do exist for on-site treatment and include spills, accidents, etc. Liabilities associated with these are significantly less since spills can be easily contained and cleaned up when on site.

Two other non-economic issues that should be considered are the eventual use of the decontaminated oil and the reliability of the disposal firm. If the oil is chemically decontaminated, the oil can be used either in transformers or as a fuel oil. Many users have raised concerns about the quality of chemically reprocessed oil. The properties of PPM's processed oil are shown below.

PPM Transformer Oil Properties

	PPM Treated Oil	Suggested Limits
Dielectric Strength, KV	38.8	>26
Color, ASTM	1.5	2 max
Acidity mg KOH/g	.045	.25 max
Specific Gravity	.883	.86 - .91
Interfacial Tension	45.3	20
Power 25°C	.016	1.0 max
Factor 100°C	.946	5.0 max
PCB Level	<2 ppm	

We believe that the oil can be safely reused in transformers. The most important factor working against reuse of transformer oil at the present time is economics. Producing fuel oil from contaminated oil is a more economic route for most utilities than going to transformer oil.

DISPOSAL ECONOMICS

The most important factor in determining the disposal option and facility design is the economics of the various options. To demonstrate the economic options available to a generator, we have included two very simple cases and generated the economics of each. In reality, the economics can vary significantly depending upon a variety of parameters.

Case 1.

50,000 gallons of contaminated oil
300 ppm PCB
600 miles to nearest disposal facility (transportaion costs of $3.25/mile)

Case 2.

6,000 gallons of contaminated oil
300 ppm PCB
600 miles to nearest disposal facility (transportation costs of $3.25/mile)

ON-SITE DISPOSAL

Three options are available to a generator for on-site disposal of the waste. These are: high-efficiency boilers, chemical destruction producing a fuel oil, and chemical destruction producing a transformer oil. On-site incineration is allowed in EPA-approved high-efficiency boilers. Initial cost estimates indicate that burning in these boilers is the most economical method of disposal; however, most utilities have avoided this option. Public opposition to power plants becoming hazardous waste disposal facilities is intense. Many utilities that have attempted taking this route have found that public opposition and ensuing expenses to defend the burning rapidly make the project economically infeasible.

Cost estimates to the generator to chemically treat PCB oils are summarized below:

	50,000 gallons ($/gal)	6,000 gallons ($/gal)
Chemical treatment (fuel oil)	1.70	2.50
Fuel value	(.90)	(.90)
Total	.80	1.60

	50,000 gallons ($/gal)	6,000 gallons ($/gal)
Chemical treatment (transformer oil product)	2.80	3.50
Transformer oil value	(1.60)	(1.60)
Total	1.20	1.90

OFF-SITE DISPOSAL

We recommend two options for off-site disposal: chemical treatment or incineration. The costs, listed below, are similar.

Oil disposal (FOB facility)	$1.10
Transportation	.33
Total	$1.43

In this option the materials are moved by tanker in 6,000-gallon lots. Transportation costs are calculated at $3.25 per loaded mile, assuming 600 miles to the facility.

Thus, of these two idealized cases, if economics is the major deciding factor, off-site disposal is preferred for the 6,000 gallons of oil, while on-site disposal producing a fuel oil product is the preferred disposal option for the 50,000 gallons of oil. The various options are summarized below, and the preferred costs are underlined.

Disposal Cost

	50,000 gallons	6,000 gallons
Off-site	$1.43	$1.43
On-site (fuel oil)	.80	1.60
On-site (transformer oil)	1.20	1.90

STORAGE FACILITY

After a decision has been made on the best method of disposal for PCB materials, a facility should be designed that best suites that option. Besides a facility, procedures should be instituted to handle and store not only PCBs but also other solvents and other wastes. Proper housekeeping can greatly reduce the size of the PCB problem by avoiding mixing of non-contaminated materials with contaminated ones.

The storage facilities should include bermed storage tanks that, for off-site disposal, hold approximately 10,000 gallons; for on-site disposal, these tanks should hold a minimum of 30,000 gallons. We found that the majority of spills of PCB oils occur when loading and unloading tankers. We therefore recommend that the loading and unloading area also be bermed. If on-site treatment is anticipated, an operational pad should also be planned.

A design we use that incorporates all these features is shown below:

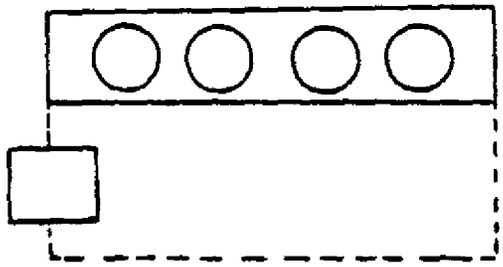

Figure 1. PCB Storage Design

Forty-eight thousand gallons of tank storage are provided in the four 12,000-gallon tanks. The tankers and the decontamination unit drive into the diked area over the ramp. All loading and unloading is done in the diked area. A chemical treatment unit should also sit in the diked area while treating. This would provide maximum protection against spills.

This design was slightly modified and used for a recent clean-up at Virginia Electric Power Company (VEPCO). Five hundred thousand gallons of oil were treated by one of PPM's mobile units. A bermed operational pad 40 feet by 80 feet was constructed to hold two storage tanks, tankers and processing equipment. The unit processed 9,000 gallons a day of oil, containing approximately 130 ppm of PCBs.

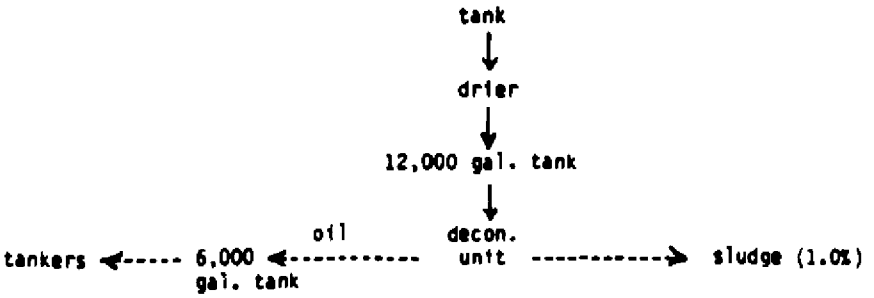

Figure 2. VEPCO Process Flow

TANK DECONTAMINATION

After emptying the 1,000,000-gallon storage tank, VEPCO was faced with the problem of decontaminating the tank. The EPA-approved procedure would require three flushes with 10 percent of the volume of the tank. This would require a minimum of 100,000 gallons of clean oil that would be considered contaminated. PPM was successful in receiving from EPA approval for an alternate procedure that greatly reduced the volume of oil needed in the flushing. The procedure included first removing all liquid and sludge from the tank, producing a "dry bottom" tank. The tank was then flushed with 10,000 gallons of oil until the PCB levels for two subsequent washes were unchanged. This was done for a minimum of three washes. Our tests showed no changes after three washes with levels at 3 ppm. This oil was removed and the tank then rinsed with another 10,000 gallons of oil. The flushing and rinsing oil was treated as PCB contaminated oil even though it was less than 50 ppm.

The procedure greatly reduced the volume of oil necessary to decontaminate the tank. After examining the procedure and PCB levels in the flushes, we felt that a better procedure would be to use several smaller volume batches of oil to flush the tank. For example, flushing the tank with five 1,000-gallon batches would have produced the same PCB-level reduction. This procedure was recommended to EPA for any future large tank clean-ups.