THERMAL DESTRUCTION

OF

CHLOROPHENOL RESIDUES

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for

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NOMENCLATURE

A   Frequency factor (s^{-1})

C   Concentration of a component (g.moles.cm^{-3})

$\bar{C}$ Average radial concentration (g.moles.cm^{-3})

C_o Concentration of a component at the entrance of the reactor (g.moles.cm^{-3})

C_{A1} Concentration of chlorophenol at the end of first stage (g.moles.cm^{-3})

C_{A*} Concentration of intermediate Complex A* at the end of first stage (g.moles.cm^{-3})

D_e Effective diffusivity ($cm^2.s^{-1}$)

D_g Molecular diffusivity ($cm^2.s^{-1}$)

E   Activation energy (cal.g.$mole^{-1}$)

GRT   Gas retention time (s)

H_6CDD Hexachloro-dibenzo-p-dioxins

H_7CDD Heptachloro-dibenzo-p-dioxins

k   Reaction rate constant (s^{-1})

L   Length (cm)

L_c Total length of curved tubing (cm)

L_s Total length of straight tubing (cm)

m   Order of reaction with respect to Component B (dimensionless)

n   Order of reaction with respect to Component A (dimensionless)

ng   Nanogram

OCDD   Octachlorodibenzo-p-dioxin

PCP   Pentachlorophenol

P_1	Ambient pressure (atm)
P_2	Exit reactor pressure (atm)
Δp	Pressure drop across reactor (atm)
R	Gas constant (cal.g.mole^{-1}.°K^{-1})
r	Radial co-ordinate (cm)
r_o	Radius of reactor (cm)
T_1	Ambient temperature (°K)
T_2	Average reactor temperature (°K)
t	Residence time in reactor (s)
T_4CP	2,3,4,5, tetrachlorophenol
TCDD	Tetrachlorodibenzo-p-dioxins
2,3,7,8 TCDD	2,3,7,8 tetrachlorodibenzo-p-dioxin
2,4,6 TCP	2,4,6 trichlorophenol
2,4,5 TCP	2,4,5 trichlorophenol
TGA	Thermogravimetric Analyzer
TDGS	Thermal Data Generation System
V	Linear axial velocity of gas at radial position r (cm.s^{-1})
$\bar{V}$	Average linear axial velocity of gas (cm.s^{-1})
V_1	Volumetric flow rate of gas at ambient pressure and temperature (cm^3.s^{-1})
V_2	Volumetric flow rate of gas at reactor pressure and temperature (cm^3.s^{-1})
V_R	Volume of reactor (mL)
W_1	Amount of sample in boat at start of run (g)
W_2	Amount of sample in boat at end of run (g)
W_3	Amount of sample in TGA washings (g)

W_4	Amount of sample in absorption solution (g)
z	Axial co-ordinate (cm)
$\P$	Geometric constant (dimensionless)
σ_t	Time based statistical standard deviation (s)
σ_z	Distance based statistical standard deviation (cm)
ω	Flow profile parameter
η	Destruction efficiency

CONCLUSIONS

Based on the results of this investigation, the following conclusions can be drawn:

1.   A system capable of studying thermal decomposition of toxic compounds under laboratory conditions has been developed. The system is able to assess the basic parameters of decomposition at a relatively modest cost. Precise thermal regimes can be maintained within the system and minimal environmental risks are involved in the laboratory experimentation. Pure compounds, industrial mixtures and contaminated residues in both solid or liquid states can be assessed.

2.   Thermal regimes up to 1200°C can be studied. The equipment is capable of generating precise thermal data up to a destruction efficiency of approximately 99 percent. A wide range of reaction environments can be provided ranging from highly oxidative to strongly reductive atmospheres.

3.   The laboratory system can generate data needed for the selection of preliminary operating conditions for pilot or full scale performance testing. Furthermore, the laboratory system can indicate the most thermally stable component of a mixture or waste and identify products of incomplete combustion.

4.   Data developed in the laboratory system can be extrapolated beyond the limits of the equipment precision (99 percent destruction efficiency) when appropriate kinetic modelling techniques are applied. For example, based on the pure chlorophenol destruction data, it is estimated that at 900°C a gas residence time not exceeding 2.9 seconds is needed to ensure complete ($>$ 99.99

percent) destruction of both T_4CP and PCP whereas extrapolated data for 2,4,5 TCP show a residence time in excess of 5 seconds would be required.

5. The results indicate that chlorophenol destruction follows first order kinetics with thermal stability decreasing, in general, in the order T_3CP, T_4CP, PCP. The experimental data for 2,3,4,5 TCP does not adhere to this pattern and cannot be readily explained.

6. Destruction efficiency of chlorophenols present in wood preserving mixtures was found to be consistently higher than would be predicted from the data developed for pure compounds.

7. For dip tank sludge, destruction efficiencies of greater than 99 percent (PCP and T_4CP) were achieved at 900°C and approximately 0.7 second GRT. Interpretation of the destruction data for the environmental samples is compounded by lack of sample homogeneity, potential of oxygen limitations due to sample ignition and effects of combustion products.

8. Significant amounts of dioxins and furans have been produced during the thermal destruction of chlorophenols at 700°C. At 900°C, similar quantitities of dioxins and furans were detected, with the exception of TCDD's which appeared to have been destroyed. Nevertheless, the concentration of highly toxic dioxins is very significant and should be of major environmental concern.

9. Data indicate that temperatures in excess of 900°C and/or residence times of more than three seconds will be necessary to accomplish significant destruction of dioxins and furans.

10.   Based on the results of this laboratory study, it can be postulated that measurable amounts of dioxins are being generated in tepee burners which operate at firebox temperatures in the range of 600 - 800°C.

RECOMMENDATIONS

Based on the results and conclusions of this work, the following areas should be addressed:

1. The basic thermal destruction data should be developed for a wide variety of organic compounds of environmental concern. Particular emphasis should be given to those compounds which are presently being disposed of by an uncontrolled incineration process. These data would enable a rational approach to the selection of preliminary operating conditions for pilot or full scale performance testing to ensure that the compounds in question are indeed thermally destroyed and no harmful byproducts are produced.

2. The conditions under which the furans and dioxins are created during thermal destruction of chlorophenols should be studied in greater detail. The variables, such as relative concentration of different chlorophenols in the mixture, reactor residence time and a more precisely defined temperature regime should be evaluated.

3. A field survey of full-scale incinerators which are burning chlorophenol contaminated wastes should be undertaken as soon as possible to assess whether significant concentrations of dioxins and furans are being released into the environment. The destruction efficiencies of the parent chlorophenols could be established at the same time.

4. A more detailed understanding of the intricacies involved in the analysis of chlorophenols, furans and dioxins in industrial samples should be developed.

1   INTRODUCTION

Safe disposal of toxic contaminants is becoming one of the major environmental issues of the 80's. One of the several approaches considered for toxic disposal is thermal destruction. This approach is particularly attractive when the toxic substances are associated with other organic materials (such as wood chips and/or concentrated organic sludges) which minimize the demand for external energy to achieve the destruction.

The Canadian wood industry is using a number of toxic compounds to protect their products from biological attack by fungi and bacteria. Some of the major wood preservatives used are chlorophenols. Approximately 3.4 million kilograms of chlorophenols are used annually in Canada as bactericides, slimicides, fungicides, herbicides and insecticides.

Some of the chlorophenols used for wood protection and preservation escape to the environment with detrimental effects due to their toxicity and persistence. As a result of environmental concern, housekeeping procedures designed to minimize the discharge of chlorophenols have been improved over the years. Wood chips and saw dust which are contaminated with chlorophenols are burned in existing boilers. This disposal technique has been used in most Canadian wood industries, particularly in British Columbia.

However, the incineration is undertaken in existing boilers which are not specifically designed for the purpose of toxic materials disposal. The thermal destruction characteristics of the individual units vary greatly from site to site and it is conceivable that some of the systems are not suited to accomplish chlorophenols destruction. Moreover, there have been reports from Europe speculating that secondary by-products of extreme toxicity (Dioxins) may be generated during incomplete destruction of chlorophenols under imperfect incineration conditions (Rappe, 1978). As a result, the technology for safe disposal of chlorophenols has been under detailed review. There is presently limited information available regarding the optimal thermal regime required for the complete destruction of various chlorophenols in incineration systems and the possibility of the formation of toxic by-products during thermal treatment of such materials.

One of the problems connected with the study of pollution control strategies for complex toxic organics is a lack of accurate and convenient analytical methods. The conventional technique for analysis of chlorophenols

involves a complex liquid-liquid extraction from the sample prior to batch injection for quantification and identification by gas chromatography and mass spectrometry, respectively (GC/MS). The liquid-liquid extraction is time consuming and prone to several problems, particularly when applied to sludges, residues, and similar sample matrices. Specifically, poor recovery of organic spikes and the formation of stable emulsions during the extraction process have been common problems. A thermal elution technique could substantially reduce the time requirements associated with solvent extraction methodology while reducing some of the problems associated with the present technique.

Development of a data base describing the conditions needed for both thermal elution and complete incineration of chlorophenols is the purpose of this study.

2   PROJECT RATIONALE AND OBJECTIVES

At the present, there are no scientific data available describing process parameters governing thermal destruction or thermal elution of chlorophenols. Ahling et al. (1977) have studied the combustion of wood preserving fluids containing pentachlorophenol at laboratory and pilot plant scale, however, their investigations were conducted under uncontrolled conditions. There are no data available in the literature on the destruction of pure chlorophenols.

There has been extensive laboratory research done by the University of Dayton, Ohio, (Duvall and Rubey, 1976) under the auspices of the U.S. Environment Protection Agency to develop gas phase destruction data for a number of complex organic compounds, such as polychlorinated bi-phenyls, Kepone and Mirex. Their work established destruction characteristics of the vaporized compounds at pre-selected temperature and residence times, examined the completeness of destruction and identified some of the decomposition products in controlled flow and high temperature air environment. The work involved evaluation of pure compounds and mixtures, which were injected into a thermal reactor system where the exact incineration residence time and temperature of the individual molecules to be destroyed could be accurately identified and maintained.

The main advantage of such an approach is the ability to evaluate the effect of process parameters with a high degree of accuracy. The disadvantage is that the results of the research are not directly related to actual industrial conditions where incineration takes place both in flame mode as well as thermal decomposition mode. However, the results are useful in establishing the relative ease of destructability of one compound from the other. Moreover, these results define the maximum destruction possible under known conditions of temperature and residence time. Products of incomplete combustion can also be identified.

The approach used in this study was to develop a larger bench scale unit, where, in addition to pure compounds, samples of actual wood preservative mixtures and contaminated sludges would be introduced. In order to achieve this goal it was decided to sacrifice some of the accuracy in the control of

operating parameters such as temperature and residence time as only approximate control can be achieved in an industrial situation.

The compounds investigated in this study were evaluated in order of increasing complexity of thermal destruction, beginning with pure compounds and then continuing with wood preserving mixtures and contaminated sludges. During the work with pure compounds, the thermal destruction characteristics were determined as a function of temperature and retention time (time interval during which the molecule was exposed to high temperature). Testing was done in a non-flame mode oxidative environment in two steps: the compound was gradually vaporized and then passed through a high temperature zone with an excess of oxygen in order to avoid the possibility of pyrolytic reactions. Vaporizing the sample prior to the thermal destruction, ensured that the individual molecules were exposed to the actual destruction temperature in the chamber.

In a pure compound system, there are no interferences from other material and the parameters governing the decomposition can be accurately defined. The data developed during the work with the pure compounds were utilized to predict the appropriate conditions for the work with the complex compounds.

All the laboratory thermal study work was designed to determine the relative importance and limits of effectiveness of the individual process variables required for safe disposal of chlorophenols in industrial situations. Although it is obvious that some scale-up investigations will be needed to prove the findings of the study under full-scale incineration conditions, every consideration was given to develop as much practical information as possible.

Based on the above rationale, the specific objectives for this investigation are as follows:

- To determine the effect of temperature on the thermal destruction of chlorophenols.

- To determine the effect of residence time on the destruction of chlorophenols.

- To determine the relationship between the process characteristics applicable to the destruction of pure compounds and complex industrial mixtures such as wood preservation liquids and contaminated sludges. To estimate the products of incomplete combustion of chlorophenols.

- To evaluate the feasibility of thermal elution technology as an analytical protocol.

3.   TECHNICAL BACKGROUND

Two basic wood treatment technologies are commonly used in Canada. One method is designed for short-term protection of wood and is referred to as "wood protection". The second method is designed for long-term protection of the wood and is generally referred to as "wood preservation".

"Wood protection" is mostly practised in British Columbia and consists of surface treatment for sap stain control during relatively short transportation periods. In general, this treatment is applied under ambient pressure.

"Wood preservation" is more widely practised and is based on chemical impregnation of the wood under pressure.

There are numerous preserving chemicals used in the wood treatment industry, such as chlorophenols and creosote, as well as oxides of copper, arsenic and chromium. In Canada, chlorophenols are most commonly used for both wood preservation and wood protection processes.

3.1   Use of Chlorophenols for Wood Treatment

Chlorophenols are widely used in the wood treatment industry due to their proven toxicity to wood destroying organisms. There are over 50 wood treatment operations in Canada and chlorophenols are utilized in the vast majority of them (Jones, 1981).

Prior to the application of the treatment, the wood has to be adequately prepared to achieve the best results. The timber is machined and dried either by air or in kilns, closed chambers and/or retorts, until the moisture is below the fibre saturation point. Alternatively, the Boulton drying process, which consists of boiling material in an oil preservative under vacuum can be used.

Wood preservation can be accomplished by a number of pressure based processes such as: Bethell, Rueping, Lowry and Cellon, all of which are quite common in Canada. The basic operating conditions of the pressure processes are summarized in Table 3.1.

TABLE 3.1   WOOD PRESERVATION - PRESSURE PROCESSES

OPERATING CONDITIONS

BETHELL PROCESS

- Initial vacuum - 22 inches of mercury

- Preservative injected till pressure is achieved

- Temperature maintained at 80 - 105°C and vacuum drawn

    The process is designed to flood the cell cavities
    with as much preservative as possible.

RUEPING PROCESS

- Air pressure (2 - 4 atmospheres) is applied for up to 1 hour

- Preservative heated to approximately 80°C is introduced and
  vacuum drawn

- Temperature increased by 4°C

    The process is designed for maximum penetration for a
    given amount of preservative.

LOWRY PROCESS

- Preservative heated to approximately 80°C is introduced
  using slight pressure and vacuum drawn

- Temperature increased by 4°C

CELLON PROCESS

- Liquified petroleum gas is used as a carrier gas for
  pentachlorophenol - pressure is built up and vacuum drawn

- Gas is evaporated and recovered

    The process impregnates the wood. The treated wood has
    the same colour and appearance as the original material.

Wood protection is usually achieved by non-pressure processes and the basic characteristics of the current technologies are shown in Table 3.2.

TABLE 3.2   WOOD PROTECTION - NON-PRESSURE PROCESSES
                        OPERATING CONDITIONS

Thermal Process Material is heated for several hours in an open tank and then quickly submerged in cold penta solution for several hours. **Dipping and Painting** Penta solution is applied by means of dipping or painting by spray or brush.

The manufacture, properties and toxicity of chlorophenols and their impurities as well as pollution control options, with the exception of thermal destruction, are described in Appendix 1.

3.2   Thermal Destruction of Chlorophenol Residues

Thermal destruction is presently being practised for the disposal of contaminated wood chips and sludges. Utilization of available heating value is the prime objective of the process. As a result, most burning of contaminated wood chips and sludges takes place in refuse (hog fuel) boilers, thermo-pile burners etc.

3.2.1   Thermal destruction of chlorophenols   At present, there are very limited scientific data regarding the thermal destruction of chlorophenols. Ahling and Johansson (1977) studied thermal destruction of chlorophenols in both pilot and full-scale experiments. The results indicate that both penta-chlorophenol and tetrachlorophenol can be almost totally destroyed at

temperatures ranging from 600 - 800°C and residence times ranging from 0.9 - 3 seconds, as shown in Table 3.3.

TABLE 3.3   SUMMARY OF RESULTS EVALUATING THERMAL DESTRUCTION
OF CHLOROPHENOLS IN PILOT AND FULL SCALE TESTS

Compound	Temperature	Residence Time	Original Concentration of Chlorophenols	% Destroyed
		PILOT SCALE		
Pentachloro-phenol	600°	3 secs.	50 mg/kg	99.995
	800°	3 secs.	15 mg/kg	99.9985
		FULL SCALE		
Tetrachloro-phenol	760°	0.9 secs.	9 mg/kg	99.9991
Pentachloro-phenol	760°	0.9 secs.	650 mg/kg	99.935

Controlled air incineration of pentachlorophenol treated wood has been conducted at the Los Alamos National Laboratory, by Stretz and Vavruska et al. (1982). No residual pentachlorophenol was found in the effluents after exposure to 980°C for a retention time of 2.5 seconds.

Field tests were conducted at a wood preserving facility by DaRos et al. (1982). Wood waste and penta creosote wastewater were co-fired in the boiler. Destruction efficiency of 96.1 and 99.97 were found for napthalene and phenol respectively.

In general, the full-scale industrial boilers currently burning chlorophenols are not operated under controlled conditions (such as exact

temperature in the incineration chamber, residence time at a given temperature) and therefore little valuable data can be obtained.

3.2.2   Production of by-products   Rappe et al. (1978) has shown that chloro-phenols contain a variety of contaminants and by-products such as poly-chlorinated phenoxyphenols, polychlorodibenzo-p-dioxins, polychlorodibenzo-furans and diphenyl ethers.   Uncontrolled open burning of leaves and wood impregnated with commercial and purified chlorophenates was investigated. Table 3.4 shows the level of dioxins in the starting materials and effluents. From the table it is clear that amounts of polychlorodibenzo-p-dioxins increased as a result of the combustion process and the distribution of dif-ferent isomers is different in each case.   The formation of polychlorodibenzo-p-dioxins could be due to dimerization of chlorophenates or by cyclization of pre-dioxins.   Dechlorination of higher chlorinated polychlorodibenzo-p-dioxins is also a distinct possibility.   Detailed studies have not been done to estab-lish the extent of polychlorodibenzo-p-dioxins formation by any of the alterna-tive routes.

TABLE 3.4   DIOXIN PRODUCTION FROM BURNING OF CHLOROPHENOL CONTAMINATED LEAVES (µg/g CHLOROPHENOL)

(Rappe 1978)

	Servarex *		KY - 5 **		2,4,6 Trichloro-phenate		Pentachloro-phenate	
	Original	Effluent	Original	Effluent	Original	Effluent	Original	Effluent
Tetra CDDS	0.7	35	0.4	30	< 0.02	2100	< 0.02	5.2
Penta CDDS	5.2	90	3.5	84	< 0.03	5	< 0.03	14
Hexa CDDS	9.5	80	5.3	82	< 0.03	1	< 0.03	56
Hepta CDDS	5.6	8	2.1	8.2	< 0.1	3	0.3	172
Octa CDD	0.7	0.3	0.3	0.4	< 0.1	6	0.9	710

* Servarex - Swedish product containing approximately 5% of 2,4,6 trichlorophenate, 50% 2,3,4,6 tetrachlorophenol and 10% of pentachlorophenol as the sodium salt.

** KY-5   - Finnish product of similar composition.

Langer et al. (1973) studied the thermal properties of chlorophenols and derivatives and concluded that decomposition of most of the chlorophenols does not lead to dioxin formation, however, the sodium salt of pentachlorophenol produced a measurable quantity of dioxins when subjected to thermal decomposition under low temperature.

No polychlorodibenzofuran or polychlorodibenzo-p-dioxin were found in the air emissions during a study of controlled incineration of wood treated with pentachlorophenol at the Los Alamos National Laboratory, (Stretz et al. 1982). Stehl's studies (1973) on the combustion products of wood and paper treated with pentachlorophenol showed no increases, but rather a decrease, in the amount of octachlorodibenzo-p-dioxin. Polychlorodibenzo-furan and polychlorodibenzo-p-dioxin were found in treating penta solution, waste sludge and the ash. The quantity determined in each sample depended on the method of analysis. It was concluded that tetrachlorodibenzo-p-dioxins were generated while octachlorodibenzo-p-dioxins were reduced by the process. It could not be concluded whether 2,3,7,8 tetrachlorodibenzo-p-dioxin was present or not. It appeared that controlled destruction in the steam boiler would be a viable method for disposal of pentachlorophenol wastewaters.

Reports summarizing the results of the field testing in Europe indicated a possibility of toxic by-products being discharged from municipal incinerator fly ash and flue gas (Olie, 1977).

Rappe (1978) reported the existence of polychlorodibenzo-p-dioxins and polychlorodibenzo furans in the fly ash from municipal incinerators and industrial heating facilities in Switzerland. Ahling and Lindskog (1980) in their studies of emission of chlorinated organic substances from burning of wood and pulp industry black liquor, concluded that inorganic chlorides result in the formation of chlorobenzenes which, in turn, form chlorophenols. The chlorophenols are the precursors for dioxins, therefore the presence of chlorophenols in flue gases from municipal wastes explains the finding of dioxins in fly ash.

Arthur D. Little Inc. (1980), in their report to the American Society of Mechanical Engineers, have reviewed the information on dioxin emissions from combustion sources. Their emphasis has been mainly on the 2,3,7,8 tetra-chlorodibenzodioxin isomer. Emission data from municipal and industrial waste incinerators in the Netherlands, Germany, Switzerland, Canada and the United States are presented.

Recently, Tiernan et al. (1982) have also quantified the tetrachloro-dibenzo-dioxins in the extract of effluent samples from a RDF (refuse derived fuel) incinerator.

The conditions needed for dioxins and furans formation are not well defined. It is established that a compound is a dioxin precursor if it meets the two following conditions (Esposito et al. 1980):

* The precursor compound must be an ortho substituted benzene ring in which one of the substituents includes an oxygen atom directly attached to the benzene ring.

* It must be possible for the two substituents, (excluding the oxygen atom), to react with each other to form an independent compound.

These conditions are satisfied by chlorophenols where the hydrogen of the hydroxyl group co-react with the other substituent (chlorine) to form hydrogen chloride, as illustrated by the following examples, (Esposito, 1980):

CHLOROPHENOL   UNSUBSTITUTED DIOXIN

2,4,6 TRICHLOROPHENOL   1,3,6,8 TETRACHLORODIBENZO—p—DIOXIN

2,4,5 TRICHLOROPHENOL → 2,3,7,8 TETRACHLORODIBENZO—p—DIOXIN + 2 HCl (variety of conditions)

2,3,5,6 TETRACHLOROPHENOL → 1,2,4,6,7,9 HEXACHLORODIBENZO—p—DIOXIN + 2 HCl (copper powder catalyst)

PENTACHLOROPHENOL → OCTACHLORODIBENZO—p—DIOXIN + 2 HCl (heating)
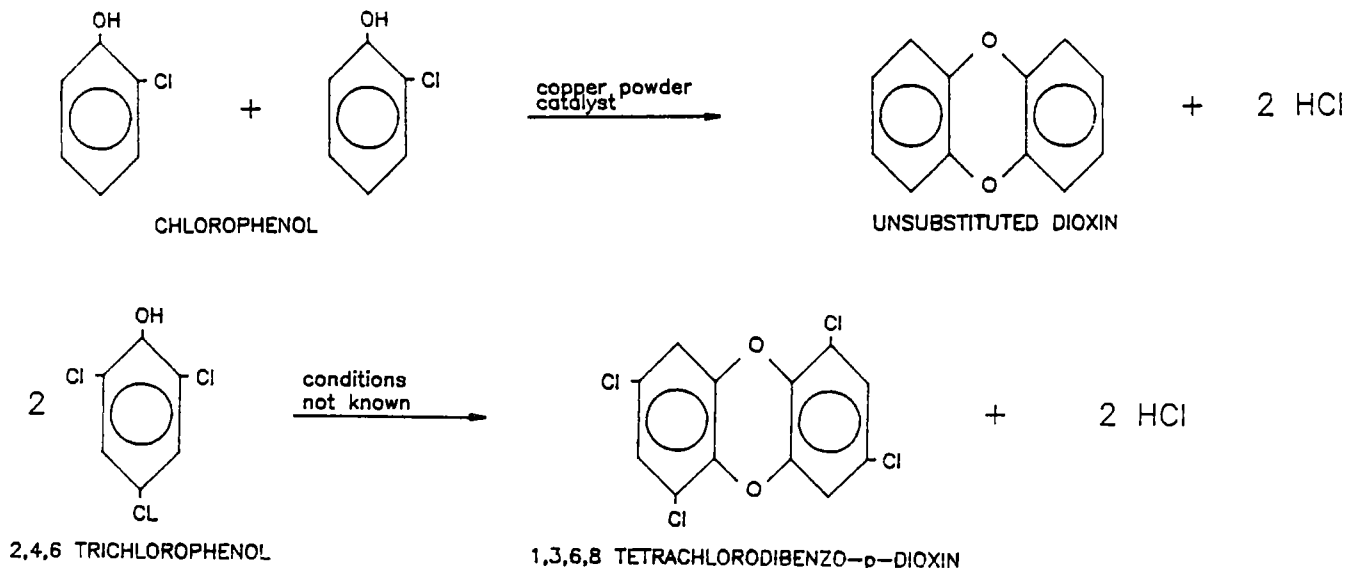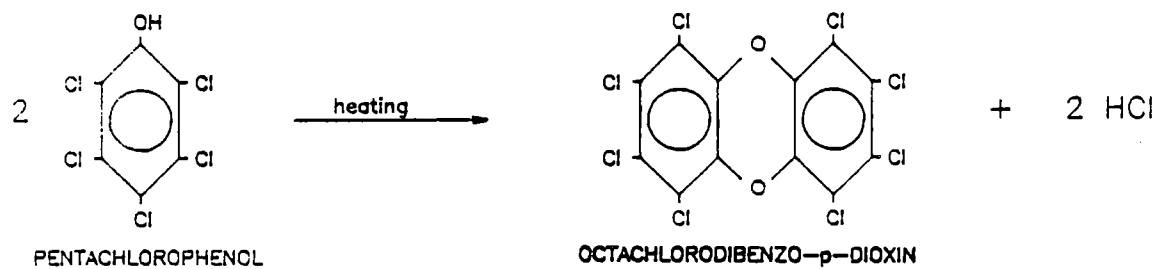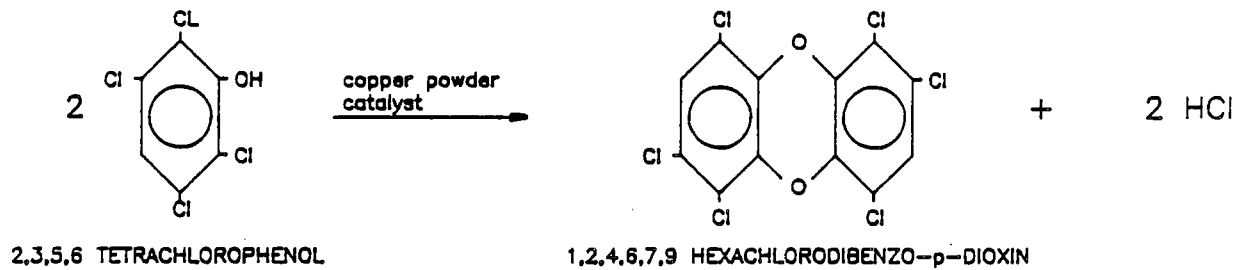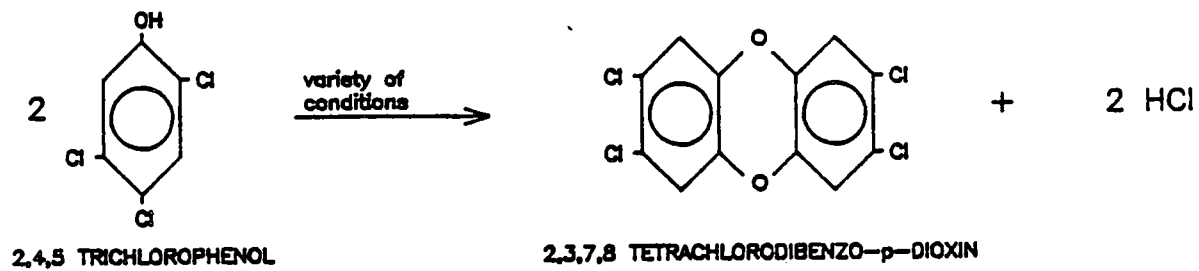
Other dioxins and similar compounds have been detected in the following reactions:

2 **2,4,5 TRICHLOROPHENOL** → **ISO PREDIOXIN** + HCl

2 **2,4,5 TRICHLOROPHENOL** → **ISO PREDIOXIN** → **FURAN**

2 **2,4,5 TRICHLOROPHENOL** → **1,4,7,10 TETRACHLORO 3,8 DIHYDROXY BIPHENYL** + Cl_2
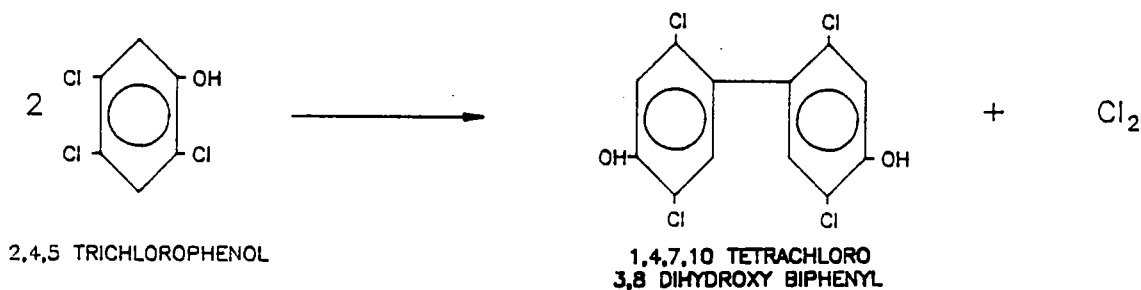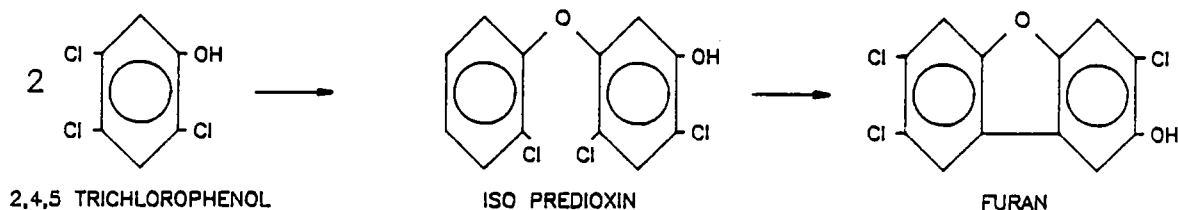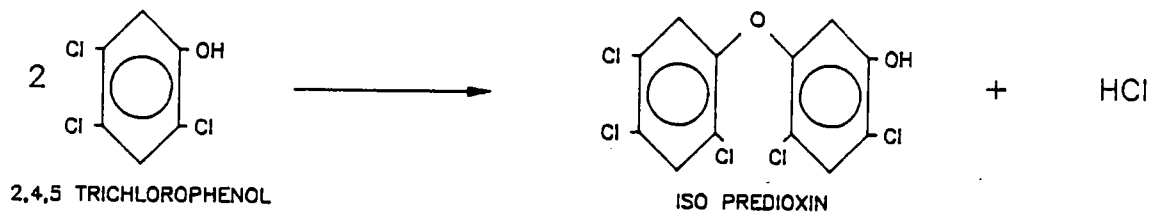
The released chlorine may react with other compounds to form higher chlorinated compounds.

Earlier it was believed that dioxins are formed by arbitrary transfer of chlorine which occurred within the energetic predioxin molecules (Boer, 1971), but now it has been proved that "Smiles Arrangement" (Gray, 1976) is often operational during dioxin creation. Some scientists (Rawes, 1979, Miller,1979 and Ciaccio, 1979) believe that an equilibrium position exists in which dioxins slowly lose or gain chlorine atoms to approach the most stable state.

It is not a necessity that the predioxin base leads to dioxin formation (Jensen and Renberg, 1972 and 1973). Predioxin appears to be more likely to occur than corresponding dioxins, as their concentration in a reaction mixture could be as much as twenty times greater than the dioxin content.

It is possible that less rigorous conditions are needed for predioxin formation and steric or electronic hindrances interfere with the final step of ring closure.

The dioxin nucleus is quite stable up to 700°C. Incinerator operating conditions currently considered adequate for destruction of chlorophenols are a temperature of 1000°C and residence time of at least 2 seconds (Tenzer, 1970, Wilkinson, 1978). With pure samples of dioxins, Kearney (1973) has shown complete destruction between 800 and 1000°C. For impure mixtures, temperatures above 800°C are important because tetrachlorodioxins may be formed from the precursor in the range of 300 - 500°C (Rappe, 1978). Uncontrolled burning of birch leaves treated with chlorophenols and commercial wood preserving formulations containing 2,4,6 tri and 2,3,4,6, tetra and penta chlorophenate led to the formation of tetra, penta, hexa, hepta and octa chlorodioxins. The same dioxins were also produced by micropyrolysis of a mixture of 2,4,6 trichloro, 2,3,4,6 tetrachloro and pentachlorophenol confirming that chlorophenols are precursors for dioxins.

3.2.3   Applicability of thermal destruction of chlorophenol residues   The data available in the literature, though incomplete, strongly suggest that thermal destruction can be a very efficient means of disposing of toxic chloro-phenol residues. However, the information, while contradictory, seems to indicate a possibility of generating undesirable by-products during incineration under less than ideal conditions. Thermal destruction profiles for pure compounds and commercial mixtures have not yet been developed, and are the basis of this investigation.

4.   DEVELOPMENT OF A LABORATORY THERMAL DATA GENERATION SYSTEM

Incineration is a thermal oxidation process and is one of the few waste management options with the capability of destroying the hazardous constituents of a waste. However, to be environmentally acceptable, incineration must have demonstrated thermal destruction capability. Development of laboratory thermal data is the first and crucial step in the demonstration of this capability.

Generation of laboratory scale thermal destruction data can be accomplished relatively easily and the data can be produced under precise thermal regimes. Additional advantages of the system include the modest cost of the testing as well as minimal environmental risks involved in laboratory experimentation.

The data generated in a laboratory system can be readily used for the following purposes:

- Selection of preliminary operating conditions for pilot or full scale performance testing.

- Identification of the most thermally stable component of a waste.

- Identification of products of incomplete combustion.

- Development of a priority list of compounds of concern.

- Provision of scientific information for public interest groups.

In general, development of laboratory thermal destruction data is a mandatory prerequisite to ensure that incineration of toxic organics is conducted in the safest and most economical manner.

4.1   Factors Affecting Incineration

The destruction efficiency (η) achieved for any specific compound in an incinerator can be defined as:

$$\eta = \frac{(\text{mass into incinerator} - \text{mass out from incinerator})}{(\text{mass into incinerator})} \times 100$$

Destruction efficiency is dependent on many factors including the following factors:

- Physical and chemical properties of a substance: The physical properties affecting destruction are the boiling point and vapour pressure of the substance. The decomposition behaviour of a substance is influenced by its reactivity with oxygen and its thermal stability.

- Atmosphere: The oxidative, inert or reductive environment in which destruction is carried out affects the extent of destruction and the products of combustion.

- Exposure temperature: The temperature at which destruction is carried out affects the decomposition of the parent compound and its products of combustion.

- Residence time: Destruction efficiency is very sensitive to the residence time of molecules in the incinerator. The incinerator volume should be such that the products of incomplete combustion will also be exposed to high temperature for a sufficient amount of time so that no harmful byproducts remain.

- Concentration: The rate of decomposition of a compound depends on its concentration in the stream entering the incinerator. For a given retention time, the destruction efficiency also becomes concentration dependent.

- Turbulence and flame effects: Turbulence and the presence of a flame affect the destruction efficiency but cannot be easily addressed in a laboratory system.

4.2   Design Requirements

Besides considering the basic process variables such as exposure temperature and residence time, other requirements of a laboratory system are as follows:

- The sample must be in vapour form before it enters the destruction chamber.

- Effluent from the destruction chamber must be captured and reliable methods must be available for analysis of products of incomplete combustion and undecomposed parent compounds.

- All transport lines should be inert to the substance to be destroyed.

- No condensation of vapours should occur on transfer lines.

The following are the basic components of a laboratory system designed to meet the above criteria:

- Gas Supply: There should be provision to admit gas at a controlled rate into the system to provide both transport of the compound and/or waste being studied as well as the appropriate environment in the destruction chamber.

- Sample Introduction: Samples introduced into the destruction chamber must be in vapour form and a constant amount of the sample should be transported to the reactor per unit of time.

- Reactor: The reactor is immersed in a high temperature zone to

provide the desired decomposition environment. The temperature variation along the reactor path should be minimized so that molecules are exposed to constant temperature during their stay in the reactor. The reactor geometry is such that the residence time of all molecules within the reactor is approximately equal. The spread in the residence time distribution should be minimal and the flow in the reactor is to approach that in an ideal plug flow reactor.

- Collection System: The products of destruction should be collected for quantification and analysis. The level of recovery achieved will influence the accuracy of mass balance calculations.

- Flow Meter: A suitable flow measuring device is necessary to determine the flow rate of the gas stream in the system.

4.3 Equipment Development and Description

4.3.1 Gas supply system

The gas serves the dual purpose of transporting the vaporized sample and providing the appropriate environment in the destruction chamber. It also controls the residence time in the reactor. The possible arrangements include an option of having different gases available in separate containers and mixing them in desired proportions. Alternatively, a gas with a tailored composition can be procured and its flow regulated through a control valve into the system. The later choice was made in the case of this study for reasons of simplicity and ease of operation.

The rate of carrier gas released from the gas reservoir is controlled by a needle valve. Gas composition is dictated by the desired environmental conditions in the reactor. Pure oxygen is used for highly oxidative conditions, carbon monoxide for reductive conditions and intermediate levels of oxygen in the carrier gas (air) or inert conditions (nitrogen) can also be supplied as needed.

4.3.2   Sample introduction (vaporization)

Sample vaporization rate is a function of temperature. If the sample is maintained at a constant temperature, vaporization will occur at a uniform rate. In order to achieve this, a stainless steel oven was fabricated to evaporate the sample. The oven was heated with electric tape allowing a constant temperature to be maintained. The disadvantages of this system were poor temperature control and the availability of a large area for sample deposition and subsequent unaccountable loss. Moreover, it involved the cumbersome process of dismantling and assembling the set-up for each run.

An alternative was to use a thermogravimetric analyzer where the sample could be vaporized at a uniform rate and the total vaporized amount accurately measured. The thermogravimetric balance contains a pan for the sample, which is attached to an electronic balance. The temperature of the sample can be precisely varied. Suitable transducers indicate the temperature and weight of the sample at any time during the run. A typical thermogram is shown in Figure 4.1.

FIGURE 4.1   TYPICAL THERMOGRAM (PCP)

SAMPLE : PCP
SIZE : 24.19 mg
RATE : 10 °C/min
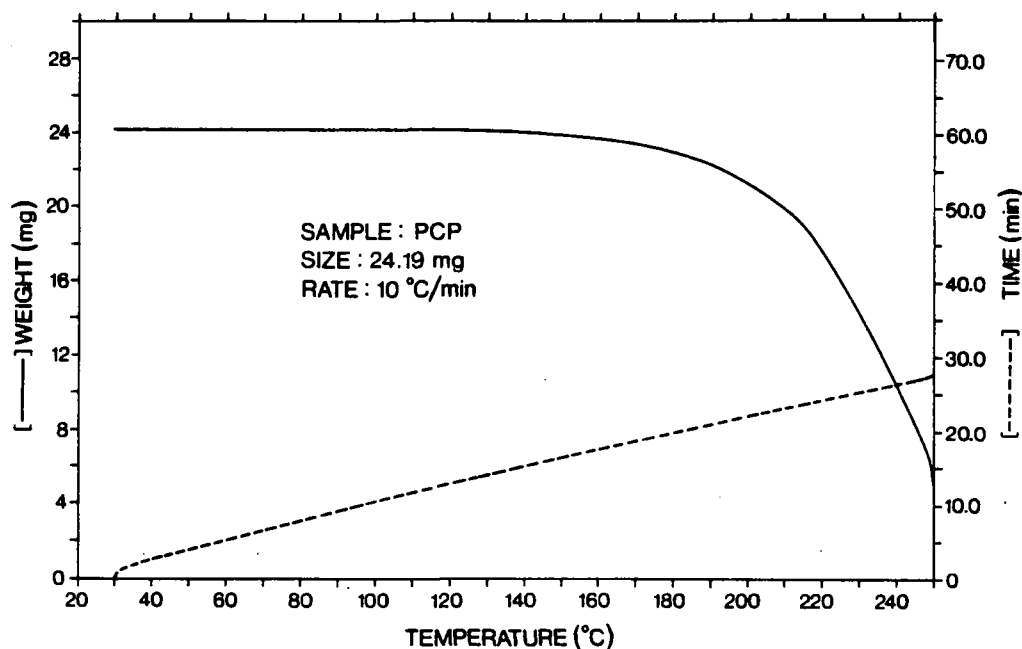
Constant temperature of the sample can be easily maintained to ensure a constant vaporization rate. The total amount of the sample vaporized is obtained by the difference in the weights at the start and at the end of the run. The carrier gas stream enters the thermogravimetric assembly and carries the vaporized sample to the reactor. A DuPont 1090 Thermal Analyzer was used as the sample vaporization stage of our system. The characteristics of the unit are given in Table 4.1.

TABLE 4.1   CHARACTERISTICS OF THE VAPORIZATION SYSTEM

Physical Nature of the Sample that can be Handled	Solid or Liquid
Maximum Amount of Sample Permissible	100 mg
Balance Sensitivity	$\pm$ 0.001 mg
Operating Temperature Range	30 - 1200°C
Linear Ramping Rates Available	2,5,10,20,50°C/min
Temperature Sensitivity	$\pm$ 0.2°C

4.3.3   Reactor

The residence time of molecules in the reactor for a given flow rate depends on reactor volume, temperature, pressure and hydrodynamics of flow. An ideal reactor is one in which all molecules spend an equal amount of time and are exposed to a constant temperature. However, these ideal conditions do not exist in practice as it is very difficult to maintain constant temperature over a long distance. As a result, a temperature gradient from one end to the other end will occur. To minimize the temperature gradient, the reactor can be either in the shape of a helical coil or in the form of a cyclic track as shown in Figure 4.2. In the case of a helical coil, secondary flow develops (Dean, 1927). Secondary flow enhances dispersion (Aris, 1956) and consequently the uniformity of the

molecules' residence time is adversely affected. Thus, to minimize secondary flow, use of a folded tube (cyclic track) reactor was selected.

FIGURE 4.2   REACTOR CONFIGURATIONS
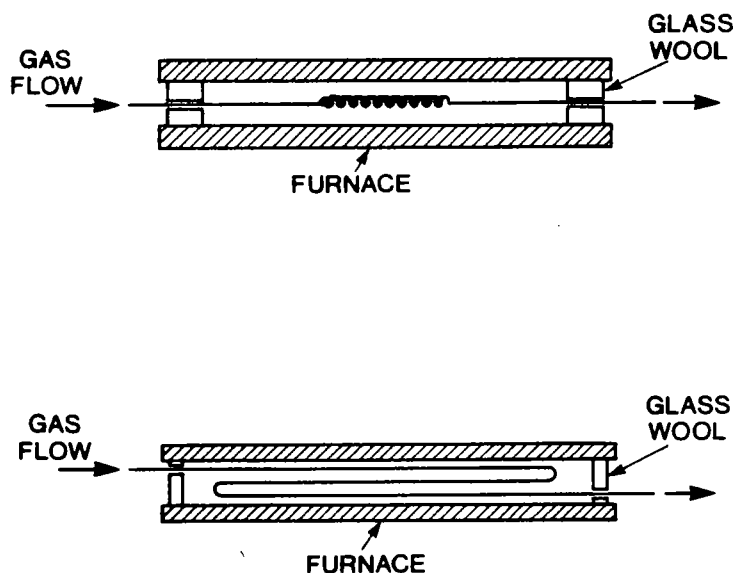
Fluids flowing in straight tubes of circular cross-section exhibit a parabolic velocity profile under laminar conditions as expressed by:

$$V = 2\overline{V} \left(1 - \frac{r^2}{r_o{}^2} \right)$$

(1)

Mass transport under these flow conditions is governed by diffusion and convection considerations and can be expressed as:

$$\frac{\partial C}{\partial t} + 2\overline{V} \left(1 - \frac{r^2}{r_o{}^2} \right) \frac{\partial C}{\partial z} = D_g \left(\frac{\partial^2 C}{\partial r^2} + \frac{1 \cdot \partial C}{r \, \partial r} + \frac{\partial^2 C}{\partial z^2} \right)$$

(2)

The solution of equation (2) is given by (Rubey, 1980), using boundary conditions at $t = o$, $C = C_o$

$$\text{and} \quad \left. \frac{\partial C}{\partial r} \right|_{r \, = \, r_o} = o \tag{3}$$

$$\overline{C} = C_o \, \exp\left(\frac{-Z^2}{4D_e \cdot t}\right) \tag{4}$$

where $\overline{C}$ is the average concentration at any cross- section. It is expressed as

$$\overline{C} = \frac{1}{\P r_o^2} \int_0^{r_o} C.2\P.r.dr \tag{5}$$

$$\text{and} \quad D_e = D_g + \frac{\overline{V}^2 r_o^2}{48 D_g} \tag{6}$$

Equation (4) is a Gaussian Distribution Function for which the distribution variance is:

$$\sigma_z^2 = 2D_e \cdot t \tag{7}$$

The distribution variance is a function of axial position; expressed as:

$$\frac{\partial^2 \sigma_z}{\partial z} = 2D_e \cdot \frac{\partial t}{\partial z} = \frac{2D_e}{\overline{V}}$$

$$= \frac{2}{\overline{V}} \left(D_g + \frac{\overline{V}^2 r_o^2}{48 D_g} \right) \tag{8}$$

At the entrance of the reactor, variance is zero

i.e.

$$\sigma_z^2 \Big|_{z=0} = 0 \tag{9}$$

Integrating equation (8) between the limits of O and L and using equation (9) we obtain:

$$\sigma_z^2 = 2 \left(\frac{D_g L}{\overline{V}} + \frac{\overline{V} r_o^2 L}{48 D_g} \right) \tag{10}$$

Time based variance is related to distance based variance by:

$$\sigma_z^2 = \sigma_t^2 \times \overline{V}^2 \tag{11}$$

Therefore, time based variance can be expressed as:

$$\sigma_t^2 = \frac{2 D_g L}{\overline{V}^3} + \frac{r_o^2 L}{24 D_g \overline{V}} \tag{12}$$

For a curved tube, equation (12) is modified according to Deelder(1978)

$$\sigma_t^2 = \frac{2 D_g L_c}{\overline{V}^3} + \frac{\omega r_o^2 L_c}{24 \overline{V} D_g} \tag{13}$$

For a folded tube reactor with straight length L_s and curved length L_c, a combination of (12 and (13) gives:

$$\sigma_t^2 = 2D_g \left(\frac{L_c + L_s}{\bar{V}^3} \right) + \frac{r_o^2}{24\bar{V}D_g} \left(\omega L_c + L_s \right) \qquad (14)$$

Under a given set of operating conditions, equation (14) can be used to calculate the residence time variance for a reactor of given length and diameter.

A cyclic track reactor shown in Figure 4.3 was fabricated and used in these studies. Its volume was measured using the mercury displacement method.

FIGURE 4.3   HIGH TEMPERATURE REACTOR
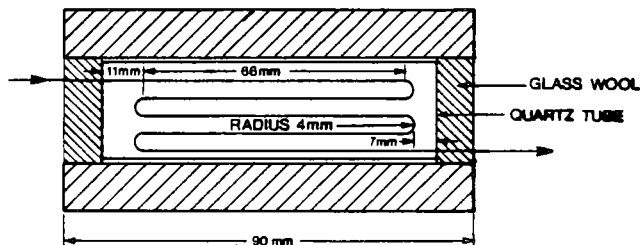
Reactor specifications are given in Table 4.2.

TABLE 4.2   REACTOR SPECIFICATIONS

Total Length of the Reactor:	398 mm
Inside Diameter of the Reactor:	2 mm
Length to Diameter Ratio:	196
Material of Construction:	Quartz
Volume of Reactor:	1.25 mL

The reactor is immersed in the high temperature zone. Figure 4.4 shows the temperature profile along the reaction path.

FIGURE 4.4 REACTOR TEMPERATURE PROFILE
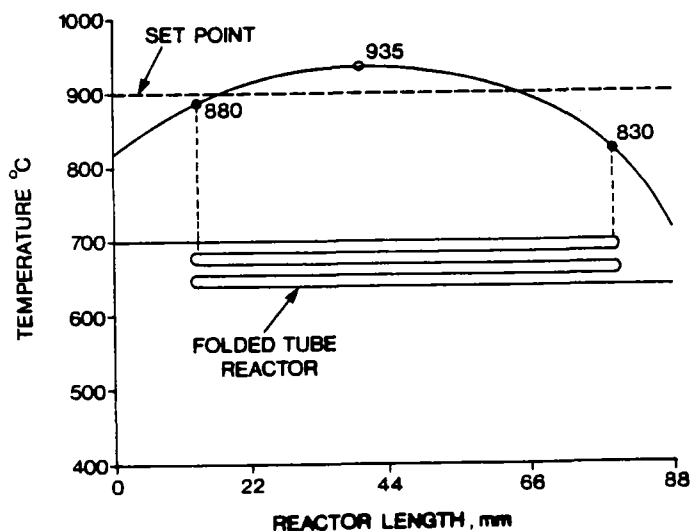
The temperature profile is not absolutely flat because end effects cannot be avoided. However, 95 percent of the reactor volume lies in the region where temperature variation is not more than 10 percent of the set point temperature. The residence time variation under extreme conditions of flow is calculated according to equation (14) and is shown in Table 4.3.

TABLE 4.3 RESIDENCE TIME VARIATION UNDER OPERATING CONDITIONS

Temperature ($^{\circ}$C)	Nominal Residence Time (s)	95% Confidence Limit (s)
500	1	0.87 - 1.13
500	3	2.76 - 3.24
900	1	0.92 - 1.08
900	3	2.72 - 3.28

Maximum deviation occurs at high temperature and at low axial velocity and is approximately 10 percent of the average residence time. The molecules passing through the reactor do not experience widespread residence times and are exposed to a relatively uniform temperature during their stay in the reactor.

4.3.4 Collection system

To capture the products of destruction from the reactor effluent, adsorption or absorption processes could be used. The suitability of the following collection systems were evaluated:

- Adsorption column containing Tenax GC

- Adsorption column containing activated carbon

- An absorption trap containing methanol

The collection systems were placed immediately after the vaporization stage and PCP was used as the target compound for recovery studies. A maximum of 9 percent of material could be recovered from Tenax GC adsorbent while recovery was only 5 percent in the case of activated carbon.

The absorption system containing methanol proved to be far superior because chlorophenols have high solubility in this solvent. Recovery tests were conducted with the absorption system under both stirred and non-stirred conditions. Ninety-nine percent recovery was obtained in the former case while only 80 percent recovery was achieved in a non-stirred system. Therefore the stirred absorption system containing methanol was chosen for product capture.

4.3.5 Flow meter

A flow meter is needed to determine the flow rate of carrier gas through the system. The flow rate can be accurately measured in the range of 1 to 60 mL/min using a bubble flow meter. As the carrier gas exits from

the system to the open atmosphere, its flow rate through the reactor can be calculated using the ideal gas law

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

(15)

where subscript 1 and 2 refer to ambient and reactor conditions, respectively.

Laminar flow conditions were always maintained in the reactor. The pressure drop across the reactor was calculated using the Hagen Poiseulle equation and was found to be very low. Therefore, the pressure measured at the exit of the reactor was almost the same as the pressure inside the reactor. A manometer connected at the exit of the reactor determines the pressure outside the reactor and the flow rate of the carrier gas in the reactor can be calculated using equation (15).

4.3.6   Transfer lines

The vaporization chamber, reactor and collection system were connected with glass lined stainless steel tubing with stainless steel unions. These transfer lines were electrically heated and well insulated to prevent heat loss to the surroundings and subsequent vapour condensation. Transfer line specifications are shown in Table 4.4.

TABLE 4.4   TRANSFER LINE SPECIFICATIONS

Inside Diameter of Tubing	= 3.5 mm
Length of Transfer Line Connecting the Reactor and the Vaporization Chamber	= 100 mm
Length of Transfer Line Connecting the Reactor with the Collection System	= 200 mm
Total Transfer Line Volume	= 2.88 mL
The Temperature Profile in Transfer Lines	= $165^{\circ} - 190^{\circ}C$

4.4   Analysis

Gas chromatography (GC), high performance liquid chromatography (HPLC) and gas chromatography/mass spectroscopy (GC/MS) were the basic analytical methods used in the course of this study, and detailed methods are available (Wastewater Technology Centre, 1983).

4.4.1   Analysis of pure samples

GC is a very sensitive and reliable method to quantify different organic components in a mixture. Chlorophenols give a very good response on an electron capture detector which uses a radioactive isotope of nickel. A Varian 3700 gas chromatograph was employed for the analysis. Very good resolution was obtained under the programmed column conditions given in Table 4.5.

TABLE 4.5   GC OPERATING CONDITIONS FOR CHLOROPHENOL ANALYSIS

Injection Port Temperature:	$300^{\circ}C$
Column:	DB.5 capillary column, 15 m long
Carrier Gas:	Nitrogen
Carrier Gas Flow Rate:	3.6 mL/min
Column Conditions:	$80^{\circ}C$ for 5 minutes
Temperature Ramp:	$4^{\circ}C/min$
Final Temperature:	$250^{\circ}C$
Time at Final Temperature:	0

4.4.2   Analysis of commercial formulations and wood wastes

Commercial formulations and wood wastes contain oil, tin oxide and other minor components. These samples and their TGA washings were analyzed by HPLC because of better resolution and reproducibility as compared to

analysis by GC. The optimum conditions for HPLC analyses conducted are shown in Table 4.6.

TABLE 4.6 HPLC OPERATING CONDITIONS FOR CHLOROPHENOL ANALYSIS

Column:	C_{18} reverse phase
Mobile Phase:	Acetonitrile/water 50:50 with 1% acetic acid
Flow Rate:	1.5 mL/min.
Detector:	High level; UV at 254 μm low level, electrochemical, 1-2V

4.4.3 Analysis of by-products of combustion

Samples were analyzed for dioxins and furans as outlined below. Sample preparation included evaporation to dryness, redissolution in chloroform and extraction with 0.05M trisodium phosphate. The resultant chloroform solution was evaporated to approximately 5 mL and run through gel permeation chromatography to accumulate dioxins and furans. This solution was evaporated to dryness and reconstituted in hexane which was then passed through an alumina column where dioxin and furan fractions were collected. This fraction was evaporated to dryness and redissolved in iso-octane. The solution was then analyzed by GC for dioxins and furans under the operating conditions shown in Table 4.7.

TABLE 4.7   GC OPERATING CONDITIONS FOR DIOXIN AND FURAN ANALYSIS

Column:	Capillary column, DB1, 30 metres
Carrier Gas:	Helium, 1- 1.5 mL/min at 80°C
Injection Port:	$250°C$
Column Temperature:	$80°C$ for 3 min.
Temperature Ramp:	$30°$/min to $220°C$ $4°$/min to $260°C$
Time at Final Temperature:	30 min.
Detector Temperature:	$300°C$

The chromatograms from selected destruction runs were examined for the potential presence of products of incomplete combustion other than dioxins and furans. Positive identification of compounds other than the parent chlorophenol, were made using GC/MS, (Wastewater Technology Centre, 1983). The operating conditions are shown in Table 4.8.

TABLE 4.8   GC/MS OPERATING CONDITIONS

GC CONDITIONS

Injection Temperature:	$300^\circ C$
Initial Temperature:	$35^\circ C$
Final Temperature:	$295^\circ C$
Initial Time:	0 minutes
Ramp Rate:	$4^\circ C/min.$
Final Time:	18 minutes

MS CONDITIONS

Quadruple Mass Spectrometer Using
Electron Impact Ionization

Electron Energy:	70 eV
Scan:	40 - 450 AMU
Scan Time:	1 second
Separator Temperature:	$300^\circ C$

4.5   System Capabilities

The system consisting of components as described in previous sections, was assembled and is shown in Figure 4.5. It was used in this study to evaluate the decomposition behaviour of chlorophenols, commercial wood preserving formulations, contaminated wood chips and sludges. The system capabilities are summarized in Table 4.9.
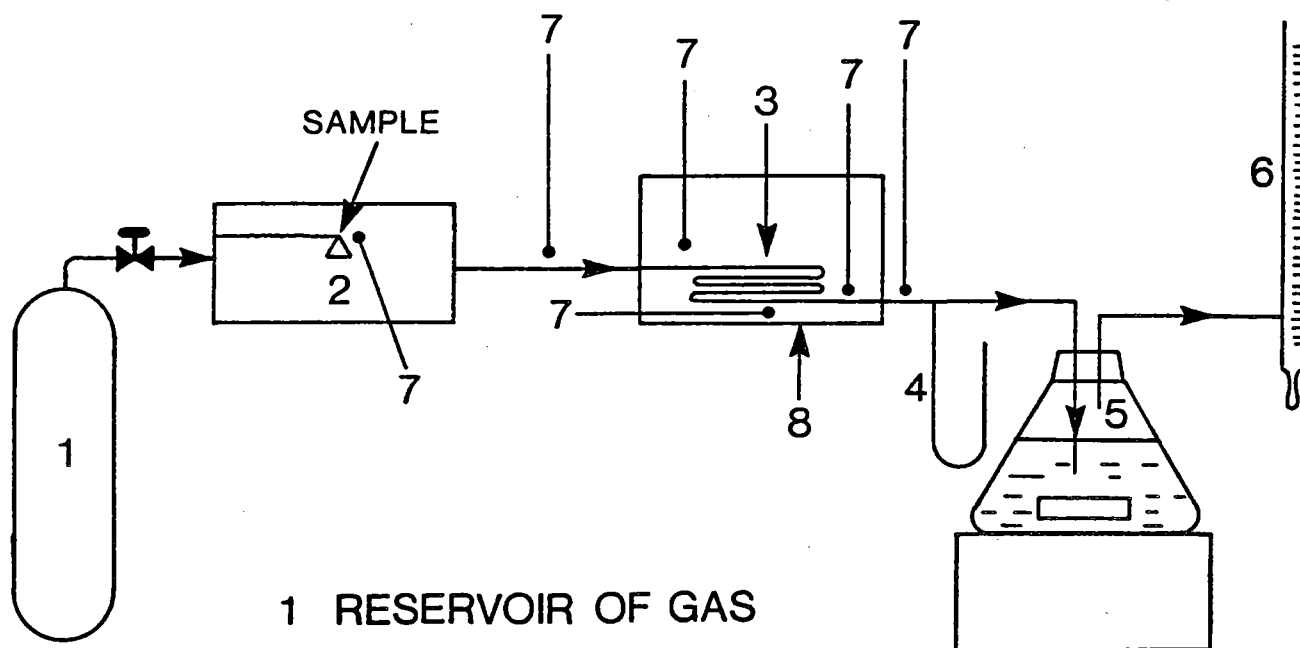
1 RESERVOIR OF GAS
2 TGA ASSEMBLY
3 QUARTZ REACTOR IMMERSED IN
  HIGH TEMPERATURE ZONE
4 MANOMETER
5 ABSORPTION TRAP
6 BUBBLE GAS FLOW METER
7 THERMOCOUPLE
8 FURNACE

FIGURE 4.5   EXPERIMENTAL EQUIPMENT

TABLE 4.9   SYSTEM CAPABILITIES

SAMPLE SPECIFICATION:	• Solid or Liquid
	• Pure Compounds
	• Environmental Samples
	• 100 mg Maximum
VAPORIZATION CHAMBER:	• $1200^{\circ}C$ Maximum
	• Variable Ramping to $50^{\circ}C/min$
	• Temperature Control $\pm 0.2^{\circ}C$
	• Ignition Capability
CARRIER GAS:	• Highly Oxidative (Oxygen)
	• Air
	• Inert (N_2)
	• Reductive (CO)
	• Or any Combination
REACTOR:	• $1200^{\circ}C$ Maximum
	• Temperature Profile $\pm 10\%$
	• 0.1 - 4.0 Second Gas Residence Time
	• Residence Time Distribution $\pm 10\%$

5.   METHODOLOGY

        The thermal data generation system is relatively simple to operate
but a standardized methodology is necessary to ensure reproducibility of
results.

5.1   Determining the Vaporization Rate

        Before any substance can be subjected to a thermal destruction
run, its volatilization rate at different temperatures must be determined.
To obtain this data the sample is vaporized in the thermogravimetric balance
where the sample temperature is varied linearly and the weight of the sample
remaining at any time is measured. The vaporization rate, as a function of
temperature, can be determined from its thermogram as shown in Figure 5.1.

FIGURE 5.1   PCP VAPORIZATION RATE
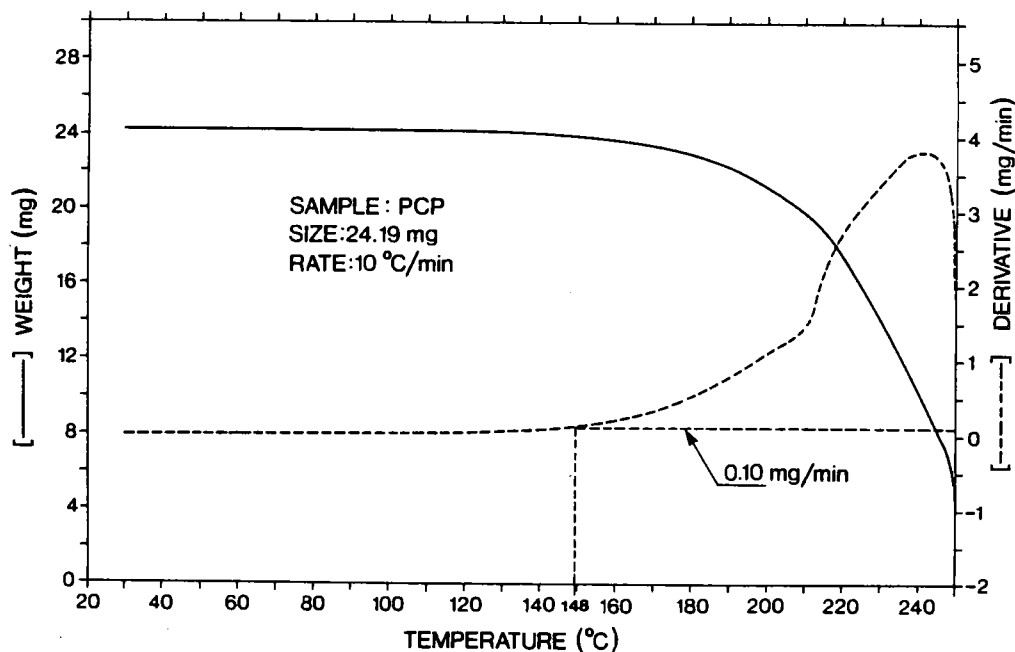
5.2   Sequence of Steps to Conduct a Run

        Equipment is assembled as shown in Figure 4.5 and the following 15
steps are followed to conduct an experiment:

i.   The compound of interest is placed in the TGA boat.

ii.   200 ml of methanol is placed in the absorption trap.

iii.   The system is air pressurized to 15 cm of mercury and any leaks detected in the system are rectified.

iv.   The reactor furnace is heated to the predetermined temperature at which destruction is to be carried out.

v.   The flow rate of the carrier gas is determined using a bubble flow meter. The fine control valve is used to increase or decrease the flow rate to attain the desired residence time of the gas in the reactor.

vi.   All transport lines are heated so that no condensation of the sample occurs during the experiment.

vii.   The stirring mechanism in the absorption trap is activated.

viii. In order to maintain the same reactor residence time as that established in Step 4, it is essential that the volume of the sample entering the reactor is negligible compared to the volume of carrier gas flowing in the system. Therefore the temperature chosen to volatilize the sample from the thermogravimetric balance is such that the volatilization rate does not exceed 1 percent of the carrier gas flow rate. The temperature of the sample is raised to the determined level and held there for the next 60 - 120 minutes.

ix.   To initiate the termination of the run, the heat supply to the sample in the TGA is switched off.

x.   When the temperature of the sample has fallen sufficiently low so

that no measurable volatilization is occurring, the absorption trap is disconnected and the heat supply to the reactor and transfer lines is switched off.

xi. Carrier gas flow is terminated.

xii. The absorption trap assembly is dismantled and washed with methanol and these washings combined with the absorption solution. The total volume is then made up to 250 mL. The solution is stored for analysis.

xiii. The TGA assembly is disconnected and the TGA chamber washed with methanol. The total volume of washings is made up to 100 mL and stored for analysis.

xiv. The thermogram generated during the run is used to establish the total amount of sample vaporized.

xv. The absorption solution and TGA washings are analyzed and different components quantified.

5.3 Calculation of Destruction Efficiency

The complexity of measuring destruction efficiency is affected by the composition and amount of the sample introduced in the system. If the sample is a pure identifiable compound and the amount used is sufficiently small, then the destruction efficiency can be directly determined from the relative height of the peaks on the chromatogram before and after the destruction process. For example, Duvall and Rubey (1976) introduced one microlitre of pure sample solution upstream of the reactor and measured the peak height of the component on a chromatogram of effluent from the reactor. Therefore destruction efficiency, in this case, is the ratio of peak height after destruction to peak height obtained under non-destructive conditions.

In our study, the calculation of destruction efficiency is based on the amounts introduced to the high temperature reactor and detected in the absorption trap. The amount introduced into the reactor is the difference in the total quantity of sample vaporized and the amount retained on the wall of the thermogravimetric chamber. Hence, in our study, destruction efficiency equals:

(amount into high temperature reactor - amount out of high temperature reactor)

(amount into high temperature reactor)

$$\text{Or: Destruction efficiency (\%)} = \frac{(w_1 - w_2 - w_3) - (w_4)}{(w_1 - w_2 - w_3)} \times 100$$

Where:
Amount of sample in boat at start of run $= W_1$ (g)

Amount of sample in boat at the end of run $= W_2$ (g)

Amount of sample in TGA washings $= W_3$ (g)

Amount of sample in absorption solutions $= W_4$ (g)

5.4   Calculations for Residence Time in the Reactor

The nominal gaseous retention time can be determined based on the average gas flow rate through the reactor. The gas law correlates the gaseous flow rate through the reactor at operating temperature and pressure to the gas flow rate at ambient conditions as follows:

$$\frac{V_1 P_1}{T_1} = \frac{V_2 (P_2 + \Delta p)}{T_2}$$

Where: V_1 = volumetric flow rate of carrier gas at ambient
pressure and temperature (mL/s)

V_2 = volumetric flow rate of the carrier gas through the
reactor at reactor pressure and temperature (mL/s)

P_1 = ambient pressure (atm)

P_2 = exit reactor pressure (atm)

Δp = pressure drop in the reactor, calculated from
Hagen Poiseulle's equation (atm)

T_1 = ambient temperature (°K)
T_2 = average reactor temperature (°K)

Residence time is defined as:

$$t = \frac{V_R}{V_2}$$

Where V_R is the volume of reactor, (mL)

6.   RESULTS

Thermal elution of chlorophenols from wood waste was studied using the laboratory thermal data generation system. Destruction behaviour of chlorophenols in their pure form as well as in commercial formulations was determined, and later compared with the destruction pattern of chlorophenols present in wastes and sludges from the wood treatment industry.

6.1   Analytical Considerations

Chlorophenols in methanol were analyzed on a Varian 3700 gas chromatograph using an electron capture detector. The detection limits shown in Table 6.1 are based on the GC operating conditions given in Table 4.5.

TABLE 6.1   GC EQUIPMENT DETECTION LIMITS

COMPOUND	DETECTION LIMIT (ng)
Pentachlorophenol	0.1
2,3,4,5-Tetrachlorophenol	0.003
2,4,6- Trichlorophenol	0.008
2,4,5- Trichlorophenol	0.004

The detectable quantity varies directly with the degree of concentration or dilution. For example, if the concentration of PCP in the absorption solution is 1.0×10^{-5} g/L (or 0.01 ng/μL) the maximum amount that can be injected into the capillary column is one microlitre which provides 0.01 ng in the detector. This amount will not be detected as the machine detection limit exceeds this quantity. As a result, the solution has to be concentrated to increase the PCP concentration above 0.1 ng/μL

$(1.0 \times 10^{-4}$ g/L). On the other hand, if the PCP concentration in the absorption solution is 10 ng/μL (0.01 g/L) one microlitre injected into the column would expose the detector to 10 ng of PCP which would overload its capacity. Consequently, the solution would have to be diluted to be within an acceptable range.

The calibration of the gas chromatograph was checked from time to time and the reproducibility was established using 2,4,5 trichlorophenol. Relative deviation for the analyses of all the chlorophenols was less than 10 percent. This level of reproducibility was considered to be compatible with the precision of the experimental set-up.

6.2   Thermal Elution

Thermal elution of chlorophenol contaminated sawdust was conducted in a similar way to a thermal destruction run with the difference that the carrier gas employed was nitrogen and the reactor was maintained at 300°C. Chlorophenol mass balances could not be established over a thermal elution run. It is probable that many parallel and series reactions take place between the chlorophenol and the constituents evolved from the saw dust. The constraints of the contract did not permit a more in-depth study of thermal elution under a variety of operating conditions. It was concluded that with the existing equipment and methodology, thermal elution was not a viable alternative to the wet chemistry techniques for determination of chlorophenols in wood products.

6.3   Thermal Destruction

6.3.1   Pure compounds

Technical grade samples of pentachlorophenol, 2,3,4,5 tetra-chlorophenol, 2,4,6 trichlorophenol and 2,4,5 trichlorophenol were supplied by Aldrich Chemical Company Inc, Milwaukee, Wisconsin and the destruction behaviour of each compound was studied separately. Figures 6.1 - 6.4 show the thermograms for each compound evaluated. Based on these thermograms, a temperature could be determined for each compound where the vaporization rate would not exceed 1 percent of the carrier gas flow rate.

FIGURE 6.1   PCP THERMOGRAM
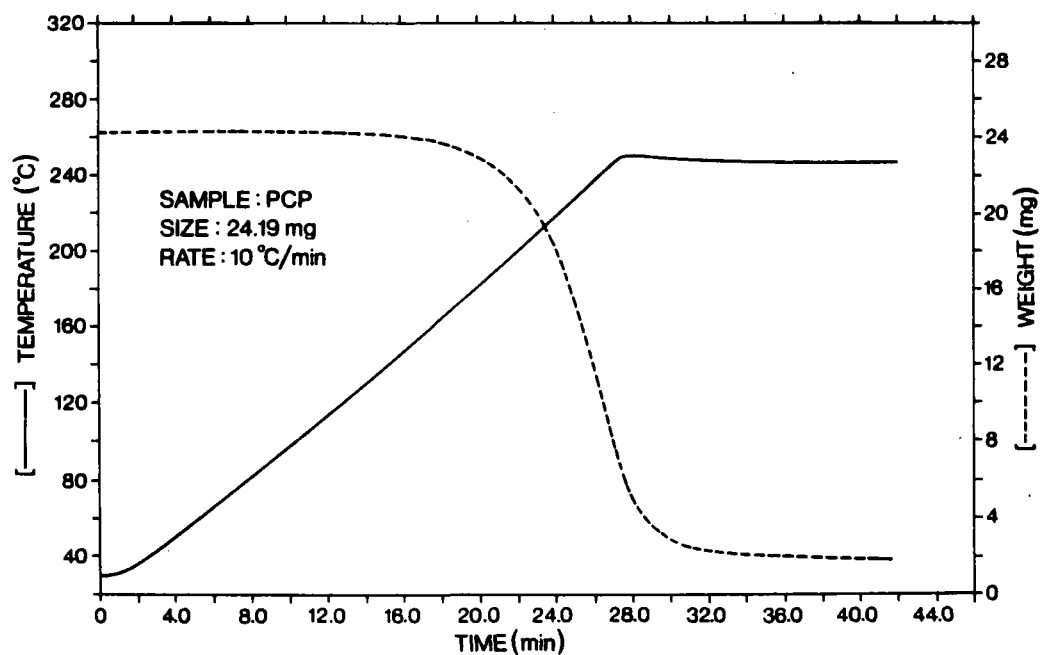
FIGURE 6.2   T$_4$CP THERMOGRAM
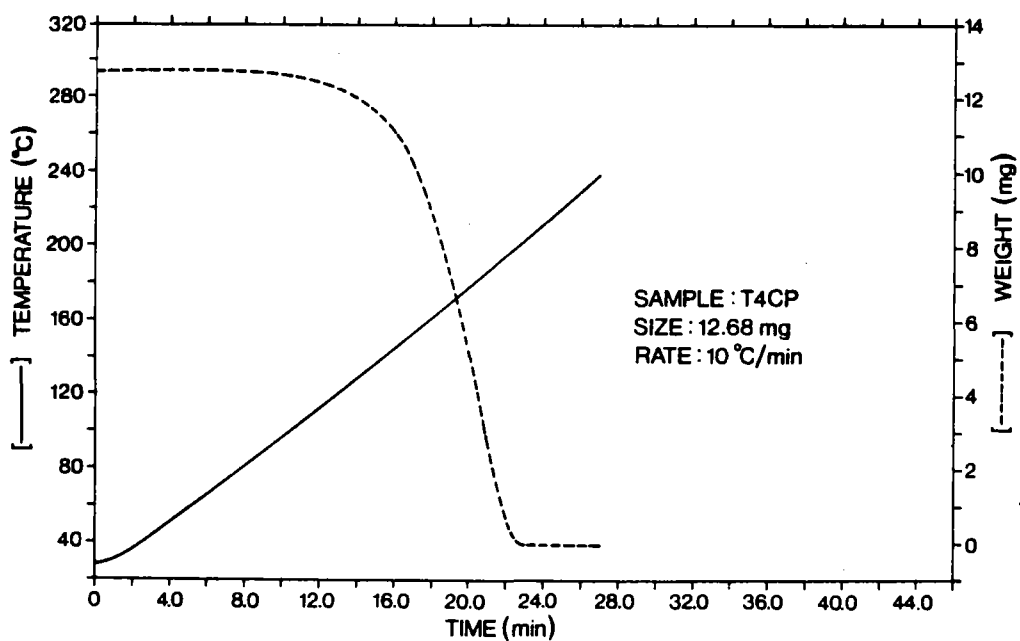
FIGURE 6.3   2,4,6 TCP THERMOGRAM

SAMPLE : 246TCP
SIZE : 22.07 mg
RATE : 10°C/min
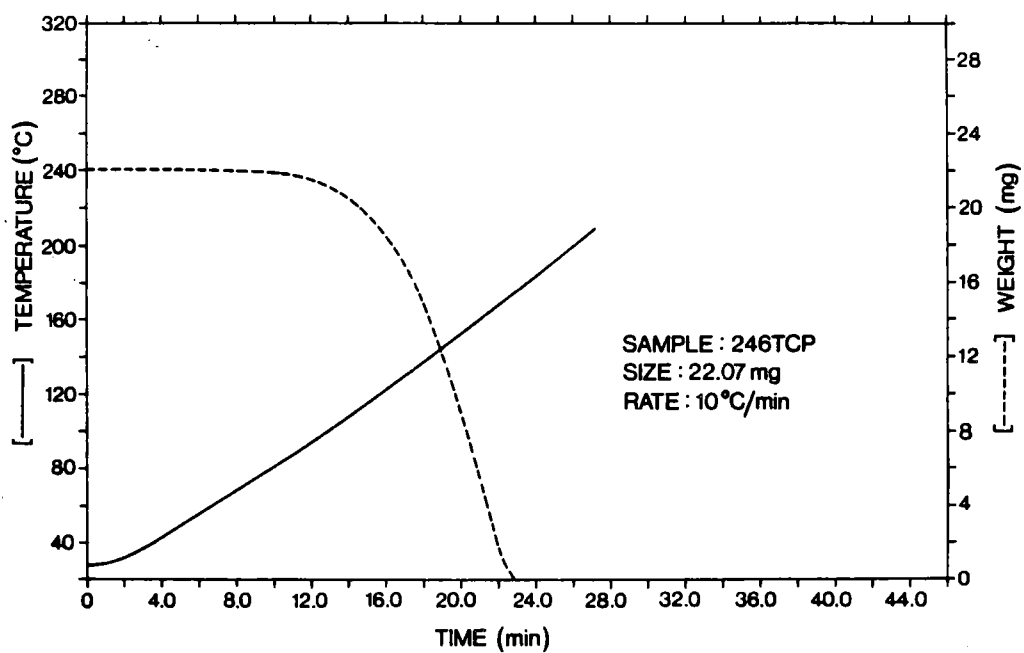
FIGURE 6.4   2,4,5 TCP THERMOGRAM

SAMPLE : 245TCP
SIZE : 17.70 mg
RATE : 10°C/min
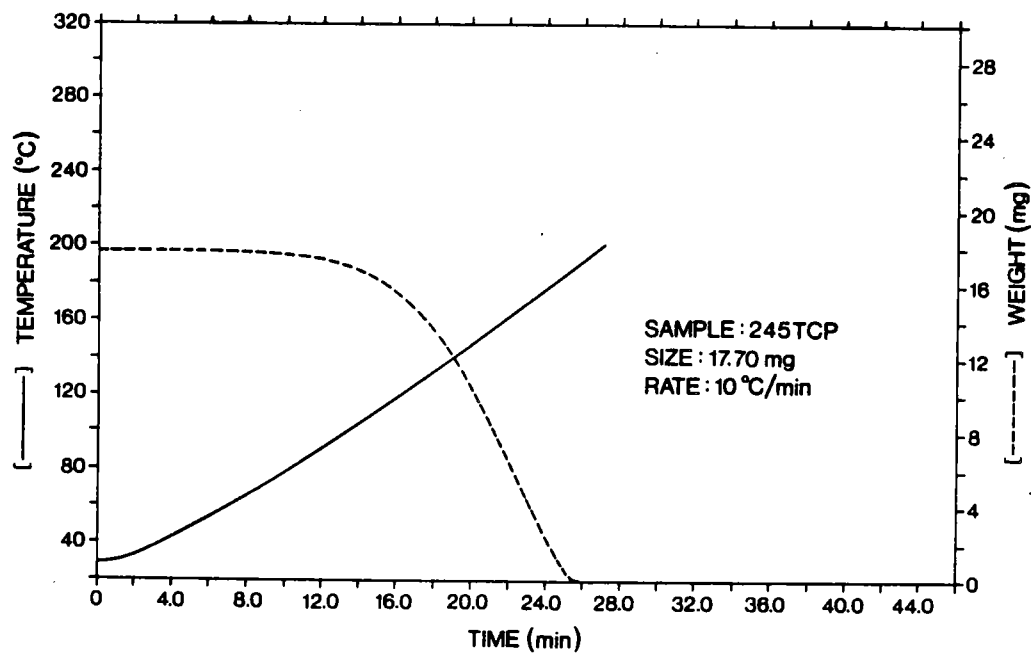
Table 6.2 shows the vaporization temperature, vaporization rate and maximum permissible vaporization rate corresponding to 1 percent of the carrier gas flow rate at 900°C for each compound.

TABLE 6.2   CHLOROPHENOL VAPORIZATION DATA

COMPOUND	PERMISSIBLE CONDITIONS		OPERATING CONDITIONS	
	TEMPERATURE* °C	VAPORIZATION RATE mg/min	TEMPERATURE °C	VAPORIZATION RATE mg/min
PCP	186	0.608	148	0.10
T_4CP	142	0.540	100	0.08
2,4,6 TCP	100	0.460	85	0.15
2,4,5 TCP	104	0.460	85	0.06

* Temperature at which vaporization rate equals 1 percent of carrier gas flow rate. Conditions shown are for worst case at 900°C and 3 sec. residence time.

The output from the TGA during a PCP destruction run is shown in Figure 6.5. It can be seen that during the run the TGA boat was maintained at 148°C and a constant sample vaporization rate was achieved.

FIGURE 6.5 PCP THERMOGRAM DURING DESTRUCTION

SAMPLE: PCP
SIZE: 18.75 mg
RATE: 10 °C/min
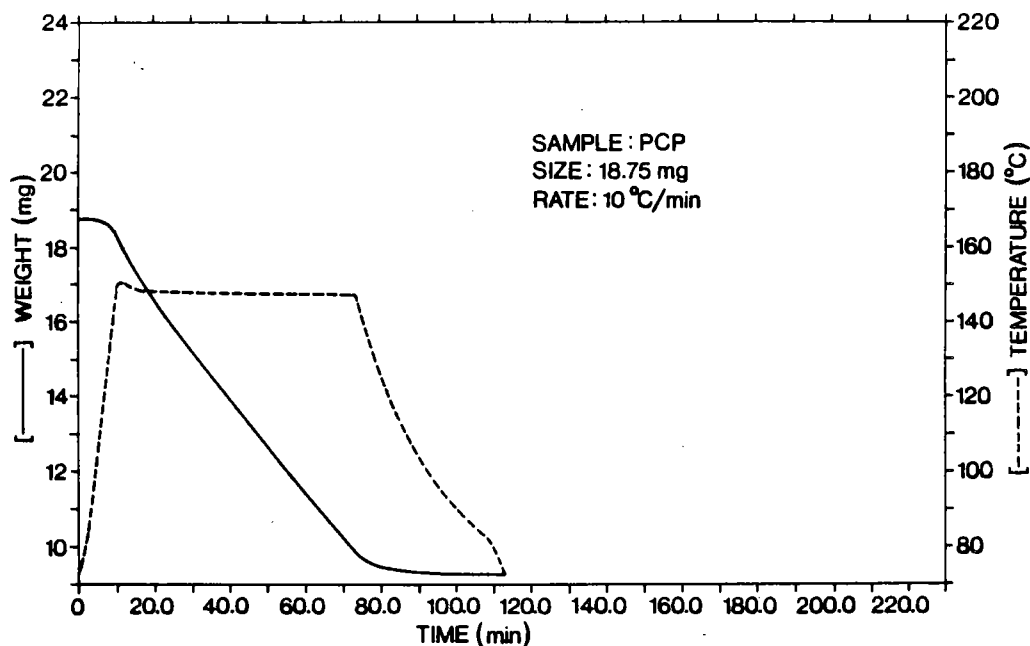
Figures 6.6 and 6.8 - 6.10 show the destruction data points as a function of residence time at different temperatures for each of the compounds tested. The rationale for data analysis and straight lines depicted on these figures is dealt with in the next section. It is quite apparent that destruction efficiency increases with an increase in either temperature or residence time.

FIGURE 6.6   2,4,6 TCP DESTRUCTION DATA
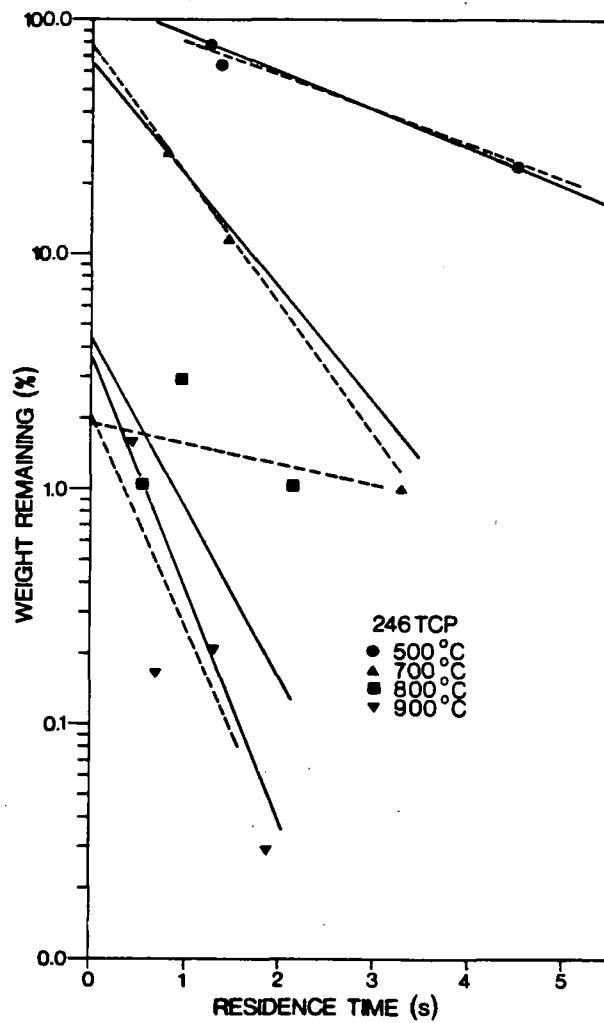
FIGURE 6.7   ARRHENIUS' PLOT OF 2,4,6 TCP
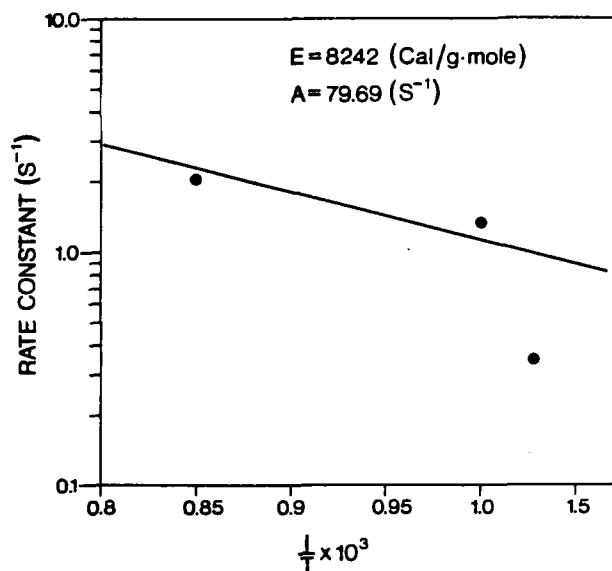
FIGURE 6.8   PCP DESTRUCTION DATA   FIGURE 6.9   T$_4$CP DESTRUCTION DATA
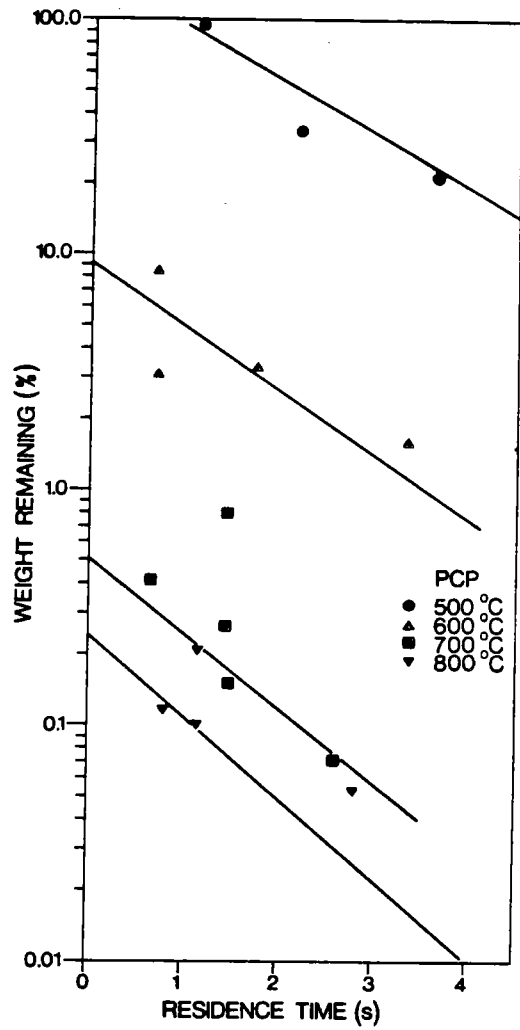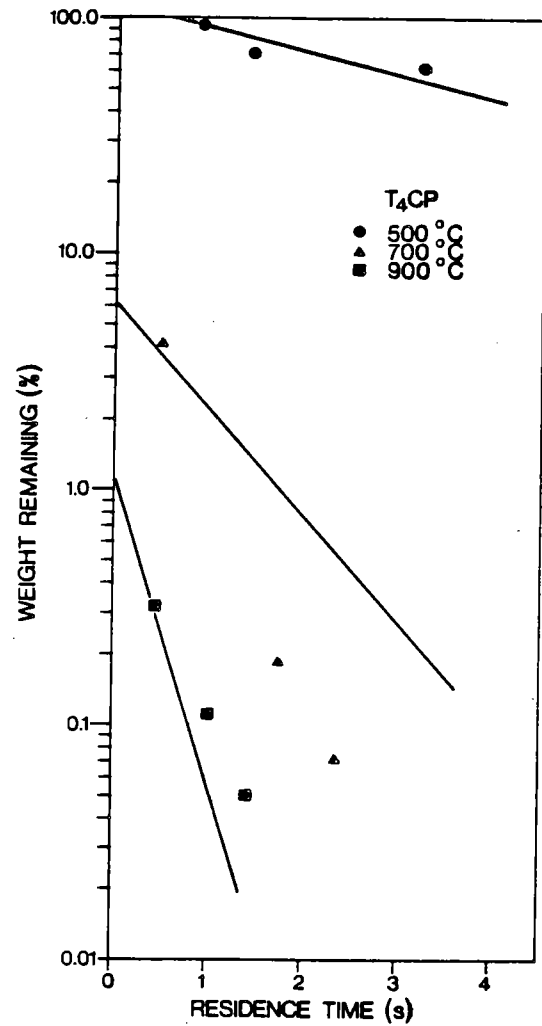
FIGURE 6.10   2,4,5 TCP DESTRUCTION DATA
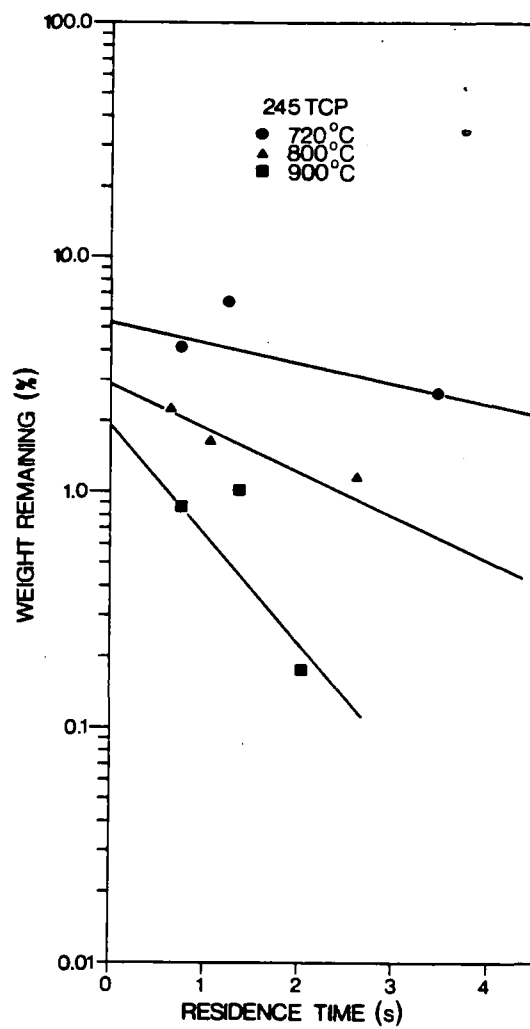
6.3.1.1 **Kinetic analysis** In a bicomponent homogeneous reaction of the type:

A + B ————⟶ Products   (1)
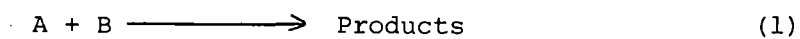
the overall concentration of reacting species at any time is given as:

$$- \frac{dC_A}{dt} = k \cdot C_A^n \cdot C_B^m \qquad (2)$$

where $- \dfrac{dC_A}{dt} =$ change in concentration of A with time $(g.moles.L^{-1}.s^{-1})$

$k =$ overall reaction rate constant $[(g.moles.L^{-1})^{1-m-n}.s^{-1}]$

$C_A =$ the concentration of A $(g.moles.L^{-1})$

$C_B =$ the concentration of B $(g.moles.L^{-1})$

$n =$ reaction order with respect to A

$m =$ reaction order with respect to B

In the present case, A is chlorophenol and B is oxygen. Under the reaction conditions employed, chlorophenols represent less than 1 percent of the mass flow rate, oxygen 23.3 percent and the remainder is inert nitrogen. The total change in oxygen concentration is negligibly small and, assuming that chlorophenol destruction is first order with respect to chlorophenol, equation (2) becomes:

$$- \frac{dC_A}{dt} = k'C_A \qquad (3)$$

where: $\qquad k' = k \times C_B^m \qquad (4)$

The solution of equation (3) with boundary condition,

at $t = o$, $C_A = C_{Ao} \qquad (5)$

is $\quad \dfrac{C_A}{C_{Ao}} = e^{-k't}$ $\qquad\qquad\qquad$ (6)

A plot of ln C_A/C_{Ao} vs. t should yield a straight line with the slope of the line equal to the overall reaction rate constant.

It is postulated that decomposition of chlorophenols proceeds in two stages. In the first stage, chlorophenol forms an intermediate Complex A* and the concentration of A drops from C_{Ao} to C_{Al} almost instantaneously. In the second stage, the intermediate Complex A* as well as remaining A decompose simultaneously as illustrated below:
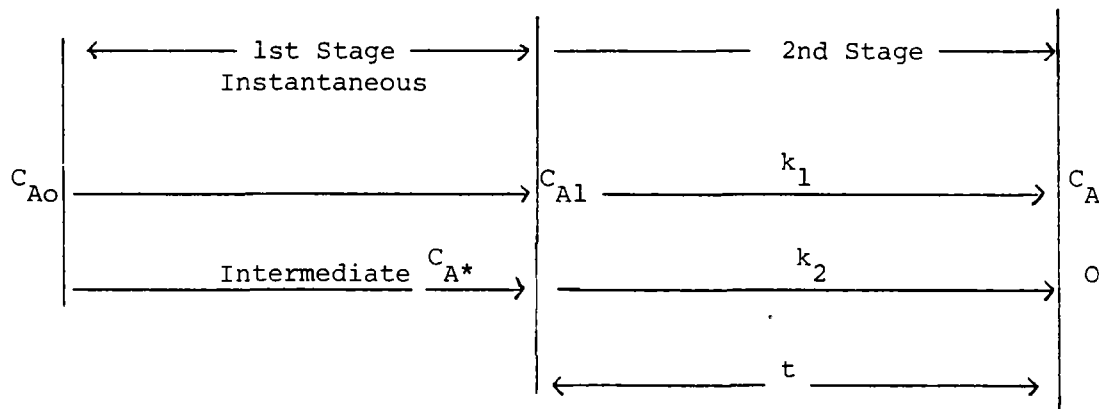
the rate of decomposition can be calculated as:

$-\dfrac{dC_A}{dt} = k_1 C_A$ $\qquad\qquad\qquad$ (7)

$-\dfrac{dC_{A*}}{dt} = k_2 C_{A*}$ $\qquad\qquad\qquad$ (8)

Assuming that $k_2 \gg k_1$, equation (7) is to be solved with boundary condition

$t = o,\ C_A = C_{Al}$ $\qquad\qquad\qquad$ (9)

The solution of (7) is therefore:

$\dfrac{C_A}{C_{Al}} = e^{-k_1 t}$ $\qquad\qquad\qquad$ (10)

Equation (10) is similar to equation (6) and the overall reaction rate constant k_1 follows Arrhenius' law:

$$k_1 = Ae^{-E/RT} \tag{11}$$

where A = Frequency factor (S^{-1})

E = Activation energy (cal/g.mole)

R = Gas Constant (Cal/g.mole/°K)

T = Temperature of reaction (°K)

$$\text{or } \ln k_1 = \ln A - E/RT \tag{12}$$

Therefore, a plot of $\ln k_1$ vs. 1/T should give a straight line with a slope equal to E/R and the intercept equal to A.

The destruction data for each compound at different temperatures was plotted as a function of time. Linear regression was used to obtain the first estimate of the slope of the line which represents the overall reaction rate constant for each temperature. An example of these first estimates are shown as dotted lines in Figure 6.6 for 2,4,6 TCP. An Arrhenius plot of rate constant estimates for 2,4,6 TCP is shown in Figure 6.7. Linear regression was used to determine E and A according to equation (12). Knowing the activation energy and the frequency factor, refined estimates of overall reaction rate constants at different temperatures were calculated. From the refined rate constants, the intercept (C_{A1}) was determined by a constrained least square fit of data points. The best estimate of destruction data, as determined by this procedure, is shown as solid lines in Figures 6.6 and 6.8 to 6.10. Since the plots are on semi-log scale, visual examination of data can be misleading. The lines do satisfy the criteria of minimum residuals under the conditions of constrained slope. Table 6.3 shows kinetic parameters and Table 6.4 shows reaction rate constants for the chlorophenols tested.

TABLE 6.3 CHLOROPHENOL KINETIC PARAMETERS

COMPOUND	E (Cal/g.mole)	A (s^{-1})
Pentachlorophenol	2349	2.38
2,4,6 trichlorophenol	8242	79.69
2,3,4,5 tetrachlorophenol	11872	487.7
2,4,5 trichlorophenol	20519	660.0

TABLE 6.4 CHLOROPHENOL REACTION RATE CONSTANTS

COMPOUND　　TEMPERATURE (°C)	REACTION RATE CONSTANTS (s^{-1})				
	500	600	700	800	900
Pentachlorophenol	0.515	0.614	0.706	0.790	0.860
2,3,4,5 tetra chlorophenol	0.219	0.519	1.035	1.86	2.98
2,4,6 tri chlorophenol	0.372	0.688	1.122	1.669	2.31
2,4,5 tri chlorophenol	0.01	0.048	0.16	0.436	1.02

The time required to achieve a certain level of destruction at any temperature can be calculated using equation 10. Figure 6.11 shows the time required to achieve 99.99 percent destruction and the same information is given in Table 6.5.

FIGURE 6.11   CALCULATED RESIDENCE TIME TO ACHIEVE
99.99 PERCENT DESTRUCTION
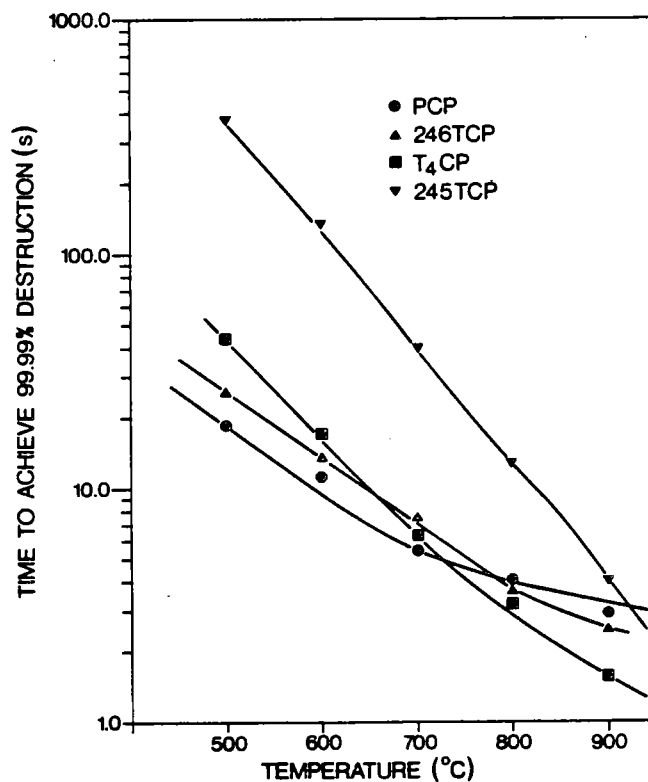
TABLE 6.5   CALCULATED RESIDENCE TIME TO ACHIEVE
99.99 PERCENT DESTRUCTION

Temp °C / Compound	CALCULATED RESIDENCE TIME (s)			
	Pentachlorophenol	2,3,4,5 Tetra-Chlorophenol	2,4,6 Trichlorophenol	2,4,5 Trichlorophenol
500	18.6	44.46	25.5	388.0
600	11.18	17.1	13.38	181.0
700	5.55	6.25	7.64	40.9
800	4.03	3.28	3.66	12.9
900	2.98	1.59	2.56	5.1

The activation energy of a reaction is an indication of the threshold energy to be overcome for the reaction to proceed. Table 6.3 suggests that the time required to achieve 99.99 percent destruction at any temperature should be in the order of:

pentachlorophenol, <2,4,6 trichlorophenol,
<2,3,4,5 tetrachlorophenol, <2,4,5 trichlorophenol

which is true up to 650°C as shown in Figure 6.11. The apparent insensitivity to temperature of pentachlorophenol and 2,4,6 trichlorophenol (i.e. linear relationship tends to tail off after 650°C) is consistent with their low activation energies.

Figure 6.12 shows the percentage of parent compound remaining at 1 second residence time at different temperatures. In most cases, the observed data shows a tailing effect, which is characteristic of first order reactions. However, it was not anticipated that the tailing effect would be observed until a much higher temperature was encountered. It is suggested that this phenomenon is an artifact resulting from the problems of analytical and experimental precision at destruction levels exceeding 99 percent. For practical purposes it is probable that the destruction profile will follow the dotted lines shown in Figure 6.12.

Comparison of results of this study and those of Ahling and Johansson (1977) shows that this study predicts higher retention times are needed for 99.99 percent destruction. The difference may be due to different reactions occurring in different modes of destruction (i.e. the presence of flame).

6.3.2   Wood preserving fluids

Two wood preserving fluids, Alchem 4135 (supplied by Alchem Limited, Burlington, Ontario) and Woodbrite 24 (supplied by Van Waters and Rogers Ltd, Richmond), were investigated. Thermograms for liquid samples are shown in Figures 6.13 and 6.14. Approximately 75 percent of the formulation comprised volatile solvents. The formulations were air dried at room temperature and the solids obtained were analyzed using high performance liquid chromatography. The chlorophenol contents of these air dried samples are shown in Table 6.6.

FIGURE 6.12   CHLOROPHENOL DESTRUCTION PROFILE
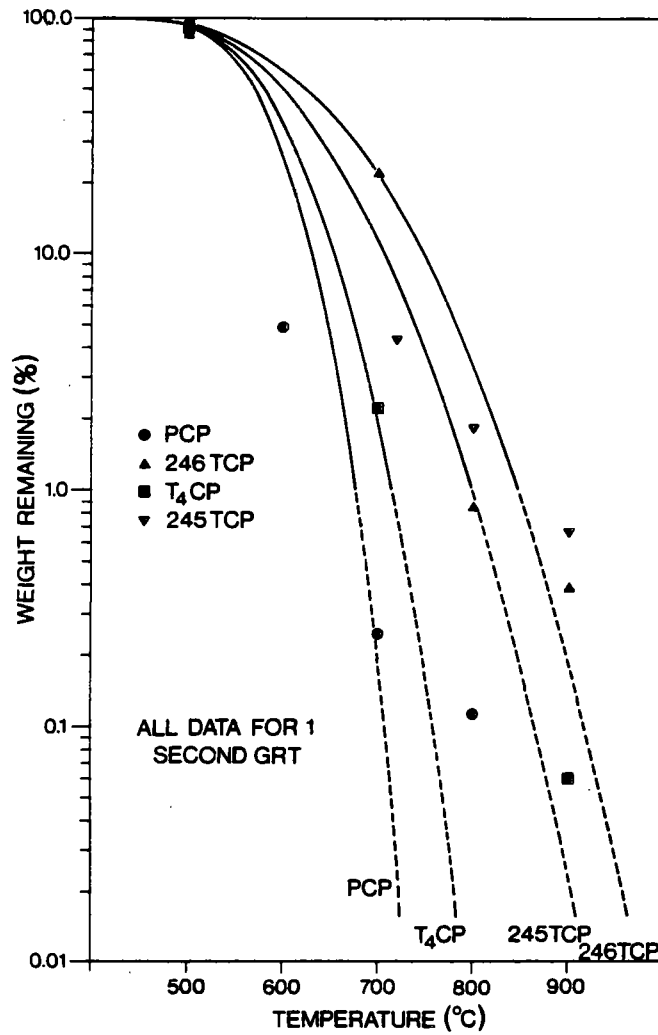
FIGURE 6.13   ALCHEM 4132 THERMOGRAM
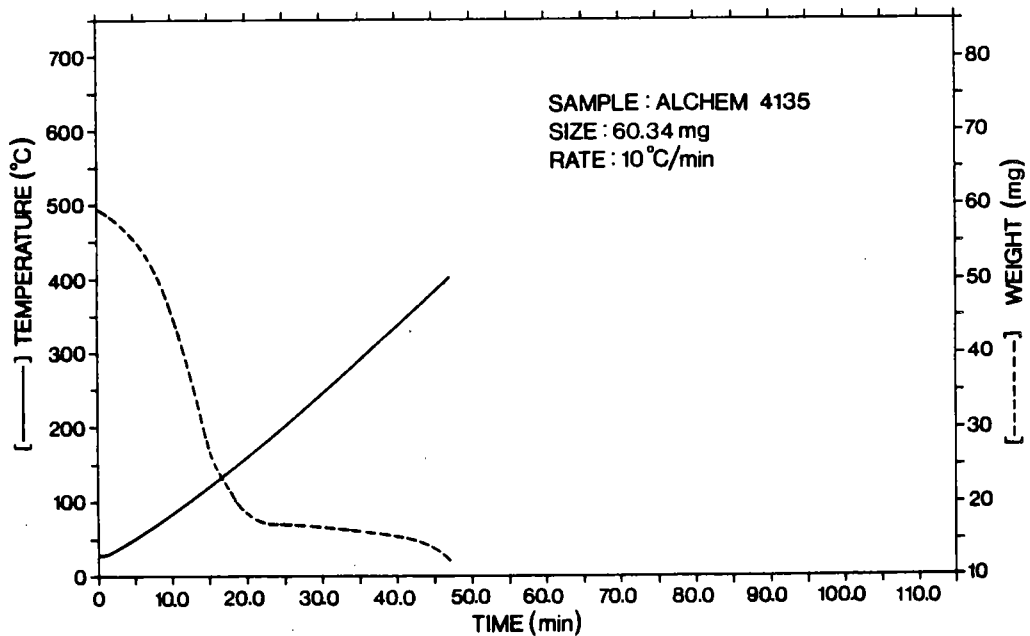
FIGURE 6.14   WOODBRITE 24 THERMOGRAM

SAMPLE: WOODBRITE 24
SIZE: 115.33 mg
RATE: 10 ℃/min
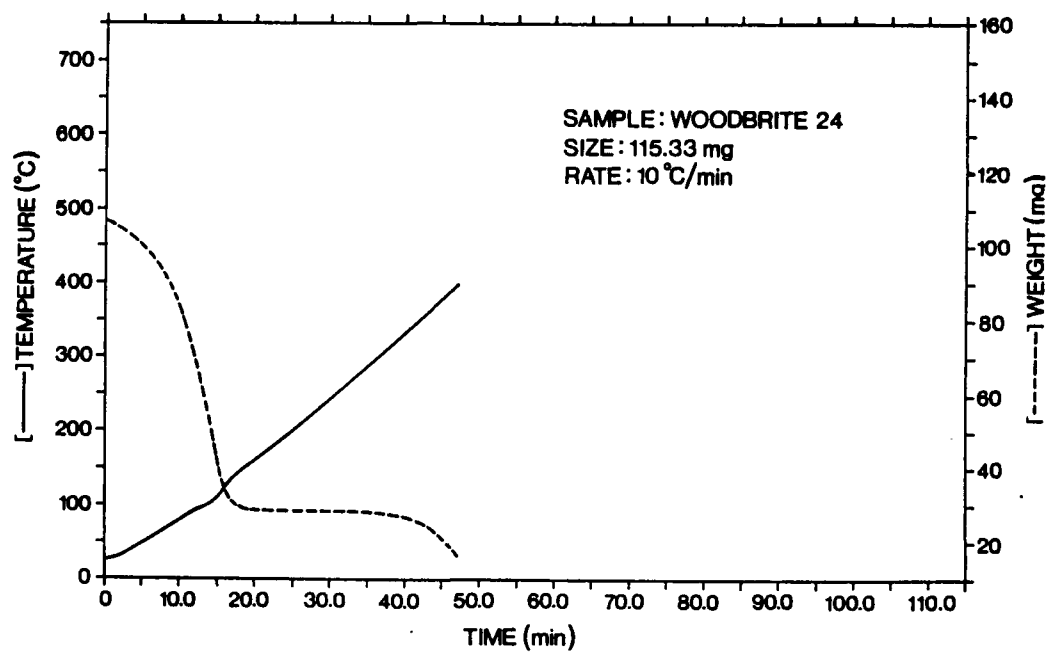
TABLE 6.6   CHLOROPENOL CONTENT OF AIR DRIED
ALCHEM 4135 AND WOODBRITE 24

	ALCHEM 4135	WOOD BRITE 24
Pentachlorophenol (%)	13.4	19.4
Tetrachlorophenol (%)	38	48

Because of the high solvent content, which might lead to partial combustion during vaporization of the sample, it was decided to use the air dried solids for destruction studies. Figures 6.15 and 6.16 show the thermograms for these solids during their respective destruction runs. Initial weight loss up to 120°C was caused by the presence of water in the formulation.

FIGURE 6.15   ALCHEM 4135 THERMOGRAM DURING DESTRUCTION
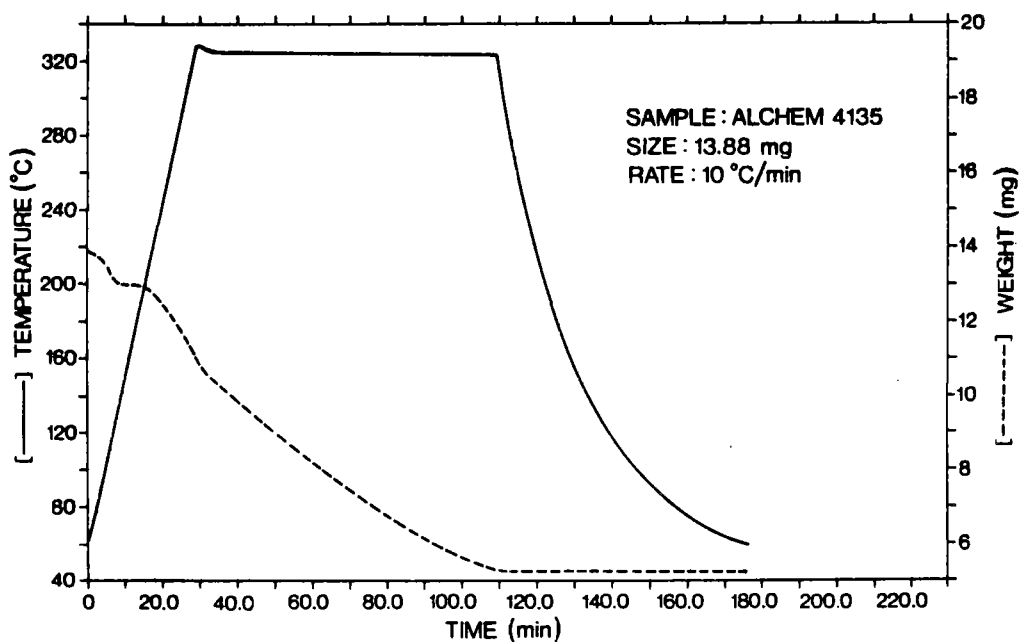
FIGURE 6.16   WOODBRITE 24 THERMOGRAM DURING DESTRUCTION
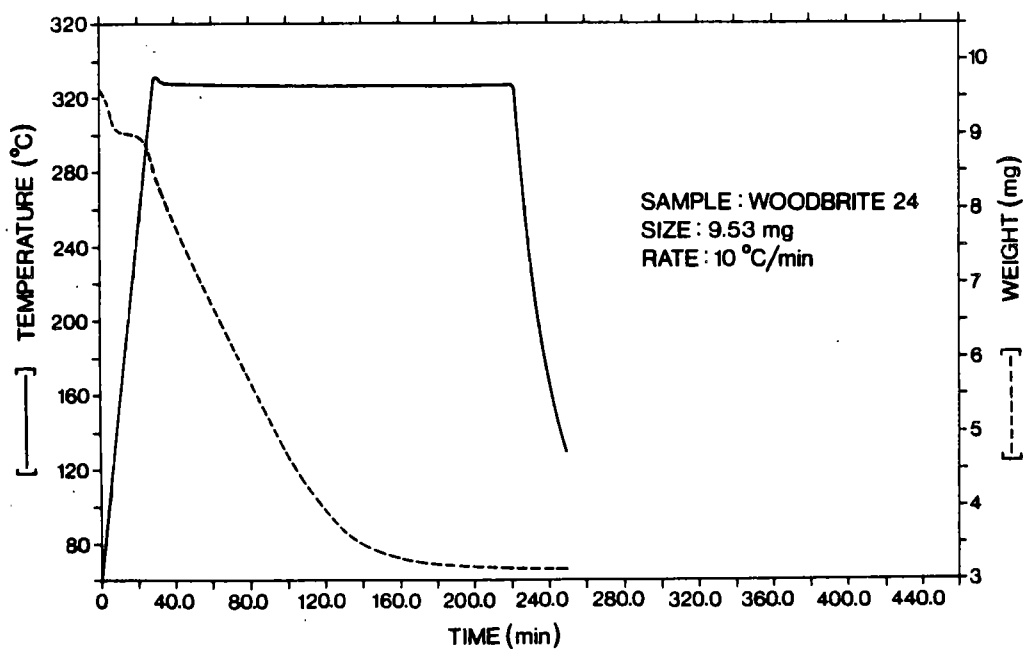
Tables 6.7 and 6.8 show the actual destruction levels achieved as well as the destruction levels predicted from the behaviour of the pure compounds as shown in Figures 6.8 and 6.9. Both Tables 6.7 and 6.8 show that the level of destruction achieved was consistently higher than would be predicted on the basis of thermal destruction studies on pure compounds. The difference may be due to the presence of other components in the formulations which seem to enhance the reaction rate.

TABLE 6.7   ALCHEM 4135 DESTRUCTION DATA

TEMPERATURE (°C)	RESIDENCE TIME (s)	PENTACHLOROPHENOL DESTRUCTION (%)		TETRACHLOROPHENOL DESTRUCTION (%)	
		PREDICTED	MEASURED	PREDICTED	MEASURED
700	0.53	99.60	99.76	96.10	99.05
700	0.95	99.75	99.79	97.70	99.94
700	1.60	99.84	>99.99	98.80	99.22
900	0.82	99.98	>99.99	99.88	99.98
900	1.26	99.99	>99.99	99.97	>99.99
900	1.66	>99.99	>99.99	99.99	>99.99

TABLE 6.8   WOODBRITE 24 DESTRUCTION DATA

TEMPERATURE (°C)	RESIDENCE TIME (s)	PENTACHLOROPHENOL DESTRUCTION (%)		TETRACHLOROPHENOL DESTRUCTION (%)	
		PREDICTED	MEASURED	PREDICTED	MEASURED
700	0.71	99.79	99.84	97.10	98.80
700	1.50	99.83	>99.99	98.70	99.70
700	3.60	99.96	>99.99	99.50	99.90
900	0.54	99.96	>99.99	99.77	99.96
900	1.50	>99.99	>99.99	99.98	>99.99
900	3.40	>99.99	>99.99	>99.99	>99.99

6.3.3   Residues

Wood chips planed from treated lumber and dip tank sludges are two
of the main chlorophenol contaminated residues in the wood treatment indus-
try.   Table 6.9 shows the levels of chlorophenols present in residues from a
typical wood protection plant.   Samples of both the wood chips and sludge
were ignited in the TGA and their products of combustion subjected to
thermal destruction at temperatures of 500, 700 and 900°C.

TABLE 6.9   CHLOROPHENOL CONTENT OF WOOD CHIPS AND DIP TANK SLUDGE

	PENTACHLOROPHENOL mg/kg	TETRACHLOROPHENOL mg/kg
Wood Chips	150	800
Sludge	4090	29000

The carrier gas used for these studies was pure oxygen to minimize
oxygen limiting conditions in the TGA during combustion.   Figures 6.17 and
6.18 are representative of thermograms for wood chips and sludge during a
run.

FIGURE 6.17   WOODCHIP THERMOGRAM DURING DESTRUCTION

SAMPLE : WOODCHIPS
SIZE : 10.69 mg
RATE : 20°C/min, O$_2$
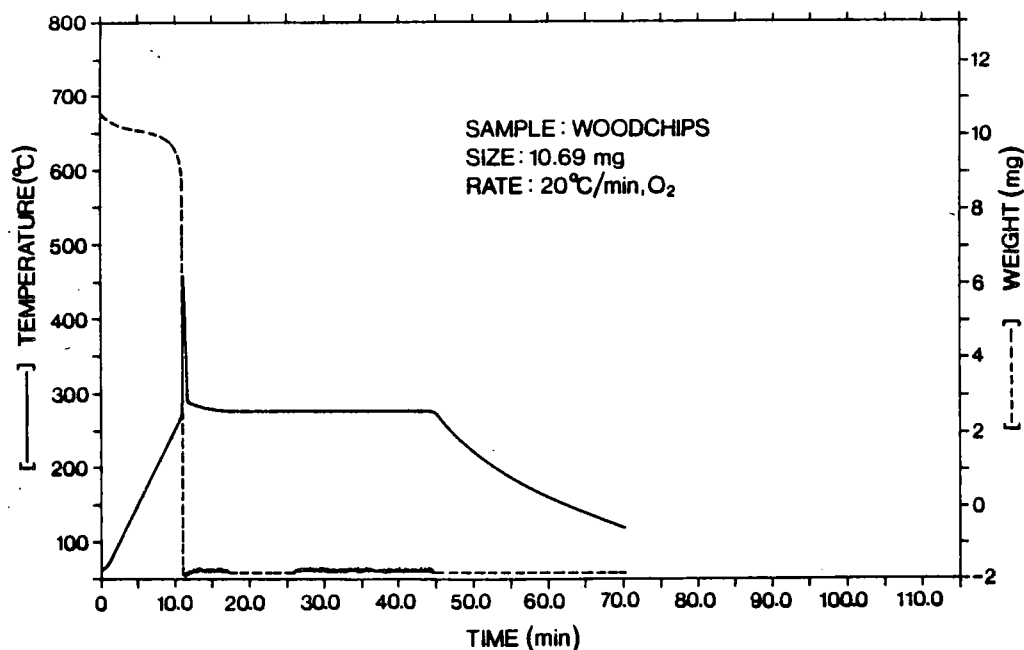
FIGURE 6.18   SLUDGE THERMOGRAM DURING DESTRUCTION
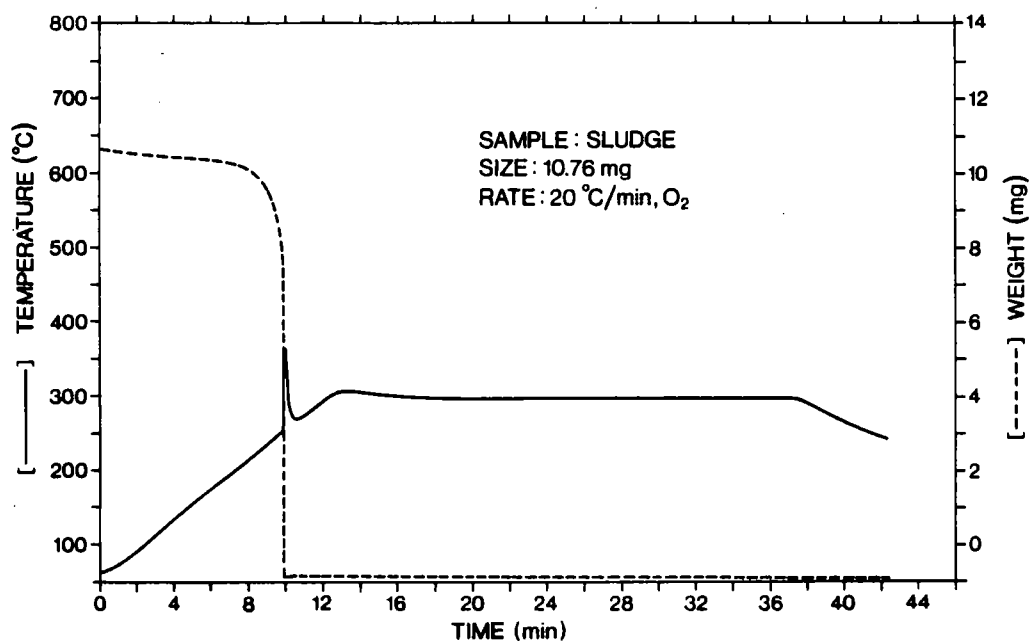
From these figures, it is clear that the wood chips ignite at approximately 275°C and sludge at about 250°C. During the combustion period, chlorophenols are evolved together with products from wood chip and sludge combustion. Subsequently this mixture enters the high temperature reactor. Table 6.10 shows the operating conditions and destruction efficiency of the system.

TABLE 6.10   DESTRUCTION DATA FOR INDUSTRIAL RESIDUES

Average Volatili-zation Rate (mg/min)	Oxygen Data		Calculated Excess Oxygen (%)	Destruction Temperature (°C)	Effective Residence Time In Reactor (s)	Percent Destruction			
	Steady State Supply (moles/min x 10^3)	Theoretical Consumption (moles/min x 10^3)				PCP		T_4CP	
						Measured	Predicted	Measured	Predicted
Sawdust									
15.0	0.94	0.828	13.5	500	0.69	61.24	2.00	69.70	3.00
17.17	0.687	0.680	1.02	700	0.73	96.46	99.70	99.58	97.10
20.66	0.649	0.60	8.16	900	0.69	95.60	99.80	95.71	99.84
Dip tank Sludge									
24.8	0.97	1.0	-3.0	500	0.64	71.82	1.00	63.62	2.00
28.4	0.71	1.1	-35.4	700	0.60	91.85	99.50	96.30	96.60
17.0	0.65	0.68	-4.4	900	0.66	99.14	99.78	99.67	99.82

The sludge data is more consistent than the wood chip data. This is probably due to the fact that the sludge is more likely to be uniformly saturated with chlorophenols. In general, and more particularly for the sludge, destruction data at 700°C or greater are of the same order of magnitude as would be predicted from pure compound data. Interpretation of the destruction data for these environmental samples is further compounded by factors such as:

- difficulty in analyzing the waste material;
- the potential of oxygen limitations due to sample ignition;
- effect of combustion (i.e. ignition) products in the subsequent high temperature reactor.

The availability of oxygen will affect the degree of destruction even when the oxygen supply exceeds the theoretical demand. This phenomenon is more pronounced as the reaction temperature increases. It is theorised that the chlorophenol destruction may be hindered by the presence of a high concentration of carbon dioxide and water which results from the combustion of the sample's organic base. A detailed calculation of oxygen consumption and related effective residence times is given in Appendix 2.

6.4   By-Products of Chlorophenol Combustion

If incineration of chlorophenols proceeded to completion, the products of combustion would be carbon dioxide, water and chlorine (or HCl). In reality, products of incomplete combustion are formed. These include lower chlorinated chlorophenols, and more importantly, dioxins and furans. Identification of dioxins and furans as products of incomplete combustion is complicated by the fact that most commercial grade chlorophenols and wood preserving fluids contain dioxins and furans as impurities in the basic formulations. Johanson (1973) and Plimmer (1973) indicate that commercial grade PCP contains between 9 and 3000 mg dioxins/furans per kg PCP.

During this study samples of PCP, 2,4,5 TCP, Alchem 4135, Woodbrite 24 and diptank sludge were analyzed for dioxins and furans and the data is shown in Table 6.11.

TABLE 6.11   <u>DIOXIN AND FURAN CONTENT OF CHLOROPHENOLS AND CHLOROPHENOL CONTAINING MATERIALS (mg/kg)</u>

HOMOLOGUE	PCP Isomers	PCP Conc'n	245 TCP Isomers	245 TCP Conc'n	ALCHEM 4135 (Dry) Isomers	ALCHEM 4135 (Dry) Conc'n	WOODBRITE 24 (Dry) Isomers	WOODBRITE 24 (Dry) Conc'n	DIPTANK SLUDGE Isomers	DIPTANK SLUDGE Conc'n
$T_4CDD + T_4CDF$	4	58			6*	26	7*	16	5	6.8
PCDD + PCDP	3	110	1	0.045	5	75	6*	69	5*	13.4
$H_6CDD + H_6CDP$	5*	370			7*	39	7*	35	4	11.8
$H_7CDD + H_7CDP$	5*	10,850	2*	0.095	6*	75	7*	52	3*	16.4
OCDD + OCDP	2	1,950			1*	77	1*	14	2*	22.0
TOTAL	19	13,338	3	0.130	25	292	28	186	19	70.4

* 2,3,7,8 positions substituted

Note that all dioxin/furan concentrations are reported as mg per kg of dry initial sample. Commercial PCP had the highest dioxin and furan content (with 19 isomers detected at a total concentration of 13,338 mg/kg). This is about four times higher than that reported in the literature. By contrast, chemically pure 2,4,5 TCP contained only 3 isomers, at a total concentration of 0.13 mg/kg. The Alchem and Woodbrite formulations, which comprise a mixture of T_4CP and PCP (50 -60% on dry weight basis) contain considerably lower total concentrations, however, the number of isomers detected is high. Diptank sludge (which was generated from Woodbrite 24 preservation) contains 2.9 percent T_4CP and 0.4 percent PCP. Comparison of the (dioxin + furan) to chlorophenol ratios for Woodbrite 24 (0.276 mg/g) and Diptank sludge (2.13 mg/g) shows an approximately 8 fold increase (based on the Woodbrite 24 dioxin/furan content, one would predict a diptank sludge concentration of only about 10 mg/kg, rather than the measured 70.4 mg/kg). This indicates preferential adsorption of dioxins and furans, which from their physical/chemical properties, is to be expected.

     Selected effluents from the thermal elution and destruction runs of 2,4,5 TCP, Woodbrite, Alchem and diptank sludge were also analyzed for dioxins and furans. This data is presented in Table 6.12 to 6.15. Two effluents generated during 2,4,5 TCP thermal destruction runs were analyzed for dioxins and furans and the data is shown in Table 6.12.

TABLE 6.12   DIOXIN AND FURAN PRODUCTION DURING 2,4,5 TCP DESTRUCTION (mg/kg)

HOMOLOGUE	Starting Material		700°C, 1 s		900°C, 3 s	
	Isomers	Conc'n	Isomers	Conc'n	Isomers	Conc'n
$T_4CDD + T_4CDF$			6*	95		
PCDD + PCDF	1	0.045	5*	108	4*	65
$H_6CDD + H_6CDF$			4	146	3	153
$H_7CDD + H_7CDF$	2*	0.095	1*	52	1*	74
OCDD + OCDF			1	14	1	27
TOTAL	3	0.140	17	415	9	319

*2,3,7,8 positions substituted

TABLE 6.13   DIOXIN AND FURAN PRODUCTION DURING ALCHEM 4135 DESTRUCTION (mg/kg)

HOMOLOGUE	Starting Material		Elution at 325°C		700°C at 0.5 s		900°C at 1.6 s	
	Isomers	Conc'n	Isomers	Conc'n	Isomers	Conc'n	Isomers	Conc'n
$T_4CDD + T_4CDF$	6*	26	8*	60	7*	4	2	0.6
PCDD + PCDF	5	75	4*	400	4*	20	6*	3.5
$H_6CDD + H_6CDF$	7*	39	4*	2500	4*	100	3*	40
$H_7CDD + H_7CDF$	6	75	4*	1500	2*	105	2*	75
OCDD + OCDF	1*	77	1*	250	1*	20	1*	15
TOTAL	25	292	21	4710	18	249	14	134.1

* 2,3,7,8 positions substituted

TABLE 6.14   DIOXIN AND FURAN PRODUCTION DURING WOODBRITE 24 DESTRUCTION (mg/kg)

HOMOLOGUE	Starting Material		Elution at 325°C		700°C at 0.7 s		900°C at 3.4 s	
	Isomers	Conc'n	Isomers	Conc'n	Isomers	Conc'n	Isomers	Conc'n
$T_4CDD + T_4CDF$	7*	16	7*	60	7*	39	3	2
PCDD + PCDF	6*	69	8*	650	5*	47	5*	2
$H_6CDD + H_6CDF$	7*	35	4*	3300	4*	450	3*	150
$H_7CDD + H_7CDF$	7*	52	2*	3400	2*	200	2*	130
OCDD + OCDF	1*	14	1*	60	1*	35	1*	25
TOTAL	29	186	22	7470	19	771	14	309

*2,3,7,8 positions substituted

TABLE 6.15   DIOXIN AND FURAN PRODUCTION DURING DIPTANK SLUDGE DESTRUCTION (mg/kg)

HOMOLOGUE	Starting Material		Ignition at 250°C		at 900°C, 0.66 s	
	Isomers	Conc'n	Isomers	Conc'n	Isomers	Conc'n
$T_4CDD + T_4CDF$	5	6.8	4	50	6*	1.4
PCDD + PCDF	5*	13.4	5	85	5*	3.9
$H_6CDD + H_6CDF$	4	11.8	3*	220	3*	20.0
$H_7CDD + H_7CDF$	3*	16.4	2*	230	2*	15.0
OCDD + OCDF	2*	22.0	1*	45	1*	2.1
TOTAL	19	70.4	16	630	17	47.4

*2,3,7,8 positions substituted

It can be seen that exposure to 700°C for 1 second results in the production of significant amounts of dioxins/furans. The 17 isomers identified, accounted for a total concentration of 415 mg/kg. This compares favourably with Rappe's data shown in Table 3.4, which indicates a total dioxin production of 2115 mg/kg at a temperature of approximately 350°C. On exposure to 900°C for 3 seconds the total dioxins/furans in the effluent were decreased to 319 mg/kg, with T_4CDD's and T_4CDF's not being evident. While Rappe indicates that T_4CDD's are the prime product of 2,4,5 TCP burning, this data indicates that upon exposure to high temperature, a series of complex reactions result in both the destruction and production of a wide variety of dioxins and furans.

The data generated from the thermal elution (at 325°C) of Alchem 4135 and Woodbrite 24, together with high temperature destruction runs, is shown in Table 6.13 and 6.14. Both sets of data indicate significant formation of penta, hexa and hepta isomers at 325°C. Exposure to thermal regimes of 700°C to 900°C reduced the levels of all isomers. However, even at 900°C significant quantities of all homologues were still present.

Data generated from the ignition (at 250°C) of diptank sludge and thermal destruction at 900°C and 0.66 second GRT are shown in Table 6.15. Ignition at 250°C resulted in a significant increase of all homologues, once again increases in penta, hexa and hepta isomers being the most pronounced. As with the wood preserving formulations, significant concentrations of all homologues were still evident after exposure to a temperature of 900°C, although the GRT of 0.66 s for diptank sludge was significantly lower than 3.4 s for formulations.

This destruction data is supported by that reported by Bumb et al. (1980) who concluded that at below 800°C destruction of T_4CDD is incomplete. The US EPA have also monitored high temperature incineration of Agent Orange and reported a 99.9 percent destruction of T_4CDD at an average temperature of 1273°C (EPA Report 600/2-7-086, April 1978).

In conclusion, these studies have indicated that significant production of dioxins and furans will occur from the burning of chlorophenol contaminated residues and that thermal regimes in excess of 900°C and 3 seconds will be required to achieve acceptable levels of control. This emphasises the dilemma with respect to incineration for control of toxic organics. While a regime of 900°C at 3 seconds GRT will provide excellent chlorophenol destruction, this data indicates that a more serious problem (i.e., dioxin production) may not have been adequately controlled.

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APPENDIX 1

MANUFACTURE, PROPERTIES, TOXICITY, FATE AND TRANSPORT

OF CHLOROPHENOLS AND THEIR POLLUTION CONTROL OPTIONS

1.   Manufacture and Properties of Chlorophenols

Chlorophenols are a family of 19 compounds, all consisting of a benzene ring, a hydroxyl group and from one to five chlorine atoms. Approximately 3.4 million kilograms of chlorophenol are used in Canada annually and it is estimated that 95 percent of the total can be attributed to the wood treatment industry. (Jones, 1981).

In excess of 2 million kilograms of chlorophenols are manufactured in Canada (Table A1.1) and a fluctuating amount is imported as shown in Table A1.2. As of June 1983, chlorophenols are no longer being produced in Canada.

1.1 Chlorophenol manufacture

Chlorophenols are manufactured either by hydrolysis of chlorobenzenes or chlorination of phenol. Chlorination of benzene gives hexachlorobenzene and, upon hydrolysis, pentachlorophenol is obtained. In the alternative process, chlorination of phenol gives a mixture of chlorophenols depending on the degree of chlorination and operating conditions such as temperature of reaction, presence of catalyst, etc.

In general, the products obtained by hydrolysis contain higher levels of impurities than chlorophenols manufactured by chlorination of phenol.

1.1.1   Manufacture of trichlorophenol   2,4,5-trichlorophenol is manufactured by hydrolysis of 1,2,4,5-tetrachlorobenzene. Hydrolysis is carried out by sodium hydroxide. Subsequent neutralization with a mineral acid forms the product. High temperature and highly alkaline conditions used in this process generally favour the production of 2,3,7,8-tetrachlorodibenzo-p-dioxin.

2,4,6-trichlorophenol is manufactured by catalytic chlorination of phenol.

TABLE A1.1   CANADIAN CHLOROPHENOL PRODUCTION

(Jones 1981)

Producer and Location	Products	-	Plant Capacity$(kg \times 10^3)$
	2,4 DCP	$2,3,4,6T_4CP$	PCP
Uniroyal Chemical Division of Uniroyal Limited, Clover Bar, Alberta	xx	450	1800

Note: 2,4 DCP = 2,4-dichlorophenol

$2,3,4,6\ T_4CP$ = 2,3,4,6-tetrachlorophenol

PCP = pentachlorophenol

xx = Plant capacity not available

TABLE A1.2   IMPORTS OF PENTACHLOROPHENOL INTO CANADA

(Jones 1981)

Country	1976 $kg \times 10^3$	1977 $kg \times 10^3$	1978 $kg \times 10^3$	1979 $kg \times 10^3$
Unidentified	188	-	77	77
West Germany	-	66	-	-
United States	370	310	468	548

1.1.2   <u>Manufacture of tetrachlorophenol</u>   Chlorination of phenol using potassium tellurate (K_2TeO_3) as a catalyst produces tetrachlorinated phenols exclusively. Isomers of tetrachlorophenol have been separated by gradient elution with ion exchange resins. The mixture is adsorbed on to Dowex 2-X-8 resin which is washed with sodium acetate, acetic acid and methanol, (Freiter, 1979).

1.1.3   <u>Manufacture of pentachlorophenol</u>   Pentachlorophenol is manufactured by chlorination of phenol at 100 - 180°C using a catalyst. The catalysts used are aluminum chloride, ferric chloride, activated carbon, quinoline or tellurium salts.

  The chlorination is carried out at a temperature between 65 - 130°C. After three to four atoms of chlorine have been substituted onto phenol, the temperature in the reactor is increased approximately 10°C above the melting point of the chlorinated mixture. Reaction time is 5 - 15 hours and catalyst concentration is critical. The hydrochloric acid gas is separated from the unrefined chlorophenol mixture which is formed by the reaction. Crude pentachlorophenol is purified by distillation under reduced pressure in the presence of amine or alkanolamine, (Watson, 1974).

  The alternative manufacturing method utilizes hydrolysis of hexachlorobenzene. This method favours the formation of dioxins. The levels of dioxins found in pentachlorophenol, manufactured by this method, are in the range of 9 - 27 mg/kg for hexachlorobenzo-p-dioxin, 90 - 135 mg/kg for heptachlorodibenzo-p-dioxin and 572 - 2510 mg/kg for octachlorodibenzo-p-dioxin (Johnson, 1973). However, 2,3,7,8 tetrachlorodibenzo-p-dioxin has not been found in pentachlorophenol. (Plimmer, 1973).

1.2   <u>Manufacture of commercial mixtures</u>

  Two types of commercial mixtures are used in Canada. A solution of sodium pentachlorophenate in water is usually utilized for wood protection while an oil based formulation of chlorophenol is used in wood preservation processes.

  Generally, the commercial mixtures are manufactured by blending the active ingredients with either water or oil. Pentachlorophenol is the

most common active agent, occasionally supplemented by the presence of tri or tetra chlorophenols. The composition of some typical wood protection formulations is shown in Table A1.3. Chlorophenol products used by the wood industry normally contain 100 - 200 ppm heptachlorodibenzo-p-dioxin and 1000 - 2500 ppm octachlorodibenzo-p-dioxin. (Woolson, 1972, Plimmer, 1973).

1.2.1   Properties of chlorophenols

The chemical formulae and relevant physical properties of the individual isomers are shown in Table A1.4. The chemical structure of the chlorophenols evaluated in this study are shown in Table A1.5. The positions of chlorine atoms with respect to the hydroxyl group and to each other provide 3 monochlorophenols, 6 dichlorophenols, 6 trichlorophenols, 3 tetrachlorophenols and 1 pentachlorophenol.

The physical and chemical properties of chlorophenols are described in the literature, (Doedens, 1977). For the purposes of this study, the most important characteristic of chlorophenols is the increase in their environmental stability and toxicity with increasing numbers of chlorine atoms in their molecule. Both stability and toxicity of chlorophenols will be addressed in specific sections later in the report.

1.2.2   Chlorophenols in the Environment

The presence of chlorophenol in the Canadian environment has been extensively documented in the literature, (Jones, 1981). Chlorophenol concentrations in the environment vary significantly. Levels of penta-chlorophenol found in the Great Lakes and in two eastern rivers near wood treatment operations, are given in Table A1.6. A typical range of chlorophenol concentration in the industrial effluents, surface waters and aquatic sediments in British Columbia is shown in Table A1.7.

As the majority of chlorophenols are used for wood treatment, it is reasonable to expect that most of the chlorophenols in the environment are connected to this use. Some evidence of this connection is documented in the literature (Tables A1.6 and A1.7).

TABLE A1.3   COMPOSITION OF INDUSTRIAL WOOD PROTECTION FORMULATIONS

FORMULATION	MANUFACTURERS' DATA* (%)	RESULTS OF ANALYSES (%)
Alchem 4135		
Sodium tetrachlorophenate	24	14.4
Sodium pentachlorophenate	-	5.6
Tributyl tin oxide	1.3	-
Woodbrite 24		
Sodium tetrachlorophenate	16.32	13.8
Sodium pentachlorophenate	7.68	5.6
Diatox		
Sodium tetrachlorophenate	19.4	-
Others	4.8	-
Wood Sheath Cherry Brown		
Sodium tetrachlorophenate	5.1	-
Others	1.5	-
Tetra Concentrate		
Sodium tetrachlorophenate	17.26	-
Others	4.67	

*   As per product label

TABLE A1.4   PHYSICAL PROPERTIES OF CHLOROPHENOLS

(Jones 1981)

COMPOUND	FORMULA	MELTING POINT	BOILING POINT
2 CP	C_6H_5ClO	9	174.9
3 CP	C_6H_5ClO	33	214
4 CP	C_6H_5ClO	43.2 - 43.7	219.8
2,3 DCP	$C_6H_4CL_2O$	57 - 59	206
2,4 DCP	$C_6H_4Cl_2O$	45	210
2,5 DCP	$C_6H_4Cl_2O$	59	211
2,6 DCP	$C_6H_4Cl_2O$	68	219
3,4 DCP	$C_6H_4Cl_2O$	68	253
3,5 DCP	$C_6H_4Cl_2O$	68 - 69	233
2,3,4 TCP	$C_6H_3Cl_3O$	83.5	Sublimes
2,3,5 TCP	$C_6H_3Cl_3O$	62	248.5
2,3,6 TCP	$C_6H_3Cl_3O$	58	272
2,4,5 TCP	$C_6H_3Cl_3O$	68 - 70.5	Sublimes
2,4,6 TCP	$C_6H_3Cl_3O$	69.5	246
3,4,5 TCP	$C_6H_3Cl_3O$	101	271
2,3,4,5 T_4CP	$C_6H_2Cl_4O$	116 - 117	Sublimes
2,3,4,6 T_4CP	$C_6H_2Cl_4O$	70	150
2,3,5,6 T_4CP	$C_6H_2Cl_4O$	145	-
PCP	C_6HCl_5O	191	309

TABLE A1.5   CHEMICAL STRUCTURE OF
CHLOROPHENOLS EVALUATED
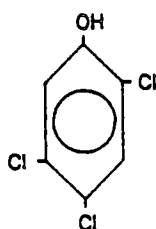
2,4,5 TRICHLOROPHENOL
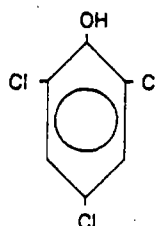
2,4,6 TRICHLOROPHENOL
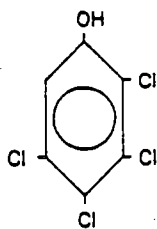
2,3,4,5 TETRACHLOROPHENOL
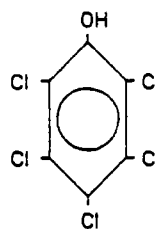
PENTACHLOROPHENOL

TABLE A1.6   PENTACHLOROPHENOL CONCENTRATIONS IN SURFACE WATERS AFFECTED BY DISCHARGE FROM THE WOOD PROCESSING INDUSTRY IN CENTRAL AND EASTERN CANADA

Location	Reference	Level of PCP	T_4CP	TCP
Domtar Wood Preserving Plant, Newcastle, New Brunswick.	Zitko and Carson 1969	0.5 - 18.3 mg/L	*	*
Salmon River, Truro, Nova Scotia	Naquadat File, Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.	0.008 - 0.38 mg/L		
Lake Superior Basin	Jones 1981	0 - 67 ng/L		
Lake Huron Basin	Jones 1981	0 - 25 ng/L		
Lake Erie Basin	Jones 1981	0 - 1700 ng/L		
Lake Ontario Basin	Jones 1981	0 - 1400 ng/L		

*   Detected but not quantified

TABLE A1.7   CHLOROPHENOL CONCENTRATIONS IN SEDIMENT, SURFACE WATER, AND EFFLUENTS ASSOCIATED WITH THE WOOD PRESERVATION INDUSTRY AT FRESHWATER AND MARINE SITES IN BRITISH COLUMBIA (Adapted from Environment Canada, 1979)

Site	Pentachlorophenol				Tetrachlorophenol				Trichlorophenol	
	Sediment (μg/kg dry wt.)		Surface Water (μg/L)	Effluent (μg/L)	Sediment (μg/kg dry wt.)		Surface Water (μg/L)	Effluent (μg/L)	Sediment (μg/kg dry wt.)	
	Average	Range			Average	Range			Average	Range
FRESHWATER										
Fraser R., Coquitlam	35.0	10-70	0.28		28.0	10-60	0.10		ND	ND
Fraser R., Coquitlam	10.8	ND-30	0.25		27.4	6-80	1.0		ND	ND-10
Fraser R., Burnaby	18.1	ND-90	TR		21.9	TR-90	0.30		ND	ND
Fraser R., Sea Island	TR	TR	TR		10.0	TR-15	0.20		ND	ND
MARINE										
Burrard Inlet, N. Vancouver	34.7	ND-240	0.75		39.8	ND-280	1.3		ND	ND
Squamish R., Squamish	52.8	14-84	2.4		98.7	46-220	5.2		52.1	5-150
Victoria	106.6	TR-500	ND		272.1	9-1600	ND		91.0	TR-170
Cowichan Bay	16.0	ND-75	TR	0.56	19.5	11-44	0.09	1.2	ND	ND
Naniamo	42.0	ND-170	TR	225	65.4	15-290	0.06	530	ND	ND
Naniamo	13.1	ND-67	3.1	ND	22.8	9-71	3.3	2.7	ND	ND
Pt.Alberni	187.9	ND-590	7.3	2760	157.3	54-370	0.22	8270	37.3	7-96

ND = Non Detectable (approx. 1/4 of limit of quantitation)
TR = Trace (present, but below level of quantitation)
Limit of quantitation - chlorophenols-sediment 5 ppb, water 0.05 ppb

Chlorophenols enter the environment via insufficiently treated effluents or due to accidental spillage. Another source of environmental contamination by chlorophenols is petrochemical drilling fluids. The sodium salt of pentachlorophenol in a concentration range of 700 - 1400 ppm is used for this purpose and drilling fluids as well as associated wastes are occasionally discharged to the environment.

1.3 Toxicity of Chlorophenols and their Impurities

The toxicity of chlorophenols is the main reason for their industrial use as anti fungal agents by the wood preserving industry. Unfortunately, chlorophenol toxicity is not specific to fungi and bacteria, but is rather general to all living organisms. Particularly, chlorophenols are highly toxic to all aquatic organisms as well as humans both on contact and as a result of ingestion.

The toxic effect of chlorophenols can be divided as follows:

    i)   Toxic effect of chlorophenols

    ii)   Toxic effect of impurities in chlorophenols

1.3.1 Toxic effects of chlorophenols

The toxic effect of chlorophenols has been well documented in the literature. The data describing the toxicity of chlorophenols to rainbow trout are shown in Table A.1.8. LC_{50} values in the range of 0.15 - 0.17 mg/L for a sodium pentachlorophenate solution were reported by several researchers (Chapman, 1969 and Alabaster, 1969). The 96 hour LC_{50} for pentachlorophenol was reported to be 0.13 mg/L (Guo, 1979). Several studies show that 5 mg/L of 2,4, 3,4, and 3,5 dichlorophenol have caused the death of all tested fish within hours.

Applegate (1957) tested the toxicity of 2,4,5 trichlorophenol and showed that while 5 mg/L killed all the tested fish in less than 2 hours, 0.1 mg/L caused no visible effects within a 24 hour period. A similar range of effect was determined for sodium pentachlorophenate.

TABLE A1.8

TOXICITY OF CHLOROPHENOLS TO RAINBOW TROUT

Chemical Compound	Test Conditions	Concentration (ppm)	Remarks	Reference
2, 4-dichlorophenol	SB, FW, LS	5.0	Dead, 3-6 h. at 12.8°C	Applegate et al (1957)
2, 6-dichlorophenol	SB, FW, LS	5.0	Dead, 13 h. at 12.8°C	Applegate et al (1957)
3, 4-dichlorophenol	SB, FW, LS	5.0	Dead, 3 h. at 12.8°C	Applegate et al (1957)
2, 4, 5-trichlorophenol (Dowicide 2)	SB, FW, LS	5.0 0.1	Dead, 0.5 - 2 h. at 12°C No effect, 24 h.	Applegate et al (1957)
Pentachlorophenol	SB, FW, LS, DCC	0.13	96 h. LC_{50} Juveniles (av. wt. 2.7 g), 14-15°C, ph 7.5-8.0	Guo et al (1979)
Sodium Pentachlorophenate (Dowicide G)	SB, FW, LS	5.0 1.0 0.1	Dead, 1 h. at 12.8°C Dead, 4 h. No effect, 24 h.	Applegate et al (1957)
Sodium Pentachlorphenate (Santobrite)	CB, FW, LS	0.17	48 h. LC_{50} 3 - 12 month old trout at 18°C	Chapman (1969)
Sodium Pentachlorophenate	CB, LS	0.15	48 h TL_m	Alabaster (1969) Kemp et al (1973)
Sodium Pentachlorophenate	SB, LS, pH 7.0 SB, LS, pH 7.0 SB, LS, pH 7.1 SB, LS, pH 5.7	0.098 0.050 0.106 0.047	96 h. LC_{50} at 12°C 96 h. LC_{50} at 11°C 96 h. LC_{50} at 12°C 96 h. LC_{50} at 10°C	Davis and Hoos (1975) (nomographic calc.)

SB = Static Bioassay   FW = Freshwater   LS = Lab Study   DCC = Dechlorinated City Water   CB = Constant Flow Bioassay

The acute toxicity of chlorophenols to mammals has also ben well documented in the literature and the results of studies conducted 'th rats are shown in Table A1.9. The data indicated that the toxicity creases with the level of chlorination, for example the LD_{50} for interp itoneal application of 2,4,5 trichlorophenol was determined to be 355 mg g while the corresponding value for pentachlorophenol was 56 mg/kg. A similar observation can be made for the oral route of application of the chlorophenols (a range of 820 - 2,960 for 2,4,5 trichlorophenol as ompared with a range of 27 - 205 for pentachlorophenol).

In general, all the chlorophenols show substantial to city to aquatic and terrestrial biota. This toxicity increases with the mber of chlorine atoms in the chlorophenol molecule.

1.3.2   Toxic effect of impurities in chlorophenols

In general, the toxicity of the impurities in chlorop nols is more profound than the toxicity of chlorophenols themselves. Di ins are commonly present as impurities in chlorophenol formulations. The are 75 possible dioxin isomers, however, only a few have been found i chloro-phenol based products. For example hexachlorodibenzo-p-dioxin hepta-chlorodibenzo-p-dioxin and octachlorodibenzo-p-dioxins are usuall present in commercial pentachlorophenol, but 2,3,7,8 tetrachlorodibenzo -dioxin has only been found in 2,4,5 trichlorophenol.

The toxicological characteristics of the dioxin isom s vary greatly. It has been shown that less than four and more than six hlorine atoms in a dioxin molecule greatly reduce toxicity. However, the resence of between four and six chlorine atoms produce highly toxic compou s.

The toxicity is enhanced by the following factors:

- 2,3,7,8 substitution
- Lateral symmetry of the molecule
- The chlorination of two adjacent carbon atoms
- The presence of available hydrogen
- The absence of steric hindrance

TABLE A1.9

ACUTE TOXICITY OF CHLORINATED PHENOLS TO RATS

TOXICANT	SEX	ROUTE	LD$_{50}$ (or as noted) mg/kg of body weight	NOTES (concentration and solvents; time till death)	REFERENCE
2,4,5-trichlorophenol	Male	O	820	20% sol'n in fuel oil	Deichmann and Mergard (1948)
		SC	2260	20% sol'n in fuel oil	Deichmann and Mergard (1948)
	Male	IP	355		Farquharson et al (1958)
	Male	O	2830		Dow Chemical Co. (1976)
	Female	O	2460		
	Male	O	2960		McCollister et al (1961)
2,4,6-trichlorophenol	Male	IP	276		Farquharson et al (1958)
3,4,5-trichlorophenol	Male	IP	372		Farquharson et al (1958)
2,3,4,6-tetrachlorophenol	Male	IP	130		Farquharson et al (1958)
Pentachlorophenol		O	27	0.5% in stanolex	Deichmann et al (1942)
		O	78	fuel oil; TDD 3-19 h 1% in olive oil; TDD, 3-11 hours	Deichmann et al (1942)
	Male	O	146		Gaines (1969)
	Male	O	205	commercial grade PCP	Schwetz et al (1974)
	Female	O	175		Gaines (1969)
	Female	O	135	commercial grade PCP	Schwetz et al (1974)
	Male	D	320		Gaines (1969)
	Female	D	330		Gaines (1969)
	Male	IP	56		Farquharson et al (1958)
		SC	90		Deichmann and Mergard (1948)
Na-pentachlorophenate	Male	INH	12	aerosol	Hoben et al (1976)

O = Oral   SC = Subcutaneous   INH = Inhalation

IP = Interperitoneal   D = Dermal   LD = Lethal dose, single administration (Deichmann et al, 1942)

TTD = Time till death (Deichmann et al, 1942)

The toxicity of different dioxin isomers has been reviewed in detail in the literature and the lethality of 2,3,7,8 tetrachloro-dibenzo-p-dioxin is shown in Table A1.10. The data indicate that 2,3,7,8 tetrachlorodibenzo-p-dioxin is approximately 1,000 times more toxic than the most toxic chlorophenol.

The teratogenicity of chlorinated dibenzo-p-dioxin compounds is shown in Table A.1.11. The data show that 2,3,7,8 tetrachloro-dibenzo-p-dioxin has substantially more pronounced teratogenicity than other dibenzo-p-dioxin compounds.

1.4   Fate and Transport of Chlorophenols

Chlorophenols are relatively persistent compounds. They can readily be transported in soil, water and air, however, they are subject to several mechanisms of degradation.

1.4.1   Fate of chlorophenols in the environment

The stability of chlorophenols in the environment has received great attention in the literature (Freiter, 1979). Three generalizations can be made from the data available:

- Chlorophenols are much more environmentally stable than the parent unsubstituted phenol.

- Stability increases with increasing degree of chlorination.

- Presence of a chlorine atom at the meta position increases the stability.

1.4.1.1   Chemical and microbial degradation   In the natural environment it is difficult to distinguish between chemical and microbial degradation

TABLE A1.10   LETHALITY OF 2,3,7,8 - TETRACHLORODIBENZO-p-DIOXIN (Schewetz et al, 1973)

Species, Sex	Administration	Time of Death, days post admin.	LD_{50} mg/kg	Dose mg/kg	Deaths/ Treated (Numbers)
Rat, male	Oral	9 - 27	0.022	0.008 0.016 0.032 0.063	0/5 0/5 10/10 5/5
Rat, female	Oral	13 - 43	0.045 (0.030-0.066)		
Guinea pig, male	Oral	5 - 34	0.0006 (0.0004-0.0009)		
Guinea pig, female	Oral	9 - 42	0.0021 (0.0015-0.0030)		
Rabbit, mixed	Oral Skin Intraperitoneal	6 - 39 12 - 22 6 - 23	0.115 (0.038-0.345) 0.275 (0.142-0.531) -	0.032 0.063 0.126 0.252 0.500	0/5 2/5 2/5 2/5 3/5
Dogs, male	Oral	9 - 15		0.30 3.00	0/2 2/2
Dogs, female	Oral	-		0.03 0.10	0/2 0/2

NOTE: Responses to individual doses are given in those cases in which an LD_{50} could not be calculated. The LD_{50} for oral administration to rabbits was calculated using the method of Litchfield and Wilcoxon (1949); the remaining values were calculated using the Weil modification.

TABLE A.1.11   TERATOGENIC EVALUATION OF CHLORINATED DIBENZO-p-DIOXIN COMPOUNDS ADMINISTERED ORALLY IN CD-1 MICE

(Courtney, 1976)

Dibenzo-p-dioxin Compound	Route	Dose/kg/day	No. of Litters	Av.No. Live Fetuses/ Litter	Av.No. Abnormal Fetuses/ Litter	% Anomalies/Total Fetuses		
						Cleft Palate	Kidney	Clubfoot
control[d]	oral	0.1 mL/mouse	15	11.0	0.8	0	1	4
2/3 mixture[a]	oral	100 ug	6	12.3	3.2	0	10[c]	9
	oral	200 ug	5	12.8	3.8	0	1	22[c]
1,2,3,4-tetrachloro-	oral	100 ug	4	11.8	0.8	2	0	2
	oral	250 ug	4	11.5	0.5	0	1	3
	oral	500 ug	5	11.6	0.2	0	0	0
	oral	1000 ug	5	11.8	1.0	0	0	0
2,3,7,8-tetrachloro-	oral	25 ug	7	10.9	4.6	3	34	3
	oral	50 ug	7	11.0	8.1	19	72	7
	oral	100 ug	6	9.7	8.3	66	71	13
	oral	200 ug	6	1.5	1.5	100	100	14
	oral	400 ug	5	0.4	0.4	100	50	50
control[b,e]	oral	0.1 mL/mouse	5	11.2	0	0	0	0
octachloro-[b]	oral	5 mg	6	11.2	0.2	1	0	0
	oral	20 mg	6	11.6	0	0	0	0

[a] mixture = 40% 2,7 dichlorodibenzo-p-dioxin and 60% 2,3,7-trichlorodibenzo-p-dioxin

[b] sacrificed day 17 of gestation: All others sacrificed day 18

[c] Courtney suggested those deviant figures were not a result of the dioxin treatment

[d] 5% anisole: corn oil

[e] 15% anisole: corn oil

due to the omnipresence of microbial life. Strufe (1968) studied the effect of the electrolytic content of water on sodium pentachlorophenate degradation. Although the solubility of sodium pentachlorophenate is not significantly affected by salts dissolved in the water, the presence of iron, lead and copper compounds leads to the formation of insoluble complex compounds and subsequent deactivation of sodium pentachlorophenate.

The biodegradability of chlorophenol was studied by Tabak et al. (1981) who reported that an activated sludge culture degraded 5 mg/L of pentachlorophenol in two weeks while four weeks was needed to achieve 98 percent degradation of 10 mg/L.

In the natural environment, Aly and Faust (1964) reported complete disappearance of 2,4 dichlorophenol from an initial concentration of 100 mg/L in lake water at neutral pH within 9 days.

There has been a substantial amount of work conducted which describes the fate of chlorophenols in soils. Chambers et al. (1963) studied the oxygen uptake of bacterial cultures in permeable soil which were exposed to chlorophenol substrates and showed that dichlorophenols were more resistant to oxidation than monochlorophenols. It was shown that pentachlorophenol at an initial concentration of 200 ppm required 205 days to achieve a 98 percent reduction.

Cserjesi (1972) reported that the degradation rate of pentachlorophenol in soils decreases with a decrease in the organic matter content of the soil. Soil texture, clay content, degree of saturation and free iron oxides were not closely related to the rate of pentachlorophenol degradation. He also pointed out that the main process for detoxification of chlorinated phenols by micro-organisms is the formation of methylated products. Similar observations were reported by Suzuki and Nose (1971).

Arsenault (1976) showed that octachlorodibenzo-p-dioxin is also biodegraded by soil. Kearney et al. (1972) summarized the findings which indicate that tetrachlorodibenzo-p-dioxin is degraded slowly in soil and tetrachlorodibenzo-p-dioxin and octachlorodibenzo-p-dioxin are not bio-synthesized by microbial reactions.

The information available in the literature suggests that, despite their strong toxicity, both chlorophenols and their industrial impurities are subject to degradation in both aquatic and soil environments.

1.4.1.2 Photochemical degradation The information in the literature strongly suggests that chlorophenols and chlorodioxins are destabilized in the environment by the affect of light. The intermediate and final by-products of the photochemical degradation were generally less toxic than the original compounds.

Hiatt (1960) determined the kinetics of photodegradation of sodium pentachlorophenate. Kuwahara et al. (1969) identified the products of photochemical decomposition of sodium pentachlorophenate as chloranitic acid, 3,4,5 trichloro-6-o-benzoquinone, 2,5 dichloro-3-hydroxy-5-p-benzoquinone, 2,6 dichloro-3-hydroxy-5-p-benzoquinone, tetrachlororesorcinol, and 3,5 dichloro-4-6-o-benzoquinone. In general, all of the products of degradation had stronger fungicidal activity but weaker phytotoxicity and lower fish toxicity than sodium pentachlorophenate. No dioxins were identified. Plimmer (1973) reported the formation of octachlorodibenzo-p-dioxin and heptachlorodibenzo-p-dioxin on irradiation of sodium penta chlorophenate, but no tetrachlorodibenzo-p-dioxin was found.

Crosby and Wong (1974) irradiated hexadecane film containing 400 ppm of pentachlorophenol floating on deionized water. No detectable photodecomposition products were found. By contrast, pentachlorophenol in deionized water degraded to 2,3,4,6 and 2,3,5,6 tetrachlorophenol and further irradiation gave 2,3 dichlormaleic acid which ultimately broke down to hydrochloric acid and carbon dioxide. Arsenault (1976) and Hamadmad (1967) confirmed separately that the presence of a solvent is mandatory for photodecomposition of pentachlorophenol. Lamparski (1980) observed that decomposition was enhanced by the presence of oil. Dobbs and Grant (1979) studied photolysis of octachlorodibenzo-p-dioxin, heptachlorodibenzo-p-dioxins and some hexachlorodibenzo-p-dioxins. The results indicated that chlorodibenzo-p-dioxins with chlorine atoms in a symmetrical position, photolyse more rapidly than those with chlorine atoms in unsymmetrical positions.

1.4.2 Transport of chlorophenols

Once released into the environment, chlorophenols can be readily transported by a number of alternative mechanisms which include: adsorption, leaching, diffusion, volatilization and atmospheric movement.

1.4.2.1   Adsorption and leaching   The adsorption and leaching charac-
teristics of chlorophenols have not been extensively investigated, but some
data on pentachlorophenol is available. Choi and Aomine (1974) showed that
adsorption of pentachlorophenol occurs on strong acid soil systems, no
matter what the mineral and organic content of the soil is. The major
factor governing adsorption is pH. Kaufmann (1976) and Green and Young
(1970) found pentachlorophenol to be most mobile at high pH and least
mobile in acid soils. Due to their low pH, humus-rich soils generally make
pentachlorophenol less soluble than it is in mineral soils.

Haque and Freed (1974) stated that the factors controlling
leaching from soil are: water solubility of the chemical, adsorption, soil
type, moisture and percolation velocity. The Weed Science Society of
America, Herbicide Handbook (1974) notes that sodium pentachlorophenate
leaches readily from soils. Stranks (1976) noted that, in general, penta-
chlorophenol does not leach from treated wood, especially if applied by an
oil carrier. However, Unligil (1968) has shown that pentachlorophenol was
removed from blocks of treated wood during steam sterilization. Similar,
but long-term leaching from wood products can probably be expected for soil
and water exposure under outdoor, hot and humid cyclical weather condi-
tions.

1.4.2.2   Diffusion and volatilization   Volatilization from the soil is
one of the important pathways for the disappearance of chlorophenols. The
volatilization rate depends on temperature, humidity, nature of soil, its
water content and air movement. As soon as loss occurs at the soil sur-
face, a concentration gradient is established and diffusion of chloro-
phenols to the surface begins.

Though diffusion does not contribute to long distance transport
in soil, it is of significance in still water. The rate of loss of a
chlorophenol from soil can, in part, be a function of the rate of evapora-
tion of water from soil, since evaporation of water accelerates the
evaporation of water soluble chlorophenol (Hartley, 1969). The
significance of volatilization as a pathway for chlorophenol transport has
not been adequately determined (Kaufmann, 1976).

1.4.2.3 <u>Atmospheric movement</u> Atmospheric movement of a chemical depends on its vapour pressure, heat of vaporization, partition coefficient between the two phases, and air velocity (Haque and Freed, 1974). Measurable quantities of pentachlorophenol detected in snow melts show aerial transport does occur (Jones, 1981). During this study, positive pentachlorophenol deposits were measured at Point Pelee National Park, Fushimi Lake Provincial Park and Kettle Lake Provincial Park. All of these sites are located far from any possible point source discharge of pentachlorophenol.

1.5 <u>Pollution Control Options</u>

Three basic types of technologies have been reported to be applicable for the control of chlorophenols. These are: physical/chemical methods, biological oxidation and thermal destruction.

Richardson (1971) has conducted an extensive survey of water treatment and disposal techniques used by the Canadian wood treatment industry. However, out of the 26 operations surveyed, as shown in Table A1.12, only three reported any data on the quality of the treated effluent. Most of the plants employed containment of the effluent in open pits or lagoons as a final treatment stage. Evaporation was claimed to be the final disposal method, however, periodic discharge of the accumulated effluent would be inevitable due to precipitation being in excess of evaporation in most of Canada. The incineration of pentachlorophenol contaminated sludges and liquids was reported in two cases.

1.5.1 <u>Physical/chemical methods</u>

A wide variety of physical/chemical methods are described in the literature.

1.5.1.1 <u>Solids/liquids separation</u> In most instances the chlorophenols are applied to the wood in conjunction with an oil-based carrier. When the oil-based chlorophenol formulations are dispersed in water the removal of the chlorophenol is related to the removal of the oil from the water. Guo <u>et</u> <u>al</u>. (1980) reported use of primary oil separation in two stages for the removal of oil-based chlorophenols at Abitibi Northern Wood Preservers

TABLE A1.12   WASTE TREATMENT PRACTICES IN THE CANADIAN WOOD TREATMENT INDUSTRY

Adapted from Richardson (1977)

PLANT NUMBER	CHEMICAL USED	VOLUME OF EFFLUENT (gal./day)	PRIMARY TREATMENT	SECONDARY TREATMENT	SLUDGE DISPOSAL METHOD	DATA ON EFFLUENT ANALYSIS
1.	P & C	Not available	Gravity separation in tank	Containment and evaporation in heated tank	Sludge trucked for land filling	Not available
2.	P	Not available	Gravity separation in tank	Containment and evaporation in pit	Not available	Not available
3.	P	15 – 20 (0.07–0.09m^3)	Gravity separation in tank	Containment and evaporation in a pond containing wood shavings	Sludge burned	Not available
4.	P, C & W	Not available	Gravity separation in tank	Boultonizing condensate by soil irrigation, steaming cond. by containment and evaporation in summer and by burial in winter	Not available	
5.	P, C & W	5,000 (23 cm^3)	Gravity separation in tank	Activated sludge biological treatment and then discharge	Sludge trucked for land filling	Untreated eff. Total phenol 1,600 ppm Treated eff. Total phenol 0.11–0.4 ppm

P – pentachlorophenol–petroleum

C – Creosote

W – Water-borne preservative

TABLE A1.12 (Continued)   WASTE TREATMENT PRACTICES IN THE CANADIAN WOOD TREATMENT INDUSTRY

Adapted from Richardson (1977)

PLANT NUMBER	CHEMICAL USED	VOLUME OF EFFLUENT (gal./day)	PRIMARY TREATMENT	SECONDARY TREATMENT	SLUDGE DISPOSAL METHOD	DATA ON EFFLUENT ANALYSIS
6.	P & C	2000 – 5000 Max. 4000 $(9-12m^3$, max. $10m^3)$	Gravity Separation Sand/polyurethane foam filtration	Activated carbon adsorption treatment then discharge	Not available	From pilot plant study, anal. of untreated effluent Before prefiltration: 500 ppm COD, 50-1100 ppm oil, 40 ppm "phenolic" equiv. and 3-60 ppm penta After carb. adsorp. "anal. limit" residuals of oils, phenols, PCP
7.	P	50-100 $(0.23-0.46m^3)$	Gravity separation	Containment and evaporation in open pit	Not known	Not available
8.	P	300-400 $(1.36-1.82m^3)$	Gravity separation	Containment and evaporation in open pit	Not known	Not available
9.	P	30 $(0.14m^3)$	Gravity separation	Containment and evaporation in open pit	Sludge trucked by commerical disposal company	Not available

P - pentachlorophenol-petroleum

C - creosote

TABLE A1.12   (Continued)   WASTE TREATMENT PRACTICES IN THE CANADIAN WOOD TREATMENT INDUSTRY

Adapted from Richardson (1977)

PLANT NUMBER	CHEMICAL USED	VOLUME OF EFFLUENT (gal./day)	PRIMARY TREATMENT	SECONDARY TREATMENT	SLUDGE DISPOSAL METHOD	DATA ON EFFLUENT ANALYSIS
10.	P	None	Not known	Not known	Sludge Burial	Not available
11.	P	Not available	Gravity separation	Containment and evaporation in open pit	Not known	Not available
12.	P	Not available	Gravity separation	Containment in septic tank	Trucked by commercial disposal company	Not available
13.	P	Not available	Gravity separation	Mixed with bunker fuel oil and incinerated	Sludge burial	Not available
14.	P	Not available	Gravity separation	Containment and evaporation in pit	Not available	Not available
15.	P & C	Not available	Gravity separation	Evaporation in tank by steam coils followed by incineration mixed with bunker fuel oil	Sludge trucked to town garbage	Not available
16.	P & C	Not available	Gravity separation Flocculation with alum & ammonia & settling	Lagooning in ditch and then discharge	Flocculated sludge, wood shavings, and sludge from lagoon burned	Not available

P – pentachlorophenol-petroleum   C – creosote

TABLE A1.12   (Continued)   WASTE TREATMENT PRACTICES IN THE CANADIAN WOOD TREATMENT INDUSTRY

Adapted from Richardson (1977)

PLANT NUMBER	CHEMICAL USED	VOLUME OF EFFLUENT (gal./day)	PRIMARY TREATMENT	SECONDARY TREATMENT	SLUDGE DISPOSAL METHOD	DATA ON EFFLUENT ANALYSIS
17.	C, P, W.	2500-3000 ($11.4-13.6m^3$) before bulk oil separation	Gravity separation	Incineration mixed with bunker fuel oil (96% efficiency)	Sludge disposed of by commercial disposal company	Not available
18.	C, P, W.	4000 ($18.2m^3$) after bulk oil separation	Gravity separation	Spray evaporation on shavings and then incineration. No scrubbing of stack gas. Plan to use cylinder condensate for scrubbing	Sludge disposed of by commercial dis-posal company	Not available
19.	P & W	200 ($0.9m^3$)	Gravity separation and Sand filtration	Filtrate for make up of water-borne preserva-tive solution	Sludge trucked by commercial dis-posal company	Not available
20.	P & C	Not available	Gravity separation	Containment and eva-poration in a pit	Not available	Not available
21.	P,C W.	Not available	Gravity and API separation and hay filtration	Lagooning in ditch and discharge. Plan - flocculation, polyure-thane filtration and activated carbon adsorption	Not available	Not available
22.	P,C W.	4000 - 7000 ($18.2-31.8m^3$)	Gravity and API separation	As above	Not available	Based on waste water vol. of 7000 gpd. API separator effluent carries 370 ppm total phenol and 1900 ppm oil to ditch.

P – Pentachlorophenol-petroleum   C – creosote   W – water-borne preservative

TABLE A1.12   (Continued)   WASTE TREATMENT PRACTICES IN THE CANADIAN WOOD TREATMENT INDUSTRY

Adapted from Richardson (1977)

PLANT NUMBER	CHEMICAL USED	VOLUME OF EFFLUENT (gal./day)	PRIMARY TREATMENT	SECONDARY TREATMENT	SLUDGE DISPOSAL METHOD	DATA ON EFFLUENT ANALYSIS
23.	P	Not available	Gravity separation	Containment and eva-poration in gravel pit	Sludge mixed with shavings and sold	Not available
24	P & C	Not available	Gravity separation	Containment and eva-poration in a pond	Sludge mixed with shavings and burned	Not available
25.	P	Not available	Gravity separation	Containment and eva-poration in a gravel field	Not available	Not available
26.	P PMC	Not available	Segregation of creosote and penta-methylene chloride effluents, gravity separation	After gravity separa-tion: incinerated or trucked by commercial disposal company	Sludge trucked by commercial dis-posal company	Not available

P - pentachlorophenol-petroleum
C - creosote
PMC - pentachlorophenol in methylene chlorine

Limited, Thunder Bay, Ontario. Richardson (1977) reported that the recovery of oil separating to the top or the bottom of the aqueous phase is widely used in the Canadian wood treatment industry as a primary control method.

Wallin et al. (1981) reported that 80 percent of the pentachlorophenol was removed by separation of the emulsified oil after lowering the pH to 4. However, coagulation with alum, ferric chloride and/or polymer resulted only in a modest reduction of chlorophenols. Lime addition of 0.75 to 2 grams/L was found to reduce oil content by about 95 percent as well as the pentachlorophenol concentration to the level of its solubility in water, (Dust and Thompson, 1971).

However, the same authors found that flocculation was only used by six of the 270 plants surveyed in the U.S. in 1974.

Richardson summarized several trials evaluating the use of air flotation for the treatment of wood preserving effluents. DAF appears to be an unsatisfactory control option due to the variable density of the oils being removed. In some trials, oil tended to migrate to the bottom of the flotation chamber rather than to the top, or else remained suspended throughout the aqueous phase.

Thurlow (1977) reported that coagulation with polyelectrolytes in combination with alum or lime followed by filtration or settling is a common procedure. COD reductions of up to 50 - 70 percent were achieved, although pentachlorophenols dissolved in water are not removed to any significant degree.

1.5.1.2 Chemical extraction Solvent extraction of pentachlorophenol with ortho-dichlorobenzene has been studied in Japan (Terai et al. 1964). Residual pentachlorophenol concentrations of less than 1 mg/L were obtained from initial concentrations of 16 to 17 mg/L. Ortho-dichlorobenzene was selected as the extraction solvent because it was readily available and it is easily separated from water by sedimentation.

Wallin et al. (1981) reported excellent results by using a mixture of No. 2 fuel oil and a cosolvent (amyl alcohol still bottoms) to extract chlorophenol from the waste. Reductions in excess of 99 percent were effected. Pilot scale trials with No. 2 fuel oil alone yielded removal efficiencies in the vicinity of 97 percent. For both systems to function

consistently, however, the waste water had to be first subjected to free oil separation and flow equalization.

1.5.1.3 Chemical oxidation Oxygen, chlorine, ozone, chlorine dioxide, potassium permanganate and hydrogen peroxide can be used as oxidants in wastewater treatment. The effectiveness of chemical oxidation depends on temperature, pH, contact time and concentration of oxidizing and reducing materials (Averill and Netzer, 1977).

The use of calcium hypochloride for the oxidation of wood treat- ment wastewater was studied by Thompson and Dust, (1972). A calcium hypochloride dosage of 1.0 g/L (as chlorine) completely oxidized 189 mg/L of phenols and reduced COD from 3,400 to 1,700 mg/L. An increase in the hypochloride dosage to 3 g/L (as chlorine) was needed to eliminate 40.7 mg/L of pentachlorophenol, which was much more difficult to oxidize than simple phenols. The prevailing degradation product of the pentachloro- phenol oxidation by chlorine was chloranil (2,3,5,6-tetrachloro-para- benzoquinone) which is a biodegradable product of relatively low toxicity. Richardson (1977) confirmed that the principal degradation product of pentachlorophenol is 2,3,4,5-tetrachloro-para-benzoquinone.

Averill and Netzer (1977) summarized the application of various chemical oxidation techniques reported in the literature. They cover the use of chlorine, chlorine dioxide, ozone and hydrogen peroxide. In general, chlorophenols can be readily oxidized under stringent conditions, however, the economics of the process are unfavourable.

1.5.1.4 Adsorption Benedek (1982) indicated that activated carbon has good affinity for pentachlorophenol and other chlorophenols. Excellent results were reported for the removal of pentachlorophenol by using acti- vated carbon columns (Guo et al. 1980). The concentration of pentachloro- phenol in the waste ranged from 0.3 to 14.9 mg/L and was reduced to an average of 0.02 mg/L in the treated effluent.

However, the system was subject to frequent breakthroughs with respect to BOD and COD. This was obviously due to the inability of the activated carbon to effectively adsorb the smaller organic molecules also present in the wastewater.

In the same study, Guo reported excellent performance of activated carbon columns as the polishing units after the biological treatment of the pentachlorophenol wastewater using the activated sludge process. The carbon adsorption system had not reached exhaustion after treatment of 550 empty bed volumes of effluent. The treated effluent had pentachlorophenol concentrations of less than 0.01 mg/L.

Excellent removal of chlorophenols was reported by Wallin (1981). Wastewater was acidified to a pH of approximately 4 and then treated with bentonite clay. Subsequently a polymeric adsorbant, Amberlite XAD-4 was used for the polishing of the effluent. The removal efficiencies for pentachlorophenol were consistently in excess of 99 percent during this pilot plant study.

Richardson (1977) monitored the performance of a dual column activated carbon system, and major findings are presented in Table A.1.13. As can be seen from Figure A1, the bulk of the oil and its associated pentachlorophenol are removed by the first column. The entire system effected a 99.8 percent removal for oil and 97.9 percent removal of pentachlorophenol. COD is removed almost equally by both columns to give a total removal of 95.6 percent. Only 23 percent of the phenols are removed by the first column, whereas the second column brings the total phenol removal to 99.9 percent.

1.5.2   Applicability of physical/chemical methods   The data reported in the literature suggest that physical/chemical methods are well suited to remove chlorophenols from liquid effluents.

Chemical extraction and chemical oxidation as well as adsorption processes are capable of achieving an excellent level of chlorophenol removal from the water phase, however, the economics of these processes are generally unfavourable.

1.5.3   Biological treatment

The removal of chlorophenols from industrial effluents using bio-treatment has been extensively studied and reported in the literature. Tabak et al. (1981) studied biodegradability of chlorophenols using a static culture flask biodegradation screening test. Much faster acclimation of

TABLE Al.13   PERFORMANCE MONITORING OF A DUAL COLUMN

ACTIVATED CARBON SYSTEM

Sampling point	Component *	Concentration		No. of daily composites
		mean (ppm)	range (ppm)	
1. Before first column	Oil	128	40-237	19
	Phenols	81	1.0-153	17
	COD	921	256-3040	19
	Penta.	4.3	1.9-8.2	10
2. After first column	Oil	9.8	0-60	19
	Phenols	62	.95-150	17
	COD	388	101-1074	19
	Penta.	0.63	0.04-5.7	10
3. After second column	Oil	0.26	0-4.9	19
	Phenols	0.10	0-0.40	17
	COD	40	3.9-95	19
	Penta.	0.09	0.02-0.32	6

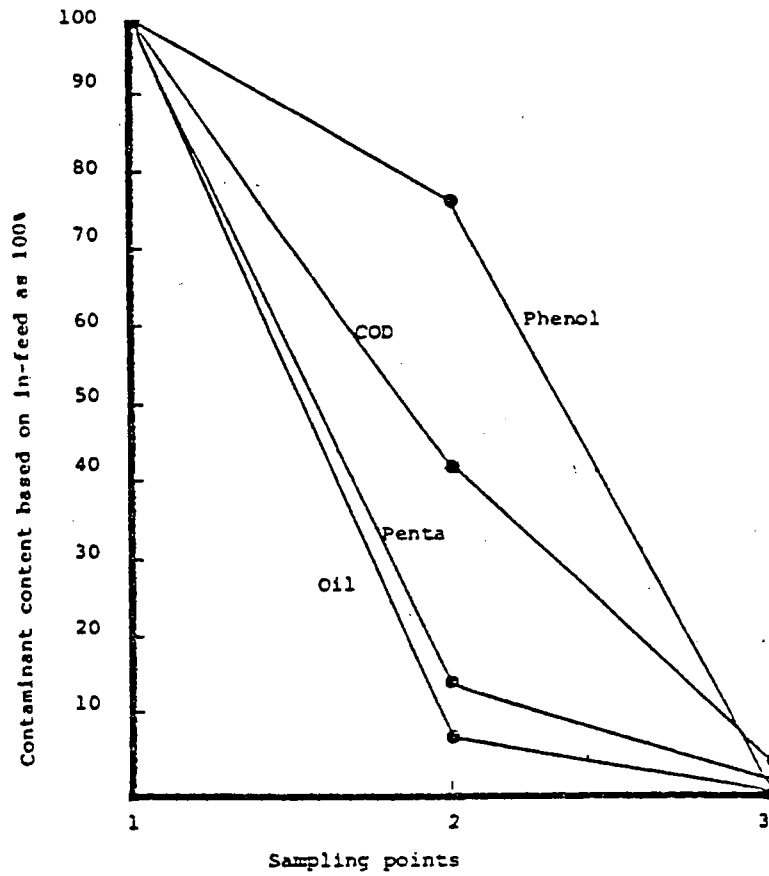* "Penta" includes both penta and tetra- chlorophenols.

FIGURE A.1   CONTAMINANT REMOVAL ACROSS A DUAL COLUMN

ACTIVATED CARBON SYSTEM

the culture was observed for 2,4,6 trichlorophenol than for pentachlorophenol under similar conditions. The results indicated that higher chlorinated phenols are much more biologically resistant to degradation than the lower phenols. For example, it took two weeks for 100 percent degradation of trichlorophenol as compared with 4 weeks for a similar degradation of pentachlorophenol.

Dust and Thompson (1973) used micro-organisms from the soil in a drainage ditch containing pentachlorophenols. After two weeks of acclimation, four continuous flow reactors, operated at hydraulic detention times of 5, 9, 20 and 38 days respectively, were fed with a solution containing 10 mg/L of pentachlorophenol and 2,400 mg/L COD. Results indicated that while the unit operated at 5 days detention time consistently removed 91 percent pentachlorophenol, the results from the other reactors were inconclusive.

Kirsch and Etzel (1973) reported that it took 25 days to achieve a 68 percent reduction of sodium pentachlorophenate at a concentration of 10 mg/L using an acclimated mixed culture.

Wallin (1981) reported that biological oxidation (laboratory and pilot scale) was not found to be an effective treatment technique because bio-adsorption rather than bio-transformation was found to be the primary removal mechanism. Removal rates continued to diminish as adsorptive capacity of the biomass was approached.

Wukasch et al. (1981) determined pentachlorophenol degradation to be a first order function of solids retention time, as long as the initial pentachlorophenol concentration was below an inhibitory level. This relationship allows prediction of effluent concentration of pentachlorophenol from a reactor operating at a given solids retention time.

Guo et al. (1980) have discussed the results of a number of studies dealing with the degradation of chlorophenols. The results of their pilot scale study using an extended aeration activated sludge plant operated at an organic loading of 0.02 to 0.06 kilograms BOD per kilogram of mixed liquor suspended solids per day, indicated excellent removal of organic contaminants such as BOD, COD and TOC from wood preserving wastewater. However, pentachlorophenol removal efficiencies were poor, resulting in an effluent that was extremely toxic to rainbow trout.

Thurlow (1977) reported that both natural and mechanically aerated lagoons are used for the treatment of wood preserving wastewaters. Long retention times and low BOD loadings are required to effect significant reduction of chlorophenols. Overflows from the lagoons are normally polished by soil irrigation. This does, however, provide the potential for contamination of the groundwater.

In general, biological processes are applicable for the treatment of wood preserving wastewaters. Sufficient acclimation of the biomass, as well as steady operation of the processes operated at high SRT is necessary to overcome the problems related to high toxicity associated with chlorophenols.

APPENDIX 2

CALCULATION OF OXYGEN CONSUMPTION AND EFFECTIVE RESIDENCE TIME

Sample Calculation for Sawdust or Sludge

Base   -   1 mg of saw dust/sludge

C   -   50% = 0.5 mg

H   -   5% = 0.05 mg

O_2 -   45% = 0.45 mg

The reactions occurring in the volatilization chamber are:

$$C + O_2 \longrightarrow CO_2 \tag{1}$$

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O \tag{2}$$

$$O_2 \longrightarrow O_2 \tag{3}$$

(from saw dust)

For one mg of saw dust, oxygen requirement for complete combustion is:

according to reaction (1) = $\dfrac{0.5}{12000}$ g.moles   (4)

according to reaction (2) = $\dfrac{0.05}{2 \times 2000}$ g.moles   (5)

according to reaction (3) oxygen generated = $\dfrac{0.45}{32000}$ g.moles   (6)

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Therefore net oxygen requirement = (4) + (5) - (6)

$$= (0.0416 + 0.0125 - 0.014) \times 10^{-3}$$

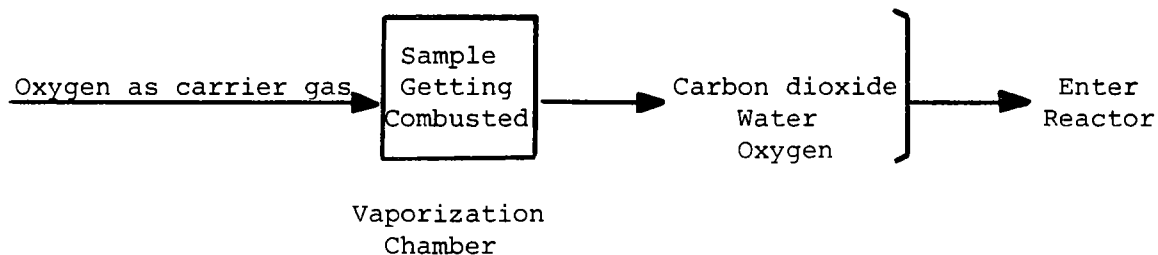$$= 0.0401 \times 10^{-3} \text{ g.moles/mg of saw dust}$$

Average combustion rate = 20.66 mg/min

Oxygen consumption rate = $20.66 \times 0.0401 \times 10^{-3}$

$$= 0.828 \times 10^{-3} \text{ g.moles/min}$$

Oxygen supply rate $= 0.943 \times 10^{-3}$ g.moles/min

Oxygen flow rate of 0.943×10^{-3} g.moles/min corresponds to 1.1 seconds of residence time in the reactor. Due to the combustion of saw dust, the total moles entering the reactor are of carbon dioxide, water and oxygen. For residence time calculations, moles of chlorophenols are negligibly small.

Oxygen as carrier gas → [Sample Getting Combusted] → Carbon dioxide, Water, Oxygen → Enter Reactor

Vaporization Chamber

According to the stoichiometry of reaction (1), one mole of carbon dioxide is produced for each mole of carbon and oxygen consumed. Stoichiometry of the second reaction shows consumption of half a mole of oxygen and formation of one mole of water for each mole of hydrogen. The oxygen present in the saw dust is available for combustion.

Oxygen supply rate = 0.943×10^{-3} g.moles/min

Saw dust combustion rate = 20.66 mg/min

Carbon dioxide generation rate = $\dfrac{20.66 \times 0.5}{12000} = 0.86 \times 10^{-3}$ g.moles/min

Water generation rate = $\dfrac{20.66 \times 0.5}{2000} = 0.51 \times 10^{-3}$ g.moles/min

Net oxygen rate = $(0.943 \times 10^{-3} + \dfrac{20.66 \times 0.45}{32000}$

$\qquad - 0.86 \times 10^{-3} - \dfrac{0.51}{2} \times 10^{-3}$ g.moles/min

$\qquad = 0.123 \times 10^{-3}$ g.moles/min

Total moles entering the
reactor = $(0.86 + 0.51 + 0.123) \times 10^{-3}$ moles/min

$\qquad = 1.493 \times 10^{-3}$ moles/min

Residence time in the reactor = $\dfrac{0.943 \times 1.1}{1.493} = 0.693$ seconds

Thus the effective residence time, during combustion of wood chips, becomes 0.693 seconds instead of 1.1 seconds.

Date Due

AUG 4 '94			