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Halogenated biphenyls, terphenyls, naphthalenes, dibenzodioxins and related products

Editor

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CHAPTER 3

Environmental pollution of air, water and soil

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3.1. Introduction

Most of the chapters in this book touch upon environmental contamination by one or more of the compounds discussed. Pollution may be heavy in localized areas where industries have discharged materials into waterways (Environmental Defense Fund, 1977; Mowrer et al., 1977) or have deposited them into dumps that are leaking. If dumps, in addition to the PCBs and other persistent chemicals, also contain solvents, their spread becomes more likely. From such point sources, contamination of the surrounding areas may be extensive and far reaching. In addition, illicit or improper disposal of such chemicals (Dunphy and Hall, 1978a, 1978b) also greatly contributes to the contamination of the environment. Open-ended uses (Chapter 1) as pesticides, flame retardants, additives in paints, to give a few examples, are another source. A number of reviews are available on this subject (IARC, 1978, WHO, 1976; NRC, 1979) for polychlorinated biphenyls, whilst much less information is available on the other compounds. All of these compounds are only very slightly soluble in water, but soluble in lipids and some organic solvents, have a low vapor pressure, and are stable and persistent. Once they have been released into the environment, they will reach the food chain where they are concentrated. Fish and wildlife are the most consistent targets for such contamination, but livestock may also become contaminated and people gradually acquire body burdens of these materials. These chemicals are not very readily taken up by plants, and because they dissolve very poorly in water, they are primarily found in sediments of polluted lakes and rivers. They are also concentrated in municipal sewer sludge if they enter waste treatment plants. If such sewer sludge is used as fertilizer, it contributes fur-

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ther to environmental contamination (Chapter 9A). They may be released into the atmosphere from municipal incinerators (Chapter 2). Their presence as contaminants in commercial products (Chapter 2) is an additional source.

3.2. Polychlorinated biphenyls

3.2.1. Air

Monitoring data is primarily only available for PCBs. Urban areas of large cities in Japan, such as Tokyo, contained 0.02 $\mu g \cdot m^3$ PCBs, while medium-sized cities, such as Matsuyama, had 0.002–0.005 $\mu g \cdot m^3$. The air around electrical appliance factories and paper recycling mills had much higher PCB levels (up to 12 $\mu g \cdot m^3$) (Tatsukawa, 1976; Tatsukawa and Watanabe, 1972).

In the United States, Kutz and Yang (1976) found that the average concentration of PCBs in samples of ambient air from suburban locations was 0.1 $\mu g \cdot m^3$.

3.2.2. Water and sediments

A national survey conducted in the U.S. showed that the PCB levels in unfiltered water samples during 1971–1974 ranged between 0.1 and 3.0 $\mu g \cdot l$ (Dennis, 1976). Kleinert (1976) estimated that the waters of Lake Michigan contain as much as 10 ng/l PCBs.

In Japan, in a survey of the surface water of Suruga Bay, near Fuji, where there are a large number of paper mills which use recycled paper, the levels of PCBs varied from 0.9 to 1.6 $\mu g/l$. Surface water in Tokyo Bay in 1973 contained as much as 0.3 $\mu g/l$ (Fukushima, 1974).

Eichner (1976) found that the PCB levels in the Rhine River and Lake Constance had increased slightly during the period 1973–75, from 0.01 to 0.075 $\mu g/l$.

The average concentration of PCBs in samples of seawater taken from 11 stations off the northwestern Mediterranean coast in 1975 was 0.013 $\mu g \cdot l$ (Elder, 1976).

Nadeau and Davis (1976) found up to 2.8 mg·l PCBs in the water and up to 6700 mg/kg in the sediments of the Hudson River in the vicinity of a factory using PCBs. Dennis (1976) reported that bottom sediments from major drainage basins throughout the U.S. and Puerto Rico contained from 1.2 to 160 $\mu g \cdot kg$.

Sediments from 1445 sites in Japan contained less than 1 mg·kg PCBs, while sediments in the rivers entering Tokyo Bay, where many factories using PCBs are located, contained up to 2.7 mg/kg (Tatsukawa, 1976; Tatsukawa and Watanabe, 1972).

Biodegradation has been a minor factor in PCB destruction for those isomers of tetra- through decachlorobiphenyl.

3.2.3. Soil

In 1972, in the United States, only 0.1% of samples contained detectable levels of PCBs. In urban areas, 12 of 19 soil samples from metropolitan areas (63%) showed detectable levels. A PCB pattern corresponding to 54% chlorine was identified in

40% of the positive samples, and a pattern corresponding to 60% was recorded in 20% of the samples (Carey and Gowen, 1976). However, the actual number of samples analyzed was small in comparison to the size of the United States.

In Japan, a nationwide survey of soil samples from 88 sites showed that 40% of samples had less than 0.01 μg g PCB, 24% had 0.01–0.10 μg g, 21% had 0.11–1.0 μg g, 7% had 1.1–10 μg g, 3% had 10.1–100 μg g and 5% had more than 100.1 μg g. As a result of contamination of soil and the atmosphere with PCBs, detectable levels have been recorded in vegetation: an analysis of PCBs in unhulled rice from 33 sites in Japan in 1972 showed that 79% had less than 0.01 μg g, 15% had 0.01–0.10 μg g, 3% had 0.11–1.0 μg g and 3% had 1.1–10.0 μg g (Tatsukawa, 1976).

3.3. Other halogenated compounds

Extensive background monitoring data for halogenated terphenyls, naphthalenes, dioxins and furans are not available. The isolated instances where environmental monitoring has been done have been in relation to special environmental contamination problems and have been discussed in the other chapters.

One open-ended use of polychlorinated terphenyls and biphenyls is in the investment casting industry. In the vicinity of one such factory in urban Chicago, Illinois, soil levels of 0.17–0.23 mg/kg were found 1000–1900 m away from the plant. The highest concentration was 13 mg/kg at a distance of 20 m from the plant. The chlorinated terphenyls most closely resembled Aroclor 5460. Most likely, contamination of the surroundings of the plant was from airborn particles (Stratton and Sosebee, 1976). Similarly, the polychlorinated terphenyls were also found in sewage sludge from a waste treatment plant which served an investment casting facility in Troy, Michigan.

Jan et al. (1978) have found 0.05–0.90 mg/kg PCT in fat and 0.005–0.80 mg/kg PCT in flesh of fish from Slovenia rivers flowing through industrial areas.

Trace amounts of PCT in the environment have also been reported from Japan (Doguchi, 1977), in a gull egg from the Rhone delta in Europe (Mestres and Illes, 1973) and in eggs and fat from herring gulls from the Bay of Fundy–Gulf of Maine area. Overall, however, the contamination of the environment with chlorinated terphenyls is not nearly as extensive at the moment as with chlorinated biphenyls.

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CHAPTER 9C

Occupational exposure

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9C.1. Introduction

Reports of illness associated with exposure to chlorinated organic chemicals of the type discussed in this book date back to the latter part of the 19th century (Herxheimer, 1899) and the early part of the 20th century (Bettmann, 1901; Wauer, 1918; Lehmann, 1905).

Extensive outbreaks following exposure to chlorinated naphthalenes occurred during World War I, but it was not until the middle of the 20th century that occupational illness from exposure to the other compounds has become a problem. Review of the available literature suggests a clinical syndrome that is produced by the halogenated biphenyls, naphthalenes, dibenzodioxins and dibenzofurans. It is presently not known whether halogenated terphenyls may cause similar problems. Some of the signs and symptoms observed following exposure to toxic levels of these compounds have been noted frequently (Table 9C.1). In all instances, the skin lesion, *chloracne*, was usually one of the first signs noted. Signs and symptoms such as weight loss, general malaise, nausea, loss of appetite, impairment of liver function, hepatic prophyria (porphyria cutanea tarda) (see Chapters 7, 8) and sensory neuropathy were less frequently reported. Other effects were occasionally associated with some outbreaks of occupational illness, but their significance is not well understood. Not all of the observed signs have been reported for all of the chemicals under discussion. Chloracne, weight loss and impaired liver function have been most frequently associated with exposure to toxic levels of these chemicals.

As outlined in Chapter 7, 2,4,5-trichlorophenol and all chemicals made from it may be contaminated with 2,3,7,8-tetrachlorodibenzodioxin. Pentachlorophenol

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TABLE 9C.1
Symptoms and signs reported after occupational exposure.

System	Lesion	Chemical	Reference[a]
General	bloodshot eyes, lassitude, headache, abdominal pain, impotence, weight loss, insomnia, alopecia, disturbance in taste	chlorinated naphthalenes	Good and Pensky, 1943
		technical pentachlorophenol	Baader and Bauer, 1951; Behrbohm, 1959
		2,3,7,8-tetrachlorodibenzodioxin	Jirasek et al., 1974
		chlorinated biphenyls	Jones and Alden, 1936
Skin[b]	chloracne, pruritus	2,3,7,8-TCDD	Kimming and Schulz, 1957
		chlorinated biphenyls	Jones and Alden, 1936
		chlorinated naphthalenes	Good and Pensky, 1943
		tech. pentachlorophenol	Behrbohm, 1959
		other tech. chlorinated phenols	Stingily, 1940; Dugois and Colomb, 1956
Liver	acute yellow atrophy, hepatocellular necrosis, mild fibrosis, fatty change, abnormal liver function, porphyria cutanea tarda	chlorinated naphthalenes (tetra-, penta-, hexa-)	Collier, 1943
		2,3,7,8-TCDD	Bauer et al., 1961; Bleiberg et al., 1964; Goldmann, 1972; Jirasek et al., 1974
		tech. pentachlorophenol	Truhaut et al., 1952; Gordon, 1956
		polychlorinated biphenyls (abnormal liver function tests)	Ouw et al., 1976
Digestive tract	anorexia, vomiting, hemorrhage	chlorinated naphthalenes	Good and Pensky, 1943; Dwyer, 1946
		2,3,7,8-tetrachlorodibenzodioxin	Hofmann, 1957; Goldmann, 1972
Peripheral nervous system	sensory neuropathy, peripheral neuritis	2,3,7,8-tetrachlorodibenzodioxin	Goldmann, 1972; Jirasek et al., 1974
Respiratory system	bronchitis, reduced vital capacity	technical pentachlorophenol	Baader and Bauer, 1951
		polychlorinated biphenyls	Warshaw et al., 1979

a. The symptoms and signs listed were observed by a number of other authors. The references listed serve merely as examples.
b. Depigmentation was reported in blacks for chlorinated naphthalenes by Cotter (1944).

may be contaminated with more highly chlorinated dibenzodioxins, dibenzofurans and hexachlorobenzene. The polychlorinated biphenyls contain trace amounts of chlorinated dibenzofurans and chlorinated naphthalenes. Whether chlorinated naphthalenes are contaminated with chlorinated dibenzodioxins and chlorinated dibenzofurans has not been established. In fact, little is known about the complete composition of the technical products that have caused outbreaks of occupational illness in the past.

The cases of chloracne which Herxheimer reported (1899) occurred in a room where caustic potash was produced by the electrolysis of potassium chloride. The chlorine was reacted with calcium to give calcium chloride. Herxheimer initially assumed that nascent chlorine had caused the dermatitis. Crow (1970a) pointed out that, although many authors clung to the nascent chlorine theory, the cause was halogenated hydrocarbons which originated from the tar lining in the absorption towers, or the anodes of tar, bitumen and charcoal that were used in the electrolytic manufacture of hydrochloric acid and similar substances. These tars were the sources of the cyclic compounds which became halogenated. Thus far, it has not been unequivocally shown whether specific isomers in the mixtures of chlorinated naphthalenes and biphenyls are the acnegenic agents and also cause some of the systemic toxic effects. Most chlorinated biphenyl mixtures are contaminated with 2,3,7,8-tetrachlorodibenzofuran which may contribute to their toxicity. Certainly the contaminants in 2,4,5-trichlorophenol and related products are the agents responsible for chloracne (Kimming and Schulz, 1957). Most likely the contaminant hexachlorodibenzodioxin in pentachlorophenol causes chloracne.

9C.2. Chloracne

Depending on the severity of the exposure and the susceptibility of the individual workers, some will develop an occupational disease commonly referred to as chloracne after having had exposure to the halogenated cyclic compounds mentioned above for several weeks or months. Following exposure to high concentrations of 2,3,7,8-tetrachlorodibenzodioxins, the onset may be more rapid. Even after a single exposure to 2,3,7,8-tetrachlorodibenzodioxins, the onset of chloracne may be delayed for several weeks, but if the exposure is severe, it may appear in as little as 2–3 days. One, or repeated short-term, exposure to 2,3,7,8-tetrachlorodibenzodioxin usually occurs during the production of 2,4,5-trichlorophenol when the reaction overheats, resulting in the increased production of the unwanted contaminant 2,3,7,8-tetrachlorodibenzodioxin. This exothermic reaction may give rise to explosions (Milnes, 1971).

The clinical features of chloracne, regardless of the type of chemical that caused it, have been most consistent. The most distinctive cutaneous lesion is the chloracne cyst (Crow, 1970b). This lesion is skin-colored and measures from 1 to 10 mm in diameter with a central opening. The other dominant lesion is the comedo (Figs. 9C.1, 9C.2). Usually these lesions start over the maxillary bone, then involve the

Fig. 9C.1. Only mild chloracne over maxillary bone is noted.

entire face, the neck and ears. Often the nose and nasolabial folds are not as extensively involved. In males, the genitalia may be involved. Furthermore, lesions may be present on the back, arms and legs, and other areas of the body, particularly where garments are in close contact with the skin. Depending on the severity, the skin contains only a few lesions (Fig. 9C.1) or the lesions are so close together that they give the skin a rough, grayish-brown appearance. The comedones and cysts can become secondarily infected and large pustules may form. Cysts may rupture and cause foreign body granulomata.

The chloracne-type skin lesion may be preceded by a faint rash which, in some cases, itches severely. In areas exposed to the sunlight, a photosensitivity-type reaction may occur and conjunctivitis with swelling of the eyelids and the rest of the facial skin may precede the development of chloracne. Since the workers are often exposed to the chloracnegenic agent, such as TCDD, as well as other chemicals, such as 2,4,5-trichlorophenol, it is not entirely clear whether the early rash is produced by the TCDD or due to the irritating effect of the 2,4,5-trichlorophenol or other substances.

Once chloracne has developed, it may remain active for many years, and particularly when secondary infections occur, deep-pitted scars may remain as a residual effect. These scars can be quite disfiguring (Fig. 9C.3). No specific treatment is available and most palliative means have not been very effective. Treatment in the

Fig. 9C.2. A worker with acute extensive chloracne.

past has included Vitamin A acid, UV light, X-ray, lancing and expressing of pustules. However, the best treatment is prevention, although dermabrasion has also been effective (Crow, 1970a).

The manufacture of these chlorinated hydrocarbons and the coating of wires and condensers with insulating materials and other industrial processes should be done in enclosed systems. Protective clothing provided by and laundered by the company should be handed out fresh daily. Shower baths after work should be compulsory and supervised. Sufficient shower facilities should be available so that workers are not delayed. Schwartz and Peck (1943) suggested synthetic wetting agents instead of soap as cleanser. They also recommended monthly skin examinations and liver function tests. In the United States, recommendations for a lower polychlorinated biphenyl standard were made by the National Institute of Occupational Health in 1977 (NIOSH, 1977) which suggests proper hygiene procedures to avoid dermal contact and recommends that occupational exposure be controlled so that no worker is exposed to PCBs at a concentration greater than 1.0 $\mu g/m^3$ of air deter-

mined as a time-weighted average (NIOSH, 1977a). The existing standards for occupational exposure to PCBs in different countries have been summarized by the International Labour Office (1970). They range from 0.5 mg/m^3 to 1.0 mg/m^3 in many countries.

It is particularly important that no potentially contaminated clothes are taken home since chloracne has been transmitted by this vehicle to other members of the family.

A skin lesion exactly like chloracne can be produced on rabbit ears or hairless mice and the muzzle of rhesus monkeys. In cattle and horses, a microscopically slightly different skin lesion which is also called hyperkeratosis or X-disease develops following exposure to compounds that produce chloracne in humans. In cattle and horses, the skin lesion is usually accompanied by hair loss in the affected areas and the epidermis is covered by a thick layer of keratin (Kimbrough, 1974; Kimbrough et al., 1977). Prior to the ability to detect chloracnegenic compounds by chemical analysis, the rabbit ear test was utilized to screen technical products for their presence (Adams et al., 1941) (see also Chapter 5).

In rabbits, monkeys and men, the microscopic appearance of the skin lesion varies, depending on the interval between last exposure and the time the biopsy was obtained. Microscopic examination of human skin biopsies from chloracne cases or tissue sections from rabbit ears with hyperkeratosis show markedly dilated hair follicles that are filled with keratin. Eventually the entire follicular appendage becomes transformed into a sac of keratin (Figs. 9C.4 and 9C.5). The sebaceous glands involute partially or completely. The epithelial cells lining the follicles and adjacent to them proliferate. Acanthosis is present and the individual prickle cells become enlarged. Polymorphonuclear leukocytes aggregate around hair follicles. This is followed by intrafollicular collections of leukocytes, microvescicles and abcesses within the follicular wall. Subsequently the follicular wall is destroyed and an abcess may develop. According to Shelley and Kligman (1957), who induced chloracne experimentally in 31 male adults with chlorinated naphthalenes, the sebaceous glands returned gradually months after the last application. Eventually, the epithelium lining the keratin-filled follicles atrophies.

Although on casual examination, chloracne resembles juvenile acne, the distribution of chloracne is quite different as is frequently the age of onset. Juvenile acne is characterized by papular eruptions due to inflammation with the accumulation of secretion of the sebaceous glands. Hyperkeratosis and atrophy of sebaceous glands does not occur in juvenile acne.

In a few instances in which workers developed chloracne following exposure to 2,3,7,8-tetrachlorodibenzodioxin, hypertrichosis and hyperpigmentation was pronounced (Jirasek et al., 1976; Bleiberg et al., 1964).

For many years, it was believed that chloracne was due to external contact and not the result of systemic exposure to the acnegenic agents. However, this belief is refuted by two episodes of accidental poisoning following ingestion of the acnegenic compounds. In one episode, 'Yusho' rice bran oil became contaminated with a

Fig. 9C.3. Residual scars subsequent to chloracne.

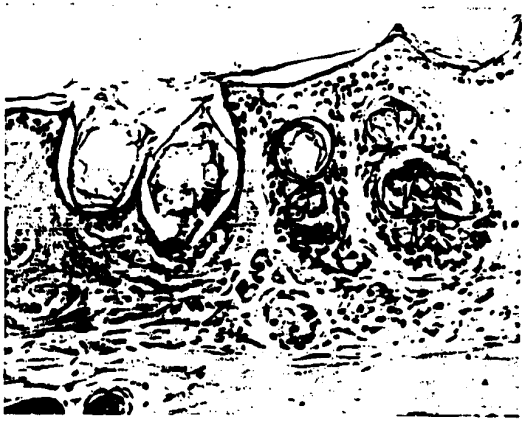

Fig. 9C.4. Follicular appendage of the skin from a normal rabbit ear.

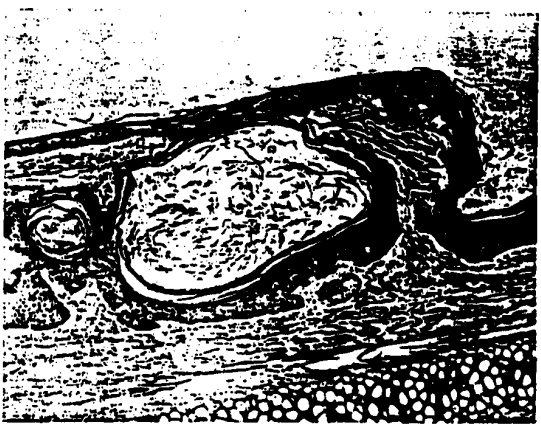

Fig. 9C.5. Follicular appendage from a rabbit ear affected by a chloracnegenic agent.

mixture of chlorinated biphenyls, quarterphenyls and dibenzofurans (Rappe et al., 1977; Miyata et al., 1978), and resulted in illness which included chloracne (Chapter 9B.1).

In 1945, six people fried vegetables in a fat-like substance thought to have been hexachloronaphthalene which they found in the bomb ruins of Berlin in Germany (Hertzberg, 1947) and subsequently developed chloracne. Similar skin lesions can also be produced in primates by oral exposure to chlorinated biphenyls or chlorinated dibenzodioxins (Barsotti and Allen, 1975; Allen et al., 1977). In rabbits, depending on the dose, application of acnegenic agents on the ear may either only result in local hyperkeratosis or at higher doses also produce a toxic effect on the liver (Kimbrough, 1977). Thus, local dermal application of these compounds, particularly the 2,3,7,8-tetrachlorodibenzodioxin may also lead to systemic disease. More recently, occupational exposure to 3,4-dichloroaniline and some herbicides made from it, such as propanil (*N*-(3,4-dichlorophenyl)propanamide) have also produced chloracne. In these instances, the toxic contaminant is tetrachloroazobenzene or tetrachloroazoxybenzene (Morse et al., 1979). These compounds are not as stable as the chemicals discussed in this book, and hence may be less of a problem.

9C.3. Presence of halogenated aromatics in human tissues and body fluids

Of all the chemicals discussed, only the chlorinated biphenyls have been measured with any frequency in human tissues. Chlorinated dibenzofurans were found in patients suffering from Yusho (Chapter 9B1) and in one instance, tissue was analyzed for 2,3,7,8-tetrachlorodibenzodioxin from a resident living in the Seveso area in Italy (Chapter 9B2). Brominated biphenyls are not as prevalent in human tissues as chlorinated biphenyls and are primarily found in the population of the state of Michigan, U.S.A. (Chapter 9A). Since the chlorinated biphenyls are lipophilic, the highest concentration is found in adipose tissue, although proportionally lower concentrations are present in other organs as well as blood. The different chlorinated biphenyl isomers are metabolized at different rates (Chapter 4) resulting in shifts in the gas-chromatographic pattern. The ratio of polychlorinated biphenyls between adipose tissue, other organs and blood varies somewhat, depending on whether exposure is current or took place in the past and whether the blood specimen was fasting. Pregnancy, weight loss and kidney disease may also affect this ratio. In order to determine the body burden of these compounds, adipose tissue would be the most suitable specimen for most of the halogenated aromatic compounds. Although appropriate for individual cases, it is usually not feasible to obtain adipose tissue samples in large population studies. In spite of the limited value of blood levels as an indicator of body burden, they can give some idea of the levels of exposure. A person with a polychlorinated biphenyl blood level of 10 ppb (μg/l) might at the most have adipose tissue levels of a few ppm (mg/kg) or less, while those with blood levels of 100 ppb (μg/l) might have adipose levels anywhere from 20 to 50 ppm (mg/kg). Since the chlorinated dibenzodioxins and chlorinated dibenzofurans, particularly the 2,3,7,8-tetra- isomer, are so extremely toxic, illness would be expected to be present at lower concentrations than for chlorinated bi-

TABLE 9C.2
Partial list of chemical companies where explosions or sudden accidental release of large quantities of TCDD has occurred during the production of 2,4,5-trichlorophenol and related products.[a]

Name of company	Place	Year	Reference
Monsanto	Nitro, W.Va., U.S.A.	1949	IARC, 1978
Badische Anilin und Soda Fabrik	Ludwigshafen, Rhein, G.F.R.	1953	Hofmann, 1957
Philips Duphar Ltd.	Amsterdam district, Haarlem, The Netherlands	1963	Dalderup, 1974a, 1974b
	Grenoble, France	1966	Dugois and Colomb, 1956
Coalite and Chemical Products Ltd.	Bolsover, U.K.	1968	May, 1973
	Hamburg, G.F.R.	1954	Schulz, 1957; Kimming and Schulz, 1957
ICMESA	Seveso, Italy	1976	Hay, 1979

a. Additional companies are listed by Hay (1979).

phenyls. These chemicals are also more polar and it is possible that their concentration in the liver may be different relative to the concentration in adipose tissue. However, this was not the case for the one resident from Seveso, Italy, who was studied in this respect (Chapter 9B2).

Low background levels of PCBs can be found in blood and other tissues of the general population of industrialized nations (Chapter 9A). Such background levels need to be considered when occupational exposure is evaluated.

Since PCBs are mixtures of chemicals, quantitation is quite difficult and a number of different ways of quantitating them have been proposed, such as adding the PCB peak heights of the gas chromatograms and comparing it to a known amount of standard (see Chapter 2). Because of these differences in quantitation, the differences in isomeric composition of the different PCB mixtures, and differences in individual susceptibility, it can presently not be predicted with certainty what a toxic blood or adipose tissue level constitutes in each case. However, in some individuals, PCB concentrations of 50 ppb (ng/g) in blood were associated with abnormal liver function tests (MMWR, 1978), while in other studies (Karppanen and Kolho, 1973), this was not the case. In capacitor plants where PCBs are heated and, therefore, volitalized, considerable respiratory exposure occurs (Table 9C.4). If PCBs are handled at room temperature as in the production and repair of transformers, dermal exposure may predominate.

Very little information is available linking PCB air levels to PCB blood levels, PCB adipose tissue levels or symptoms (Table 9C.3). Since PCB air levels may fluctuate a great deal, air monitoring may not adequately reflect exposure.

No published information is available on the presence of halogenated naphthalenes and terphenyls in workers. Neither have the chlorinated dibenzodioxins or dibenzofurans been extensively measured in the occupational setting.

TABLE 9C.3
PCB concentrations in the occupational environment and in blood of workers exposed to PCBs.

Duration of PCB exposure	PCB levels		Effects reported	Reference
	Environmental (mg/m^3)	Blood (ppb)		
Not known	10	–	unbearable irritation	Elkins, 1959
4–6 mo.	5–7	–	chloracne	Puccinelli, 1954
<1–20 yr.	0.2–1.6	370, ave.	chloracne, hyperpigmentation, liver injury	Hasegawa et al., 1972
2.5 yr. ave.	not reported	820. ave.	chloracne	Kitamura et al., 1973
2.5–18 yr.	0.013–0.27	36–286	irritation, liver injury	Levy et al., 1977
14 mo.	0.1	–	chloracne, liver injury	Meigs et al., 1954
2–23 yr.	0.32–1.44	>200	chloracne, liver injury	Ouw et al., 1976
Up to 15 yr.	not reported	7–300	chloracne, elevated triglycerides	Hara et al., 1974 Hara et al., 1975
	<1	74–1,900	no effect	Karppanen and Kolho, 1973

9C.4. Polychlorinated biphenyls

Chlorinated biphenyls (PCBs) were introduced into industry around 1929 and in the early 1930s. They were primarily used as dielectric fluids in capacitors and transformers. In capacitor plants, the chances of being exposed to PCB vapors were greater than in transformer plants. Later, the use of polychlorinated biphenyls expanded to other areas (Chapter 1). One of the first reports on health effects of polychlorinated biphenyls was made by Jones and Alden (1936). These authors examined 17 of 23 workers that were engaged in the production of polychlorinated biphenyls. All of the workers had chloracne. The chloracne involved the face, genitalia, trunk and extremities in many of the workers. Prior to the outbreak of chloracne in the plant, the electrical property of the chlorinated biphenyls had fallen below specifications and the color of the product had deepened. It was not determined whether this was caused by a change in the chemical composition of the material. The symptoms of illness in the report were more extensively described in the first worker that presented himself with chloracne. This worker complained of lassitude, loss of appetite and loss of libido. Unfortunately, it is not clear from the report whether a more than cursory attempt was made to determine systemic health effects. In 1937, Drinker et al. reported their efforts to determine whether chlorinated biphenyls had systemic health effects. Their studies were prompted by three fatal cases of jaundice in workers who had been exposed to chlorinated naphthalenes and chlorinated biphenyls. In only one of these three cases is the presence of chloracne mentioned. Exposure in all three instances was to tetra- and pentachloronaphthalene and 10% chlorinated biphenyls. Drinker et al. (1937) mention and warn against the use of carbon tetrachloride as a solvent since it may have additive toxic effects on the liver. Following these studies, a tabulation of 14 chlorinated hydrocarbons with permissible safe concentrations in the air of work-rooms was made (Drinker, 1939). Over the years, other cases of chloracne following exposure to chlorinated biphenyls were reported in the literature. Most of these involved exposure to vapors which developed when polychlorinated biphenyls or mixtures of chlorinated terphenyls were heated (NIOSH, 1977).

At times, the skin rashes that workers developed were accompanied by pruritus. Some of these workers had other complaints, such as burning of the eyes, nose and throat, dry throat, nausea and dizziness. Many of the workers were also exposed to trichlorobenzene. Meigs et al. (1954) reported chloracne in workers who had had exposure to polychlorinated biphenyl vapors for 5–14 months. The concentration of polychlorinated biphenyls in the workers' breathing zone was determined to be 0.1 mg/m^3. Evidence of slight liver injury was also present in these workers. Air level determinations in the earlier outbreaks of chloracne were not reported. Only recently have better and more accurate methods of PCB quantitation been developed. Thus, Ouw et al. (1976) found air levels in a capacitor plant which ranged from 0.32 mg/m^3 Aroclor 1242 (PCBs) to 1.44 mg/m^3. Workers in this environment complained of burning of the eyes, face and skin, and persistent body

odor. Nineteen of the 34 workers were employed in an impregnating room and had heavy exposure while the remainder of the workers assembled Aroclor dipped capacitor components and had less exposure. One worker suffered from chloracne and five complained of eczematous rashes. A few of the workers had abnormal liver function tests, elevated serum protein levels and others showed low levels of serum α_1-globulin. These workers had a mean PCB blood level of about 400 ppb (μg/kg). The control group in this study had no detectable PCB blood levels. This lack of PCB background levels in the general population of New South Wales was explained by the fact that environmental pollution with PCBs in that part of the world is much lower.

In most studies of workers with chloracne, evidence of liver injury was also found and in one study, abnormal liver function tests were present in workers who did not have chloracne (NIOSH, 1977). Elevated serum triglycerides have been found in exposed workers in the United States (Fishbein et al., 1979) and in Japanese studies. Similarly, Smith et al. (1978) found slightly elevated triglyceride levels and lower high and low density lipoproteins in workers slightly and moderately exposed to PCBs when fasting plasma levels were compared to controls. Similarily, Sak and Ahlers (1977) observed significantly elevated serum concentrations of triglycerides, total cholesterol and phospholipids in workers occupationally exposed to polychlorinated biphenyls. Many factors can influence serum lipoprotein levels (Beaumont et al., 1970), such as diet, excessive alcohol consumption, pregnancy, exercise, emotional stress, smoking, estrogens, other hormones and medications, such as salicylates. In addition, hyperlipoproteinaemia also occurs in a number of common diseases, such as hypothyroidism, insulin-dependent uncontrolled diabetes, nephrotic syndrome, biliary obstruction, pancreatitis, dysglobulinemia, or auto-immune hyperlipoproteinemia. It would be of great importance to determine whether halogenated biphenyls and related compounds do generally also have such an effect as a few studies suggest, and at what exposure levels this effect occurs.

Animal studies suggest that lipid metabolism in the liver may be affected by halogenated biphenyls (Kimbrough et al., 1972).

Another effect of PCBs on the liver is the induction of *mixed-function oxidases*. This has been studied extensively in animals. Alvares et al. (1977) determined that in 5 workers occupationally exposed to Aroclor 1016, a PCB mixture primarily composed of di-, tri-, tetra- and pentachlorobiphenyls, plasma antipyrine half-life was significantly lower than in matched controls. These workers had been exposed to Aroclor 1016 for at least 2 years and had no obvious signs or symptoms of PCB poisoning, such as chloracne or abnormal clinical liver function test results. Other health effects that have been reported more recently are eye and upper respiratory irritation. Thus, Warshaw et al. (1979) studied a group of 326 workers in a capacitor plant with a mean employment of more than 15 years and a mean age of 41.1 years for males and 47.3 years for females. Work-related eye or upper respiratory irritation was reported by 48% of the workers, and 10% had experienced tightness in the chest. Spirometric studies were conducted on 309 workers; 66 of them were

dropped from the study because of exposure to talc, textile dust or asbestos, leaving 243 for analysis. In males, there were about twice as many smokers and exsmokers as nonsmokers. In females, the proportion of nonsmokers was higher. Thirty-four of the workers (14%) had a reduced vital capacity and 27 of these demonstrated a restrictive pattern of impairment (FEV/FVC >0.7). According to Warshaw et al. (1979), the prevalence of restrictive impairment in the capacitor workers is comparable only to that found in asbestos workers. The vital capacity in PCB workers that had no opportunity to be exposed to asbestos should be studied to confirm these findings.

No conclusive evidence has thus far been reported which demonstrates that occupational exposure to PCBs has caused an increased incidence of cancer.

Bahn et al. (1976) reported results of a preliminary investigation. This study consisted of a search of chart records of a group of 51 research and development employees and 41 refinery plant employees at a New Jersey petrochemical facility. Between 1949 and 1957, these workers had been exposed to Aroclor 1254, a PCB mixture composed of chlorinated biphenyl homologs from mono- to heptachlorobiphenyl. Three melanomas and two carcinomas of the pancreas were found. This incidence was significantly higher than the expected rates. Since exposure to other chemicals also occurred and since the cohort was small, further studies are necessary to determine whether PCBs have caused cancer in humans. A retrospective mortality study conducted by the U.S. National Institute of Occupational Health (CDC) may provide additional information in the near future.

9C.5. Chlorinated naphthalenes

Following the early reports of chloracne which were caused by chlorinated tar products (Herxheimer, 1899; Bettman, 1901), the second episode of outbreaks of occupational chloracne occurred during the first World War following exposure to the chlorinated naphthalenes. Chlorinated naphthalenes (halowaxes) were used in the production of gas masks. Wauer (1918) referred to chloracne as 'pernakrankheit'. The term 'perna' originated from '*per*chlor*na*phthalin'. The chlorinated naphthalenes were also used to impregnate fabric and to make soles for shoes (Teleky, 1927). After World War I, this use of chlorinated naphthalenes stopped. A few years later, the chlorinated naphthalenes were used in the mining industry as water and fire resistant insulating material for detonators. This resulted in outbreaks of chloracne in 1926 and 1927 among workers that produced such detonators (Teleky, 1927). Subsequently, around 1930, chlorinated naphthalenes (Mayers and Silverberg, 1938) and chlorinated diphenyls were used as insulating material for cables and condensers. In the United States, several hundred cases of illness following exposure to chlorinated naphthalenes were reported. Among them were several deaths due to acute yellow atrophy of the liver (Jones, 1941; Sulzberger et al., 1934, Flinn and Jarvik, 1936). However, such cases were isolated and it is possible that such additional factors as infectious viral hepatitis may have contri-

buted to the disease. Since workers in many instances were exposed to mixtures of chlorinated naphthalenes and biphenyls, it was not clear what actually caused the systemic illness. The industries concerned then initiated a study of the toxicity of these products (Drinker et al., 1937). This resulted in improved occupational hygiene and the establishment of exposure limits at the work place and the use of lower chlorinated substances which seemed to cause less health effects. During World War II, chlorinated naphthalenes and chlorinated biphenyls were extensively used in the ship-building industry. Painting the surface of the ships with these chemicals neutralized them against magnetic contact mines. Furthermore, the chlorinated naphthalenes were also used as insulating material for cables. In this industry, illness was observed not only in the workers who insulated the cables, but also in the workers who handled the cables after they had been manufactured. Although the use of chlorinated naphthalenes has declined, they are still used occasionally because of their low cost. Weber (1969) reported chloracne in the cable industry where chlorinated naphthalenes were used. Kleinfeld et al. (1972) described an episode in 1972 where 92 workers were exposed to a mixture of tetra- and penta-chloronaphthalenes in the manufacture of insulated electrical coils. In many of the industrial processes, the chlorinated naphthalenes were heated, producing vapors to which the workers were exposed. Although the fact that these compounds caused chloracne had been known for years, the serious systemic effects were not generally recognized until the 1930s and 1940s. The first complaints of the workers were digestive disturbances, burning of the conjunctivae, and in some instances sexual impotence and haematuria (Von Wedel et al., 1943). Other complaints were blood-shot eyes, lassitude, headaches, abdominal pain, weight loss, insomnia, alopecia, and disturbances in taste (Good and Pensky, 1943). A number of case reports appeared in the literature in the '30s and '40s describing patients who worked with chlorinated naphthalenes, developed acute yellow atrophy of the liver and died (Greenburg et al., 1939). Cotter (1944) described a number of such cases. Most of these patients were exposed to chlorinated naphthalenes for several weeks to several months before they became ill. In many instances, chloracne was not recorded in the case reports, and in some instances it was pointed out that it was not present. The following account by McLetchie and Robertson (1942) gives a description of the typical clinical course of these workers:

"This 41-year-old female was admitted with a history of nausea, vomiting, and jaundice of four weeks duration. She had been employed for the past six months at a process which exposed her to fumes of chlorinated naphthalenes. A number of her coworkers had developed an acneform dermatitis, but there was no other case of jaundice. About 8 weeks before admission, the patient began not to feel well and noticed that in the evening, her feet and ankles became swollen. Permanent puffiness developed around the eyes. Two weeks later, she became breathless on slight exertion, jaundice developed four weeks prior to admission. Shortly after onset of jaundice, troublesome nausea developed. However, she did not lose any weight. Vomiting also occasionally occurred. The patient noticed that her urine was

becoming darker while her stools were grayish in color. Physical examination on admission revealed a well-nourished patient which showed no signs of any great discomfort and was mentally alert. A definite but not deep icteric tinge of the skin and conjunctivae was present and a faint purpuric rash was noted on the legs and lower abdomen. There was also slight edema around the ankles and puffiness of the tissues around the eyes. The physical findings were essentially negative except for a slight increase in the area of cardiac dullness and a slightly diminished liver dullness. The urine was dark brown and contained bile. On the third day after admission, the patient became drowsy and the jaundice increased in intensity. Muscular twitching of all limbs developed. A patchy-brown discoloration of the skin over the arms and the chest was noted. The patient continued in coma, the pulse rapidly increased in rate, and she died on the fifth day after admission. On post-mortem examination, two pints of straw-colored fluid were found in the peritoneal cavity and there was marked edema of the loose retroperitoneal tissues. The liver was very small, shapeless, collapsed under a wrinkled capsule, soft in consistency with few firm nodules scattered throughout. The nodules varied in size from a few millimeters to 2.5 cm in diameter. The liver weighed 650 grams (normal 1,500 grams). On section, the nodules were of a dull-yellow color. The intervening soft tissue was mainly red. The gallbladder was normal; the stomach contained much dark-brown mucus. The kidneys were stained deep green, and the heart revealed moderate hypertrophy and slight dilitation of the right ventricle. The cardiac valves showed chronic rheumatic endocarditis. On histologic examination, the liver showed a varying picture of acute damage, fibrous proliferation and regeneration. Large areas of autolyzed, necrotic, hepatic parenchyma were noted. Islets of surviving epithetial tissue in areas with collapsed sinusoids where dead hepatocytes had been resorbed were noted. In these areas, congestion, hemorrhage, and round cell infiltration was also present. Furthermore, small areas of liver parenchyma were surrounded by bands of young connective tissue which contained many poorly formed bile ducts. The pancreas showed minute ares of necrosis in the pancreatic fat. No other findings of note were made."

The livers of the fatal cases reported by Cotter (1944) showed in many areas complete absence of hepatic cells, bile duct proliferation, hemorrhage, and an inflammatory reaction. None of his cases showed typical chloracne although one patient had a papular rash of the forearms. Cotter points out that in blacks, depigmentation of the skin may be one of the early manifestations of illness. Another interesting observation among the seven cases reported by Cotter was the fact that one worker became jaundiced after a year of working with chloronaphthalenes. He was transferred to a department where he did not come in contact with these chemicals and his jaundice subsided, but recurred when he was put back on his original job. Although in most of these instances, the workers were exposed to vapors of chlorinated naphthalenes, Peck (1944) noted an increasing incidence of acne-like lesions in electricians who were installing cables on ships during the second world war. These cables had been coated with chlorinated naphthalenes and chloro-

diphenyls. The chloracne was usually found in electricians engaged in stripping (the coated cables). The halowax which was stripped off was impregnated in asbestos which was wrapped around the wires as insulation.

Experimental studies were carried out with the chlorinated naphthalenes which caused outbreaks in different working situations. These mixtures were composed of chlorinated naphthalenes with various percentages of chlorination. Teleky (1927) pointed out that in factories where the substances used contained only 14% chlorine, the incidence of chloracne was much reduced. In one of the companies, the health status of the workers was greatly improved when naphthalenes with only 7–8% of chlorine were substituted for those with higher percentages of chlorine. A number of experimental studies stimulated by the health problems observed in workers exposed to these chlorinated naphthalenes demonstrated that the penta- and hexachloronaphthalenes seemed to be the most toxic. This experimental work also indicated that mixtures of chlorinated naphthalenes with chlorinated diphenyls increased the toxicity of these materials (Von Wedel et al., 1943). During that time, the most extensive studies were done by Bennett et al. (1938). In these studies, the trichlornaphthalenes were less hepatotoxic than the higher chlorinated compounds and the chlorinated diphenyls were considered to be the most toxic of all. However, no chemical analyses for any of these compounds were performed at the time to determine whether any toxic impurities might be present. Similarly, Shelley and Kligman (1957) tested a number of halowaxes for acnegenic potential in humans. The following mixtures of chlorinated naphthalenes were tested:

Mono- and dichloronaphthalenes (Halowax 1000), tri- and tetrachlornaphthalenes (Halowax 1001), penta- and hexachlornaphthalene (Halowax 1014), heptachlornaphthalene (Halowax 1052) and octachlornaphthalene (Halowax 1051). Of these, only the mixture of penta- and hexachlornaphthalene produced chloracne. The other four chlorinated naphthalene mixtures were without effect. However, Mayers and Silverberg (1938) reported a series of patients who had developed chloracne after being exposed to a mixture of tri- and tetrachlornaphthalenes. Again, no chemical analysis of this particular mixture was done. On the other hand, studies in rabbits injected with mixtures of tri- and tetrachlornaphthalene, or tetra- and pentachlornaphthalene or penta- and hexachlornaphthalene only showed liver damage when they were given the penta- and hexachlornaphthalenes, but not when they were given the mixtures of the other chlorinated naphthalenes. Thus, most of the clinical observations as well as the available experimental data seem to indicate that the penta- and hexachloronaphthalenes are the most toxic components of the mixtures of chlorinated naphthalenes.

9C.6. Contaminants (chlorinated dibenzodioxins and chlorinated dibenzofurans)

Chlorinated dibenzodioxins and chlorinated dibenzofurans are contaminants of a number of commercial products (Chapters 1, 2). The only documented episode of substantial exposure of humans to chlorinated dibenzofurans occurred in Japan,

and these subjects were also exposed to polychlorinated biphenyls (Chapter 9B1). It is known that products such as pentachlorophenol are contaminated with chlorinated dibenzodioxins and chlorinated dibenzofurans, but in the published reports dealing with occupational exposure to technical pentachlorophenol no efforts have been made to distinguish the effects of these trace contaminants from those of pentachlorophenol per se. Through the efforts of Kimming and Schulz (1957), it is known, however, that to a large extent, illness caused by technical 2,4,5-trichlorophenol and all products made from 2,4,5-trichlorophenol is actually caused by TCDD. TCDD is the most toxic isomer of the group of chlorinated dibenzodioxins (Chapter 5).

Occupational exposure to TCDD may occur in the production of 2,4,5-trichlorophenol and all products for which 2,4,5-trichlorophenol is used as starting material. In addition, exposure to commercial products contaminated with TCDD may also result in illness.

Two types of exposures have occurred in these occupational settings. Workers may be exposed daily to TCDD during normal production of 2,4,5-trichlorophenol and its end products. In this type of setting, chloracne developed gradually in some workers after they have been exposed for several weeks or months. In addition, these workers may also show systemic illness.

The other type of occupational illness has a more sudden onset. When 2,4,5-trichlorophenol is produced from tetrachlorobenzene, unless the reaction is carefully controlled, it may overheat and result in an explosion of the reaction vessel. Once the temperature of the reaction exceeds 160°C, increasing amounts of TCDD are also formed. Exposure of workers to TCDD during the explosion and subsequently during clean-up operations has often been quite heavy and has resulted in the onset of chloracne in a week or two, sometimes accompanied by systemic illness. A number of such episodes have been published in the literature and some are listed in Table 9C.2. Clean-up crews and maintenance men are particularly endangered.

Acute symptoms occurring after such accidents have consisted of headaches, nausea and dizziness. Rarely, severe itching, redness and swelling of the face or other areas of the skin may develop, and swelling of the eyelids with conjunctivitis may also be present. Within two or three weeks chloracne develops and systemic illness, such as weight loss, easy fatigueability and aching muscles, particularly in the lower extremities and chest, may be present. Other complaints often recorded were insomnia, irritability and loss of libido. The liver may become tender and enlarged, and sensory changes, particularly in the lower extremities, have been observed. Total serum lipids may be increased and the prothrombin time may be prolonged. Symptoms may be quite persistent, particularly the severe aches and pains which are manifestations of peripheral neuropathy and the fatigueability (IARC, 1978; Bauer et al., 1961; Bleiberg et al., 1964; May, 1973; Jensen and Walker, 1972; Oliver, 1975). Unfortunately, since chloracne is the most obvious manifestation of TCDD poisoning, the systemic effects have been less well studied

and reported. While in some episodes, chloracne seems to be the only significant health effect (May, 1973) in most episodes, systemic illness was also noted. Unfortunately, a number of these episodes either have not been published at all or have only been insufficiently reported, such as the accident which occurred in Nitro, West Virginia, in 1949 or the health effects observed in the Philips Duphar Co. in the Netherlands. The reports made by Bauer et al. (1961), Schulz (1957), Bleiberg et al. (1964), Oliver (1975), Goldman (1972) and Jirasek et al. (1976) describe systemic effects in more detail. Most of the persons exposed in industrial settings were exposed to a mixture of chemicals, such as 2,4,5-trichlorophenol, TCDD, 2,4,5-trichlorophenoxyacetic acid, and, in the episode reported by Jirasek (1976), also to pentachlorophenol. It is, therefore, not clear whether all effects were solely caused by TCDD. Only the two laboratory workers studied by Oliver (1975) had exposure to pure TCDD.

Systemic illness is usually reported only in workers with chloracne. However, Jirasek et al. (1976) cite 4 workers with systemic illness without chloracne. From the other published reports, it is not clear whether all exposed workers were examined for systemic illness or whether they were selected on the basis of chloracne which may have led to the prhaps erroneous assumption that in humans, illness caused by TCDD must always be accompanied by chloracne.

Jirasek et al. (1976) found that a number of their patients had porphyria cutanea tarda. In addition to the chloracne, hypertrichosis and hyperpigmentation were noted. Abnormal liver function test results (elevated SGOT and SGPT) were obtained for 11 of 80 patients. In more than half of the workers, total cholesterol, total lipids, and phospholipids were elevated. Urinary uroporphyrins were elevated in 23 workers. Thin layer chromatography showed that urinary 8- and 4-carboxyporphyrin were increased. Both liver and urine fluoresced under UV light. A peripheral neuropathy was documented in 17 of these workers. In 4 workers, localized effects on the central nervous system were also observed. In the outbreak reported by Bleiberg et al. (1964), a number of workers had, in addition to chloracne, abnormal excretion of urinary uroporphyrins, hirsutism, and hyperpigmentation. Six years later, in a followup study of the same plant, only one worker had persistent uroporphyrinuria (Poland et al., 1971). In addition, a number of authors (Schulz, 1957; Bauer et al., 1961; Jirasek et al., 1976; Oliver, 1975) observed a neurasthenic syndrome characterized by a lack of drive and vigor, sleep disorders, emotional instability and diminished libido or potency (Kleu and Goltz 1971).

Bauer et al. (1961) studied three groups of workers in Germany who had developed chloracne and/or systemic illness after working in the production of chlorinated phenols. Liver biopsies of three workers showed in one instance a fatty liver with slight fibrosis and an inflammatory reaction, and in two instances, 'perihepatic' changes and a brown pigment which stained partially positive for iron. A liver biopsy from another showed a gray pigment which was not positive for iron.

Among the long-term followup studies reported thus far in workers exposed to

TCDD is one by Thiess and Goldmann (1976). Of the 53 original workers exposed to TCDD in 1953, 22 were still employed by BASF in 1976; 3 workers received partial compensation – 1 for persistent chloracne, 1 for residual paresis of the left leg, and 1 because of deafness. Apart from residual scars, the other 18 workers had no persistent skin lesions in 1976. Causes of death were as follows: 2 – myocardial infarct, 4 – cardiovascular decompensation, 4 – carcinoma of different sites, 1 – mitral stenosis, 2 – suicide, 1 – bleeding of the esophagus. As mentioned, one worker had died earlier (Goldmann et al., 1972). No information was given on the 16 retired workers. This study illustrates how persistent the chloracne may be in some individuals.

Recently, a followup study was also conducted on the workers in Nitro, West Virginia (Zack and Suskind, 1980) in which the acute symptoms initially suffered by the workers were described. Aside from the symptoms and signs already mentioned, 4 of 6 workers who were examined in 1949 and 1950 had an enlarged liver and a delayed prothrombin time at that time. A regression of symptoms and signs was observed in these workers when they were reexamined in 1953. The mortality experience of 121 of these workers who had developed chloracne following the explosion in 1949 was also reported. Among this group of workers, 32 deaths were recorded against 46.41 expected. There were 9 deaths from malignant neoplasms with 9.04 expected. There were 5 lung cancer deaths versus 3.02 expected, 1 skin cancer death with 0.15 expected, and 3 deaths from neoplasms of lymphatic and hematopoietic tissue.

A followup examination of 11 of 23 workers who had first become sick in 1953/1954 following exposure to TCDD were reexamined in 1976 (Krause and Brassow, 1978). The chloracne had completely disappeared in only 2 workers. Seven of the 11 still complained of epigastric pain, nausea and intolerance of alcohol. Six of the 11 had an enlarged liver which was not present when they were examined in the 1950s and 6 of the 11 had at least one abnormal liver function test. Furthermore, Hardell and Sandström (1979) have reported an increased incidence of mesenchymal tumors in workers who were either exposed to technical 2,4,5-trichlorophenol or 2,4,5-trichlorophenoxiacetic acid. The problem with all of these studies is that the number of cases examined is small. Hardell and Sandström tried to control for that by conducting a case control study where they matched 4 controls to each case by age, sex and locality. However, by excluding all control cases with cancer, they may have biased their study.

Another chlorinated phenol, pentachlorophenol, is used extensively as a wood preservative and fungicide. This product is contaminated with chlorinated dibenzodioxins and chlorinated dibenzofurans, but usually with the hexa-, hepta- and octahomologs (Chapter 2). Occasionally, workers engaged in the production of pentachlorophenol have also developed chloracne (Baader and Bauer, 1951) and complaints such as neuralgic pain in the lower extremities, persistent bronchitis and eye irritation (Behrbohm, 1959). The bronchitis seems to be more prevalent in workers exposed to technical pentachlorophenol than to the other technical products

discussed in this chapter. Workers dealing with wood preservatives again experience mixed chemical exposure. Other chemicals used in such industries include organic arsenic and tin compounds, copper derivatives and creosotes. Pentachlorophenol per se is an uncoupler of oxidative phosphorylation and, like 2,4-dinitrophenol, increases the metabolic rate, resulting in hyperthermia, profuse sweating and weight loss. A number of fatalities following exposure to pentachlorophenol have been described (Mason et al., 1965, Bergner et al., 1965). In these cases, absorption of several hundred mg of pentachlorophenol has usually occurred in severe or fatal poisoning and pentachlorophenol blood levels as high as 10–20 ppm (μg/g) have been measured soon after exposure. On the other hand, workers in wood-treating plants may reach pentachlorophenol blood and urine concentrations as high as 10–20 ppm without symptoms of toxicity (Casarett et al., 1969). Simultaneous exposure to heat may make workers more susceptible to the toxic effects of pentachlorophenol. Since pentachlorophenol is used extensively, detection of ppb (ng/g) concentrations of pentachlorophenol in blood or urine must be considered to represent background levels which are frequently detected in the general population (Bevenue et al., 1967; Casarett et al., 1969). In some fatal human cases, hepatocellular necrosis was observed (Truhaut et al., 1952; Gordon, 1956). Whether these effects resulted from the simultaneous exposure to toxic contaminants in pentachlorophenol has never been investigated (see also Chapters 2 and 5). Vacuolation of hepatocytes was also noted in livers of infants who were accidentally exposed to technical-grade pentachlorophenol in a nursery (Robson et al., 1969).

9C.7. Chlorinated terphenyls and brominated compounds

Essentially no information is presently available on halogenated terphenyls and only one preliminary study on workers exposed to brominated biphenyls has been conducted (Kay, 1977). In addition, Bahn et al. (1980) examined 35 workers of a total cohort of 86 men who had been engaged in the manufacture of decabromobiphenyl and decabromobiphenyl oxide. A total of 89 control subjects were chosen from steel workers and wire men. Studies of thyroid function revealed four cases of primary hypothyroidism in the 35 exposed workers and in none of the controls. This represented a prevalence of 11.4% which is statistically significantly higher than the background incidence of 2.8% found in males in the United Kingdom. Since the group of subjects studied was small, additional studies will have to be done to determine how prevalent hypothyroidism is following exposure to these types of compounds.

Summary

The occupational diseases caused by halogenated biphenyls, terphenyls, naphthalenes, dibenzodioxins and dibenzofurans were reviewed. Occupational illness has primarily occurred following exposure to 2,3,7,8-tetrachlorodibenzodioxin, chlorin-

ated biphenyls and chlorinated naphthalenes. The health problems associated with exposure to these compounds include chloracne, liver disease, porphyria cutanea tarda, and neuropathies. Not much is known about the other compounds mentioned.

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Detoxication
of Hazardous Waste

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PURPOSE AND SCOPE OF THIS BOOK (PREFACE)

A great variety of treatment techniques can be applied to solve our current pollution problems. The chapters in this book demonstrate that detoxication of hazardous waste can be achieved by creative adaptation of existing, fundamental knowledge by workers with a multidisciplinary outlook. However, the actual implementation of the technical solutions often depends on the necessary interaction with nonscientific members of society and on numerous value judgments and decisions about risk levels, potential consequences and political realities.

This book, based on a symposium by the Division of Environmental Chemistry of the American Chemical Society, focuses on the detoxication of hazardous waste as an alternative and/or a complement to storage and destruction techniques. The book contains four sections:

1. incineration and waste management;
2. treatment, recovery and destruction of polychlorinated biphenyls (PCB);
3. a case study of the destruction of dioxins; and
4. the biological detoxication potential of genetic engineering, microbial and enzymatic techniques.

Section 1 describes the design and operation of multipurpose industrial incinerators for regional waste treatment centers. The question of destruction of hazardous components and their removal efficiency as a function of operating conditions of the incinerator is discussed, and the ranking of hazardous compounds for incinerability is debated in several fundamental chapters. The concern about the potential emission of toxic combustion by-products such as polychlorinated dioxins and furans is addressed and illustrated by data on the emission of these compounds during incineration of PCB.

Section 2, on PCB detoxication, illustrates the diversity of possible approaches to treating a specific type of waste and serves as a model for detoxication of other pollutants. Land- and ocean-based, molten salt, diesel, and cement kiln incineration have been tested. Plasma arc and other high-temperature processes have been explored. The treatment of PCB-contaminated transformer fluids illustrates the role of detoxication in recovery and reuse of valuable chemicals. PCB destruction by organometals, ultraviolet light, alkali metal alkoxides and chemical reduction are feasible and have been tested by numerous investigators.

No compounds, other than perhaps PCB, have achieved the public recognition and fear of polychlorinated dibenzodioxins. The case study of a project that destroyed 7 kg of tetrachlorodibenzodioxin in a complex, hazardous waste illustrates how social values, political judgments and legal requirements affect attempts to detoxicate hazardous waste. In addition, the project demonstrates clearly that the technical expertise exists to solve even the most difficult pollution problem.

Section 4 focuses on the future by examining the exciting potential of selected mutation or genetic engineering of microorganisms to detoxicate hazardous waste, and contaminated soils, lagoons or groundwaters. Also, enzymes may catalyze slow chemical reactions for treating pollutants.

Although these biological methods appear attractive, many problems still must be overcome. In the meantime, we have available a wealth of fundamental knowledge that can be adapted to pollution problems by chemists, engineers, microbiologists, physicists, geologists, toxicologists and many others. At present, implementation of technical solutions is being delayed by legal, political and societal discord and arguments. A number of solutions to diverse pollution problems are offered in this book. I hope that these solutions can demonstrate what can be accomplished if we have the will to actually solve the problem of hazardous waste.

Jurgen H. Exner

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I thank Dr. R. B. Pojasek for suggesting the possibility of this book, B. Monopoli for her tireless editorial assistance and my family for accepting many lost weekends.

Jurgen H. Exner manages the research and development activities of IT Enviroscience, Knoxville, Tennessee, the consulting and engineering division of IT Corporation, a national waste management company headquartered in Wilmington, California. He received a PhD in Organic Chemistry from the University of Washington in 1968 and a BS from the University of Minnesota in 1963. During the last seven years he has assessed waste profiles and disposal options for wastes from chemical and pharmaceutical manufacturers. He has developed and implemented processes for recovery, treatment or detoxication of organic residues, metals, halogenated aromatics and toxic gases. His most recent accomplishment was to develop and carry out a process for destroying the highly toxic tetrachlorodibenzodioxin in a hazardous waste. His work in hazardous waste treatment and disposal and in organometal, carbanion and cation chemistry has been published in 21 articles and talks. He has been granted seven patents from his work at Dow Chemical and IT Enviroscience.

Dr. Exner organized and was chairperson of a two-day symposium of detoxication of hazardous waste at the 182nd National Meeting of the American Chemical Society, New York, August 1981. Dr. Exner was the 1981 chairman of the East Tennessee Section of the ACS. He is a member of Phi Beta Kappa, Tau Beta Pi and Phi Lambda Upsilon.

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INTRODUCTION

Disposal of toxic wastes is a global problem that industrialized nations now have begun to confront in a systematic fashion. Public awareness has led to the passage of the Resource Conservation and Recovery Act (RCRA) of 1976, which regulates disposal and restricts what can be stored permanently in the ground. Such regulations are changing slowly the economics of waste disposal and, at long last, the potential benefits of source control, and recovery and recycle of waste, are being pursued earnestly. Only after rigorous investigation of recovery and recycle should landfilling or destruction alternatives be deemed appropriate. Nonetheless, these alternatives, especially underground storage, remain economically attractive. Still, increasing long-term legal liabilities and the potential for groundwater contamination are forcing a shift from storage to treatment or total destruction. This book, which is based on a symposium by the Division of Environmental Chemistry of the American Chemical Society, focuses on detoxication of hazardous waste as an alternative and/or an addition to storage and total destruction techniques.

Wastes can be detoxicated by chemical, physical or biological techniques. These methods can also be used to modify wastes destined for landfill or total destruction by incineration. Preferably, detoxication allows recovery and reuse of the valuable chemicals in hazardous waste. Detoxication techniques are generally carried out in small and economical equipment; therefore, treatment can be carried out at the location where the waste is generated or located. The portability of detoxication equipment should allow its use during cleanup of abandoned dump sites. Detoxication of contaminated soil is especially attractive because incineration or landfill disposal is so expensive. Suitable soil detoxication procedures would be ideal methods for cleanup of spills.

In a democratic society, hazardous waste is understandably as much a political as a scientific issue, and legal, social and political issues do affect

the technical solutions that can be applied to solve pollution problems. There is no "typical waste," and there are thousands of toxic chemicals. Our present legalistic industrialized society has attempted to characterize hazardous wastes rigorously without much concern about the degrees of hazard. Hazardous waste under RCRA is defined as those materials that are ignitable, corrosive, reactive or toxic. Ignitable wastes are those that can give off heat, smoke and particulates, or disperse toxic pollutants and by-products through the environment. Corrosive wastes are those that can cause injury to tissue, or, through destruction of containers, be released to the environment. Reactive wastes are those that can detonate or give off toxic gases by reaction with water or air. Toxicity is the most elusive criterion used in classifying hazardous wastes. The U.S. Environmental Protection Agency (EPA) extraction procedure (EP toxicity) requires that chemical concentrations in the extract do not exceed the National Interim Primary Drinking Water Standards by more than 100. This definition assumes dispersion of the pollutant through a landfill into groundwater and is limited to well defined chemicals. Toxicity of chemical wastes must take into account the acute and chronic effects of chemicals. Generally, acute (short-term) criteria for oral, inhalation and dermal toxicity are considered to be death in humans at low doses, dermal LD_{50} (rabbit) of less than 200 mg/kg, oral LD_{50} (rat) of less than 50 mg/kg, inhalation LD_{50} (rat) of less than 2 mg/l, or any serious irreversible illness. The impact of chronic (long-term) toxicity effects poses exceedingly difficult questions because of uncertainties surrounding the no-effect level, a concentration threshold below which no carcinogenicity, mutagenicity, teratogenicity, or plant and animal toxicity exists. A great deal of controvery surrounds the concept of a threshold to toxicity. Consequently, risk assessments must be carried out to estimate the potential for harm due to the discharge of a waste to the environment. Also, of course, there is a direct correlation between the degree of concern over a pollutant and its detectability, persistence, degradation, migration or bioaccumulation in the environment.

In the final analysis, however, society decides which chemicals are toxic. The chapters in this book focus on polychlorinated biphenyls (PCB) (which were specifically regulated in the United States in 1979 under the Toxic Substances Control Act), priority pollutants specified in the Clean Water Act of 1977, and the hazardous constituents associated with RCRA. The detoxication methods described in this book are designed to convert wastes or specific constitutents in the waste to residues that present a reduced risk of health or environmental danger and which are more acceptable to society.

The book is divided into four sections: incineration and waste manage-

ment; treatment, recovery and destruction of PCB; a case study of the destruction of dioxins; and the biological detoxication potential of genetic engineering, microbial and enzymatic techniques.

In the United States, treatment of hazardous wastes at regional waste management centers is a common and economical disposal method. Major improvements in capability and degree of detoxication can be achieved by the integration of various chemical engineering unit operations with multipurpose thermal oxidation complexes. Consequently, the new waste management complexes are much more sophisticated than existing facilities. In addition, typical engineering operations (such as carbon adsorption, distillation, steam or air stripping, precipitation and coagulation, and biological treatment) are combined to pretreat, detoxicate and recover waste constituents. Stabilization of inorganic wastes is necessary before landfilling, to reduce their environmental impact, but the general applicability of stabilization suffers from poorly conceived testing procedures and public misconceptions. Incinerators are the heart of regional waste management facilities and, until recently, little hard scientific information was available about efficiency of destruction and chemical processes within the burning chamber. RCRA has affected the design of hazardous waste incinerators by requiring specific destruction and removal efficiencies. At the moment, there is considerable debate about ranking the incinerability of hazardous compounds. Nevertheless, incineration of wastes to carbon dioxide and inorganic constituents offers the most flexible, economical detoxication methods for a wide variety of nonrecoverable hazardous wastes. In addition, incineration allows energy recovery as useful heat. However, considerable public opposition to new incinerators presently exists. One reason for concern is the potential emission of toxic combustion by-products such as polychlorinated dioxins and furans. Any understanding of the chemical processes, stability of hazardous wastes and performance characteristics of various incinerator designs could demonstrate the effectiveness of thermal oxidation and thereby alleviate public concern.

In 1979 concern over the stability of PCB led to stringent restrictions on the incineration of PCB. When PCB disposal was mandated, regulations prescribed greater than 99.99% destruction by oxidation above 1200°C for more than two seconds. Yet, approval of PCB incineration facilities was not granted until the question of polychlorinated dibenzodioxin and dibenzofuran emissions had been addressed. This question had been raised by scientists who postulated the formation of polychlorinated dibenzodioxins during any combustion of chlorine-containing fuels. Sophisticated analyses of vent emissions during test burns of PCB at two incinerators in 1981 provided experimental data on dibenzo-

dioxin and -furan emissions. Risk analyses of the emission of low concentrations of chlorinated dioxin and furans on human health suggested low potential hazards. Subsequently, the incinerators were approved by EPA for disposing of PCB under the conditions of the test burns.

During this same testing period, a number of other PCB destruction processes were explored. Actually, PCB detoxication illustrates the diversity of possible approaches to treating a specific type of waste. The large number of processes can serve as a model for detoxication of other pollutants. Ocean-based, molten-salt, diesel and cement kiln incineration were proposed and tested. Plasma arc and other high-temperature processes were explored. PCB-contaminated waste oil was burned in high-efficiency boilers.

Detoxication of PCB-contaminated transformer fluids provides a splendid example of the benefits of detoxication in recovery of valuable chemicals. After PCB are removed from transformers, replacement fluids become contaminated by the slow leaching of residual PCB. The resulting transformer fluids generally contain less than 500 ppm of PCB. Several approaches to removing PCB from these fluids have been proposed, tested in pilot plants, and two are in commercial operation. The first approach uses anion radicals, such as naphthyl sodium, to abstract chlorine from PCB to form dechlorinated coupling products and salt. Two processes based on this approach are available in mobile units. A second approach uses superoxides of sodium polyethylene glycoxide to perform nucleophilic displacements on PCB. A third method dehydrochlorinates PCB by exposure to ultraviolet light. All of these processes apply fundamental chemistry of halogenated aromatic hydrocarbons to solve environmental problems and to recover valuable chemicals. The ultimate fate of all PCB in the environment is degradation by microorganisms and exposure to sunlight.

In the United States, detoxication of high concentrations of PCB, such as pure PCB or its mixtures with trichlorobenzenes, is geared toward destruction, despite the loss of large quantities of chemicals. In other parts of the world (e.g., Japan), different economic criteria and social values lead to a different approach. Extensive work by the Japanese on the reduction of PCB by hydrogen in the presence of metal catalysts appears to be achieving the goal of converting PCB to high-quality, useful diphenyl.

Social values, political judgments and legal requirements play major roles in any attempt to detoxicate hazardous wastes. No compounds, other than perhaps PCB, have achieved the public recognition and fear of the polychlorinated dibenzodioxins, often described as the most toxic

synthetic chemical known to man. This class of compounds, an impurity formed during preparation of chlorophenols, achieved notoriety during the Vietnamese war and because of several industrial accidents. The most serious of these incidents, a release of a reactor contents containing about 2 kg of tetrachlorodibenzodioxin (TCDD), led to the evacuation of the Italian town of Seveso in 1976. It seems appropriate, then, to describe a case study of a project that destroyed 7 kg of TCDD in a complex, hazardous waste. The experience gained during this project can be used as a model for other detoxication projects. The technical success required a multidisciplinary effort of organic and analytical chemists, chemical engineers, toxicologists and industrial hygienists. The destruction process was implemented by technical people working closely with lawyers, doctors, government regulators, politicians and the public. In addition to serving as a model, this project teaches one other important point: the technical expertise exists to solve even the most difficult pollution problem. However, the societal or corporate will to solve the problem must be asserted.

Microorganisms in biological activated sludge systems have long served to degrade organic chemicals in aqueous waste streams. The application of selected microorganisms to detoxicate pollutants in hazardous waste or contaminated soils, lagoons or groundwaters is generating a great deal of interest. In addition to selected mutation of microorganisms, the potential for developing new pollution control technologies by genetic engineering is exciting. Enzymes also can offer sufficient catalytic activity to allow the use of otherwise slow chemical reactions in the detoxication of pollutants.

In summary, disposal of hazardous waste presents varied problems that can be addressed by detoxication procedures. The fundamental knowledge to carry out detoxication exists, but it must be adapted creatively to specific problems by chemists, engineers, microbiologists, physicists, geologists, toxicologists and many others working together. Implementation of the solution requires interaction with nonscientific members of society, value judgments, decisions about risk levels and potential consequences, and political realities. We can solve the problem of hazardous waste if we, as a society, have the will and make the commitment.

SECTION 1

INCINERATION AND WASTE MANAGEMENT

CHAPTER 1

HAZARDOUS WASTE DETOXICATION AT CONTRACT WASTE MANAGEMENT FACILITIES

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This chapter focuses on hazardous waste processing technologies at existing and future contract hazardous waste management facilities. The IT Corporation Northern California Treatment System Complex (NCTSC) is described to illustrate hazardous waste detoxication* technologies used in an existing facility. This facility represents existing application of technology and employs a broad spectrum of detoxication and treatment techniques, ranging from incineration to chemical treatment of wastes. The IT Corporation Ascension Parish Hazardous Waste Management Facility (APHWMF) illustrates integrated hazardous waste detoxication techniques under design for a future contract hazardous waste management facility. This facility, which will be the most technologically sophisticated regional hazardous waste detoxication facility in

*"Detoxication" refers to transformation of a toxic compound into a less toxic product; "detoxification" is a reduction in the degree of poisoning of an organism, as in the detoxification of an inebriate [1].

the western world when completed in 1984, has received state of Louisiana operating and federal construction permits.

The first section of this chapter deals with waste detoxication at the NCTSC; the second section deals with waste detoxication technologies planned for the APHWMF. Each section includes a brief summary of the appropriate facility as a whole, with emphasis on the treatment technologies employed and their integration. These summaries are followed by discussions of each major treatment technology by unit operation. Emphasis is placed on the expected or proven performance of various technologies with limited discussions of equipment design parameters. In addition, the importance of integration of technologies for efficient detoxication of a broad spectrum of wastes will be discussed.

HAZARDOUS WASTE DETOXICATION TECHNOLOGIES AT NCTSC

NCTSC is an integrated operation designed to detoxicate, destroy, treat or dispose of >80 million gal/yr of industrial hazardous wastes generated in Northern California. The complex meets many of the waste treatment and disposal needs of area industries by processing wastes that industries cannot handle themselves, and consists of a treatment facility with solar ponds in Martinez, California, and a landfill with ponds in Benicia, California.

A variety of waste management technologies are used in the complex, ranging from incineration of hazardous waste vapors and liquids to landfill of inorganic sludges. The design and operating philosophy of the facility is to recover useful chemicals (primarily oils) and energy values (combustion of waste solvents to generate steam) from wastes, to destroy toxic materials such as phenols, sulfides and cyanides, and then to dispose of remaining residues in a secure landfill or solar evaporation ponds.

Figure 1 is a simplified flow diagram showing the interrelationships between major segments of the NCTSC. The main processing facility, located in Martinez, California, includes all operations shown in Figure 1, except for the Benicia landfill and several solar evaporation ponds. The Martinez facility, which includes support facilities such as a laboratory, maintenance shop, and utility supply and distribution systems, has the appearance of a typical chemical processing plant.

After passing a predisposal selection process, liquids or slurries are received at Martinez, and solids, at Benecia. Examples of the type of wastes normally received at the NCTSC are listed in Table I. The wastes primarily are delivered in 5000-gal vacuum trucks, logged in and

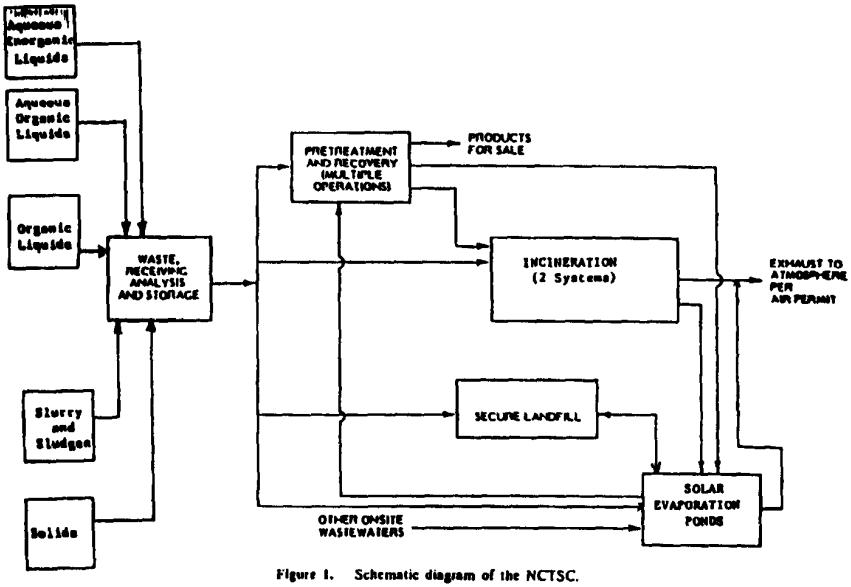

Figure 1. Schematic diagram of the NCTSC.

Table 1. Industrial Waste Categories Processed at NCTSC and Representative Examples

Group	Classification	Example
I	Aqueous Inorganic Liquid	
	Nonmetallic salts	Na_2SO_4, $NaNO_3$
	Acid	HF, HNO_3, H_2SO_4, H_3PO_4
	Acid with heavy metals	HNO_3 + $Fe(NO_3)_2$
	Alkali	NaOH
	Alkali with heavy metals	NaOH + lead
	Cyanide	NaCN, KCN, $Cd(CN)_2$, $Zn(CN)_2$
	Reactive (bleach, sulfide)	Mercaptans, H_2S, Na_2S
	Brine	NaCl
II	Aqueous Organic Liquid	
	Biodegradable organic	Acetone, MEK, acetic acid
	General organic	Phenol
	Organic and heavy metals	
III	Organic Liquid	
	Light hydrocarbon	Hexane, gasoline
	Hydrocarbon with water	Jet fuel
	Chlorinated hydrocarbon	Not accepted
	Polychlorinated aromatics	Not accepted
	Other halogenated hydrocarbons	Not accepted
	Other substituted hydrocarbons	Mercaptans
	Oil (heavy hydrocarbon)	Crude oil with light ends
	Organic with heavy metal	Tar with nickel catalyst
IV	Slurry/Sludge (Liquid/Solid)	
	Organic/organic	Waste oils
	Organic/heavy metals	
	Aqueous/heavy metals	Cooling tower sludge with chromium
	Aqueous/inorganic nonmetallic	Aqueous calcium carbonate
	Aqueous/biological	Biological treatment plant sludge
	Organic/inorganic	Oil spill cleanups
	Aqueous/organic	Aqueous amines
V	Solids	
	Organic	High-molecular-weight alcohols
	Inorganic	Spent calcium chloride drying agent
	Inorganic with organic	Used insulation
	Heavy metal	Spent catalysts containing metals
	Contaminated trash	Empty chemical bags
	Organic heavy metal	

analyzed. Based on the results of this analysis, an appropriate treatment method is selected, and the waste is discharged to storage, treatment tanks, the landfill or ponds. Analysis and treatment evaluation tests are performed in a laboratory facility equipped with appropriate analytical instrumentation and bench-scale testing equipment.

Most wastes delivered to Martinez require pretreatment before ultimate disposal at Benicia or in solar evaporation ponds. These wastes are processed in the pretreatment and recovery units of the Martinez facility. Wastes amenable to oil or chemical recovery are treated by conventional operations, such as filtration, settling, drying, evaporation and chemical reaction. These treatments yield oil and solvents usable as fuel. Wastewaters from these operations are placed in solar ponds for evaporation. Organic sludges are landfilled in Benicia.

Aqueous wastes containing phenols, mercaptans, sulfides, cyanides or organic solvents are processed by multipurpose equipment typical of the chemical industry. Organic solvents and other volatiles are stripped from aqueous wastes by air and/or steam. Phenols, mercaptans and sulfides are oxidized by hydrogen peroxide to less hazardous compounds. Cyanides are oxidized by chlorine to carbon dioxide and nitrogen. Sludges are partially dewatered by gravity thickening in lagoons and vertical tanks to reduce aqueous loads to the landfill.

An incineration complex consisting of two high-temperature thermal oxidation trains is the major energy recovery/vapor emission control system for the Martinez facility. The primary incineration system (incineration I) is used to destroy vapors collected from treatment operations and holding tanks, waste solvents, waste oils, and other combustible and pumpable waste liquids. The much smaller incineration II backs up the primary system, and is used primarily to incinerate vapors collected from waste holding tanks.

Finally, pretreated wastewater generated onsite and certain aqueous wastes received at the site are deposited in solar evaporation ponds. As water evaporates from the ponds, the remaining solids concentrate and are removed and placed in the Benecia landfill.

Not all of the treatment and disposal processes mentioned above are truly waste detoxication technologies. All, however, are required to yield an effective economical contract waste disposal facility. Thus, the technologies employed at the facility and the manner in which they are interconnected yield effective, economical waste treatment. The waste detoxication technologies at NCTSC fall into the categories of waste pretreatment/recovery and incineration. Technologies falling into the former category are air/steam stripping, chemical treatment (oxidation, neutralization), solvent recovery and oil reprocessing.

Waste Pretreatment/Recovery

The pretreatment and recovery systems operate in a batch mode and fractionate and/or detoxicate certain types of wastes to yield nontoxic residues and usable products. (Figure 2 is a schematic of the various systems.) The principal types of wastes directed to the pretreatment and recovery systems include dilute aqueous wastes, aqueous-organic liquids and organic liquids (see Table 1). These wastes are either sent directly to the appropriate detoxication technology from vacuum trucks or transferred to the appropriate treatment system from onsite storage tanks.

Aqueous wastes from pretreatment/recovery operations are sent directly to solar evaporation ponds or processed through the air/steam sparging system and subsequently sent to ponds as the lab analysis dictates. Organic/inorganic residues are ultimately landfilled at Benecia, and organic products are sold or burned in the incinerator.

Vapors from storage, treatment or handling procedures are collected in the vent system and burned in the incinerators. Steam is generated by combustion of these gases and organic waste liquids and is used in the solvent recovery unit and the air/steam sparging unit.

Chemical Treatment

Cyanide Treatment System. The cyanide treatment system is designed to remove cyanide from liquid wastes by converting free cyanide to carbon dioxide and nitrogen gas and by precipitating combined forms of cyanide. The process involves chlorination, pH adjustment and precipitate removal.

There are two types of cyanides in the majority of the waste cyanide loads received at the Martinez facility: free (CN^- ions in solution) and combined (e.g., ferrocyanide complexes) cyanide. Oxidation by chlorine at pH 10 converts all free cyanide and most combined cyanide to the cyanate form, which is much less toxic than the original cyanide. This cyanate subsequently is further oxidized at pH 8.5–9 in the presence of free residual chlorine to CO_2 and N_2. The only combined cyanide that is not readily oxidized even by excess chlorine is sodium or potassium ferrocyanide. This complex, because of its stability, is not excessively toxic and is removed by precipitation at pH 5.5–6.0.

A simplified flow diagram of the cyanide destruction system is shown in Figure 2. The system consists of (1) a batch cyanide treatment tank and recirculation pump, and (2) sodium hydroxide, sulfuric acid and chlorine storage and delivery systems. The cyanide treatment tank is connected to the main vent system to collect gases (CO_2, N_2 and sometimes NH_3) and

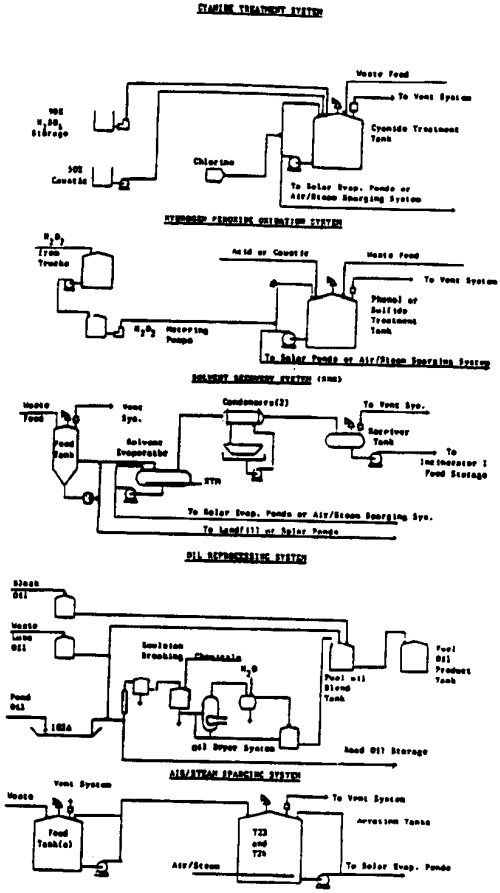

Figure 2. NCTSC pretreatment and recovery systems.

to control inadvertent hydrogen cyanide evolution if the solution becomes acidic.

Hydrogen Peroxide Oxidation. The hydrogen peroxide unit is used on a batch basis to oxidize phenols and sulfides in aqueous wastes. Phenol is oxidized by hydrogen peroxide at pH 6–7 to volatile organic acids and ultimately to carbon dioxide and water with a ferrous sulfate catalyst. At alkaline pH, sulfides are oxidized by hydrogen peroxide to water and sulfates.

Figure 2 shows a simplified flow diagram of the hydrogen peroxide oxidation unit. All tanks are connected to the vent control system, so that any vapors released during oxidation will be incinerated rather than emitted to the atmosphere. Sulfide-containing and phenol wastes are unloaded directly into separate treatment tanks. If a wastewater is excessively acidic, an appropriate amount of caustic is added. Once pH adjustment has been completed, the appropriate amount of hydrogen peroxide and ferrous sulfate are metered into the treatment tanks to achieve the desired oxidation. Treatment tank contents are recirculated during hydrogen peroxide addition to ensure rapid mixing and, thus, uniform oxidation. Such recirculation also occurs during tank pH adjustments. On completion of oxidation, treatment tank contents are air/steam sparged to reduce volatiles or discharged directly to solar evaporation ponds.

Neutralization. Aqueous acids, such as 25% HNO_3, H_2SO_4, HF and H_3PO_4, are received onsite in 5000-gal vacuum trucks and stored in lined, horizontal steel tanks. The acids are metered from these tanks to treatment tanks containing appropriate amounts of caustic. Vapors emitted during neutralization enter the vent system. Neutralized wastewater is normally sparged with air/steam to remove volatiles and subsequently placed in solar evaporation ponds.

Solvent Recovery System

The solvent recovery system (SRS) is a batch system designed to recover high-quality burnable solvent from waste solvent loads containing too much water and/or solids to be burned directly. The solvent recovered by this system is blended with other hydrocarbon fuels and burned directly. The system is designed to process hydrocarbon solvents and oxygenated hydrocarbons, but cannot handle chlorinated solvents.

The SRS is shown in Figure 2. It consists of a vertical, cone-bottom, waste solvent storage/feed tank, a solvent evaporator tank, vapor

condensers, and an overheads receiver and associated pumps, piping, valves and vent collection equipment.

Solvent wastes are processed in the SRS on a batch basis. First, solvent wastes are loaded into the vertical cone-bottom tank. Solids settle in the tank's cone bottom and are gravity-fed to an oil storage pond and eventually landfilled. Second, a batch of solvent from the tank is drained by gravity and pumped into the evaporator tank. Solvent is evaporated by direct steam injection, condensed in the overhead condensers and collected in the receiver tank. The contents of the receiver tank are then pumped to the incinerators for thermal oxidation. Water and sludge remaining in the evaporator are transferred to other tanks, where they are contacted with additional steam and air to remove trace levels of volatiles. Finally, the water is pumped to a solar evaporation pond.

Air/Steam Sparging System

The air/steam sparging system is used to strip volatile organic materials out of wastewater before ultimate disposal in a solar evaporation pond. The system consists of an air compressor, air and steam delivery piping, air and steam sparger nozzles, and two aeration/treatment tanks. The system is shown in Figure 2.

Oil Reprocessing System

This facility consists of a number of heated tanks, an evaporator (oil dryer) and a chemical treatment system. Equipment is designed to remove water from waste lube and slop oils, and break emulsions so that the oil can be reused as fuel. Heat is supplied to the evaporator and treatment tanks by a recirculating hot oil system that uses waste oil as fuel.

Figure 2 contains a simplified flow diagram of the oil reprocessing operation. Pond and other slop oils are received by trucks and placed in a special pond. Oil is skimmed off the top of this pond, filtered, deemulsified and dried by heat application or chemical addition, filtered again and placed in an intermediate tank. The oil from this tank is blended with dry-filtered waste lube oil and waste black oil to make No. 4 fuel oil for sale.

Incineration

Two incinerators destroy hydrocarbon vapors collected from storage and treatment tanks in the vent system and waste organic liquids received directly onsite or recovered in the SRS system and the oil reprocessing

facility. In addition, the incinerator produces steam to be used in the SRS unit and in the air/steam sparging system.

Vent System

The vent system is a closed system of storage and treatment tanks with associated piping that carries vapors from the tanks through venturi scrubbers to the incinerators (Figure 3). With incinerator I on-line, tank vapors and air (supplied through atmospheric dampers) are drawn into the incinerator by a blower. The atmospheric dampers are automatically opened once the scrubber blowers are energized and automatically closed after the scrubber blowers are secured. In-line, manually operated dampers are designed to meter air- and vapor flow from specific tank farm areas. Pressure/vacuum valves are situated on each vented tank and correct any high- or low-pressure conditions. Spark arrestors are installed at each vented tank and prevent vent line flashbacks from spreading to the holding, storage or processing tanks and eliminate the spread of potential tank fires or explosions.

Incinerator I

Incinerator I burns recovered waste fuels and vapors given off from holding and processing tanks. The heat produces steam in the boiler (heat exchanger) chamber. This steam production allows effective treatment of wastes containing high hydrocarbon vapor phase (HCVP) in the air/steam sparger system and enables recovery of waste solvents and fuels in the SRS system. This incinerator is shown schematically in Figure 3.

The incinerator is designed to operate at combustion chamber temperatures of 1500–2000°F and flue gas residence times on the order of 0.5 sec. These conditions assure adequate destruction of the nonhalogenated hydrocarbon liquids and vapors.

Incinerator II

Incinerator II prevents toxic and/or air polluting materials from entering the atmosphere by incineration and caustic scrubbing of vapors drawn through the vent system. This unit must be running any time incinerator I is not operating. Incinerator II consists of the equipment shown in Figure 3.

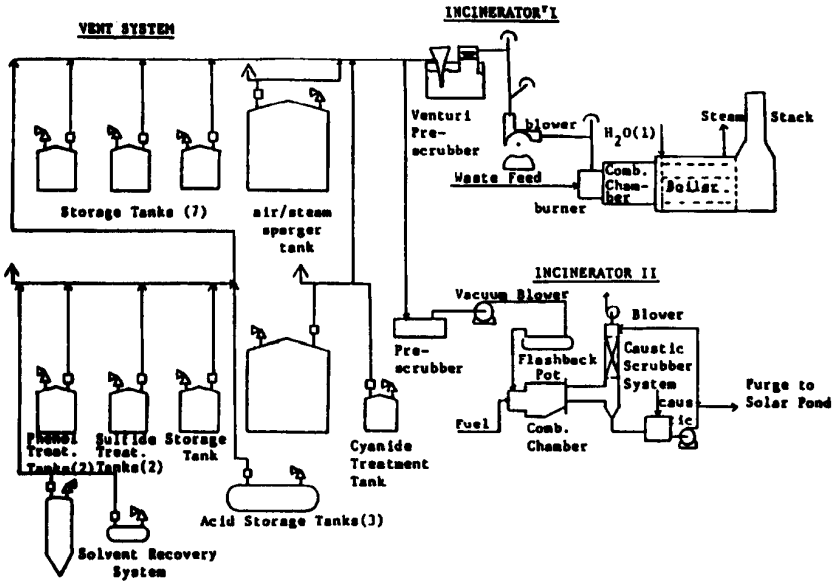

Figure 3. Simplified flow diagram of NCTSC incineration/vent system.

HAZARDOUS WASTE DETOXICATION AT APHWMF

APHWMF will be a fully integrated operation to detoxicate, destroy or reclaim approximately 80 million gal/yr (350,000 ton/yr) of industrial hazardous wastes generated in the Ascension Parish, Louisiana, area. The site will be located in Ascension Parish, Louisiana, on a 1000-ac site bordering the Mississippi River, but will occupy only 150 acres of the site. The facility will process a broad spectrum of hazardous wastes from local industry. These wastes will vary widely in physical and chemical properties. Table II lists the categories of wastes expected to be handled at the facility as determined by surveys of selected area industries. Table III lists typical compounds the facility is expected to process.

Figure 4 is a simplified flow diagram showing the interrelationships between major facility segments. The integrated nature of the facility is evident, with effluents, residues and energy from waste pretreatment, wastewater treatment and incineration being transferred from one process area to another to achieve destruction or detoxication of wastes in an economical manner.

Wastes will be received at the facility in the form of solids, liquids or slurries and, as shown in Figure 4, will be delivered to the plant, received, logged in, analyzed and stored. Based on analysis, an appropriate treatment method will be determined, and the waste will be designated for processing under rigorously controlled conditions by the most appropriate treatment operation. These analytical and treatment evaluation tests will be performed onsite in a modern laboratory equipped with sophisticated analytical instrumentation and bench-scale testing equipment.

Many wastes will be candidates for pretreatment, either for recovery or to improve the overall economics involved in downstream processing of the materials. Wastes amenable to oil and/or chemical recovery will be processed using the conventional operations, settling, drying, distillation and chemical reaction, as required with steam generated by incineration of wastes in the incineration system. This procedure will yield oil that can be used to fuel the incinerators, lube-oil blending stock, and industrial-grade chemicals and solvents. Wastewater and organic sludges generated from these operations will be processed or destroyed onsite.

Aqueous wastes containing small amounts of hazardous pollutants will be pretreated by multipurpose equipment typical of the chemical processing industry. The wastes will be processed by physical means (e.g., extraction, steam stripping or carbon adsorption), or chemical treatment methods. Wastewater effluents from these units will be processed in a wastewater treatment plant on site. Organic material will be incinerated.

Table II. APHWMF Waste Profile

Group	Classification	Percentage of Total Waste Represented by Each Category
I	Aqueous inorganics	0
II	Aqueous organic liquids	
	Organic (acid)	
	Organic (alkali)	
	Organic (salt)	
	Percentage of total waste	17
III	Organic liquids	
	Light hydrocarbons	
	Hydrocarbon with water	
	Chlorinated hydrocarbons	
	Substituted hydrocarbons	
	Oils (heavy hydrocarbons)	
	Percentage of total waste	33[a]
IV	Sludges	
	Organic/organic	
	Aqueous/heavy metal	
	Aqueous/inorganic nonmetal	
	Aqueous/biological	
	Organic/inorganic	
	Aqueous/organic	
	Percentage of total waste	46
V	Solids	
	Organic	
	Inorganic	
	Inorganic with organic	
	Heavy metal	
	Contaminated trash	
	Organic/heavy metals	
	Percentage of total waste	5
	Approximate total waste (ton/yr)	350,000

[a]Includes 40,000 ton/year waste crankcase and lube oils from the area.

Sludges will be dewatered and/or dried to reduce the aqueous loads on incineration equipment and, thus, reduce energy consumption. Equipment planned for this service includes belt filters for dewatering dilute sludges and indirect steam dryers for further moisture reduction.

Table III. Typical Organic Chemicals Expected to Be Processed at APHWMF

Aldehydes/Alcohols/Ketones
Acetaldehyde
Methanol
Methyl ethyl ketone
Chlorinated Aliphatics
Carbon tetrachloride
Ethylene dichloride
Methylene chloride
Trichloroethane
Chlorinated Aromatics
Chlorotoluene
Chlorobenzene
Chlorinated Olefins
Vinyl chloride
Aromatics
Benzene
Toluene
Amines
Diphenylamine
Toluene diamine
Carboxylic Acids
Propionic Acid
Phenols
Phenol

An incineration complex of three high-temperature thermal oxidation trains is the heart of the treatment facility. A broad profile of offsite organic wastes plus onsite residues from recovery/pretreatment will be destroyed. Two large (90-million-Btu/hr) rotary kiln/secondary combustion systems will receive solids, liquids, gases and slurries. The third specialty incinerator will receive a limited profile of pumpable wastes. One rotary kiln will be equipped with a heat recovery boiler for steam generation. The incineration units will have secondary combustion chamber configurations designed to provide a minimum residence time of 2 sec at 1000 or 1200°C. Flue gas from each incinerator will be treated separately to remove particulates and acid gases before discharge. The four-stage, state-of-the-art gas cleaning technology includes wet scrubbing techniques (quench, venturi, packed bed) and wet electrostatic precipitation. Inorganic sludges and noncombustible materials will be

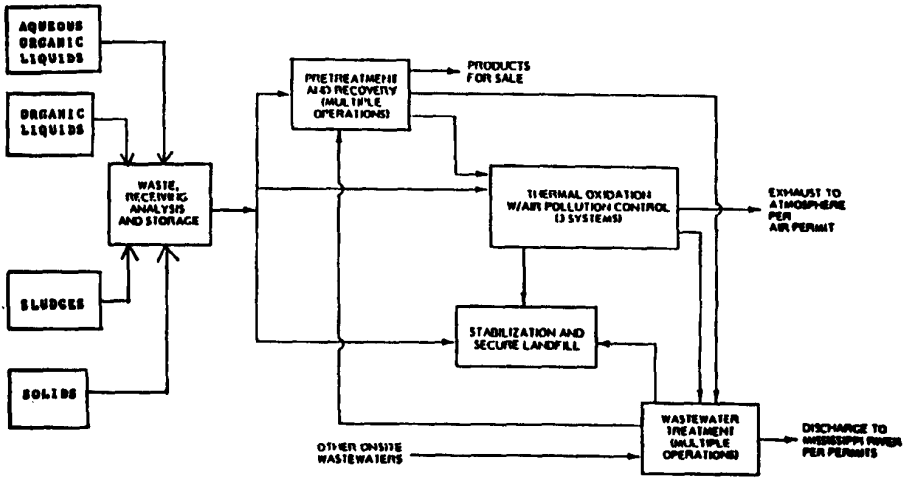

Figure 4. Schematic diagram of the APHWMF.

stabilized and confined in an onsite secure landfill along with inorganic residues and fly ash solids from incinerator flue gas cleaning systems.

Finally, treatment will be provided for wastewater generated onsite from all the processing units, in addition to site-related waters such as surface runoff and sanitary wastes. Treatment processes for different streams will include physical/chemical removal methods, such as clarification, pH adjustment, carbon adsorption and activated sludge biological treatment, for pollutant destruction or removal. Treated, monitored wastewaters will be discharged to the Mississippi River. Other support facilities necessary for a complete and operable facility include such ancillaries as plant administration, personnel services, maintenance shops, fire protection, security, utility supply and distribution, and effluent/emission monitoring.

Pretreatment and Recovery

The pretreatment and recovery systems include four primary processing areas with different functions and equipment:

1. Aqueous waste pretreatment includes several independent unit operations designed to remove or destroy selected pollutants in dilute aqueous wastes.
2. Sludge-slurry processing consists of equipment to remove water from sludges and slurries.
3. Chemical recovery provides equipment for fractionating organic liquid wastes.
4. Oil reprocessing is a complete multistage oil re-refining plant to convert various waste lubricating oils to lube blending stock and fuel.

Figure 5 is a simplified block diagram of the pretreatment and recovery system showing the four areas and major flows into, from and between these areas.

The pretreatment and recovery systems are necessary in the overall facility to:

- improve ultimate disposal and treatment performance and reduce costs;
- increase effective overall facility capacity;
- reduce the use of purchased fuel for incineration; and
- reclaim valuable chemical constituents of waste mixtures.

In addition to processing offsite wastes, this system enables treatment of wastes generated onsite, such as waste-activated sludge from the biological treatment system and aqueous effluents.

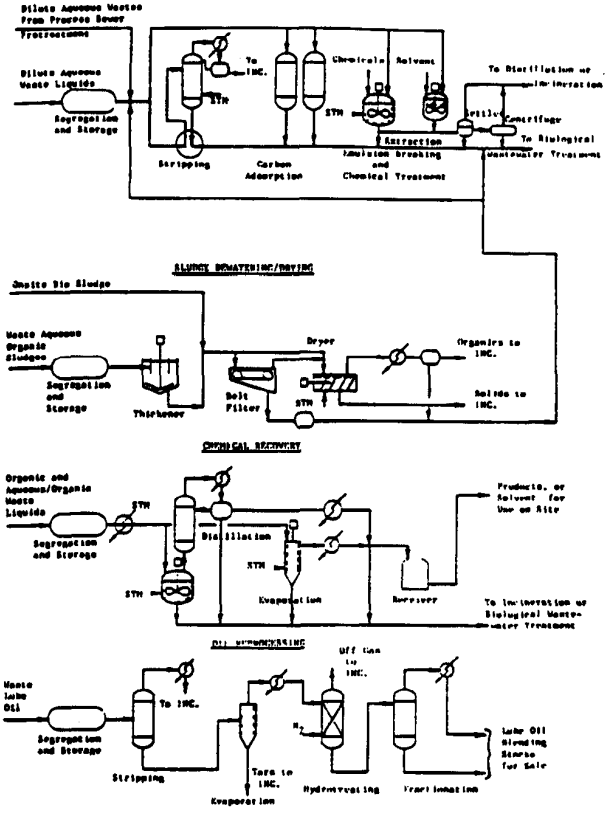

Figure 5. APHWMF pretreatment and recovery systems.

Aqueous Waste Pretreatment

The purposes of aqueous waste pretreatment are:

- removal from wastewater of regulated pollutants that cannot be removed by conventional biological wastewater treatment (resulting in detoxication of the wastewater);

- prevention of deleterious effects of toxic pollutants to the facility's biological wastewater treatment plant;
- prevention of air emissions or hazards caused by sewering volatile, flammable or odorous pollutants; and
- production of high-quality organic fuel fractions for incineration.

In general, the pretreatment area will receive Class II dilute aqueous wastewaters that are not effectively treatable by biological means (see Table 11). The wastes are expected to contain priority pollutants, e.g., cyanide, heavy metals or toxic organics such as pesticides. Types of wastes may include very dilute slurries, emulsions and brines.

Technologies chosen to treat this variety of waste types include a selection of versatile, conventional unit operations that are applicable for removing pollutants from water. The four basic pretreatment processes include:

1. steam stripping;
2. carbon adsorption with in-place, nondestructive steam or solvent regeneration;
3. liquid/liquid extraction; and
4. emulsion breaking and chemical treatment.

Each technology is discussed below in sequence, with emphasis on those that detoxicate/destroy hazardous wastes to yield less toxic wastewater.

Steam Stripper

The steam stripper will treat continuously up to 80 gal/min of aqueous streams containing organics that are moderately volatile and that range in concentration up to the organic solubility level. Due to the corrosion-resistant construction of the stripper and associated equipment, aqueous streams over a broad range of pH values will be acceptable for treatment. However, streams containing a significant quantity of suspended solids or streams that foam when heated will not be treated.

Feed will be transferred to the stripper column through a shell-and-tube feed/bottoms cross exchanger (see top of Figure 5). The feed will enter the stripper column where it will be contacted countercurrently with steam. Vapors stripped from the feed will pass into a shell-and-tube type overhead condenser where they will be condensed and then flow into a vertical decanter tank. Condensed vapors will either be refluxed back to the stripper column or incinerated. The unstripped portion of stripper feed will flow out the column bottom and be pumped to biological wastewater treatment via the feed/bottoms cross exchanger.

Pollutants with a Henry's law constant of 10 or more will undergo 99% or greater removal in the stripper. For pollutants with Henry's law constants close to 10, which require a higher steam-to-feed ratio, the feed rate to the stripper will be adjusted down to achieve corresponding treatment efficiency. Conversely, aqueous streams containing organics with Henry's law constants greater than 10 require a lower steam-to-feed ratio to achieve 99% removal and therefore can be fed at a higher flowrate to the stripper.

Carbon Adsorption

The aqueous waste pretreatment carbon adsorption system is designed to treat up to 50 gal/min of wastewater based on a typical loading range of 0.1–0.3 lb of adsorbable organic per pound of carbon. The loading will vary considerably with the concentration of adsorbable compound, and adsorption and activated carbon characteristics. The loading could be much lower than 0.1 lb/lb without necessarily affecting the performance. An average removal of 99% of the adsorbable organic from the aqueous waste stream is expected.

The carbon adsorption system consists of carbon columns with auxiliary pumps, tankage and piping for series and parallel operation of the columns and for inplace solvent or steam regeneration of the carbon (Figure 5). Typically, wastewater is fed continually to one column until it is saturated with organics, at which point it is switched to regeneration. Throughput can be increased by operating the two columns in parallel and feeding batchwise. Treated wastewater from the columns flows to biological wastewater treatment. Organic compounds removed during regeneration are incinerated.

Solvent Extraction

Solvent extraction is a separation technique involving contacting a water-immiscible solvent with wastewater. A certain degree of separation occurs when some of the pollutant transfers from the wastewater to the solvent. Separation of the solvent from the extracted pollutant by distillation enables recycle and reuse of the solvent.

Aqueous wastes selected for extraction at APHWMF normally contain organics that exhibit a reasonable partition coefficient in typical extracting solvents. Compounds that are likely candidates for extraction generally will have low water solubility. However, selective solvents can be effective in removing polar, low-molecular-weight compounds, which

have higher water solubility. Solvent extraction will be used for treatment of aqueous wastes with solute concentrations from 10 to about 0.1%.

Solvent extraction will be carried out at APHWMF in three 8000-gal, jacketed vessels. The raffinate will be pumped to the stripper or biological wastewater treatment, while the extract will be distilled in the recovery section.

Emulsion Breaking and Other Chemical Treatment

Typical oil-water and water-oil emulsions can be deemulsified by altering one or more of the physical/chemical characteristics of the emulsion. Methods of deemulsification include temperature elevation, pH adjustment, or addition of acidic soaps or polyvalent salts. After an emulsion is broken, conventional physical separation techniques can be used to separate organic and aqueous phases and/or solids.

Wastes for emulsion breaking can include a wide variety of oil-in-water or water-in-oil mixtures. Solids often are dispersed in the emulsion. Examples of emulsions include pesticide-water mixtures, oil-water sludge mixtures from refineries and solvent-water-solid mixtures from tank cleaning or other processes.

Wastes for chemical treatment will vary significantly. Wastewaters containing fats, oils, ethers, acid sludges, pesticides and carbohydrates are typical candidates for acid or caustic hydrolysis. Wastewaters suitable for chemical oxidation may contain compounds such as cyanide, pesticides and sulfides. Chemical precipitation will treat wastes containing metals and most inorganic ions, although specific organic salts also may be precipitated. Various treatment methods and equipment are suited for wastewaters containing a wide range of contaminant concentrations. Emulsion breaking and chemical treatment are carried out in the same process equipment used for solvent extraction.

Sludge Processing

Dewatering and drying processes separate the solids portion of sludges and slurries from the liquid (aqueous) portion. The resultant separated streams are much easier to dispose of than the original mixture. The dewatered and/or dried solids have a high enough fuel value and low enough water content that they can be incinerated readily in a rotary kiln. Without processing, aqueous sludges and slurries would require substantial auxiliary fuel for incineration.

Dewatering

Sludges and slurries containing a low concentration of solids are subjected to two dewatering steps—thickening and belt filtration (see Figure 5). The solids content is increased from below several percent solids to an intermediate range of 10–15% solids by separating and removing most of the liquid in these two steps. In the thickening step, 80,000 ton/yr of low-solids sludge, with an average solids content of 0.5–1.3%, is thickened to yield sludge with an average solids content of about 3–5%. This sludge is then processed by belt filter presses to yield moist sludge cake with an average solids content of 10–15%. The two-step dewatering process will remove 80–90% of the total water in the original sludge or slurry. An average of 98% solids retention is expected.

Drying

The types of sludges identified in the APHWMF waste profile as applicable for direct dryers are (1) dewatered, waste-activated sludge from offsite sources; (2) other dewatered primary wastewater treatment sludges; (3) primary, oily sludges from American Petroleum Institute (API) storage tanks and the bottoms from refinery API separators; and (4) powdered carbon wet cake containing traces of organic and inorganic contaminants. The solids content of these wastes may vary from 10 to 20%, depending on offsite treatment techniques. These materials will be combined with wastes from onsite dewatering and dried in indirect steam heated, jacketed dryers.

The dryers are sized to process about 80,000 ton/yr of high-solids sludges. They are horizontal troughs with rotating center shafts that drive attached paddles to agitate and recirculate the bed of dried solids in the trough. Heat is transferred into the moving solids through both the jacket wall and the walls of the hollow paddles. Up to three twin-agitator, Porcupine®-style dryers will be used. The dryers will produce a wet solid with 50–60% moisture. The consistency, melting point, thermal stability, presence of organics and moisture of the feed are major factors in the degree of drying that is appropriate.

Chemical Recovery

The purpose of the chemical recovery system is to:

- recover and/or modify selected wastes if the market or recycle value of waste constituents is greater than their potential value as fuel to the incinerator;

- upgrade or separate selected wastes streams so that the overall fuel will be enhanced; and
- recover and/or purify the carbon adsorption regenerant and the extraction solvents from the pretreatment section for reuse in that area.

In general, the chemical recovery system consists of two batch-distillation units and a wiped film evaporator. The system I distillation unit can carry out atmospheric batch distillations. The system II distillation unit is capable of carrying out vacuum and pressure distillation and continuous steam stripping. The evaporation unit can evaporate solvents and/or light hydrocarbon fuels from such viscous wastes as heavy tars and still bottoms or from contaminated solvents.

System I distillation has been designed to treat a wide variety of liquid waste mixtures, with emphasis on the organic liquid constituents identified in the waste profile (see Table III for example compounds). Wastes will be distilled if reasonably pure mixtures of the major organic constituents can be obtained economically by batch distillation and if a market for the products exists.

System II distillation is expected to handle the recovery of the carbon regeneration solvent and the extraction solvent from aqueous waste pretreatment. The bottoms produced from the recovery of these solvents will be transferred to the incinerator feed storage tanks for disposal.

An analysis of the available vapor-liquid-equilibrium and vapor-pressure data for potential waste constituents indicated that the average reflux ratio required for batch distillation of all wastes is 2.0. The system is designed accordingly.

The evaporation process is sized to treat at least 1000 lb/hr (20,000 lb/day) of wastes. The capacity for a given waste feed depends on various factors, such as viscosity, heat of vaporization and amount of solvent to be evaporated. The performance of the evaporation and distillation systems is linked with the overall performance of the facility only because it may change the waste load constituency to the ultimate treatment or disposal areas, especially the incineration area. Waste candidates will be chosen on the basis of recovery economics (product or fuel value). Evaporation processes such as those in this facility have been used for many years and are being used increasingly by generators (solvent users) and waste solvent reclaimers.

Oil Reprocessing

A separate system to reprocess 5–10 million gal/yr of waste oils will produce salable products from waste oils purchased from generators or

collectors. All residues and effluents from waste oil reprocessing, which may contain hazardous materials, will be transferred, treated and disposed of in the appropriate area of the overall facility.

APHWMF will receive two major types of oils. Industrial automotive crankcase and machine lube oils will be collected for recovering the lube-oil fraction as lube-oil base stock. Other slop oils, waste oils and oil-water mixtures will be processed to recover fuel values in the pretreatment (emulsion-breaking) incinerator or for potential resale, if removal of the bulk of water and suspended solids cannot be accomplished through phase separation in waste storage.

The APHWMF oil reprocessing system is a waste lube-oil re-refinery. A simplified flow diagram of the process is shown in Figure 5. The process begins with storage and settling and includes distillation steps to remove low-boiling contaminants, evaporation to remove high-boiling contaminants, hydrotreating for purification by removal of sulfur, chlorine and nitrogen contaminants, and a distillation section to separate the oil product into different viscosity grades. The various products are stored in appropriate tankage in the oil reprocessing area for shipment or transfer to incinerator feed storage for auxiliary fuel.

Incineration System

Purpose of the Incineration Complex

The purpose of the incineration complex is to completely destroy organic compounds by high-temperature thermal oxidation and then remove any resulting inorganic residuals from the flue gases as ash or scrubber water slurries/solutions. These objectives are achieved by applying the most advanced U.S. and European state-of-the-art combustion and gas cleaning technology available.

Incinerators 1 and 2 are nearly identical two-chamber rotary-kiln systems. Each has a rotary-kiln primary combustion chamber that is capable of handling containerized wastes in up to 85-gal drums, bulk solid wastes, pumpable liquid wastes, slurries and sludges. A secondary combustion chamber capable of handling pumpable liquid wastes follows the kiln. Incinerator 3 is a single-chamber system capable of handling pumpable liquid or slurry wastes with similar performance and air pollution control systems as incinerators 1 and 2.

The thermal oxidation systems in the APHWMF facility consist of two rotary-kiln incinerators (units 1 and 2), a third, pumpable liquid/slurry incinerator (unit 3), and associated waste feed and flue gas cleaning systems. The waste profile used to design the complex required a nominal

duty capacity of 90 million Btu/hr from each of the three incinerators. The waste profile consists of solids, liquids and sludges that must be balanced properly to minimize use of auxiliary fuels and to optimize destruction efficiency. The waste pretreatment methods previously described are a necessary part of the incineration operations for efficient treatment of an overall set of wastes similar to that shown in Table II.

After wastes have been identified, categorized, and blended or segregated, they are fed into the appropriate incinerator for thermal destruction. Incinerators 1 and 3 each contain a quench chamber that cools the gases, removes large particles and washes acids from the flue gas. Incinerator 2 has a waste-heat recovery system after the incinerator that produces high-pressure steam before the gases enter the quench chamber. All three incinerator trains have sophisticated gas-cleaning systems that remove SO_2, HCl and submicron particulates. Following gas cleaning, each train has its own induced-draft fan and exhaust stack. Recycle and fresh makeup water are used in the quench and gas-cleaning systems, and purge water is sent to the heavy metals removal system. Ash from the three incinerators is stabilized and landfilled.

Rotary Kiln and Secondary Combustion Chamber

The thermal oxidation (incineration) portion of the total system is designed into two separate chambers—the rotary-kiln primary combustion chamber and the stationary-hearth secondary combustion chamber. The rotary kiln is an ~ 11-ft-diameter-by-40-ft-long, refractory-lined, horizontal, rotating cylinder equipped with a variable-speed drive. There are burner nozzles for incinerating pumpable liquid or slurry wastes and a continual gas pilot burner to ensure a constant source of ignition. A combustion air blower and a pilot air blower provide air for combustion at the burner nozzles, and the overfire excess air is drawn down the feed chute into the kiln by the negative pressure created by the large induced draft fan at the end of the process (Figure 6).

Containerized and bulk solids are charged down the feed chute into the kiln by gravity through air locks. The liquid burners are fired cocurrently, and combustion products flow from the kiln into a refractory-lined mixing chamber and on into the secondary combustion chamber. Both ends of the kiln are sealed to minimize air leakage into the kiln. Ash and slag move slowly through the kiln, driven by the rotation of the cylinder, and fall out the end of the kiln into a water-filled ash quench trough. A drag chain conveyor moves the ash to a screen for separation into fine and oversize fractions. The fine fraction drops into a dumpster box for transportation to the stabilization area, and the oversize materials (burned out

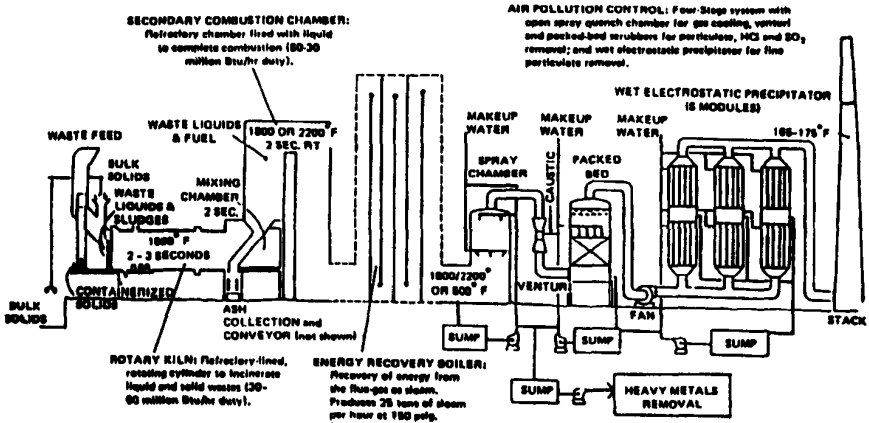

Figure 6. Rotary kiln thermal oxidation system.

drums and clinkers) drop into a dumpster box for transportation to the inert material landfill.

The secondary combustion chamber is made up of three separate sections. The horizontal section contains two waste liquid burner nozzles, a continuous pilot burner, a combustion air blower and an atomization air blower. The chamber is refractory-lined and is designed to receive the combustion gases from the kiln to complete the combustion process. The gases then flow from the horizontal section into the vertical section, which ensures completion of the combustion process.

Next, the gas retention section allows hot gases to further mix and fragment. Completion of the combustion process is ensured by increased temperature, additional retention time, gas turbulence and flame contact.

The overall combustion system is rated at a nominal 90 million Btu/hr. Throughput is a function of the temperatures, excess air and combustible portion (organic carbon) of the waste. With the kiln operating at flue gas temperatures of 1500° F and the secondary chamber at 1800° F, about 60 million Btu/hr are fired in the kiln and 30 million Btu/hr in the secondary chamber. The Btu/hr ratio is reversed, however, when the secondary is fired at 2200° F while the kiln is maintained at 1500° F, as would be necessary to meet guidelines for incinerating chlorinated aromatics. Increasing the operating temperature of the kiln is desirable to increase the quantity of solids and sludges handled by the system; however, tradeoffs exist, since increasing the temperature may rapidly shorten the life of the refractory due to the combination of heat and attack of salts and alkalies.

An average overall excess air level of 100% is designed into the system to promote complete oxidation and to provide a cushion for combustion surges such as those generated when bulk quantities of rapidly combustible materials are fed into the system. Most of the excess air is introduced into the kiln, where contact between combusting solids and air is not as efficient as contact between atomized liquids and air. The excess air level in the kiln is approximately 150%. Although the operating temperatures dictate the level of excess air, because air is a heat sink, water in the feed also acts as a heat sink and therefore reduces the level of excess air at a given temperature.

Flue Gas Cleaning System

The flue gas cleaning equipment is designed to meet Resource Conservation and Recovery Act (RCRA) regulations for HCl and particulate removal. A pH-controlled scrubber is included to remove SO_2. With the pH-controlled scrubber in the system, >99% HCl removal is achieved. A

venturi scrubber and wet electrostatic precipitators are incorporated for particulate removal.

After the quench chamber, the flue gases flow to a venturi scrubber. A pressure drop of 30–40 in. water column (w.c.) is maintained over the venturi for optimum particulate removal efficiency. A packed demister/scrubber sized to remove water droplets, HCl and SO_2 follows the venturi. The water from the venturi and demister flows to another integral sump, where it is pH-adjusted and recycled to the venturi and demister. Fresh process water is also added to the demister through a distributor.

The driving force for moving flue gases through the entire system is provided by an 80,000-acfm induced-draft fan located behind the venturi/demister. Three wet electrostatic precipitators connected in parallel remove any remaining submicron particulate matter from the flue gases. The cleansed gases leaving each of the three precipitators are combined and sent to a free-standing exhaust stack for discharge into the atmosphere.

The pH-adjusted overflow water from the quench sump and the venturi-packed scrubber/demister sump flows to the main sump. From there it is pumped to the heavy metals removal system. The sump overflow is the purge water from the air pollution control system and can be adjusted to maintain the desired suspended and dissolved solids levels in the recycle water systems.

Waste Heat Boiler

Incinerator 2 is identical to incinerator 1 except that it has a heat-recovery boiler located between the secondary combustion chamber and the quench chamber. The boiler is used to extract energy from high-temperature combustion products to produce up to 368-psig steam with 130° F superheat.

The energy-recovery technology that is being applied originated in Europe, where identical boiler systems have been in continuous operation for more than 15 years on large chemical waste incinerators and several industrial processes. The waste heat boiler is a basic, water tube type. The peripheral boiler housing heat-transfer surfaces (walls) use natural circulation for movement of the deionized boiler feed water. The internal heat-transfer surfaces are arranged in the housing and operated by forced circulation of the deionized feed water. Forced circulation operation of the internal heating surfaces is necessary to accommodate heat-load fluctuations. The bottom of the boiler is designed as an ash discharge facility and made of tube-web-tube construction. It is designed to be cleaned manually during normal operation of the boiler. The steam drum

is located on the boiler roof and has a reserve capacity of 10 min. The drum's internal baffles ensure that the steam quality is in accordance with the required steam quality specifications.

Rotary Kiln Incinerator Performance

The incineration process, including thermal oxidation and flue gas cleaning equipment, will meet the performance requirements of Louisiana law and the U.S. Environmental Protection Agency (EPA) RCRA incinerator standards published on January 23, 1981 (and proposed EPA incinerator standards). Compliance with current RCRA requirements includes achievement of: (1) 99.99% destruction and removal efficiency (DRE) of organic constituents; (2) 99% HCl removal efficiency; and (3) particulate emissions of less than 0.08 gr/dscf adjusted to 12% CO_2.

Stabilization and Landfill

The waste stabilization treatment process detoxicates inorganic chemical residues by intimately mixing them with a carefully compounded portion of treatment additives. The slurry sets into a rigid, inert rock-like cast within 6 hr to 3 days after compounding and mixing. This rock-like form, through physical and chemical interactions, binds into an inert mass and detoxicates the toxic or environmentally harmful species in the waste.

The inorganic waste stabilization process used at APHWMF can be described generically as a cement-pozzolanic solidification process. In this process lime, fine-grained siliceous (pozzolanic) material such as fly ash and cement are added to the waste in specific combination and sequence to achieve the best and most economical treatment for the specific waste being treated. A number of additional ingredients may also be used, depending on the type of waste being treated, to enable the process to achieve optimum end-product stability.

Function and Interface with Other Major Treatment Areas of APHWMF

Stabilization is the final treatment process at APHWMF for inorganic wastes and/or inorganic residues (incineration ash, metals sludge from wastewater treatment) from onsite treatment facilities before the material is permanently interred in the secure landfill. Stabilization treatment converts the material to its least soluble and most environmentally inert form. This stabilization is accomplished by improving the handling and

physicochemical characteristics of the waste, decreasing the surface area across which transfer or loss of contained pollutants can occur, minimizing the solubility of any pollutants contained in the waste and detoxicating contained pollutants.

Stabilization facilities receive the bulk of waste to be stabilized in the form of ash from the incinerators and as heavy metal sludge from the wastewater treatment area. The ash is received in dumpster boxes, and the heavy metal sludge is received as a water slurry via direct pipeline and as a semisolid filter cake contained in dumpster boxes. Offsite materials destined for stabilization without pretreatment are routed directly to stabilization unloading stations after laboratory confirmation and acceptance procedures. Stabilized waste is transferred to the landfill by truck or pipeline.

The stabilization process is suitable for all inorganic wastes and organic-contaminated wastes that can be incorporated homogenously into an aqueous phase by dissolution, suspension or absorption. Generally, the maximum acceptable level of organics in the waste is a few percent by weight. Plant policy is that organic wastes will not be treated by stabilization or interred in the landfill. The process is especially effective in treating all heavy metals, including arsenic and mercury and asbestos.

Stabilization Technology

The APHWMF stabilization process (Figure 7) is carried out on a batch basis. Liquid wastes are stored in tanks fabricated of appropriate materials. Bulk solid wastes are stored in separate bunkers. Raw materials used in the treatment process are stored in bunkers and storage silos and on pallets. The liquid storage tanks have agitators to prevent solids from settling and to maintain homogeneous mixtures in the tanks.

The first stage in the process is to blend, homogenize and pretreat a variety of wastes available from storage. In this way, interactions between the various wastes can be employed to bring the waste mix to the desired state before formulation of the treatment mix. After neutralization and pretreatment of reactive wastes, appropriate quantities of compatible liquid and solid wastes are blended in a stock pretreatment tank. Solid materials are passed through a crusher to reduce the particle size. Appropriate quantities of lime and fly ash are blended thoroughly to prepare the mixture for the final product formulation. At this point the mixture has a pH >9 and contains 10–40% total solids. The mixture must contain the proper ratio of solids to water so that adequate water of hydration is available for the solidifying reactions. The bulk of water

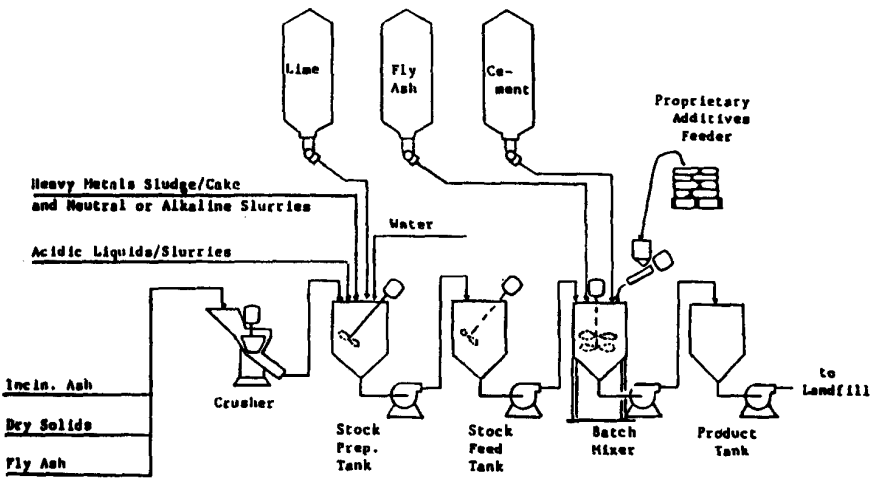

Figure 7. API HWMF stabilization process.

needed is obtained by mixing in heavy metal slurry containing only about 2–4% solids from heavy metals treatment. After the stock is thoroughly blended, samples are taken and tests are run in the laboratory to determine the characteristics of the batch and the formulation necessary to produce a satisfactory final product. The prepared stock is then transferred to a stock feed tank.

Weighed quantities of premixed stock from the stock feed tank are mixed with weighed quantities of additives (fly ash, cement and proprietary additives) in a batch mixer according to the formulation determined by the laboratory. The mixture is then blended by a high-speed shear mixer before being discharged to the product tank.

The prepared product is a thick slurry similar to wet masonry mortar. This slurry is pumped from the product tank directly to the landfill placement area via pipeline. At the landfill, the material is cast into a single monolithic mass containing about one week's production. In about 6 hr to 3 days the material converts to a rock-like mass. Rainwater falling on uncured material runs off the surface without affecting the properties of the material. The placed material sets even if submerged in water. The placement procedure strives to produce a solid monolith to exclude environmental interactions with the placed material. The larger the treated monolithic mass, the greater the proportion of the waste isolated from any environmental interactions.

Stabilization System Performance

The treatment performance of the stabilization process is measured by the characteristics of the stabilized waste product. The stabilized waste product has the following characteristics:

- Physical appearance—the stabilized product sets to form a hard, rock-like monolith. The material is nonflammable, nonodorous, nonputrescible and unattractive to vectors.
- Permeability—the coefficient of permeability is less than 1×10^{-6} cm/sec, which is less than concrete and equivalent to compacted clay.
- Leaching—the concentration of heavy metals in the leachate is typically less than 1 ppm.
- Strength—the unconfined compressive strength is greater than 200 psi.
- Density—the density of the stabilized product ranges 65–85 lb/ft^3.

Landfill

The APHWMF landfill is not used for detoxication of hazardous wastes, but simply as a repository for detoxicated inert residues. As such,

it is not described here except to state that it is a secure landfill designed and operated to state of Louisiana and RCRA standards.

Wastewater Management Systems

The APHWMF wastewater management system will consist of seven areas designed to treat, detoxicate or handle specific onsite wastewaters. The seven major areas are shown in Figure 8 and can be categorized into four systems:

1. a system for treatment of wastewaters contaminated with specific inorganic compounds such as metals (heavy metals removal);
2. a system for treatment of wastewaters contaminated with organic compounds (pretreatment, biological oxidation and carbon adsorption);
3. a system for handling stormwater; and
4. a system for retention of treated effluent until its suitability for discharge has been proven by analysis (final effluent handling).

All areas will be integrated to provide treatment flexibility, since on occasion wastewater or effluent normally containing only inorganic compounds may become contaminated with organics or vice versa. Only the first two areas, however, are described here, since they employ detoxication technologies.

Technologies to Detoxicate Wastewater Contaminated with Toxic Inorganics

The first treatment system, shown at the top of Figure 8, consists of heavy metals removal. This treatment area will process the largest volume of wastewater of any system (up to 2000 gal/min). It will be operated principally to remove 500–2000 ppm of dissolved metals and suspended solids from incinerator scrubber purge water. It will have the capacity, however, to treat other wastewater that may be contaminated with metals or suspended solids, such as landfill leachate and runoff. The major unit operations and detoxication technologies employed by this system are pH adjustment, flocculant aid addition, clarification, filtration and sludge handling.

All waste streams feeding the heavy metals removal area first flow into a main sump. From this sump, wastewater is pumped through three evaporative cooler/sulfite oxidizers and into a cooling sump. Cooled wastewater from this sump subsequently flows into a pH adjustment basin, where the pH of the wastewater is adjusted by addition of caustic or acid to precipitate metal hydroxides. Alum is also added to aid in

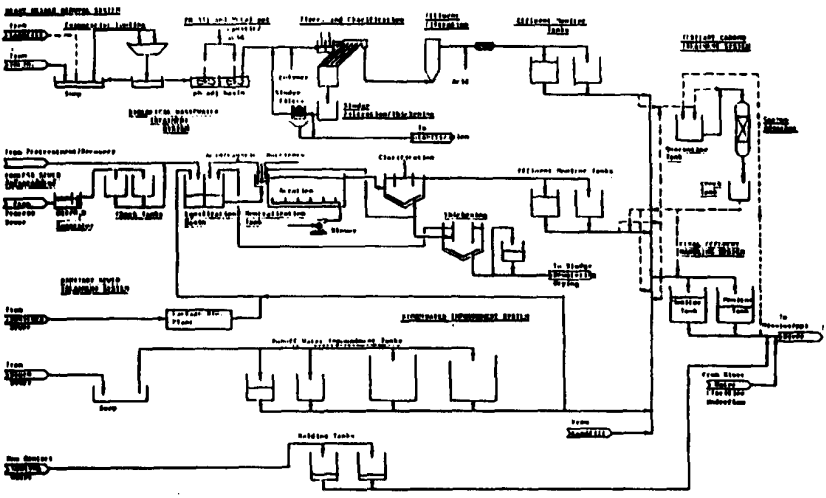

Figure 8. Simplified flow diagram of APIIWMF wastewater treatment/handling system.

flocculating the hydroxides. Wastewater from the pH adjustment basin is pumped into two rapid-mix/flocculator tanks. Here it is combined rapidly with polymer solution to aid flocculation. The wastewater solution overflows into the flocculation compartments of the tank, where flocculation of precipitated metal hydroxide particles is encouraged by the slow mixing action of flocculator agitators.

Thoroughly flocculated wastewater exits the rapid-mix/flocculator tanks by overflowing into one of two gravity clarifier/thickeners. Flocculated solids settle to the bottom of the thickeners, and supernatant liquor, low in metals and solids, overflows at the top. On exiting the clarifier, the supernatant liquor flows by gravity through one of six sand filters, where practically all residual suspended solids are removed. A backwash stream flows from the filters to the pH adjustment basin to keep the filters clean. Wastewater exiting the sand filters is expected to be of acceptable effluent quality in all respects, i.e., less than 5 ppm total suspended solids (TSS), and less than Louisiana state water discharge limits for toxic metals. It will, however, be detained in holding tanks until its suitability for discharge has been confirmed by analysis.

Metal hydroxide particulate and other suspended solids removed from wastewater in the clarifiers will be thickened in the clarifier thickening section. Some of this thickened sludge will be pumped directly to stabilization, and the remainder will be filtered in a plate-and-frame filter press. The filter cake will be transported to stabilization.

Technologies for Detoxication of Organic-Contaminated Water

Process Sewer Pretreatment. Aqueous wastes from the process sewer will be pretreated before they enter the biological wastewater treatment system. The wastewaters expected to enter process sewer pretreatment come from operations such as tank cleaning, building and equipment washdowns, laboratory testing and sample analysis, truck washouts, and other miscellaneous operations. These wastewaters will pass through an oil/water/grit separator (see Figure 8, second line) and enter one of two holding tanks. Water contained in such a tank will be analyzed to determine its treatability. Depending on the analytical results, wastewater normally will be pumped to biological treatment. However, it also may be pumped to aqueous wastes pretreatment, where unit operations such as steam stripping, carbon adsorption, solvent extraction or chemical treatment will be used to remove nonbiodegradable and purgeable organics.

Sanitary Sewer Treatment. Sanitary sewage from lavatories, change rooms and toilets will be degraded in a packaged biological treatment unit shown on the third line of Figure 8. Effluent from the unit will be disinfected with ozone and then discharged into the biological wastewater treatment system.

Biological Wastewater Treatment System

The primary "end of the line" organic wastewater treatment unit at APHWMF is the biological wastewater treatment system. Wastewater from various areas will be detoxicated to reduce degradable organics, biochemical oxygen demand (BOD) and suspended solids. The principal unit operation of the system is an extended aeration activated sludge system. Ancillary unit operations include equalization, neutralization and waste sludge thickening as shown in Figure 8, second train.

Oxygen transfer and mixing will be provided by a submerged aeration system. Static aerators will be mounted on the bottom of each aeration tank on approximately 8-ft centers. Air will come from three blowers, and the flow to each aeration tank will automatically be adjusted by a modulating valve controlled by the dissolved oxygen concentration in the individual tank. Nitrogen required for the biological treatment process will be supplied by metering 50% aqueous urea solution into the neutralization tank. Phosphorus required for biological treatment will be supplied by metering 85% phosphoric acid into the neutralization tank.

Thickened sludge will be removed from the bottom of the clarifier by a suction withdrawal mechanism and will be pumped to the aeration tank distribution channel. Thickened waste-activated sludge (WAS) from the sludge thickener will be pumped to the WAS holding tank or to sludge dewatering/drying for dewatering. Supernatant from the sludge thickener will flow by gravity to a supernatant wet well and will be pumped to the equalization tanks.

Clarified effluent from the secondary clarifiers will flow into either of two check tanks. These check tanks will retain clarified effluent for a sufficient time to determine if it has been treated adequately. If it has been treated adequately, it will be discharged into the final effluent handling check tanks. If it has not been treated adequately, it will be pumped to tertiary carbon treatment for final polishing.

The biological treatment system will process up to 400,000 gal/day of wastewater containing 1000–7500 ppm of BOD and produce an effluent containing 50–225 ppm of BOD.

Tertiary Carbon Treatment

The tertiary carbon treatment system is to be used on an as-needed basis to treat off-specification aqueous effluents from all other wastewater treatment systems. The system is designed to treat an average of 400 gal/min of wastewater through two carbon columns operated in parallel. The quantity of wastewater that each carbon column can effectively process depends on a number of factors. The most important factors are the types of organics in water feeding the column and their concentrations, the dynamic loading of organics at the breakthrough point, and the concentration of suspended solids in the feed. The design case is for a total organic concentration of about 20 ppm in effluent feeding the columns, suspended solids concentrations of 20–160 ppm, and a conservative dynamic loading of 0.01 lb total organics/lb carbon at breakthrough.

Stormwater Impoundment

The third major handling system shown in Figure 8 is the stormwater impoundment area. This system will consist of devices to segregate, convey, store and analyze rainwater to determine its appropriate disposition, and then dispose of it by discharge to final effluent handling or to one of the treatment systems discussed above.

Final Effluent Handling

The remaining system shown in Figure 8 is final effluent handling. Treated effluents from heavy metals removal, stormwater impoundment and biological wastewater treatment are contained and held in this area for up to 12 hr until analysis indicates their suitability for discharge or need for retreatment. If retreatment is needed, the combined effluents will be pumped to a quarantine tank in the tertiary carbon treatment area. If the treated effluent meets permit standards and is suitable for discharge, it will be monitored and then combined with uncontaminated riverwater, clarifier underflow and noncontact cooling water. This combined stream will then be discharged to the Misssissippi River.

SUMMARY AND CONCLUSIONS

The present detoxication technologies of the NCTSC facility include air/steam stripping, chemical treatment, solvent recovery, oil reprocess-

ing and incineration. Detoxication technologies described for the future (APHWMF) facility include steam stripping, carbon adsorption, solvent extraction, chemical treatment, sludge dewatering/drying, chemical recovery, incineration, stabilization and wastewater treatment.

The technologies planned for future facilities are extensions or improvements of those currently used. For example, the steam stripper described for the future facility performs a function similar to the air/steam sparging system of the current facility, but is much more efficient. Similarly, the solvent recovery system of the future facility is much more efficient and sophisticated than that of the present solvent recovery system. In addition, the integrated nature of the future facility is an extension of the current facility, since such integration is essential to applying waste detoxication technologies economically to hazardous waste management on a contract basis.

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CHAPTER 2

CHEMICAL PROCESSES IN THE INCINERATION OF HAZARDOUS MATERIALS

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The underlying phenomenon associated with incineration is a series of complicated chemical changes. Historically, however, the subject has been dominated by physical considerations and the experience of long practice. This is hardly surprising, since the conversion of a complex, ill defined conglomeration of principally organic substances to light gases and ash is not a process that lends itself to detailed chemical considerations. Furthermore, in the absence of environmental regulations or energy constraints, hardly any chemical expertise is necessary. Recent events [1] mandating incineration as a primary disposal tool for hazardous wastes and the possibility that hazardous substances may be formed in combustion processes [2,3] suggest the necessity for a closer look at the chemical basis of incineration. Such information can lead to prediction or at least classification and thus ultimately to the appropriate strategies for measurement, abatement and foundation for new approaches. This approach can mean important savings in terms of proper measurement methodology as well as decreased needs for large-scale testing.

This chapter will begin by giving a qualitative picture of how a large polyatomic molecule breaks down under incinerator conditions from the

point of view of elementary processes. We next attempt to make these concepts quantitative, first in terms of thermodynamic equilibrium and then from a more detailed consideration of the rates (or at least the relative rates) of the pertinent elementary processes. We will pay particular attention to sources of data and the availability of estimation schemes. These concepts will then be applied to chemicals that are of interest in a hazardous waste context. Finally, we will list a number of unanswered questions and suggest certain types of experiments that will help provide a proper methodology and data base for design and operational purposes in the incineration of hazardous wastes.

REACTION MECHANISMS

If one considers the decomposition of a complex polyatomic molecule in the hostile environment of an incinerator, the basic processes are stepwise breakdown of the molecule to smaller and/or oxygenated species together with the alternative possibility of buildup to large species culminating in soot formation. Figure 1 gives a pictorial description. In a sense, the incineration process can be characterized as a race between destruction of reactants to smaller species and the side reactions yielding unwanted products. The individual elements that govern these transformations are the elementary reactions. These are processes that occur as written, in contrast to global reactions (such as $7\ O_2 + 2Br_2C_3H_3Cl \rightarrow 4HBr + 2HCl + 6CO_2 + 2H_2O$), which express the chemistry of the combustion in terms of the overall conversion. Treatment in this form is appropriate only if the rates are assumed to be infinitely fast or as a basis for an empirical analysis of experiments. Only through elementary processes can one derive the type of general picture that is transferable to all conditions and systems. In seeking a more general solution, the required information base is correspondingly increased. Nevertheless, because one is dealing with elementary processes, the possibility of extrapolation and interpolation is enlarged. Furthermore, all elementary processes are not equally important in any given process; thus, identification of key reactions can lead to simplification. Finally, we note that the treatment of combustion processes in terms of elementary reactions is and has been for many years the state-of-the-art [4].

In terms of elementary processes and for present purposes there are only two broad classes of reaction types: unimolecular and bimolecular. As evidenced by the name, the former is represented by processes of the type:

where the rate of destruction can be written as $dHz/dt = -k_{uni}Hz$. Bimolecular reactions deal with the attack of reactive species on a molecule:

$$R + Hz \rightarrow \text{product(s)}$$

and the rate of destruction is now $dHz/dt = -k_b(R)(Hz)$. The former is conceptually the simplest of all kinetic processes. It involves a molecule at a particular temperature having sufficient internal energy so as to cause rupture of its bond(s) within the time scales of the experiments. The rate constant k_{uni} is a fundamental property of the molecule itself, in the same sense as infrared spectrum or boiling point. Unimolecular reactions can be classified in terms of bond rupture, complex fragmentation and isomerization processes [5].

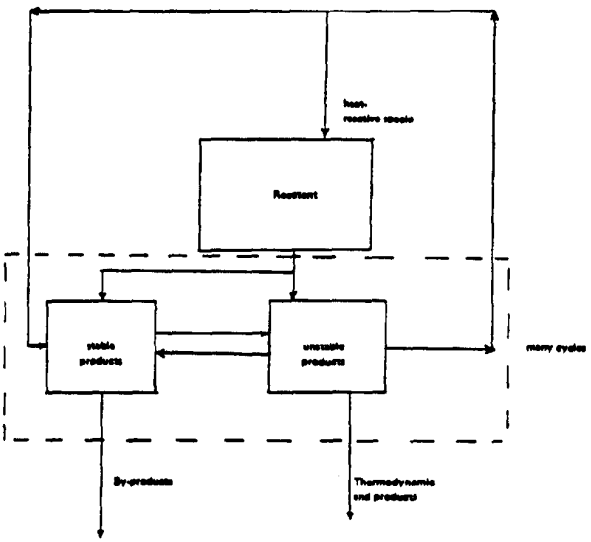

Figure 1. General mechanism for the disintegration of a polyatomic molecule under incineration conditions.

For present purposes we will be interested primarily in the first two reaction types. Within these groupings, related molecules behave in a consistent manner. Structural characteristics control molecular stability, thus providing a basis for prediction. Under certain circumstances, unimolecular reactions can have a pressure dependence [6]. The nature of this phenomena is well understood, and if the pressure-independent behavior (at sufficiently high pressures) is known, appropriate corrections can be made. For all except the smallest of molecules, we do not believe that this phenomenon is of major importance under incineration conditions. The situation with respect to bimolecular reactions is made more complicated by the multiplicity of possible reaction species. Thus, the rate of destruction depends on the constituents of the reactive systems, as opposed to the situation for unimolecular processes, where only the physical properties, principally temperature, are of concern. The two distinct types of bimolecular reaction of interest are addition and metathesis [5]. The former leads to the formation of larger species and is related to unimolecular reactions through the equilibrium constant. In certain cases, addition leads to a sufficiently thermally hot molecule (chemical activation) and a subsequent cracking step occurs. This phenomenon also can be handled within the context of unimolecular rate processes. Metathesis is concerned with the transfer of an atom or group of atoms from one molecule to another. As in the unimolecular situation, structural features govern reactivity, thus providing a basis for prediction.

EQUILIBRIUM CONSIDERATIONS

The earlier discussion has been developed on the basis of considering the incineration process from the viewpoint of elementary reactions. As has been indicated, the present data base is insufficient for derivation of a complete solution. In this and subsequent sections we will attempt to summarize existing data and indicate how they may be used in the present application. Thermodynamics permits a powerful zero-order description of any system. Results are rigorous, assuming that equilibrium is achieved. At the very least they set important constraints on the range of possibilities. Furthermore, the data base is available, and the procedures for calculations are well established and have been used widely in combustion contexts. The data base given by Stoll and Prophet [7] represents the essential source of all thermodynamic data on atomic, diatomic and small polyatomic species. For the larger polyatomics there are two outstanding compilations, by Cox and Pilcher [8] and Stull et al. [9]. More importantly, with the existing values as a basis, it is possible to estimate with high accuracy the thermodynamic properties of practically

Table I. Calculated and Literature Values for Heats of Formation of Substituted Benzenes

	$-CH_3$		$-Cl$		$-F$	
Substitution	Calc.	Lit.	Calc.	Lit.	Calc.	Lit.
1,2,3-	-2.73	-2.26 ± 0.29	2.18		-111.39	
1,2,4-	-3.15	-3.31 ± 0.26	0.48		-114.46	
1,3,5-	-3.74	-3.81 ± 0.33	-0.02		-118.79	
1,2,3,4-	-10.22	-10.02	-1.95		-150.52	
1,2,3,5-	-10.64	-10.71	-3.05		-154.22	
1,2,4,5-	-10.47	-10.82	-3.65		-153.59	
Penta-	-17.72	-17.80	-5.09		-188.28	-193.59 ± 0.35
Hexa-	-24.53	-20.75 ± 0.62	-6.14	-8.6 ± 2.3	-220.97	-228.49 ± 0.29

Table II. Thermodynamic Functions for 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin

Temp.	cal/(mole°K)			kcal/mole			
(°K)	C_p°	S_T°	$-(G_T^\circ-H_0^\circ)/T$	$H_T^\circ-H_0^\circ$	ΔH_f°	ΔG_f°	Log K_p
200	40.95	94.75	72.45	4.46	-81.83	-58.34	63.735
298.16	56.67	114.11	83.02	9.27	-82.49	-46.67	34.199
300	56.84	114.46	83.21	9.37	-82.50	-46.43	33.815
400	69.94	132.67	93.33	15.74	-82.87	-34.33	18.755
500	80.39	149.44	102.90	23.27	-82.98	-22.18	9.694
600	88.53	164.85	111.96	31.74	-82.94	-10.02	3.651
700	94.88	179.00	120.54	40.92	-82.78	2.12	-0.662
800	99.87	192.00	128.67	50.67	-82.51	14.23	-3.886
900	103.85	204.00	136.38	60.86	-82.21	26.30	-6.386
1000	107.06	215.12	143.71	71.41	-81.77	38.34	-8.377
1100	109.68	225.45	150.67	82.25	-81.27	50.31	-9.995
1200	111.85	235.09	157.31	93.33	-80.72	62.25	-11.335
1300	113.66	244.11	163.65	104.61	-80.19	74.15	-12.463
1400	115.18	252.59	169.70	116.05	-79.67	86.00	-13.423
1500	116.47	260.59	175.49	127.64	-79.16	97.80	-14.247

all polyatomic molecules. In view of current interest in polychlorinated aromatics, we have been estimating the thermodynamic properties of many such compounds [10]. Table I summarizes estimated heat of formation data for a number of halogenated species and comparisons with direct determinations. It should be noted that at higher temperatures (of interest for incinerator operation), accuracy requirements for energy quantities are much less severe than for ambient conditions. Table II is a typical JANAF-type [7] data sheet for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. With such information and appropriate ancillary data from the literature, heat of combustion and adiabatic flame temperatures can be

computed. More significantly, one can calculate the equilibrium distribution of species for arbitrary temperature, pressure and initial composition. Our calculations for a variety of the polychlorinated aromatics indicate that at temperatures in excess of 500°C, the reaction is thermodynamically complete. Except for greater stability with increased chlorination there is no single compound with special stability characteristics.

The fact that much higher temperatures are required in practice to effect destruction shows that at the lower temperatures at least, equilibrium is not achieved and the reactions are kinetically controlled. This does not rule out the possibility that in certain subsets of the entire system local thermodynamic equilibrium is in fact achieved. This local equilibration should be particularly true for small inorganic radicals, which can undergo fast reactions with each other. This assumption is widely used in the analysis of combustion systems, and we will employ this as a means of estimating radical concentrations at high temperatures. Furthermore, as implied earlier, coupling thermodynamic information with the rate of reaction in one direction permits, through detailed balance, calculation of the reverse rate. Finally, thermodynamic properties of stable compounds are the basis for calculation of transition state properties leading to predictions of mechanisms and rates [11,12]. They are thus the quantitative basis for high-accuracy structure-reactivity relations.

QUANTITATIVE ASPECTS OF DECOMPOSITION PROCESSES

In the most general terms, the destruction of a hazardous waste Hz in an incinerator can be described by the relation

$$-dHz/dt = k_{uni}[Hz] + (\sum_i k_{bi}R_i)[Hz]$$

where k_{uni} = unimolecular rate for decomposition
k_{bi} = bimolecular rate constant for attack of specie R_i on Hz.

Rearranging, we can write

$$\int_{Hz_i}^{Hz_f} -dHz/Hz = ln\ Hz_i/Hz_f = \int_0^{\tau} [k_{uni} + (\sum_i k_{bi}R_i)]dt$$

where τ is the residence time in the incinerator. The U.S. Environmental Protection Agency (EPA) requirement for 99.99% destruction efficiency is equivalent to setting a value of 9.212 for the logarithmic term in the relation. Within this context, the problem becomes one of finding the conditions where the integral involving k_{uni}, $\Sigma k_{bi}R_i$ and T is in excess of 9.212.

Consider first the situation where unimolecular processes are the predominant mode of decomposition. In this case, assuming a reasonably uniform temperature situation and the usual incinerator residence time of approximately 1 sec, and since $9.212 \leqslant k_{uni} = A_\infty \exp(-E_\infty/RT)$, we arrive at the minimum temperature as tabulated in Table III. A_∞ and E_∞ values given here cover virtually the complete range of such values.

Study of the rates of unimolecular decomposition processes has long been a favorite pastime of chemical kineticists. Outstanding collections of information are given by Benson and O'Neal [11] and Robinson and Holbrook [6]. Comparison of the data in these reviews and the numbers in Table III clearly demonstrates that under the stated incinerator conditions, most of the organic molecules will decompose on the basis of thermal stability considerations alone. In view of the large literature, one expects direct determinations for a number of hazardous materials. In other cases, the existing data can be used for extrapolation and prediction. An examination of the situation with respect to the rates of cleavage of a single chemical bond is instructive. In this case, two reactive radicals are formed. Since the activation energy for recombination is known to be negligible, the bond dissociation energy is the activation energy for dissociation. The relationship between this quantity and chemical reactivity has focused important research efforts in this direction. For the present purpose it is sufficient that extensive tables of such quantities [13–16] or the equivalent heats of formation of the radicals exist. A typical sampling can be found in Table IV [14–18]. When this is combined with the experimental observation that the preexponential factor per bond broken is in the range of 10^{15}–$10^{16.5}$/sec, where the range of values increase from dissociation, to polyatomic + atom, to polyatomic + diatomic, to polyatomic + polyatomic, one can determine readily from Table III the approximate conditions to achieve the appropriate destruction limits. Furthermore, except for resonance stabilization effects,

Table III. Temperature (°K) Necessary to Assure 99.99% Destruction Assuming Unimolecular Mechanism and Arrhenius Rate Expression [$k = A_\infty \exp(-E_\infty/RT)$] for Incinerator Residence Time of ~1 sec

A_∞ (/sec)	E_∞ (kcal)							
	40	50	60	70	80	90	100	110
10^{12}	792	990	1188	1386	1584	1782	1980	2178
10^{13}	726	908	1089	1271	1453	1634	1815	1980
10^{14}	670	838	1006	1173	1341	1509	1676	1844
10^{15}	622	778	934	1090	1245	1401	1556	1713
10^{16}	581	727	872	1017	1163	1308	1453	1599
10^{17}	545	681	818	954	1090	1226	1362	1499

Table IV. Some Typical Bond Energies of Polyatomic Compounds [14–18]

Radicals	H	F	Cl	Br	I	OH	NH_2	NO_2	NO	CH_3
CH_3	104	109	84	70	56	91	87	60	44	88
C_2H_5	100		83	70	55	93	86	60	44	87
iC_3H_7	97	108	83	70	55	93	87		46	86
tC_4H_9	96		84	71	55	96	88		45	82
C_2H_3(vinyl)	115		99		68					107
C_3H_5(allyl)	90		72	56		82				77
C_6H_5	111	125	95	80	64	110	104	70	52	100
$C_6H_5CH_2$	89				44	81				80
CH_2Cl	102		79							
$CHCl_2$	99		77							
CCl_3	96		70	56					32	88
CH_3O	104					44		44	41	88
C_6H_5O	87									80
CH_2CO	87	118	83	67	50	108	99			86
NH_2	107						65			83

substitutions to the bond being broken at positions greater than α have very little consequence on the bond dissociation energies. Thus, the range of compounds covered in such a listing is far larger than the compounds directly involved.

For the present purposes, primary interest is focused on the fastest process that will destroy a molecule. In the framework of unimolecular decompositions, complex fragmentations (where simultaneous cleavage and formation of bonds occur) frequently provide a low-energy channel for decomposition, in comparison to direct breaking of a single bond. Our understanding of complex fragmentations is considerably less than for direct bond breaking. As was the case for bond-breaking processes, an important factor to remember is that these reactions involve localized properties. Thus, except for substitution near the reactive site, rate parameters can be considered to be invariant.

As an example of these ideas, consider the situation with respect to a wide variety of chloroalkanes as summarized in Table V. The primary mode of decomposition is the four-center elimination of hydrogen chloride to form the appropriate alkene. In contrast, the bond cleavage reactions involving C-C and C-Cl bonds are all in the neighborhood of 80 kcal. This lowered activation energy more than compensates for the two-order-of-magnitude drop in A factors. Thus, molecular elimination is the primary decomposition mechanism. Note particularly the similarities in rate parameters for the decomposition of a particular type of alkyl chloride molecule. This trend is carried over to the bromides and iodides.

Table V. Rate Expressions (/sec) for the Decomposition of Alkyl Chlorides [11]

$C_2H_5Cl \rightarrow C_2H_4 + HCl$	$10^{13.45}\exp(-55{,}000/RT)$
$nC_3H_7Cl \rightarrow C_3H_6 + HCl$	$10^{13.6}\exp(-55{,}150/RT)$
$nC_4H_9Cl \rightarrow C_4H_8 + HCl$	$10^{13.2}\exp(-56{,}5000/RT)$
$iC_3H_8Cl \rightarrow C_3H_6 + HCl$	$10^{13.6}\exp(-51{,}100/RT)$
$sC_4H_9Cl \rightarrow C_4H_8 + HCl$	$10^{14.0}\exp(-50{,}600/RT)$
$tC_4H_9Cl \rightarrow C_4H_8 + HCl$	$10^{13.8}\exp(-45{,}000/RT)$
$tC_5H_9Cl \rightarrow C_5H_{10} + HCl$	$10^{13.7}\exp(-44{,}000/RT)$

We next consider bimolecular channels for hazardous chemicals destruction. The greater complexities inherent in this situation have been discussed earlier. Indeed, it is not possible to examine this problem with the same rigor as in the unimolecular case. However, it is possible to make some reasonable estimates. The basic model that will be considered is that of a high-temperature oxidative system at equilibrium, and we seek to estimate the lifetime of a thermally stable molecule in this environment. The equilibrium hypothesis, which should be of considerable validity, immediately yields species concentration. Of particular concern are OH, O and H concentrations. These are the most important high-temperature-reactive species, in the sense that most larger radicals are thermally labile and/or less reactive. Figures 2 to 4 represent equilibrium H, OH and O mole fractions at various temperatures at 1 atm and equivalence ratios of 0.5, 1.0 and 2.0, respectively. It is immediately clear that, with respect to bimolecular removal, attention must be focused on H and OH attack. The lack of accurate high-temperature rates for these processes introduces another uncertainty into these considerations. However, OH attack on organic substrates is one of the key processes in tropospheric chemistry. Thus, there is a large data base of information at room temperature, from which certain inferences can be drawn. It should also be noted that since incineration of hazardous wastes is usually carried out with large excesses of air, the OH contribution to bimolecular destruction must be quite important.

Two publications [17,18] have summarized the current state of knowledge on rates and mechanisms of OH attack on organic substrates. From a mechanistic viewpoint there are two processes to be considered: addition and abstraction of hydrogen atoms. For the former, under incineration conditions, the overall process must also involve fragmentation subsequent to addition. Table VI represents a sampling of recent information of OH reactions with organic compounds at or near ambient conditions. With respect to addition, the salient feature is the electrophilic nature of the OH attack on the unsaturates, leading to drastic lowering of

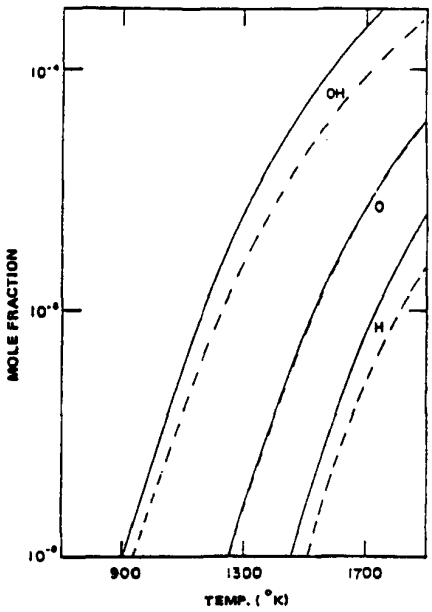

Figure 2. Equilibrium OH, O and H mole fractions at 1 atm pressure for stochiometric (ψ = 1) reaction with CH_4 (——) C_6H_6(----) in 5% Cl_2.

the rates with increasing halogenation. With respect to abstraction, the strength of the bond being broken obviously is an important factor. An empirical equation [19] has been proposed that directly relates rates with bond dissociation energy. Thus, the bond dissociation data summarized in Table III clearly are of greater applicability than merely for the prediction of unimolecular decomposition rates. It should be noted that the OH abstraction reactions under discussion all involve H-atom transfer. This is because for the halides, the overall reaction process is too endothermic. Another factor that makes the OH data useful is that, as far as addition is concerned, it tracks O-atom processes [6]. Thus, on a relative basis, these two processes can be lumped together. To use this information at incinerator conditions, accurate methods for extrapo-

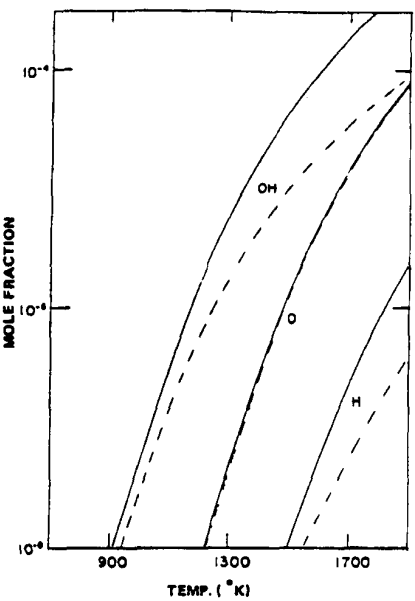

Figure 3. Equilibrium OH, O and H mole fractions at 1 atm pressure for fuel-lean (ψ = 0.5) reaction with CH_4(——) and C_6H_6(----) in 5% Cl_2.

lation are needed. The temperature dependence that has been determined covers very narrow ranges near ambient, and the accuracy of projected results at the higher temperatures is therefore uncertain. One does note, however, the difference in the directions of the temperature dependence in the sense that the addition processes usually have negative activation energies. In other words, the rate goes down with temperature. Probably a more appropriate functional form is a $(1/T)^n$ dependence. Furthermore, there is increasing evidence that for OH abstraction reactions there is a positive curvature in the Arrhenius plots. In general, one would expect that addition processes will be slower than abstraction under incineration conditions.

We next consider H-atom processes [19,20]. We have noted previously that, under most hazardous waste incineration situations, the presence of

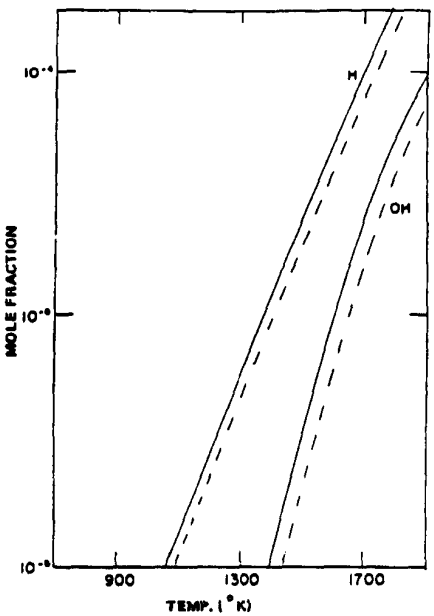

Figure 4. Equilibrium OH and H mole fractions at 1 atm pressure for fuel-rich (ψ = 2.0) reaction with CH_4(——) and C_6H_6(----) in 5% Cl_2 (0-atom mole fraction is less than 10^{-8}).

excess air makes it unlikely that it will be of importance. However, in the presence of mass transfer problems, substances may well pass through oxygen-deficient environments. Hydrogen atom abstraction reactions are characterized by higher A factors and activation energies than comparable OH reactions. The consequence is that, at incineration temperatures, their rate constants are close to that for OH attack. The general trends for H abstraction are dependent on the appropriate C-H bond dissociation energy. With respect to addition, H atom rates at room temperature do not follow the general trends characteristic of OH attack. Indeed, variations appear to be small. The equilibrium concentration of H atoms in air-lean systems is lower than OH concentrations in air-rich situations (see Figures 2 to 4). The consequence is that destruction rates will be

Table VI. Typical Rates of OH Attack on Organic Substrates [6]

Compounds	Rate Const. at 298°K (liter/mol-sec)	Rate Parameters A (liter/mol-sec)	E (kcal)
CH_4	5.4E6	2.4×10^9	3600
C_2H_6	1.6E8	1.1×10^{10}	2400
nC_4H_{10}	1.8E9	8.4×10^9	1000
iC_4H_{10}	1.7E9	4.8×10^9	769
CH_3F	1E7		
CH_3Cl	2.2E7	1.8×10^9	2400
CH_2Cl_2	9E7		
$CHCl_3$	8E7	2.4×10^{10}	2254
HCHO	7.2E9	6×10^9	175
CH_3OH	6E8	—	—
CH_3CHO	9E9	4.2×10^9	-510
CH_3SH	1.8E10	5.4×10^9	-790
CH_3NH_2	1.2E10	6×10^9	-455
C_2H_4	3.6E9	7.2×10^8	-900
C_3H_6	1.6E10	2.4×10^{10}	-1100
$2C_4H_8$	4.2E10	6×10^9	-1100
CH_2CHCl	4.2E9	6×10^8	-800
$CHClCH_2Cl$	1.8E9	3×10^8	-900
C_2Cl_4	1E8	6×10^9	2400
C_6H_6	9E8		
C_6F_6	1.3E8		

slower. For the same extent of conversion one expects that an increase of at least 150°K is required.

A direct consequence of the above is a model involving hazardous waste destruction of the more thermally labile compounds by unimolecular decomposition and the more stable components by radical attack. An estimate of the temperature that divides the two classes of compounds can, in conjunction with the data in Table III, give some idea of the compounds belonging to each class. Figure 5 represents equilibrium OH mole fraction at various equivalence ratios and chlorine concentrations. To within a factor of three, this can be represented by:

$$OH \approx 10^{-1.7} \exp(-35{,}000/RT) \text{ mol/l}$$

If we now examine the data on the rates of OH attack on organic substrates, we can estimate that, at incinerator conditions, bimolecular rate constants will be of the order of $10^{9\pm1}$ liter/mol-sec. The consequence is that to obtain the pseudo-unimolecular rate constant of 9.212, we need a temperature of the order of 1230°K. If one now considers the results from Table III, it is seen that for bond cleavage reactions, unimolecular

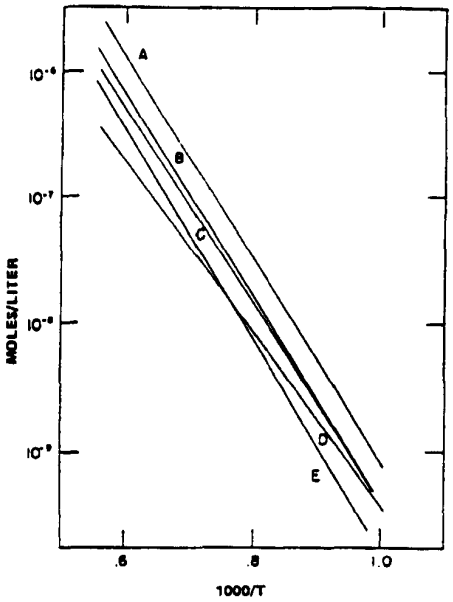

Figure 5. Equilibrium OH concentration for various reaction conditions as a function of temperature. A = CH_4, ψ = 1.0, Cl_2 = 0%; B = CH_4, ψ = 1.0, Cl_2 = 5%; C = C_6H_6, ψ = .5, Cl_2 = 5%; D = C_6H_6, ψ = 1.0, Cl_2 = 0%; E = C_6H_6, ψ = 1.0, Cl_2 = 5%.

decomposition will be quite important for compounds with their weakest bonds in the 80- to 85-kcal range. This range covers many of the larger organics with their numerous aliphatic C-C bonds. Since the rates of most known complex fragmentation processes are faster than comparable bond cleavage reactions, molecules with such decomposition channels will also decompose via unimolecular mechanisms. Thus, radical attack is of major importance only for a limited class of compounds: specifically, simple aromatics and other unsaturated molecules without organic substituents, and the simplest one- or two-carbon saturated systems.

The present treatment can be extended simply to the problem of the production of hazardous waste during combustion if one extends the

criteria of 99.99% destruction to requiring similar extent of decomposition for the products that are formed. In general, this requirement will mean the use of slightly larger unimolecular rate constants as the criteria that must be met, perhaps of the order of ~20 to take into account the fact that products have residence times half that of the reactant. This assumes a constant rate of product formation from a precursor.

APPLICATION TO HAZARDOUS MATERIALS INCINERATION

The model that has been developed is a very idealized one. Aside from the assumptions that have been described, the analysis has been carried out on the basis of completely homogeneous gas-phase systems. Direct application is rendered uncertain by the neglect of mass- and heat-transfer effects. Thus, a molecule trapped in a particulate matrix may not be heated to the incinerator temperature or be attacked by a reactive radical. The most effective use of such information will occur in situations in which such effects may be cancelled out. A likely possibility is the setting up of a scale of incinerability and providing guidance for the kind of "test burns" that can qualify the operation of an incineration for a whole range of other compounds. This possibility will be especially true for systems with well defined unimolecular channels for decomposition, since the temperature necessary fo 99.99% conversion with a 1-sec residence time provides a well defined parameter. The lack of accurate high-temperature information on OH and H rates makes calculated relative numbers of such processes somewhat uncertain. For the present purposes, we believe that OH reactivity is of greater importance, and the appropriate variables should be C-H bond strength and (in the case of addition) extent of halogen substitution. On this basis Table VII gives a ranking of some hazardous organic compounds [21]. It should be emphasized that for the fuel-rich systems, where H-atom reactions are important, chlorinated aromatics may be less stable in comparison to the pure aromatics. This difference emphasizes the provisional nature of the ranking and indicates the need for additional high temperature rate data on such processes.

EPA has issued interim regulations for the burning of hazardous waste [1]. A suggested procedure for proof of the satisfactory performance of hazardous waste incinerators involves the selection of the principal organic hazardous constituents and the demonstration of 99.99% destruction efficiency for these compounds. It is thus highly dependent on the proper estimate of incinerability. EPA representatives have more recently [22] suggested a ranking based on heat of combustion. The rationale

Table VII. Incinerability Rankings of Some Hazardous Compounds [21]

Rank	Compound[a]	Rationale	Rank (ΔH_c,comb)
1	Hexachlorobenzene	All C-H bonds in excess of	9
2	Pentachlorobenzene	110 kcal, C-Cl bonds ~95 kcal;	7
3	Chlorobenzene	OH addition is major destruc-	26
4	Benzene	tion mode and is dependent	38
5	Naphthalene	on substituents on unsaturated	37
6	Vinyl chloride	structure	20
7	Chloromethane	C-H bonds are in the 90- to	13
8	Ethylene diamine	95-kcal range; all other	33
9	Dichlorophenol	bonds are greater than 80 kcal;	16
10	Resorcinol	assume that OH abstraction	24
11	Chlorotoluene	is controlling	29
12	Formaldehyde		21
13	Acetaldehyde		25
14	Acrolein		30
15	Dimethylphthalate	Bond breaking processes in	
16	Methylethyl ketone	the 60- to 80-kcal range;	
17	Allyl alcohol	unimolecular decomposition	
18	Chloroform	is controlling mechanism	
19	Bromomethane		
20	Dinitrobenzene		
21	Trinitrobenzene		
22	Tribromomethane		
23	Hexachloropropene		
24	Hexachloropentadiene		
25	Bromoacetone		
26	Hydrazine		
27	Methylhydrazine		
28	1,2-Dichloroethane	Low energy pathway through	
29	1,2-Dichloropropane	complex fragmentation into	
30	Hexachlorocyclohexane	stable molecules: $A_\infty \sim 10^{12}$–10^{14}/sec, $E_\infty \sim 45$–55 kcal	
31	Di-*n*-butylphthalate		
32	Ethyl carbamate		
33	1,2-Dibromo-2-chloropropane		
34	Methyliodide	Fragmentation into radicals	
35	1,2-Diphenyl hydrazine	brought about by very weak	
36	Nitroglycerine	bonds; 40–55 kcal range.	
37	*N*-Nitrosodiethyl amine	A-factor $\geq 10^{15}$/sec	
38	2-Butanone peroxide		

[a] The compounds are divided into groups purely for present convenience; when one considers all the compounds in the EPA listing there will obviously be many overlaps.

behind this ranking is that a higher heat of combustion requires a higher flame temperature and presumably a greater capacity to consume itself. The connction between flame temperature and heat of combustion is, of course, not necessarily true. It also must be pointed out that in the particular application in mind, a mixture is being burned; thus, this "driving force" is never manifested. Indeed, through control of auxiliary fuel and equivalence ratios, temperature is a variable that can be adjusted. Furthermore, heat of combustion is a thermodynamic quantity and is definitely not a parameter associated with the activation process that controls molecular stability. A very straightforward way of demonstrating the inappropriateness of the heat of combustion for this purpose is to cite the fact that a variety of explosives, near explosives and propellants (nitroglycerine, trinitrobenzene, hydrazine) are more difficult to destroy than most of the organic compounds in the listing. For example, benzene and polynuclear aromatics are considered among the easiest compounds to incinerate, and the limits of incinerability are almost completely set by benzene and hexachlorobenzene.

The ranking that has been presented here is vastly different from that proposed by EPA. It makes no claim with regard to exact quantitative accuracy. It would displace the listings of compounds supposedly difficult to decompose that are ranked ahead of hexachlorobenzene, simply because most of these will decompose by unimolecular processes at lower temperatures. They will be placed behind benzene. Nitro, nitroso and peroxide compounds are considered among the most labile due to their weak C-N, O-N and N-N bonds. Basically, there is very little concordance at all between the two rankings, except for the greater difficulty to be expected for the incineration of increasingly chlorinated aromatic compounds. Unfortunately, we are not aware of any burn data that can resolve these discrepancies. They are, however, so large that it should not require many experiments to differentiate beteen the two scales.

The present analysis suggests that in terms of the hazardous wastes given in the EPA tabulation, aromatic compounds (particularly the polychlorinated variety) are the most difficult to burn. The capacity to destroy such species is indicative of conditions that can easily destroy other compounds. Indeed, the usual presence of low-energy unimolecular decomposition channels makes most hazardous materials rather easy to destroy, and for systems free of chlorine, considerably lower temperatures can perhaps be used. Nevertheless, it should be pointed out that all of the above is based on extrapolations and interpolations. Direct experimental verification would be useful. Of special importance are high-temperature reactions of radicals with aromatic systems. Furthermore, since aromatic compounds are the inevitable by-products of combustion situations, a

better understanding of how such compounds are formed could dictate the proper strategies for prevention. The above also holds for the effect of chlorine, both with respect to the effect in aromatization or the chlorination of such substances. All of this, of course, is intimately tied to dioxin and related problems. Without some degree of information on mechanisms and rates, the only alternative is to raise continually the incinerator temperature. In terms of material capabilities, additional environmental problems and costs, there are definite limitations.

In terms of direct experimental verification of scales of incinerability, we believe it is possible to devise laboratory-scale experiments that can mimic actual burn conditions. The work of Duvall et al. [23] represents an excellent start in this direction. However, interpretation of such results must be handled with care. Thus, although the general trends with respect to stability and chlorination on the aromatic structure agrees with our expectations, this agreement may well have been brought about by decreasing amounts of hydrogen in the system. This hydrogen decrease has the effect of drastically lowering OH concentrations and leading to a less "hostile" environment. What is needed is exploration of the full range of conditions, in terms of C/H and equivalence ratios, likely to be encountered during incineration.

In view of the present conclusion that unsaturated chlorides are probably the most difficult organic substances to incinerate, a detector that can detect such compounds in real time would prove to be an ideal instrument for monitoring of completeness of hazardous waste incineration. It should be emphasized that throughout the course of this study, we have discovered no special features with respect to the stability of the most toxic chlorinated dioxins or benzofurans either from a thermodynamic or kinetic point of view. One would therefore question the necessity of carrying out expensive determinations of the presence of individual isomeric compounds.

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CHAPTER 3

COMBUSTION CHARACTERISTICS OF CHLORINATED HYDROCARBONS

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Combustion of chlorinated hydrocarbons (CHC) is an attractive treatment process for ultimate disposal of chemical wastes bearing these compounds. Destruction of CHC via combustion brings about a number of special problems, in which very little fundamental work has been done. Consequently, present CHC incineration technology involves a high degree of empiricism, and is a costly operation. Therefore, developing a better understanding of the fundamental scientific principles of CHC combustion is important for the design and operation of reliable and efficient incinerators.

Previous CHC combustion research can be divided into two major categories:

1. Research was conducted involving a number of large-scale test runs in existing combustion facilities such as rotary kilns, fluidized beds etc., mainly under the auspices of the U.S. Environmental Protection Agency (EPA). Except for specific operating guidelines, these tests did not produce any fundamental data on CHC combustion.
2. The fundamental combustion characteristics of a number of CHC were studied mostly due to their flame inhibition characteristics. However, because chlorinated hydrocarbons are not as powerful as other halogenated species as inhibitors, they were not studied thoroughly.

Additional work under milder thermal conditions also exists in which solid or liquid catalysts were used to promote combustion. There are a number of proprietory designs and catalyst formulations for catalytic combustion of CHC.

Despite the lack of sufficient prior work in the literature, available information and recent research in our laboratories indicate a number of important features of the CHC combustion, such as low flame combustion rates and high soot formation propensities, when compared to non-CHC and the presence of staged combustion phenomena at atmospheric pressure. These and related subjects will be discussed in this chapter.

In examining the fundamental combustion properties of CHC, it is important to isolate the effects related to transport phenomena, to get an accurate understanding of the chemical rates and mechanisms involved. This can be achieved by studying premixed systems in which the fuel and the oxidant are mixed to molecular homogeneity such that diffusional problems are minimized. In catalytic combustion, additional precautions must be taken to ensure that there are no transport limitations, both within and outside the catalyst structure. Premixed, gas-phase systems will be considered in this chapter, unless otherwise noted.

GENERAL THERMODYNAMIC CONSIDERATIONS

Combustion reactions of conventional hydrocarbons, i.e., without halogens, have been documented in many sources [1,2] and will not be repeated here. The presence of chlorine brings in a number of additional features that influence the combustion characteristics of CHC compounds.

Thermodynamics of CHC combustion are complex because of the incomplete understanding of the chemistry involved, i.e., the intermediates and products of combustion are not fully known. However, one can still examine CHC combustion from a heuristic point of view and develop an insight into the overall process. If a general CHC compound is designated by $C_xH_yCl_z$ (where x = 1, y = 1 and z = 3 for $CHCl_3$), the overall combustion stoichiometry can be defined for $y > z$ by:

$$C_xH_yCl_z + \left(x + \frac{y - z}{4}\right) O_2 = xCO_2 + zHCl + \frac{y - z}{2} H_2O \qquad (1)$$

For CHC compounds in which $y < z$, the formation of molecular chlorine must be considered as:

$$C_xH_yCl_z + xO_2 = xCO_2 + yHCl + \frac{z-y}{2} Cl_2 \quad (2)$$

In practical operations, the formation of Cl_2 is undesirable because it is highly corrosive, and it is relatively difficult to remove from stack gases. Thus, auxiliary fuel with sufficient hydrogen content may be needed to suppress Cl_2 formation. The most suitable auxiliary fuel, with the highest hydrogen content, is methane, with the following overall stoichiometry for combustion:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (3)$$

Suppression of Cl_2 formation by auxiliary fuel can best be illustrated by examining the Deacon reaction:

$$H_2O + Cl_2 = 2HCl + 0.5\ O_2 \quad (4)$$

Higher temperatures favor the equilibrium formation of HCl, and this, combined with the use of sufficient amounts of auxiliary fuel (as manifested by the formation of H_2O) should minimize the formation of Cl_2 if the amount of excess oxygen present in the system is not high.

If methane is used as the auxiliary fuel, the overall combustion stoichiometry for the mixture will be as the following:

$$C_xH_yCl_z + \frac{1}{R} CH_4 \left(\frac{2}{R} + x + \frac{y-z}{4}\right) O_2 = \left(x + \frac{1}{R}\right) CO_2 + zHCl + \left(\frac{2}{R} + \frac{y-z}{2}\right) H_2O \quad (5)$$

where R = CHC-to-methane molar ratio

The use of auxiliary fuel is frequently needed not simply to suppress chlorine formation, but also to increase the heat of combustion of the mixture for effective incinerator operation. In Figure 1 the lower heats of combustion (LHC) of a variety of CHC are shown as a function of chlorine content of the CHC compound [3]. It is extremely difficult to stabilize flames using air when the heat of combustion of a fuel mixture is less than about 4000 kcal/kg. Clearly, there are incinerator configurations, such as vortex burners, fluidized beds and catalytic units, that can sustain combustion even when lower-LHC mixtures are used. However, they frequently have other constraints, such as the unacceptably low maximum temperature limits of operation, which allows them to be suitable only under special circumstances.

Another important parameter one must introduce is the equivalence-ratio (ϕ) of the fuel-oxidant mixture, frequently defined as the ratio of actual to stoichiometric fuel/oxygen ratios. This can then be written for Equation 5 as:

$$\phi = \frac{(\frac{2}{R} + x + \frac{y - z}{4})}{\text{actual } O_2} \quad (6)$$

Therefore, for $\phi = 1$, the actual O_2 present in the system corresponds to the exact stoichiometric oxygen requirements based on Equation 5, and $\phi > 1$ and $\phi < 1$ correspond to fuel-rich and fuel-lean systems, respectively.

The products of combustion of CHC in premixed systems principally depend on temperature, equivalence ratio of the original mixture and chemical structure of the parent CHC compound. As will be discussed later, the low combustion rates and high sooting characteristics of CHC bring in additional constraints on the design and operation of practical systems. One cannot examine combustion thermodynamics without due regard to the actual chemical kinetics and mechanisms involved; indeed, many of the pollutant emissions from incinerators can be traced to rate processes rather than thermodynamic limitations.

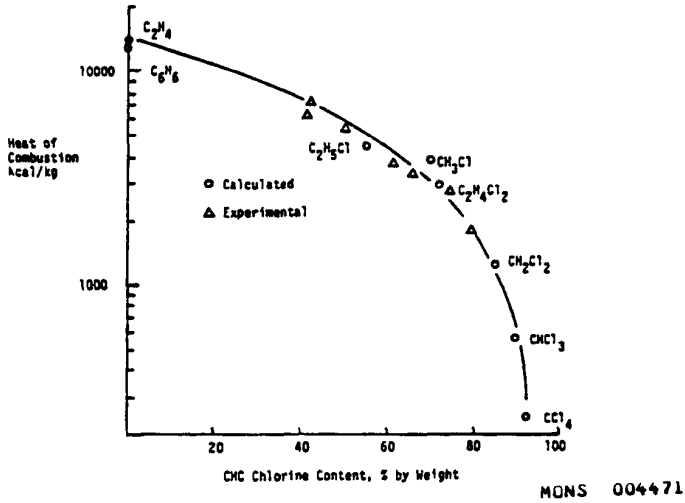

Figure 1. Effect of chlorine content on heat of combustion.

In CHC combustion, pyrolysis of the parent molecules must be considered first, due to the relatively weak C-Cl bond. This pyrolysis frequently involves the formation of relatively stable intermediate molecules followed by a degenerate branching step. The intermediates that form influence the product distribution as much as the original CHC molecules. Examples of such pyrolysis reactions are the following:

$$CCl_4 = C(s) + 2\ Cl_2 \quad (7)$$

$$CH_2Cl_2 = C(s) + 2HCl \quad (8)$$

$$CHCl_3 = C(s) + HCl + Cl_2 \quad (9)$$

$$C_2H_3Cl = C_2H_4 + HCl \quad (10)$$

Table I shows the bond dissociation energies of a variety of CHC and provides a comparison with the conventional hydrocarbon systems. As can be seen, the energy required to remove a chlorine atom from a CHC is less than that for hydrogen or the scission of a C-C bond. The dechlorinated species can then undergo a variety of reactions. For example, they can recombine to form other CHC compounds, undergo further pyrolysis, oxidize or polymerize (see below). The exact scenario is quite complex, and no attempt will be made here to enumerate all the possibilities. Indeed, such an attempt will be highly speculative due to our incomplete understanding of the chemistry involved.

Table I. Bond Dissociation Energies of Compounds Relevant to CHC Combustion

Parent Complex	Bond Strength (kcal/g-mol at 298° K) H	Cl
H-	104	103
Cl-	103	58
CH_3-	104	84
C_2H_5-	98	81
C_3H_7-	95	81
C_4H_9-	92	81
C_6H_5-	110	95
$C_6H_5CH_2$-	85	69
CCl_3-	96	73
CH_3CO-	86	82
CN-	120	97
OH-	119	60
C_6H_5CO-		74
CH_2Cl-	101	
$CHCl_2$-	96	
C_2HCl_4-	94	
CH_2=CH-	108	91

From a global point of view, the formation of HCl and Cl_2 would be expected to constitute the bulk of the chlorine-bearing species in the combustion products. They are related to each other through the Deacon reaction discussed above (Equation 4). It is important to note, however, that in practical systems, Cl_2 concentrations above those predicted by the Deacon equilibria have been observed [4].

Depending on the mixture equivalence and H/Cl ratios, chlorine can also end up in many different compounds. For fuel-rich systems, the presence of CO will be unavoidable. The CO can then react with chlorine to form phosgene as shown below:

$$CO + Cl_2 = COCl_2 \tag{11}$$

or carbonyl monochloride:

$$CO + 0.5Cl_2 = COCl \tag{12}$$

Although higher temperatures favor the presence of CO rather than $COCl_2$ or COCl, their potential production in chlorine-rich systems cannot be ruled out. Many CHC in mixtures with air have been shown to yield $COCl_2$ readily in the presence of Fe, Cu, Zn and Al catalysts at relatively low temperatures [5]. Carbon tetrachloride yields $COCl_2$ at a temperature as low as 100°C in the presence of iron, while $CHCl_3$, C_2HCl_3, $C_2H_4Cl_2$, C_2Cl_4 have given recognizable amounts of phosgene around 300°C.

Possible reactions of chlorine with carbon species at high temperatures may include:

$$C_2(g) + Cl_2 = 2\ CCl(g) \tag{13}$$

$$0.5C_2(g) + Cl_2 = CCl_2(g) \tag{14}$$

However, the products of Equations 13 and 14 can be converted to other species with the formation of HCl:

$$CCl(g) + H_2O = HCO + HCl \tag{15}$$

$$CCl_2(g) + H_2O = HCOCl + HCl \tag{16}$$

As the equivalence ratio is increased in fuel-rich systems, soot—polycyclic aromatic hydrocarbon (PAH)—formation is favored. As will be discussed more thoroughly in the following sections, the propensity of PAH formation increases as the chlorine content of the mixture is increased. Therefore, one must consider critically the formation of higher-molecular-weight pollutants as an integral part of an incinerator design and operation. In particular, combustion of CHC has been reported to have the potential to produce chlorinated dioxins, most notably the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) [6,7]. The exact conditions

under which chlorinated dioxin compounds are formed are not clear. However, the general observation is that TCDD concentrations in the soil in areas with CHC combustion activities are higher than elsewhere [6]. Therefore, it appears that CHC combustion processes may be a likely source for the generation of chlorinated dioxins. It is difficult to explain the formation of trace organic compounds/pollutants in combustion by thermodynamics, and their occurrence in practical devices is a manifestation of the rate limitations present, rather than of equilibrium conditions in these systems.

To suppress the formation of carbon-based pollutants in combustion, excess oxygen is frequently used in incinerators. However, the use of large amounts of excess oxygen will be unsuitable in CHC combustion, due to a number of reasons. First, as shown by the Deacon reaction the excess oxygen will induce more Cl_2 formation (Equation 4), which is undesirable. Second, the deviation of ϕ from 1 decreases the flame temperature and therefore the rates of combustion, resulting in potential operating difficulties. Third, the use of excess air will decrease the energy utilization efficiency. It should be remembered that as the equivalence ratio is decreased the actual increase in the heat capacity of the mixture will be much higher due to the presence of nitrogen in air.

Under fuel-lean conditions, the oxygen can undergo reactions with chlorine as:

$$Cl_2 + O_2 = 2ClO \quad (17)$$

$$Cl_2 + 0.5O_2 = Cl_2O \quad (18)$$

$$0.5Cl_2 + O_2 = ClO_2 \quad (19)$$

Additional chlorine reactions may involve the following:

$$CO_2 + Cl_2 = CO + Cl_2O \quad (20)$$

$$H_2O + ClO = HOCl + 0.5H_2 \quad (21)$$

$$H_2O + Cl_2 = HOCl + HCl \quad (22)$$

$$HCl + H_2O = HOCl + H_2 \quad (23)$$

All of the reactions presented above involve stable species, some of which may or may not exist in incinerators, depending on specific operating conditions. CHC oxidation at high temperatures also brings in the reactions of radicals, which one must consider in evaluating the thermodynamic aspects of combustion. Principal reactions that involve radicals of hydrogen and/or chlorine include:

$$H + HCl = H_2 + Cl \quad (24)$$

$$Cl + HCl = H + Cl_2 \quad (25)$$

$$Cl_2 = Cl + Cl \quad (26)$$

$$HCl = H + Cl \quad (27)$$

Dissociation of HCl into its atoms is quite unlikely even under extreme temperatures; thus, the main source of Cl radicals is probably establishment of the equilibrium for reaction as in Equation 24. Indeed, this criterion was used in assessing the inhibition characteristics of various halogens in flames [8].

Principal radical reactions also involving oxygen include:

$$Cl + O_2 = ClO_2 \quad (28)$$
$$Cl + ClO_2 = 2ClO \quad (29)$$
$$O + ClO_2 = ClO + O_2 \quad (30)$$
$$O + ClO = Cl + O_2 \quad (31)$$
$$2ClO = Cl + ClO_2 \quad (32)$$
$$2ClO = Cl_2O_2 \quad (33)$$
$$HCl + O_2 = Cl + HO_2 \quad (34)$$
$$Cl + HO_2 = HCl + O_2 \quad (35)$$
$$H + ClO_2 = ClO + OH \quad (36)$$

Furthermore, some of the reactions that include carbon are:

$$Cl + COCl = CO + Cl_2 \quad (37)$$
$$Cl + CH_4 = HCl + CH_3 \quad (38)$$
$$H + CH_3Cl = HCl + CH_3 \quad (39)$$
$$O + CH_3Cl = CH_2Cl + OH \quad (40)$$
$$OH + CH_3Cl = CH_2Cl + H_2O \quad (41)$$
$$OH + CCl_4 = CCl_3 + HOCl \quad (42)$$

It should be remembered that the equations presented above are meant to illustrate some of the possible reactions in which chlorine and chlorine-bearing compounds can participate, and they represent a fraction of the total set of reactions characterizing the overall combustion process. In principle, one may be able to incorporate some of the reactions presented above into a reaction set describing the oxidation characteristics of a well-studied nonchlorinated fuel, such as CH_4, CO or H_2, to develop a better understanding of the CHC combustion process.

CHC combustion may also involve the production of NO_x under certain operating conditions. Catalytic combustors probably are less susceptible to NO_x formation, due to milder temperatures. The oxides of nitrogen can then react with chlorine-bearing species. Examples of such reactions are:

$$ClO + NO = Cl + NO_2 \quad (43)$$
$$ClO + NO_2 = ClONO_2 \quad (44)$$
$$NO + Cl = NOCl \quad (45)$$
$$2NOCl = 2NO + Cl_2 \quad (46)$$

$$Cl + NOCl = NO + Cl_2 \quad (47)$$
$$HCl + NO_2 = HNO_2 + Cl \quad (48)$$
$$NO + ClO_2 = NO_2 + ClO \quad (49)$$
$$NO_2 + ClO_2 = NO_2 + ClO \quad (50)$$
$$CH_3Cl + NO_2 = CH_2Cl + HNO_2 \quad (51)$$
$$HCl + NO_2 = HNO_2 + Cl \quad (52)$$

Clearly, the reactions presented above are far from being complete, as they were compiled to illustrate the complexity of the reaction system at hand and to provide examples.

The equilibrium constants for some of the reactions presented above are shown in Figure 2 (see Table II for the legend), together with some of the reactions that are common to conventional hydrocarbon combustion systems [2]. It must be remembered again that many combustion systems are not simply characterized by equilibrium considerations, and they are also influenced by the rate processes. Despite these limitations, however, thermodynamics must be considered for the effective design and reliable operation of incinerators.

GENERAL KINETIC CONSIDERATIONS

CHC possess a number of unique combustion properties that distinguish them from other combustion reactions. One of the most important of these properties is that some CHC compounds, especially those with high chlorine contents, show two-stage flame combustion at atmospheric pressure. Although this is not an usual phenomenon, as many hydrocarbon systems possess two-stage combustion under certain conditions, it is relatively rare to find them at atmospheric pressure. The presence of two-stage combustion in CHC systems can probably be attributed to the relatively less strong C-Cl bond in these compounds (see Table I). Low-temperature flames are then probably initiated by the formation of Cl radicals by pyrolysis, and then sustained by sets of chain reactions involving a degenerate branching step [9].

Because the C-Cl bond is relatively weak, it is not surprising that chlorinated compounds promote low-temperature oxidation rates of conventional hydrocarbon systems when they are mixed together. Many CHC not only increase the preflame combustion rates of non-CHC, but they also decrease the ignition temperature of the mixture [10].

Although CHC promote oxidation rates at low temperatures, they inhibit hydrocarbon combustion at higher temperatures. Indeed, CHC compounds are better known as flame inhibitors, as they suppress

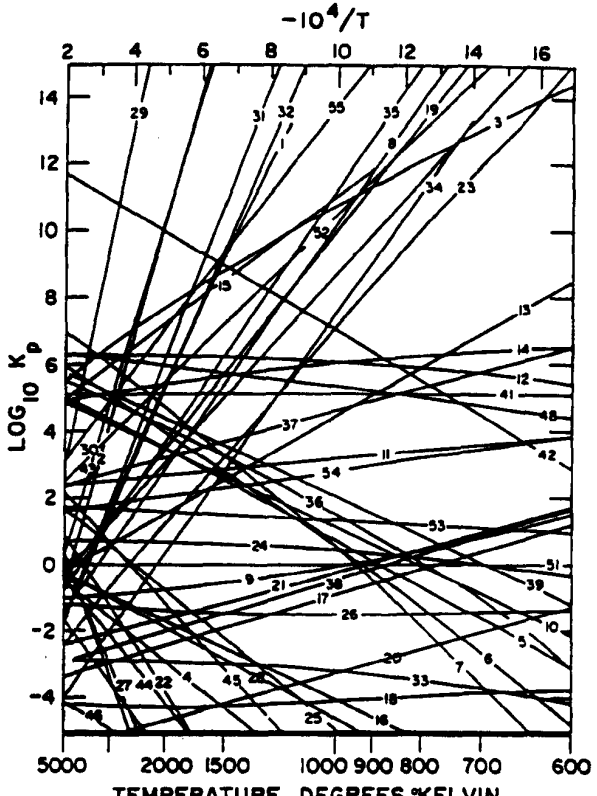

Figure 2. Equilibrium constants for reactions relevant to CHC combustion (see Table II).

Table II. Reactions of Interest in CHC Combustion

Carbon Reactions [2]

1. $0.5C_2(g) = C(s)$
2. $C(g) = C(s)$
3. $C + 0.5O_2 = CO$
4. $C + 0.5N_2 = 0.5C_2N_2$
5. $C + 2H_2O = CO_2 + 2H_2$
6. $C + H_2O = CO + H_2$
7. $C + CO_2 = 2CO$
8. $CO + 0.5O_2 = CO_2$
9. $CO + H_2O = CO_2 + H_2$
10. $CH_4 = C + 2H_2$
11. $0.5C_2H_4 = C + H_2$
12. $HCHO = CO + H_2$
13. $0.5C_2H_2 = C + 0.5H_2$
14. $1/3\ C_3O_2 + 1/3\ H_2O = CO + 1/3\ H_2$

Nitrogen and Oxygen Reactions [2]

15. $O_2 = 1.5O_2$
16. $0.5N_2 + 0.5O_2 = NO$
17. $NO + 0.5O_2 = NO_2$
18. $NO + 0.5N_2 = N_2O$
19. $H_2 + 0.5O_2 = H_2O$
20. $0.5N_2 + 1.5H_2 = NH_3$

Sulfur Reactions [2]

21. $0.5S_2(g) = S(l)$
22. $SO_2 = SO + 0.5O_2$
23. $SO_2 + 3H_2 = H_2S + 2H_2O$
24. $0.5SO_2 + 2/3\ H_2S = 0.5S_2(g) + 2/3\ H_2O$
25. $H_2S = HS + 0.5H_2$
26. $CO + H_2S = COS + H_2$

Radical Reactions with No Chlorine [2]

27. $C + 0.5N_2 = CN$
28. $CH_4 = CH_3 + 0.5H_2$
29. $2N = N_2$
30. $N + O = NO$
31. $2O = O_2$
32. $2H = H_2$
33. $0.5H_2 + O_2 = HO_2$
34. $OH + O = HO_2$
35. $OH + 0.5H_2 = H_2O$

Chlorine Reactions

36. $COCl_2 = CO + Cl_2$
37. $COCl = 0.5Cl_2 + CO$
38. $2HCl + H_2O_2 = 2H_2O + Cl_2$
39. $CCl_4 = C + 2Cl_2$
40. $C_2Cl_2 = 2C + Cl_2$
41. $C_2Cl_4 = 2C + 2Cl_2$
42. $C_2Cl_6 = 2C + 3Cl_2$
43. $2C + Cl_2 = 2CCl$
44. $C + Cl_2 = CCl_2$
45. $0.5Cl_2 + 0.5O_2 = ClO$
46. $0.5Cl_2 + O_2 = ClO_2$
47. $CO_2 + Cl_2 = CO + Cl_2O$
48. $CH_2Cl_2 + H_2O = HCHO + 2HCl$
49. $Cl_2 = 2Cl$
50. $HCl = H + Cl$
51. $H + HCl = Cl + H_2$
52. $H + Cl_2 = Cl + HCL$
53. $Cl + CH_4 = HCl + CH_3$
54. $Cl + ClO_2 = 2ClO$
55. $O + ClO_2 = ClO + O_2$

combustion rates at elevated temperatures, i.e., temperatures above ~800°C. The inhibitory effects of CHC compounds are generally accepted to be due to their free radical scavenging characteristics. Scavenging is defined as a process that converts reactive radicals, such as H, OH and O, into stable molecules and/or less reactive radicals. During high-temperature combustion, many such radicals form and participate in the reaction network.

The most important chain branching reaction in combustion is:

$$H + O_2 \rightarrow OH + O \quad (53)$$

Chlorinated compounds compete successfully for H radicals at moderately high temperatures and render them less reactive, for example by reactions such as:

$$Cl + H \rightarrow HCl \quad (54)$$

$$HCl + H \rightarrow H_2 + Cl \quad (55)$$

$$Cl_2 + H \rightarrow HCl + Cl \quad (56)$$

$$CH_3Cl + H \rightarrow CH_3 + HCl \quad (57)$$

$$HCl + OH \rightarrow H_2O + Cl \quad (58)$$

This results in decreased combustion rates, best manifested by the decrease in measured laminar burning velocity. As the temperature is further increased, the inhibitory effects of chlorinated compounds diminish, because now the H, OH and O radical-forming reactions with their higher activation energies can successfully compete with the scavenging reactions [11].

CHC also have a higher propensity for soot formation due, in part, to the weak C-Cl bond strength and the free radical scavenging characteristics of chlorine and chlorine-bearing species; this propensity seems to be directly proportional to the chlorine content of the mixture.

In the remainder of this section, chemistry and mechanism of CHC combustion, laminar burning velocity, and soot formation will be presented in more detail. Although these topics are highly interrelated, they will be discussed in separate sections to enhance the presentation of the important features involved in the combustion of CHC.

Chemistry and Kinetics of CHC Combustion

Although the presence of two stages in CHC combustion has been demonstrated experimentally, the actual chemistry and mechanisms involved in the overall process are poorly understood. However, there is considerable literature on two-stage combustion aspects of conventional hydrocarbons, and an insight to CHC combustion can be obtained by examining that previous work [1,12].

The two-stage combustion phenomenon is frequently discussed in the same context with "cool flames." The underlying principles are probably similar; however, the relative temperature ranges can be quite different.

The general feature of two-stage combustion is that although an explosive reaction occurs during the first stage of combustion, it falls short of proceeding to completion. Instead, the reaction is self-quenching, and a fraction of the total available enthalpy of combustion is released. Analysis of the intermediate products in non-CHC systems showed the presence of peroxides and aldehydes. Although a long controversy existed as to the relative importance of RO_2H vs RCHO as the active intermediate, it is well documented now that hydroperoxides are the autocatalytic intermediates, and that aldehydes are the important fuel source in the intermediate region. Under certain circumstances, the first stage terminates in complete combustion, i.e., it leads to the second stage.

On a temperature-pressure (TP) diagram for a given mixture composition, the existence of cool flames and two-stage combustion can best be illustrated by identifying the zones of multiple ignition temperatures at an isobar. Such a diagram is shown in Figure 3. Regions to the right of the

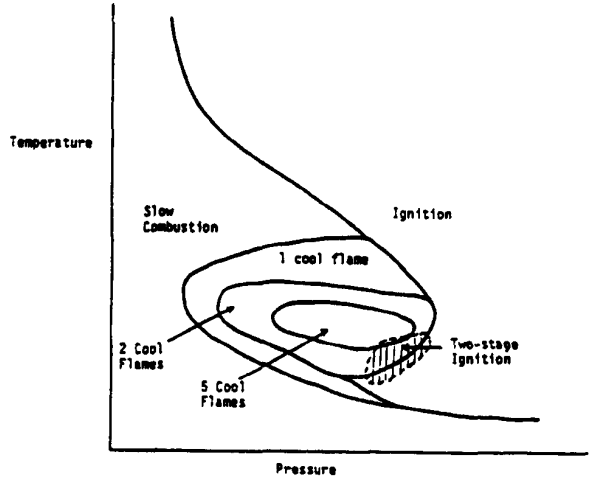

Figure 3. Combustion phenomena associated with CHC and hydrocarbon oxidation.

cool flames are regions where fast ignition may set. Regions to the left correspond to slow reactions, which are unimportant in combustion.

An important feature of two-stage combustion is that although there is an appreciable temperature increase along the first stage, the reaction rate does not appear to accelerate. In fact, the rate after the first flame is slower than just before. This behavior corresponds to what is called as the "negative" temperature dependency for the reaction. The rate of reaction, instead of increasing with temperature, decreases. This clearly indicates that self-quenching must be chemical in origin. One possible explanation to this observation is the presence of two reactions in series, with the second one having a significantly higher activation energy [1,13]. On the other hand, one can also explain the two-stage phenomenon by introducing a set of chain reactions with a degenerate step that is responsible for the delayed second combustion stage [1,9,13].

The combustion mechanisms suggested for CHC compounds, although they are very few, can also be categorized according to the two approaches described above. Hoare et al. [14], in studying the oxidation of methylene chloride at temperatures above 500°C in static and flow systems, discovered that the overall stoichiometry of the reaction tended to be:

$$CH_2Cl_2 + 0.5O_2 = CO + 2HCl \qquad (59)$$

but the products also included CO_2, H_2O, $C_2H_2Cl_4$, C_2HCl_3, C_2Cl_4, $C_2H_2Cl_2$, $CHCl_3$, CCl_4, HCHO and Cl_2. They noted the similarity of CH_2Cl_2 combustion to pyrolysis and suggested the following reaction mechanism:

$$CH_2Cl_2 + Cl \rightarrow CHCl_2 + HCl \qquad (60)$$

[primary chain]

$$CHCl_2 + CH_2Cl_2 \rightarrow CHClCHCl + HCl + Cl \qquad (61)$$

$$CHClCHCl + O_2 \rightarrow H_2O + CO + CCl_2 \qquad (62)$$

[degenerate branching]

$$CHClCHCl + Cl \rightarrow C_2HCl_2 + HCl \qquad (63)$$

$$C_2HCl_2 + O_2 \rightarrow 2CO + HCl + Cl \qquad (64)$$

$$CCl_2 + CH_2Cl_2 \rightarrow 2CHCl_2 \qquad (65)$$

$$CH_2Cl_2 + H_2O = HCHO + 2HCl \qquad (66)$$

$$2CH_2Cl_2 \xrightarrow{\text{wall}} CHCl_2CHCl_2 \xrightarrow{\text{wall}} CHClCCl_2 + HCl \qquad (67)$$

[chain termination]

$$2CCl_2 \xrightarrow{\text{wall}} C_2Cl_4 \qquad (68)$$

It was also suggested that CHCCl can act as a degenerate branching agent. Clearly some of the reactions in this set, such as Equations 62 and 64, must occur in a number of steps, as it is improbable that they represent elementary reactions. Although the mechanism presented above explains some of the pathways for production of intermediate species, such as C_2Cl_4 and HCHO, it fails to provide an explanation for the formation of species such as $COCl_2$ and ClO under fuel-lean conditions. At 533°C, the maximum reaction rate was correlated with:

$$-\frac{d}{dt}[CH_2Cl_2]\Big|_{max.} = k[CH_2Cl_2]^2[O_2]^{0.9} \qquad (69)$$

A somewhat similar reaction mechanism involving simple intermediates was postulated by Kaesche-Krischer [15] for two-stage combustion of CH_2Cl_2 and C_2HCl_3. Accordingly, CH_2Cl_2 combustion involved:

$$CH_2Cl_2 + O_2 \rightarrow CO_2 + H_2 + Cl_2 \qquad \text{first stage} \qquad (70)$$

$$H_2 + Cl_2 \rightarrow 2HCl \qquad \text{second stage} \qquad (71)$$

Similarly, two-stage combustion of trichloroethylene was postulated to be:

$$C_2HCl_3 + 2O_2 \rightarrow HCl + CO_2 + CO + Cl_2O \qquad \text{first stage} \qquad (72)$$

$$CO + Cl_2O \rightarrow CO_2 + Cl_2 \qquad \text{second stage} \qquad (73)$$

Obviously the reactions demonstrated in Equations 70 to 73 are far from being elementary reactions. The simple oxidation mechanisms suggested above are highly unlikely, in view of fast H_2-Cl_2 and CO-Cl_2 reactions. In the absence of any oxygen CH_2Cl_2 quantitatively decomposes to C and HCl as:

$$CH_2Cl_2 \rightarrow C(s) + 2HCl \qquad (74)$$

Equation 74 proceeds with a considerable induction period at temperatures above 500°C, with the formation of other CHC carbon intermediates similar to the ones discussed earlier.

Thermal decompositions of tetrachloroethane and trichloroethylene have been studied by Barton and Howlett [16]. Reaction networks similar

to the ones corresponding to CH_2Cl_2 were postulated, with provisions made for the formation of higher CHC compounds such as:

$$C_2H_2Cl_4 + Cl \rightarrow C_2HCl_4 + HCl \quad (75)$$

$$C_2HCl_4 \rightarrow C_2HCl_3 + Cl \quad (76)$$

$$C_2HCl_3 + Cl \rightarrow C_2Cl_3 + HCl \quad (77)$$

$$C_2Cl_3 \rightarrow C_2Cl_2 + Cl \quad (78)$$

$$(C_2Cl_2) \rightarrow (C_4Cl_4),(C_6Cl_6) \quad (79)$$

Chlorine-photosensitized oxidation of trichloroethylene has been studied by Huybrechts and Meyers [17] at low temperatures and the following reaction mechanism was proposed:

$$C_2HCl_3 + 0.5O_2 = CHCl_2COCl \quad \text{[overall reaction]} \quad (80)$$

$$Cl_2 \xrightarrow{\text{light}} 2Cl \quad (81)$$

$$Cl + C_2HCl_3 \rightarrow C_2HCl_4 \quad (82)$$

$$C_2HCl_4 + Cl_2 \rightarrow C_2HCl_5 + Cl \quad (83)$$

$$C_2HCl_4 + O_2 \rightarrow C_2HCl_4O_2 \quad (84)$$

$$C_2HCl_4O_2 + C_2HCl_4 \rightarrow C_2HCl_4O_2C_2HCl_4 \quad (85)$$

$$2C_2HCl_4O_2 \rightarrow C_2HClO_2C_2HCl_4 + O_2 \quad (86)$$

or

$$2C_2HCl_4O_2 \rightarrow 2C_2HCl_4O + O_2 \quad (87)$$

$$C_2HCl_4O \rightarrow C_2HCl_3O + Cl \quad (88)$$

$$C_2HCl_4 \rightarrow \text{termination} \quad (89)$$

There have been a number of studies published on homogeneous gas-phase oxidation of chlorethylenes in relation to the problems of atmospheric pollution [18,19]. Most of these studies were done under mild thermal conditions and the reactions were initiated using light, mercury sensitization or ozone. The reaction mechanisms developed have essentially been the extension of the mechanisms proposed by Huybrechts and Meyers [17] and the interested reader is referred to the general review of the subject given by Sanhueza et al. [19]. From the foregoing discussions, it is clear that CHC oxidation and pyrolysis are quite similar, and that both processes would be expected to occur simultaneously under actual incinerator operating conditions.

As discussed above, CHC combustion involves many reactions, in series and in parallel. Although the specific reactions present in a given system may be difficult to identify, one may break down the overall chemical event into a set of elementary chemical reactions. In recent years, the quantity and quality of experimental data on elementary reactions that are encountered in combustion have reached a point where it has become possible and reasonable to develop models to simulate actual combustor performance. Indeed, with respect to conventional hydrocarbons many compilations of such reaction sets exist [20,21]. Rate constants for various elementary reactions involving chlorine are given in Table III. These are mainly compiled from Kondratiev [21] and Baulch et al. [22]. It can be noted that the activation energies of the reactions that involve the H radical are moderately low (i.e. reactions 92 to 98), as discussed earlier with respect to the radical scavenging characteristics of chlorine-bearing compounds at moderately high temperatures.

There is also a considerable patent literature on the solid-catalyzed combustion of gaseous CHC. The use of noble-metal catalysts, such as Pt, Pd and Ru, and oxides of metals such as Fe, Cu, Cr, V, U, Al, Mo and W were reported to convert CHC compounds into combustion products in a temperature range of 20–1000°C, depending on the particular catalyst formulation used and the CHC present [23]. Although the fundamental aspects of CHC combustion are understood poorly, the existing patent literature suggests the technical feasibility of this method as an effective means for the incineration of CHC. Some CHC oxidation characteristics, such as their relatively higher oxidation rates compared to conventional hydrocarbons, as discussed earlier, will probably be valid under catalytic combustion conditions; however, the presence of solid surfaces and lower temperatures must be taken into consideration.

In summary, although some previous work exists, our understanding of the chemical mechanisms and rates involved in CHC combustion is insufficient to make any definitive remarks. It is clear, however, that reactions involved are very complex, and to develop a realistic picture one must consider sets of branching reactions both in series and parallel to account for the processes occurring in the combustion of CHC.

Burning Velocities of CHC

The laminar flame propagation velocity, or the burning velocity (u_b), is one of the most important physicochemical properties of a combustible mixture. It is the velocity at which the flame front travels relative to the unburned mixture and provides an insight into the overall rate of

Table III. Rate Constants for Reactions Involving Chlorine [k = AT^n exp($-E_a/RT$) cm^3/mol-sec]

	Reaction	$\log_{10}A$	n	E_a	Temperature Range (°K)
90	$HCl + M \rightarrow H + Cl + M$	12.82	0	71	1600–2800
91	$O + HCl \rightarrow OH + Cl$	12.84	0	6.7	298–720
92	$H + CH_2Cl_2 \rightarrow HCl + CH_2Cl$	13.04	0	6.1	298–460
93	$H + Cl_2 \rightarrow HCl + Cl$	15.0	0	2.2	300–1100
94	$H + HCl \rightarrow H_2 + Cl$	13.6	0	4.5	298–1000
95	$H + ClO \rightarrow OH + Cl$	12.88	0.68	4.8	
96	$H + ClO \rightarrow HCl + O$	12.77	0.67	13.	
97	$H + CCl_4 \rightarrow HCl + CCl_3$	11.34	0.5	3.45	
98	$H + Cl + M \rightarrow HCl + M$	17.94	-1	0	
99	$OH + HCl \rightarrow Cl + H_2O$	12.35	0	1	200–500
100	$Cl_2 + M \rightarrow Cl + Cl + M$	13.37	0	46.9	1550–2800
101	$Cl + Cl + M \rightarrow Cl_2 + M$	14.35	0	-1.8	195–520
102	$Cl + O_3 \rightarrow ClO + O_2$	13.17	0	0.4	200–400
103	$Cl + ClO_2 \rightarrow ClO + ClO$	13.56	0	0	298
104	$O + Cl_2 \rightarrow Cl + ClO$	12.40	0	2.7	174–602
105	$O + ClO \rightarrow Cl + O_2$	13.76	0	0.36	200–500
106	$ClO + ClO \rightarrow$ products	12.1	0	2.6	295–600
107	$NOCl + M \rightarrow NO + Cl + M$	15.11	0	32	800–1500
108	$Cl + COCl \rightarrow CO + Cl_2$	15.11		3.3	300–600
109	$O + CH_2Cl \rightarrow OH + CH_2Cl$	13.25	0	7.93	353–949
110	$O + CCl_4 \rightarrow COCl_2 + Cl_2$	10.23	0	4.5	278–370
111	$O + CH_2 + ClCH_2Cl \rightarrow 2\ HCl + CO + CH_2$	13.08	0	5.5	353–473
112	$Cl + H_2 \rightarrow HCl + H$	13.9	0	5.5	298–1000
113	$Cl + CH_4 \rightarrow HCl + CH_3$	7.04	1.97	1.5	200–500
114	$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	14.1	0	0.98	349–560
115	$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$	13.5	0	3.1	323–432

116	$Cl + CH_3Cl \rightarrow Cl_2Cl + CH_3$	14.0	0	25.1	350-475
117	$Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$	13.4		2.96	273-563
118	$Cl + CH_2Cl_2 \rightarrow Cl_2 + CH_2Cl$	14	0	21.4	360-475
119	$Cl + CHCl_3 \rightarrow HCl + CCl_3$	12.84	0	3.35	286-593
120	$Cl + CCl_4 \rightarrow Cl_2 + CCl_3$	13.93	0	20.0	303-425
121	$Cl + C_2H_5Cl \rightarrow HCl + CH_2ClCH_2$	13.05	0	1.5	303-453
122	$Cl + C_2H_5Cl \rightarrow HCl + C_2H_4Cl$	13.51	0	1.50	273-488
123	$Cl + C_2H_5Cl \rightarrow HCl + CH_3CHCl$	13.55	0	1.40	303-453
124	$Cl + C_2H_5Cl \rightarrow Cl_2 + C_2H_5$	14.3	0	21.5	303-453
125	$Cl + C_2H_4Cl \rightarrow HCl + C_2H_3Cl$	13	0	3.0	654-740
126	$Cl + C_2H_4Cl_2 \rightarrow HCl + CH_2CCl_2$	12.95	0	1.9	323-423
127	$Cl + C_2H_4Cl_2 \rightarrow HCl + CH_2CHCl_2$	13.00	0	3.4	303-458
128	$Cl + C_2H_4Cl_2 \rightarrow HCl + CHClCH_2Cl$	13.80	0	3.1	323-432
129	$Cl + C_2H_4Cl_2 \rightarrow Cl_2 + C_2H_4Cl$	14.3	0	21.3	303-458
130	$Cl + CH_3CCl_3 \rightarrow HCl + C_2H_2Cl_3$	12.40	0	3.6	323-428
131	$Cl + CHCl_2CH_2Cl \rightarrow HCl + CCl_2CH_2Cl$	12.95	0	3.1	323-428
132	$Cl + CH_2ClCHCl_2 \rightarrow HCl + CHClCHCl_2$	13.5	0	3.7	333-413
133	$Cl + C_2H_3Cl_3 \rightarrow Cl_2C_2H_3Cl_3$	14.3	0	20.6	323-428
134	$Cl + CH_2ClCCl_3 \rightarrow HCl + CHClCCl_3$	12.80	0	3.55	323-423
135	$Cl + CHCl_2CHCl_2 \rightarrow HCl + C_2HCl_4$	13.10	0	3.4	323-438
136	$Cl + C_2H_2Cl_4 \rightarrow HCl + C_2HCl_4$	13.8	0	3.3	323-438
137	$Cl + C_2Cl_6 \rightarrow Cl_2 + C_2Cl_5$	14.3	0	19.5	360-480
138	$C_2H_4Cl \rightarrow C_2H_4 + Cl$	16.9	0	23.6	360-480
139	$C_2H_3Cl_2 \rightarrow C_2H_3Cl + Cl$			21.5	635-758

combustion. However, despite its definitional simplicity, measuring the burning velocity of a combustible mixture is far from being trivial. This problem must be discussed further.

Burning velocity can most easily be related to the rate of combustion reaction by considering one-dimensional systems. The theoretical approaches that have been used to calculate u_b can be categorized into three groups, depending on whether they consider thermal diffusion, mass diffusion or combined effects for flame propagation [24]. Thermal theories of flame propagation are based on the assumption that diffusion of reactive species in the flame zone is not important in promoting ignition, which occurs mainly due to the heating of the reactant gases. This assumption simplifies mathematics considerably, and explicit expressions for u_b can be obtained by integrating a differential energy balance equation. If first- and second-order combustion rate expressions are assumed, the following expressions for the burning velocity are obtained:

$$u_b^2 = \frac{2\lambda c_p A}{\rho_o L^2} \frac{T_o}{T_f} \left[\frac{RT_f^2}{E}\right]^2 \exp\left[-E/RT_f\right], \text{ for a first-order reaction} \quad (140)$$

$$u_b^2 = \frac{4\lambda c_p^2}{\rho_o L^2} An_o \frac{T_o}{T_f} \left[\frac{RT_f^2}{E}\right]^3 \exp\left[-E/RT_f\right], \text{ for a second-order reaction} \quad (141)$$

where λ = thermal conductivity
c_p = specific heat
ρ_o = unburnt gas density
L = heat of combustion
E = activation energy
A = rate preexponential factor
n_o = initial concentration
T_o, T_f = initial and flame temperatures, respectively

In equations 140 and 141, the square of the burning velocity principally has the Arrhenius temperature dependency. This dependency clearly demonstrates the intimate relationship between the combustion rate and the burning velocity, and serves as an important reference point.

For flames involving highly mobile, reactive species, such as H, the thermal theory falls short of explaining the observed burning velocities. Therefore, diffusion of species also must be introduced into the picture. Again, the extreme case of flame propagation, in which the diffusion of species is the only source of ignition, can be treated mathematically quite well if it is assumed that thermodynamic equilibrium exists at the flame zone [25]. The burning velocity can then be given by the following expression:

$$u_b^2 = \sum_j \frac{k_j\, n\, x_j\, D_{jm}}{x_p\, B_j} \qquad (142)$$

Here, k_j is the specific rate, which can be considered to have an Arrhenius temperature dependency, resulting in the following expression for u_b:

$$u_b^2 \sim \exp\,[-E/RT_f] \qquad (143)$$

Equation 143 is of the form shown in Equations 140 and 141, and shows the general correlation to be expected between burning velocity and flame temperature.

There are also mathematical models that have been developed utilizing the vital concepts in both the thermal and species diffusion theories. However, although they do provide more accurate results with a smaller number of assumptions, the models are mathematically complex and fail to provide an immediate physical insight into the processes involved.

In CHC combustion, one would initially expect the thermal theory of ignition to be adequate to describe flame propagation. This is due to the radical scavenging characteristics of chlorine-bearing compounds discussed earlier. Because CHC flames will be deficient in radicals such as H, OH and O, one would not expect any significant diffusion of species into the preflame zone. Indeed, inhibition studies have revealed that CHC compounds broaden the precombustion zone and force the main reaction zone into a narrower region [26].

Measurement of the burning velocity can be accomplished using a variety of methods, and many excellent reviews exist on this subject [27,28]. Most notable are the methods using Bunsen cones, flames in tubes, soap bubbles, constant volume explosions and flat flame burners. Although there is still a lack of consensus as to the most appropriate technique, the Bunsen cone method with a suitable photographic system has been used most frequently, because its simple experimental setup, the rapidity of data acquisition and the reasonable quality of data it yields when compared to other, more sophisticated methods. According to this method, burning velocities are determined by dividing the volumetric flowrates of the unburned gas mixture to the flame front areas, which are determined from the enlarged pictures of the flame zone [29].

The combustion of chlorinated hydrocarbons requires either oxygen-enriched air or an auxiliary fuel to sustain stable, open flames. Kaesche-Krischer [30] reported the burning velocities of chlorinated methanes and trichlorethylene in an atmosphere with varying oxygen contents. The effect of oxygen content on the burning velocity is significant, due to changes in flame temperature, as shown in Equation 140. As the oxygen content in the air is increased (i.e., inert nitrogen content is decreased) the flame temperature also increases due to decreased mixture heat capacity.

Figures 4 and 5 show how the burning velocity of CH_3Cl and CH_2Cl_2 vary as a function of the mixture equivalence ratio, with the oxygen content of the air as the parameter. The figures show the typical inverted U shape, with the burning velocity establishing its maximum value around stoichiometric conditions. Furthermore, they show the negative effect of chlorine content on the burning velocity. It is important to note that for atmospheric air (21% O_2), burning velocities are extremely low (less than 10 cm/sec), which may result in flame stability problems. Both $CHCl_3$ and CCl_4 failed to produce a stable Bunsen flame even when pure oxygen

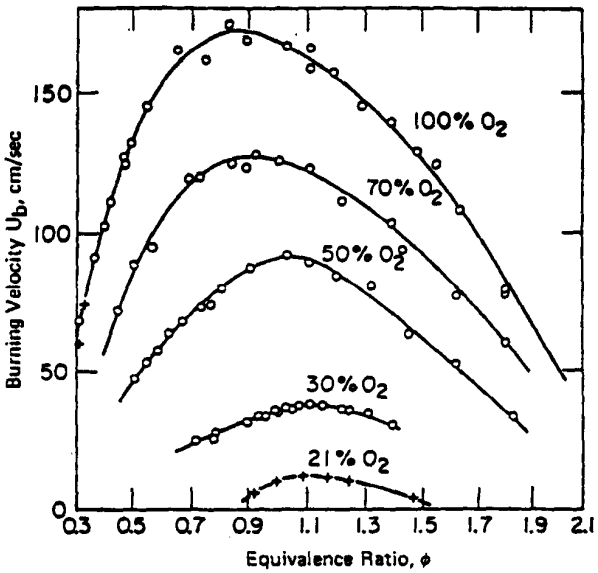

Figure 4. Burning velocities of CH_3Cl in oxygen-enriched air [30].

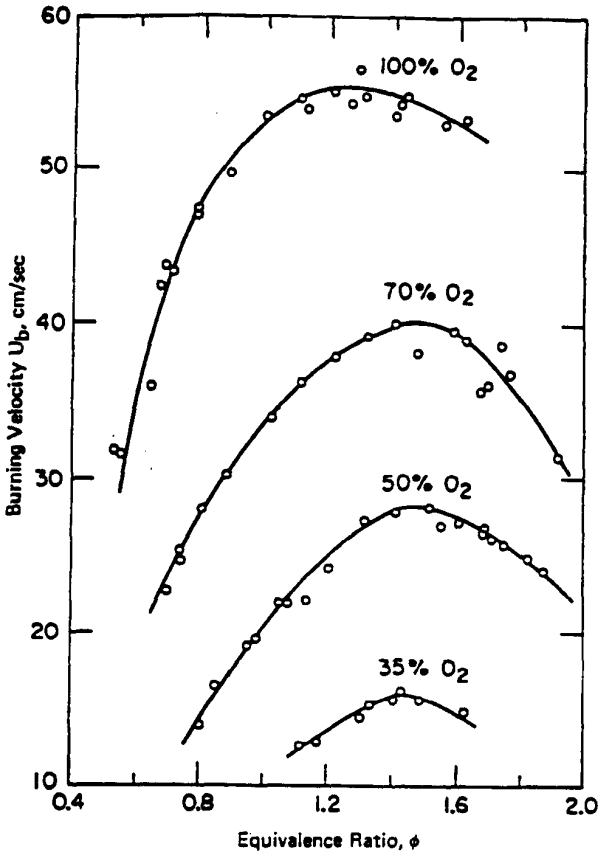

Figure 5. Burning velocities of CH_2Cl_2 in oxygen-enriched air [30].

was used, thus indicating burning velocities to be lower than those obtained for CH_3Cl and CH_2Cl_2.

The burning velocity of trichlorethylene is shown in Figure 6. Unlike CH_3Cl and CH_2Cl_2, C_2HCl_3 does not have as sharp a peak in burning velocity. In fact the equivalence ratio seems to influence u_b minimally, probably due to the nonoxidative, pyrolytic decomposition nature of the first stage of its combustion.

Although the burning velocities of CHC in oxygen-enriched environments are extremely important, they fall short of utility in practical systems. Consequently, one must also examine CHC burning velocities in mixtures with an auxiliary fuel and air. Besides providing important practical results, extrapolation to no-auxiliary-fuel conditions can also yield information on the individual burning rates of CHC.

In this regard, Garner et al. [31] examined how chlorinated methanes and HCl inhibited the burning velocities of propane/air mixtures when present in quantities less than 1%. They concluded that the order of effectiveness in reducing the burning velocity was $HCl < CH_3Cl < CH_2Cl_2 < CHCl_3 < CCl_4$ (Figure 7). Morrison and Scheller [32] reported the amounts of various chlorinated methanes needed to reduce the burning velocity of stoichiometric *n*-hexane/air mixtures by 30%.

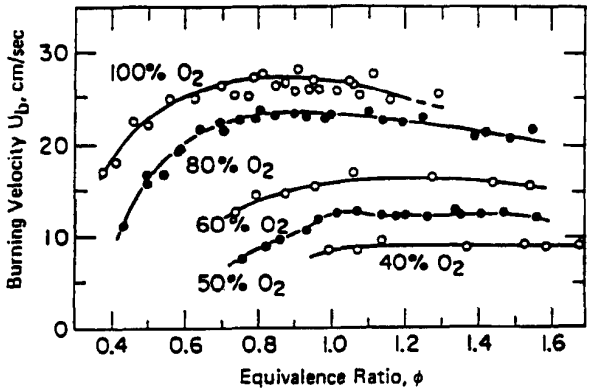

Figure 6. Burning velocities of C_2HCl_3 in oxygen-enriched air [15].

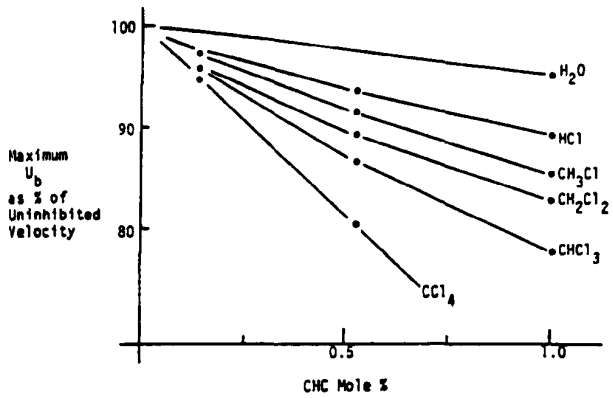

Figure 7. Inhibition of propane-air flames by various chlorinated compounds [31].

They reported an order of inhibition effectiveness similar to that of Garner et al. [31].

Experiments in our laboratories with various CHC in mixture with methane and air show somewhat similar trends. As seen in Figures 8 and 9, burning velocities decrease significantly when the CHC/methane ratio is increased, as well as when the chlorine content of the CHC compound is increased for a given equivalence ratio. Furthermore, as the chlorine content of the CHC is increased, the resulting u_b vs ϕ curve flattens more, indicating the lessened influence of oxygen concentration on the combustion process [29].

From the examination of burning velocity data on CHC systems, it can be concluded that these systems undergo combustion relatively slowly when compared to conventional hydrocarbons. As a conseqence, complete combustion of CHC would require longer reaction times and/or higher operating temperatures to achieve the same degree of destruction as non-CHC.

Soot Formation of CHC

Formation of carbon and/or soot in flames is of considerable practical importance. Soot formation is undesirable because its formation is often

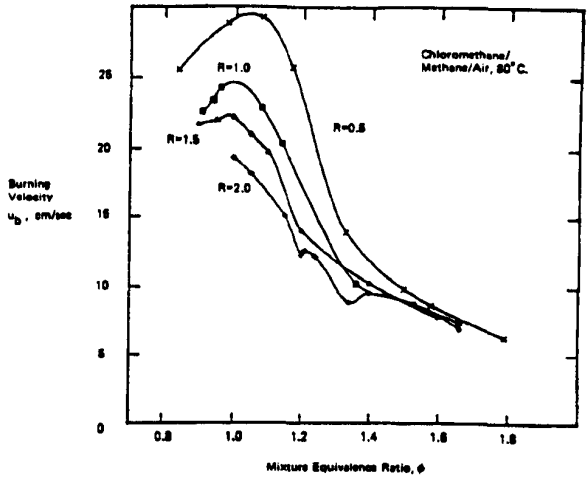

Figure 8. Burning velocities of CH_3Cl/CH_4/air mixtures.

related to the production of toxic compounds such as PAH or chlorinated dioxins, which pose a potential threat to human health and the environment. Soot formation is also undesirable because its presence indicates the conditions of incomplete oxidation and the loss of overall energy efficiency in practical combustors. Furthermore, from the esthetic viewpoint, soot formation is not desirable. However, under some conditions, soot formation is desirable, as carbon aids radiation from the flames thus increasing the efficiency of heat transfer in combustors.

Soot formation is a rate-determined process, and its formation is detected if rates of carbon formation are higher than the rates of carbon gasification. The presence of soot is most easily and directly observed through the presence of yellow luminosity in flames. In this regard, conventional hydrocarbons have been studied quite extensively, and a number of reviews exist in the literature discussing the many aspects of soot formation in flames generated by carbon-, hydrogen- and oxygen-bearing fuels [33,34].

Research with CHC compounds to date principally involved examination of conventional hydrocarbon flames doped with CHC additives, with

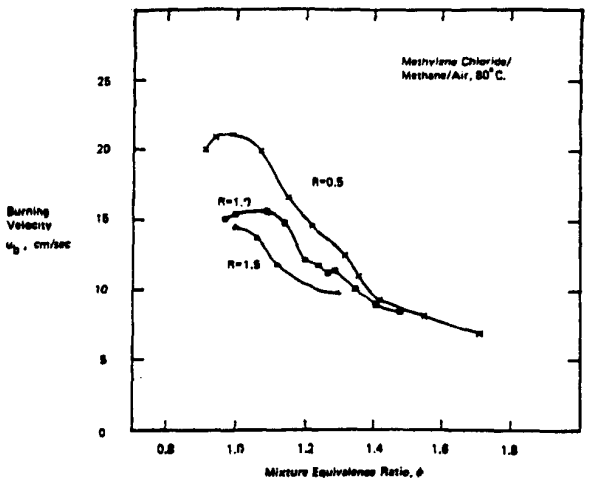

Figure 9. Burning velocities of CH_2Cl_2/CH_4/air mixtures.

the general observation that CHC compounds tend to promote soot formation. Street and Thomas, [35] using a Bunsen burner system, showed that the addition of Cl_2 or CCl_4 increases the amount of premixed air required to suppress carbon formation in benzene/air and kerosene mist/air flames. Garner et al. [31] studied the effects of additives, such as CH_2Cl_2, $CHCl_3$ and CCl_4, on the sooting characteristics of *n*-heptane/ and methylcyclohexane/air diffusion flames, and concluded that as the proportion of chlorine in the additive molecule is increased, so is the effectiveness of the compound in promoting the rate of soot formation. Carbon formation in premixed chlorobenzene air flames was investigated by Scully and Davies [36], who reported higher soot yields from the chlorobenzene system when compared to its nonhalogenated analog (benzene). Wright [37], using a well stirred reactor, reported the critical oxygen-to-carbon (O/C) ratios for incipient carbon formation to be 1.7, 1.75 and 1.75 for chlorobenzene, chlorotoluene and benzylchoride, respectively. In comparison, the critical O/C ratios were 1.75 for benzene and 1.71 for toluene.

The sooting aspects of CHC and their influence on the behavior of conventional hydrocarbons is again related to the free radical scavenging characteristics of the chlorine and chlorine-bearing compounds. The reduction in reactive radical concentration in the preflame zone leads to two relevant events: (1) a decreased radical attack on the fuel molecules before they enter the flame zone (thus, intact fuel may not have sufficient residence time for combustion), and (2) fuel molecules will have more time to undergo pyrolysis. Clearly, this combination of events is conducive to soot formation. Although the exact mechanism of facilitation of soot formation by chlorine-bearing compounds is not clear, these compounds play a dominant role in shaping the behavior of hydrocarbon flames.

Sooting limits of various chlorinated methanes and ethylenes in mixtures with methane and air are shown in Figures 10 and 11 [38]. These limits are presented in terms of the overall mixture critical equivalence ratios (ϕ_c) in accordance with the combustion stoichiometry shown in Equation 5.

The negative sloping trends of the data are consistent with the nonsooting aspects of methane-air mixtures (R = 0.0) and the expected sooting characteristics of the CHC. At low CHC/methane ratios, all chlorocarbons appear to induce soot at about the same equivalence ratio.

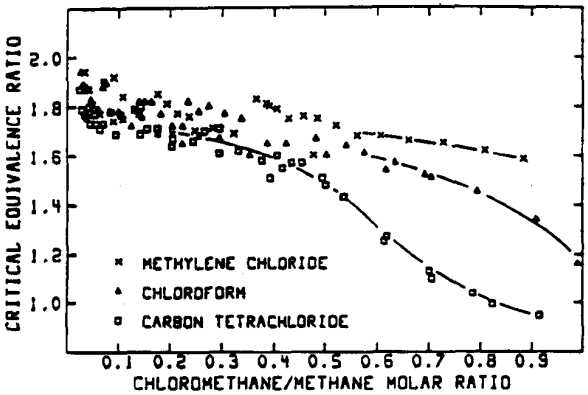

Figure 10. Soot formation limits of chloromethanes in methane and air.

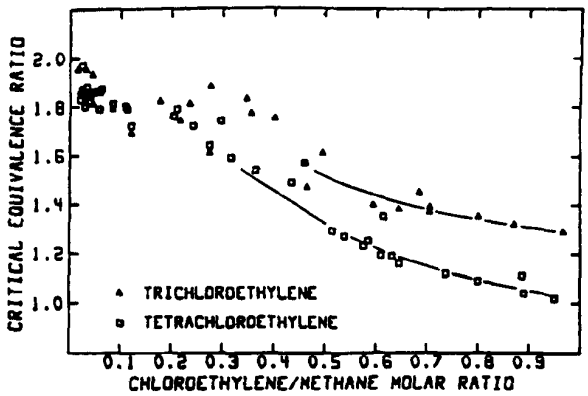

Figure 11. Soot formation limits of chloroethylenes in methane and air.

However, as the mixture is made proportionally more rich in CHC, the differences of individual components become more apparent. This observed variation can probably be attributed to the expected differences in flame temperatures and chlorine contents of the various CHC compounds examined. The sooting tendencies of CHC seem to be proportional to the chlorine content of the compound. The higher the chlorine substitution in a given series, the lower the critical equivalence ratio at which soot formation is first observed.

The results are in agreement with the soot formation mechanism involving pyrolysis of the CHC compounds with rapid dechlorination first, as the C-Cl bond is relatively easy to break, followed by combination of the carbon residues to form soot particles. The dechlorination phenomenon combined with the OH, O and H radical scavenging characteristics of chlorine and chlorine-bearing compounds in the early stages of the flames are all related, and they result in an earlier formation of solid carbon residues in the flames. Senkan et al. discussed the limits of soot formation in CHC/methane/air [38].

Despite the lack of understanding of the exact mechanism of soot formation, it is clear that chlorine-bearing compounds promote both the

limits and rates of carbon formation in flames. Therefore, these properties of CHC compounds must be considered in the design and operation of incinerators.

SUMMARY

Although the fundamental combustion characteristics of CHC are not understood sufficiently well to make definitive predictions on the chemistry, mechanism and rates of CHC oxidation, some general characteristics can still be established.

Available information indicates that CHC combustion is relatively fast at low temperatures and relatively slow at moderately high temperatures when compared to conventional (nonchlorinated) hydrocarbon combustion. Therefore, higher temperatures and/or longer residence times are needed to ensure complete destruction of CHC compounds in practical combustion systems.

Limited research also indicates that potential for soot and particulate formation in chlorinated hydrocarbon systems is again greatly enhanced when compared to that of conventional hydrocarbons. Because of this, new constraints on excess air requirements must be considered in the design and operation of reliable incinerators.

In the design of practical systems the combustion of original chlorinated hydrocarbon compounds and their decomposition products must be considered. Some chlorinated compounds can produce intermediate species that are more stable than the parent CHC molecules, and this possibility must not be overlooked.

ACKNOWLEDGMENTS

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CHAPTER 4

IMPACT OF THE RESOURCE CONSERVATION AND RECOVERY ACT ON THE DESIGN OF HAZARDOUS WASTE INCINERATORS

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Passage of the Resource Conservation and Recovery Act (RCRA) in 1976 ushered in a new era of hazardous waste regulation. The U.S. Environmental Protection Agency (EPA) currently estimates that 67,000 generating facilities, handling some 43 million wet metric tons of hazardous waste (HW) will be regulated in 1981 [1]. Approximately 10–20% of this hazardous waste is being incinerated in about 850 industrial and commercial HW incinerators [2,3]. Between 1981 and 1985, possibly 50–100 new industrial and commercial HW incinerators may need to be designed and installed to meet the disposal pressure caused by RCRA [2].

Subtitle C of RCRA requires "cradle-to-grave" accountability for HW materials. Wastes will be tracked and regulated from their generation point through storage, transportation, and final treatment and/or disposal. One of the key Subtitle C sections is Section 3004, "Standards for Owners and Operators of Hazardous Waste Treatment, Storage and Disposal Facilities." This section includes standards for treatment alternatives, which include incineration, landfill, surface impoundments, landfarming, chemical, physical and biological treatment, and underground injection. This chapter will discuss the impact of RCRA Section 3004 on the design of industrial and contractor HW incineration systems.

SUBTITLE C HISTORY

The proposed Section 3004 incineration regulations, first published in the December 18, 1978, *Federal Register* [4], contained specific incineration technical performance and design standards. These performance and design standards mandated criteria such as combustion temperature, retention time, carbon monoxide combustion efficiency, toxic component destruction efficiency and exhaust gas removal requirements for halogens and particulates. During the allowable comment period, industry responded strongly to some of the proposed performance and design standards, indicating that the combined EPA and industry incineration data base used to set the standards was poor and in need of further development and documentation. Consequently, when EPA published the revised Section 3004 regulations in the May 19, 1980, *Federal Register* [5], the incineration performance and design standard approach had been replaced with a proposed three-phase regulatory program.

The May 19, 1980, Phase I standards were interim status standards (Part 265), which regulated the operation of existing HW incinerators. The general requirements for incineration in Part 265 basically involve improving existing incineration facility operating procedures. Some of the required improvements involve startup, waste analysis, monitoring and inspection. The intent of the interim status standards was to improve the operation of existing incinerators during the interim period before the existing system undergoes the RCRA trial burn permitting process required by the Phase II incineration regulations.

Phase II incineration standards were published in the January 23, 1981, *Federal Register* [6]. The January 23, 1981, Part 264 incineration regulations set forth three performance standards that must be met by new HW incinerators during a trial burn test. The three performance standards involve principal organic hazardous constituent (POHC) destruction, exhaust gas HCl removal and maximum particulate emission limitation.

The Part 264 standards for regulation of HW incinerators imposed essentially identical permitting and operational requirements on both new and existing facilities. However, because of industry comments expressing concern over the costs associated with retrofitting and upgrading existing incinerators, the EPA temporarily suspended the effective date of the Part 264 regulations for existing incinerators [3]. After reexamination of the issues involved, the EPA will either lift the suspension or initiate new rulemaking for existing HW incinerators [3]. In the meantime, existing HW incinerators will be regulated by the Part 265 interim status rules [6].

The Phase III HW incineration standards are to be based on an extensive evaluation of trial burn data from new and existing incinerators.

Since the trial burn requirements for existing incinerators have been suspended temporarily, the schedule for the proposed Phase III HW incineration regulations has been delayed. According to EPA, most of the specific quantitative design, operation and performance requirements for the Phase III regulations will be issued only when adequate technical support for these standards can be established firmly. Establishing the technical support data for the Phase III standards could take five or more years of intense development activity.

A regulatory impact analysis (RIA) is now being compiled for the Part 264 HW incincerator regulations for existing and new HW incinerators. The draft RIA is expected to be ready for public review by April 1983 [3] and may result in changes to the Part 264 regulations.

The ultimate HW incineration rules may include two changes from the present Phase II regulations. These changes may incorporate risk assessment procedures and the use of risk assessment procedures to allow site-specific variance of 99.99% destruction removal efficiency (DRE) [6,7]. The variance would allow <99.99% DRE for certain facilities and require >99.99% DRE for other facilities, based on emissions and facility location. An evaluation of the impact of the January 23, 1981, performance standards on the design and operation of new HW incineration systems is presented in the following sections.

RCRA INCINERATOR PERFORMANCE STANDARDS

The main HW incineration performance standards are listed in Section 264.343 of the January 23, 1981, regulations [6]. The key points of these standards, summarized in Table I, have had significant impact on the design of HW incinerators.

Table I. Summary of Performance Standards from Part 264 of the RCRA Hazardous Waste Incineration Regulations [6]

Section	Standard/Criteria	Requirements
264.343a	POHC DRE	POHC destruction of 99.99% by weight based on waste POHC feed rates and combustion gas POHC emission rate measured after air pollution control equipment
264.343b	HCl removal	99% HCl removal required when incinerating hazardous waste containing more than 0.5% chlorine
264.343c	Particulate emission	Particulate emissions after air pollution control equipment must not be greater than 0.08 gr/dscf when corrected to 12% CO_2

Continuous measurement of the concentrations of POHC, HCl and particulates in a stack gas is currently beyond the state-of-the-art. Therefore, compliance with the performance standards given in Section 264.343 can only be measured during a trial burn by using established and newly developing stack sampling techniques.

The January 23, 1981, HW incineration regulations require that a new facility perform a compliance trial burn before starting normal operation, to prove compliance with the performance standards and to establish normal incinerator operating conditions [6]. The trial burn requirements are listed in Part 122 of the January 23, 1981 *Federal Register* [6] and are summarized in Table II. The POHC DRE criterion is the most significant of the three perfogmance standards listed.

Table II. RCRA Trial Burn Requirements [6]

Trial Burn Plan
Trial burn plan must include:
Analysis of wastes (heat of combustion, viscosity, Appendix VIII constituents)
Detailed description of incineration system
Detailed trial burn test schedule
Detailed trial burn test protocol (relevant test parameter variation)
Description of emission control equipment and operating conditions during trial burn tests
Procedures for rapid waste shutoff and incinerator shutdown during test burn equipment malfunction
Trial Burn Review and Approval
Possible EPA request for additional information
EPA determination of:
POHC
Trial burn plan is likely to achieve objectives
Trial burn will not present imminent hazard to humans
Trial Burn Testing/Analytical Requirements
POHC and organic chlorine waste feed
Exhaust gas emissions of POHC, CO_2, CO, HCl, particulate and hazardous combustion by-products
Quantitative analysis of scrubber water, ash residues, and other residues for POHC
POHC mass balances
Calculation of POHC DRE
Calculation of HCl removal efficiency
Computation of particulate emissions
Identification, sources and control of fugitive emissions
Measurement of average, maximum and minimum temperatures and air feed rates
Continuous measurement of CO in exhaust gas
Certification by applicant that test results and submissions were performed as per the approved test burn plan

POHC Destruction Removal Efficiency

DRE Definition

The concept and selection of POHC is an important part of the incineration regulations. POHC, which are to be determined during permit trial burns, are to be selected by the EPA permit writers from the RCRA Appendix VIII constituents present in the wastes to be incinerated [6]. Appendix VIII is a list of about 370 organic and inorganic hazardous chemicals first published in Part 261 of the May 19, 1980, *Federal Register* [5]. The Appendix VIII constituents have been defined by the EPA as substances that scientific studies have shown to have toxic, carcinogenic, mutagenic or teratogenic effects on humans or other life forms [8]. The actual number of Appendix VIII chemicals is higher than 370, because more than 30 of the Appendix VIII constituents are chemical groups such as isomers or salts. For example, the constituent listed as chlorinated benzenes represents all the possible isomers (monochlorobenzene through hexachlorobenzene). The most recent version of Appendix VIII appears in the May 20, 1981, *Federal Register* [9].

The POHC selection process will be based on the concentration of Appendix VIII constituents in the incineration waste feed and on the degree of difficulty of incinerating the Appendix VIII constituents. The Appendix VIII constituents in the waste feed that have the highest concentration and are the most difficult to incinerate will be designated by the EPA permit writer as POHC. Those Appendix VIII constituents that represent the greatest degree of difficulty of incineration (highest thermal oxidation stability) will be the ones most likely to be designated as POHC [6].

The POHC DRE standard (Section 264.343a) requires that a HW incinerator must achieve a DRE of 99.99% for each POHC designated by the EPA permit writer, although the number of Appendix VIII constituents that will be designated as POHC is not specific in the regulations. The DRE during the trial burn is determined for each POHC according to:

$$DRE = \frac{(W_{in} - W_{out})}{W_{in}} \times 100\% \qquad (1)$$

where W_{in} = mass feed rate of a POHC in the waste stream feeding the incinerator
W_{out} = mass emission rate of the same POHC present in exhaust emissions before release to the atmosphere

As can be seen from Equation 1, each DRE is based on the weight of feed rate of each POHC into the incinerator and the emission rate of each POHC in the HW incineration combustion gas measured after going through the incineration system's air pollution conctrol (APC) equipment. The DRE calculation does not include any POHC present in either the incinerator ash or any APC effluents such as scrubber water. The DRE calculation includes only the stack emission of the original POHC that was fed into the HW incinerator and does not consider combustion by-products or products of incomplete combustion (PIC).

The DRE is also a function of the APC system. In incineration systems equipped with wet scrubbers such as venturis, uncombusted POHC with high aqueous solubility and low vapor pressures will have high potential for being removed. With wet scrubbers or dry APC equipment (such as electrostatic precipitators or baghouses), uncombusted POHC that are adsorbed on soot and particulate will be removed from the combustion gas along with the particulate collected by the APC equipment.

Considerations Related to 99.99% DRE

There are many complex considerations associated with the design of hazardous waste incinerators so that a DRE of 99.99% is always achieved. Many of these factors are often poorly understood by the industrial and regulatory community, and their importance therefore may be overlooked. The effects of high combustion temperature and extended high-temperature residence time are generally acknowledged as important. These two important criteria, however, are only part of the design, and attention to time and temperature alone can be a critical error.

The 99.99% DRE performance standard emphasizes the need for good combustion chamber design relative to turbulent mixing of unburned POHC and hot, oxygen-rich combustion gases outside the flame envelope. The combustion reaction rate in a flame envelope is several orders of magnitude faster than the combustion reaction rate under flameless conditions. This increased reaction rate is probably due to the formation of highly reactive free radicals in the high-energy flame environment. The reaction rate under flameless conditions outside the flame envelope is slower and involves different thermal oxidation reaction mechanisms [10]. Even though most of the POHC destruction probably occurs in the flame envelope, attainment of the final amount of destruction necessary to achieve a 99.99% DRE also depends on good turbulent mixing outside the flame envelope. Therefore, designing a HW incineration to incorporate both turbulent mixing and flame contact is important.

In addition to the considerations of turbulent mixing and flame contact, other thermal oxidation mechanisms are important. These mechanisms include atomized liquid droplet evaporation rates, particulate melting and vaporization rates, and adsorption of uncombusted chemicals on soot particles and particulate. All these rate processes produce a situation in full-scale HW incineration in which thermal oxidation reaction kinetics are not limiting, but other practical factors, such as the degree of turbulent mixing, droplet evaporation rate and soot formation, are rate-limiting [12]. These factors have not been studied and evaluated extensively, but they play an important part in the attainment of 99.99% DRE. The design of a HW incineration system for maximum flexibility with high temperature, adequate residence time, good turbulent mixing capabilities and careful consideration of each of these other factors appears to be necessary to achieve 99.99% DRE-thermal oxidation stability for high (TOS) Appendix VIII constituents.

Thermal Oxidation Stability

TOS is a key concept of the January 23, 1981, HW incineration regulations [6]. EPA has stated that those Appendix VIII constituents that are most difficult to incinerate (highest TOS) will be the chemicals most likely to be designated as POHC [6]. Any designer of HW incinerators must therefore have some idea of the TOS of different Appendix VIII and other chemicals during the design process.

EPA has recommended heat of combustion as a TOS indicator [12], apparently because heat of combustion data and estimation techniques are available for all Appendix VIII constituents. In the EPA heat of combustion model, TOS is inversely proportional to the heat of combustion. The higher the heat of combustion, the lower the TOS of the Appendix VIII constituent.

Two publications indicate that the concept of heat of combustion as a TOS indicator may not be a very good one [11,13]. For example, Tsang and Shaub point out that, according to the heat of combustion TOS indicator, acknowledged high-TOS chemicals such as benzene, polynuclear aromatics and polychlorinated biphenyls (PCB) have lower thermal oxidation stabilities than highly unstable chemicals such as nitroglycerine and trinitrotoluene (TNT) [13]. Cudahy et al. statistically correlated flameless vapor-phase thermal oxidation DRE data for 15 chemicals with various parameters such as the autoignition temperature (AIT) and the heat of combustion [12]. Table III summarizes the results of the statistical analysis. The laboratory DRE data were expressed as T99.99/2, the temperature necessary to achieve a 99.99% DRE for a particular chemical

Table III. Results of Linear Regression Analysis for Correlation of T 99.99/2

X Parameter	Y Parameter	(R) Correlation Coefficient	R^2
Autoignition Temperature (°C)	T 99.99/2	0.94	0.88
Ionization Potential (eV)	T 99.99/2	0.80	0.64
Heat of Ion Formation (kJ/mol)	T 99.99/2	0.74	0.55
Molar Heat of Combustion (J/mol)	T 99.99/2	0.62	0.38
Activation Energy (kJ/g-mol)	T 99.99/2	0.42	0.19
Heat of Combustion (J/g)	T 99.99/2	0.39	0.15
Flash Point (°C)	T 99.99/2	0.22	0.05
Heat of Formation @ 298°C (kJ/mol)	T 99.99/2	0.21	0.04
Free Energy @ 298°C (kJ/mol)	T 99.99/2	0.08	0.006

Table IV. Approximate Order of TOS According to AIT for Various Nonsubstituted Organic Families

Family	Basis	TOS
Polynuclear Aromatics	Naphthalene	Highest
Biphenyls	Biphenyl	
Aromatics	Benzene	
Aromatic Ring N	Pyridine	
Methanes	Methane	
Straight Chain Paraffins	Ethane	
Straight Chain Olefins	Ethylene	
Hydrazines	Hydrazine	Lowest

at a 2-sec residence time. The T99.99/2 was calculated based on laboratory-derived, first-order kinetic constants, assuming Arrhenius temperature dependence for the reaction rate constant.

As can be seen from Table III, AIT had a correlation coefficient (R) of 0.94, and the heat of combustion had an R of 0.39. These correlation coefficients indicate that the AIT is a far better indicator of TOS than heat of combustion in flameless combustion. However, because of the lack of T99.99/2 data under flame combustion conditions, the validity of AIT as a TOS indicator for flame combustion incineration systems presently is still in question.

Assuming that the AIT is a good indicator of TOS in flame combustion, certain useful guidelines based on AIT values can be drawn about the TOS of various chemical families present in Appendix VIII. The approximate relative TOS, based on AIT values of eight chemical families that account for about two-thirds of the Appendix VIII constituents, are shown in Table IV [11]. The approximate impact of substitution on the TOS of these families is shown in Table V. The AIT data base is not large

Table V. Impact of Group Substitution on Thermal Oxidation Stability

Group Substitution	Thermal Oxidation Stability		
	High	Medium	Low
F, Cl	X		
Br, CN, CNO, OH, NH_2, $\overset{O}{\overset{\|}{C}}$-OH, H	X	X	
CH_3, NO_2		X	
C_2H_5, C-O-C, OCH_3, $\overset{O}{\overset{\|}{C}}$, S, SO_4			X

enough to define more clearly the impact on TOS of the seven groups classified as high and medium. As a general rule, except for chlorination, multiple substitution appears to lower TOS. Halogenated organics are a particularly important subgroup of Appendix VIII. About one-third of the approximately 340 organic Appendix VIII constituents contain either chlorine, fluorine or bromine. Based on AIT values, the following tentative guidelines can be drawn for the TOS of halogenated organics [11]:

1. Chlorinated aromatics such as chlorobenzene, PCB and chloronaphthalene appear to have the highest TOS values of any of the Appendix VIII constituents.
2. Halogen substitution seems to increase TOS in the following order: F > Cl > Br.
3. Halogenation does not increase the TOS of all organic compounds. Halogenation of straight-chain olefins, for example, may result in a TOS decrease.
4. For aromatic compounds, TOS appears to increase with increasing halogen substitution up to maximum halogen substitution.

Table VI summarizes the published AIT values for organic Appendix VIII constituents [14,15]. AIT values were found for only about 20% of the organic Appendix VIII constituents. The lowest reported AIT values are listed for the chemicals in Table VI.

HCl Removal (Section 264.343b)

According to RCRA, an incinerator burning HW containing more than 0.5% chlorine must remove 99% of the HCl from the exhaust gas [6]. For HW incinerators that are fed waste profiles containing organic

Table VI. AIT Values of Appendix VIII Constituents [10]

Phenol	715.
Dichloromethane	662.
o-Dichlorobenzene	648.
Chlorobenzene	638.
Diphenylamine	634.
Chloromethane	632.
Hexachlorobutadiene	618.
Aniline	615.
Resorcinol	608.
Cresylic Acid	599.
Benzyl Chloride	585.
Phthalic Anhydride	584.
1,2,4-Trichlorobenzene	571.
Acetophenone	570.
Cresol	559.
2-Chloronaphthalene	558.
1,2-Dichloropropane	557.
Dimethyl Phthalate	556.
Formic Acid	539.
Hydrocyanic Acid	538.
2-Picoline	538.
Bromomethane	537.
Naphthalene	526.
Acetonitrile	524.
Acrylamide	524.
Methyl Ethyl Ketone	515.
Benzene	498.
1,1,1-Trichloroethane	486.
Nitrobenzene	482.
Toluene	482.
Pyridine	482.
Acrylonitrile	481.
Maleic Anhydride	477.
Vinyl Chloride	472.
1,1-Dichloroethane	458.
Vinylidene Chloride	458.
1,1,2-Trichloroethene	457
Ethylene Oxide	429.
Isobutyl Alcohol	427.
Formaldehyde	424.
Methyl Methacrylate	421.
1,2-Dichloroethane	413.
Epichlorohydrin	411.
Trichloroethylene	410.
Di-n-butyl Phthalate	403.
Acetyl Chloride	390.
Allyl Alcohol	378.
Creosote	336.

Table VI, continued

Ethyleneimine	322.
Propyl Amine	318.
1,2,3-Trichloropropane	304.
Acrolein	278.
Nitroglycerin	270.
Hydrazine	270.
Hydrogen Sulfide	260.
Nicotine	244.
Paraldehyde	238.
Benzotrichloride	211.
Crotonaldehyde	207.
Methyl Hydrazine	194.
Dimethyl Sulfate	188.
Acetaldehyde	185.
1,4-Dioxane	180.
Phosphine	100.
Carbon Disulfide	90.

chlorine levels of greater than 5–10% by weight, this standard should be economically achievable using traditional equipment such as venturi scrubbers, tray towers and packed beds. The EPA background document [16] summarizes HCl removal data for eight full-scale chemical waste incinerators. Seven of the eight achieved 99% or greater HCl removal efficiency, and the eighth system came close [16].

The HCl removal performance standard as written will be expensive and difficult to achieve for HW incinerators that are burning waste profiles in the 0.5- to 5-wt % range. Under the proposed regulation an incinerator system operating at 1832° F, 145% excess air and incinerating 0.50 wt % organic chlorine will not be required to wet-scrub HCl and will produce a combustion gas containing about 130 ppm_v of HCl. The same facility incinerating 0.51 wt % organic chlorine will, however, be required to wet-scrub the combustion gas to a stack level of 1.3 ppm_v of HCl. Typical water scrubbing systems can generally get down to a measured level of about 20 ppm_v of HCl. Demonstrating removal of HCl to the 1.3-ppm_v range will be very difficult and expensive, requiring costly alkaline scrubbing and possibly sacrificing process reliability due to potential hardness precipitation and plugging of equipment. For these small systems, an HCl emissions limitation based on stack concentration rather than removal efficiency makes more sense.

For systems with higher waste organic chlorine contents, the 99% performance standard is readily achievable. The main impact of the HCl

performance standard on the design of HW incineration systems will be the necessary addition of packed bed or tray-type absorption systems to the APC system and the use of alkaline scrubbing solutions.

Particulate Emission Limitation (Section 264.343c)

The January 23, 1981, HW incineration regulations include a particulate emissions limitation performance standard [6]. This standard states that an incinerator burning HW must not emit particulate matter exceeding 0.08 gr/dscf when corrected to 12% carbon dioxide (CO_2). Particulate concentrations in the exhaust gas of 0.08 gr/dscf corrected to 12% CO_2 are achievable. To be met consistently, however, careful waste characterization, feed control, flue gas preconditioning and selection of the optimal gas cleaning and mist elimination systems are required. Venturi scrubbers, for example, will require pressure drops in the range of 40–80 in. water column (w.c.) to meet the criteria. The electrical power cost for such a system operating under induced draft is quite high, however, and must be considered carefully. At a system pressure drop of 72 in. w.c. and at 70% fan motor efficiency, approximately 160 hp will be required for each 10,000 acfm to the fan.

In many cases, test burns may be desirable to develop specific air pollution design criteria, particularly if the waste profile contains organic phosphorus, metal salts and substantial quantities of inorganic salts. The use of emerging technologies such as wet electrostatic precipitators and high-pressure fluid jets should be investigated as a means of reducing fan horsepower requirements and improving particulate removal efficiences.

In the January 23, 1981, particulate performance standard, no detail is given on how CO_2 should be determined for particulate correction. This important area needs clarification because of the possibility of CO_2 absorption in alkaline wet scrubber solutions before exhaust gas sampling. Since sampling of hot combustion gas for CO_2 is complex and hazardous, sampling after the wet scrubbing system is recommended if reliable CO_2 exhaust gas concentrations can be determined. An example is given below to illustrate the importance of correct CO_2 determinations. For accurate CO_2 sampling (6% CO_2 = correct value)

$$\frac{0.04 \text{ gr}}{\text{dscf}} \times \frac{12\%}{6\%} = \frac{0.08 \text{ gr}}{\text{dscf}} \text{ corrected to } 12\% \ CO_2 \qquad (2)$$

For inaccurate CO_2 determination (5% CO_2 = incorrect value)

$$\frac{0.04 \text{ gr}}{\text{dscf}} \times \frac{12\%}{5\%} = \frac{0.096 \text{ gr}}{\text{dscf}} \text{ corrected to } 12\% \, CO_2 \qquad (3)$$

RCRA OPERATING AND MONITORING REQUIREMENTS

The January 23, 1981, HW incineration regulations specify monitoring requirements that must be performed by a permitted incinerator during normal operation [6]. These requirements include areas that typically have not been monitored during waste incineration and therefore will need to be developed by industry and equipment vendors. According to Section 264.345b, during normal operation an incinerator must be operated within certain permitted limits for waste feed rate, CO exhaust gas concentration, combustion temperature and combustion air feed rate. If any of these permit limits are exceeded, the waste feed rates to the incinerator must automatically be shut off (Section 264.345e). Continuous tracking or monitoring of waste feed rate, CO and combustion air feed rate represent difficult technical design problems.

Waste Feed Rate (Section 264.345b2)

A rotary kiln incineration system designed for liquid and solid waste feeds such as those shown in Table VII can operate under many different feed rate conditions. Continuous monitoring and tracking of the waste feed rates for the seven general liquid and solid waste categories shown in Table VII is very difficult and expensive [17]. Periodic analysis of these seven waste streams for multiple POHC or 370 Appendix VIII constituents as implied by Section 264.341 [6] also is impractical and cost-prohibitive [17]. EPA must clarify and simplify these waste feed rate operating requirements and make them more practical.

Table VII. Typical Waste Categories for a HW Incinerator

Primary combustion chamber organic liquids
Secondary combustion chamber organic liquids
Aqueous organic liquids
Solids/bulk
Solids/drums or fiber packs
Sludges/bulk
Sludges/drums or fiber packs

Air Feed Rate (Section 264.347a1)

The January 23, 1981, regulation states that the incineration permit will have acceptable limits for the air feed rate based on trial burn data. The permitted air feed rates must be monitored on a continuous basis (Section 264.347a1) [6]. This operating requirement seems to be concerned with combustion retention time. However, air feed rate is poorly defined and must be redefined in a more practical way. One reason the air feed rate regulation must be modified is that measurement in some liquid/solid incineration systems is difficult. For example, in an induced-draft rotary-kiln incineration system, part of the combustion air enters the system through the solids feed chute and the rotary-kiln seals. This air is very difficult to measure. To alleviate this situation, air feed rate permit limits could be replaced by some retention time indicator that could be measured more easily and would be reasonably simple and accurate. EPA could investigate the feasibility of the following directly proportional retention time indicators:

- incinerator combustion gas flowrate,
- major induced or forced draft fan flowrate or motor current, and
- incineration system pressure drop

Any of these techniques regulates combustion retention time more simply than permit limits on air feed rate.

Carbon Monoxide Monitoring (Section 264.347a2)

Analytical equipment does not exist for the continuous determination of specific Appendix VIII constituents in a stack gas. EPA therefore plans to monitor the organic destruction efficiency of RCRA-permitted HW incinerators by monitoring combustion temperature and CO levels continuously as indicators of good combustion. If the combustion temperature drops below permitted limits or the exhaust gas CO concentration rises above permitted levels, the HW feeds must automatically shut off.

Nondispersive infrared radiation (NDIR) is the analytical method referenced by the EPA for continuous monitoring of CO in exhaust gases. The analytical method and instruments, however, must be selected carefully for operation under the specific waste gas conditions. Other analytical techniques, such as gas chromotography with flame ionization detection and electrochemical transducer methods, should be considered. The analytical techniques should be considered. The analytical techniques

should be evaluated relative to the exhaust gas characteristics for the following factors:

- particulate interference,
- water vapor interference,
- system durability (resistance to corrosion),
- maintenance requirements, and
- gas sample preparation requirements.

Stack Monitoring

The January 23, 1981, regulations require continuous exhaust (stack) gas monitoring only for CO [6]. However, other factors, such as the Clean Air Act (Prevention of Significant Deterioration) and state air regulations, may require continuous stack monitoring for other gaseous compounds. Among likely candidates are nitrogen oxides, sulfur oxides, hydrocarbons, oxygen and CO_2. Technology exists today to continuously measure these compounds in a combustion gas. However, stack sample preparation technology is often difficult and complex because of the high levels of water vapor in HW incinerator stack gases that have been wet-scrubbed for acid gas and particulate removal.

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CHAPTER 5

USING SOLIDIFICATION AS A WASTE DETOXICATION PROCESS

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For some reason, solidification has not widely been thought of as a detoxication process. Some may argue that this process simply prepares a waste for landfilling in a secure facility. However, solidification has been used successfully for waste detoxication for more than ten years. There are many feasible solidification processes. These processes are either commercially (i.e., privately owned) or generically available. They can be utilized at the waste generation site or at a waste management facility offsite. There are even mobile solidification units available for use at uncontrolled waste sites or inactive lagoons. This versatility may account for the recent reawakening in interest for this often misunderstood technology.

The U.S. Environmental Protection Agency (EPA) defines "treatment" as:

> any method, technique, or process which is designed to change the physical, biological character or composition of any hazardous waste or to render such waste nonhazardous, safer for transport, amenable for recovery, amenable for storage, or reduced in volume.

Solidification is not a disposal technique. Beyond the physical encapsulation properties that are inherent in most processes, some processes chemically bind or "fix" certain inorganic species to the crystalline

matrix. The quicklime process generates great heat, thereby disinfecting (i.e., through biological process) or even thermally oxidizing organics. Finally, asphalt processes may account for significant volume reduction. This chapter examines how the treatment process of solidification leads to detoxication.

DETOXICATION

When many materials are disposed of improperly, various toxic components are leached from them. These toxics are then able to find their way into surface or groundwaters. Solidification reduces the surface area of the waste, thereby dramatically reducing the leachable fraction, even if there is no fixation or other reaction that may further retard elutriation of the toxics. Toxicity, in a strict sense, requires the toxic component to enter a pathway and reach a receptor in a sufficient amount and over a sufficient period of time to cause a toxic reaction. Solidification reduces the probability of this happening, even if the material is not chemically destroyed.

EPA defines two types of hazardous waste: one that fails the characteric tests of ignitability, corrosivity, reactivity and end product (EP) toxicity; and one that appears on an EPA hazardous waste list. If one solidifies the first type of hazardous waste, and the product passes the characteristic tests that it failed as raw waste, it is no longer hazardous. Therefore, if a waste fails the EP toxicity test but after solidification it no longer fails the test, the waste has been detoxicated.

Solidification of a listed waste is a different matter. Under the present regulations, no amount of any treatment can automatically make these wastes nonhazardous. The applicant must petition the EPA under 40 CFR, Parts 260.20 through 260.22 for "delisting" of a treated waste. This delisting procedure involves the submission of a petition by certified mail to an EPA Regional Administrator. The petition must include:

1. petitioner's name and address;
2. statement of petitioner's interest in the proposed action;
3. description of the proposed action; and
4. statement of the need and justification for the proposed action, including any supporting tests, studies or other information.

The information to be supplied under point 4 above constitutes the major portion of a delisting study. The report should address the following points, as specified in Part 260.22, to show that the waste in

question does not exhibit the characteristic(s) that caused it to be listed as generically hazardous:

1. name and address of the laboratory facility performing the sampling or tests of the wastes;
2. names and qualifications of the persons sampling and testing the waste;
3. dates of sampling and testing;
4. location of the generation facility,
5. description of the process and feed materials producing the waste and an assessment of whether such processes, operations or feed materials can or might produce a waste that is not covered by the demonstration;
6. description of the waste and an estimate of the average and maximum monthly and annual quantities of the waste covered by the demonstration;
7. discussion (where applicable) of the factors delineated in 40 CFR Part 261.11(a)(3);
8. description of the methodologies and equipment used to obtain the representative samples;
9. description of the sample handling and preparation techniques, including techniques used for extraction, containerization and preservation of samples;
10. description of tests performed (including results);
11. names and model numbers of the instruments used in performing the tests; and
12. generator's certification statement.

EPA has reviewed a number of delisting petitions concerning solidification and has published its findings and conclusions in the *Federal Register*. Removing from the EPA list a treated waste removes the waste at the point of treatment from the regulations regarding disposal. Because of the potential cost savings, delisting provides an incentive for the use of solidification and other detoxication technologies.

PROCESS CONTROL

Unfortunately, any treatment process is only as good as the means utilized to ensure its proper operation and maintenance (O&M). When petitioning the EPA or a potential host community, the petitioner for a potential facility site must be able to demonstrate O&M control in five critical areas:

1. waste collection and prescreening,
2. waste pretreatment,
3. addition of solidification agent,
4. mixing, and
5. handling and/or disposal

Each of these areas as they relate to the use of solidification as a detoxification process will be described briefly below.

Waste Collection and Prescreening

As with any other treatment process, it is important to have the waste generator segregate waste streams that have undesirable qualities for the particular solidification agent that will be utilized. Some Portland cement processes do not readily tolerate certain types of organics, which act as retarding or accelerating agents. Because of the vast variety of different solidification processes, proper prescreening can find a suitable match between waste type and solidification agent. However, economics may then dictate the preferential use of another treatment option. Prescreening is also required as part of the ongoing effort to make certain that the process receives no surprises with respect to waste stream characteristics.

Waste Pretreatment

Some wastes can be solidifed directly, while others must be pretreated. Physical pretreatment process units required by some solidification units include thickening, dewatering, calcination and incineration. To reduce the extraction of toxics from the solidifed waste, pretreatment for cyanide destruction and chromium reduction are usually required. Neutralization, often with another waste, can cut down on the amount of caustic solidification agent required. When pretreatment is required, prescreening is often repeated to be certain the waste is ready for solidification.

Addition of Solidification Agent

There are at least six categories for solidification agents as described in the literature. These categories are:

- cement or silicate-based,
- lime-based,
- thermoplastic-based,
- organic polymer-based,
- ceramic-based, and
- encapsulation

Each of these processes has its own requirements for addition of the solidification agent. A wide variety of different feed equipment is utilized. The amount of additive probably will be dictated by cost-effectiveness (after meeting the minimum specifications of the EPA structural integrity and EP toxicity leaching tests). Other specifications may be required, depending on the end use of the material if it is nonhazardous and not landfilled.

Mixing

Solidification is often conducted in a large batch reactor or in a smaller container. The versatility of the process also allows it to be used in situ at an abandoned hazardous waste site. The mixing required must be compatible with both the application and the solidification agent utilized. Proper mixing is essential to obtain a homogeneous end product. Random sampling will be required of all processes after solidification, as unreacted waste could spoil the testing results. Mixing must also be monitored carefully so the system does not accidentally "freeze up" with solidified material.

Handling and/or Disposal

To repeat a statement made above, solidification is not a disposal technology. If the end product is sampled and found to be "hazardous," the material must be disposed of in a secure chemical landfill. There are those who want all solidified wastes to be managed in such a facility. However, if the treated waste is nonhazardous, a landfill designed to a lesser specification may be all that is required for proper management. There are a number of productive uses of solidified wastes that provide increased cost-recovery incentives for the use of this process. Some of these demonstrated uses include: land reclamation, roadbed aggregate, artificial reefs, parking lot pavement, impermeable municipal landfill liners, and landfill cover and capping material.

ONSITE VS OFFSITE TREATMENT

A controversial choice confronting every hazardous waste generator is where the wastes should be handled for treatment. Offsite regional treatment offers economies of scale and the possibilities for use of other wastes for neutralization and pretreatment. A potential problem is that the waste will be mixed with other wastes, and there is the question of future joint liability. Wastes must also be manifested with this option, if they are hazardous.

Onsite treatment gives the generator more control over processing and handling of his own wastes. It may also remove some of the manifesting requirements. Some treatment technology vendors operate exclusively in one mode or the other. Other vendors operate in either mode, to suit the needs of a customer. Legal and economic factors must be weighed carefully by the waste generator before deciding which route to take.

In the area of abandoned site cleanup, the same controversy takes the form of containment vs removal. A variety of solidification processes have been demonstrated for direct in situ containment. Other processes require removal and processing through a mobile unit before onsite recontainment. Some processes have end products that never set hard but remain friable to permit future removal to an alternative site. This remarkable versatility has recently led to the placement of solidification on many of the remedial action priority lists.

PROBLEMS SITING SOLIDIFICATION FACILITIES

Despite the proven detoxication of certain wastes and the remarkable versatility of this category of processes for waste treatment, the public has been unwilling in many cases to accept disposal of the product other than in a secure chemical landfill. Numerous vendor claims have gone unheeded. The public repeatedly asks the questions:

- What will be released to the environment when the solidified product is not placed in a fully contained landfill?
- How much of each toxic component will be released per unit mass?
- What will happen to the mass and the rate of leaching over time?

It is easy to become confused over the leaching data submitted to regulatory officials by many vendors. Over time, a variety of different testing methods have been used. There is no set pattern or even mention of the ratio of waste additive. Finally, the end product is not made to a consistent physical constant. How is one to compare the data or determine whether it is suitable for the planned management scenario? The EPA EP toxicity test settles the problem with variable testing protocols, but there is little agreement as to its representativeness or precision. The American Society for Testing and Materials (ASTM) has established a subcommittee of their D34 Waste Disposal Committee to look into these questions.

Some progress has been made by ASTM to examine the leaching test and the physical constants that will be necessary to provide answers to the first two public questions. However, this process is slow and not necessarily directed at providing siting assistance. Someone other than vendors needs to address these questions soon; unfortunately there appears to be no attempt in the United States to provide such an answer.

The public has often been told that the treated waste is like cement. The layperson is used to seeing cement crack on roads and bridges and will strongly doubt vendor claims concerning the durability of the end

product over time when properly managed. Accelerated environmental testing is perhaps the most controversial aspect of testing solidified-product durability. Most environmental tests, which are designed to be representative of environmental conditions, are slow to generate useful data, and the testing process cannot be accelerated. However, just as the aerospace industry tested the long-term lifespan of critical components with accelerated techniques, a similar approach must be applied to solidified wastes. Some groundwork for this testing has been laid in Europe, but little is presently being done in the United States. U.S. vendors must overcome their reluctance and devise these tests, have them approved by an independent group, and submit standard samples for independent accelerated testing to avoid costly secure landfilling of "nonhazardous" products.

CONCLUSIONS

Solidification has only been used for waste treatment for the past 10 years. Encouragement is needed to bring the technology to the point where the public's questions can be answered with credibility. A quote, which appeared in the *Federal Register* (October 8, 1980), sets the tone for this movement:

> Hazardous waste management is a new and developing field. The relatively recent concern with the dangers presented by the disposal of hazardous waste has spawned new efforts in the scientific and engineering community to develop new technologies that are capable of recycling, treating and safely disposing of these materials. EPA wants to encourage innovation in hazardous waste management. In devising regulations, therefore, it is important to avoid rigid approaches that stifle the development of new technologies.

Hopefully, state and local regulators will endorse this excellent advice in the development and application of their hazardous waste management programs. However, they will require independent data on the process proposed for each of the waste types or mixtures handled by each facility. A detailed O&M manual must be submitted before plant operation to serve as an independent check of operations by the regulators entrusted in monitoring the facility. A concerted effort must be made now to move in this direction before the adverse publicity of multiple siting failures makes credible generation of the necessary data a fruitless exercise. As described above, solidification is a versatile process, capable of detoxifying hazardous wastes. The hazardous-waste manager must give the process every consideration when selecting a treatment sequence for a waste stream.

SECTION 2

POLYCHLORINATED BIPHENYLS: TREATMENT, RECOVERY AND DESTRUCTION

CHAPTER 6

SUMMARY OF POLYCHLORINATED BIPHENYL TREATMENT ALTERNATIVES

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Technical progress on important problems continues rapidly during the time that a book is prepared. Consequently, this brief chapter intends to summarize the available polychlorinated biphenyl (PCB) destruction methods as of April 1982. This update, based on telephone surveys and company responses, is not necessarily complete.

Commercial incineration of PCB is being carried out by Ensco in El Dorado, Arkansas, which is in the process of tripling its capacity, and by Rollins Environmental Services, in Deer Park, Texas. In December 1981 Chemical Waste Management carried out a test burn on its incineration ship, the Vulcanus, in the Gulf of Mexico. The analytical measurements from this test have not been published, and EPA approval has not been granted. Rockwell now offers for sale its molten-salt incinerator, which operates at about 700°C and destroys PCB. Various tests on destroying PCB in cement kilns are examining the emissions of principal organic compounds. Test runs with 1600 g PCB in the plasma torch have verified a minimum of 99.9999% destruction. No dioxins were found in the offgases from this test, and a demonstration unit is being planned.

Decontamination of PCB-contaminated transformer fluids continues as an active area of commercial interest. Acurex and SunOhio have gained EPA approval in several EPA regions for detoxicating transformer fluids and expect nationwide approval within the year. Several mobile treatment plants are available to treat at the waste site fluids

containing 100–1000 ppm of PCB. The organometal processes can convert the transformer fluid to a useful fuel (Acurex) or a reusable transformer fluid (SunOhio).

The Franklin Institute process (NaPEG), which consists of nucleophilic displacement of chlorine by a superoxide radical anion at elevated temperatures, has been tested in a pilot plant at a Philadelphia utility. Much of the current effort is being directed toward chemical treatment of PCB-contaminated soil by spraying the reagent on the soil. The results and environmental consequences are unclear at this time. Microbial degradation of PCB-contaminated soils is being pursued by several investigators.

Brunnelle, of General Electric, reported on a simple, phase transfer-catalyzed process for destroying PCB. PCB solutions can be treated with small amounts of the methyl ether of polyethylene glycol in the presence of potassium hydroxide. The substitution products are formed within one hour at 60°C, and a continuous, pilot-plant unit operating at 100°C and a residence time of 15 min has verified the laboratory data. The substitution products, not strictly PCB by the legal definition, may be biodegradable.

It appears, then, that three years after PCB regulations took effect, the technology is available, finally, to carry out the intent of the regulations. Also, this area of work demonstrates clearly that many different approaches can be taken to solving pollution problems.

CHAPTER 7

FEDERAL POLYCHLORINATED BIPHENYL REGULATIONS

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Since the mid-1960s, when polychlorinated biphenyls (PCB) were first found to pose a threat to wildlife, the chemicals have been found widely distributed in low concentrations throughout the United States. From the late 1960s until the early 1970s, the federal government approach to the PCB problem was fragmented. The U.S. Department of the Interior Bureau of Mines (BOM), responsible for water pollution, and the Department of Health, Education and Welfare (HEW), responsible for human health, undertook some PCB research, but no programs addressing the basic problems were initiated. In 1969 the Council on Environmental Quality (CEQ) was formed; and in 1970, the U.S. Environmental Protection Agency (EPA). Both began work on the PCB problem. CEQ was the catalyst in the formation of a federal interagency task force to coordinate the federal PCB effort. In May 1972 the task force issued a report concluding that PCB contamination was ubiquitous and represented an unquantified but undisputable hazard, and that the use of PCB should be restricted to essential applications that involve minimal direct human exposure [1].

Once this report was issued, programs aimed at correcting the PCB problem were begun. In 1971 Monsanto, the sole domestic commercial producer of PCB, voluntarily restricted sales of PCB to "closed-system uses," thereby limiting sales to manufacturers of transformers and

capacitors [2]. Monsanto also introduced what it felt was a less toxic PCB mixture, Aroclor 1016. The EPA recommended raising water quality standards to reduce PCB levels to less than 0.01 ppb. In February 1973 the Organization for European Community Development (OECD) issued a directive that recommended limiting the worldwide use of PCB. EPA designated PCB as toxic substances and set a national effluent standard pursuant to Section 307(a) of the Federal Water Pollution Control Act Amendments of 1972 (PL 92-500). In 1973 the Food and Drug Administration (FDA) published regulations limiting the use of PCB in food and feed facilities and establishing temporary tolerances for PCB levels in many food and feed items [3]. In February 1977 EPA banned PCB discharges into waterways by capacitor and transformer manufacturers, and finally in 1976 the Toxic Substances Control Act (TSCA) (PL 94-469) was passed by Congress, requiring regulation of PCB.

EPA REGULATION OF PCB UNDER TSCA

TSCA Requirements

TSCA is a law to regulate commerce and protect human health and the environment by requiring testing and necessary-use restrictions on certain chemical substances. TSCA designates one class of chemicals in particular for regulation. This class of chemicals is PCB.

Section 6(e) of TSCA specifically requires EPA to regulate the manufacture (including importation), processing, distribution in commerce, use, disposal, and labeling of materials containing PCB. These mandates were implemented in a phased manner, with the marking and disposal rules to be promulgated first. Accordingly, in February 1978 EPA regulated the disposal and marking of PCB (40 CFR Section 761, *Federal Register* 43:7150). This rule required the marking of many PCB items still in service, and set up a system for the proper disposal of PCB. On May 31, 1979, EPA instituted a ban on the manufacture, processing, distribution in commerce and use of PCB (*Federal Register* 44:31514).

There are four "exceptions" to the bans instituted on May 31, 1979. The first two are very broad; the remaining two apply only to specific situations. First, TSCA applies, by statute, only to those uses of PCB that are not considered "totally enclosed." EPA, in the May 31, 1979, regulation, considered the following uses "totally enclosed": (1) use (except servicing) of intact, nonleaking PCB transformers and PCB-contaminated transformers; (2) use (except servicing) of intact, non-

leaking PCB capacitors. Second, EPA set a standard of 50 ppm PCB concentration, below which most PCB are not regulated. Third, TSCA provided for EPA to grant authorizations for nontotally enclosed uses that present little or no risk to human health or the environment. Among the authorizations granted are: (1) servicing of transformers, electromagnets and mining equipment; (2) use of PCB in heat transfer systems, hydraulic systems and railroad transformers; (3) use as a mounting medium in microscopy; and (4) use in small quantities for research and development. Finally, TSCA provided for EPA to grant exemptions to certain manufacturers, processors and distributors in commerce of PCB. To be granted an exemption, two broad criteria set by Congress must be met:

1. An unreasonable risk of injury to health or the environment would not result.
2. Good faith efforts have been made to develop a chemical substance that does not present an unreasonable risk of injury to health or the environment and that may be substituted for PCB.

Activities Since Promulgation

Exemptions

More than 400 petitions for exemptions from the prohibitions of TSCA Section 6(e)(3)(A) have been filed. Approximately 40 of these seek exemptions for the manufacture of PCB at concentrations greater than 50 ppm; nearly all of these involve processes where PCB are produced as a by-product in the manufacture of other materials. The remaining exemption petitions are for processing or distribution in commerce of PCB. In the case of manufacturing exemption petitions filed for activities that were ongoing as of January 1, 1979, and processing and distribution petitions filed for activities which were ongoing as of July 1, 1979, the activities for which exemptions are sought may be continued until EPA rules on the petitions. For petitions submitted after the filing deadlines, EPA will decide on a case-by-case basis whether or not to accept them for consideration. The late petitioner must show good cause as to why the petition was submitted after the filing deadline. Of those petitions accepted, only those activities that EPA determines were underway before the dates the bans went into effect will be allowed to continue until EPA rules on the pending petitions. Therefore, persons who wish to begin a PCB manufacturing, processing or distribution in commerce activity that was not underway at the time the bans went into effect may not initiate the activity until EPA rules on the exemption request [4].

Open Border Policy

The Ban Rule also established an Open Border Policy, which permitted import and export of PCB wastes for purposes of disposal for a period of one year. On May 1, 1980, EPA announced that it was ending the Open Border Policy and closing all U.S. borders to shipments of PCB wastes. This decision was made because it had become apparent that few other nations were actively seeking to develop adequate disposal facilities of their own. EPA announced that it would reopen U.S. borders to shipments of wastes to and from any nation that entered into a bilateral agreement with the United States on standards for disposal of PCB. Such an agreement is presently being discussed with Canada. No other nation has sought an agreement.

Exports of PCB for use in other nations are permitted only if the activity was ongoing as of July 1, 1979, a petition for a distribution exemption is on file and a proper TSCA Section 12(B) export notice is submitted. If the activity was not ongoing as of July 1, 1979, an exporter must obtain an exemption from EPA before he may initiate his export.

Food and Feed Amendment

On May 9, 1980, EPA proposed to amend the Ban Rule to prohibit the use of PCB items (including PCB large high- and low-voltage capacitors, PCB transformers, PCB-contaminated transformers, PCB heat transfer systems, and PCB hydraulic systems) in facilities manufacturing, processing, or storing fertilizers or agricultural pesticides. EPA issued this proposed rule under the authority of Section 6(a)(5) of TSCA. FDA and the U.S. Department of Agriculture (USDA) published similar proposals, with each agency's proposal covering its area of legal reponsibility in order to cover the entire food, feed and agricultural chemical industry.

On May 6, 1981, EPA published a *Federal Register* notice placing the proposal in abeyance. This decision was made in part because of the October 30, 1980, decision of the U.S. Court of Appeals for the DC Circuit, which is discussed later in this chapter.

ENVIRONMENTAL DEFENSE FUND CHALLENGE

Shortly after the final PCB Ban Rule was published in the *Federal Register*, the Environmental Defense Fund (EDF) challenged the validity

of the Ban Rule in a petition for review to the U.S. Court of Appeals for the DC Circuit. EDF sought review of the Final Ban Rule on three points: (1) EDF challenged the determination by EPA that certain commercial uses of PCB are "totally enclosed," a designation that exempts those uses from regulation under TSCA; (2) EDF claimed that the EPA acted contrary to law when it limited the applicability of the regulation to materials containing PCB concentrations greater than 50 ppm; and (3) EDF challenged the decision by EPA to authorize the continued use of 11 nontotally enclosed uses of PCB.

In its October 30, 1980, decision, the Court of Appeals found no substantial evidence in the record to support EPA's classification of electrical transformers, capacitors and electromagnets as "totally enclosed" uses, or to support EPA's establishment of the cutoff under which only materials containing 50 ppm or more PCB are regulated. The Court of Appeals therefore remanded these portions of the regulations to EPA for further proceedings. However, the Court of Appeals upheld EPA's authorizations of the 11 nontotally enclosed uses of PCB.

Because invalidation of these parts of the Ban rule by the Court of Appeals would have brought into full effect absolute prohibitions against manufacture, distribution in commerce, processing and use, EPA and other parties to the litigation requested that the Court of Appeals stay its mandate until new regulations could be promulgated. In two orders, issued on February 12 and April 13, 1981, the Court of Appeals granted that request, subject to certain conditions.

Totally Enclosed Issues

The February order dealt with the issue of totally enclosed uses of PCB. The Court of Appeals stayed the effectiveness of its judgment that that portion of the regulations is invalid, subject to several conditions. First, the stay is for a period of 18 months and applies only to those who comply with the prescribed interim inspection and maintenance procedures known as the Interim Measures Program. Second, the Edison Electric Institute (EEI) is to conduct a study to provide EPA with information it will need for further rulemaking regarding uses of PCB in electrical equipment. Third, EPA must announce its new rulemaking in an Advance Notice of Proposed rulemaking (ANPR) and must promulgate a final rule within six months of receipt of the EEI study. (The ANPR was published March 10, 1981.) Finally, the parties must make a progress report to the court on October 1, 1981.

The 50-ppm Issue

The court's April order dealt with the 50-ppm issue, that part of the court's decision that invalidated the 50-ppm regulatory cutoff. The court stayed its mandate with respect to this portion of its decision for 18 months and ordered EPA to undertake two parallel activities during the period of the stay.

The first activity applies to chemical manufacturing processes that generate PCB, but release no PCB. It also includes chemical manufacturing processes that release PCB only as constituents of wastes that are incinerated or disposed of in EPA-approved landfills, or held for such disposal. On May 20, 1981, EPA published an ANPR relating to the possible exclusion of manufacture of PCB in these processes from the prohibitions of TSCA Section 6(e)(3)(A). EPA must promulgate a final rule with respect to this potential exclusion within the 18-month period of the stay or advise the Court of Appeals of its reasons for not promulgating a final rule along with plans and a schedule for any further action.

The second activity applies to manufacturing, processing, distribution in commerce and use of PCB in concentrations less than 50 ppm (other than the creation of PCB in those processes described above). EPA also published an ANPR regarding this activity on May 20, 1981. By March 13, 1982, EPA must advise the court of its plans for further action and its schedule for such action.

ENFORCEMENT

When the first PCB rule, covering marking and disposal, became effective in April 1978, EPA began an active PCB compliance monitoring program under the direction of the Pesticides and Toxic Substances Enforcement Division. The program was expanded when the PCB Ban Rule, which incorporated provisions of the marking and disposal rule, became effective in July 1979.

Since April 1978 more than 2000 PCB compliance monitoring inspections have been conducted. EPA's limited resources for inspections have been augmented by the use of contractors to perform some of those activities. Most of the cases have involved violations of marking, storage and disposal requirements. In many instances, EPA's activities required cleanup of spilled PCB material in addition to the payment of civil penalties. A number of hazardous waste cases also have involved PCB; in those instances, joint injunctions have been sought under TSCA and other EPA statutes.

TSCA is a relatively new statute, and the PCB rule was the first major regulatory program established under its authority. The PCB rule was also the first major field enforcement effort, and what has been learned from this effort has helped shape all subsequent TSCA enforcement programs.

The final PCB enforcement strategy is to minimize the release of PCB into the environment. The release of PCB can occur in two ways: (1) improper disposal of PCB items and liquids when they are taken out of service; and (2) uncontrolled discharge caused by leaks and spills from inservice, stored or transported items.

In the enforcement strategy, compliance monitoring inspections are allocated among the 11 economic sectors and industries that control the vast majority of PCB now in use. The sectors identified in the strategy are: utilities; chemicals; metals; papers and lumber; mining; food; stone, clay and gas; textiles; automobiles; railroads; and commercial buildings. Inspection allocations were based on a number of considerations, including forecasts of expected retirement or rebuilding of PCB equipment, industry structure characteristics, degree of awareness of PCB requirements by industry members, and cost of compliance.

The emphasis in the inspections is on reviewing required PCB storage and disposal records to ensure proper ultimate disposal and on examining the condition and location of PCB equipment to detect any evidence of uncontrolled discharge. The penalties assessed against facilities found in violation are related directly to the degree of hazard posed, and companies may also be required to clean (in some instances at great cost) areas contaminated with PCB.

A strategy for enforcing the Interim Measures Program is in draft form. That strategy augments the overall PCB strategy by adding checks for compliance with the new program while conducting regular PCB inspections. A more intensive monitoring effort is directed at utilities and food and feed facilities through a review of randomly selected records required by the Interim Measures Program.

DISPOSAL

Incinerators and Boilers

The key to success for EPA's program of regulatory control of PCB is the availability of adequate disposal facilities. Many of EPA's efforts have been directed toward approval of incinerators and encouraging verifica-

tion burns in high-efficiency boilers. The evaluation of data from test burns in incinerators and boilers is handled by the ten regional EPA offices. Public opposition to PCB incineration and the question of toxic by-product formation have caused regional administrators to proceed very cautiously with approval of incinerators and boilers.

In January 1981 EPA approved the first two commercial incinerators: one in Deer Park, Texas, owned by Rollins Environmental Services, and the other in El Dorado, Arkansas, owned by the Energy Systems Co. (ENSCO). EPA has a very thorough plan to monitor operations at these two facilities.

EPA anticipates the testing and approval of the incinerator ship Vulcanus. The major steps in the approval are completion and acceptance of an environmental impact statement evaluating the impact of the incinerator on the ecology of the area of the ocean where the burning will occur, and locating suitable staging and transfer facilities ashore. Should this incinerator be approved for use in the United States, a major portion of the high-concentration liquid PCB that are in storage could be incinerated in one or two trips.

EPA has provided for the disposal of low concentration (50–500 ppm) liquid PCB waste. This waste is usually mineral oil removed from electrical transformers. It can be burned in high-efficiency boilers meeting certain technical criteria. These boilers operate with very good combustion characteristics and have been shown in repeated tests to achieve very high destruction efficiencies for PCB without emitting toxic combustion by-products. Seven boilers in the United States have disposed of contaminated mineral oil.

Alternative Disposal Techniques

In promulgating the disposal regulations, EPA allowed approval to be granted for alternative methods that are equivalent to incineration. The alternative method must achieve a level of performance equivalent to incineration or destruction in a high-efficiency boiler, and a written request for approval must be submitted. Before approval is granted, the applicant must show that the method of destroying PCB will not present an unreasonable risk of injury to health or the environment. One such alternative method has been approved.

Many researchers and entepreneurs have sought solutions to the problem of PCB disposal using a wide range of techniques, including chemical destruction, catalytic decomposition and a variety of thermal destruction methods other than conventional incinceration.

To date only one company has built and tested a full scale commercial

unit using new technology. SunOhio, based in Canton, Ohio, has constructed a mobile PCB chemical destruction unit (PCBX) and demonstrated the capabilities of their system in a test conducted for EPA officials. Treatment of PCB-contaminated mineral oil reduced the PCB concentration to a nondetectable level. Due to the mobility of the PCBX system, SunOhio is seeking the approval of all ten regional administrators so they can offer their disposal services nationwide. At this time SunOhio has received approvals to dispose of mineral oil contaminated with PCB in Regions I, IV and VII.

The PCBX disposal system has some interesting features. It does not produce emissions to air or discharges to water. It is portable, allowing the PCB to be treated onsite, thereby eliminating extra handling or transportation of the wastes. Finally, because PCBX is mobile, it should minimize opposition from local communities—opposition that fixed-site facilities have often encountered. Because PCBX presently is approved only for low-concentration mineral oil, it is not the answer to all aspects of the PCB disposal problem, but it does illustrate the potential that exists in the area of emerging technology.

Landfilling of Capacitors

EPA recognized in the Ban Rule that the best method for disposal of large PCB capacitors (those containing more than 3 lb PCB) is incineration. However, no incinerators were available at the time the Ban rule was promulgated. Anticipating that an incinerator would be approved by January 1, 1980, EPA authorized landfilling of capacitors until that date. However, as no commercial incinerators were approved by January 1, 1980, EPA extended the authorization of landfilling until March 1, 1981. The extension included a provision that the authorization subsequently could be extended at the discretion of the Assistant Administrator for Pesticides and Toxic Substances if inadequate disposal facilities were available. The first incinerator capable of shredding capacitors was approved March 1981. A request by a group of electric utilities for a further extension of landfilling grace period was denied on July 28, 1981.

ADDITIONAL INFORMATION

The EPA has an Office of Industry Assistance which distributes publications and answers questions to help people understand the Toxic Substances Regulations. They may be reached by calling the toll-free number 800-424-9065 during Washington business hours, or the local number, 554-1404.

REFERENCES

1. "PCBs and the Environment," Interdepartmental Task Force on PCBs, COM 72.10419, U.S. Government Printing Office (1972).
2. "PCBs in the United States—Industrial Use and Environmental Distribution," U.S. EPA Criteria and Standards, EPA-560/6-76-005.
3. U.S. Code of Federal Regulations, Vol. 21, Sections 3.93, 122.10.
4. *Federal Register*, 45, p. 14247, March 5, 1980.

CHAPTER 8

TREATMENT AND DESTRUCTION OF POLYCHLORINATED BIPHENYLS AND POLYCHLORINATED BIPHENYL-CONTAMINATED MATERIALS

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Polychlorinated biphenyls (PCB) were among the earliest classes of compounds to be identified as hazardous and to be banned by law. As such, they have become in many people's minds the epitome of "hazardous waste." This has made them difficult to control and manage safely. Because of the uncertainty and fear generated by the present attitude toward PCB, there is a shortage of facilities available for their legal disposal or destruction. This chapter evaluates the legal, technical and regulatory status of PCB and their control. It evaluates the various technologies available for their destruction from viewpoints of efficacy and potential for solution of these problems.

PCB REGULATIONS

PCB were first introduced by the Monsanto Company in 1929. Because of their thermal, biological and chemical stability, and high dielectric constant, this group of chemicals achieved widespread use. There are 209 different chlorinated biphenyls, referred to collectively as PCB. PCB were used as dielectric fluids in capacitors and transformers, as heat transfer

fluids, and as hydraulic fluids. Between 1930 and 1975, 1.253 billion pounds of PCB fluids were sold in the United States. Of this amount, 77% (965 million lb) was used for electrical equipment, largely by the electric utility industry.

In 1976 the Toxic Substances Control Act (TSCA), PL 94-469, established a framework for regulating hazardous chemicals. PCB were specifically identified for regulation by TSCA. In the May 31, 1979, *Federal Register* [1], the U.S. Environmental Protection Agency (EPA) promulgated rules for "PCB Manufacturing, Processing, Distribution in Commerce and Use." These rules prohibited the manufacture of PCB and their use in almost all nonenclosed applications.

The regulations created a unique situation, wherein large quantities of relatively pure materials require safe disposal. In addition, very stringent rules for storage, shipping and disposal were set. For the purposes of this chapter, PCB wastes can be broken down into the following categories:

- PCB solids consist largely of shredded capacitors, drained transformers and other PCB-contaminated solid materials. These may be landfilled at present.
- PCB liquids encompass liquids contaminated with PCB at a concentration of 500 ppm or greater. The only legal method of disposal is destruction in high-efficiency incinerators or cement kilns.
- PCB-contaminated liquids are oils containing 50–500 ppm PCB. They legally may be burned in high-efficiency boilers or be landfilled.

As can be seen, the PCB regulations permit PCB and PCB materials to be landfilled or burned only in special incinerators, cement kilns or boilers. They also allow the Regional Administrator to approve other alternative technologies to be used if he finds that they do not "present an unreasonable risk of injury to health or the environment" and if "its level of performance is equivalent to Annex I incinerators or high efficiency boilers." This is somewhat difficult to interpret, as it does not define what specific criteria the alternative technologies must meet. This chapter will discuss several specific destruction methods.

DESTRUCTION TECHNOLOGIES

There are many methods available for the destruction of PCB. Land disposal, which is basically a confinement rather than a destruction procedure, is not discussed here. Treatment procedures can be split into two generic groups: combustion technology and chemical detoxification technology. The specific combustion technologies to be discussed here are

- Liquid injection incinerators,
- Rotary kiln incinerators,
- High-efficiency boilers (for 50 to 500-ppm PCB),
- Cement kilns,
- Fluidized bed incinerator,
- Molten salt incinerator,
- Pyrolysis, and
- Ocean based incineration;

In addition to combustion technologies, chemical technologies (including wet oxidation and chemical dechlorination), and exotic technologies (such as microwave plasma destruction) will also be discussed.

Before discussing the various types of technology available to destroy PCB, it is necessary to examine the pitfalls existing that proposed PCB-disposal operations have encountered and potential methods of overcoming them. These are:

1. Exposure of new people to a (perceived) risk has been the most difficult problem to overcome. Basically, the people in the vicinity of the disposal facility perceive themselves as being exposed to an added risk and object to the facility. Even if the people are convinced that the facility will destroy the PCB completely, they object to "the danger of shipping the PCB through their neighborhood." The problem boils down to the statement "waste disposal facilities are needed, and are a good idea, but not near where I live." It might be added that people five or more miles from a proposed facility have been known to object to it because they feel that it is too close to them. Even when existing industrial facilities (i.e., cement kilns, boilers, etc.) have been involved, there has been tremendous local citizen and government opposition. A direct result of this concern is a concern for decrease in the property values. After all, a perceived risk does make this property less desirable. The ideal PCB destruction technology is one that is capable of being moved to or located at the site where the PCB wastes are being stored.

2. Verification of destruction is best summarized by the statement: "We're sure you can destroy the PCB during the test when all these scientists and engineers are running the process, but how can we be sure you will destroy them during operation—we all know that breakdowns occur?" In addition, there are the problems associated with hazardous products of combustion, (HPC): those materials, such as chlorodibenzofurans and chlorodioxins, that form or are suspected of forming when PCB are burned. Combustion is largely an uncontrolled chemical process. As a result, almost any organic material can conceivably be formed. While such an extreme concern seems unwarranted, it must, nevertheless, be considered in the selection of a technology. The technology of choice

should utilize well understood and controllable destruction methods. Furthermore, the technology of choice should operate in a batch mode. This operation will make it possible to analyze chemically the outflows before release or discharge.

3. Gaseous emissions are released from some sort of stack, which is often associated in people's minds with heavy volumes of noxious smoke. This perception contributes to making people who live miles from the facility fearful of it. To overcome these concerns, the ideal PCB destruction technology should have no gaseous emissions and only small volumes of aqueous effluent. It is recognized that no technology is capable of managing all forms of PCB and still satisfy these criteria for successful implementation; however, as the following discussions will show, there are certain technologies which, for specific important applications, come very close to meeting these criteria.

COMBUSTION TECHNOLOGIES

Currently, the only legal method for disposal of liquid PCB is combustion in a high-efficiency incinerator or cement kiln. Incinerators must meet the following conditions:

1. either: 1200°C, 2-sec dwell time and 3% excess oxygen, or 1600°C, 1.5-sec dwell time and 2% excess oxygen;
2. combustion efficiency of 99.9%; and
3. PCB emissions less than 1 mg/kg PCB destroyed; 99.9999% destruction removal efficiency (DRE).

Only the last condition applies to cement kilns, as the temperature, dwell time and excess oxygen in the kiln are all greater than these minima. Cement kilns are considered to be an acceptable method of destroying PCB. In 1976 a series of tests was conducted at St. Lawrence Cement in Canada [2]. These tests showed that the destruction achieved was in excess of 99.9996%. Another set of tests, performed in Sweden [3], by Ahling, showed a destruction efficiency in excess of 99.99998%. These values were indicative only of the sensitivity of the measurement method used. No PCB were found. Based on these tests, the PCB regulations permit the use of cement kilns for PCB destruction. No such facility in the United States or Canada has been given a permit for destroying PCB to date, largely because of local opposition.

The chlorine from the PCB is converted to hydrogen chloride, which then combines with the alkali in the cement. As a result, cement kilns do not require auxiliary equipment for HCl removal. The sodium, potassium

and calcium chlorides formed are emitted with the particulate in the gas stream. They are captured by the air pollution control equipment or emitted to the environment through the stack.

PCB regulations permit the use of high-efficiency boilers for the destruction of PCB-contaminated mineral oil—less than 500 ppm PCB. The restrictions placed on the boiler are:

1. The boiler is rated at a minimum of 50 million Btu/hr.
2. The carbon monoxide in the flue gas is 50 ppm or less for a natural gas- or oil-fired boiler, or 100 ppm or less for a coal-fired boiler.
3. The excess oxygen in the stack is greater than 3%.
4. The waste is less than 10% by volume of the total fuel feed.
5. The waste may only be fed when the boiler is at its full operating temperature—not during startup or shutdown.
6. The boiler must be monitored continuously for carbon monoxide and excess oxygen. If less than 30,000 gallons of waste oil are burned per year, this monitoring may be replaced by CO and O_2 measurements every 60 minutes.
7. The quantities burned and feed ratio of the fuel and waste must be monitored every 15 minutes.
8. If the CO and O_2 values fall below the specified amount, waste feed must cease.
9. Approval for such burns must be given by the EPA Regional Administrator.

The regulations require additional reporting and monitoring conditions. Although the number of boilers burning PCB-contaminated oils in the United States is unknown, it is very low. The vast majority of the utility industry is simply storing its contaminated oil.

PCB solids, such as drained transformers, PCB-impregnated capacitors or PCB-contaminated soil, may be landfilled. Before landfilling, free liquid must be drained from equipment (such as transformers) and the equipment must be rinsed with a volume of PCB-free mineral oil equal to that drained from the equipment. Landfilling, of PCB solids is illegal and likely to remain so.

To date, despite these permissible options, only two facilities for the disposal of PCB liquids and one for PCB solids have been approved. Local opposition and siting problems are a large part of the reason for this, although the concerns described earlier factor into the situation.

The problem of greatest concern is products of incomplete combustion (PIC), which are formed in trace quantities. When PCB are burned, chlorinated dibenzofurans (CDBF) can be formed. These results have been corroborated in field tests, although these tests have only shown the CDBF to be in the ash. CDBF have been identified in the stack gases in very low concentrations. Tests on incinerators have identified dioxins in the stack gases. This uncertainty regarding highly suspect classes of chemicals has made the regulatory authorities extremely cautious and has delayed the issuance of permits for the incineration of PCB. The nine combustion technologies are summarized in Table I.

Table 1. Types of Combustion Equipment for PCB Destruction

Type of Equipment	Applicable Waste Type	Comments
Liquid Injection Incinerator	Liquid PCB, PCB-contaminated oils, some aqueous PCB materials	The most developed incineration systems can achieve in excess of 99.9999% DRE
Rotary Kiln Incinerator	All physical forms	Very highly developed; can achieve in excess of 99.9999% DRE
High-Efficiency Boilers	PCB-contaminated waste oils (500 ppm)	Tests show better than 99.99% DRE
Cement Kilns	Liquid PCB, PCB-contaminated oils	Tests have shown in excess of 99.999998% DRE
Fluidized-Bed Incinerator	Liquid PCB, high-viscosity systems, shredded PCB-saturated paper	Only pilot-scale tests have been done; may not be capable of reaching high temperatures; scrubbers for HCl may not be required at times
Molten-Salt Incinerator	Liquid PCB, shredded PCB-saturated paper	Experimental, not fully tested yet
Pyrolysis		Too low temperature, not generally applicable to PCB
Ocean-Based Incineration	PCB liquids, PCB-contaminated oil	Only developed and tested for liquid injection; may eliminate siting problem but siting of land-support facilities may be a problem; potentially expensive

CHEMICAL DESTRUCTION METHODS

Liquid-Phase Chemical Destruction Techniques

It appears that some form of liquid-phase chemical destruction technique will come closest to overcoming the four objections to implementation of a technology. This is shown by comparing technology classes to the four problems in implementation of PCB destruction technology discussed earlier:

1. Liquid-phase systems are smaller than gas-phase systems and, thus, can be taken to the source of the PCB.

2. Liquid-phase chemical reactions are controlled much more easily than are gas-phase reactions such as combustion. The condition for the destruction can thus be more readily duplicated and hence predicted with greater reliability.
3. Liquid-phase reactions can be run in a batch mode, so that discharges can be analyzed before release.
4. Because of their smaller volume, liquid-phase systems tend to have only small quantities of air emission.

To chemically destroy PCB, it is not necessary to break completely the biphenyl structure. The degree of hazard, and chemical and biological stability of PCB increase with the number of chlorine atoms on the biphenyl molecule. As a result, dechlorination appears to be a possible alternative to total destruction. This is highly desirable because cleavage of the aromatic biphenyl structure requires a very high energy of activation, and therefore, requires a much higher temperature than does dechlorination. On the basis of this analysis, we can, thus, draw conclusions:

1. If we want to break the biphenyl structure, only some form of combustion can provide the necessary conditions.
2. If dechlorination of the molecule is adequate, low-temperature wet chemical processes can be used.

The liquid-phase processes that are (at least potential) candidates for the destruction of PCB or PCB-contaminated materials are:

1. sodium/naphthalene/tetrahydrofuran dechlorination or variations thereof;
2. sodium metal dechlorination;
3. sodium/polyethylene glycol (NaPEG) dechlorination;
4. oxidative processes such as wet oxidation or ultraviolet (UV)/ozonation; and
5. catalytic dehydrochlorination

In addition, there are concentration techniques available (both adsorption and absorption) for reducing the PCB contamination of oils.

Sodium Treatments

The first three processes are very similar in nature. They are all based on variations of the use of metallic sodium to dechlorinate organics, a procedure that is well known. In fact, this method has been used to analyze organics for chlorine. The use of sodium/naphthalene/tetrahydrofuran system was brought to the attention of EPA by Goodyear Tire and Rubber Corporation of Akron, Ohio. They have used it for dechlorination of ~100- to 150-ppm PCB-contaminated hydraulic and heat transfer oils. It is applicable to the similar dechlorination of any PCB-contaminated oil.

Variations of this process have been adapted to different types of PCB-containing material by Acurex Waste Technologies Corporation, General Electric, SunOhio and others.

Goodyear's process uses the sodium naphthalene synthesis of Scott et al. [4]. The process involves preparation of a deep green reactive complex of naphthalene and sodium in tetrahydrofuran by melting sodium (melting point, 98° C) in a nitrogen-blanketed hydrocarbon oil, chilling rapidly to produce "sodium sand" (fine spherical particles) and adding a tetrahydrofuran (THF) solution of naphthalene to the cooled slurry. The reagent takes about an hour to form and is added to the oil that is to be treated.

Treatment of an oil containing 300 ppm of PCB at ambient temperature required approximately one hour, after which water was added to destroy the excess sodium. The oil is then vacuum-stripped to recover the THF and naphthalene, and further distilled, leaving the sodium chloride, sodium hydroxide and the nonhalogenated polyphenyls as still bottoms, which are presumably safe for incineration. The purified transformer or heat transfer oil contained less than 10 ppm PCB. SunOhio has successfully treated transformer oils containing up to 500 ppm PCB. Acurex has treated oils containing approximately 1000 ppm during an EPA demonstration and up to 10,000 ppm (1%) PCB during tests. SunOhio and Acurex have succeeded in bringing the final PCB concentration in the oil to below detectable limits, about 1 ppm.

These are not the only such processes in existence. EPA has been funding a project at the Franklin Institute [5] that is exploring the use of a "reactive sodium-glycolate-oxygen solution" to destroy PCB. In the Franklin Institute process, the reagent is prepared by dissolving sodium into polyethylene glycol-400. The reagent is then added to the contaminated oil, and air or oxygen is bubbled through the system. The reaction is run at 130° C. Destructions similar to that using the Goodyear process have been reported. The Franklin Institute claims that water does not inhibit the dechlorination reaction; however, this result was not confirmed by Napier [6] of Union Carbide at Oak Ridge National Laboratories. The Franklin Institute is now investigating the applicability of this process to PCB-contaminated soils.

At the University of Waterloo (Ontario), Smith and Bubbar [7] have applied the sodium naphthalide reagent to destruction of undiluted PCB containing up to 55% Cl. They treated a PCB (Aroclor® 1254) containing 54.58% total chlorine, achieved 99.8%, which left approximately 2000 ppm PCB after six hours at room temperature. A higher excess of sodium might have brought this down below the level required in the United States; however, this has not been verified experimentally as yet.

Other sodium treatments have existed for a number of years. The sodium dispersion methods developed by U.S. Industrial Chemicals Company [8] uses the "Dispersator" (a modified Waring blender), Manton-Gaulin homogenizer or other high-shear mixer. Dispersion is assisted and stabilized by the presence of a dispersion aid such as calcium stearate; dispersion is carried out under a nitrogen blanket. The sodium particles range from submicron to 200 μ in diameter [9]. Dispersions of 50% sodium by weight are easily produced by this technique and, because of the high surface-to-volume ratio, reactivity is extremely high. In dehalogenation reactions, only about 10% excess sodium is required; additional savings may be realized by eliminating the naphthalene and ether required by the other processes, although a small amount of naphthalene may be employed to "activate" the sodium surface. This approach has not, however, been successful in achieving the low final PCB concentration required by EPA.

Other wet processes that have been or may be used for PCB destruction are wet air oxidation and combined UV light/ozonation [10].

Wet Oxidation

Briefly, wet oxidation is accomplished by adding air or oxygen to an aqueous mixture of organics under pressure and elevated temperature. Pressure serves the dual purpose of keeping the aqueous phase in liquid form and increasing the partial pressure of the oxygen so as to increase the amount of oxygen dissolved in the liquid. Because the temperature involved is considerably lower than for incineration, and also because much less water is vaporized, wet oxidation may require less energy than incineration.

The temperature ranges encountered during wet oxidation are very wide and range from a low of about 300° F for simple sludge conditioning systems to a high of 600° F. Since the pressure of the reactor must be greater than the vapor pressure of the waste at the operating temperature equipment, pumping and pressure control costs increase rapidly when temperatures exceed approximately 450–500° F. The residence time for these systems ranges from about five minutes to as much as one hour. Generally, as the temperature is increased, the residence time decreases.

While no work has been identified on PCB specifically, Baillod et al. [11] decomposed pentachlorophenol in such a system. The results of their work are not encouraging. First, the temperature and pressures were high, about 600° F. Second, they identified a number of products of incomplete destruction in significant quantities. As a result, at present, wet oxidation could, at best, be considered a pretreatment step.

UV Light/Ozonation

The combination of UV light and ozone has shown some success in destroying PCB in aqueous systems. The concept was proposed in 1977 to EPA by Westgate Research; however, because of the high suspended solids likely to be encountered in actual systems, such a process is not likely to be successful.

Adsorption and Extraction

The final technology to be discussed is adsorption and extraction processes. It is possible to extract the PCB from contaminated oils by the use of a suitable solvent. Napier [6] found furfural to have potential application. Neoprene has also been used in an attempt to adsorb PCB. Napier found this to be ineffective. These concentration techniques must be used in conjunction with other methods for destroying PCB.

Chemical treatment techniques are summarized in Table II.

Table II. Types of Liquid-Phase Systems for PCB Destruction

Type of Chemistry	Applicable Waste Type	Comments
Sodium Naphthalide	Liquid PCB, PCB-contaminated oil	This is well established chemistry; the process has been optimized commercially for PCB contaminated oil; costs are very high when pure PCB are treated; can be mobile-mounted; no emissions; low effluent volume; potential for fire is moderate; cannot tolerate free water
NaPEG	Liquid PCB, PCB-contaminated oil, possibility for PCB-contaminated soil, possibility for PCB solids	In laboratory state; development under EPA grant; potentially useful in the presence of water; requires oxygen and process can release hydrogen; plant safety factors need investigating
Sodium Metal	PCB-contaminated oil	Untested as yet but may be promising from theoretical considerations
Oxidative Processes	PCB-contaminated soils, PCB in an aqueous stream	Degree of destruction is a function of temperature and pressure; for PCB destruction, estimated

Table II, continued

Type of Chemistry	Applicable Waste Type	Comments
		required temperature and pressure are in excess of 600°F and 400 psi for wet oxidation, but have not been tested; use of water in supercritical state may have potential; UV-ozonation has had limited laboratory-scale success
Catalytic Dehydrochlorination	Was not successful	Evaluated by EPA project, found not to produce sufficient level of degradation
Adsorption on Neoprene Rubber	PCB-contaminated oils	This process is being marketed; tested at Oak Ridge National Laboratories; wash found not to be effective for adsorbing the PCB from the oil
Adsorption or Extraction	PCB-contaminated materials	New area; tested at Oak Ridge National Labs; about 20 solvents tested; furfural found to have potential

CONCLUSION

There are many technologies that appear capable of destroying PCB. The problems that are usually encountered, however, are rarely technical. In almost every case considered, the problem has been public acceptance of the disposal facility, with objections falling into three categories: (1) exposure of new people to a (perceived) risk, (2) inability to verify destruction during normal operation, and (3) fear of dispersion of pollutants.

Liquid-phase destruction systems appear to embody those attributes that best satisfy the above criteria. These methods appear to stand the best chance of being accepted by the public and of solving the disposal problems associated with PCB.

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CHAPTER 9

INCINERATION OF CHEMICAL WASTES CONTAINING POLYCHLORINATED BIPHENYLS: ASSESSMENT OF TESTS CONDUCTED AT ROLLINS ENVIRONMENTAL SERVICES, DEER PARK, TEXAS, AND ENERGY SYSTEMS COMPANY, EL DORADO, ARKANSAS

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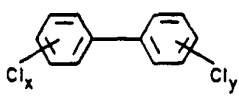
The Toxic Substances Control Act (TSCA) of 1976 prohibits the manufacture of polychlorinated biphenyls (PCB) and greatly restricts the uses of these compounds. In 1979 the U.S. Environmental Protection Agency (EPA) published guidelines [1] governing continuing use of certain PCB and disposal of PCB-containing materials. The guidelines for disposal are:

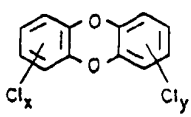
- Liquids containing <50 μg PCB g are not regulated.
- Liquids and solids containing 50–500 μg PCB/g may be deposited in an EPA-approved landfill, incinerated in a high-efficiency boiler (producing >50 million Btu steam/hr) or in an EPA-approved incinerator.
- Capacitors and liquids containing 500 μg PCB/g or higher levels of PCB must be incinerated.

The physical, chemical and toxicological properties of PCB form the basis for these regulations.

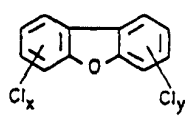
The characteristic inertness of PCB to thermal degradation (which makes them ideally suited for use as dielectrics and heat transfer fluids) and the resistance of these compounds to degradation in the environment have resulted in a distinct increase in the concentrations of PCB in the environment and in man [2]. This persistence of PCB in the environment, coupled with toxicological effects recently attributed to these compounds, have provided EPA the impetus for PCB regulation. The molecular structures of PCB (Figure 1) are quite similar to those of the chlorinated



Polychlorinated Biphenyls



Chlorinated Dibenzo-p-dioxins



Chlorinated Dibenzofurans

Figure 1. Molecular structures of PCB, chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans.

dibenzo-*p*-dioxins (CDD) and chlorinated dibenzofurans (CDF), some of which are known to be extraordinarily toxic. Indeed, recent reports have appeared that indicate that the PCB can, on heating, be converted into CDD and CDF [3]. It is not surprising, therefore, that the toxicologic properties of some PCB are similar to those of some CDD and CDF [4,5].

The resistance of PCB to thermal degradation makes efficient incineration of these compounds quite difficult. Moreover, the possibility of interconversions of the PCB to CDD and CDF, which can occur during incineration [6], makes it mandatory to ensure that incineration of these compounds is accomplished under optimum conditions. In recognition of this fact, EPA has specified that incinerators used for disposing of PCB must be operated at very high temperatures. Even under such conditions, however, it has not been established that emissions of toxic compounds, such as CDD and CDF, are essentially precluded. Recently, EPA conducted test burns of PCB at two chemical waste destruction facilities in the United States in an effort to assess the efficiency of incineration as a destruction technique for PCB. This chapter describes the two incinerators used in these tests and the relevant operating parameters. In addition, the sampling and analytical procedures developed and implemented to determine levels of toxic chlorocarbons (primarily CDD/CDF) emanating from the stacks of the two incinerators during these tests are discussed. Finally, the levels of CDD/CDF that were determined to be present in the stack effluents are reported, and the results of the risk assessment for the incinerators that was accomplished by EPA using the latter data are summarized.

DESCRIPTION OF THE INCINERATOR FACILITIES AND TESTS CONDUCTED

The incinerator facilities employed for the PCB destruction tests described here are located at El Dorado, Arkansas, and Deer Park, Texas, and are operated by Energy Systems Company (ENSCO) and Rollins Environmental Services, respectively. The two incinerators, which are somewhat similar in terms of operating capabilities, are depicted schematically in Figures 2 and 3. A detailed description of these incinerators has been provided in the plan for testing developed by the EPA's sampling contractor, TRW [7], and will be mentioned only briefly here, to provide a basis for discussion of the various types of samples that were collected during the monitoring tests.

The incineration system utilized by Rollins consists of a rotary kiln and a liquid injection burner, both feeding a common afterburner. Tempera-

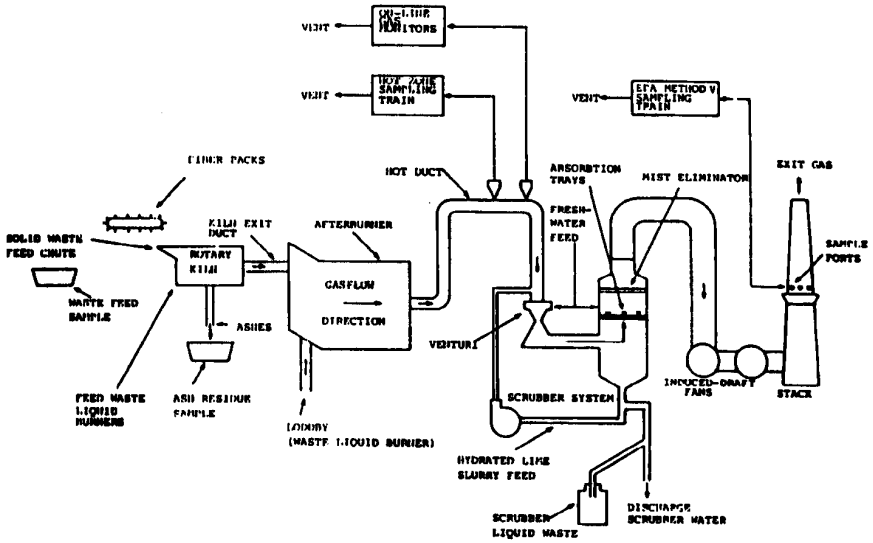


Figure 2. Schematic of Rollins Environmental Services incinerator.

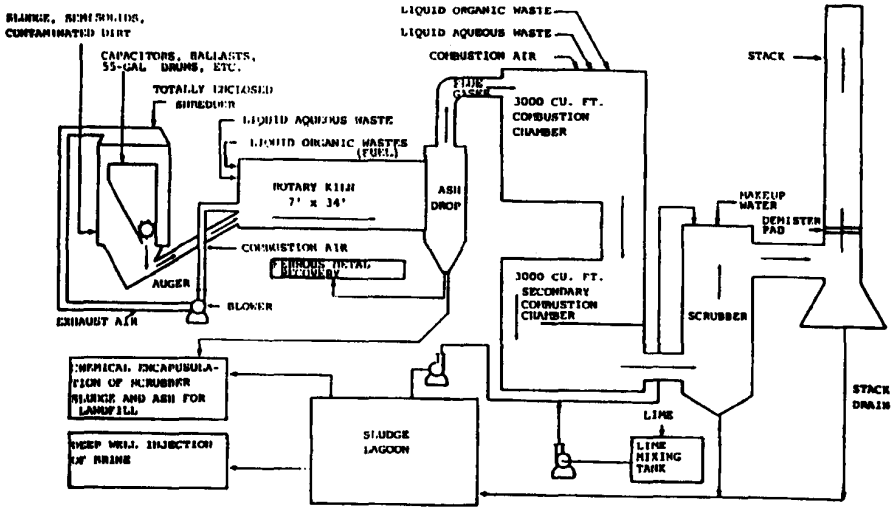


Figure 3. Schematic of the ENSCO incineration system.

tures attainable in these three burners are normally 1300–1500°C. The overall retention time of the incineration system is 2–3 seconds. Solid wastes can be fed into the rotary kiln by conveyor (although no solids were burned during the tests described here), while liquids and sludges are pumped into the kiln or into the liquid injection burner. Natural gas is used as an auxiliary fuel for initial heatup and to provide supplemental heat for incineration of low-heat-capacity wastes. No. 2 fuel oil is also used to provide heat for burning materials such as PCB, and is mixed with the PCB before the waste is fed into the incinerator. Gaseous emissions from the combustion of solid and liquid wastes are controlled by a venturi scrubber. Lime is injected to neutralize the scrubber water, which is then admitted to settling ponds, where the water is analyzed and subjected to further treatment, if necessary, before discharge into the Houston ship channel. Exhaust gases are also routed through absorption traps and a mist eliminator before entering the 30-m exhaust stack.

The incineration system used by ENSCO is also capable of combusting both solid and liquid wastes. This incinerator consists of a rotary kiln, in which combustion temperatures of 1200–1500°F are attained, and in which the retention time for solid material is approximately 1 hr and the gas retention time is approximately 4 sec. Liquid wastes, water and natural gas can also be injected into the front end of the kiln. Ash is removed from the end of the kiln by a drag chain and placed in steel drums for storage. Gases evolved from the rotary kiln pass into an afterburner that consists of two separate combustion chambers. Residence time in the primary chamber is approximately 2.2 sec, and temperatures of 2250–2340°F are typically maintained there. Most of the organic waste materials are destroyed in this region. Molten slag resulting from the combustion settles on the chamber floor and is removed through a slag trap. The secondary combustion chamber is baffled to facilitate gas mixing, and the residence time in this chamber is approximately 2 sec, while the temperature is typically 1400°F. The total residence time for gases in both chambers is about 4.5 sec. The scrubber at the ENSCO facility is also a venturi jet type. Gases evolved from the combustion chamber are quenched with lime and caustic solution as they enter the bottom of the scrubber. This treatment removes particulates and neutralizes acidic gases such as HCl. Spent scrubber liquor is transferred to a holding tank which then overflows to a sludge lagoon. Spent scrubber solution is available for recycling. After neutralization, the combustion gases pass through the venturi section of the scrubber, in which recycled scrubber water is sprayed to facilitate particulate removal. Ultimately, sludge and liquids from the lagoon are discarded by deep-well injection.

Sampling and monitoring were accomplished by the sampling contractor during three different modes of operation at each of the incinerators tested. The materials combusted and the conditions for each of these tests are as follows.

Test 1

For test 1, each incinerator was operated under the conditions at which incineration is normally conducted. Temperatures in this case were not necessarily maintained at 1200°C as required for PCB incineration. At the Rollins plant, the materials combusted were liquid chlorinated hydrocarbon wastes, such as vinyl chloride still bottoms. At the ENSCO plant, shredded capacitors (solids, but not containing PCB) were incinerated, along with chlorinated hydrocarbon wastes, such as pesticide process wastes, as well as paint and ink manufacturing wastes.

Test 2

For test 2, the materials combusted at the Rollins incinerator consisted of the same types of materials as described for test 1, along with liquid PCB wastes. Similarly, at ENSCO, the test 2 incinerator feed included the normally processed wastes (as in test 1) along with liquid PCB and shredded PCB-containing capacitors. Combustion temperatures for test 2 were maintained near 1200°C at both plants, as required by EPA regulations for incineration of PCB.

Test 3

For test 3, the materials combusted at Rollins consisted of a mixture of liquid PCB wastes and clean fuel oil. At the ENSCO plant, the materials incinerated during test 3 included liquid PCB wastes and PCB-containing capacitors, mixed with diesel fuel. Again, temperatures were maintained at the levels required for PCB incineration.

SAMPLING PROCEDURES AND TYPES OF SAMPLES COLLECTED

The sampling procedures and apparatus utilized in the monitoring tests at the Rollins and ENSCO incinerators have been described in detail in documentation prepared by TRW [7], and only those aspects which relate

to the samples ultimately analyzed by Wright State University will be summarized briefly here.

Stack Effluent Samples

Stack effluents were collected by using a modified EPA Method 5 sampling train, shown schematically in Figure 4, which consisted of a glass probe (capable of being heated to 250°F), followed by a series of three glass impingers (the first containing 100 ml of distilled water, the second containing 200 ml of distilled water, and the third, empty), a sorbent trap containing XAD-2® resin, a sorbent trap containing Florisil®, and a fourth impinger containing silica gel. A schematic representation of the traps is shown in Figure 5. The train was backed by appropriate gauges, valves, meters and a pump, for controlling and monitoring flow through the train. No filter was inserted between the probe and impingers, so any particulates collected entered the impingers and

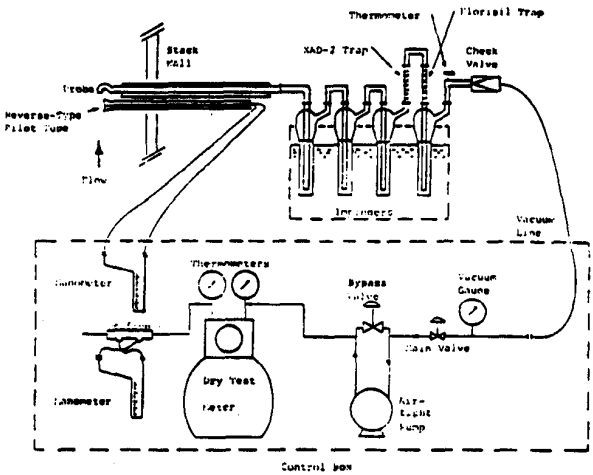


Figure 4. Modified method V train used to sample combustion effluents from the ENSCO and Rollins incinerators.

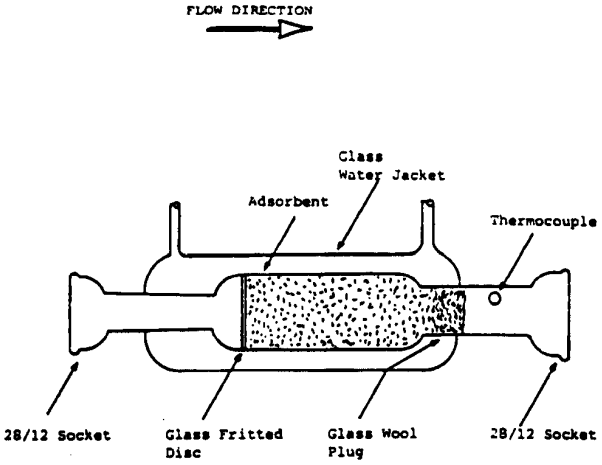


Figure 5. Schematic of sorbent trap employed in the modified method V train.

were immersed in the liquids. The impingers were cooled by immersing them in an ice bath to condense moisture from the stack effluent stream. The sorbent traps were also cooled by circulating chilled water through the exterior jackets. The sorbent traps incorporated a glass fritted disc on one end, which retained and supported the sorbent bed, and the sorbent was held in place by a glass wool plug at the other end of the trap. The traps, as well as the probe and the impingers, were interconnected using standard glass ball and socket joints, which were not greased for these tests. All components of the sample train were rigorously cleaned, using standard procedures, before use.

On termination of a stack sampling event, the probe was removed from the stack and the train was disassembled. The nozzle and glass probe were rinsed with approximately 100 ml of acetone and 100 ml of hexane, and the interior surfaces were scrubbed with a nylon brush. The rinses and any materials removed from the probe were transferred to a prerinsed amber glass bottle and the bottle was sealed with a Teflon®*-lined cap.

*Registered trademark of E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware.

The contents of the first three impingers were pooled by pouring the liquids into a single amber glass bottle. The interior chamber of each impinger was rinsed successively with 30 ml acetone and 30 ml hexane and these rinse solutions were placed in the same bottle containing the collected impinger liquids. Rinsings of connector tubing were also placed in this container, which was sealed with a Teflon-lined lid. The XAD-2 and Florisil sorbent tubes were removed and sealed by placing mating ground glass caps on the end joints of each tube. Appropriate solvent and water blank samples were also collected during the tests and placed in sealed amber glass bottles. Several method blank samples were also obtained by charging and assembling a complete train, then dissassembling the train components (unused) and collecting the appropriate samples.

From the foregoing, it is seen that five types of samples requiring analyses for CDD, CDF and PCB result from the stack sampling. These types include the probe wash, impinger catch and rinses (composite), XAD-2 resin traps, Florisil traps, and solvent and method blanks.

Solids and Liquid Samples

Concurrent with the stack sampling, samples of appropriate solids and liquids relevant to the incineration process (feed materials, combustion products, emission control equipment samples) were also collected by simple grab sampling. Such samples were collected at appropriate intervals during the incineration tests, and were placed in prerinsed amber glass bottles and sealed with Teflon-lined caps. The time and resources allotted to Wright State University for this project by EPA permitted analyses of very few of the latter samples, and none of the data relevant to these are presented here.

ANALYTICAL METHODOLOGY

Sample Handling and Preparation

Samples collected as described above were shipped from the sampling sites to the Brehm Laboratory, Wright State University. Certain liquid samples from the sampling trains (probe rinses and impinger samples) contained two distinct layers: in one case, suspended solid material was visible. After allowing such samples to stand for a period sufficient to effect complete separation of the layers, each layer of these samples was removed to a separate amber glass sample container fitted with a Teflon-

lined lid, so that each phase could be analyzed separately. The quantities of the liquid phases varied considerably from sample to sample, and in a few instances, only one layer was present. It is not known whether these variations were due entirely to leakage of the sample containers (which did occur in many samples) or to variations in the sampling train operation and rinsing procedures applied in the field. The separated liquid layers were subsequently processed as described below and analyzed.

The XAD-2 resin and the Florisil traps were sealed with glass caps by field sampling personnel, and the traps were shipped intact to the Brehm Laboratory. Before analysis of the trap contents, the XAD-2 resin or Florisil was removed from each trap and transferred to a clean amber glass vessel fitted with a Teflon-lined cap. Each individual sample was thoroughly mixed before removing an aliquot for analysis in an effort to ensure homogeneity and representative sampling. In all cases, both the XAD-2 resin and Florisil appeared to contain substantial quantities of water (although the quantity varied from sample to sample) and the solid sorbents were agglomerated and difficult to remove from the traps. In fact, some quantities of the sorbents adhered tenaciously to the inner surfaces of the traps and could not be removed. The quantities remaining could not be determined and related to the original weight of resin, because the weights of the individual traps prior to packing and the weight of the water absorbed by the solid sorbent in each trap, could not be determined reliably. Consequently, there is uncertainty in the reported analytical results arising from the fact that these data do not take into account the residues of the sorbents left in the traps. However, the quantities of these residues were generally small (probably less than 2 g). No attempt was made to dry the XAD-2 or Florisil samples before analysis, since it was thought that this also might lead to loss of volatile chemical compounds trapped on these sorbents. The total weights of the sorbents taken for analysis also were determined, and by relating these aliquots to the total quantity of sorbent removed, the total burden within the trap of the compounds analyzed could be determined.

Another factor that bears on the accuracy of the reported data for the XAD-2 resin and Florisil traps should also be mentioned. It was observed that the glass frits of the traps received by the Brehm Laboratory had been perforated, and in some cases exhibited nonuniform holes of varying sizes. Apparently, according to information received from the sampling contractor, the frits were perforated during the actual sampling tests because the frits plugged and the desired flowrate through the sampling train could not otherwise have been achieved. These observations raise questions about the uniformity of exposure of the solid sorbents to the

gas stream during the sampling process. The colorations observed in various parts of the traps also raise similar questions. Several of the traps from the tests at the ENSCO plant exhibited a pronounced red-brown coloration on the frit and on the glass wool plugs at the other end of the solid sorbent bed, but the sorbent itself appeared to have retained its characteristic stark white color. This was observed for both the XAD-2 resin and the Florisil traps. Similarly, many of the Rollins traps exhibited a bright yellow color on the frits and the glass wool plugs at the other end of the sorbent bed, but the sorbents themselves appeared to be stark white with no indication of the yellow color. In the case of traps originating from test 3, at the ENSCO site, the frit was covered with an oily residue (gray in color) but again the resin appeared to be "clean."

As noted above, small quantities of the solid sorbents could not be removed from the traps. Also, the colored contaminants that appeared on the glass frits of the traps as well as other solid deposits on the trap walls remained in the traps after the bulk of the sorbents had been removed. Since it is important to know whether or not these residues may include CDD, CDF or PCB, attempts were made to extract these residues from one trap by immersing the entire trap (after the sorbent had been removed) in a very large soxhlet apparatus and employing the extraction procedures described below. The extract was subsequently analyzed to determine content of the compounds of interest and was found to contain insignificant concentrations of CDD/CDF.

A few of the solid samples (feed materials, etc.) were analyzed as received. Aliquots of these were removed from the sample vessels in which the samples were received and weighed. Again, attempts were made to ensure that a reasonably representative sample was selected, but with the coarse solid feed materials (for example, shredded capacitors) and the viscous scrubber samples there is no certainty that this was achieved.

Analytical Methods Development and Testing

At the outset of this program, analytical methods to accomplish quantitative measurements of the CDD, CDF and PCB in samples of the type collected in this assessment had not been demonstrated. In fact, a complete survey of combustion effluents for all classes of CDD and CDF had not been reported by any laboratory in the United States. Related studies [8] reported quantitative data on CDD, including some information on isomeric composition of the tetrachlorinated dibenzo-*p*-dioxins (TCDD), for effluents from a municipal refuse incinerator. Other workers had also reported the results of comprehensive studies of CDD in various combustion products [9,10]. The samples collected in the Rollins/

ENSCO tests, however, encompass a much broader array of sample types than have previously been examined in such surveys. Accordingly, it was necessary to develop and test the efficacy of analytical procedures that could be applied for the required analyses.

The approach adopted by this laboratory for developing the needed analytical procedures entailed initial application of methodology similar to that which we have applied previously for combustion products and other hazardous waste samples containing CDD. To gauge the efficacy of these procedures, portions of samples were spiked with known quantities of $^{37}Cl_4$-2,3,7,8-TCDD, and other stable isotopically labeled CDD, and the samples were then analyzed to determine the recovery of these CDD. If recoveries were not acceptable (usually a minimum recovery of 50% of the added labeled internal standard was used as a criterion of acceptability), the extraction and/or cleanup procedures were modified, and another spiked sample aliquot was analyzed using the modified methods. This procedure was repeated until recovery of the added CDD was acceptable. It was not possible to accomplish the same type of tests for the CDF, because no labeled CDF was available or could be obtained for use as an internal standard in the studies reported here. A limited number of experiments were conducted with CDF using the method of standard additions, in which a given sample was analyzed before and after addition of a known quantity of an unlabeled CDF standard. The methods ultimately developed and validated for the determinations reported here are described in the following sections.

The extent to which information on the CDD and CDF isomers present in the samples could be obtained was limited by the availability of pure standards of the isomers which could be used for comparisons of gas chromatographic retention times and mass spectral response. Of the total 75 CDD and 135 CDF isomers which are possible, only 33 CDD and 10 CDF were available in our laboratory at the time of this study. A listing of these is given in Table I. In addition, it is seen that four other isotopically labelled CDD are on hand.

Extraction of Samples and Preliminary Separation of CDD, CDF and PCB from Other Matrix Constituents

The procedures developed and applied for extraction of the samples and preliminary separation of the compounds of interest are as follows.

Table I. CDD and CDF Isomer Standards Available at the Brohm Laboratory at the Time of the ENSCO and Rollins Studies

1-Chlorodibenzo-*p*-dioxin	$^{37}Cl_4$-1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin
2-Chlorodibenzo-*p*-dioxin	Octachlorodibenzo-*p*-dioxin
2,7-Dichlorodibenzo-*p*-dioxin	$^{37}Cl_8$-Octachlorodibenzo-*p*-dioxin
2,3-Dichlorodibenzo-*p*-dioxin	2,4-Dichlorodibenzofuran
1,2,4-Trichlorodibenzo-*p*-dioxin	3,6-Dichlorodibenzofuran
Tetrachlorodibenzo-*p*-dioxins (all 22 isomers)	2,8-Dichlorodibenzofuran
$^{37}Cl_4$-Tetrachlorodibenzo-*p*-dioxin	1,2,4-Trichlorodibenzofuran
^{13}C-2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	1,2,4,8-Tetrachlorodibenzofuran
^{14}C-2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	2,3,7,8-Tetrachlorodibenzofuran
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin	1,2,4,7,8-Pentachlorodibenzofuran
1,2,4,6,7,9-Hexachlorodibenzo-*p*-dioxin	1,2,4,6,7,9-Hexachlorodibenzofuran
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin	1,2,3,4,6,8,9-Heptachlorodibenzofuran
1,2,3,4,6,7-Hexachlorodibenzo-*p*-dioxin	Octachlorodibenzofuran
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin	

Extraction

Liquid Samples. Measure the total volume of the liquid sample. Transfer approximately half of the total sample (or up to 40 ml) to a precleaned 125-ml amber glass bottle. Add appropriate quantities of the internal standards [$^{37}Cl_4$-2,3,7,8-TCDD and $^{37}Cl_4$-1,2,3,4,6,7,8-heptachlorodibenzodioxin (HpCDD)]. Add 40 ml of petroleum ether, seal the vessel tightly with a Teflon-lined cap, and agitate the vessel vigorously on a laboratory shaker for a period of one hour. Proceed with cleanup and liquid chromatographic (LC) separation.

Solid Samples. Accurately weigh an aliquot of the XAD-2 or Florisil sorbent (or other solid sample) corresponding to approximately half of the total sample (typically 5–13 g), place this in a precleaned glass thimble, and add appropriate quantities of the internal standards ($^{37}Cl_4$-2,3,7,8-TCDD and $^{37}Cl_4$-1,2,3,4,6,7,8-HpCDD), directly to the sample in the thimble. Insert the thimble into a precleaned soxhlet apparatus, charge the soxhlet reservoir with 100 ml of benzene, and apply heat to the reservoir to extract the sample. Continue extraction for a period of 16 hours. Remove the extract and concentrate to a volume of about 5 ml using a Snyder column. Transfer the concentrate to a precleaned 125-ml

glass bottle and add 40 ml of petroleum ether. Proceed with cleanup and LC separation.

Cleanup and LC Separation

Add 50 ml of bidistilled water to the vessel containing the sample extract, reseal the vessel and agitate for ten minutes. Allow the vessel to stand for a period sufficient for the aqueous and organic layers to separate completely, and remove and discard the aqueous layer.

Using the same procedure as applied in the preceding paragraph, wash the extract successively with 50-ml portions of 20% KOH, bidistilled water, concentrated H_2SO_4 (except in this case agitate mixture for 15 min), and bidistilled water, in each case discarding the washing agent. The acid washing procedure is repeated until the acid layer is visually colorless.

Add 5 g of anhydrous sodium sulfate to the washed extract and allow it to stand, to remove residual water. Transfer the extract to a centrifuge tube and concentrate to near-dryness by placing the tube in a water bath at 55°C, and passing a gentle stream of filtered, prepurified N_2 over the solution.

Prepare a glass macrocolumn, 20 mm o.d. x 230 mm in length, tapered to 6 mm o.d. on one end. Pack the column with a plug of silanized glass wool, followed successively by 1.0 g silica, 2.0 g silica containing 33% (w/w) 1 *M* NaOH, 1.0 g silica, 4.0 g silica containing 44% (w/w) concentrated H_2SO_4 and 2.0 g silica. Quantitatively transfer the concentrated extract from the previous paragraph to the column and elute with 45 ml hexane. Collect the entire eluate and concentrate to a volume of 1–2 ml in a centrifuge tube, as before.

Construct a disposable LC minicolumn by cutting off a 5-ml Pyrex® disposable pipette at the 2.0-ml mark and packing the lower portion of the tube with a small plug of silanized glass wool, followed by 1 g of Woelm basic alumina, which has been previously activated for at least 16 hours at 600°C in a muffle furnace, and cooled in a desiccator for 30 minutes just before use. Quantitatively transfer the concentrate from the previous paragraph onto the LC column, rinse the centrifuge tube consecutively with two 0.3-ml portions of 3% CH_2Cl_2-in-hexane, and also transfer the rinses to the chromatography column.

Elute the column with 10 ml of 3% (v/v) CH_2Cl_2-in-hexane and retain the eluate for PCB analysis. Elute the column with 10 ml of 50% (v/v) CH_2Cl_2-in-hexane and retain the eluent for analyses for CDD and CDF.

Elute the column with 5 ml CH_2Cl_2 and retain the eluate to check for retention of CDD and CDF on the column.

Concentrate each of the retained fractions to a volume of approximately 1 ml by heating the tubes in a water bath while passing a stream of prepurified N_2 over the solutions, as described above. Quantitatively transfer the concentrated fractions into separate 2-ml microreaction vessels, splitting each fraction so that half goes into each of two sample vessels. (The contents of one vessel are analyzed for CDF, and the contents of the other for CDD.) Evaporate the solutions in each of the microreaction vessels almost to dryness, using the procedures just mentioned, rinse the walls of each vessel with 0.5 ml CH_2Cl_2, and reconcentrate just to dryness.

Approximately 1 hour before gas chromatographic/mass spectrometric (GC/MS) analysis, dilute the residue in each microreaction vessel with an appropriate quantity of benzene (depending on the anticipated quantities of analytes in each vessel) and gently swirl the solvent in the vessel to ensure dissolution of CDD, CDF and PCB.

If preliminary GC/MS screening analysis of the sample indicates the presence of potential interfering compounds (e.g., those that obscure the CDD, CDF or PCB signals) or other sample matrix constituents having very long GC retention times, then additional sample cleanup or fractionation is required using high-performance liquid chromatography (HPLC). The HPLC used for this purpose is described below. The sample is injected into the HPLC apparatus and appropriate fractions are collected, as determined in advance, by injecting pure CDD and CDF standards and measuring the retention times of these.

Analysis of Sample Extracts Using GC/MS

Two separate GC/MS methods of analysis were employed in this study, one utilizing low-resolution gas chromatography/high-resolution mass spectrometry (LRGC/HRMS), and the other utilizing high-resolution gas chromatography/low-resolution mass spectrometry (HRGC/LRMS). For determination of total TCDD in the extracts of the samples, LRGC/HRMS was employed. This technique provides a generally reliable quantitative indication of the total levels of TCDD present in the analyte (assuming that the instrument response is the same for all TCDD isomers), but does not yield information regarding the quantities of specific TCDD isomers present. For these analyses, a modified AEI MS-30 mass spectrometer, operated in selected-ion monitoring (SIM) mode,

is used. This technique utilizes a specialized step-scan circuit and associated electronic hardware developed in this laboratory and described in previous publications. Both m/z 319.8966 and 321.8936 are monitored as indicators of TCDD during the period when TCDD elute from the gas chromatograph. Thus quantification of the TCDD detected can be based on the signal observed at either mass. The theoretical ratio of m/z 319.8966 to m/z 321.8936 resulting from CDD (based on the known isotopic abundances of ^{35}Cl and ^{37}Cl and the numbers of Cl substituents in the molecular ion) is 0.77, and the experimentally observed ratio should be essentially the same as the theoretical ratio. This isotope ratio is another criterion that the data should satisfy to certify with confidence that TCDD is indeed detected. Since the ion signal at m/z 327.8846, which arises from the $^{37}Cl_4$-2,3,7,8-TCDD internal standard added to all samples prior to processing, is also monitored concurrently with the two masses typical of native TCDD, and the quantification of native TCDD is actually based on the ratios of the signals at m/z 320 and m/z 322 to that at m/z 328, the TCDD data obtained are inherently "recovery-corrected." This is, of course, one of the chief reasons for using an internal standard, and results in improved accuracy. The percent recovery of the internal standard is specified in the data listings solely for the purpose of illustrating the overall efficiency of the analytical procedure.

For determining the total concentrations of each of the various other classes (penta- through octachlorinated) of CDD and CDF in the sample extracts, a sophisticated HRGC/LRMS technique was employed. A complex, computer-controlled SIM scheme was used for this purpose and the compounds in each extract were quantified during two separate GC/MS runs. The ions monitored during these GC/MS analyses for each group of CDD and CDF are listed in Table II, while the sequences of GC and MS operations are shown in Tables III and IV for the two runs. These procedures permit the monitoring of ion masses characteristic of each class of CDD and CDF during the appropriate GC retention time interval. As expected, the monochlorinated CDD and CDF have similar retention times. However, use of a 50-m wall-coated open tubular fused-silica GC column provides optimum separation and minimizes overlap of individual compounds. As mentioned earlier, of the 75 possible CDD and 135 possible CDF, authentic standards of only a limited number are available in our laboratory for use in calibration (see Table I). Therefore, most of the CDD and CDF peaks observed in the analyses of the sample extracts cannot be assigned to a specific isomer. Thus, in arriving at a quantitative estimate for a given class of CDD or CDF, the areas of the mass chromatographic peaks appearing at the appropriate retention times, and having the appropriate mass spectral response, were summed

Table II. Ion Masses Monitored Using SIM GC/MS for Simultaneous Determination of Mono- through Octachlorinated Dibenzo-*p*-dioxins and Dibenzofurans

Class of Chlorinated Dibenzodioxin or Dibenzofuran	Number of Chlorine Substituents (X)	Monitored m/z for Dibenzofurans $C_{12}H_{8-x}OCl_x$	Monitored m/z for Dibenzo-*p*-dioxins $C_{12}H_{8-x}O_2Cl_x$	Approximate Theoretical Ratio Expected on Basis of Isotopic Abundance
Mono-	1	202.019[a]	218.013[a]	1.00
		204.016	220.011	0.35
Di-	2	235.980[a]	251.974[a]	1.00
		237.977	253.972	0.69
Tri-	3	269.941[a]	285.940[a]	0.99
		271.938	287.937	1.00
Tetra-	4	303.902[a]	319.897[a]	0.77
		305.899	321.894	1.00
			327.885[b]	
			[256.933][c]	0.21
			[258.930][c]	0.20
Penta-	5	337.863[a]	353.858[a]	0.57
		339.860	355.855	1.00
Hexa-	6	373.821	389.816	1.00
		375.818	391.813	0.87
Hepta-	7	407.782	423.777	1.00
		409.779	425.774	1.00
			431.765[b]	
Octa-	8	441.743	457.738	0.86
		443.740	459.735	1.00

[a]Molecular ion peak.
[b]$^{37}Cl_4$-labeled TCDD and HpCDD standard peaks.
[c]Ions that can be monitored in TCDD analyses for confirmation purposes.

and compared to the corresponding area observed from injection of a known quantity of a calibration standard of the same class. In general, a single CDD or CDF isomer of each chlorinated group (monochlorinated, dichlorinated, etc.) was used in the calibration process. However, since all 22 TCDD isomers are available in this laboratory, it is possible to make a reasonably definitive identification of most of the TCDD isomers present in the samples, because the techniques employed permit complete separation of most of these isomers.

Sample extracts expected to contain PCB were also subjected to HRGC/LRMS analysis, using SIM. PCB standards representative of several classes of PCB (mono- through decachlorinated) were used to calibrate the GC/MS and to determine appropriate GC retention time

Table III. Sequence of Operations in GC/MS (MS-25) Analyses of CDD and CDF in First Injection of Sample Extract

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temperature Program Rate (±°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Compounds Monitored
0.00	Injection, splitless	190			
1.50	Turn on split valve	190			
2.00	Begin temp. program to 220°C	190	5		
4.50	Open column flow to MS	202	5		
5.00	Start program 1: sweep = 100 ppm; time on each mass = 0.15 sec	205	5	202.019	Mono-Cl furans
				204.016	Mono-Cl furans
				218.013	Mono-Cl dioxins
				202.011	Mono-Cl dioxins
8.00	Column reaches isothermal hold	220			
8.75	Stop program 1	220			
9.50	Start program 2: sweep = 100 ppm; time on each mass = 0.15 sec	220		269.941	Cl_3 furans
				271.938	Cl_3 furans
				285.940	Cl_3 dioxins
				289.937	Cl_3 dioxins
16.00	Stop program 2				
16.75	Start program 3: sweep = 125 ppm; time on perm mass = 0.2 sec; time on ^{37}Cl-TCDD = 0.07 sec	220		327.885	^{37}Cl-labeled TCDD
				337.863	Cl_4 furans
				339.860	Cl_4 furans
				353.858	Cl_4 dioxins
				355.855	Cl_4 dioxins
25.00	Begin temp program to 235°C	220	5		
30.00	Stop program 3	235			
45.00	Start program 5: sweep = 175 ppm; time on each mass = 0.35 sec	235		407.782	Cl_5 furans
				409.779	Cl_5 furans
				423.777	Cl_5 dioxins
				425.774	Cl_5 dioxins
				431.765	^{37}Cl-labeled HpCDD
60.00	Stop program 5				
95.00	Return GC to to initial temp				

Table IV. Sequence of Operations in GC/MS (MIS—25) Analyses of CDD and CDF in Second Injection of Sample Extract

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temperature Program Rate (A°C/min)	Ions Monitored by Mass Spectrometer (m/e)	Compounds Monitored
0.00	Injection, splitless	190			
1.50	Turn on split valve	190			
2.00	Begin temp program to 220°C	190			
4.30	Open flow to MS	202	5		
6.00	Start program 2: sweep = 100 ppm; time on each mass = 0.15 sec	210	5	235.980	Cl_4 furans
				237.977	Cl_4 furans
				251.970	Cl_4 dioxins
				253.972	Cl_4 dioxins
8.00	Column reaches 220°C; hold isothermal	220			
12.00	Stop program 2	220			
12.75	Start program 4: sweep = 100 ppm; time on ^{13}C mass = 0.15 sec; time on ^{37}Cl-TCDD = 0.05 sec	220		303.902	Cl_5 furans
				305.899	Cl_5 furans
				319.897	Cl_5 dioxins
				321.894	Cl_5 dioxins
				327.885	^{37}Cl-labeled TCDD
24.00	Stop program 4	220			
25.00	Begin temp program to 235°C	220	5		
26.50	Start program 6: sweep = 150 ppm; time on each mass = 0.25 sec	225	5	373.821	Cl_6 furans
				375.818	Cl_6 furans
				389.816	Cl_6 dioxins
				391.813	Cl_6 dioxins
45.00	Stop program 6	235			
46.00	Start program 7: sweep = 175 ppm; time on each mass = 0.035 sec	235		407.782	Cl_7 furans
				409.779	Cl_7 furans
				423.777	Cl_7 dioxins
				425.774	Cl_7 dioxins
				430.765	^{37}Cl-labeled HpCDD
60.00	Stop program 7	235		441.743	Cl_8 furans
70.00	Start program 8: sweep = 225 ppm; time on each mass = 0.03 sec	235		443.740	Cl_8 furans
				457.738	Cl_8 dioxins
				459.735	Cl_8 dioxins
90.00	Stop program 8				
95.00	Return to initial temp	235			

parameters and sensitivities for each PCB class. The mass spectral ions indicative of each PCB class that were monitored at the appropriate retention time are shown in Table V. The same monitoring sequence was applied to the sample extracts to estimate the quantities of total PCB of each class that were present.

Immediately before analysis, each sample extract was diluted to the desired volume (typically 10–50 μl) and 1- to 10-μl aliquots of each sample extract were injected via a microsyringe into one of the gas chromatographs.

Specific details follow of the apparatus, operating conditions and experimental parameters for the GC/MS analyses reported here.

Parameters for LRGC/HRMS Analysis of Sample Extracts

Instrumentation. A Varian 3740 gas chromatograph coupled through an Associated Electric Industries (AEI) silicone membrane separator to a modified AEI MS-30 mass spectrometer. Modifications to the MS-30

Table V. Ion Masses Monitored Using SIM GC/MS for Simultaneous Determination of Mono- through Decachlorinated PCB

Class of Chlorinated PCB	Number Chlorine Substituents	Ions Monitored (m/z) for PCB [$C_{12}H_{10-x}Cl_x$]
Mono-	1	188.039
		190.036
Di-	2	222.000
		223.997
Tri-	3	255.961
		257.958
Tetra-	4	289.922
		291.919
Penta-	5	325.880
		327.877
Hexa-	6	359.841
		361.839
Hepta-	7	393.802
		396.800
Octa-	8	427.763
		429.761
Nona-	9	463.722
		465.719
Deca-	10	497.683
		499.680

include a new ESA power supply and incorporation of a custom-built step-scan circuit driven by a Nicolet 1074 Signal Averaging Computer. Four masses are rapidly scanned at the retention time of the dioxin or furan of interest.

Conditions for the Gas Chromatograph. The column was a 1.8-m × 2-mm i.d. glass column packed with 1.5% OV-101 on Gas Chrom Q (100/120 mesh). The carrier gas was helium at a flowrate of 30 ml/min. The temperatures were injector, 250°C; column, 220°C; transfer lines, 285°C.

Conditions for the Mass Spectrometer. Ionizing voltage was 70 eV; static resolution was 1:12,500 (10% valley); source envelope pressure was 5×10^{-5} torr; analyzer pressure was 5×10^{-6} torr; source temperature was 250°C; membrane separator temperature was 215°C; transfer line temperature was 270°C; and ions monitored were m/z 319.8966, 321.8936, 325.8805 and 327.8846.

Parameters for HRGC/LRMS Analysis of Sample Extracts

Instrumentation. A Perkin-Elmer Sigma III gas chromatograph was coupled through a custom-fabricated interface, including a single-stage glass jet separator, to a Kratos MS-25 mass spectrometer equipped with a DS-50SM Data System.

Conditions for the Gas Chromatograph. The column was a 50-m WCOT (OV-101) silica capillary column. The carrier gas was hydrogen, at 30 lb head pressure. The column temperature was programmed from 190 to 220°C at 5°C/min, hold at 220°C for 20 min. The interface temperature was 250°C. Splitless injection was used.

Conditions for the Mass Spectrometer. SIM mode was used. (For m/z monitored and details of instrumental procedures see Tables II to V.) Ionizing voltage was 70 eV; accelerating voltage was 4 kV.

High-Performance Liquid Chromatography

The apparatus and instrumental parameters applied for HPLC fractionation of sample extracts are specified below.

Parameters for HPLC Fractionation of Sample Extracts

Instrumentation. A Varian Model 5021 Microprocessor Controlled High-Performance Chromatograph was equipped with CDS-111L Data System.

Parameters. Pressure was maintained between 10 and 250 atm. A 25-μl injection loop was used. The guard column was a 37-μ Vydac SC reverse-phase, 4.0 cm × 0.4 cm i.d. The analytical column comprised two Du Pont Zorbax-ODS columns, each 25.0 cm × 0.6 cm i.d. The temperature of the guard column was 20° C; in the analytical column, 50° C. Detectors were: fixed UV, 254 nm, 0.01 absorbent units full scale (AUFS); Varichrom UV-Vis: TCDD, 235 nm, 0.01 AUFS, HxCDD, HpCDD, 245 nm, 0.01 AUFS.

Reagents and Chemicals

The following reagents and chemicals were utilized in the procedures outlined above:

- reagent-grade potassium hydroxide, anhydrous sodium sulfate and sulfuric acid (J. T. Baker Chemical Co. or Fisher Scientific Co., Fairlawn, NJ)
- distilled-in-glass methanol, hexane, methylene chloride and benzene (Burdick and Jackson, Muskegon, MI)
- Omnisolve-quality, low-boiling petroleum ether (Matheson, Coleman, and Bell, Cincinnati, OH)
- Activity Grade I Woelm basic alumina (ICN Pharamaceuticals, Cleveland, OH)
- bidistilled water from all-glass distillation apparatus (Brehm Laboratory)
- prepurified nitrogen (Airco, Inc., Montvale, NJ).

Standards employed in this work were obtained from the following sources:

- 1-chlorodibenzo-*p*-dioxin (Analabs, Inc., North Haven, CT)
- 2-chlorodibenzo-*p*-dioxin (Analabs, Inc., North Haven, CT)
- 2,7-dichlorodibenzo-*p*-dioxin (Analabs, Inc., North Haven, CT)
- 2,3-dichlorodibenzo-*p*-dioxin (Analabs, Inc., North Haven, CT)
- 1,2,4-trichlorodibenzo-*p*-dioxin (Analabs, Inc., North Haven, CT)
- 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (Analabs, Inc., North Haven, CT)
- $^{37}Cl_4$-2,3,7,8-TCDD (KOR Isotopes, Cambridge, MA)
- 2,3,7,8-TCDD and other TCDD isomers (Dow Chemical Co., Midland, MI, and H. R. Buser, Swiss Federal Research Station, Wädenswil, Switzerland)
- 1,2,3,7,8-PCDD (KOR Isotopes, Cambridge, MA)
- 1,2,3,4,7,8-HxCDD (Dr. A. Poland, University of Rochester, NY)
- 1,2,4,6,7,9-HxCDD (Dr. A. Poland, University of Rochester, NY)

- $^{37}Cl_4$-1,2,3,4,6,7,8-HpCDD (KOR Isotopes, Cambridge, MA)
- OCDD (Analabs, Inc., North Haven, CT)
- $^{37}Cl_8$-OCDD (KOR Isotopes, Cambridge, MA)
- 2,4-dichlorodibenzofuran (All CDF obtained from Food and Drug Administration, Washington, DC)
- 2,8-dichlorodibenzofuran
- 1,2,4-trichlorodibenzofuran
- 1,2,4,8-tetrachlorodibenzofuran
- 2,3,7,8-tetrachlorodibenzofuran
- 2,3,6,8-tetrachlorodibenzofuran
- 1,2,4,7,8-pentachlorodibenzofuran
- 1,2,3,5,7,9-hexachlorodibenzofuran
- 1,2,3,4,5,8,9-heptachlorodibenzofuran
- octachlorodibenzofuran

Quality Assurance

As is the case for all analytical programs conducted in our laboratory, all analytical measurements were accomplished in accordance with good laboratory practice. An extensive quality assurance program is established and followed for all projects such as those described here. This program includes analyses of solvent and method blanks, analyses of internally spiked control samples, and determinations to validate the efficacy of the analytical procedures applied, as already described. Quality control for the individual analyses reported here was also provided on a continuing basis for CDD determinations because of the incorporation of known quantities of labeled TCDD and HpCDD internal standards into each sample before analysis.

RESULTS AND DISCUSSION

Total TCDD and TCDF

Results obtained from the determination of total TCDD and TCDF in the stack effluents (that is, in the individual sampling train samples) from the tests at Rollins are reported in Tables VI and VII, respectively. Corresponding data for the tests at ENSCO are reported in Tables VIII and IX. The data for total TCDD and TCDF are reported separately, because these results were considered by EPA to have greatest relevance for the estimation of health risks in connection with the incineration tests, and were the first results obtained by the Brehm Laboratory in this study.

Table VI. Results of Analyses of Rollins Incinerator Stack Effluent Samples for TCDD (PCB Destruction Tests)

Test and Sample Train Number	TRW Sample Number	Sample Type	Native TCDD Detected in Entire Sample (ng)			Minimum Detectable Quantity (ng)	Percent Recovery[a]
			m/z 320	m/z 322	Average		
1; 1	6-0581	Impinger[b]	1.61	1.97	1.79	0.43	100
1; 1	6-0582	Probe wash	3.16	4.51	3.84	0.43	100
1; 1	6-0583	XAD-2 resin	0.53	2.09[c]	1.31	0.43	100
1; 1	6-0584/6-0585[d]	Florisil	0	0	0	0.70	44
2; 1	6-0605	Impinger[b]	0	0	0	0.27	75
2; 1	6-0606	Probe wash	1.32	1.52	1.42	0.27	129
2; 1	6-0607/6-0608[d]	XAD-2 resin	0	0	0	0.38	107
2; 1	6-0609	Florisil	0	0	0	0.48	79
3; 2	6-0643	Impinger[e]	0	0	0	0.90	100
3; 2	6-0644	Probe wash[e]					
3; 2	6-0645	XAD-2 resin	0	0	0	0.30	80
3; 2	6-0646	Florisil	0	0	0	0.35	58

[a] Based on $^{37}Cl_4$-2,3,7,8-TCDD added as internal standard.

[b] Upper layer (apparently hexane fraction) only.

[c] Incompletely resolved interference at m/z 322 results in elevated signal.

[d] Composite.

[e] Sample contained only one layer, which appeared to be the acetone-water layer; upper hexane layer observed in other samples was completely absent.

Table VII. Results of Analyses of Rollins Incinerator Stack Effluent Samples for TCDF (PCB Destruction Tests)

Test and Sample Train Numbers	TRW Sample Number	Sample Type	Quantity of Total TCDF in Entire Sample[a] (ng)	Apparent Number of TCDF Isomers[b]	Quantity of Apparent 2,3,7,8-TCDF[c] (ng)	Minimum Detectable Quantity of TCDF (ng)	Percent Recovery[d]
1; 1	6-0581	Impinger[e]	3.5	6	0.7	0.08	100+
1; 1	6-0582	Probe wash	5.0	7	0.5	0.15	100
1; 1	6-0583	XAD-2 resin	3.0	8	0.3	0.15	100
1; 1	6-0584/6-0585[f]	Florisil	0	0	0	0.08	1
2; 1	6-0605	Impinger[e]	6.0	9	0.8	0.1	72
2; 1	6-0606	Probe wash	14	8	1.4	1.0	122
2; 1	6-0607/6-0608[f]	XAD-2 resin	2.0	9	0.25	0.07	100
2; 1	6-0609	Florisil	0	0	0	0.09	85
3; 2	6-0643	Impinger[g]	0	0	0	0.2	100+
3; 2	6-0644	Probe wash[g]	0	0	0	0.5	60
3; 2	6-0645	XAD-2 resin	2.0	8	0.2	0.1	72
3; 2	6-0646	Florisil	0	0	0	0.4	50

[a] Based on summation of the areas of all mass chromatographic peaks observed in a selected TCDF retention time window, while monitoring m/z 304 and 306. It is assumed that the instrument response determined by calibrating with an authentic 2,3,7,8-TCDF standard is the same for all TCDF isomers.

[b] The number of discrete mass chromatographic peaks observed in the TCDF window. Since all TCDF isomers are not available for determination of GC retention times, it is not known whether or not each peak represents more than one isomer. The number cited is therefore the minimum number of TCDF isomers that can be present in the sample.

[c] Determined on the basis of the mass chromatographic peak which has a retention time corresponding to that of the 2,3,7,8-TCDF isomer. Other TCDF isomers may also be included in this peak.

[d] Based on $^{37}Cl_4$-2,3,7,8-TCDD added as an internal standard.

[e] Upper layer (apparently hexane fraction) only.

[f] Composite.

[g] Sample contained only one layer which appeared to be the acetone-water layer; upper hexane layer observed in other samples was completely absent.

Table VIII. Results of Analyses of ENSCO Incinerator Stack Effluent Samples for TCDD (PCB Destruction Tests)

Test and Sample Train Number	TRW Sample Number	Sample Type	Native TCDD Detected in Entire Sample (ng) m/z 320	m/z 322	Average	Minimum Detectable Quantity (ng)	Percent Recovery[a]
1; 1[b]	6-0528	Probe wash	0.617	0.149	0.158	0.062	146
1; 2	6-0529	XAD-2 resin	0.088	0.122	0.105	0.062	104
1; 2	6-0530	XAD-2 resin	0	0	0	0.073	85
1; 2	6-0531	Florisil	0	0	0	0.062	128
2; 1	6-0560	Impinger[c]	0.400	0.551	0.476	0.22	45
2; 1	6-0561	Probe wash	0	0	0	0.25	99
2; 1	6-0562	XAD-2 resin	0	0	0	0.38	134
2; 1	6-0563	Florisil	0	0	0	0.66	57
3; 1	6-0574A	Impinger[c]	0	0	0	0.35	71
3; 1	6-0574B	Probe wash	0	0	0	0.21	98
3; 1	6-0574C	XAD-2 resin[d]	0	0	0	0.20	94
3; 1	6-0574D	Florisil (1 of 2)	0	0	0	0.20	122
3; 1	6-0574E	Florisil (2 of 2)	0	0	0	0.45	46

[a] Based on $^{37}Cl_4$-2,3,7,8-TCDD added as internal standard.
[b] Impinger sample from this series was broken when received by Wright State.
[c] Upper layer (apparently hexane fraction) only.
[d] The other XAD-2 resin trap was not received by Wright State.

Table IX. Results of Analyses of ENSCO Incinerator Stack Effluent Samples for TCDF (PCB Destruction Tests)

Test and Sample Train Numbers	TRW Sample Number	Sample Type	Quantity of Total TCDF in Entire Sample[a] (ng)	Apparent Number of TCDF Isomers[b]	Quantity of Apparent 2,3,7,8-TCDF[c] (ng)	Minimum Detectable Quantity of TCDF (ng)	Percent Recovery[d]
1; 2[e]	6-0528	Probe wash	0	0	0	1	50
1; 2	6-0529	XAD-2 resin	0	0	0	1	[h]
1; 2	6-0530	XAD-2 resin	0	0	0	0.1	70
1; 2	6-0531	Florisil	2.0	4	0.5	0.4	100
2; 1	6-0560	Impinger[f]	4.0	3	1.0	0.5	45
2; 1	6-0561	Probe Wash	0.5	2	0.2	0.09	75
2; 1	6-0562	XAD-2 resin	1.5	5	0.3	0.05	100+
2; 1	6-0563	Florisil	0	0	0	0.08	100
3; 1	6-0574A	Impinger[f]	0	0	0	0.5	100+
3; 1	6-0574B	Probe wash	0	0	0	0.2	100+
3; 1	6-0574C	XAD-2 resin[g]	0	0	0	0.08	100
3; 1	6-0574D	Florisil (1 of 2)	0	0	0	0.4	51
3; 1	6-0574E	Florisil (2 of 2)	0	0	0	0.09	95

[a] Based on summation of the areas of all mass chromatographic peaks observed in a selected TCDF retention time window, while monitoring m/z 306 and 306. It is assumed that the instrument response determined by calibrating with an authentic 2,3,7,8-TCDF standard is the same for all TCDF isomers.

[b] The number of discrete mass chromatographic peaks observed in the TCDF window. Since all TCDF isomers are not available for determination of GC retention times, it is now known whether or not each peak represents more than one isomer. The number cited is therefore the minimum number of TCDF isomers which can be present in the sample.

[c] Determined on the basis of the mass chromatographic peak which has a retention time corresponding to that of the 2,3,7,8-TCDF isomer. Other TCDF isomers may also be included in this peak.

[d] Based on $^{37}Cl_4$-2,3,7,8-TCDD added as an internal standard.

[e] Impinger sample from this series was broken when received by Wright State.

[f] Upper layer (apparently hexane fraction) only.

[g] The other XAD-2 resin trap was not received by Wright State.

[h] Recovery could not be determined on basis of low resolution MS analysis because of unresolved interference at m/z 320.

As mentioned earlier, the total TCDD results were obtained by LRGC/HRMS, while the total TCDF data were obtained by HRGC/LRMS.

As noted above, the results obtained for total TCDD do not permit any definitive conclusions with respect to the composition of TCDD positional isomers. Some information on this topic was obtained however, for TCDD and TCDF from capillary-column HRGC/LRMS measurements. These results are discussed below. The data for total TCDD and TCDF shown in Tables VI and VII (Rollins tests) indicate that these compounds were detected in the train samples from tests 1 and 2, but generally were not found in the train samples from test 3. The same observations are applicable to the ENSCO data (Tables VIII and IX). One possible conclusion that can be drawn from these observations is that the "normal" chlorocarbon wastes incinerated by these two plants are the source of the TCDD (since these were burned in both tests 1 and 2), whereas incineration of the PCB (which were the only chlorocarbons burned in test 3) did not yield TCDD. There is no obvious rationale for the curious pattern of the TCDD results (for example, the observation of TCDD in the impinger, probe wash and XAD-2 resin samples from one test, whereas only the probe wash sample or the impinger sample contained TCDD in other tests). Possibly, this reflects erratic sampling procedures (as discussed earlier) or variations in the washing of the train components by the field sampling contractor. Alternatively, temperature fluctuations in various sections of the train might account for some of these observations. Similar peculiarities are apparent in the patterns observed for the total TCDF data.

Data for both the TCDD and TCDF are reported as total quantities present in each type of sample analyzed. Since the volumes and weights of the various samples varied considerably, and since these could not be related to original volumes and weights (these were not available, and in any case, leakage and/or loss of unknown quantities of most samples occurred during shipment) it was not possible to calculate concentrations of TCDD and TCDF present in the samples from the analytical data determined by our laboratory.

Isomeric Composition of TCDD and TCDF

Data on the isomeric composition of the TCDD and TCDF present in representative Rollins and ENSCO samples were also obtained in the present study from the HRGC/LRMS measurements. For these latter determinations, a 50-m capillary GC column was utilized, which is capable of resolving many of the tetrachlorinated isomers. For example, Figure 6 shows SIM mass chromatographs obtained for a mixture of 12

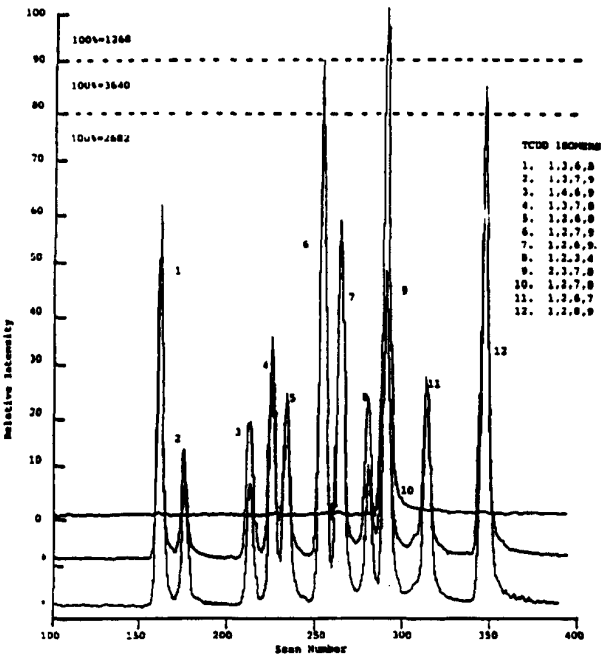


Figure 6. Selected-ion mass chromatograms obtained by HRGC/LRMS for 12-isomer TCDD standard mixture. Masses monitored were: * = 256–259; # = 319–322; 0 = 327–328. Numbering of peaks corresponds to isomer identifications shown at right.

TCDD isomers by monitoring sequentially nominal m/z 257 and 259 (the sum of these is displayed); nominal m/z 320 and 322 (sum of these is displayed); and nominal m/z 328 in one GC/MS run. Corresponding displays obtained from the HRGC/LRMS analyses of TRW sample number 6-0660 (Rollins test 2, train 1, probe wash sample) and sample number 6-0660 (ENSCO test 2, train 1, impinger sample) are shown in Figures 7 and 8 (the numbering of peaks corresponds to that shown in Figure 6). By comparing the observed sequence of peaks in these runs with that observed for the standard isomer mixture (Figure 6), and by

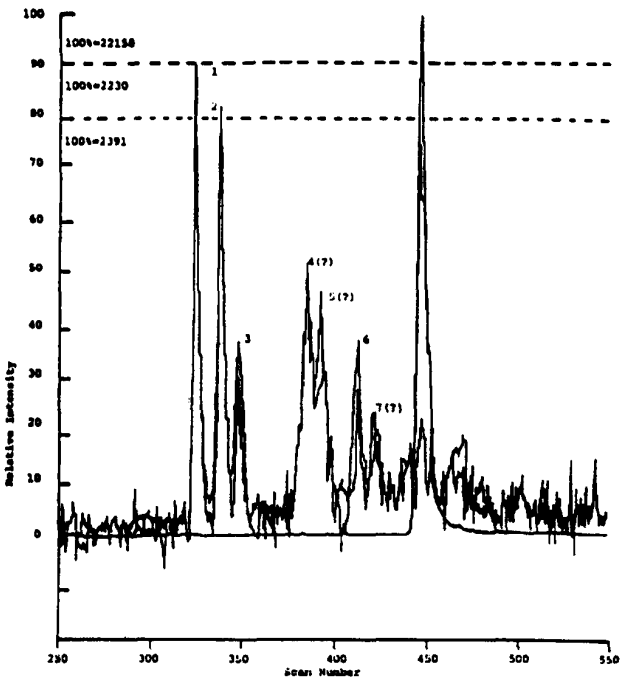


Figure 7. Selected-ion monitoring mass chromatograms obtained from HRGC/LRMS analysis of Rollins test 2, train 1 probe wash sample (TRW No. 6-0606) showing TCDD isomer peaks. Numbering and symbols are given in Figure 6. $^{37}Cl_4$-2,3,7,8-TCDD was added as an internal standard.

utilizing other related GC data obtained in our laboratory, it is possible to identify positively four of the TCDD isomer peaks detected in the analyses of these two samples. It is known from the results cited above that each of these four isomers is completely resolved from the other 21 TCDD isomers, and identification of these isomers is unequivocal using the experimental conditions employed here. These isomers and their relative quantities (percents of the total TCDD) are listed in Table X for

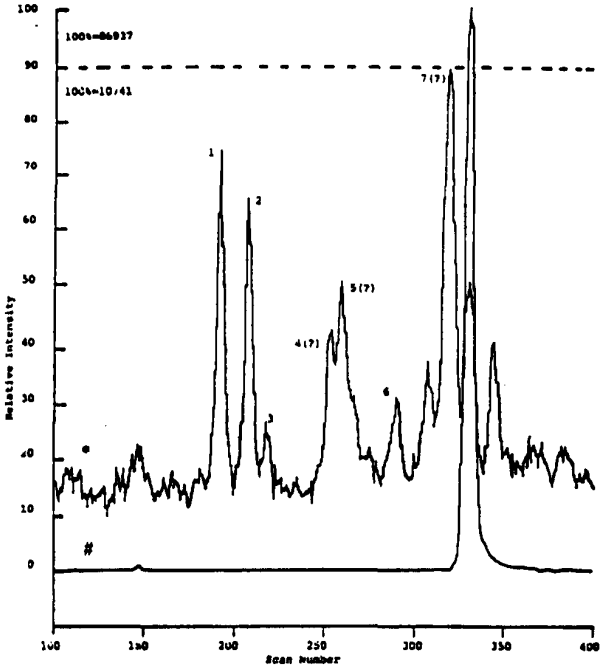


Figure 8. Selected-ion monitoring mass chromatograms obtained from HRGC/LRMS analysis of ENSCO test 2, train 1 impinger sample (TRW No. 6-0560) showing TCDD isomer peaks. Numbering of isomer peaks is given in Figure 6. $^{37}Cl_4$-2,3,7,8-TCDD was added as an internal standard. Symbols: * = 319-322; # = 327-328.

the two samples indicated. Several of the other isomer peaks shown in Figures 7 and 8 also correspond in retention time to specific isomers included in our 12-isomer mixture, but other data obtained in this laboratory indicate that these isomers are not uniquely resolved from the other TCDD isomers, and so the identifications of these other peaks are tentative. Under the presently utilized experimental conditions, the 2,3,7,8-TCDD isomer is also resolved from most other TCDD isomers,

Table X. TCDD Isomers Determined in Stack Effluent Samples from Incineration Tests at Rollins and ENSCO

Test and Sample Train Numbers	TRW Sample Number	Origin	TCDD Isomers Detected	Percent of Total TCDD
2; 1	6-0606	Rollins Environmental Services	1,3,6,8-	25
			1,3,7,9	22
			1,3,6,9	9
			1,2,7,9	9
			Others[a]	35
2; 1	6-0560	ENSCO	1,3,6,8	20
			1,3,7,9	18
			1,3,6,9	3
			1,2,7,9	5
			Others[b]	54

[a]TCDD are also observed at retention times corresponding to the 1,3,7,8-, 1,2,6,8- and 1,2,6,9- isomers, but these isomers are apparently not completely resolved from several other TCDD isomers which could also account for these peaks.

[b]TCDD are also observed at retention times corresponding to the 1,3,7,8-, 1,2,6,8- and 1,2,3,4- isomers, but these peaks may also be accounted for by several other isomers.

and since no mass chromatographic peak was detected at the 2,3,7,8-TCDD retention time, it is therefore possible to state that, within the limits of detection applicable here (500 pg) 2,3,7,8-TCDD is *not* detected in the effluent samples analyzed. It seems probable that the isomeric composition of the TCDD in the other effluent samples would be essentially the same as those detected for the two samples just discussed.

Less definitive data on the isomeric composition of the TCDF could be obtained, because only three TCDF isomer standards were available for calibration (1,2,4,8-, 2,3,6,8- and 2,3,7,8-TCDF). Thus, although a TCDF peak is observed at the retention time corresponding to that of 2,3,7,8-TCDF in the mass chromatograms of many of the samples, completely unequivocal assignment of this peak is not possible at present. The quantities of the TCDF component that is "apparently" 2,3,7,8-TCDF are listed in Tables VII and IX, along with the data for total TCDF. Again, it must be emphasized that this assignment is tentative.

Total Higher-Chlorinated CDD and CDF

Using the complex sequence of HRGC/LRMS procedures described above, the complete series of higher-chlorinated CDD and CDF (total penta- through octachlorinated) were determined in representative Rollins and ENSCO samples. Examples of mass chromatograms typical

of those obtained in the course of these complete GC/MS scans are shown in Figures 9 and 10. Figure 9 shows the mass chromatograms resulting from injection of a mixture of three TCDF standards. The corresponding mass chromatograms for an actual sample (TRW number 6-0606) showing the responses for various TCDF contained therein are shown in Figure 10. Similar calibration data and corresponding MS data for actual samples were obtained for all the other classes of CDD and

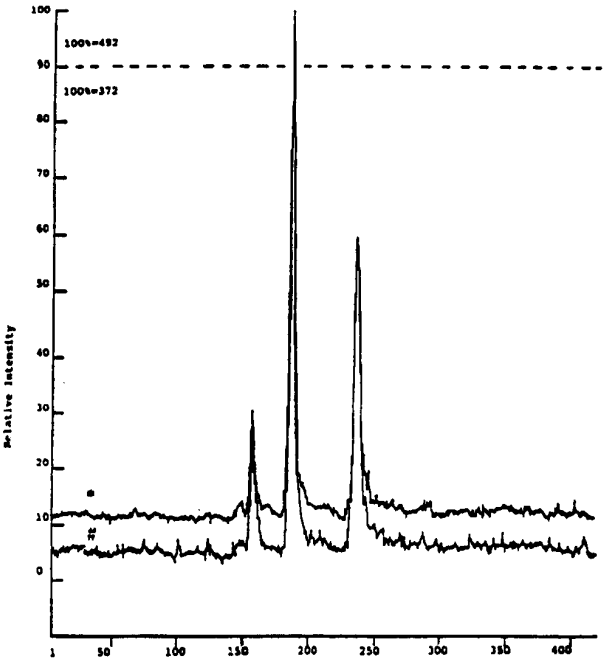


Figure 9. HRGC/LRMS mass chromatogram results obtained for calibration standard containing tetrachloridibenzofurans (2,3,7,8-, 1,2,4,8- and 2,3,6,8-TCDF). Symbols: * = 303-304; # = 305-306.

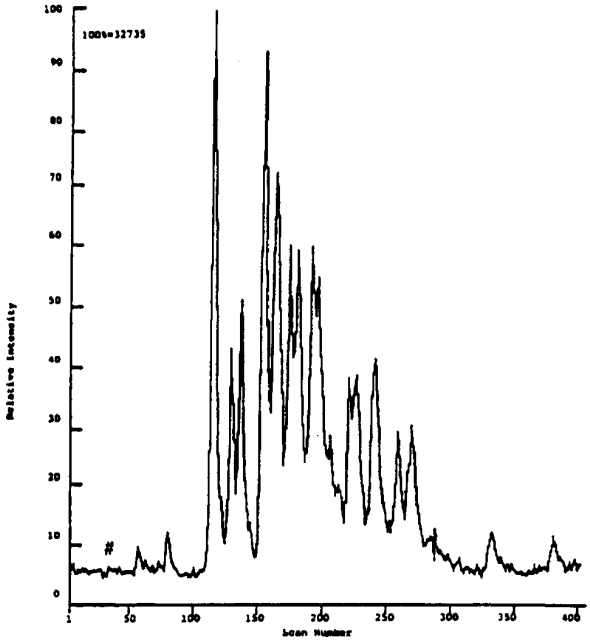


Figure 10. HRGC/LRMS mass chromatogram obtained in analysis of TCDF in Rollins test 2, train 1 probe wash sample (TRW No. 6-0606. Symbol: # = 303-306.

CDF. The CDD and CDF isomer standards utilized in obtaining the calibration data included:

- 1-chlorodibenzo-*p*-dioxin;
- 2,7-chlorodibenzo-*p*-dioxin
- 1,2,4-trichlorodibenzo-*p*-dioxin;
- 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and all 22 TCDD isomers;
- $^{37}Cl_4$-2,3,7,8-tetrachlorodibenzo-*p*-dioxin;
- 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin;
- 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin;
- octachlorodibenzo-*p*-dioxin;

- 2,4-dichlorodibenzofuran;
- 1,2,4-trichlorodibenzofuran
- 2,3,7,8-tetrachlorodibenzofuran;
- 1,2,4,8-tetrachlorodibenzofuran;
- 1,2,4,7,8-pentachlorodibenzofuran;
- 1,2,4,6,7,9-hexachlorodibenzofuran; and
- octachlorodibenzofuran.

The quantities of total CDD and CDF of the various chlorinated classes in two representative samples [the test 1, train 1, probe wash sample from Rollins (TRW number 6-0582), and the test 2, train 1, impinger sample from ENSCO (TRW number 6-0560)] as determined from the HRGC/LRMS data described above, are listed in Tables XI and XII, respectively. It appears that the quantities of CDF in these samples generally exceed the quantities of the corresponding CDD. The significance of these observations and their bearing on the combustion mechanisms is not apparent, and is difficult to determine in the absence of data on other chemical constituents in the effluents and feed materials.

Polychlorinated Biphenyls

In the limited time permitted for the analyses of samples collected in this survey, it was possible to analyze only a single sample for PCB content. The sample analyzed was a Florisil trap sample from Rollins test 2, train 1 (TRW number 6-0609), and the results are shown in Table XIII. Typical mass chromatograms obtained for a mixture of PCB standards and for this sample in the course of these analyses are shown in Figures 11 and 12. Similar data were obtained for other classes of PCB. Clearly, several classes of PCB were detected in the sample. The estimated quantities of the various PCB present are given in Table XIII.

RESULTS OF RISK ASSESSMENT PERFORMED BY EPA

The data obtained during the course of the complex analyses described above were employed by EPA to accomplish risk assessments for both the ENSCO and Rollins incinerators. The bases for these risk assessments (which estimate the hazards to human health resulting from emissions from these incinerators) are described in detail elsewhere [11], and only the general approach and conclusions derived by EPA are summarized here.

The risk assessment calculations were based solely on the levels of total TCDD and total TCDF provided to EPA by this laboratory [12] and

Table XI. HRGC/LRMS Data on Total CDD and CDF (Tetra- through Octachlorinated) in Test I, Train I, Probe Wash Sample (TWR Number 6-0582) from Incineration Tests at Rollins

CDD/CDF[a]	Number of Apparent Isomers[b]	Quantity of Total CDD/CDF Detected in Total Sample (ng)[c]	Minimum Detectable Quantity (ng)	Percent Recovery[d]
TCDD	[e]			100[f]
PCDD	4	4	0.3	
HxCDD	2	1	0.5	
HpCDD	1	2	2	100[f]
OCDD	1	5	3	
TCDF	7	5	0.2	
PCDF	6	30	0.3	
HxCDF	4	25	0.5	
HpCDF	2	12	2	
OCDF	1	10	3	

[a] Prefix designations are: T = tetra-; P = penta-; Hx = hexa-; Hp- = hepta; O = octa-.

[b] Since only a limited number of CDD and CDF isomers are available (see Tables I and II), it is not possible to demonstrate for most of the classes of CDD and CDF that all isomers of a given chlorinated group (for example, the pentachlorinated isomers; there are 14 PCDD) are completely resolved by using the GC conditions employed here. Therefore, it is not certain that each peak of the family observed for a given chlorinated group corresponds to a single isomer. Hence, the terminology "apparent" is used which designated the number of GC peaks observed for a given chlorinated group of CDD and CDF.

[c] Results are corrected for recovery on the basis of recovery of added internal standards.

[d] Recoveries for CDD were estimated on the basis of recovery of two internal standards added to the samples prior to processing. These standards are $^{37}Cl_4$-2,3,7,8-TCDD, the recovery of which was assumed to be indicative of the recoveries of native PCDD and lower-chlorinated CDD (that is, mono- through penta-CDD), and $^{37}Cl_4$-1,2,3,4,6,7,8-HpCDD, the recovery of which was assumed to be indicative of the recoveries of native HxCDD and higher-chlorinated CDD (that is, hexa- through octa-CDD). No isotopically labelled CDF were available, and so the recoveries of CDF could not directly be assessed. However, recoveries of CDF are probably on the same order as the corresponding CDD.

[e] Not determined in the HRGC/LRMS analyses; these data were obtained by LRGC/HRMS and are reported in Table VII.

[f] Refers to recovery of ^{37}Cl-labeled standards mentioned in footnote d.

described here. These data, in turn, were used in calculating the mass emission rates for TCDD and TCDF during the various test burns conducted at Rollins and ENSCO. To estimate the probable airborne concentrations of TCDD and TCDF that would result from these emissions, a computer modeling scheme was employed. The calculations ultimately yielded an estimate of the TCDD/TCDF concentrations in the

Table XII. HRGC/LRMS Data on Total CDD and CDF (Tetra- through Octachlorinated) in Test 2, Train 1, Impinger Sample (TWR Number 6-0560) from Incineration Tests at ENSCO

CDD/CDF[a]	Number of Apparent Isomers[b]	Quantity of Total CDD/CDF Detected in Total Sample (ng)[c]	Minimum Detectable Quantity (ng)	Percent Recovery
TCDD	[e]			100[f]
PCDD			1	
HxCDD			2	
HpCDD			6	100[f]
OCDD			8	
TCDF	3	4	0.5	
PCDF	6	20	1	
HxCDF			2	
HpCDF			6	
OCDF			8	

[a] Prefix designations are: T = tetra-; P = penta-; Hx = hexa-; Hp- = hepta; O = octa-.

[b] Since only a limited number of CDD and CDF isomers are available (see Tables I and II), it is not possible to demonstrate for most of the classes of CDD and CDF that all isomers of a given chlorinated group (for example, the pentachlorinated isomers; there are 14 PCDD) are completely resolved by using the GC conditions employed here. Therefore, it is not certain that each peak of the family observed for a given chlorinated group corresponds to a single isomer. Hence, the terminology "apparent" is used which designated the number of GC peaks observed for a given chlorinated group of CDD and CDF.

[c] Results are corrected for recovery on the basis of recovery of added internal standards.

[d] Recoveries for CDD were estimated on the basis of recovery of two internal standards added to the samples prior to processing. These standards are $^{37}Cl_4$-2,3,7,8-TCDD, the recovery of which was assumed to be indicative of the recoveries of native PCDD and lower-chlorinated CDD (that is, mono- through penta-CDD), and $^{37}Cl_4$-1,2,3,4,6,7,8-HpCDD, the recovery of which was assumed to be indicative of the recoveries of native HxCDD and higher-chlorinated CDD (that is, hexa- through octa-CDD). No isotopically labelled CDF were available, and so the recoveries of CDF could not directly be assessed. However, recoveries of CDF are probably on the same order as the corresponding CDD.

[e] Not determined in the HRGC/LRMS analyses; these data were obtained by LRGC/HRMS and are reported in Table VII.

[f] Refers to recovery of ^{37}Cl-labeled standards mentioned in footnote d.

breathing zones of persons living near the incinerators. From the latter results, by utilizing a number of "worst case" assumptions, and by taking into account the risk factor associated with breathing air containing 2,3,7,8-TCDD [13,14], EPA concluded that the risk of additional cancers in the population exposed to the emissions from the ENSCO incinerator ranges from 1 to 4 in 10,000,000. Similarly, the risk of additional cancers

Table XIII. HRGC/LRMS Data on PCB in Test 2, Train 1, Florisil Sample (TRW Number 6-0609) from Incineration Test at Rollins

Class of Chlorinated PCB (No. of Chlorine Substituents)	Number of Apparent Isomers[a]	Quantity of PCB Detected in Total Sample (ng)[b]	Minimum Detectable Quantity (ng)
Monochlorinated (1)			0.1
Dichlorinated (2)	3	10	0.3
Trichlorinated (3)	8	15	0.3
Tetrachlorinated (4)	4	3	0.5
Pentachlorinated-Decachlorinated (5-10)		C	

[a] Only a limited number of PCB isomers are available for use in establishing GC retention times and sensitivities for PCB, and so it could not be demonstrated that all isomers of a given chlorinated class are resolved using the GC conditions employed here. Therefore, it is not certain that each peak of the family observed for a given chlorinated group corresponds to a single isomer. Hence, the terminology "apparent" is used, which designates the number of GC peaks observed for a given chlorinated group of PCB.

[b] Assumes that the sensitivities of all isomers of a given chlorinated class are the same. These data are not corrected for recovery, since no isotopically labelled PCB were available to establish recoveries for the method used.

[c] Some Cl_5-Cl_{10} PCB are probably present, but there were too many interferring MS peaks to reliably determine these.

in the population exposed to the emissions from the Rollins incinerator was estimated to range from 1 to 180 in 10,000,000. EPA ruled that these risks were negligible and therefore, in early 1981, granted approval for the ENSCO and Rollins plants to continue incineration of high-level PCB wastes.

It is concluded from this assessment, therefore, that under proper conditions, incineration is a viable procedure for destruction of PCB wastes.

ACKNOWLEDGMENT

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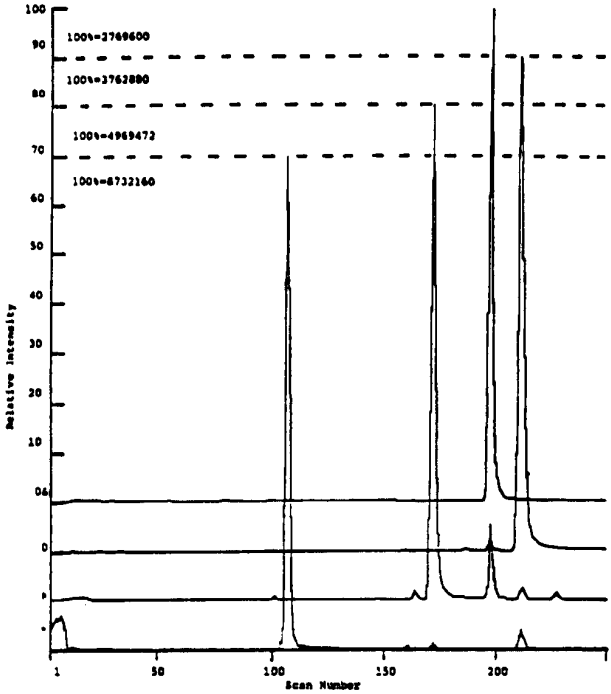

Figure 11. Selected-ion mass chromatograms obtained from HRGC/LRMS analysis of a mixture of mono-, di-, tri- and tetrachlorinated PCB standards. Symbols: * = 188-192; # = 222-225; O = 255-258; & = 289-292. See Table V for listing of isomer masses corresponding to each PCB class.

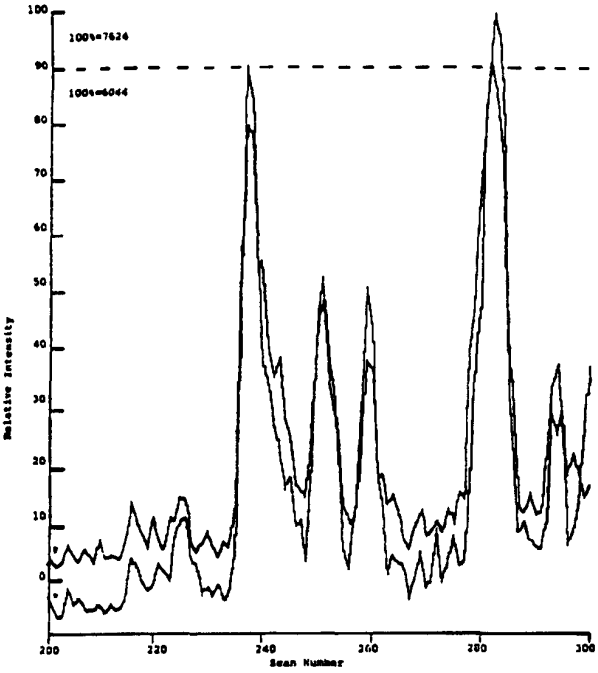

Figure 12. Selected-ion mass chromatograms obtained from HRGC/LRMS analysis of ENSCO test 2, train 1 Florisil sample (TRW No. 6-0609) for tetrachlorinated PCB.

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CHAPTER 10

ULTIMATE DISPOSAL OF POLYCHLORINATED BIPHENYLS

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Polychlorinated biphenyls (PCB) present a difficult problem for conventional waste disposal systems. They are very stable chlorinated organic molecules that require long dwell times at high temperatures to effect thermal destruction. Present incineration guidelines suggest a 2.0-sec dwell at 1200°C or a 1.5-sec dwell at 1600°C. These combinations are difficult to achieve in incinerators, yet can be easily achieved in a plasma system. However, these guidelines may be extremely conservative for a plasma system, for two reasons. First, since radiative heat transfer proceeds as a function of the fourth power of the temperature differential, a plasma system is capable of transferring energy approximately six million times faster than conventional incineration. Second, organic chlorides are known to dehalogenate when excited by ultraviolet (UV) light. It thus may be conceived that a plasma system possesses properties conducive to ultimate destruction of organic halogens such as PCB. A test was conducted to qualify this belief, and a further $400,000 test program,

funded by the Ministry of the Environment of the Province of Ontario, is presently under way for toxic waste destruction at the Royal Military College in Kingston, Ontario.

PCB COMPOSITION AND USES

PCB is the name given to a series of aromatic organochlorine homologs and isomers having the chemical composition $C_{12}H_{10-n}Cl_n$. PCB is a double benzene ring linked by a C-C bond and having 10 possible chlorine substitutions per molecule. Theoretically, this configuration results in 210 PCB isomers, having low water solubilities, low volatilities, and a high degree of resistance to chemical and thermal degradation. In general, solubility and volatility decreases with increasing chlorine substitution, whereas resistance to breakdown increases. A further important property of PCB is high solubility in organic solvents. The chemical stability of PCB coupled with excellent electrical insulating capabilities led to extensive use as dielectric fluids in capacitors and transformers. PCB were also used as hydraulic and heat transfer fluids, as wax and pesticide extenders, in carbonless reproduction paper and in other minor applications. Since the discovery of the toxic effects of PCB, their use has been limited to closed systems where release into the environment is minimal.

Commercial production of PCB started in 1929, 48 years after the first reported chemical synthesis of these compounds [1]. In North America, the sole producer was Monsanto, which supplied 99% of U.S. and Canadian requirements. Monsanto marketed a range of PCB products, trademarked Aroclor, which contained varying mixtures of chlorohomologs. For example, Aroclor® 1254, which has an average chlorine *content of 54%, contains four homologs in varying amounts.*

Total U.S. production to date has been estimated at 1.45 billion pounds, reaching an annual high of 85 million pounds in 1970. Monsanto's voluntary ban on production for open system usage in 1970–1971 reduced annual production to 40 million pounds. Production ceased in 1977. Canadian imports have been estimated at 75 million pounds plus an unknown amount imported in the form of finished electrical goods [2].

PCB IN THE ENVIRONMENT

PCB are ubiquitous in the environment. They have been found in ocean sediments, the atmosphere, and a large number of terrestrial and aquatic

locations, including both polar icecaps. Of local concern is the Great Lakes ecosystem, which contains among the highest recorded ambient PCB levels. For example, in Lake Ontario, the water has a measured concentration of 45 ppt, the sediment has 72 ppb and certain fish more than 2.5 ppm. Ontario citizens have the highest PCB residues in Canada: males have 1.125 ppm and females, 0.859 ppm in adipose tissue [3].

The major routes of PCB into the environment are leaks from sealed or partly sealed systems, spills and losses during manufacture, vaporization or leaching from PCB-containing formulations, and disposal of waste PCB [4]. The presence of PCB in the atmosphere and in areas remote from heavily industrialized locations indicates that atmospheric transport is the major route of global dispersion. In large ecosystems, PCB input from atmospheric deposition is the greatest source of contamination, exceeding point sources such as sewage treatment plants and industrial sites [5-7].

In an aquatic environment, PCB spread through the water column from the air-water interface to the bottom sediment. Aquatic fauna accumulate PCB through equilibrium partitioning and food sources, the latter predominating in higher trophic levels. Because of the chemical inertness and resistance of PCB to metabolism, magnification within the food chain has been observed. Predatory fish have the highest concentration factors, about 10^6. Concentration factors for water, sediment, and plankton in Lake Ontario are $1:2500:10^5$ [8-11]. The principal source of PCB uptake in humans is the diet [12]. Although fish provide the greatest input, PCB have been found in small concentrations in poultry, meat, produce, dairy products, food wrapping and other household articles [13].

PCB are truly pervasive in the environment and will remain so for a long period of time. Temporal trends show no discernable evidence of a decrease in ambient PCB concentrations, despite the Monsanto ban.

TOXICOLOGY OF PCB

PCB are not particularly toxic in acute or short-term testing. Very high dosages are necessary to induce a lethal response in most trophic levels. However, chronic exposure to sublethal concentrations combined with high lipid solubility and resistance to metabolism can result in PCB accumulation and a toxic response. Synergistic effects of other contaminants and environmental stresses are not fully understood, but they may intensify the toxic effects of PCB.

In zooplankton and marine algae, PCB in 10-ppb concentration have

been observed to alter community growth rates by as much as 80%. Growth of algae greater than 8 μm was inhibited by an order of magnitude, changing the population distribution. The community had not fully recovered after 10 days in a PCB-free environment [14-18].

Higher forms of aquatic life also showed toxic responses. Concentrations of 10 μg/l caused decreased shell growth in oysters and higher mortality rates in shrimp and several types of fish. Reproductive success of Atlantic salmon and rainbow trout has been affected adversely by high PCB residues in eggs. Pathological repsonses to sublethal dosages of PCB were found in livers, kidneys and spleens of experimental fish.

Birds have also been studied widely to determine the effects of PCB poisoning. Species reproductive success has declined as a result of eggshell thinning. PCB are but one of several organochlorine substances, such as DDT and Mirex, that are implicated. Highest body residues are found among raptors and birds whose chief source of food is fish [11].

In Japan, a PCB poisoning incident known as "yusho" provided information on the effects of PCB to humans. Rice oil, contaminated with 1000 ppm PCB, was ingested by about 1200 people. Total body burdens were about 2 g, resulting in PCB concentrations of up to 75 ppm in subcutaneous fat. Patients complained of constant abdominal pain, poor appetite and general fatigue. External symptoms of poisoning were acneform eruption, pigmentation, swelling of eyelids, eye discharge and deformation of nails. The principal organs affected were the liver and skin [19].

There is a small body of evidence to link PCB with carcinogenesis. Rats developed benign lesions in the livers and experienced an increase in the number of cells in the liver whereby the bulk of the organ was increased. These reactions are similar to effects of known hepatocarcinogens prior to the appearance of carcinoma. Among yusho patients, 9 of 22 deaths in subsequent years were caused by malignant neoplasms, suggesting a possible excess of deaths from cancer [11,19].

LEGISLATION AND DISPOSAL

As a result of a recommendation by the Organization for Economic Cooperation and Development (OECD), and after many national studies, many countries imposed restrictions on PCB use and disposal. In Canada, this responsibility is divided among the various levels of government. The Canadian government has issued guidelines on storage, handling and disposal of PCB, although no disposal technology is in place. These guidelines permit release of PCB to the environment in low

concentrations such as road oiling with oil contaminated with less than 25 ppm of PCB [20]. Such guidelines will only increase the environmental burden of PCB and may encourage dilution as a solution to the present toxic waste storage problems.

Approximately 450,000 kg of PCB plus an unknown amount of contaminated solids are presently awaiting ultimate disposal in Canada. Ontario, with 91% of this total, has no licensed disposal site. With disposal stockpiles growing at an annual rate of 500,000 kg, it is clear that an effective method of disposal is urgently required.

PLASMA ARC TECHNOLOGY

Plasmas have been referred to as the fourth state of matter, because they do not always behave as either a solid, liquid or gas. A plasma may be defined as a gas consisting of charged and neutral particles, having an overall charge of approximately zero, which exhibits collective behavior [21,22]. Within the universe, as much as 99% of matter, including stars and interstellar space, is in the plasma state [23]. On earth, plasmas are much less prevalent, but the aurora borealis, lightning bolts, fluorescent and neon lights, and arc welding are common examples. They all exhibit a common property of plasmas, an ability to readily conduct electricity.

Electrical arcs are used in day-to-day applications in arc welding. Arc welders are characterized by very short arcs and by electrodes that are quickly destroyed by the process. To create longer arcs, an innovation was required to increase the stability of the discharge at the higher voltages. Initially, the plasma arcs destroyed themselves in a matter of minutes. Subsequent developments have led to plasma arcs that do not destroy the electrode, while producing a transferred plasma arc with excellent dimensional stability. Arcs in general require a great deal of maintenance, primarily because they are uncontrollable at elevated voltages, and therefore require huge amounts of current to develop large amounts of power. The development of a marketable plasma torch was undertaken to reverse the high-current/low-voltage requirement. The torch at the royal Military College Plasma Arc Research Facility demonstrates very clearly the success of that effort. Plasma systems no longer need to destroy themselves and require only very little maintenance.

The plasma arc can best be understood by thinking of it as an energy conversion and transfer device. A low-pressure gas is used as the medium through which an electrical current is passed. The type of gas used is relatively unimportant in creating the discharge, but will affect the

ultimate products formed. In passing through the gas, electrical energy is converted to thermal energy by absorption by the gas molecules. The gas molecules are activated into ionized atomic states with equivalent temperatures of about 50,000° K. In relaxing from these activated states, radiation is given off for absorption by material fed into the plasma.

As a result of energy absorption, waste feed materials are atomized and ionized as they interact with the decaying plasma species. This process is one of molecular fracture rather than a chemical oxidation reaction typical of incineration. The products that result are simple because the activated states are atomic. This reflects the much more energetic nature of the radiation supplied by the plasma discharge compared to the oxidation processes involved in combustion. Furthermore, the volume of gaseous products is much less than the volume produced in combustion and thus greatly reduces the scale of commercial equipment. Figure 1 shows the reaction vessel, the liquid feeding apparatus and the product gas scrubbing system presently being used for plasma pyrolysis of liquid waste material.

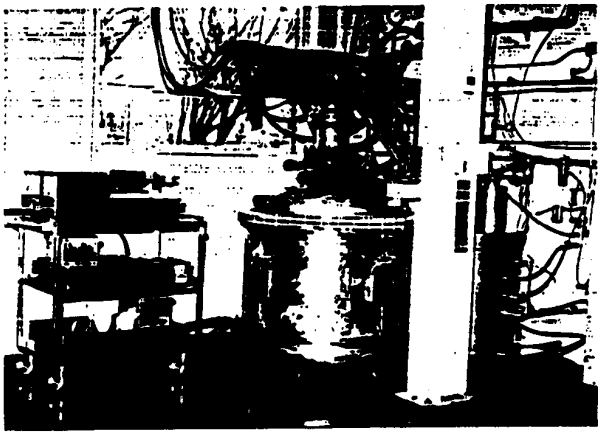

Figure 1. Reaction vessel system.

The reaction vessel is fabricated from stainless steel and is refractory-lined to limit heat loss to less than 10% of the applied power. The plasma torch, which is inserted through the top of the vessel, is rated from 60 to 350 kW and is water-cooled to prevent torch destruction. The gas scrubbing system consists of a water-injected venturi scrubber, a wet cyclone and a scrubbing water reservoir as shown in the schematic of the system in Figure 2.

Water from the scrubber reservoir is injected into the venturi at a rate of 15 liter/sec to quench hot product gas from 900° C down to 50° C, and to wet carbon soot entrained in the product gas stream. The wetted gas then passes through the cylcone, where > 99% of the water is extracted from the product gas. The extracted water is returned to the 200-liter scrubber reservoir, where it is cooled before being recirculated through the scrubbing system. The entire product gas stream then passes through the glass impinger network, which is designed for a gasflow approaching 40 liter/sec. The impinger network is chilled with ethylene glycol and dry ice to promote exceptional trapping of organic species produced during pyrolysis of liquid wastes. The impinger network is shown in Figure 3.

An integral part of the application of this plasma arc technology is the computerized pyrolytic simulation model based on kinetic equilibrium. If plasma forces rapid atomization of organic compounds injected into the

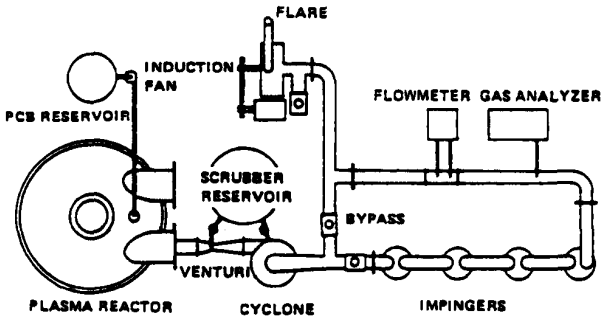

Figure 2. Schematic of PCB test equipment.

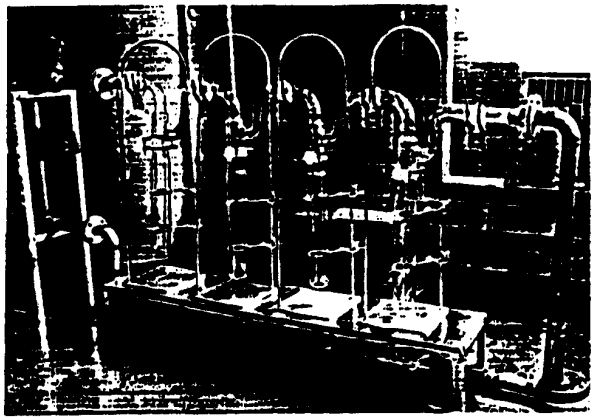

Figure 3. Impinger network.

plasma, then recombinations of new molecules from the atomic species formed should be predictable based on kinetic equilibrium. The computer model is used to predict the composition of products formed from waste feedstocks and the amount of plasma energy required to effect pyrolysis. Equilibrium and material balance equations are used to determine the concentrations of product species formed over a range of equilibrium temperature for selected operating conditions. Changes in enthalpy between the feedstock and the output products are used to predict the quantity of plasma energy required adiabatically for the pyrolysis of organic matter. This approach to predicting the performance of the plasma pyrolysis process has been tested and supported with experimental data which is published elsewhere [24]. This computer simulation is used to determine suitable test conditions.

INITIAL PCB TESTING

The first test was conducted to demonstrate qualitatively the destruction of a 27,000-ppm concentration of PCB in toluene [25]. During the test, 1.6% of the product gas was continuously drawn through a dual ethylene glycol impinger system, with a rated capture efficiency of 99.6%. The gas was also monitored by an infrared (IR) analyzer for methane, carbon dioxide and carbon monoxide concentrations. Subsequently, PCB analysis by gas chromatography (GC) was carried out on the impinger liquids.

A Miran 80 single-beam infrared spectrophotometer was used for quantitative analysis of the product gas for CO, CO_2 and CH_4. The gas flowed continuously through the 1-cm cell at 8 liter/min, with analyses performed at 1-min intervals. Each wavelength was scanned approximately 15 times during each analysis. An Intel 8080A microprocessor then applied Beer's law to the measured absorbances and the absorbance constants stored in memory to calculate the concentration of each component.

A Varian Aerograph Model 920 gas chromatograph equipped with a thermal conductivity detector was used for analysis of impinger fluid for PCB presence. The helium carrier gas flowed at a rate of 90 ml/min, through the 13-ft × 1/4-in. copper chromatographic column packed with 5% S.E. 30 on Chromosorb P. The isothermal temperature settings were 295° C for the injector, 265° C for the column and 310° C for the detector. A filament current of 180 mA was used in the thermal conductivity detector.

An Askarel sample consisting of Aroclor 1254 and trichlorobenzene in the ratio of 68 ± 2% (as analyzed by the Ontario Research Foundation) was used to determine the characteristic chromatogram of the Aroclor 1254 and the limits of detection. From a standard solution of 68 mg in 5 ml of spectranalyzed hexane, five 10-μl and three 1.0-μl samples of solution were analyzed. The effective lower limit of detection was judged to be 10 μg of Aroclor 1254.

A typical chromatogram of a 10-μl injection is shown in Figure 4, and a chromatogram of the extracted impinger residue is shown in Figure 5.

Assuming the worst case, that the gas chromatograph results represent PCB only, integration of the curve showed that no more than 10 mg of PCB were collected in the impingers. The destruction efficiency is conservatively estimated to be greater than 99% from this qualitative test. A comparison of the two chromatograms presented clearly shows the conservative nature of the claim made to the destruction of the Aroclor 1254.

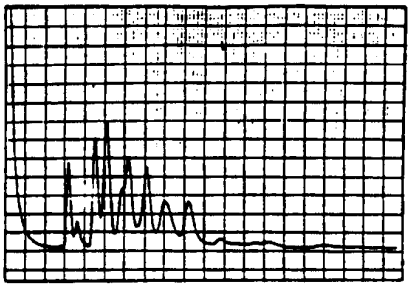

Figure 4. Chromatogram of 10 μl Aroclor 1254.

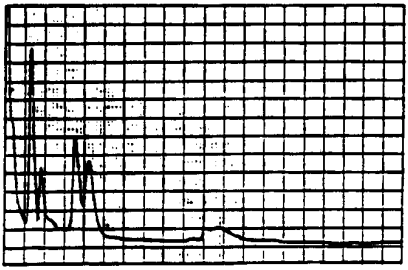

Figure 5. Chromatogram of impinger residue.

Although this test was qualitative in nature, it yielded a number of significant observations. The results indicated that the plasma torch was capable of destroying PCB with a high degree of efficiency. It was evident that the principal limitation to the determination of the destruction efficiency was the efficacy of the sampling and analysis procedures

and not the plasma torch. Specifically, the sampling and analysis phase did not incorporate 100% offgas testing, the identities of the organic compounds in the GC scan were unknown and the impinger did not ensure 100% PCB collection. The adiabatic plasma energy required for pyrolysis was less than 0.6 kWh/kg of solution and represents only about 10% of the fuel value of this waste feedstock.

To improve the analytical results, several steps are necessary. Since these results are based on one test, more tests are obviously required to ensure repeatability. High resolution and high sensitivity will require a gas chromatograph with a better detector, such as an electron capture detector (ECD). A gas chromatography/mass spectrometry/computer (GC/MS/COMP) system will be necessary to identify the extraction residue, assuming it is not PCB. With the financial assistance of the Ontario Ministry of the Environment, we have begun a comprehensive testing program.

COMPREHENSIVE TESTING PROGRAM

A series of tests has been conducted using ethanol, methanol and methanol with trichlorobenzene as liquid wastes. The purpose of these tests was to demonstrate the performance of the plasma system and to establish the degree to which energy and material balances could be determined. These feedstocks were used as precursors to future PCB tests to minimize any pollution dangers. Computer simulations based on waste atomization and kinetic equilibrium reformations were conducted before each test to establish suitable test conditions.

Although many chlorinated organic destruction demonstrations have shown a reduction in concentration of the waste of interest in the test effluent, few have been able to identify the location of the chlorine and complete a chlorine balance (even on a macroscopic basis). If a chlorine balance can be demonstrated, the perceived dangers of producing large quantities of other harmful organic chlorides during the destruction of PCB compounds are greatly minimized. Rather than using PCB to attempt a complete chlorine balance, mimicking ring-structured compounds such as chlorobenzenes can be used to test the ability of the experimental apparatus to capture chlorine compounds.

According to computer simulations of the destruction of a solution of trichlorobenzene in methanol (500 g in 3 liters) virtually all the chlorine should form hydrogen chloride. Minor amounts of other chlorine compounds formed should be present in concentrations of less than 5 ppm. If the computer model is accurate, hydrogen chloride would be found in the scrubbing water reservoir and the trace amounts of other chlorinated compounds should be isolated in the impinger network.

Changes in the pH of the scrubber reservoir during the test sequence were used to estimate the extraction of hydrogen chloride from the product gas. Obviously, unless some neutralization of the pH in the reservoir is simultaneously carried out, the rate of hydrogen chloride removal in the venturi will diminish as the pH of the scrubbing water drops. Nevertheless, the initial rate of pH change can be used to predict the rate at which hydrogen chloride is captured in the venturi, and can be compared to the theoretical production rate to determine the efficiency of the scrubbing. Additional tests with neutralization of the hydrogen chloride eliminated carbonic acid interference, which is prevalent at high pH values, and provided total chlorine mass information.

For the tests using trichlorobenzene in methanol, where no neutralization is carried out, the initial rate of change of pH showed that the venturi scrubber mechanism was better than 98% effective in extracting the hydrogen chloride. Without neutralization and based on total change in pH, approximately 70% of the chlorine could be accounted for in the scrubber reservoir. However, with neutralization, using sodium hydroxide, more than 96% of the mass of chlorine could be accounted for in the scrubbing water. It is believed that problems with scrubbing water pumps and reduced fluid flows during the last minutes of these tests are responsible for allowing the escape of a minor amount of hydrogen chloride during these tests. Neutralization was carried out so as to maintain only slightly acidic conditions in the scrubbing reservoir to minimize interference from carbonic acid.

Trace analyses for trichlorobenzene in the scrubbing water reservoir showed a presence of less than 0.00013 of the mass of trichlorobenzene fed to the system during each test. It is perceived that this material enters the scrubbing system as a result of the shutdown procedure rather than short-circuiting of the waste during the test. Impinger residue analyses showed no confirmed presence of trichlorobenzene based on GC/ECD findings. However, if the area under the chromatogram spanning the theoretical location of trichlorobenzene is used as an indicator of the residue, less than 0.0001 of the material survived the plasma system. This

gives a destruction efficiency greater than 99.99%. The estimate of the impinger residue presently is believed to be high by several orders of magnitude.

More than 80% of the energy injected into the system can be accounted for by direct measurement. The remaining 20% cannot be practically measured, but is consistently accounted for by wall losses from the test system and energy added to the thermal mass of the system. The energy balance calculations support the theoretical change in enthalpy predicted for the feedstocks by the computer simulation.

The 12 chlorobenzenes were selected as mimicking compounds because they have a wide range of solubilities and vapor pressures and can be mixed to give elemental compositions identical to commercial PCB. Two of the three trichlorobenzenes are also present in the Aroclors. Chromatographic separation of the 12 chlorobenzenes is easily accomplished using capillary column GC, and their quantification is easily possible. Thus, material balances and destruction efficiencies could be readily determined while minimizing the risk of social displeasure associated with this work.

During each test, a combination of 4- and 9-in.-diameter impingers was used. Internal calibration to determine impinger trapping efficiency was conducted during each test by injecting known amounts of monobromobenzene. The larger impingers were packed with 20-mm Raschig rings and contained 500 ml of ethylene glycol as a wetting agent. At the end of each test, each impinger was injected with a known quantity of orthodibromobenzene to be used as an indicator of the effectiveness of the extraction procedure. Extraction efficiency was better than 99%, and impinger trapping efficiency was comparable. Additional work is now underway to improve material balances and determination of destruction efficiencies with PCB testing commencing in fall 1981.

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CHAPTER 11

CHEMICAL DESTRUCTION OF POLYCHLORINATED BIPHENYLS IN TRANSFORMER OIL

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One consequence of the restrictions on the use of polychlorinated biphenyls (PCB) enacted into law by Congress in 1976 and subsequently promulgated into regulation by the U.S. Environmental Protection Agency (EPA) has been to create a need for nearly total removal of trace-level PCB from some still uncertain fraction of the 1.5 billion gallons of specially refined mineral oil (10C oil) currently in use in U.S. transformers. A known generic approach to selective destruction of aromatic chlorides like PCB in hydrocarbon media at low temperatures consists of treatment with reactive anion radicals, formed by interaction of sodium metal with an electron carrier in an aprotic cation-complexing solvent or as an intermediate in a free radical chain reaction. Experimental evaluation of the interactions of a number of sodium/electron carrier/solvent systems with 10C oils containing 125–800 ppm of Aroclor® 1254 or 1260 showed that most of the sodium adduct was consumed by reaction with the 10C oil rather than with the PCB, particularly when only low levels of ion-complexing solvent were present. Marked reductions in solvent requirements could be achieved, however, by forming the presumed

adduct in situ, e.g., by simply stirring together the PCB-containing oil, finely dispersed sodium, catalytic quantities of an electron carrier (such as benzophenone or naphthalene) and an ion-complexing solvent, such as diglyme (DGM). Using various specimens of PCB-containing 10C oil that had been used in transformers, removal of PCB to gas chromatographically undetectable levels (0 ± 2 ppm) could thus be effected in simple process equipment within a few minutes at room temperature.

ORIGIN OF NEED FOR REMOVING TRACE PCB FROM 10C OIL

Between the mid-1930s and 1977, two generic types of dielectric fluids were used in the manufacture of ordinary, liquid-filled, industrial, utility and distribution transformers. The more widely used of these was 10C oil. This is a specially refined mineral oil derived from naphthenic base crudes from certain wellfields. It was selected for its arc-quenching ability (i.e., its ability to consume hydrogen atoms generated by corona via addition reactions rather than H_2-producing H-abstraction reactions) and its resistance to autoxidation in use. Chemically, it consists of the same sort of complex mixture of hydrocarbons as found in a low-viscosity lube oil, but with an aromatic content of 15–30% (depending on source), provided mainly by alkyl benzenes and naphthalenes, and a sulfur content of 0.03–0.24%.

The less commonly used type bore the generic name "askarel" (which denotes any nonflammable dielectric fluid) and a variety of manufacturers' trade names, such as General Electric's "Pyranol" and Westinghouse's "Inerteen." Askarels, being more expensive than 10C oil, were used only where the fire hazard was considered sufficient to warrant the extra cost, for example, in transformers for indoor commercial or industrial use, or in transformers used on railroads. Virtually all of the askarels used consisted of mixtures of PCB (usually, Aroclors 1254 or 1260, which were themselves complex mixtures of PCB homologs and isomers averaging five or six chlorines per biphenyl residue, respectively) and polychlorinated benzenes (mixed isomers of tri- and/or tetrachlorobenzene).

Generally speaking, both oil- and PCB-filled transformers were manufactured and repaired in common facilities. As a result, trace levels of each type of dielectric often found their way into transformers of the other type. For many years such contamination attracted no attention, because it did not affect the performance of a specific dielectric in its designed use.

Beginning in 1966, however, it was discovered that PCB were highly persistent in the environment and were accumulating to ppm levels in fish and fish-eating wildlife around the world. As a result, in the early 1970s there were (1) voluntary restrictions by manufacturers on the sale of PCB, which were allowed only for totally enclosed uses, such as in capacitors and transformers; (2) provision of incineration facilities for destroying returned scrap PCB; and (3) development of biodegradable types of PCB for capacitor use.

Subsequently, however, investigation [1] of an outbreak of "yusho" disease in Japan traced it to the consumption of rice oil that had accidentally been contaminated with heat exchanger fluid, which consisted of a PCB that had been pyrolyzed to a mixture of polychlorinated quaterphenyls and dibenzofurans. Consumption of this oil resulted in transient accumulations of undecomposed PCB in the victims' adipose tissues, chronic accumulation of some toxic penta- and hexachlorodibenzofuran isomers in their livers, and chronic manifestation of chloracne symptoms. This evidence of human hazard led to widespread demands for tight controls on PCB use in Japan, Sweden, Canada and the United States.

In response, Congress enacted the Toxic Substances Control Act (TSCA), of 1976 which generally banned PCB manufacture, importation, distribution, processing or use, and directed EPA to define procedures for the marking and disposal of residual stocks. In regulations promulgated in 1979, EPA set forth such procedures, but excluded from the disposal requirements PCB contained in intact, nonleaking capacitors or transformers and mixtures containing PCB at concentrations less than 50 ppm. As a result of a court challenge by the Environmental Defense Fund, however, EPA is currently reexamining these exclusions.

The 1979 regulations themselves, however, already mandate special ultimate disposal procedures for somewhere between 300 and 600 million gallons of the 10C oil that is currently in service in transformers or transformer systems, because of contamination with more than 50 ppm of PCB. Since 10C oil is a valuable commodity, for which production capacity is only about 100 million gallons per year, it would seem desirable to develop methods for decontamination and reuse of this oil, rather than simply to dispose of it.

In principle, removal of PCB from mineral oil could be effected by a separation or destruction process. The former would separate the oil into two fractions: a PCB mixture for separate disposal and a PCB-depleted oil for reuse. The latter would solve the PCB disposal problem and give a reusable oil in a single step; therefore, it presumably would be preferable. However, current EPA regulations have been interpreted to require that a

PCB destruction method that is an alternative to disposal by incineration must achieve an equivalent level of performance, or >> 99% destruction. Thus, reusable oil prepared by a PCB separation process may contain up to 50 ppm PCB, the lower limit for legally defined "PCB contamination," but that prepared by a PCB destruction process must contain no PCB, within the limits of analytical uncertainty, currently defined as about 2 ppm.

In summary, although it is impossible to predict future regulatory developments in this area, current requirements create an immediate need for small-scale, decentralized facilities for processing batches of oil provided by transformer repair and servicing operations. The challenge facing the chemist is to devise treatment processes that will consistently remove PCB down to levels below 50 ppm, if done by separation, or to 0–2 ppm, if done by PCB destruction.

PRIOR USE OF SODIUM OR ANION RADICALS TO DESTROY PCB

PCB are generally unreactive materials. Many of their past applications were, in fact, based on their great thermal and chemical inertness. About the only class of chemical reactions they are known to undergo at low temperatures are electron transfer processes effected by anion radicals, such as the sodium adducts of certain aromatic hydrocarbons.

The use of metallic sodium itself is apparently effective only at elevated temperatures. A Japanese patent [1] reports that 6 hr at 120°C was required for the removal of PCB from kerosene, or 2 hr if catalytic quantities of isopropanol were added. A Goodyear report [2] indicates that heating with molten sodium to 300°C for 6 hr was required for the removal of PCB from a heat transfer oil.

Conversely, the intensely colored solutions prepared by dissolving sodium metal in solutions of certain aromatic hydrocarbons in aprotic, cation-complexing solvents such as tetrahydrofuran (THF) or DGM are known to react readily with organic halides. The deep blue adduct of sodium and biphenyl is frequently used as an analytical reagent for quantitatively converting organic to inorganic chlorides, and the deep green adduct of sodium and naphthalene has been reported to act similarly on the PCB [3].

Two reports [2,4] have described the reaction between this 1:1 sodium:naphthalene adduct (naphthalenide anion radical) and PCB in THF solution at 60°C in some detail. From examining these reports and the prior literature [5] it becomes evident that a number of types of

chemical reactions can occur in such systems. These generic types of interactions, summarized in Table I, include the reversible formation of 1:1 (Equation 1) and sometimes 2:1 (not shown) adducts between the sodium and electron carrier; a variety of forms of attack on the solvent system, including hydrogen abstraction, alkoxide elimination and metallation processes (Equation 2); reductive dechlorination of the aromatic halide, presumably via electron transfer followed by fragmentation, which produces inorganic chloride and aryl radicals (Equation 3); occasional reduction of the aryl radical by hydrogen abstraction or metallation (Equations 4 and 5); and a variety of radical recombination processes (Equations 6–9). The reported data [4] on the interaction between preformed sodium naphthalenide and various Aroclors in THF solution indicates a net consumption of PCB, naphthalene and THF in roughly comparable molecular proportions and the formation of chlorine-free, soluble resinous products, which we may presume to have been complex mixtures of species derived from various recombination processes, (Equations 6–9).

Table I. Generic Types of Reactions Known to Occur During Interactions Among Sodium Metal (Na), Cation Carriers (B), Electron Carriers (C), and Aromatic Chlorides (ArCl) in Organic Media

Adduct Formation	
$Na + xB + C \rightarrow NaB_x^+ + \cdot C^-$	(1)
Solvent Attack, Metallation	
$\cdot C^- + RH \rightarrow \cdot R, R^-, CR^-$, etc.	(2)
Dechlorination	
$\cdot C^- + ArCl \rightarrow C + Cl^- + \cdot Ar$	(3)
Aryl Radical Reduction	
$\cdot Ar + RH \rightarrow \cdot R + ArH$	(4)
$\cdot Ar + \cdot C^- \rightarrow C + Ar^-$ ($+ H_2O \rightarrow ArH$)	(5)
Aryl Radical Recombination	
$2 \cdot Ar \rightarrow Ar_2$	(6)
Mixed Radical Recombination:	
$\cdot Ar + \cdot R \rightarrow ArR$	(7)
$\cdot Ar + \cdot C^- \rightarrow ArC^-$ ($+ H_2O \rightarrow ArCH$)	(8)
$\cdot R + \cdot C^- \rightarrow RC^-$ ($+ H_2O \rightarrow RCH$)	(9)

Several papers have described light- [6], radiation- [7] or peroxide-initiated [8] free radical chain reactions between alkali, isopropanol and PCB to give inorganic chloride, acetone and biphenyl. These processes have been presumed to proceed by a pathway analogous to that of the Sherman mechanism [9]: the reversible formation of isopropoxide (Equation 10), its conversion to the anion radical (Equation 11) and attack of the latter on PCB (Equation 12):

$$Me_2CHOH + OH^- = H_2O + Me_2CHO^- \quad (10)$$

$$Me_2CHO^- + {\cdot}Ar - ArH + {\cdot}Me_2CO^- \quad (11)$$

$$Me_2CO^- + ArCl - Cl^- + Me_2CO + {\cdot}Ar \quad (12)$$

The process of Equation 11 is obviously analogous to that of Equation 4, and that of Equation 12 is analogous to Equation 3. From the latter we may conclude that ketone as well as hydrocarbon anion-radicals are capable of attacking PCB molecules at low temperatures.

The question of how well an anion radical-mediated PCB destruction process might perform in a medium that was predominantly 10C oil rather than a cation-complexing solvent is not resolved by either of these bodies of prior literature. In such a medium one might expect the adduct formation equilibrium (Equation 1) to be shifted to the left; solvent attack processes (Equation 2) to be favored over PCB attack (Equation 4); and possible complications from radical reduction processes (Equations 4 and 5), which would mean that incompletely dechlorinated PCB molecules would still appear in the gas chromatogram as PCB, albeit of lower degrees of chlorination, rather than as constituents of a nonvolatile resin.

ASSESSMENT OF SODIUM ADDUCT-PCB INTERACTIONS IN 10C OIL

To assess the pattern of interactions among sodium adducts, PCB and 10C oil, 0.5 *M* solutions of various 1:1 and 2:1 adducts were prepared by stirring together under nitrogen the appropriate quantities of sodium metal (40% dispersion in light mineral oil, from Matheson, Coleman, and Bell), the selected cation-complexing solvent (dried over a Linde 4A molecular sieve), and the selected electron carrier. The resulting intensely colored solutions were then added, a few milliliters at a time, to 100-ml portions of askarel-contaminated 10C oil, with stirring under nitrogen at room temperature. After the color disappeared from each portion of the adduct, and before addition of the next portion, a sample of the oil was removed for gas chromatographic determination of its PCB content,

which was done by comparing eight of the more prominent peak heights with those in Aroclor 1254 or 1260 standards.

Generally speaking, decolorization of the first few milliliters of added adduct occurred almost instantly in all cases, but with no change in PCB levels, indicating consumption of the adduct by traces of highly reactive non-PCB species such as H_2O, O_2 or carboxylic acids. The colors of subsequent portions of the adducts generally persisted for 1-5 minutes, except in the case of the 1:1 sodium-benzophenone adduct (sodium diphenylketyl), which reacted more slowly.

The titration curves obtained by plotting % PCB removed as a function of the relative amount of adduct added exhibited the general features shown in Figure 1. In most cases, as illustrated in the lower part of Figure 1, the initial flat was followed by a pseudo-linear decline of PCB with added adduct until a rather sharply defined point of PCB disappearance was reached. In all such cases, there appeared to be little difference in the relative reactivities of the different PCB isomers; the individual peaks in the gas chromatogram maintained roughly the same relationship to each other as they declined. Conversely, during titration with the 1:1 sodium-benzophenone adduct (upper curves, Figure 1), disappearance of species in the Cl_6-Cl_8 biphenyl range was accompanied by an initial sharp rise in concentration of those in the Cl_4-Cl_5 range, and then followed by a slow and incomplete disappearance of the lower homologs. Evidently, this reagent was far more reactive with higher- than with lower-chlorinated biphenyl homologs, and some constituent of the reaction system, presumably benzhydrylate (by analogy to Equation 11), was capable of transferring hydrogen to the radicals formed from the higher homologs so as to give the reduced products observed.

Returning to the more usual case, where there were no complications arising from partial reduction of PCB, the first notable feature of the titration curves shown at the bottom of Figure 1 was their low slopes, which indicated that most of the sodium adduct was being consumed by reaction with species other than PCB. Similar behavior has also been reported for reactions of sodium naphthalenide/THF with PCB in heat transfer oil [2]. The second significant feature was their roughly linear (rather than hyperbolic form), indicating that the *relative* rates of attack on PCB must have been increasing with increasing volumes of titrant solution in the medium. The latter point was also illustrated by the comparative titrations of 10C oil solutions containing 120 and 800 ppm of PCB; it generally required only 2-5 times as much titrant to destroy seven times as much PCB.

The approximate relative efficiencies of a number of different adduct-solvent combinations in the removal of Aroclor 1254 or 1260 from 10C oil

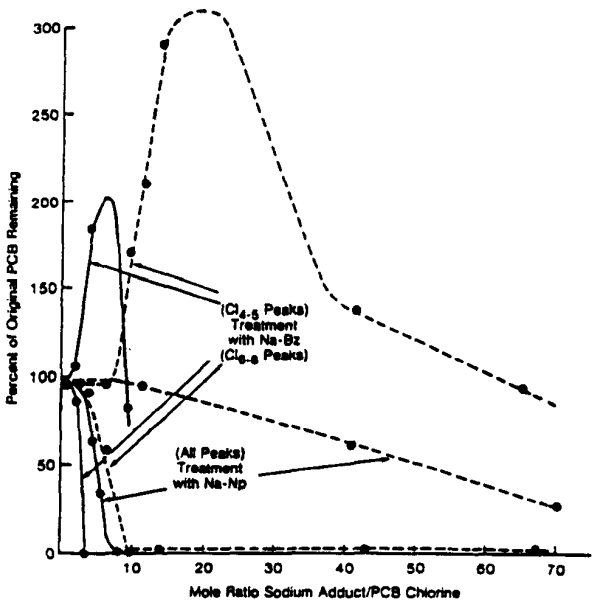

Figure 1. Changes in PCB levels resulting from titrations of 10C oils containing Aroclor 1254 (----), 120 ppm, or Aroclor 1260 (———), 800 ppm, with 0.5 *M* solutions of sodium adducts of benzophenone (Bz) or naphthalene (Np) in diglyme or tetrahydrofuran, respectively, at room temperature.

are shown in Table II. Generally speaking, the relative activities in attacking the less reactive PCB species (rather than unidentified components of the 10C oil), as indicated by the quantities of the adduct solutions that had to be added to achieve complete removal of the PCB, were roughly comparable for the 1:1 sodium:naphthalene adduct, the 2:1 sodium:biphenyl adduct and the 2:1 sodium:benzophenone adduct. They were somewhat higher for the 2:1 sodium:naphthalene adduct, which formed a very slowly reacting black suspension in the system, decidedly higher for the removal of the more highly chlorinated PCB homologs by the 1:1 sodium:benzophenone adduct, and decidedly lower for the removal of the lower homologs (i.e., all PCB) by that adduct.

Table II. Approximate Effectiveness of Various 0.5 *M* Sodium Adduct Solutions in Destroying PCB[a] in 10C Oil at Room Temperature

Adduct Former[b]	Na-Adduct Ratio	Solvent[b]	PCB Type[c]	PCB Conc. (ppm)	ΔPCB/ΔNa	% Soln. for 99% Δ PCB (v/v)
Bz	1:1	ETH	1260	800	0.06[e]	f
Bz	1:1	THF	1260	800	0.04[e]	f
Bz	1:1	DGM	1260	800	0.08[e]	f
Bz	1:1	DGM	1254	120	0.4 [e]	f
Bz	1:1	TGMT	1260	800	0.9 [e]	f
Bz	2:1	TGMT	1260	800	0.7 [e]	>>10
Np	1:1	THF	1260	800	0.03	20
Np	1:1	GLM	1260	800	0.02	>20
Np	1:1	DGM	1254	120	0.003	>25
Np	2:1[g]	DGM	1260	800	0.05	8[g]
Bp	1:1	THF	1260	800	0.002	>>20
Bp	2:1	GLM	1260	800	0.02	15

[a] As measured by disappearance of gas chromatographic peaks in range characteristic of Cl_4–Cl_8 biphenyls. Unless noted (e), all such peaks disappeared at approximately same rate.

[b] Key: Bz, benzophenone; Np, naphthalene; Bp, biphenyl; ETH, ether; THF, tetrahydrofuran; DGM, diglyme; TGMT, 1:2 tetraglyme-toluene; GLM, glyme.

[c] Aroclor 1260, mainly mixture of C_3–Cl_7 biphenyls; Aroclor 1254, mainly mixture of Cl_4–Cl_8.

[d] Ratio of moles PCB lost per mole adduct sodium added determined from approximate slope near middle of titration curve.

[e] Data for peaks in Cl_6–Cl_8 biphenyl range only.

[f] Not yet demonstrated that any quantity of the 1:1 Na-Bz adduct solution sufficient to remove the less highly chlorinated PCB homologs.

[g] Presumed adduct formed by dispersing solid Na-in-naphthalene dispersion (Coronet Chemical Co.) in diglyme; formed black suspension rather than solution: reactions with PCB/10C required several hours rather than minutes.

Several rather poorly reproducible experiments using tri- or tetraglyme (which are apparently harder to obtain in consistent purity) suggested higher ΔPCB/ΔNa ratios than exhibited in runs using DGM as the ion-complexing solvent; conversely, somewhat lower ratios were shown by monodentate complexers such a THF or diethylether (Table II).

The overall conclusion drawn from these experiments was that if one desired to destroy the PCB in 10C oil with reasonable speed and efficiency by adding to the oil a near-saturated solution of a reactive sodium adduct, roughly 20 volumes of adduct solution would be required per 100 volumes of oil, almost regardless of the choice of adduct or PCB level in the oil. Since the effective ion-complexing solvents are all about 10 times as costly as 10C oil, and since they would almost certainly alter its dielectric

properties and thermal stability if appreciable amounts were left in oil destined for reuse, it was evident that any practical use of preformed adduct solutions for PCB removal would have to be followed by some reasonably efficient recovery of the ion-complexing solvent.

CATALYZED SODIUM PROCESS FOR DESTROYING PCB IN 10C OIL

To determine whether such substantial needs for ion-complexing solvents in the reaction system could be reduced, we conducted a number of experments in which prior formation of the adduct was eliminated. In these experiments, various types and levels of electron carriers, cation-complexing solvents, and commercial sodium dispersions were added to Aroclor 1260-containing 10C oil with stirring under nitrogen at room temperatures, and the mixture was checked periodically for disappearance of both sodium and PCB.

It was observed that there was considerably more batch-to-batch variation in the reactivity of the sodium dispersions than was encountered during preparation of the sodium adducts in ion-complexing media. Most freshly opened commercial samples appeared to react completely with the 10C/PCB/electron carrier/ion carrier mixtures within an hour, leaving only a fine gray haze of suspended sodium chloride particles. However, in a few cases, reaction was complete within a few minutes, and some older dispersion specimens did not react at all. Evidently, in media consisting of 10C oil containing only 1–5% of ion-complexing solvent, the reaction with electron carrier was more sensitive to inhibition by oxide films on the dispersed sodium particles than in those composed by solvent alone. The rate of sodium disappearance did appear to be related to the quantity of cation-complexer present, but this proportionality was difficult to quantify because of the variability in the dispersion reactivity. Sodium disappearance was accompanied by that of the PCB in roughly the same proportions as observed using solutions of the preformed adducts, i.e., most of the sodium was consumed by reactions with constituents of the 10C oil rather than with PCB, hence, large excesses of sodium were still required for complete PCB removal.

Reaction of the sodium with PCB and 10C oil depended not only on the presence of the anion carrier, but also on that of the electron carrier. In parallel experiments using 10C oil containing 800 ppm Aroclor 1260, 5% DGM, and 0.23% sodium with or without 0.32% naphthalene, elimination of the PCB required an hour in the first case and a week in the second. Even in that latter case, an electron carrier may have been

involved: most 10C oils are known to contain some alkyl naphthalenes, and the reaction medium in this case did exhibit the typical deep green color of a 1:1 naphthalene adduct by the end of the week. We have also learned, from another laboratory where this process was being checked, that some Texaco 10C oils, which are particularly high in alkyl naphthalenes, do not require naphthalene addition for successful dechlorination [10].

A number of parallel runs were made using either benzophenone or naphthalene as the electron carrier, without revealing any significant differences in reaction rates or efficiency of PCB removal. In both cases, the Cl_4–Cl_7 biphenyl isomers all disappeared at roughly the same rate without evidence of stepwise reduction, and the reactions proceeded without ever developing more than traces of the intensely colored 1:1 adducts. From these, we concluded that the reactive intermediate was some species other than the 1:1 adduct present in the preformed solutions used earlier, and instead was probably either a soluble 2:1 adduct or else some sort of a surface complex.

The performance of the sodium/naphthalene/DGM system on a number of different specimens of PCB-containing 10C oil, all taken from transformers returned for service work, is summarized in Table III. From these data it was concluded that contaminants arising during transformer use would not seriously interfere with use of this system for PCB removal.

Table III also points out that in some runs, which were examined by electron-capture gas chromatography just after the disappearance of the dominant Cl_4–Cl_7 biphenyl peaks of the Aroclor 1254 or 1260, there remained some weak peaks in the retention range covered by the Cl_2–Cl_4 biphenyl peaks of Aroclor 1016. A few of the peaks had retention times similar to those of 1016, and we could not exclude the possibility that such mixtures contained trace of the lower-chlorinated biphenyls, in addition to other electron-capturing species, such as sulfur compounds or autoxidation products. Fortunately, on continuation of the sodium treatment, these enigmatic peaks disappeared in all cases.

To examine the feasibility of process scaleup, a 55-gal drum was equipped with a lid, stirrer and provision for flushing with nitrogen. In a typical experiment, this was charged with 40 gal of PCB-containing 10C oil (which was pumped in through a 30-in. column of 1/16-in. pellets of Linde 4A molecular sieve, #87956, to remove any water present), 4 lb of a 20% dispersion of sodium in mineral oil (Coronet Chemical Co., Newark, NJ) and a solution of 1 lb naphthalene in 2 gal DGM (diethylene glycol dimethyl ether; Ansul Chemical Co., Marietta, WI). Gas chromatographic analysis showed the initial level of Aroclor 1260 to be 852 ppm; after 15 min, 17.6 ppm; after 60 min, 1 ppm.

Table III. Reductions in PCB Levels Resulting from Stirring Randomly Selected Specimens of Used PCB-Containing 10C Oil with Diglyme, Naphthalene and Dispersions of Sodium Metal (0.24% w/v; 0.10 *M*) Under Nitrogen at 24°C

Initial Aroclor 1260 (ppm)	% (v/v) Diglyme Solution Added[a]	Initial Naphthalene in 10C Oil[a] (*M*)	Reaction Time (min)	% Reduction in PCB	
				Lower Peaks[b] (1% of Initial 1260)	Higher Peaks[c] (99% of Initial 1260)
930	5	0.025	30	92	100
434	3	0.015	30	98	100
434	3	0.015	30	98	100
410	3	0.015	40	98	100
410	3	0.015	40	92	100
180	3	0.030	30	98	100
180	3	0.030	30	100	100
180	5	0.025	30	100	100
180	5	0.025	30	99	100
372	3	0.030	30	98	100
372	3	0.030	30	100	100
372	5	0.025	30	98	100
372	5	0.025	30	98	100
336	2	0.010	30	99	100
336	2	0.010	60	96	100
336	3	0.015	10	99	100
333	1	0.010	15	92	91
333	1	0.010	30	99	100
333	2	0.020	15	100	100

[a] Naphthalene introduced into 10C oil by adding 1-5% (as indicated) of 0.5 or 1.0 *M* solution in diglyme.
[b] Electron capture gas chromatographic peaks mainly in range characteristic of trichlorobiphenyls; some, but not all, corresponding to positions of peaks in Aroclor 1016.
[c] Peaks mainly in range characteristic of penta-, hexa- and heptachlorobiphenyls.

A portion of the resulting Na-treated, but unwashed, oil, which was initially almost clear except for the NaCl haze, and no more colored than the original 10C oil, was allowed to stand with exposure to air for several weeks. As a result, the oil developed a purple color and deposited most of its sodium salts as a black precipitate that appeared reddish-purple in thin layers. This deposit, after filtration and washing with hexane, reacted with water without gas evolution to produce sodium hydroxide and a light yellow, water-insoluble, hydrocarbon-soluble resin.

Examination of this resin by gel permeation chromatography showed a broad, weakly bifurcated peak, with the two maxima at positions corresponding to those of linear polymers with molecular weights of 310 and 620, respectively. (On the same columns, 10C oil itself gave an asymetrical

peak, having a centroid and a maximum at points corresponding to polymers of molecular weights 242 and 161, respectively; the actual average molecular weight of 10C oil is about 250.) Examination by gas chromatography showed the lower-molecular-weight population to be a very complex mixture, and field desorption mass spectrometry indicated a detectable peak at almost every mass number between 150 and 350. The UltraViolet (UV) spectrum of the resin resembled that of an alkyl benzene, with a sharp maximum near 272 mμ, but with some broadening on either side. The nuclear magnetic resonance (NMR) spectrum indicated an aromatic/aliphatic proton ratio of 0.43. The infrared spectrum revealed prominent carbonyl and hydroxyl (i.e., carboxylic acid?) bands in a specimen that had been aged a year; however, these were less evident earlier. It was concluded that the precipitated purple salt was probably an autoxidation product derived mostly from metallation and coupling products of various constituents of the 10C oil (e.g., via processes like Equations 2 and 9), rather than from those of the PCB.

However, the available data do permit certain conclusions to be drawn regarding the nature of the PCB conversion products. First, it is evident from the absence of stepwise reduction products (which were easily detected in the case of treatments with preformed sodium diphenylketyl) that aryl radical reduction reactions (Equations 4 and 5) must be rather unimportant in these heterogeneous systems. Second, the absence of any high-molecular-weight polycondensates or insoluble polybiphenyl gels indicates that aryl radical recombination reactions (Equation 6) must also be unimportant. According to classical polymer gelation theory, gelation in a polycondensation of hexafunctional monomers should occur when the reaction is only 20% complete. In addition, we might note that no gelation has been reported even in systems using high concentrations of PCB [2,4], which would favor aryl-aryl coupling; hence such coupling would appear particularly unimportant in systems where the PCB levels are only 100–1000 ppm. Accordingly, we conclude that most of the radicals generated by the removal of the chlorines from the PCB molecules must be consumed via mixed radical recombination processes (Equation 7 and 8), and hence that the PCB conversion product must consist of an extremely complex mixture of molecular species, each of which contains a single biphenyl nucleus linked to 4–7 aralkyl hydrocarbon, dihydronaphthalene or glycol ether residues. Such a product would be similar to asphalt in its chemical and environmental properties.

It is thus apparent that catalyzed sodium processes of the types just described are capable of removing PCB from transformer oil down to the levels sought by the EPA without the formation of objectionable products. Moreover, such processes are capable of being carried out in a

single step at room temperature in simple process equipment and hence are suitable for small-scale, decentralized operations. A minimal objective of such operations would be to render scrap transformer oil acceptable for sale as fuel. Still undetermined is whether the 10C oil treated by this or any of the alternative PCB-removal processes, all of which tend to alter the levels of multicyclic hydrocarbons and/or sulfur compounds, as well as those of the PCB and chlorobenzenes, still possesses the long-term oxidative and dielectric stability required for reuse in transformers; however, active research on this question is currently in progress [10].

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CHAPTER 12

LIGHT-ACTIVATED REDUCTION OF CHEMICALS FOR DESTRUCTION OF POLYCHLORINATED BIPHENYLS IN OIL AND SOIL

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Successful commercialization of synthetic halogenated organics began in the early twentieth century. Since that time, halogenated organics have been used in a wide variety of products, including pesticides, plastics, heat transfer fluids and dielectrics. Ecological damage caused by halogenated organics in the environment was first brought to public attention in 1962, with the publication of *Silent Spring* [1]. Since this publication, a large amount of research has been conducted to determine the environmental dangers of these compounds. In general, the halogenated organics are highly persistant in the environment. They also tend to bioaccumulate and cause devastating damage to certain species of wildlife and, ultimately, man. Probably the most insidious of the halogenated compounds produced by man are the polychlorinated biphenyls (PCB). These compounds were widely used as dielectrics in transformers and capacitors, and as heat transfer agents in heat exchangers from 1929 through 1978. In 1978 the U.S. Environmental Protection Agency (EPA) published its proposed rules, which prohibited the manufacture, processing, distribution and use of PCB except in totally enclosed systems [2]. However, the problem that still remains is how to safely dispose of the billions of

gallons of waste transformer oil containing PCB and how to remove the PCB from the environment.

Atlantic Research Corporation (ARC) has addressed the problem of destruction of halogenated organics in wastes and the environment with the development of the light-activated reduction of chemicals (LARC) process. This process was originally developed for destruction of Kepone; however, research has shown that the destruction of PCB extracted from soils and in transformer oils is economically feasible with the LARC process.

LARC is a patented process [3] that uses ultraviolet (UV) light in the 1850- to 4000-Å region in combination with hydrogen gas and optimized photochemical conditions to effect dehalogenation of complex chlorinated and brominated organic molecules. UV light initiates the photochemical process by homolytic cleavage of the carbon-halogen bonds. The conditions are optimized to maximize this cleavage and the resultant formation of a carbon-hydrogen bond. Mass spectral data from LARC reactions run in deuterated solvents show that the hydrogen for the reduced organic may come either directly from the hydrogen gas or from the solvent, depending on the solvent involved. In either case, hydrogen gas plays a significant role in the photoreduction process since the same reactions with nitrogen substituted for hydrogen proceed at much slower rates.

The LARC process has been applied to reductive dehalogenation of several compounds, of which the most environmentally significant are Kepone in water and PCB from soils and in oils. This chapter discusses research on LARC degradation of PCB from soils and in oil conducted at ARC.

EXPERIMENTAL

Two LARC reactors were used in this research: a single-lamp tube reactor and a 64-lamp pilot unit. These reactors are shown in Figures 1 and 2. Both reactors contain low-pressure UV lamps with 95% of their output at 2537 Å. The lamps are surrounded by quartz sleeves, which allow greater than 90% transmission of the 2537-Å light. The hydrogen gas is introduced into the reactors via 2.0-μ fritted stainless steel spargers. The pertinent reactor parameters are:

	Tube Unit	Pilot Unit
Number of Lamps	1	64
Capacity (liters)	0.600	40
Light Path Length (mm)	5.33	6.35
Radiant Energy at Lamp Sleeve Surface (mW/cm^2)	36,300	29,400
Hydrogen Flowrate (liter/min)	0.26	1.9

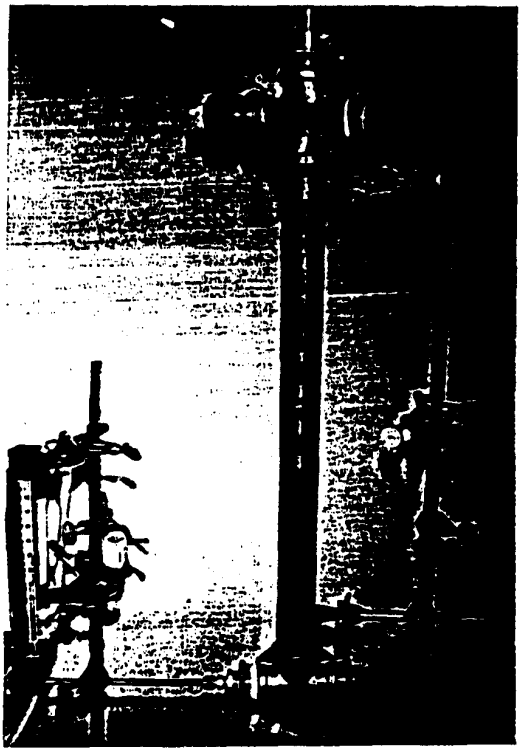

Figure 1. Single-lamp LARC reactor.

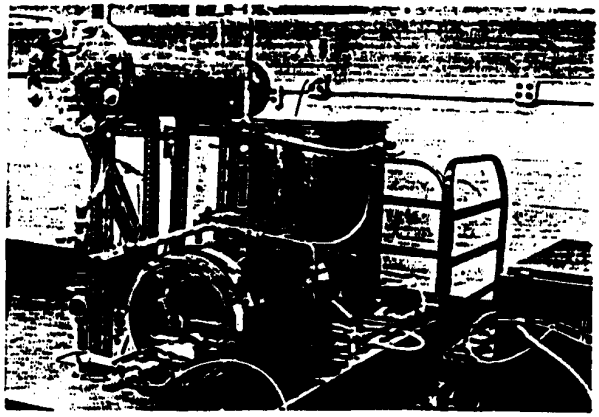

Figure 2. Pilot LARC reactor.

Both units are capable of flow-through or bath-recycle operation.

Analysis for PCB and PCB degradation products was performed on a Hewlett-Packard 5880 or Varian 3700 gas chromatograph (GC) with electron capture detector (ECD) for PCB and flame ionization detector (FID) for biphenyl. The following gas chromatogaphic conditions were used:

- column: 1.95% OV 17/1.5% OV 210 on Anakrom Q;
- temperature: injection port—300°C; oven—programmed from 135 to 225°C at 20°C/min; ECD or FID—300°C; and
- carrier gas: nitrogen at 25 ml/min

Before GC/ECD, the PCB-containing solutions were diluted with benzene to a PCB concentration less than 2 ppm.

PCB IN SOIL

If LARC is to be useful for destruction of PCB in soils, the PCB must first be extracted from the soil. Several solvents were evaluated for their

ability to extract the PCB from soil without previous treatment and for their ability to act as a LARC solvent. A clay soil containing approximately 2000 $\mu g/g$ of Aroclor 1242 was used in this investigation. The Aroclor 1242 had been spilled on this soil approximately 10 years previous to the extraction experiments. Of the potential solvents with suitable UV transmission characteristics for LARC, the low-molecular-weight alcohols were found to be the most suitable extractants. Methanol, ethanol and isopropanol all yielded >88% extraction efficiencies with each extraction step.

The extract was then filtered, as shown schematically in Figure 3. Solid sodium hydroxide was added to the filtrate, and the filtrate was subjected to LARC treatment. The extracted soil can then be returned to the original site. Excess alcohol can be removed from the soil by blowing warm air over the filter or by seeding the soil with an actively growing culture of *Pseudomonas* sp. After LARC degradation of the PCB, the alcohol can be reused after distillation to remove the PCB degradation products, sodium chloride and biphenyl.

The effectiveness of methanol, ethanol and isopropanol as LARC solvents for Aroclor 1242 was then determined. As shown in Figure 4, isopropanol was the best of the three solvents, with 85% of the PCB degraded after a 20-min reaction time. In methanol or ethanol, only 43 and 74%, respectively, of the Aroclor 1242 was decomposed after 20 min.

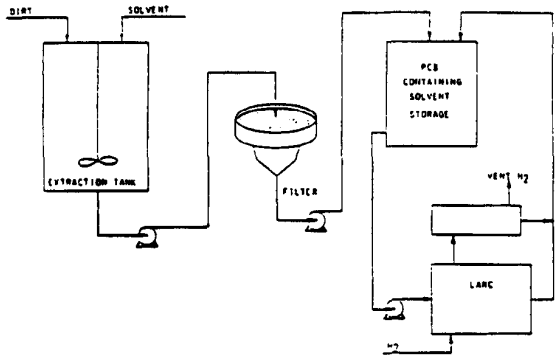

Figure 3. Schematic of extractor/LARC procedure for removal of PCB from soil.

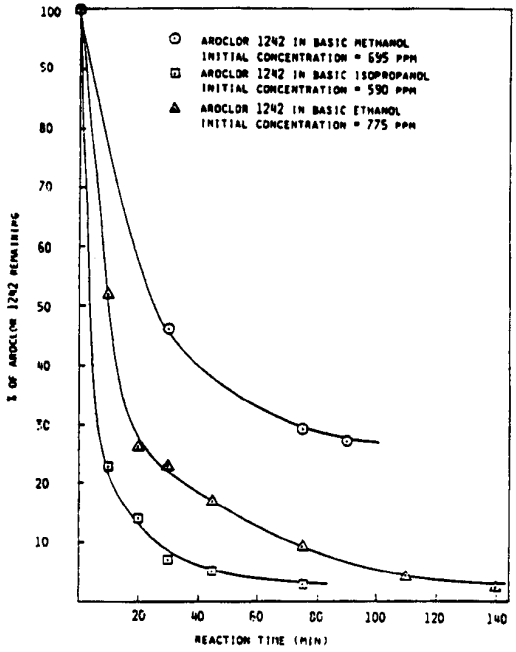

Figure 4. LARC degradation of Aroclor 1242 in various solvents.

The rates of LARC reduction of the various Aroclors (1242, 1254 and 1260) extracted from soil were investigated. Isopropanol was used for the extractions, and solid sodium hydroxide was dissolved in the isopropanol extract before LARC. The single-lamp reactor was used in most of these studies. For comparison purposes, a run was made in the pilot unit using the Aroclor 1260 basic isopropanol extract. The results of this investigation are presented in Figures 5 and 6. The plot of $ln\ C_o/C$ vs reaction time shows an initial and final degradation rate. The rate constants calculated from these plots are:

	Aroclor	k_i (min^{-1})	k_f (min^{-1})
Single Lamp Reactor	1242	0.080	0.0206
	1254	0.086	0.046
	1260	0.112	0.032
Pilot Reactor	1260	0.238	0.056

The initial degradation rates appear to increase with increasing chlorination of the biphenyl, i.e., with higher Aroclor number. The final degradation rates are 25–50% of the initial rates. Dechlorination of Aroclor 1260 initially proceeds about twice as fast in the pilot unit as in the single-lamp

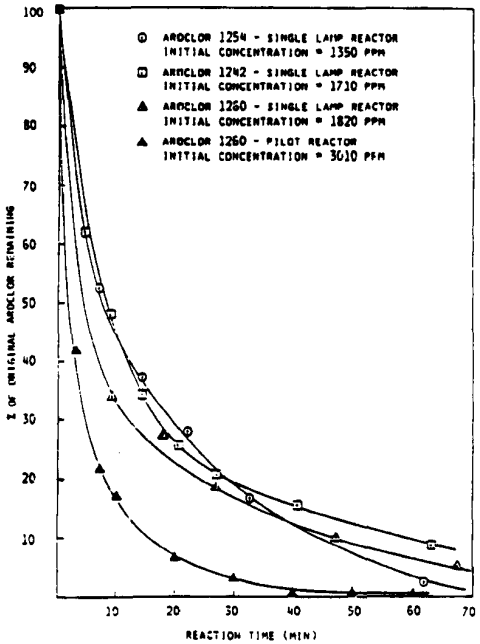

Figure 5. LARC degradation of Aroclor 1242, 1254 and 1260.

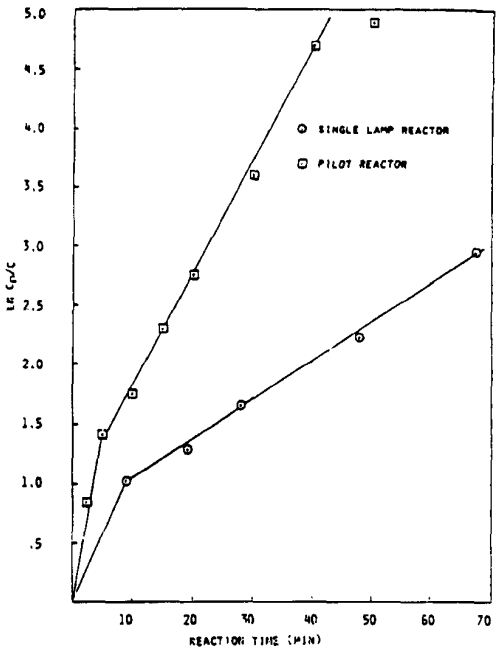

Figure 6. Comparison of degradation rates of Aroclor 1260 in the single-lamp and pilot reactors.

reactor. This increased degradation in the pilot unit is due to the higher light flux and optimized temperature and flow pattern.

Several experiments were conducted to determine the practical upper concentration limit for LARC degradation of Aroclor 1260 in basic isopropanol. The practical maximum initial concentration is approximately 3500 ppm. Concentrations $\leq$5000 ppm can be employed. However at higher concentrations, the reaction rate declines due to the increased amount of the interfering biphenyl final product.

PCB IN OILS

Before LARC can be successfully used for degradation of PCB in oils such as transformers and heat exchanger fluids, several basic problems associated with photochemical degradation of PCB in mineral- and silicon-based oils must be overcome. These problems include:

- UV light-absorbing oil degradation products are present in many transformer fluids.
- Most of the oils are not good hydrogen sources.
- Some of the oils are too viscous for adequate dispersion of the hydrogen gas.
- The PCB degradation product is a yellow-brown polymer substance that also absorbs UV light.

Cleanup of the transformer fluids to remove the brown to black UV light-absorbing oil degradation products can be accomplished with chromatographic processes. Commercial transformer cleanup operations use fuller's earth or some other chromatographic medium to remove these degradation products from the oil. Transformer oil cleaned up by these processes should be of sufficient clarity for LARC degradation of PCB.

Several diluents were evaluated to decrease the viscosity of the transformer oils and to provide a good hydrogen source to aid the LARC reaction:

Constituents	Ratio
Oil:Hexane:Isopropanol	5:3.75:1.25
Oil:Isopropanol:Hexane:Diethylether	8:1:0.5:0.5
Oil:Tetrahydrofuran	7:3
Oil:Tetrahydrofuran	8:2
Oil:Tetrahydrofuran	9:1
Oil:Tetrahydrofuran:Basic Methanol	8:1.5:0.5
Oil:Tetrahydrofuran:Isopropanol	7:2:1

For these experiments, clean mineral oil was used as the oil. The oil mixtures were spiked with Aroclor 1260 to give initial PCB concentrations of 1000–2000 ppm. In all cases, the rate of LARC destruction of PCB was faster than for PCB in the mineral oil alone. The addition of tetrahydrofuran further improved the PCB degradation rate over that of the hexane formulations. The rates for Aroclor 1260 degradation did not vary with the amount of tetrahydrofuran added in the tested 10–30% range. The addition of basic methanol also did not improve the PCB degradation rate over that of the 9:1 oil:tetrahydrofuran mixture. The addition of isopropanol to the oil:tetrahydrofuran mixture significantly improved the initial degradation rate (Figure 7).

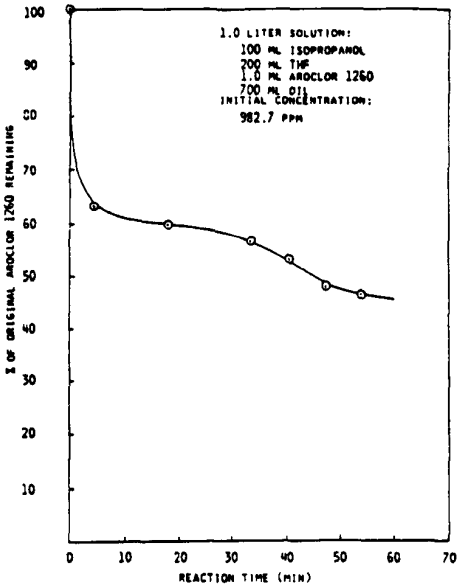

Figure 7. LARC degradation of Aroclor 1260 in oil.

The reaction mechanism appears to be rapid dechlorination of the PCB with concurrent formation of hydrochloric acid and a nonchlorinated yellow-brown substance that is believed to be a polyphenylene. No evidence of chlorinated furans or chlorinated dibenzofuran was found in mass spectra of the degradation products.

As shown in Figure 7, formation of the yellow-brown substance significantly inhibits further degradation of the Aroclor 1260, and must be removed. Several solvent extraction procedures have been evaluated for removal of this substance. One method that appears to work satisfactorily is a proprietary aqueous extraction technique. The reaction products from the experiment in Figure 7 were subjected to batch extraction and retreated by the LARC process. The results, shown in Figure 8, indicate that this extraction procedure does remove the

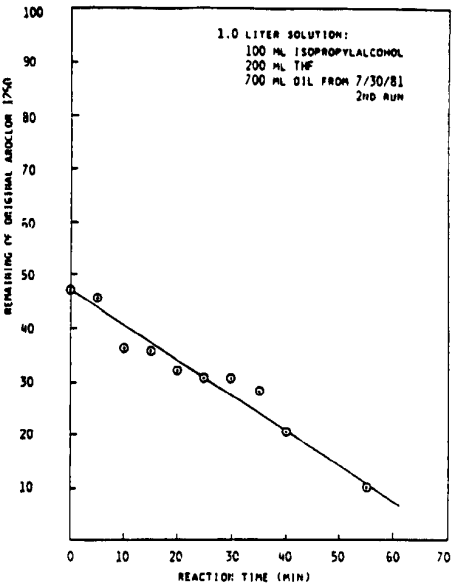

Figure 8. Continued LARC degradation of Aroclor 1260 after extraction of polyphenylene product.

interfering product and allows the PCB degradation to proceed at a reasonable rate. ARC is investigating a continuous extraction method for removing the yellow-brown substance from the oil.

CONCLUSIONS

LARC degradation of PCB extracted from soil with isopropanol is a feasible process. Degradation of PCB in transformer oil requires both cleanup of the initial oil and removal of the yellow-brown final product before LARC degradation of PCB in this medium is effective. Cleanup of the transformer oil is commercially available technology. Removal of the

degradation product is effective in a batch process. Continuous extraction of this degradation product is currently under evaluation.

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CHAPTER 13

CATALYZED WET OXIDATION OF HAZARDOUS WASTES

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Small chemical companies and formulation operations have always been faced with the difficult problem of economically treating low-volume aqueous and organic hazardous wastes. Economies of scale for thermal incineration or biological treatment can be achieved only by large-volume waste streams. Small waste generators therefore must use commercial waste disposal services. However, many companies desire to have total control over the cost and proper disposal or destruction of their wastes. Therefore, a hazardous waste treatment process that is capable of destroying and/or detoxicating low-volume waste streams at reasonable cost to the waste generator is desirable. There are a number of existing treatment methods that are capable of either completely (using expensive reagents) or partially (using an inexpensive reagent) destroying hazardous wastes. However, there is a treatment process under development that combines the advantages of a number of treatment methodologies into a system that offers the small hazardous waste generator an alternative to offsite disposal or treatment services. The process, catalyzed wet oxidation (CWO), harnesses the potential of powerful oxidizing species to oxidize organics to carbon dioxide, water and inorganic salts with the economy of using the oxidation potential of oxygen.

The CWO process is based on a U.S. patent [1] which demonstrates the use of nitrate and bromide or iodide ions in an acidic solution to catalyze

the oxidation of organics by oxygen. The catalyst system originally was developed for oxidizing soluble organics in aqueous wastes, but has been modified to permit its application to insoluble organic residues. An improved catalyst system for these applications is described in another U.S. patent [2].

WET OXIDATION OF ORGANICS

The concept of wet combustion of organics is aimed at reducing the energy required for treating a waste, and uses an inexpensive and readily available reagent: oxygen or air. The energy reduction is twofold. The first savings results from a lower operating temperature than other destruction processes (for example, thermal incineration, which requires temperatures up to 1200°C to destroy chemical wastes). The second savings of a wet combustion process results from organic oxidation in the aqueous phase, rather than in a vaporized or gas phase, which requires energy for vaporizing the water associated with the waste. The chemistry of wet oxidation [3] relies on the formation of free radicals, which oxidize the organics. Oxidation of the organic results in the formation of additional organic radicals that propagate the reaction sequence:

$$RH + O_2 \rightarrow R^{\cdot} + {}^{\cdot}OOH \quad (1)$$

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot} \quad (2)$$

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \quad (3)$$

There are two major considerations in maximizing the rate of the above reactions: oxygen availability and the formation of radicals. Although oxygen availability in aqueous solution is very low at room temperature because of solubility and diffusion limitations, oxygen availability is much greater at wet oxidation temperatures (315°C) [4], and is no longer rate-limiting. However, the main limitation for wet oxidation processes is the formation of radicals, which is considered to be a relatively slow and probably rate-limiting step. Radical formation via reaction of molecular oxygen (Equation 1) with the organic molecule is one of the postulated sources of radicals that initiate the organic oxidation sequence. Another postulated source of radicals is an equilibrium between water and oxygen that generates hydroxyl radicals, a very powerful oxidant.

Both conditions for radical formation are met in commercially produced wet oxidation systems. To achieve these conditions, operating temperatures of 220–320°C with corresponding pressures of 1000–2500 psig are required. The CWO process addresses these considerations by

using the bromide-nitrate catalyst to achieve similar or better organic destruction rates at lower temperature and pressure.

CATALYTIC WET OXIDATION

The catalysts used in the CWO process are capable of accelerating the chemical sequences that occur in wet combustion processes through a series of reactions with oxygen and specific bromine and nitrogen compounds. The major impact of the catalyst system is to lower the temperature of the organic destruction process. These reactions and the chemical species produced perform the same basic functions already described in wet combustion chemistry. The mechanisms by which the catalysts operate have been postulated after extensive experimentation with the aqueous bromide-nitrate catalyst, and examination of the literature on the reported mechanism for wet combustion of organics in aqueous solution to obtain an understanding of how the CWO process achieves faster destruction rates for waste organics.

The first of the three roles performed by the catalyst system is to increase the transfer of oxygen into the aqueous medium at relatively low temperatures. Although this transfer occurs in uncatalyzed wet combustion, it is a slow process, due to the low solubility of oxygen at temperatures below 200°C. The bromide-nitrate catalyst system accelerates the transfer of oxygen into solution through the complex reactions of the oxides of nitrogen and their solubility in the aqueous catalyst solution:

$$2\ NO + O_2 \rightleftharpoons 2\ NO_2 \tag{4}$$

$$2\ NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3 \tag{5}$$

$$H_2O + HNO_3 + 2\ NO \rightleftharpoons 3\ HNO_2 \tag{6}$$

$$HNO_2 + HBr \rightleftharpoons NOBr + H_2O \tag{7}$$

These reactions and subsequent reactions with bromine/bromide species provide the formation of radicals for the oxidation of waste organics. The principal radical species used in CWO is not the product of oxygen-organic reactions found in wet combustion systems, but is postulated to be a bromine anion radical. This radical is a strong oxidant capable of abstracting hydrogen from organic molecules. Once radicals are formed, the chemistry becomes similar to conventional wet oxidation, except that the CWO catalyst system has the ability to generate other radical species. It is postulated that the formation and use of the bromine anion radical is responsible for the increased destruction rate of organic compounds by

CWO. When the three roles of the catalyst system (oxygen fixation, radical generation and organic oxidation are tied together, it becomes apparent that the bromide-nitrate catalyst system reactions depend on maintaining the proper relationship between liquid catalyst species, gaseous catalyst species, oxygen and the organics to be oxidized.

EXPERIMENTAL RESULTS

The data were generated from experiments in a titanium reactor [5]. The experiments consisted of batch reactions with a variety of organic compounds over varying conditions of time, temperature and catalyst mixtures. After extensive experimentation with the catalyst system, two conclusions were reached. The first conclusion was that the bromide-nitrate catalyst system was capable of destroying organic compounds at much lower temperatures than uncatalyzed wet oxidation. This is demonstrated in Table I. Destroying organics at lower temperatures reduces the operating temperature and resulting pressure of the treatment process. Lower pressures and temperatures reduce the waste treatment cost by lowering the capital cost of the equipment and minimizing operational problems such as corrosion. For certain organic wastes, the operating temperature and pressure are low enough to permit waste treatment using conventional chemical process equipment. This capability makes CWO an attractive waste treatment alternative for small chemical production or formulation operations.

CWO can destroy certain hazardous wastes that are immune to conventional wet oxidation. These compounds are typically very stable and require higher temperature and longer reaction times to achieve acceptable destruction rates. Two polychlorinated biphenyls (PCB), tetrachlorodibenzo-*p*-dioxin (TCDD) and the CWO reaction conditions are listed in Table II. Although the temperatures and reaction times are much

Table I. Organic Destruction by Catalyzed and Conventional Wet Oxidation[a]

	Reaction Time (min)	Organic Destruction	
		Wet Oxidation	CWO
Acetonitrile	30	5%	90%
Diphenyl Hydrazine	30	19%	73%
Pentachlorophenol	30	7%	99%
o-Xylene	60	54%	94%
DDT	60	10%	60%

[a]Reaction temperature: 165°C; catalyst mixture: 0.5% Br^-, 5.0% NO_3^-, 0.25% Mn.

Table II. CWO Destruction Rates for Hazardous Wastes

	Temperature (°C)	Reaction Time (min)	Percent Destruction
Aroclor 1016	200	120	87.8
Aroclor 1254	250	120	97.0
TCDD	200	240	99.5

higher for these waste compounds, it is possible to design a mobile batch reactor process that can destroy hazardous wastes at the waste site. This concept avoids the risks associated with transport of hazardous waste and eliminates the problem of finding a disposal company capable of responsibly destroying the waste.

CONCLUSIONS

CWO can destroy a wide variety of waste compounds. The process destroys organic chemicals at much lower temperatures than conventional wet oxidation systems. The milder operating conditions and resultant process design options make CWO an attractive waste treatment alternative, especially for small waste generators who wish to maintain economic and legal control of their wastes. The improvements associated with the catalysts of the wet oxidation process were achieved through an understanding of the process chemistry and the identification of limiting reactions. Subsequent improvements, such as the bromide-nitrate catalyst, not only reduced the operating conditions and treatment cost, but also expanded the list of wastes suitable for treatment by the process. As we continue to deal with the problems of hazardous wastes and stricter government regulation, we must look at the process chemistry to improve the performance of waste treatment.

ACKNOWLEDGMENTS

We recognize the dedicated efforts by J. Johnson and D. Demott in collecting experimental data. Dr. J. R. Moyer and Dr. R. W. Diesen, Dow Chemical Company, Midland, Michigan, developed the initial catalyst system and made other valuable contributions.

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CHAPTER 14

KINETICS MODEL AND SIMULATION OF CONCENTRATION VARIATIONS OF SPECIES OF POLYCHLORINATED BIPHENYLS INVOLVED IN PHOTOCHEMICAL TRANSFORMATION

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Polychlorinated biphenyls (PCB) are potentially toxic and carcinogenic compounds whose large-scale use over the years has made them ubiquitous in the environment. A recent study by the National Academy of Sciences indicates that total U.S. PCB use as of 1976 was 6.1×10^8 kg [1]. The Atlantic Ocean appears to be a major sink for PCB, accounting for 80% of the PCB burden in the environment. Many freshwater lakes and rivers also serve as sinks for PCB.

Most PCB released into the hydrosphere are expected to end up either adsorbed onto sediment or resting as sludges at the bottom of rivers, lakes and oceans. Transport of PCB in rivers is thought to take place by solution and readsorption onto sediment, and by transport of sediment itself.

Atmospheric transport plays a major role in the worldwide dissemination of PCB [2-5]. Most of the transport of PCB to the North Atlantic is thought to be atmospheric. PCB transport to freshwaters, such as Lake Michigan, is also thought to have an important atmospheric component. PCB released directly into the atmosphere adsorb onto particulates and are transported with the prevailing winds. Particle fallout and precipitation deposit the PCB on land or into a body of water. PCB were presumably released in highest concentrations during 1960–1976, primarily to the air and water near urban, industrialized areas. However, current data show measurable levels of PCB in air, freshwater and marine samples from both industrialized and remote areas, suggesting that contamination is still occurring [6]. The sources of contamination by these chemicals generally include agricultural runoff; municipal applications; and direct discharges into rivers, estuaries and coastal waters by municipal and industrial activities; and power plants [4]. In general, laboratory photodecomposition of lower-chlorinated PCB isomers in both polar and nonpolar solvents reveals a potential parallelism to the environmental mechanisms that could effectively degrade these contaminants [7].

PCB are similar to many chlorinated pesticides, which are known to bioaccumulate to high concentrations in the higher trophic levels. Commercially prepared PCB exist as seven complex mixtures that contain a total of at least 54 chlorinated hydrocarbons (biphenyl). If introduced into the aquatic environment as combinations of the seven mixtures, the system may be considered to be an aqueous solution containing in excess of 50 nonelectrolytes. By including the aquatic organisms and other natural and manmade suspended solids, photodecomposition becomes a primary concern. The toxicity of this system to aquatic communities may be due to photochemical products of oxygenated compounds such as chlorodibenzofurans. Since photochemical products of PCB may be toxic and can accumulate in living organisms, even trace amounts of these compounds may have deleterious effects at higher trophic levels.

Since PCB mixtures occur dispersed in rivers, estuaries and seawater at levels up to 150 ng/l [6,8], appropriate conditions exist for hydroxylation and dibenzofuran-forming environments. Indeed, the notable absence of the lower-chlorinated biphenyls from most environmental samples suggests an important role of photodecomposition in the environmental fate of PCB, the interpretation of their source and movement, and prediction of toxic effects on aquatic life [8]. Photolysis of PCB at wavelengths >290 nm (i.e., sunlight) indicates the environmental significance of such nonbiological degrdation [9]. Due to an interesting set of attributes of PCB, two sets of environmental consequences exist. Most PCB species are

nonvolatile and hydrophobic in aquatic environments. Thus, they will either cluster as aggregates of drops in water or reside at the surface in the hydrophobic, nonpolar, hydrocarbon thin-films that spread over the surface. This latter condition increases exposure of PCB to the ultraviolet radiation of the sun, thus maximizing photochemical decomposition. In an aqueous environment, they would be subject to hydroxylation and subsequent potential formation of chlorinated dibenzofuran. Such conversion, however, is far less likely in the environment than reductive dechlorination.

Creation of free radicals by sunlight allows environmental replacement of chlorines by hydroxy groups from water without the intervention of alkali when this occurs at the *ortho* position (found to be the most preferred for chlorine loss). The resulting 1-hydroxychlorobiphenyl is perfectly positioned to allow oxygen to bond to an *ortho* position on the other ring. This results in formation of the potentially most important class of contaminant in PCB mixtures: the highly toxic chlorodibenzofurans [8]. Dispersal in seawater implies that all but a small fraction of the soluble PCB will be too deep to be affected by photolysis by the sun. Thus, the general inertness of PCB combined with the results of gradient distribution due to differential solubility implies that PCB will probably persist in the marine environment.

The photochemical kinetics model was developed to predict the change in concentrations and formation of predominant PCB under the influence of sunlight in a microsurface layer of aquatic environments. The rate constants of the photochemical reactions and initial concentrations of each chemical species are considered in the kinetic model. The computer code uses the reaction rate constants, average surface temperature and pH of the complex photochemical reactions in surface waters. The kinetics model incorporates the most important photochemical reactions that are known to occur when PCB are discharged into the aquatic environment over relatively long periods of time.

PHOTOLYSIS

One of the most ecologically significant degradation processes of PCB is photolysis in aquatic environments. The accepted route for the photochemical excitation of PCB isomers in the 280- to 320-nm region occurs by a transition of electrons in the ground state to an excited state. From the excited state, which can be singlet, double and triplet multiplicity, the carbon halogen bond undergoes fission, giving rise to aryl and hydrogen radicals. The radicals then abstract hydrogen from the medium or

dimerize. In addition, a hydrogen halide can also be detected. Before bond fission, an alternative reaction between the excited state and nucleophilic species can occur, giving the appropriate substitution product at the C-X bond.

Photochemically induced degradation of isomers and commercially synthesized mixtures of PCB has been reported [10,11]. Reaction rate comparisons in oxygen-saturated and degassed solutions indicated a marked reduction in rates in the presence of oxygen. The cleavage mostly takes place on the 2,2',6,6', *ortho* chlorine substituents. Since biphenyl has a planar excited state geometry, coplanarity between the rings increases conjugation and stabilizes excited state molecules. The *ortho* chlorine substitutes sterically hinder the coplanarity between the phenyl rings. These groups are specifically cleaved in preference to substituents at the *meta* and *para* positions.

It is possible that fission of the *ortho* chlorine substituents is due to stabilization of the transition state by complexation of the leaving halogen atom with the system of the other phenyl ring. Thus the *ortho* position, being closest to the ring, would facilitate cleavage. Substitution by the solvent could occur via nucleophile attack on the triplet or attack on a radical cation. Photolysis of PCB in aqueous solutions showed that dehalogenation and substitution products were accompanied by chlorinated biphenylenes and the highly toxic chlorinated dibenzofurans.

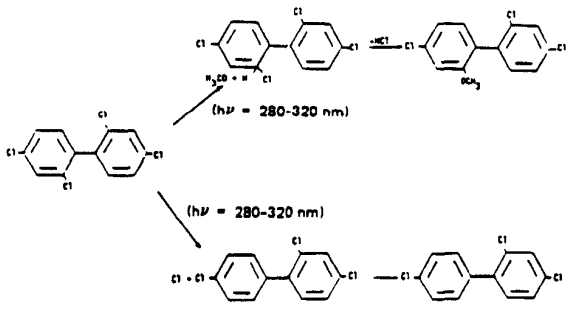

Figure 1. Photochemical dehalogenation of 2,2',4,4'-tetrachlorobiphenyl [9].

Thus, photochemical degradation can both detoxify PCB in aqueous conditions due to the formation of lower-chlorinated PCB isomers, and toxify with the formation of the more toxic chlorinated dibenzofuran and chlorobiphenylol photoproducts. Different pathways operating to give replacement of chlorine by hydrogen and methoxy groups and intermediates inferring the corresponding mechanism are shown in Figure 1.

PHOTOCHEMICAL KINETICS COMPUTATIONAL METHOD

The formulation of the complex photochemical reactions of differential equations reduces to equations for a single-stage photochemical kinetics process [12]. The differential equations for the changes in the reactant concentrations are derived directly from the stoichiometic equations. In the photolysis process, the reactions are assumed to be irreversible and displaced toward formation of the reaction products.

The values of the parameters of reactions and the special initial diluted concentrations were determined on the basis of measured data and theoretical considerations of the photochemical reactions. Most of the photochemical reactions that are known to occur when PCB are exposed to UV irradiation (280–320 nm) and/or sunlight were included in the model.

The photochemical kinetics model uses the basic principle of "law of mass" and considers the photolysis reactions in terms of reaction rates. It predicts the variation of net rate of formation and consumption of the chemical species in the system based on their initial diluted concentrations. The kinetics code calculates the depletion of chemical species as a function of photolysis rates, pH and temperature, and simulates the variations of concentrations as a function of time.

RESULTS AND DISCUSSION

The photochemical kinetics study shows that the chemical nature of the compounds formed in the photolysis process depends mainly on the presence of *ortho*- and *para*-chlorobiphenyls in aquatic systems. Concentration variations of PCB in aquatic environments under the influence of sunlight may not be detectable by conventional measurement techniques. Also, there are analytical difficulties in measuring the highly toxic photolysis products of dibenzofurans in the aquatic environments.

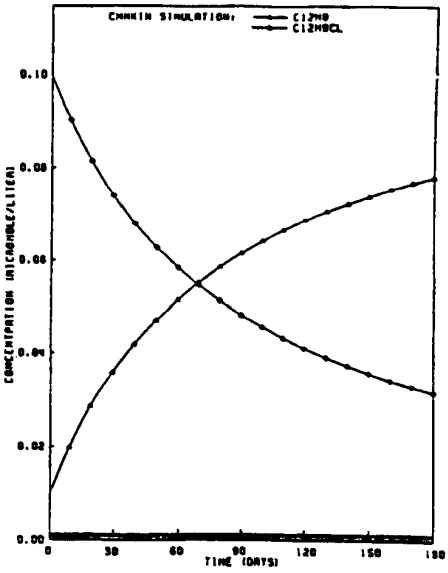

Figure 2. Concentration variations of 4-chlorobiphenyl within a body of water and thin films along the surface of water in six months.

Simulation of a small variation in concentration of the PCB under the influence of sunlight that may not be detectable by the conventional measurement techniques is shown in Figures 2 and 3. Photochemical reactions give three types of products, depending on environmental conditions: (1) chlorine is replaced by hydroxy groups in aqueous systems, (2) chlorine is replaced by hydrogen (reductive dechlorination) in nonpolar systems, and (3) chlorine is replaced by hydroxy groups in polar systems. From the results above it is apparent that dechlorination of biphenyls in aquatic environments proceeds very slowly, with consumption of *ortho*- and *para*-chlorobiphenyl. The results of this study also show that highly chlorinated biphenyls are more stable under the influence of sunlight than less chlorinated biphenyls. The exact reason for the differences in persistence of the highly chlorinated biphenyls is not known, as loss of chlorine is related to the action of hydroxy groups in aqueous systems.

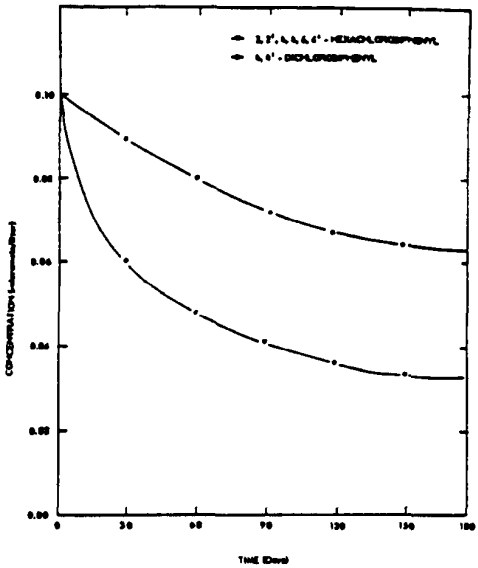

Figure 3. Concentration variations of 2,2',4,4',6,6'-hexachlorobiphenyl and 4,4'-dichlorobiphenyl.

The environmental significance of the formation of chlorinated dibenzofurans is threefold: (1) *ortho*-chlorobiphenyls can be hydroxylated by radiation (sunlight) when they are syspended in aqueous media; (2) the products are converted to chlorinated dibenzofurans; and (3) rates of formation of chlorinated dibenzofurans by this process are the same as their rates of degradation, leading to steady concentrations. The chlorodibenzofurans formed from chlorobiphenyl under photochemical conditions lead to oxygenated products in six months. Dechlorination of PCB exposed to sunlight was also observed to a certain extent. Irradiation of 2,8-dichlorodibenzofuran resulted in slow dehalogenation in aqueous suspension.

These limited results do not allow direct comparison of environmental dibenzofuran degradation rates with rates of photochemical degradation

observed for some chlorodibenzofurans. However, it seems possible that most isomers will not accumulate excessively in the environment (with the possible exception of a 2-chlorinated dibenzofuran).

ACKNOWLEDGMENTS

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SECTION 3

DESTRUCTION OF DIOXINS: CASE STUDIES

CHAPTER 15

CHLORODIBENZODIOXINS AND CHLORODIBENZOFURANS: AN OVERVIEW

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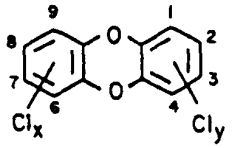
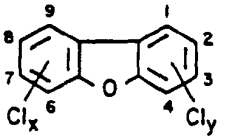
Chlorodibenzodioxins (CDD) and chlorodibenzofurans (CDF) are two series of tricyclic aromatic compounds that exhibit similar physical and chemical properties and that apparently induce similar biological effects. Generalized structures of the CDD and CDF and the numbering according to the position of chlorine substituents on the rings are shown in Figure 1. The number of chlorine atoms in the molecule can range from one to eight; therefore, a large number of positional isomers are possible. The total number of CDD is 75, and there are 135 CDF. The numbers of CDD and CDF isomers as a function of the number of chlorine atom substituents are indicated in Table I.

In the past few years, widespread concern has arisen with respect to contamination of the environment by CDD and CDF. This concern has been prompted in part by observations, principally based on animal studies, that indicate that certain of the CDD and CDF exhibit potent toxicity. In addition, it has been recognized that, since the CDD and CDF are present as contaminants in numerous commercial chemicals that have been or are being produced and used in large quantities [1], the potential for extensive environmental contamination by these compounds is very great. Moreover, CDD and CDF generally are quite stable, chemically and thermally, and are reasonably soluble in several common organic solvents (selected physical properties of two representative chlorinated



Chlorinated Dibenzo-p-dioxin



Chlorinated Dibenzofurans

Figure 1. Generalized structures of CDD and CDF.

Table I. Numbers of CDD and CDF Isomers as a Function of the Number of Chlorine Substituents

Number of Chlorine Atoms	Number of CDD Isomers	Number of Isomers
1	2	4
2	10	16
3	14	28
4	22	38
5	14	28
6	10	16
7	2	4
8	1	1

dioxins are shown in Table II). There is some evidence to suggest that the CDD and CDF are accumulating in the environment, and that these compounds persist for considerable periods.

The purpose of this chapter is to give a concise overview of the present status of knowledge of the CDD and CDF, as a prelude to discussions of

Table II. Physical Properties of Two Chlorinated Dioxins

	2,3,7,8-TCDD	OCDD[a]
Empiric Formula	$C_{12}H_4Cl_4O_2$	$C_{12}Cl_8O_2$
Percent by Weight		
C	44.7	31.3
O	9.95	7.0
H	1.25	
Cl	44.1	61.7
Molecular Weight	322	459.8
Melting Point (°C)	305	130
Decomposition Temperature (°C)	>700	>700
Solubilities (g/l)		
o-Dichlorobenzene	1.4	1.83
Chlorobenzene	0.72	
Anisole		1.73
Xylene		3.58
Benzene	0.57	
Chloroform	0.37	0.56
n-Octanol	0.048	
Methanol	0.01	
Acetone	0.11	
Dioxane		0.38
Water	2×10^{-9}	

[a] Octachlorodibenzo-*p*-dioxin.

various methods of destroying these compounds or detoxifying wastes in which they are contained, which are presented in other chapters in this book. More comprehensive reviews of this subject can be consulted for additional details [1–3].

TOXICITY AND HEALTH EFFECTS OF CDD AND CDF

The toxicity of chemical compounds is usually assessed on the basis of tests with animals. Frequently, in these tests, large doses of the material being tested are administered in an attempt to compress the time scale for response. This testing may result in misleading conclusions, because such massive doses are usually unrealistic in terms of the doses that would be encountered in typical real-world exposures. Moreover, since toxic response is a function of the pharmacokinetics and the adaptive charac-

teristics of each particular animal system, the response of different animal species to a given chemical may, and frequently does, vary markedly. All of these considerations lead one to conclude that it is extremely difficult, if not impossible, to extrapolate toxicologic data from one animal species to another, particularly to humans. Still, animal tests are one measure of the toxicity of chemicals, and some CDD and CDF have been tested in this manner. On this basis, as shown by the comparison in Table III [4,5], the acute toxicities of at least some CDD [in particular, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD)] are comparable to or exceed the toxicities of several well known poisons, and these rank among the most lethal chemical compounds known to man. It has also been observed that the LD_{50} doses for various CDD isomers, based on tests with guinea pigs and mice, differ substantially, depending on the number and location within the molecule of the chlorine atom substituents (Table IV). Of the CDD isomers tested, the 2,3,7,8-TCDD is recognized to be the most toxic. The acute toxicities of CDF have been less extensively investigated, but the LD_{50} values for 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) and 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-PCDF) appear to be similar to those for the more toxic CDD, that is, 1–100 μg/kg for the most sensitive animal species.

Table III. Toxicities of Selected Poisons[a]

Substance	Molecular Weight	Minimum Lethal Dose (mol/kg)
Botulinum Toxin A	9.0×10^5	3.3×10^{-17}
Tetanus Toxin	1.0×10^5	1.0×10^{-17}
Diphtheria Toxin	7.2×10^4	4.2×10^{-12}
2,3,7,8-TCDD[b]	322	3.1×10^{-9}
Saxitoxin	372	2.4×10^{-8}
Tetrodotoxin	319	2.5×10^{-8}
Bufotoxin[c]	757	5.2×10^{-7}
Curare	696	7.2×10^{-7}
Strychnine	334	1.5×10^{-6}
Muscarin[c]	210	5.2×10^{-6}
Diisopropylfluorophosphate	184	1.6×10^{-5}
Sodium Cyanide	49	2.0×10^{-4}

[a] Source: Pland and Kende [4]. These data were compiled by Mosher et al. [5], and the values indicate only relative toxicity. It should be noted that the values deal with different species, routes of administration, survival times and, in one case, mean lethal dose rather than minimum lethal dose. Except where noted, administration was by the intraperitoneal route in mice.

[b] LD_{50} on oral administration in the guinea pig.

[c] Intravenous injection in the cat.

Table IV. Acute Toxicities of Chlorodibenzodioxins [1]

Number and Positions of Chlorine Substituents	LD_{50} (μg/kg)[a]	
	Guinea Pigs	Mice
2,8-Di-	>300,000	
2,3,7-Tri-	29,444	>3,000
2,3,7,8-Tetra-	0.6–2.0	284
1,2,3,7,8-Penta-	3.1	338
1,2,4,7,8-Penta-	1,125	>5,000
1,2,3,4,7,8-Hexa-	72.5	825
1,2,3,6,7,8-Hexa-	70–100	1,250
1,2,3,7,8,9-Hexa-	60–100	>1,440
1,2,3,4,6,7,8-Hepta-	>600; 7,180	
1,2,3,4,6,7,8,9-Octa-		$>4 \times 10^6$

[a] All values are for oral doses; test period is 30 days.

Table V. Summary of Toxic Effects of 2,3,7,8-TCDD on Several Animal Species[a] [1,6]

	Mice	Guinea Pigs	Monkeys (Female)
Thymus Involution	+++	+++	+++
Spleen Reduction (white pulp)	+	+	+
Bone-marrow Hypoplasia	±	++	+
Liver, Megalocytosis, Degeneration	+++	-	-
Bile-duct Hyperplasia	±	±	+++
Testicular Degeneration	++	+++	N/A
Renal-pelvis Hyperplasia	-	++	+
Urinary-bladder Hyperplasia	-	++	-
Adrenal-cortical Atrophy (Zona Glomerulys)	-	++	-
Hemmorhage			
Intestinal	+	+	-
Adrenal	-	++	-
Ascites	++	-	+
Cutaneous lesions	-	-	+++

[a] Key: -no effects; + mildly affected; ++ moderately affected; +++ severely affected.

A summary of the observed biological effects of 2,3,7,8-TCDD on mice, guinea pigs and monkeys is presented in Table V [1,6]. While the effects and their severity vary to some extent among these species, as already noted, in general the major organs affected are the thymus, liver and spleen, along with the reticuloendothelial system. Reproductive functions are also affected in some animals, and pronounced developmental effects in offspring have been observed. In some animal species,

2,3,7,8-TCDD is fetotoxic (or embryotoxic), teratogenic and even carcinogenic [1]. A particularly apparent response to this compound observed in rabbits, monkeys and man is an acnegenic eruption (termed chloracne in man).

TCDD causes marked alteration of normal enzyme activity in certain laboratory animals. It is a highly potent inducer of aryl hydrocarbon hydroxylase (AHH), as well as the mixed-function oxidases and the cytochrome P_1-450 (P-448) enzymes of the liver, lung, placenta and kidney, in mice and rats [1]. It also appears that TCDD may potentiate the adverse action of other toxic materials, or even cause another seemingly innocuous agent to exhibit toxicity [1].

There are relatively few data concerning the distribution of CDD and CDF within animal tissues and organs or excretion of these compounds following administration. Some studies with TCDD indicate that in rats, excretion is largely via the feces, and that accumulation occurs principally in the fat and liver, with smaller amounts in the spleen, bone, heart, lungs, testes and kidney [1]. Most TCDD is apparently not metabolized by the rat, or at least metabolism of this compound occurs very slowly, and the metabolites have not been identified reliably.

Information on the effects of human exposure to CDD has been obtained principally from epidemiological studies of persons exposed as a result of accidents in chemical plants or by exposure to contaminated foods, materials or areas. A summary of the major accidents occurring in trichlorophenol (TCP) plants in the past several years is given in Table VI [7]. The most notable episode involving CDD contamination in recent years was the explosion that occurred at the Icmesa trichlorophenol plant located in Seveso, Italy, where TCP and 2,3,7,8-TCDD were dispersed over a wide area. Approximately 5000 persons were exposed in this accident [1,2]. Shortly after the accident, chloracne (a well-known symptom of acute CDD toxicity) was observed in some 134 persons. Other disorders reported included hepatic and coronary insufficiency, chronic bronchitis, muscular weakness, irritability and nervousness, urinary and pancreatic disorders, porphyria cutanea tarda, hyperpigmentation and hirsutism and chromosomal damage. A later followup study detected peripheral nerve damage and polyneuropathy in some of the exposed individuals [2].

TCDD is also known to be an inducer of delta-aminolevulinic acid (d-ALA) and AHH in man. Probably this accounts for stimulation of production of certain porphyrins, which are ultimately excreted in the urine. The distribution of CDD and CDF within the human body and the modes of elimination have not been established, nor are the metabolic pathways or metabolites (if any) known. Reproductive effects of CDD

Table VI. Accidents in Chemical Plants Manufacturing TCP [7]

Date	Manufacturer	Country	Personnel Injured	Cause of Accident
1949	Monsanto	U.S.	117	Overheating leading to explosion
1952/1953	Boehringer	W. Germany	37	Exposure during manufacturing process
1953	Badische Anilin und Soda Fabrik AG (BASF)	W. Germany	55	Overheating leading to explosion
1953/1971	Rhone Poulenc	France	97[a]	Exposure during manufacturing process
1956	Hooker	U.S.	Staff employees	Overheating
1960	Diamond Shamrock	U.S.	Figure unknown	Overheating
1963	Philips Duphar	Holland	30	Overheating leading to explosion
1964	Spolana	Czechoslovakia	72	Exposure during manufacturing process
1964	Dow Chemical	U.S.	30	Exposure during manufacturing process
1968	Coalite and Chemical Products	U.K.	79	Overheating leading to explosion
1970(?)	Bayer	W. Germany	5	Exposure during manufacturing process
1972/1973	Chemie/Linz	Austria	50	Exposure during manufacturing process
1976	Icmesa (Givaudan)	Italy	106 children	Overheating
Before 1976	Thompson Hayward	U.S.		Overheating leading to explosion

[a] Including 17 injured in a 1956 explosion and 21 in 1966. Source: A. Hay, "Accidents in Trichlorophenol Plants: A Need For Realistic Surveys to Ascertain Risks to Health", in "Health Effects of Halogenated Aromatic Hydrocarbons", W. J. Nicholson and J. A. Moore, Eds. *Ann. N.Y. Acad. Sci.* 320:1-730 (1979).

and CDF in humans also have not been determined, in part because of the complicating factors caused by the many other hazardous organic compounds to which man is exposed.

The most notable reported episode involving human exposure to CDF occurred in Japan in 1968 as a consequence of the accidental contamination of rice oil used for cooking with polychlorinated biphenyls (PCB); subsequently, CDF were shown to be present in small quantities in the PCB [8]. This incident, which has come to be known as the "yusho" incident, involved more than 1200 persons. There were several near-term symptoms, including chloracne. Many of these symptoms were similar to those cited above for CDD [2]. By the end of 1977, some 51 of the exposed population had died; 11 of these were identified as resulting from malignant neoplasms of the stomach, lung, liver, breast or lymphatic system, or combinations of these [2]. Tissues (principally from the livers) of the victims of this accident were analyzed for CDF, as were samples of the PCB contaminant in the rice oil. A comparison of the results showed that many of the same CDF isomers were present in both the PCB contaminant and the liver tissues, and further indicated that certain CDF isomers, particularly those having all the lateral (2-, 3-, 7- and 8-) positions chlorinated, were preferentially retained in human tissues [8]. This is one of the few instances in which such compounds have been implicated unquestionably in severe human health effects.

In several animal studies, PCB have been implicated as inducing toxic effects in animals, but in some of these investigations, it has not been clear to what extent PCB were contaminated with CDF, and the causative agent or agents are therefore uncertain.

SOURCES AND ACCUMULATION OF CDD AND CDF IN THE ENVIRONMENT

As mentioned earlier, major sources of CDD and CDF detected in the environment are industrial chemicals. More recently, however, it has been recognized that these compounds are present in the effluents from various combustion processes. The principal environmental sources of CDD/CDF thus far identified include [1]:

1. chemical products for which the normal manufacturing process generates these compounds as by-products, and which are widely used in the environment (pesticides, wood-treating products, etc.);
2. uncontrolled manufacturing processes, which result in releases of CDD and CDF (explosions of reactors);

3. improper disposal of chemical manufacturing wastes or products containing CDD and CDF (landfills, waterways);
4. incineration of municipal, commercial and industrial wastes;
5. ordinary combustion processes (wood-burning and others); and
6. accidents (fires, spills, etc.).

Perhaps most important among the mass-produced chemicals which are known to be contaminated with CDD and CDF are the *ortho*-chlorophenols, particularly TCP and pentachlorophenol (PCP). TCP has been used widely as a preservative, bactericide, fungicide and algicide in many industrial products, and is the starting material used in the manufacture of a series of industrial and agricultural chemicals, notably the herbicide 2,4,5-T, and the related products, silvex, ronnel and hexachlorophene, a bactericide. PCP is extensively utilized in wood-preserving processes. CDD and CDF that have been detected in various chlorophenols and related pesticide products are listed in Table VII. The probable mechanism by which chlorodioxins are formed in the synthesis of *ortho*-chlorophenols is a thermally induced condensation reaction of two molecules of the sodium or potassium chlorophenate, such as that exemplified in Figure 2 for the production of 2,3,7,8-TCDD in the manufacture of 2,4,5-TCP. A so-called "predioxin," a phenoxyphenate or substituted diphenyl ether, may be an intermediate in this reaction. Similar condensation reactions can account for the formation of hexa- (HxCDD), hepta- (HpCDD) and octachlorodibenzo-*p*-dioxins (OCDD) in the manufacture of PCP (Figure 3).

The extensive occurrence of CDD and/or CDF in such widely used commercial chemicals as chlorophenols, their derivatives and PCB provides a clear indication of the need for adequate methods for destruction of chemical wastes and related materials that result from manufacture of these chemicals. Obviously, improper disposal of such chemical wastes can lead to extensive environmental contamination. Prominent examples of this that have received recent attention are the Love Canal area in Niagara Falls, New York, where several major chemical dumps are located, and a 2,4,5-T/2,4-D manufacturing plant site located in Arkansas. Levels of TCDD typically found in environmental samples from these sites are shown in Table VIII. Applications of excessive quantities of herbicides contaminated with TCDD, as in South Vietnam during the conflict there and at various military sites in the United States during this period, or the contamination of the environment resulting from such events as the TCP reactor explosion at Seveso, Italy, can also result in elevated levels of TCDD in plants and animals (including humans) present at such sites (Table IX [9]).

As already noted, CDF are also present as contaminants in some PCB

Table VII. Higher Chlorodibenzodioxins CDD and Chlorodibenzofurans CDF Detected in Chlorophenols and Related Pesticides [1,2]

Product	CDD Detected[a]					CDF Detected[a]				
	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Tetra-	Penta-	Hexa-	Hepta-	Octa-
TCP	-	-	-	-	-	+	+	+	+	-
Tetrachlorophenol	+	+	+	+	+	+	+	++	++	+
PCP	-	-	+	++	++	-	-	++	++	++
2,3,5-T	++	ND	++	-	-	ND	ND	ND	ND	ND
Silvex	+	ND	-	-	-	ND	ND	ND	ND	ND
2,4-D[b]	-	ND	+	-	-	-	-	-	-	-
Erbon	-	ND	-	-	++	ND	ND	ND	ND	ND
Sesone	-	ND	+	-	-	ND	ND	ND	ND	ND

[a]Concentration ranges: ++ = >10 ppm; + = 0.5-10 ppm; - = <0.5 ppm; ND = not determined.
[b]Recent analyses by Wright State University.

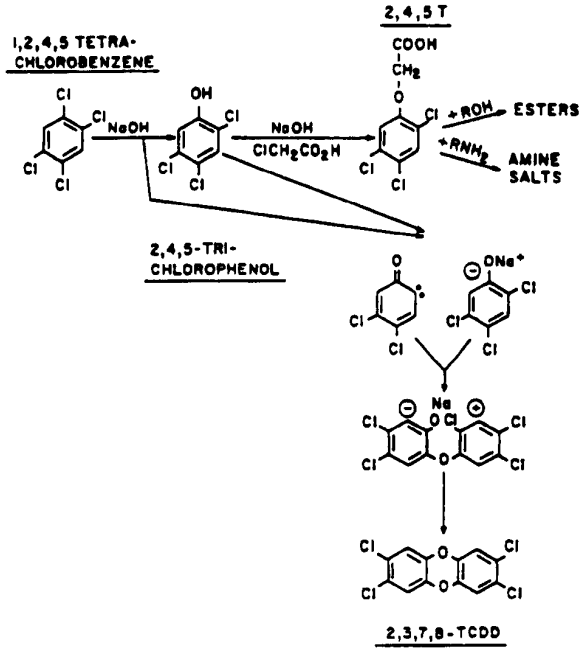


Figure 2. Reactions involved in synthesis of 2,4,5-trichlorophenol and related products (2,4,5-T and derivatives) showing formation of 2,3,7,8-TCDD as a by-product.

formulations [2]. In addition, it is known that pyrolysis of PCB at certain temperatures (obviously lower than the temperatures required for complete destruction) yields CDF as products [3]. The reaction scheme for formation of CDF from pyrolysis of 2,2',4,4',5,5'-hexachlorobiphenyl, for example, is as shown in Figure 4. An instance in which a PCB formulation (also containing hexachlorobenzene) was incinerated under conditions leading to formation of substantial quantities of CDD and CDF occurred in Binghamton, New York. This episode occurred as a

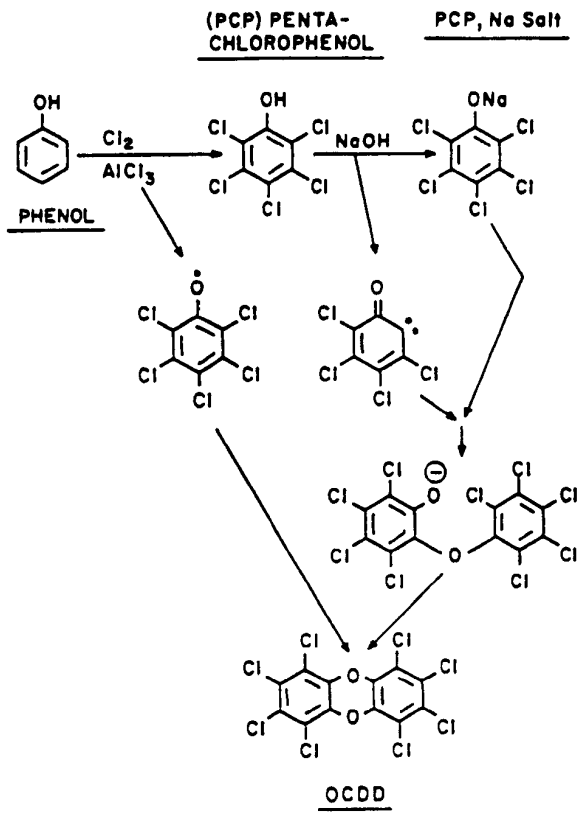


Figure 3. Reactions involved in synthesis of PCP and derivatives showing formation of octachlorodibenzodioxin as a by-product.

result of a transformer fire in the basement of a large office building. Soot samples and wipes of surfaces in nearby areas showed rather large concentrations of CDD and CDF, as indicated by the data shown in

Table VIII. Levels of TCDD in Various Environmental and Biological Samples Analyzed by the Brehm Laboratory of Wright State University

Sample Description	Native TCDD Detected
Hazardous waste landfill soil/sludge, New York state	300–199,000 ppt
Trichlorophenol manufacturing waste, still bottom, Arkansas	22,000 ppt
Blood sample from workers involved in cleanup of *ortho*-chlorophenol spill in tank car derailment, Missouri	7–28 ppt
Blood sample from Vietnam veteran	41 ppt
Bovine	10 ppt
Municipal refuse-fired incinerator, New York state (on particulate emissions)	15 mg/hr
Soot from wood-burning fireplace	0.65 ppb
Agent Orange	0.1–60 ppm
2,4-D (several manufacturers)	0.2–1.3 ppb

Table IX. TCDD Levels in Wildlife in Seveso, Italy, Area Following TCP Accident[a]

Animal	No. of Samples Analyzed	Tissue	Positive	TCDD Level (ng/g) Average	Range
Field Mouse	14	Whole body	14/14	4.5	0.07–49
Hare	5	Liver	3/5	7.7	2.70–13
Toad	1	Whole body	1/1	0.2	
Snake	1	Liver	1/1	2.7	
		Adipose tissue		16.0	
Earthworm[b]	2	Whole body	1/2	12.0	

[a] Source: Fanelli et al. [9], referenced in Esposito et al. [1].
[b] Each sample represents a 5-g pool of earthworms.

Table X for a wipe sample [10]. In still another instance, incineration of wood-treatment wastes containing PCP, and probably related CDD/CDF or precursors of these, in an incinerator that apparently provided less-than-optimum conditions for destruction, yielded ash residues containing relatively large quantities of CDD/CDF (see Table XI). Another chapter in this book [11] presents a more detailed discussion of the recent assessment of destruction of PCB by incineration under conditions where

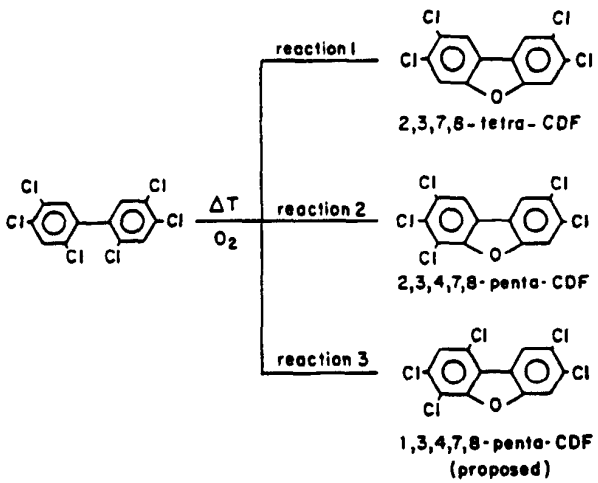


Figure 4. Reactions leading to formation of CDF from pyrolysis of 2,2',4,4',5,5'-hexachlorobiphenyl.

high destruction efficiency was achieved and the level of CDD/CDF in the combustion effluents were within limits which the U.S. Environmental Protection Agency (EPA) deemed acceptable.

ANALYSES OF CDD/CDF IN ENVIRONMENTAL SAMPLES

The extraordinary toxicity of some CDD and CDF dictates the need for analytical capabilities that can detect and quantify picogram quantities of CDD and CDF. At the same time, great analytical methods specificity is required, because several other prominent contaminants that persist in environmental samples (e.g., PCB and DDE) can interfere with the determination of CDD and CDF. The analytical capability described has only been realized within the past 3–4 years, and it is now possible to reliably determine parts-per-trillion levels of CDD and CDF in many

Table X. Results of HRGC/LRMS Analysis of Wipe Sample from Area Contaminated by Transformer Fire for Tetra- Through Octachlorinated Dibenzo-*p*-dioxins and Dibenzofurans

CDD/CDF[a]	Apparent Isomers[b]	Quantity of CDD/CDF Detected (ng/wipe)	Minimum Detectable Quantity (ng per isomer)
TCDD	ND	ND	0.10
	$^{37}Cl_4$-2,3,7,8		
PCDD	ND	ND	0.10
HxCDD	ND	ND	0.20
HpCDD	1,2,3,4,6,7,8-	0.65	0.20
	1,2,3,4,6,7,9-	0.45	0.20
	Total	1.1	0.20
	$^{37}Cl_4$-1,2,3,4,6,7,8-		
OCDD	1,2,3,4,6,7,8,9-	1.0	0.20
	$^{37}Cl_8$-OCDD		
TCDF	1,2,4,8-	2.0	0.10
	2,3,6,8-	3.1	0.10
	2,3,7,8-	9.6	0.10
	Other isomers (8)	35.8	0.10
	Total	50.4	0.10
PCDF	1,2,4,7,8-	5.2	0.10
	Other isomers (13)	11.8	0.10
	Total	17.0	0.10
HxCDF	1,2,4,6,7,9-	1.6	0.20
	Other isomers (12)	43.6	0.20
	Total	45.2	0.20
HpCDF	1,2,3,4,6,8,9-	2.7	0.20
	Other isomers (4)	4.6	0.20
	Total	7.3	0.20
OCDF	1,2,3,4,6,7,8,9-	7.3	0.20

[a] PCDD = penta-CDD; HxCDF = hexa-CDF; HpCDF = hepta-CDF; OCDF = octa-CDF.
[b] See text for discussion.

types of environmental and biological samples, hazardous chemical wastes, and chemical formulations. The Brehm Laboratory, Wright State University, has been one of the major contributors to the development of this highly sophisticated analytical methodology. In general, the analytical procedures now applied for definitive determinations of CDD and CDF isomers entail the following:

Table XI. HRGC/LRMC Analytical Results for CDD/CDF in Ash Sample from Incineration of Wastes Containing PCP[a]

CDD/CDF	Total Number of Apparent Isomers	Total Detectd (ng/g)	Minimum Detectable Concentrated (ng/g)
MCDF	3	75	0.1
DCDF	8	25	0.3
TrCDF	8	15	0.6
TCDF	7	7	0.5
PCDF	5	8	1
HxCDF	5	5	1
HpCDF	2	6	1
OCDF	1	2	1
MCDD	1	1	0.1
DCDD	4	5	0.3
TrCDD	5	2	0.6
TCDD	4	4	0.2
PCDD	5	32	1
HxCDD	5	81	1
HpCDD	2	117	1
OCDD	1	198	1

[a]Recent analyses by Wright State University.

1. extraction of CDD and CDF from the sample matrix using organic solvents,
2. preliminary separation of CDD and CDF from other constituents of the matrix, which also have been extracted (including other chlorinated materials) using acid-base treatments and liquid chromatography with alumina, silica gel and/or other suitable columns;
3. further fractionation of the CDD and CDF using normal and reverse-phase high-performance liquid chromatography (HPLC); and
4. analyses of the prepared extracts containing CDD and CDF using capillary-column gas chromatography/mass spectrometry (GC/MS). Both low- and high-resolution mass spectrometry may be used in this analysis, depending on the sample.

The application of this complex analytical procedure is tedious and costly, but such a procedure is necessary to obtain definitive data on the CDD and CDF isomers at the extremely low (parts-per-trillion) concentration levels at which these must be detected. The results of such an analysis are well illustrated by data obtained from analysis of the ash sample resulting from incineration of PCP wood-preserving process wastes, which are shown in Table XI. Interestingly, the TCDD isomers detected in this sample were 1,3,6,8,- 1,3,7,9-, 1,3,7,8- and 1,2,3,4-TCDD.

No 2,3,7,8-TCDD was found. Similar analyses have recently been accomplished by the Brehm Laboratory on stack effluents from incineration of municipal refuse, and on effluents from incineration of wastes containing PCB. The latter work is discussed more fully and the detailed analytical techniques are also described in another chapter in this book [11].

ENVIRONMENTAL TRANSPORT AND NATURAL DEGRADATION OF CDD

Considerable work has been done in an effort to assess the extent of degradation and transport of CDD in the environment [1], although the conclusions from these studies are not entirely clear. Although biodegration of TCDD does not seem to be a particularly important process, both TCDD and OCDD appear to be effectively photodegraded by both natural sunlight and artificial ultraviolet (UV) radiation [1]. Transport of TCDD in soil, water and air has been investigated, but since the results depend on so many environmental factors (e.g., type of soil and organic content, temperatures and organic content of water, and method of dispersal in air), the conclusions are not straightforward. It appears, however, that TCDD can migrate to some extent in soils, especially porous, sandy soils. Transport of CDD/CDF can occur in the air, especially if these compounds are sorbed on airborne particulates. It is also clear that transport of CDD/CDF can occur by runoff of surface waters and or leaching into groundwaters, which ultimately may contaminate lakes, rivers and streams. In the latter instance, TCDD appears to accumulate largely in sediments, although the content of other organic compounds in natural waters also affects the concentration of CDD/CDF therein. Finally, as discussed earlier, CDD/CDF can bioaccumulate in some plants, animals and fish exposed to these compounds; obviously, this may also result in transport and, ultimately, dispersion of these compounds in the environment. There are few baseline data on concentrations of CDD/CDF in the environment, however, except where high levels of CDD/CDF are anticipated because of massive contamination episodes such as those described earlier

DESTRUCTION OR DETOXICATION OF CHEMICAL PRODUCTS AND WASTES CONTAINING CDD/CDF

Among the methods applied in attempts to destroy or detoxicate wastes containing CDD and/or CDF are conventional incineration, photolysis,

radiolysis, ozonolysis, catalytic dechlorination and biological treatment. Several of these techniques and their application to such chlorinated compounds are discussed in more detail in several other chapters in this book. These chapters clearly demonstrate that considerable success has been achieved in devising environmentally acceptable methods for destroying or detoxifying hazardous wastes containing CDD and/or CDF.

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CHAPTER 16

SELECTED LEGAL ASPECTS OF A DIOXIN DETOXICATION PROJECT

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On a summer afternoon in 1974, Godfrey Moll, Plant Manager of the Syntex Agribusiness chemical production facility in Verona, Missouri, rapped on the side of an old 20-foot-tall steel tank, which had been sitting idle on the premises for many years. Syntex had purchased the plant, including the steel tank, in 1969. Moll assumed that the tank was empty because Syntex had never used it, but his knocking on the tank wall was inconclusive. Consequently, he carefully lowered a small flask into the tank and, to his surprise, it came up filled with a dark sludge material. Moll calculated from the size of the tank that it contained approximately 4300 gallons of this material, which was the consistency of heavy motor oil. Laboratory analysis of the sludge increased his surprise considerably: the 4300 gallons of sludge contained approximately 343 ppm of dioxin.

It soon became evident what had happened. In the late 1960s North Eastern Pharmaceutical and Chemical Company, Inc. (NEPACCO) leased a portion of the Verona plant from the company that then owned it. Under this lease, NEPACCO was entirely responsible for disposing of its own wastes and trash, and agreed to operate at all times in conformity with applicable laws and regulations. NEPACCO's activities at the plant included the production of hexachlorophene. One step of that manufacturing process, which involved the purification of trichlorophenol (TCP), apparently produced dioxin as an unwanted by-product.

Syntex Agribusiness later acquired the Verona plant subject to the existing lease with NEPACCO. NEPACCO ran into financial difficulties when hexachlorophene, its main product line, was essentially removed from the market by the Food and Drug Administration (FDA) and soon thereafter NEPACCO allowed its corporate charter to lapse.

In short, in violation of its lease, NEPACCO had apparently simply abandoned the dioxin-containing wastes in the tank and, after Syntex purchased the facility, had gone out of business.

The first-priority activity, from legal as well as other perspectives, was to provide additional safety precautions for the tank. A reinforced concrete dike, capable of containing the entire contents of the tank should it leak, was constructed beneath it; a building was erected over it; and a wire fence was put up around it. After the area was safely secured, Syntex turned its attention to finding a suitable way to resolve the problem.

The overriding consideration for Syntex in searching for and selecting a disposal method was the safety of the public, its employees and the surrounding area. Syntex was dissappointed many times in its search. Several plans for disposal by incineration at appropriate facilities had to be abandoned because Syntex was not allowed to transport the wastes across state lines. At one point, the possibility of incineration at sea on the ship Vulcanus was also explored. This option met with two main obstacles: the unwillingness of state and federal authorities to allow transportation across state lines and the unwillingness of the Vulcanus to handle what it viewed as a small quantity of waste. In general, as the hazards of dioxin became more publicized, fewer and fewer consultants or contractors were willing to become involved in the disposal of this material. However, despite these difficulties, Syntex continued to search for a disposal method, and began exploring the possibility of detoxicating the NEPACCO wastes onsite.

INTERDISCIPLINARY EFFORTS

Early in 1978, Syntex entered into a contract with IT Enviroscience (formerly known as Dow/Hydroscience) to undertake a three-phase program. Phase I was a technology review by IT Enviroscience to discover feasible methods of onsite reduction and recommend a method for further development; phase II involved laboratory development and refinement by IT Enviroscience of the method which they recommended; and phase III was the detoxication of the NEPACCO wastes.

Syntex convened a Blue Ribbon Committee to make an independent evaluation of the IT Enviroscience recommendations and to guide its

progress in this endeavor. The Committee consisted of 5 academic and industrial experts in photochemistry, chemical engineering, process analysis and reaction kinetics. When it became evident that the process that IT Enviroscience was likely to recommend would involve photolysis, two experts in this specialty were immediately added to the Blue Ribbon Committee.

Syntex also, of course, continued to apply intensively the expertise of its own employees in many disciplines. They included chemical engineers, civil engineers, process engineers, research chemists, analytical chemists, industrial hygienists, toxicologists, physicians, insurance specialists, fire protection specialists and lawyers.

As I have stated, safety of the public, its employees and the surrounding area was Syntex' primary consideration. This consideration weighed heavily against any process requiring operation at high temperatures or pressures. The process ultimately proposed by IT Enviroscience was extraction of dioxin from the NEPACCO wastes followed by ultraviolet (UV) photolysis of the extractant material. The process had the advantages of operating at essentially ambient pressures and temperatures, as well as being amenable to batch processing, which enabled careful regulation of the amount of wastes being treated at any given time. The proposed process was reviewed and approved by the Blue Ribbon Committee in 1979.

WHY LAWYERS?

On the surface, the destruction of these wastes appears to be more a scientific than a legal challenge. There was no litigation pending nor even threatened concerning these materials. Why, then, were lawyers an integral part of the team?

The involvement of legal counsel began very early in the detoxication project, in fact, at the point of decision as to whether there was even going to be such a project. The initial question was whether to focus efforts on pointing out Syntex' lack of responsibility for the presence of the materials or, instead, to turn directly to an attempt to clean them up.

On one hand, Syntex had not generated or disposed of the wastes in question. NEPACCO, which created the wastes and abandoned them at the Verona chemical plant nine years before, was out of business and had not existed as a corporation since 1974. Syntex found itself involved in this matter because it purchased the plant in Verona from another company, which had earlier leased part of the plant to NEPACCO for the manufacture of hexachlorophene. Clearly, a strong basis existed for

declining any responsibility whatsoever, on the grounds that Syntex did not generate the hazardous materials or place them in the tank.

On the other hand, militating in favor of Syntex' attempt to detoxicate the materials created by others was a factor that was and continues to be of paramount importance to Syntex: safety. Syntex evaluated the comparative safety (and attendant legal exposures) involved in processing the materials vs leaving them where they were, in a protected steel tank. Even though the wastes were protected in their tank, with its dikes and fences, they still might be affected by such events as tornados, deliberate damage or leakage due to eventual deterioration of the tank. They were, in the final analysis, located on what had become Syntex property and the company felt an obligation to deal with them.

Another important factor weighed very heavily in the decision to proceed to detoxicate the materials: Syntex wished to act as a good corporate citizen and to alleviate a possible source of concern and anxiety both in the community in which its plant was located as well as in surrounding communities. Accordingly, it was decided to seek a way to detoxicate the materials.

Of course, involvement of lawyers in the project did not cease once the decision was made to detoxicate the sludge. During process development and before startup, lawyers were active in a number of areas. First, considerable effort was expended on maintaining liaison and rapport with responsible officials of the U.S. Environmental Protection Agency (EPA) as well as state and local agencies. As a part of this liaison activity, lawyers often served as problem-solvers to help avoid and overcome possible impasses and to help gather and synthesize information from the various disciplines in a manner that would be responsive to EPA's concerns. For example, numerous meetings were held as the development of the process progressed, to keep EPA officials in Washington, DC, and the Regional Office in Kansas City informed. As the process was selected and refined, specific documentary submittals were provided. At one point, 17 multifaceted written questions were posed by EPA. A four-inch-thick, item-by-item response by Syntex elicited an even larger number of questions from EPA. Soon, however, the questions began to decrease in both number and scope until finally, on May 19, 1981, EPA authorized Syntex to begin processing. The actual commencement date of the processing took place only two weeks later than the startup goal that Syntex had set almost a year before. Syntex feels that the timely startup of this process provides a good example of the kind of results that industry and government can accomplish by working cooperatively together.

In a second, related, area, there was considerable legal activity involved in obtaining the requisite federal, state and local permits. For example, approximately 55 days before processing was scheduled to begin, a regulation was promulgated under the Toxic Substances Control Act (TSCA) requiring 60-day notice to EPA before any dioxin disposal could commence. The regulation was actually designed to halt another company's dioxin disposal project, which EPA apparently thought ill advised. Unfortunately, the regulation's prohibitions reached beyond that one company and, at least literally, encompassed Syntex' proposed processing. After extensive negotiations and correspondence, EPA again cooperated with Syntex by finding that the notification requirement had been met, partly on the basis that Syntex had been keeping EPA informed for several years of its progress toward detoxication. Again, the spirit of cooperation and openness between Syntex and EPA had made it possible to overcome a problem that otherwise might have halted or delayed the project.

A third area of legal activity involved the protection of confidential proprietary process information. The contract with IT Enviroscience obligated Syntex to maintain certain process information as confidential. Yet EPA felt it could not approve the process without such information. Considerable negotiation and correspondence enabled a mutually satisfactory resolution of these competing needs.

A fourth area of legal activity involved the preparation of contracts with IT Enviroscience, the Blue Ribbon Committee members and other consultants. The sensitive nature of the project and the involvement of confidential process information made the task particularly challenging. Another group of issues requiring the application of legal effort involved establishing shutdown authority, emergency procedures and EPA representation at the processing site. Finally, considerable time was spent coordinating public involvement, including town meetings, press conferences and briefings of officials, including the mayor of Verona and U.S. senators.

During the successful operation of the detoxication process, input by lawyers continued along lines similar to those described above, particularly in the areas of maintaining liaison with EPA and coordinating the efforts of consultants. Fortunately, the process operated with a minimum of hitches, so no further legal activity was necessary with regard to such issues as shutdown authority or emergency procedures.

LAWYERS' INTERACTION WITH OTHER DISCIPLINES

One way to conceptualize the lawyer's role in such situations is to say that he or she can be responsible for removing or addressing certain obstacles and problems so that scientists and other experts are allowed to focus their expertise on resolving the scientific and technical aspects of the situation. Prime examples of this traditional role for a lawyer might include obtaining permits and drafting contracts. These activities represent an important aspect of a lawyer's traditional role in such situations. Conceptualizing the interaction among the disciplines in such a limited fashion, however, vastly undervalues the extent of symbiotic interplay that is essential to the success of such a project. The several disciplines involved did not simply work on separate, parallel tracks. Instead, many key decisions involved a collegial process that brought together several areas of expertise, including legal. One example may help illustrate this point.

The design of environmental and personnel sampling protocols and the selection of the accompanying analytical methods required an extensive iterative dialog among lawyers, analytical chemists, industrial hygienists and others. Such a system had to meet several conflicting demands. On one hand, the samples had to be sufficient in number to rebut allegations of dioxin release or injury, have sufficient sensitivity to meet legal standards and be frequent enough, with short analytical turnaround times, to enable rapid identification of any problems. On the other hand, these environmental sampling and analytical efforts could not be so numerous, sensitive or frequent as to interfere with the analysis of process samples, prolong excessively the turnaround time, extend the duration of the detoxication processing, or increase unacceptably the possibility of obtaining misleading false positive results. The pooled expertise of several disciplines, based on extensive discussion, was necessary to balance these variables.

Unfortunately, shortly before the detoxication processing was completed, another NEPACCO dioxin disposal site was discovered in a trench on a Missouri farm several miles from the Verona plant. Once again it was decided to clean up the materials rather than to focus efforts on pointing out Syntex' lack of responsibility for the presence of the materials. Based on the lessons of the Verona detoxication effort, another interdisciplinary team, including lawyers, was assembled, and a plan for site cleanup was approved by EPA. The cleanup effort at this new site is now well underway.

In retrospect, Syntex' efforts to act in a responsible manner and as a good corporate neighbor have been well received. A U.S. senator for the state of Missouri, after being personally briefed in Washington about Syntex' proposed detoxication effort, commented that the program "represented the highest degree of corporate care and concern." The Chamber of Commerce for a nearby town passed a resolution thanking Syntex for its "caring attitude . . . and moral and unselfish stance." Finally, Douglas M. Costle, then the head of EPA, traveled to Missouri to hold a press conference complimenting Syntex for its "responsible and constructive actions." Comments such as these helped confirm that the correct choice had been made more than seven years earlier to tackle this difficult hazardous waste disposal problem.

CHAPTER 17

PROCESS FOR DESTROYING TETRACHLORODIBENZO-*p*-DIOXIN IN A HAZARDOUS WASTE

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Polychlorinated dibenzo-*p*-dioxins (PyCDD) are extremely toxic compounds [1,2] that have been involved in several highly publicized accidents such as the Missouri Horse Arena episode in 1971 [3], the Seveso release in 1976 [4], and in the controversies surrounding the use of Agent Orange and trichlorophenoxyacetic acid herbocides. The 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) isomer is one of the most toxic chemicals known toward certain species of animals. In 1974, the presence of tetrachlorodibenzodioxins was confirmed in a waste storage tank at a chemical plant in Verona, Missouri. The waste resulted from production of hexachlorophene by North Eastern Pharmaceutical and Chemical Co. (NEPACCO). NEPACCO became defunct in 1971 and the tank and contents reverted to Syntex (U.S.A.) Inc. After the discovery of the contents of the tank, public and political opposition to transportation and destruction of this politically sensitive waste prevented land- or sea-based incineration. Consequently, IT Enviroscience was retained to examine treatment options for this waste that could be used at the plant site. The objective was to decrease the hazard of the stored waste to the surrounding community of Verona, Missouri, by developing a safe, effective method to reduce the approximately 7 kg of dioxin in about 4600 gal of waste.

Development of the destruction process and the ultimate destruction of the waste involved a three-phase project that illustrates the social, economic, political, technical and legal aspects of waste detoxication projects. In addition, this project illustrates the multidisciplinary nature of the technical solutions to these difficult waste problems. The technical solution relied on the experience of analytical, organic, physical and inorganic chemists; chemical, civil and process engineers; industrial hygienists and toxicologists; and medical personnel.

EXPERIMENTAL

Safety, Health and Environmental Considerations

TCDD is teratogenic, has a high acute toxicity, and causes severe chloroacnogenic response on skin contact [5]. Work was carried out in an isolated work area in accordance with safe handling recommendations [6]. Standard laboratory emergency procedures were altered to separate potentially contaminated apparatus and personnel from the rest of the laboratory. Skin contact was minimized through the use of disposable coveralls and rubber gloves. Goggles and face shields were worn during nonroutine laboratory manipulations. Personal hygiene was enforced by requiring showers and clothing changes when workers left the isolated work room. Chemical manipulations were carried out in a well ventilated hood. The minimum air velocity at the face of the hood was 100 ft/min, and under normal working conditions the velocity ranged 150–200 ft/min. Liquid and solid wastes were placed into a plastic bottle. Glassware was placed into metal cans. Slightly contaminated materials, such as gloves and towels, were placed into a 55-gal drum. Used coveralls were placed into a second drum. These drums were sealed and disposed of by incineration.

All persons working with TCDD were given complete baseline physicals, with special attention given to liver function and skin condition. These physicals were followed semiannually for a minimum of one year after completion of the project.

Analytical

Gas chromatography (GC) analyses were carried out on a Hewlett-Packard 5750 with flame ionization detection (FID). A 10% OV-101 on

80/100 mesh Chromosorb WHP glass column, 10 ft × 2 mm, was used at 230°C. Nitrogen flowrate was 30 ml/min; detector temperature was 270°C, injector temperature was 250°C, and the sample volume was 2 μl. TCDD retention time was 9.5 min.

GC/electron capture detection (ECD) analyses were carried out on a Hewlett-Packard 5710 with a ^{63}Ni detector. A 1.5% SP-2250/1.95% SP 2401 on Supelcoport 100/120 glass column, 6 ft × 2 mm, was used at 220°C. Carrier flow (5% methane/95% argon) was 20 ml/min, detector temperature was 330°C, injector temperature was 250°C, and sample volume was 1 μl using an autoinjector.

High-pressure liquid chromatography (HPLC) was carried out on a Perkin-Elmer LC-55 using a 250 × 6.2-mm Zorbax ODS column (Dupont) at 50°C. The eluent was methanol at 2 ml/min. The UV detector was set at 235 nm, connected to a recorder deflecting full scale at 0.01–0.02 absorbance units.

GC/mass spectrometry (MS) analyses were performed on a Finnigan Model 3200 coupled to a System Industries 150 data package, which permits continuous acquisition during chromatography. Analyses were carried out with a 6-ft × 2-mm glass column packed with 3% OV-101 on 80/100 mesh Chromosorb WHP. Conditions for qualitative analyses were: 120°C for 2 min, 120–250°C at 8°C/min; injector, 290°C; separator, 290°C; helium flow, 30 ml/min; sample volume 2 μl. Quantitative analyses were carried out isothermally at 250°C.

Isopropyl alcohol (IPA) in hexane was analyzed on a Perkin-Elmer Sigma 3 FID, using an 8-ft × ⅛-in. 100/120 mesh Porapak stainless steel column. The column temperature was 150°C; detector, 200°C, injector, 200°C; and the N_2 flowrate was 25 ml/min. Ultraviolet (UV) spectra were obtained on a Perkin-Elmer 202 Ultraviolet-Visible Spectrophotometer.

Materials

Solvents were obtained from Burdick and Jackson (distilled in glass) or Fisher HPLC grade. Alumina was Brockman activity I, 80–200 mesh or Fisher A-540. Silica gel was Fisher ACS reagent, 100–200 mesh. NEPACCO waste was hand-delivered to the Knoxville laboratory.

TCDD Standard

TCDD (>99%), 6.1 mg, obtained from the Dow Chemical Company, was transferred quantitatively into a 50-ml volumetric flask. The solid was dissolved in *o*-xylene. Triphenylethylene (Aldrich) in *o*-xylene was

added as an internal standard at 21 mg/l. Dilutions were made volumetrically and standards were stored in septum bottles sealed with Teflon®-lined caps and covered with aluminum foil.

Column Chromatographic Purification of TCDD Samples

Several procedures were used throughout the course of the work:

1. Basic alumina, 4.0 g, was added to 4 ml of *n*-hexane in a 1- × 10-cm glass column. To a 5.0-ml aliquot of a hexane extract of the NEPACCO waste, 71.2 mg/l (356 μg) TCDD was added, and the hexane was collected. A 20-ml aliquot of 2% v/v methylene chloride/hexane was placed on the column and collected. No TCDD was detected in this fraction. TCDD was eluted with a 20-ml portion of 50% methylene chloride/hexane, and the solution was concentrated to 6.3 ml (4.4 g). TCDD concentration was 56 mg/l, 352 μg, a recovery of 99%.
2. A 1- × 10-cm column was packed with 1.0 g of silica gel and 4.1 g of 44% w/w sulfuric acid/silica gel. A second column, 1 × 30 cm, was packed with 6.0 g Fisher A-540 alumina, which had been activated at 130°C for 20 hr. A small layer of anhydrous sodium sulfate was placed upon the alumina. The photolysis residue was reduced in volume by about 2.0–2.5 times. To this concentrate was added 260 μl of a 66-mg/l solution of TCDD in hexane. Analysis by GC/FID gave 9 mg/l TCDD in the spiked solution. A 2.0-ml aliquot was placed on the acidic silica gel, and the material was eluted directly onto the alumina column with 45 ml of hexane. The alumina column was eluted with 20 ml of 20% v/v methylene chloride/hexane. The solvent was evaporated to dryness in a 5-ml cone-bottom vial and dissolved in 2 ml of hexane. A 100-fold dilution of this sample gave 7.2 μg/l (87%) of TCDD by GC/ECD.

Analysis of NEPACCO Waste Extracts

Into a 125-ml separatory funnel was placed 8.04 g (~5.8 ml) of NEPACCO waste, then 30 ml of 15% w/w aqueous sodium hydroxide and 30 ml of hexane were added successively. The mixture was shaken for about 30 sec, and the separated, lower, black aqueous phase was added to a second 125-ml separatory funnel. The volume of the hexane layer was determined with a graduated pipet, and the hexane layer was analyzed by GC/FID. The caustic layer was extracted five more times with 30-ml portions of hexane. Each hexane layer was analyzed; however, extracts 3–6 were reduced in volume by 5–16 times before GC/FID analysis. All remaining extracts were combined to yield 66 ml of hexane extracts, which contained 40 mg/l TCDD (2640 μg) by GC/FID and 33 mg/l by GC/MS. Column chromatography by method 1 gave 43 mg/l of TCDD by GC/FID. Addition of the six extract analyses gave 2760 μg TCDD.

Analysis of Photolysis Mixtures by Column Chromatography and HPLC Followed by GC/ECD

A sample of photolysis effluent from a photolysis run was spiked with TCDD to make a 620-μg/l solution. A 1- × 10-cm column was packed with 2 g of silica gel and 2 g of 44% H_2SO_4/silica gel, then 3.0 ml of the photolysis solution was placed on the column and eluted with 35 ml of hexane. The sample was concentrated to 3 ml, and a 67-μl sample was injected onto the HPLC. Fractions of the eluate were collected over the time interval consistent with retention times of a standard (5–8 min). The eluate was collected in a 25-ml volumetric flask which contained 1 ml of hexane. The solution was then washed with enough 1% w/w aqueous sodium bicarbonate so that the hexane layer separated in the neck of the volumetric flask. The hexane was withdrawn with a disposable pipet, and the aqueous methanol solution was extracted with three successive 1-ml portions of hexane. The combined hexane layers were reduced to 0.1 ml in a cone-bottom vial and analyzed by GC/ECD.

Scaleup Photolysis

A 4655-ml aliquot of extracts from the first three extraction scaleup experiments was placed into a 5-liter, 3-necked flask equipped with a quartz light-well through the center neck, a magnetic stirring bar and a reflux condenser connected to a trap filled with water. Technical-grade IPA (85 ml) was added, the solution was stirred magnetically, and a 450-W Hanovia mercury lamp was inserted in the light-well and switched on. Samples were removed for dioxin and chloride ion analyses. Chloride ion was determined by extracting a 20-ml sample with 10 ml of water. The water and the water in the scrubber were analyzed by ion chromatography on a Dionex Ion Chromatograph using a 0.0024-*M* sodium carbonate/0.003-*M* sodium bicarbonate eluent at 3 ml/min through a 6- × 250-mm cation suppressor column followed by a 3- × 150-mm anion separator precolumn followed by a 3- × 500-cm anion separator column.

Miniplant Operation

Into a 4-liter, jacketed, glass resin kettle equipped with an agitator ("crow's foot") and condenser, was placed 1050 ml of 15% w/w sodium

hydroxide solution and 1250 ml of technical-grade hexane. NEPACCO waste [322 g (~233 ml)] was added, and the bottle was rinsed with an additional 250 ml of 15% sodium hydroxide. The mixture was heated to 42°C and stirred at 17,000 rpm for 20 min. After settling occurred, the top hexane layer was transferred by pump to a 3-liter, jacketed glass vessel. Successive extractions were performed with 610 and 305 ml of hexane, and the first five hexane extracts were combined in the photolysis reservoir. To this solution was added 56 ml of technical-grade IPA, and the yellow solution was pumped at 65–100 ml/min from the bottom outlet of the reservoir through a 250-ml photochemical reaction vessel into the top of the reservoir. The photochemical reactor was equipped with a 450-W medium-pressure, Hanovia mercury-vapor lamp in a water-cooled immersion well and a reflux condenser. Sampling valves in the Teflon® lines allowed inlet and outlet samples to be taken at various time intervals. After 3.5 hr, the light was turned off, a condenser was placed on the photolysis reservoir, and the brown solution was distilled by heating with water/ethylene glycol. Distillation began at 59° C, and about 100 ml of distillate was collected when the vapor temperature reached 65°C. The temperature gradually rose to 65°C during the distillation.

To the caustic raffinate in the extractor was added with stirring 1294 g of 20.8% w/w sulfuric acid. The mixture separated into a brown aqueous layer (~2400 ml) and a black oil at the bottom.

RESULTS AND DISCUSSION

Composition of NEPACCO Waste

Characterization of wastes is the basis for any rational waste treatment process. Knowledge of the waste composition provided the key to successful treatment in this case. The tank contained the distillation residue from trichlorophenol purification. Presumably, trichlorophenol had been manufactured by treatment of tetrachlorobenzene with sodium hydroxide in ethylene glycol at 150 and 200°C. Therefore, by-products from trichlorophenol production, phenols and TCDD were expected, and analytical procedures were based on these expectations. Solvent extraction of the waste gave a base-soluble fraction and a neutral organic fraction containing TCDD. GC/MS analysis of these fractions revealed 42 different components. Figure 1, the reconstructed GC/MS chromatogram of the base-soluble fraction, shows a variety of hydroxyl and

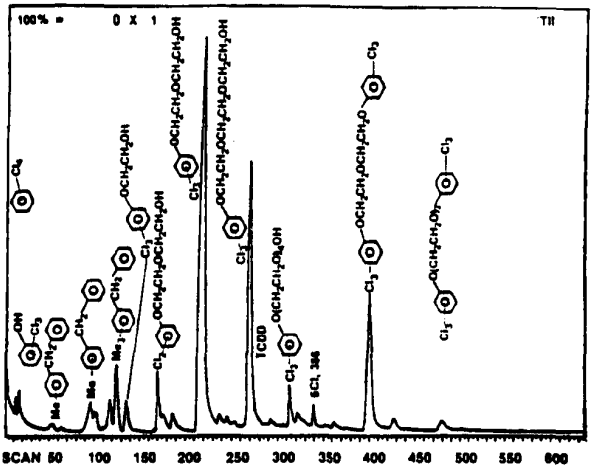


Figure 1. Reconstructed gas chromatogram for fraction of waste extracted into 15% methylene chloride/benzene.

ethylene glycol derivatives of tetrachlorobenzene. The major portion of the base-soluble fraction, about 50% w/w, was trichlorophenol. The neutral fraction, shown in Figure 2, contained methylated benzylbenzenes (presumably impurities in tetrachlorobenzene), ethers of trichlorophenol and diethylene glycol, ethylene glycol and diethylene glycol derivatives of tetrachlorobenzene, tetrachlorobenze, and TCDD. These compounds are consistent with the manufacture of trichlorophenol by hydrolysis of tetrachlorobenzene.

TCDD was confirmed by GC/MS by matching GC retention times to within 0.1 min of a standard, and by the relative intensities at m/e 320 (74), 322 (100) and 324 (48). In addition, various purification techniques allowed GC/EC quantification. Purification methods, adapted from those described by Lamparski et al. [7], consisted of liquid chromatography through acid-treated silica gel, silica gel and alumina. Impurities were separated by elution with hexane, and dioxin was collected in 20% methylene chloride/hexane. The nominal TCDD concentration in the

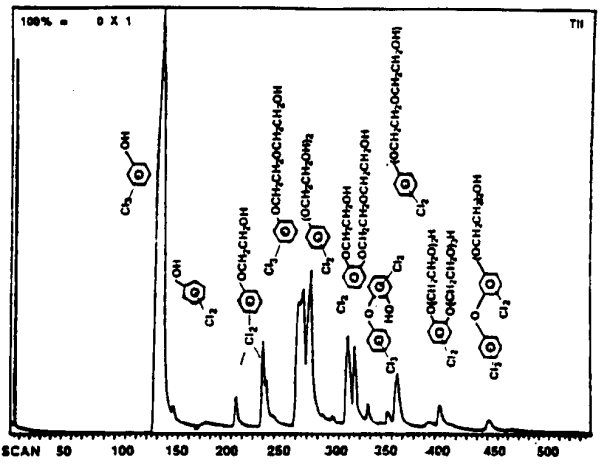


Figure 2. Reconstructed gas chromatogram for base-soluble fraction after extraction with 15% $MeCl_2$/PhH.

waste was 343 ng/g; however, collection of a representative waste sample from the tank was complicated by the dangerous nature of this waste and extreme difficulties in obtaining representative, homogeneous samples.

Process Selection

In addition to the analysis of the NEPACCO waste, three destruction processes (catalyzed wet oxidation, photochemical reduction and chemical treatment) were examined during the first phase of this project. The first two processes were tested experimentally and achieved a dioxin destruction of greater than 99% in preliminary lab experiments. Conceptually, catalyzed wet oxidation of the NEPACCO waste involved minimal handling, only one reaction vessel, and led to only inorganic, aqueous residues. However, this process used technology still under development and involved high pressure, a safety consideration. On the other hand, the

extraction-photolysis process destroyed only the dioxin, the most dangerous component of the waste, left an organic residue and required several pieces of equipment and several stages of operation. On the positive side, the photolysis process used typical chemical engineering unit operations at ambient temperature and pressure under close process control. Because of the overriding factor of safety, the extraction-photolysis process was selected for further development.

Extraction-Photolysis

This TCDD destruction process is based on two important operations. First, dioxin must be separated from the majority of the waste components by extraction with a suitable solvent. In addition to being selective in removing dioxin, the solvent extraction process also must remove >99.9% of the dioxin from the distillation sludge. Second, photolytic dissociation of the carbon-halogen bond must occur efficiently.

The ability to separate dioxin from other chlorinated waste components is highly solvent-dependent. Figure 3 shows UV spectra of NEPACCO waste extracts in hexane, tetrachloroethylene and *o*-xylene. At dioxin concentrations of 1.2 mg/l, xylene and tetrachloroethylene extracts contain approximately 4 and 2.5 times more by-products, respectively, than hexane extracts. Hexane extraction of the NEPACCO waste removed the dioxin and about 2% w/w of other chlorinated waste material. Greater than 99.9% extraction efficiency was achieved by successive batch extractions.

Photolytic dissociation of aromatic halides occurs under the influence of sunlight or UV light [8–10]. Sunlight or simulated sunlight degrades chlorodioxins in the presence of hydrogen donors [11, 12]. Pure TCDD in methanol decomposed 50% in 4–8 hours when exposed to simulated sunlight [13]. In addition, di- and trichlorodibenzodioxins degrade faster that TCDD [13]. Chlorinated dibenzofurans, compounds closely related to dioxin, also are reduced by dechlorination and polymer formation [14]. Thus, the literature data demonstrate that TCDD is dechlorinated by UV light. However, photolysis rates can be affected by light-absorbing impurities, radical inhibitors and, of course, fouling of the light-wells.

The rate of photolysis and the products formed are primary concerns in any successful photolysis detoxication process. Figure 4 shows the rate of decomposition of dioxin in a hexane extract of NEPACCO waste. These experiments were carried out in photochemical reaction vessels with medium-pressure mercury-vapor lamps immersed in water-cooled wells.

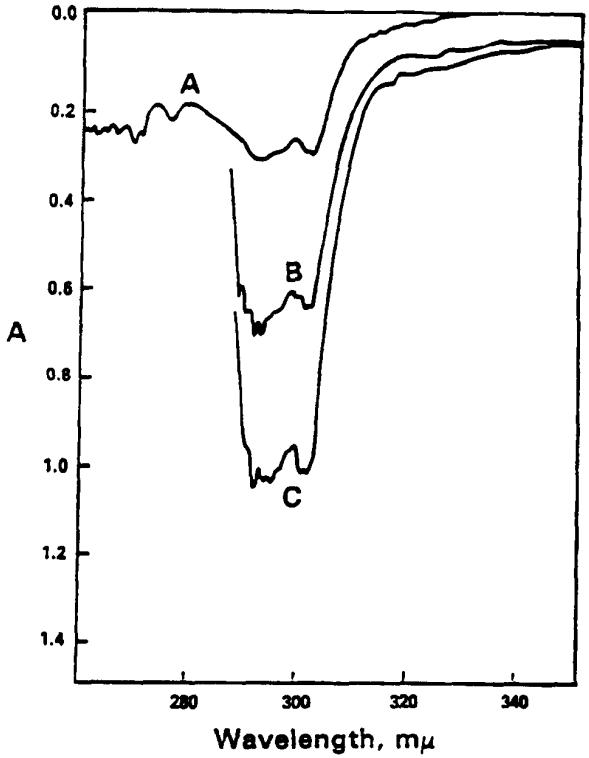


Figure 3. UV spectro of TCDD extracts of NEPACCO waste: (A) hexane: (B) tetrachloroethylene: (C) *o*-xylene.

The photodecomposition rate is pseudo-first-order over a concentration range of five orders of magnitude. However, early work showed a marked rate decrease at about 99% TCDD reduction. This decrease in the rate of decomposition of dioxin was due to the fouling of the light-well by

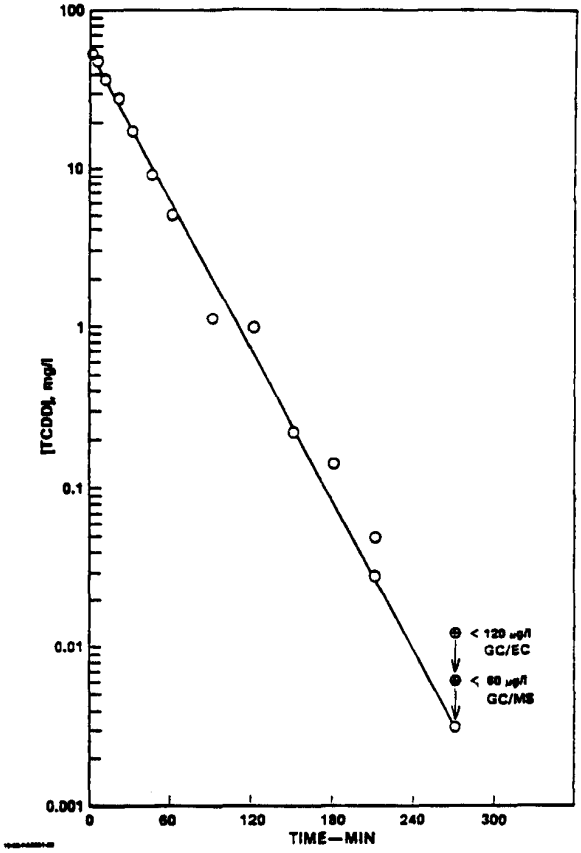


Figure 4. Rate of dioxin disappearance on UV irradiation.

oligomers of hexane. These polymeric photolysis by-products presumably arise after hydrogen abstraction from hexane. Further incidences of light-well coating were prevented by adding other hydrogen donors, such as isopropyl alcohol, to the solution. The presence of isopropyl alcohol allowed the high degree of TCDD destruction shown in Figure 4 without affecting the rate of reaction. The rate of photodecomposition also is temperature-independent. These findings are consistent with rate-determining C-Cl bond breakage followed by reduction of the dioxin radical via hydrogen abstraction from the solvent.

Although photolytic conversion of dioxin to more highly toxic compounds seemed unlikely, care was taken to examine the reaction products of the photolysis of the NEPACCO waste extracts. Extensive GC/MS analyses supported the postulated TCDD decomposition path shown in Figure 5 and were consistent with data of Botre [15] and Plimmer et al. [16]. Exposure of TCDD and the other chlorinated organics in the hexane solution to UV light successively dechlorinates these compounds. Figure 6, the reconstructed gas chromatograms of photolysis solutions at different irradiation times, shows the disappearance of many chlorinated compounds that exist in hexane extracts of NEPACCO waste. For example, the disappearance rate of the diethylene glycol derivative of trichlorophenol is 0.54 times that of TCDD and follows similar first-order kinetics. When a photolysis sample was concentrated, a dark oil separated from hexane. This acetone-soluble oil contained ethoxylated phenol consistent with dechlorination reactions. No chlorinated compounds were detected at the end of exhaustive photolysis by GC/MS or direct-probe mass spectrometry.

No gas evolution occurred during photolysis. A sample of the vapor space above the photolysis solution was examined by GC/MS. Hexane and hexane isomers were major components, and IPA and traces of 2-chloropropane and acetone were present. The hydrogen chloride formed during photoreduction remained in solution. Photolysis of NEPACCO waste extracts yielded about 3.6 times the theoretical amount of hydrogen chloride based on TCDD. These data are consistent with dechlorination of dioxin and of the other organic components present in the hexane extracts.

Engineering Considerations

Conversion of laboratory data to full-scale plant design is always difficult. In this case, the high toxicity of the dioxin-containing waste prevented normal scaleup methods involving pilot-plant examination.

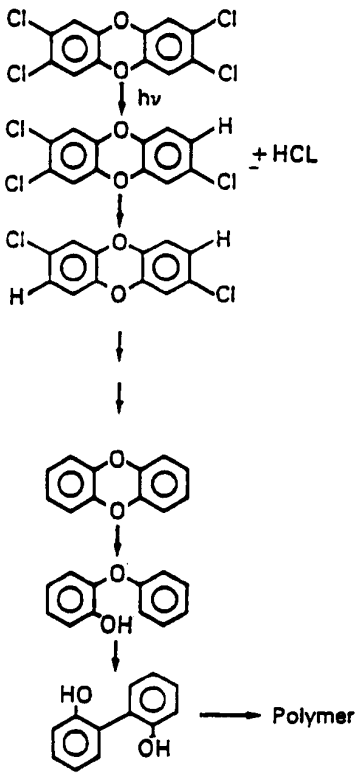
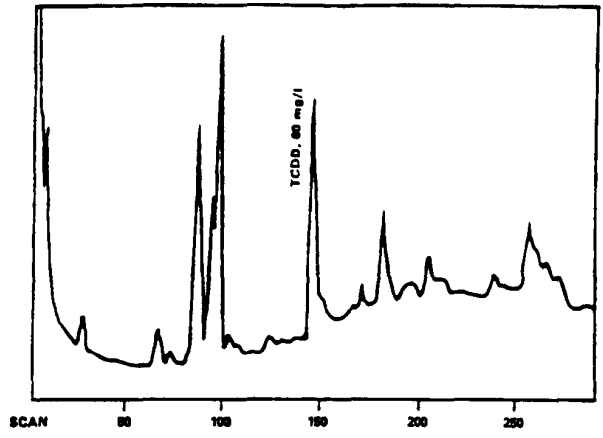
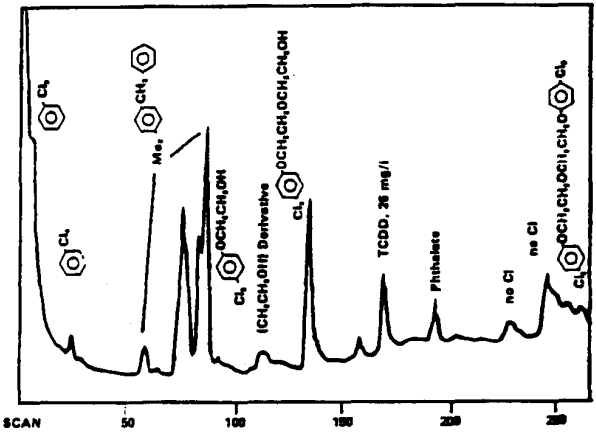


Figure 5. Photoreduction products of TCDD.

Consequently, great care was required in designing a laboratory mini-plant that was safe, protected the worker and the environment and provided adequate scaleup data from 2 liters to 2000 gal, a factor of >3000. The full-scale extractor at Verona was intended to be an existing, 2000-gal glass-lined reactor. A laboratory version of this vessel was


TCDD, 60 mg/l
SCAN
80
100
150
200
250


Cl2
CL
Me2
CH3
OCH2CH2OH
Cl2
ICH2CH2OH Derivative
OCH2CH2OCH2CH2OH
Cl2
TCDD, 25 mg/l
Phthalate
no Cl
no Cl
OCH2CH2OCH2CH2O
Cl2
Cl2
SCAN
50
100
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250

designed carefully using a similarity approach to scale down to a 3-liter glass laboratory vessel. The proposed large-scale reaction vessel had an impeller-to-tank diameter ratio of 0.56, a tank height-to-diameter ratio of 1.32, an impeller tip speed of 1348 ft/min, and a Reynolds number of 5.3 × 10^6. The corresponding laboratory extraction vessel was designed to have an impeller-to-tank diameter ratio of 0.52, a tank height-to-diameter ratio of 1.03, an impeller tip speed of 1360 ft/min, and a Reynolds number of 0.4 × 10^6. In addition, a retreating curve impeller was fabricated to maximize scaleup similarity. The mixing action in the laboratory extractor was visually similar to that of the 2000-gal reactor.

The following aspects were examined for photolysis scaleup: (1) optical density of TCDD solutions; (2) lamp characteristics, such as intensity, spectral distribution, spatial arrangement, commercial availability and safety features; and (3) interference by UV absorbers or fouling of the light-well. Hexane extracts of NEPACCO waste absorb UV light in the 200- to 320-nm region. Dioxin's absorption bands are at 235 and 306 nm.

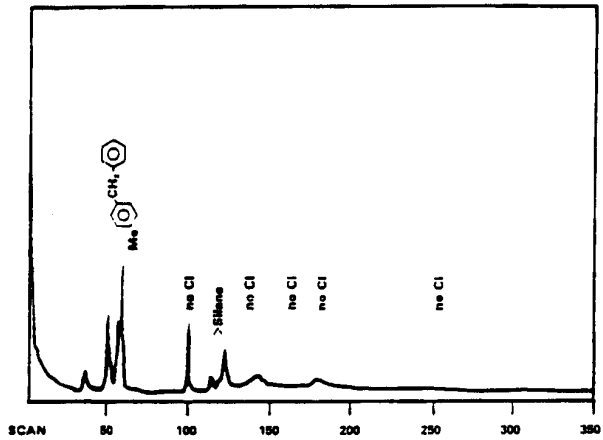

Figure 6. Reconstructed gas chromatograms for 10% isopropyl alcohol/hexane photoreduction after (A) 11 min; (B) 21 min; (C) 300 min.

Molar extinction coefficients are about 4.5×10^5 M^{-1} -cm^{-1} and 6×10^3 M^{-1} -cm^{-1} at 235 [17] and 306 [11] nm, respectively. However, hexane extracts of NEPACCO waste have apparent extinction coefficients in the 290- to 310-nm range that are 2–6 times higher than those calculated for pure dioxin. This increase in light absorption is presumably due to absorption by other trichlorophenol derivatives extracted from the waste. Thus, 99% of the available UV light is absorbed within a very short distance from the light-well. This high solution absorptivity dictated the choice of the photolysis reactor design. Photochemical and safety considerations led to the use of annular flow reactors with a batch recycle reactor system [18] in which the photolysis solution is pumped from a reservoir through a light reactor. The operational characteristics of a batch recycled reactor are described by:

$$C = C_o^{-\alpha t f/V_r}; \quad \alpha = 1 - e^{-kV_r/f} \tag{1}$$

where C_o = initial dioxin concentration
t = reaction time
f = pumping rate
V_v = reservoir volume
V_r = reactor volume
k = reaction rate constant

Analysis of Equation 1 shows that pumping rate and reservoir and reactor volumes affect the reaction time, and that reaction time to achieve specific dioxin destruction is inversely proportional to reservoir volume. Practical considerations of available equipment fixed the reservoir to reactor volume, and the pumping rate was set at a relatively low 5 gal/min per light reactor for safety reasons. Because of the high absorbtivity of the solution, good mixing in the light was crucial to allow transport of dioxin from the bulk solution to within 1–5 mm of the light-well surface. Turbulent flow was also necessary to minimize deposition of photolysis products and fouling of the light-well. In the miniplant reactor, Reynolds numbers of about 100 were achievable, compared to the expected number of 14,500 in the full-scale system. With the exception of the inability to provide turbulent flow in the laboratory reactor, all other parameters such as residence time and flowrates, were similar to those projected for the full-scale system.

In addition to physical and spatial scaleup considerations, the spectral distribution of suitable lights had to be examined. Since dioxin in hexane absorbs light below 320 nm, the light intensity in that region for the laboratory lamps had to be comparable to industrial lamps. Industrial

UV lights and 450-W laboratory lamps have similar power outputs per unit area both in total power and in power available below 313 nm. The 100-W laboratory lamp, although convenient to use in preliminary laboratory experiments, has considerably lower power flux than the other lamps. Comparison of batch photolyses with the 450-W and 100-W lamps showed that the high-intensity lamp decomposed dioxin at a rate 12.9 times faster than the lower-intensity lamp. This observation is in accord with the fact that the 450-W lamp has a power output 11.6 times that of the 100-W lamp below 313 nm. Based on the data from the 450-W scaleup runs and the observation that all usable light is absorbed within 10 mm of the light-well, it was calculated that eight 10-kW lamps would be able to reduce a 6600-liter batch of hexane extract containing 40 mg/l of dioxin by 99.79% in 22 hours.

Operation of Destruction Process

At the conclusion of the laboratory and miniplant experiments, the third phase of the project—engineering, construction and operation—began. Careful process engineering provided piping and instrument diagrams and equipment, piping and instrument specifications. This work incorporated careful planning for worker and environment protection by providing engineering controls, such as:

- leak-proof pumps and piping connections;
- minimization of pumps by pressure transfers;
- separate diked process areas;
- a vent system with pressure reliefs;
- flame arrestors; and
- an emergency blowdown tank.

Careful attention to operating procedures and redundant instrumentation minimized the potential for misoperation and spills.

Detailed engineering design provided the final aid to plant construction. During the construction phase, the process and engineering were reviewed extensively by IT Enviroscience, Syntex and an EPA task force. A series of public meetings explained the process to town residents, and careful safety, industrial hygiene, environmental and emergency procedures were put in place. A laboratory was equipped onsite for process control.

EPA approval was received on May 19, 1980. After a one-week startup period and additional troubleshooting, 160-gal batches of NEPACCO waste were run through the destruction process in five 2-week operating

periods. Six extractions of the waste reduced the dioxin content from 343 to 0.2 ppm. Generally, photolysis reduced the dioxin concentration to less than 0.1 mg/l, with optimum photolysis times of about 20 hours. About 700 process samples, many at the ppb dioxin level, were analyzed to control the processing. Air sampling at the single process vent confirmed that no dioxin (less than 0.01 $\mu g/m^3$) was emitted to the atmosphere during operation.

SUMMARY

The extraction-photolysis process for destroying TCDD in a hazardous waste was implemented in full-scale plant operation within 19 months of initial laboratory experiments. A 3000X scaleup of data from laboratory to full-scale plant was successful. Procedures developed for handling the very toxic dioxin prevented personnel exposure and environmental contamination. None of the extensive contingency procedures needed to be implemented. About 7 kg of dioxin were destroyed with 99.94% efficiency, and a significant hazard to the population of Verona, Missouri, and surrounding communities was removed.

ACKNOWLEDGMENTS

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CHAPTER 18

ENVIRONMENTAL HEALTH AND SAFETY CONSIDERATIONS FOR A DIOXIN DETOXICATION PROCESS

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Successful, environmentally safe destruction of nearly 4300 gallons of dioxin-laden sludge containing 343 ppm of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) was a significant challenge. Syntex Agribusiness Inc. engaged the consultant services of IT Enviroscience, Inc., to help develop a unique extraction-photolysis process to remove and subsequently destroy the dioxin from a complex, tar-like sludge residue. This residue was the resultant still bottoms from a high-vacuum distillation of trichlorophenol (TCP). The material had been generated by a firm, the North East Pharmaceutical and Chemical Company (NEPACCO), which leased a portion of a chemical plant that was later purchased by Syntex.

Syntex' primary goal for development of such a detoxication process was the safety of the public, its employees and the surrounding community. It was necessary to break new technological ground to develop a suitable, inherently safe dioxin detoxication process. Of the various processes considered, the extraction photolysis process conducted at moderate temperatures and ambient pressure accommodated most closely the safety criteria established.

An interdisciplinary team of Syntex scientists, technical experts in environmental health and safety, a Blue Ribbon Committee of academic and industry consultants, and several members from various govern-

mental agencies all worked to help plan, design and refine this process. More than 13 lb of dioxin (343 ppm) was safely detoxicated to < 0.2 ppm—a reduction greater than 99.9%. Because of the known toxicity of TCDD, strictly regimented environmental, health and safety guidelines were implemented for the conduct of the process operation to ensure that the environment, workers and surrounding area were adequately protected. Figure 1 depicts the range of activities that were covered.

ENVIRONMENTAL WASTE STREAMS

The extraction photolysis process for dioxin detoxication was designed to minimize the amount of contaminated waste streams generated. In terms of air emissions, the sole vent for the photolysis process was from a packed caustic scrubber unit capable of treating any evolved gases, nitrogen purge gas or displaced airspace volumes arising from various process transfer operations. The vent was monitored continuously for organic vapor emissions by an alarm system designed to sound whenever levels greater than 25% of the lower explosion limit (LEL) for hexane, the key extracting solvent, were exceeded. The alarm never sounded during process operation. A portable organic vapor analyzer was available to detect system leaks, to determine solvent vapor levels associated with possible drips or spills, and to serve as a calibration check for the fixed, continuous alarm system. Additional periodic air sampling studies at the process vent were conducted by IT Enviroscience during strategic operations to further verify that there were no emissions of dioxin. A modification of the U.S. Environmental Protection Agency (EPA) Method V for analyzing particulate emissions from stationary sources was used to analyze for dioxin using both filter and impinger techniques. Results of these studies confirmed emission levels of hexane well below predicted levels, and no detectable dioxin releases. Two fixed air sampling stations were established at upwind and downwind process area perimeter locations to provide continuous dioxin monitoring. Additionally, five other plant site areas were sampled continuously to further verify that there had been no dioxin release. No detectable levels of dioxin (analytical limits of < 0.005 μg) were found at any of these fixed sampling points. Finally, as will be discussed further below, personal monitoring was conducted by filter cassettes and personal sampling pumps. Again, no dioxin was detected.

In terms of liquid or aqueous waste emissions, Table 1 summarizes typical waste analyses for the three process-generated waste streams. The neutralized oil and the still bottoms streams were kept isolated in separate

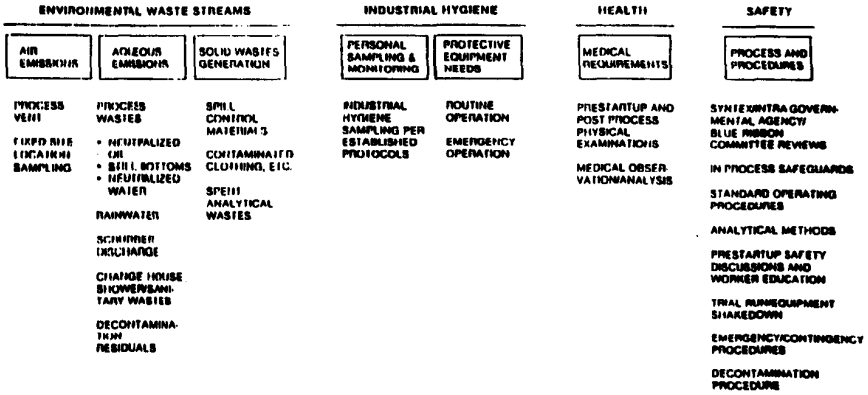

Figure 1. Environmental health and safety considerations for a dioxin detoxication

Table I. Summary of Typical Environmental Waste Streams from Dioxin Detoxication Process

Waste	Quantity		Approximate Composition	
	gal	lb	Dioxin (ppm)	Other (%)
NEPACCO wastes fed to process	160	1841	343	50% trichlorophenol; 50% ethylene glycol derivatives
Neutralized oil and still bottoms residue after processing	175	1937	0.2	50% trichlorophenol; 50% ethylene glycol derivatives; hexane traces
Neutralized water after processing	672	6411	<0.002	13% Na_2SO_4; 1-3% isopropyl alcohol and ethylene glycol derivatives; 84-86% water

steel storage tanks within the diked detoxication process area, pending final EPA approval for ultimate disposal. The neutralized water waste was stored in a concrete diked open-top tank located proximal to the detoxication process area wherein further natural degradation of any remaining low-level TCDD residues could occur by ultraviolet (UV) rays from sunlight. A separate 10,000-gal storage tank was available to contain rainwater that gathered within the detoxication process area. Scrubber discharges were either reused as part of the neutralization step during the extraction process, or neutralized and sent directly to the concrete diked tank. Aqueous wastes generated from the change house were approved by EPA for treatment in an onsite wastewater system. Solvents used in processing, when they became contaminated, were detoxicated in the extraction photolysis process, and the resultant material was recycled into subsequent batches. At the end of processing, the final detoxicated solvent residuals were placed into a tank pending approval by EPA for ultimate disposal. Any solid wastes generated from spill absorption procedures, disposal of possibly contaminated work clothing, boots, gloves or goggles, or spent analytical operations, (e.g., disposable laboratory clothing, gloves and burettes) were kept isolated, and contained in marked 55-gal covered drums, pending EPA approval of final disposal procedures.

INDUSTRIAL HYGIENE

The focus for worker protection of the detoxication process operators included a comprehensive education concerning all the potential hazards

associated with the process and an emphasis on the need for protection of any exposed skin surfaces at all times. The process was designed for 24-hour operation, using a four-shift-per-day staffing of two process operators per shift inside the detoxication process, and a Syntex process supervisor stationed outside the secured area who oversaw the operation for technical suitability, sample gathering and analysis, and emergency response requirements. The emphasis for process operation was on step-by-step control by experienced, knowledgeable personnel throughout the detoxication process.

Access to the detoxication area could be gained only by authorized workers passing through a change house. All workers removed their street clothes on the clean side of the change house and put on fresh work clothes supplied by Syntex on the process side of the change house. The detoxication process operators were strictly trained to conduct certain industrial hygiene protocols during each shift of operation. One operator per shift had a personal sampling pump attached to his belt that pulled approximately three liter/min of air through a labeled filter cassette clipped onto his shirt collar to monitor his breathing zone for dioxin. Additionally, an organic vapor badge was worn by the same operator to substantiate that there was no overexposure to any solvents (primarily hexane). Each operator rotated every other day wearing the pump, filter and organic vapor badge. The operator wearing the industrial hygiene equipment was required to take any necessary in-process samples. The operators were trained to calibrate the pump at the end of the shift, to log in and out pertinent sample information, and to record any unusual events that may have occurred during the shift. The filter samples, vapor badges and logged information were routinely transferred from the process side to the clean side of the change house for subsequent chemical analysis. None of the filters analyzed (analytical limits of < 0.005 μg) indicated any detectable levels of dioxin, and the threshold limit values (TLV) of the process solvents (TLV of hexane = 100 ppm; TLV of isopropyl alcohol = 400 ppm) were not reached.

The process operators were required to wear supplied uniforms, chemical-resistant gloves, chemical safety goggles, safety shoes and hard hats. In addition, for any emergency operations (e.g., handling spills, process line disruption or fire), procedures required the operator to wear chemical wet suits, boots, taped sleeves and pant legs, face shields and suitable respiratory protection equipment. A self-contained breathing apparatus (SCBA) was designed to be the first-line respiratory protection for any emergencies, particularly under conditions where aerosolization of dioxin might be expected to occur. Four SCBA units each capable of 30 min minimum air-supply were available from the process side of the change house, with an additional four air-supply tanks also kept readily

available. Chemical cartridge respirators were issued and appropriately fit-tested for each person for use in emergencies that might result in exposures to organic solvent releases that would not be expected to contain TCDD, e.g., hexane or isopropyl alcohol. Fortunately, there were no situations necessitating the use of any of the emergency equipment.

The supplied uniforms were routinely laundered and dried by the process operators after each shift, using the washer and dryer located on the process side of the change house. Obviously, soiled white uniforms were not laundered, but were disposed of as solid wastes in marked and covered 55-gal drums located near the change house; any soiled gloves, safety goggles, hard hats, safety shoes, etc., were not reused or decontaminated, but were also disposed of in this manner. All operators were required to shower before going back to the clean side of the change house at the end of shift. Additional industrial hygiene restrictions forbade food, beverages or smoking in the detoxication process area, and dictated complete adherence to all change room procedures and routine inspection and maintenance of all respiratory protection equipment. The analytical laboratory personnel located in a segregated laboratory immediately outside the detoxication process area were also required to follow strict industrial hygiene practices such as wearing disposable gloves and laboratory uniforms, restricting access to their work areas, and showering before leaving the isolated work area.

HEALTH

A comprehensive medical examination was conducted on all detoxication operation personnel before start-up. Table II summarizes the key parameters for medical examination and evaluation. Certain employee medical health anomalies, based on a physician's analysis and evaluation of the parameters identified in Table II would preclude a person from working within the actual detoxication process and have him assigned outside this area. Each operator chosen to work within the detoxication area satisfactorily met all the health requirements. Following final

Table II. Employee Medical History/Physical Examination Selected Evaluation Parameters

History of nervous disorders, drinking habits
Evidence of preexisting chronic illnesses
Evaluate skin/liver function
Assess suitability to wear respiratory protective equipment

shutdown of the detoxication process, all the process operators and supervisors were given postprocess physical examinations as part of Syntex' ongoing state-of-the-art health surveillance program. A comprehensive evaluation by an interdisciplinary team of Syntex physicians, epidemiologists, toxicologists, industrial hygienists and statisticians found no adverse health effects. This review included comparing individual and grouped medical results to other nondioxin process chemical operators at the Syntex plant. During process operation, a local physician in the community who had conducted the prestartup physical examinations was available to provide medical assistance on a routine or emergency basis as required for those people engaged in the detoxication process.

SAFETY

All steps designed to provide for safe operation were required to have been completed before startup of the detoxication process. A comprehensive review of the detoxication process by a Blue Ribbon Committee encompassing expertise in photochemistry, chemical engineering process analysis and reaction kinetics was completed before startup. Several governmental agencies, including EPA, the National Institute for Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administration (OSHA), the Missouri Department of Natural Resources and FDA participated with key Syntex managers in ongoing review meetings, detailed process flowsheet analysis and a final onsite walk-through of the detoxication facility before granting startup approval. Numerous safeguards were integral to the basic design of the process, including moderate-temperature and ambient-pressure processing, totally enclosed process operation, diked and sumped process area, nitrogen transfer operations, isolated cooling water sources, small batch sizes, outdoor process operation, corrosion-resistant tanks and piping, explosion-proof equipment, outdoor safety showers, and complete protective enclosure of the highly contaminated dioxin waste storage tank. Within the detoxication process, all reaction vessels were equipped with flame arrestors, and vented to a caustic scrubber system. All reaction vessels were connected to a bump tank via individual reactor pressure-relief devices. The entire process was color-coded for ease of reaction vessel and pipeline identification, and the photolysis light system was designed to shut down automatically in the event of an emergency.

Before startup, detailed standard operating procedures were drafted and compiled for all aspects of the batch detoxication process in a format

similar to that used in regular in-plant manufacturing processes. Analytical methods and procedures were developed and formalized for routine in-process sample analysis of the process waste streams listed in Table 1, and for monitoring extraction efficiency and extent of the photolysis reaction. All of the analytical samples were taken through special liquid-sampling valves, transferred to a locked sample box at the perimeter of the detoxication process area, and subsequently transported to the analytical laboratory just outside the process area in a specially designed, absorbent-filled bucket carried by the outside process shift supervisor.

Detailed safety training programs were conducted to educate all process workers on personal safety and industrial hygiene procedures, use of routine and nonroutine protective and respiratory equipment, change room procedures, firefighting techniques, hazardous spill control, medical monitoring programs, emergency shutdown and contingency procedures, and process sampling and transfer procedures. Each worker received nearly 40 hours of classroom instruction and training on all aspects of the detoxication process. Following the classroom training, the entire detoxication process was tested using hexane and water solutions containing no dioxin. The operators received onsite training in taking analytical samples and operating the photolysis system, and conducted several mock firefighting exercises before startup.

A comprehensive contingency plan was drafted and approved by EPA in the event of a major spill, fire, explosion, tornado or offsite release of materials. The plan included measures for immediate shutdown of the process, containment, and subsequent action to alert the nearby population. A highly trained, commercially available chemical cleanup service was on call to assist in any emergency during detoxication process operation. Fortunately, no such emergencies arose during the process operation. Nearly a dozen town meetings were held in the small community of Verona, Missouri, where the detoxication process was located, to assure the local people of the safety of the operation, and that public health and other considerations had been considered and more than adequately met. Comprehensive decontamination procedure protocols were developed for final cleanout of all process piping and vessels, with subsequent wipe test analyses to be conducted to verify that decontamination was complete.

Additional safety precautions included continuous monitoring and recording of prevailing wind conditions, and establishment of definitive spill containment procedures using cob meal, a readily available absorbent at the Syntex plant, to absorb any liquid discharges. Other security measures required 24-hour guard duty at the entrance to the plant site, limited plant access for non-Syntex personnel, and a completely fenced-in area surrounding the detoxication process.

Onsite representation of EPA Region VII was present throughout the operation to monitor the day-to-day events of the detoxication process operation. Periodic sample splits were provided to EPA to assay and confirm the extent of detoxication. All results from laboratory samples analyzed by IT Enviroscience and Syntex personnel were made available to EPA. EPA established its own perimeter and area monitoring air sampling protocols as an independent verification of the safe operation of the detoxication process. EPA results confirmed that there had been no release of dioxin.

CONCLUSION

Operation of the dioxin detoxication process in an environmentally safe manner resulted from a successful combination of industry, government and academic expertise working toward a common goal. The primary objective of achieving and maintaining safety for the environment, operating personnel and the surrounding community was achieved. None of the extensive contingency plans for emergency protection of the public health and the environment needed to be implemented. Operating procedures, analytical methodologies, environmental, health and safety considerations, and emergency/contingency procedures are viewed as innovative, and should serve as models for the new and evolving field of hazardous waste management. Successful completion of this project demonstrates that technical expertise coupled with corporate responsibility can interact to solve some of the difficult hazardous wastes problems that face us today. The complex system of environmental and personal monitoring controls required for this detoxication process confirm, through the absence of any negative environmental impacts, the effectiveness of the precautions taken.

SECTION 4

BIOLOGICAL DETOXICATION: GENETIC ENGINEERING, MICROBIAL AND ENZYMATIC TREATMENT

CHAPTER 19

OPPORTUNITIES FOR DEVELOPMENT OF NEW DETOXICATION PROCESSES THROUGH GENETIC ENGINEERING

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The U.S. Environmental Protection Agency (EPA) Advanced Environmental Control Technology Research Center (AECTRC) at the University of Illinois has conducted a planning study to assess the opportunities and problems of developing new pollution control technologies using genetic engineering. The goal of this study was to document the scientific basis for the genetic engineering approach to pollution control, and to develop recommendations for a research policy to promote it. To achieve this goal, three working papers were assembled, each dealing with one of the following subjects:

1. description of problems potentially amenable to the genetic engineering approach;
2. description of the genetic engineering technologies available for creation of new solutions to these problems;
3. selective description of factors limiting natural biodegradative processes, especially those that potentially may be manipulated by genetic engineering to create new pollution control technologies.

Each of these papers was reviewed by nationally recognized experts. In May 1981 these experts were brought to the University of Illinois to participate in a workshop that was organized around a discussion of the working papers. In addition, each paper was reviewed by a number of outside scientists and engineers.

A detailed description of the conduct of this study, the content of the working papers and the major conclusions from the workshop have been published [1]. The responses of the workshop participants and the outside reviewers have been used to formulate policy recommendations that were transmitted to AECTRC in September 1981.

Information from the AECTRC study relevant to biological detoxication of pollutants is assembled here, along with comments on the genetic engineering approach and possible barriers to the development of such new treatments.

RELATION OF DETOXICATION TO WASTE TREATMENT

To view detoxication from the perspective of the AECTRC genetic engineering planning study, it is necessary to recall that the fundamental axiom of toxicology states that all compounds are toxic if given to a test organism at a sufficiently high dose [2]. Thus, chemical compounds may differ in the concentration required to exert a deleterious influence on an organism, but all compounds potentially are toxic. By definition, compounds that exert deleterious influences on living organisms are said to be toxic to those organisms. Compounds are only toxic, therefore, with reference to some organism. From the anthropocentric, environmental perspective of this chapter, discussion will be limited to environmental pollutants that potentially may affect human health.

Detoxication is the transformation of a toxic substance into a less toxic product. Studies that determine the quantitative toxicity of a group of closely related compounds often find that one or a few substituent groups on the molecule impart the greatest fraction of the toxicity. For instance, nitroso- or chloro- substituents on a molecule frequently increase mammalian toxicity. Therefore one important mechanism of detoxication is the removal of the most toxic substituents. Primary biodegradation, a simple, biologically catalyzed change in a molecule that alters its chemical identity, can accomplish detoxication; similarly, mineralization of the compound (ultimate biodegradation) can also accomplish detoxication. Unfortunately, primary biodegradation can sometimes increase the toxicity of a compound by converting a less toxic substituent to a more toxic form. Reduction of aromatic nitro- groups to hydroxylamine and sequential methylation of mercury (Hg^{+2}) by anaerobic microbes in sediments are examples.

In addition to biodegradation, pollution treatment often reduces the toxic manifestations of a compound by diluting the toxicant or by physical sequestration of the toxicant into a phase not in contact with the

organism. Neither of these approaches to treatment alter the chemical composition or the inherent toxicity of the compound.

GENETIC ENGINEERING AND DETOXICATION

Improvements in the biodegradation of toxic pollutants through genetic engineering will ultimately rest on certain kinds of genetic manipulations that have only recently become possible. These manipulations include (1) rearrangement of genes from almost any source in microorganisms of almost any species; (2) amplification of the number of gene copies in an organism and concomitant amplification of the level of protein products made from those genes; (3) circumvention or alteration of control on the expression of particular genes; and (4) site-specific (gene-specific) mutagenesis to delete genes from an organism or to alter the characteristics of the gene product (enzyme), including changes in substrate specificity and kinetic constants.

The ways in which such manipulations might be used to develop organisms with enhanced or novel biodegradative capabilities can best be illustrated by considering a specific example. One broad class of compounds with a great potential for toxicity and widespread exposure to the human population are the manmade halogen-containing compounds. In general, these compounds are biodegraded in the environment much less readily than their nonhalogenated analogs. A brief examination of the genetics and enzymology of dehalogenation will illustrate many of the ways by which genetic manipulation might enhance the degradation of some of these compounds.

The enzyme-catalyzed destruction of the carbon-halogen bond was reviewed by Goldman [3], and there have been few important additions to this literature since that time. Briefly, Goldman identified two groups of dehalogenases, one whose primary function appeared to be dehalogenation and a second, which catalyzed dehalogenation but whose normal cellular function did not involve halogenated substrates. The first group consisted primarily of enzymes in aerobes catalyzing the hydrolytic displacement of halide from aliphatic acids (hydrohalidases) and enzymes in anaerobes catalyzing removal of HCl from DDT (dehydrohalidases). Hydrohalidases that are specified by plasmid-borne genes have been reported in *Moraxella* sp. [4,5]. Several kinds of hydrohalidases have been described [3]; each typically attacks a small group of closely related substrates.

The second group of enzymes were termed adventitious dehalogenases by Goldman, since the dehalogenation seemed to be an extrinsic and

fortuitous function. The primary function of these enzymes is not dehalogenation. They are, however, able to remove the halogen as a result of the usual reaction that they catalyze. Adventitious dehalogenases often produce a chemically unstable form of the halogen, such as halohydrin, which then decomposes spontaneously to release halide. An example is fumarase, which can accept fluorofumarate and produce 2-fluoromalate. This compound then rearranges to form oxaloacetate and fluoride [6]. The mechanism of halogen removal by other adventitious dehalogenases is less well defined. Oxygenases are frequently able to displace halogen from halogenated analogs of their normal substrates. Examples include the dioxygenase that removes fluoride from *ortho*-fluorobenzoate [7] to produce catechol and the lactonizing enzyme that displaces chlorine from 4-chloro-*cis,cis*-muconic acid to yield *cis,cis*-muconolactone during the catabolism of 2,4-dichlorophenoxyacetic acid [8,9]. The halogen that is removed occurs at the particular position on the molecule attacked by the oxygenase. Goldman has given examples of several other adventitious dehalogenation enzymes, and has suggested that close scrutiny of other isolated enzymes for the ability to accept and dehalogenate analogs of their normal substrates may reveal many more examples.

The existence of adventitious dehalogenases in an organism is not in itself sufficient for efficient detoxication of a compound. A halogenated environmental pollutant must be taken up by an organism and the compound must reach the dehalogenase in a form able to be metabolized by it. Thus, all halogenated intermediate molecules formed from a halogenated compound must be tolerated and transformed by all of the enzymes on a pathway leading to the dehalogenase step. Halogenated intermediates that are not accepted as substrates by these enzymes will prevent the compound from arriving at the dehalogenase in a form that can be metabolized. Also, if an enzyme preceding the dehalogenase can bind a halogenated intermediate but not metabolize it, the halogenated intermediate may act as an inhibitor of that enzyme, reducing the metabolism of its normal substrate and potentially poisoning the cell. For these reasons, the existence of an adventitious dehalogenase in an organism is merely a prerequisite for effective destruction of a halogenated pollutant.

To modify an organism for efficient dehalogenation, the molecular biologist can, in principle, select mutant forms of enzymes tolerant of halogen-substituted substrates. Studies extending the substrate specificity of an amidase suggest that mutation and selection can easily modify that portion of an enzyme's structure concerned with substrate recognition and binding, without affecting the structure of the active site [10]. Thus, halogen substitution at some distance from that part of a substrate bound

to the active site of an enzyme should be more easily tolerated. Since most mutant enzymes acquiring a dehalogenation activity have altered active sites, they are more difficult to select than enzymes simply tolerant of halogenated substrates. Mutations affecting the active site of an enzyme are less likely to occur and harder to isolate. In these mutants, a small fraction of the protein determining the critical structure of the active site is involved. It is well known that even minor changes in bond angles and distances in an active site often strongly reduce catalytic activity.

Recent advances in mutagenesis and selection facilitate isolation of halogen-tolerant mutants. Site-specific mutagenesis permits alteration of only specific regions of DNA, improving the yield of mutants in a desired gene. Timmis described various ways of performing in vitro site-specific mutagenesis [11] and Kleckner et al. [12] described the uses of transposons for site-specific mutagenesis. A continuous culture has been adapted specifically for selection of mutants catalyzing dehalogenation by Senior and co-workers [13,14]. They grew a carbon-limited culture of *Pseudomonas putida* on propionate in the presence of a fivefold excess of 2,2-dichloropropionate (dalapon). The propionate, called the carrying substrate, sustained the culture. Any mutants able to dehalogenate dalapon and use it as a carbon source would have a greater carbon pool available to it, should grow faster and displace the parental type from the chemostat. Adaptations of this technique in concert with site-specific mutagenesis hold great promise for the adaptation of existing catabolic pathways to recalcitrant analogs.

An elegant example of extension of a pathway by introduction of the genes for enzymes degrading halogenated substrates was described by Reineke and Knackmuss [15]. They observed that a *Pseudomonas* species carrying the TOL plasmid (a self-replicating unit of DNA, specifying the enzymes for the degradation of xylenes and toluic acids via catechol [16]) was able to metabolize both 3- and 4-chlorobenzoic acid to the corresponding chlorocatechols. The enzymes apparently accept chlorobenzoates as analogs of the corresponding toluic acids. The plasmid-specified enzymes could not accept chlorinated catechols, however, and the further metabolism of the chlorobenzoates was blocked at this step. Reineke and Knackmuss [15] were also aware of a *Pseudomonas* strain B13 that was able to mineralize 4-chlorocatechol, but which was unable to oxidize chlorobenzoic acids to chlorocatechol. By introducing the TOL plasmid into strain B13 and selecting for growth at the expense of 3- or 4-chlorobenzoic acids, they obtained a derivative strain that could mineralize either of these benzoic acids. This strain apparently possessed mutations in regulatory functions that allowed expression of plasmid-encoded functions through catechol and chromosomal functions there-

after. It was then used in further mutation and selection studies to extend the range of substrates subject to dehalogenation. Bull's strategy was used; a mutagenized culture was grown in a chemostat in the presence of 3-chlorobenzoate, a carrying substrate and a variety of other chlorinated benzoates not normally used by the strain. The nonutilized substrates were chosen so that single dehalogenations would allow the organisms to metabolize them. In this way, mutants were isolated that could mineralize 3,5-dichlorobenzoic acid. Neither the TOL-bearing strains or strain B13 had previously attacked this compound. It must be recognized, however, that most of these alterations required a detailed knowledge of the molecular genetics of the catabolic pathway being manipulated. This implies a substantial investment in basic research before similar manipulations could be undertaken in uncharacterized species.

Mutants might be improved further by increasing production of the enzyme of interest. This improvement can be accomplished by selecting constitutive mutants (mutations in regulatory genes that lead to continual synthesis of specific proteins), recombining the genes for the enzyme with strong promotors, as described by Timmis [12], and amplifying the number of copies of the relevant genes in an organism by using multicopy plasmids or gene duplications [11]. All of these manipulations could result in an increased carbon flux through the cell, allowing a simple selection on the basis of enhanced growth rate.

Once a particular pathway has been developed, existence of transmissible plasmids suggests a strategy to introduce it to indigenous organisms. Just as acquisition of the TOL plasmid extended the range of substrates utilized by strain B13, acquisition of a plasmid with a suite of genes specifying an entire catabolic pathway for a particular xenobiotic might quickly acclimate microflora without requiring colonization by an introduced organism. While the facility of plasmid transfer in nature is not well documented, plasmid spread under laboratory conditions can be explosive.

ECOLOGICAL CONSIDERATIONS

Barriers to the development of pollution control technologies based on genetic engineering are more likely to be found in the process of bringing an engineered organism to a polluted environment and having it function successfully in that environment than in the process of developing the organism itself. The genetic engineering industry was born from basic research in DNA enzymology and plasmid biology that grew into a set of tools for manipulating DNA. This industry is now integrating fermenta-

tion technology and molecular biology for the production of previously unavailable biochemicals. The development of pollution control technologies would require a similar coordination of microbial ecology with molecular biology. In contrast to fermentation technology, however, microbial ecology at the moment is a science less able to make predictions. In particular, the microbial ecologist cannot yet evaluate the possibility of success of efforts to establish engineered microbes in contaminated environments. This situation is a consequence of the complexity of the ecology of microbes and the small amount of attention historically paid to this subject.

In contrast to the development of the genetic engineering industry producing novel biochemicals, pollution treatment technologies based on engineering organisms are stalled temporarily by the uncertainties attendant on gene transmission from introduced, engineered organisms or the competitiveness of such microbes in the environment and their potential for establishment. Few direct attempts have been made to evaluate gene transmission from altered organisms to indigenous organisms or to evaluate their potential for establishment in nature. One such study was undertaken to evaluate the probability of escape of genetically debilitated organisms used for research or commercial production of biochemicals [17,18]. This work demonstrated the fragility of organisms like *X*1776 when exposed to the environmental conditions typically found in temperate climates. It also attempted to evaluate the potential of such organisms to colonize the mammalian gut. Since *X*1776 is debilitated by design, it is understandable that this work failed to demonstrate establishment. This does not necessarily reflect the potential of organisms normally resident in aquatic and terrestrial environments, especially if these organisms have had only minimal genetic alteration. Lack of experimental information, however, does not allow a conclusion to be drawn.

A number of companies exist that sell microorganisms claimed to improve or enhance the biodegradation of various components of waste streams in waste treatment facilities or of pollutants in situ in the environment. This apparent source of information on the effectiveness of introduced organisms has been found to be of little value. It is in the interest of these companies to know whether organisms introduced into a resident microflora can colonize or transmit relevant genes to indigenous microbes. Data on the use of one of these commercial microbes has shown that establishment and effective biodegradation can occur when these organisms are introduced into a lab-bench aeration basin lacking a resident microbial population [19]. We are unaware, however, of any information clearly showing the effectiveness of these organisms intro-

duced into normally operating full-scale aeration basins or natural environments having an active resident microflora. None of the information called to our attention and purporting to demonstrate the effectiveness of seeding with these products meets normal criteria for a scientific experiment, especially with regard to the controls. Superficially, most of these data appear to show small improvements in treatment when a facility is seeded with these organisms. This is either not supported by analysis of the data, or the experimental design is inadequate to conclude that the effect was due to the added microorganism rather than other, uncontrolled factors. From information that we examined it was impossible to determine whether these introduced microorganisms can establish themselves and significantly enhance treatment in a normally operating facility or a polluted environment.

Exploratory studies should be undertaken by interested scientists to evaluate the colonization potential of introduced microorganisms in habitats such as aeration basins, and an evaluation of gene transmission to resident microbes following seeding with an engineered strain. Such experiments must be undertaken with adequate controls and carried out in a manner that recognizes and measures changes in the performance of the treatment facility dependent only on the introduction of the engineered strain. Concomitant with this direct experimental approach, basic research is needed to develop understanding of the factors affecting the success of introduced microbes. Historically, the establishment of introduced microorganisms has been studied in the context of infection and disease, with the single exception of the inoculation of soil with *Rhizobium*. Of course, in this case the establishment of the introduced organism depends on the presence of a special habitat, the legume root.

Many kinds of physical and biological factors have been recognized as important for the success of an introduced microbe. Obvious factors include the availability of adequate nutrients, acceptable pH, oxygen tension, and presence or absence of light. Manipulation of these factors should not be overlooked as a means to enhance degradation of a pollutant. For example, degradation of Arctic oil spills apparently can be accelerated by relieving phosphorus and nitrogen starvation of microbes associated with them [20]. Additional factors of special relevance to waste treatment and biodegradation include concentration of the pollutant, occurrence of the pollutant in mixtures of more easily metabolized and/or toxic compounds, availability of water, and sorption of compounds and microorganisms to surfaces.

The relationship of the concentration of a compound in bulk solution to its rate of biotransformation has been neglected frequently by the molecular biologist interested in enhancing biodegradation through

genetic manipulation. Most microorganisms used for studies of biodegradation are selected for their ability to degrade the compound of interest and to do so in a manner that is convenient to study. They are obtained from enrichment cultures with the target compound as sole or principal source of carbon and energy at a concentration that can support rapid growth. Because they can grow rapidly when exposed to abundant substrates, these organisms are sometimes called "eutrophs" (from the Greek *eutrophos*, meaning well nourished). The complementary group of slow growing organisms capable of surviving on very low substrate fluxes (called oligotrophs from the Greek *oligo*, meaning few or scant, plus *trophos* meaning fed) are not often isolated by this method.

Most of the organisms used in basic molecular biology, e.g., typical *Enterobacteriaceae* and *Pseudomonadaceae*, are eutrophs unable to effectively catabolize single substrates at parts-per-billion concentrations, even if they may grow on the same substrate at parts-per-million concentrations. Many toxic or persistent pollutants of concern in the environment are present at parts-per-billion concentrations and therefore are more likely to be attacked by oligotrophs, if at all. There is very little fundamental information regarding the biochemical adaptations of oligotrophs that permit them to succeed under low nutrient conditions, but a basic outline of their characteristics has been published [21]. At least cursory consideration should be given to the concentration of a target pollutant in a contaminated environment when planning the genetic alteration of an organism to enhance its attack on the pollutant.

Another basic microbial adaption that should receive at least passing attention is the tolerance of the engineered microbe for environmental stresses. Stresses of particular importance in waste streams and polluted environments are reduced water activity and the presence of toxicants. Any particular microbial species can tolerate only a limited range of water activity. These limitations are well known and widely exploited for the preservation of food (e.g., pickling brines and sugar syrups). In waste streams and polluted environments, water activity may be reduced by salts or partially water-soluble solvents (solvents can be biocidal both from a reduction in water activity and by direct solvent action on microbial membranes). Bacteria use at least two genetically controlled strategies to function in reduced water activity environments [22]. The first is the synthesis of enzymes that function normally only at elevated ionic strengths. The second is the synthesis of internal solutes, especially proline and glutamate, that raise the internal osmolarity so as to balance the external environment, but without interfering with normal metabolic functions. Because the latter adaptation probably involves fewer genes, it appears to be more amenable to alteration by genetic manipulation.

Fungi, which are generally better able to tolerate reduced water activity than are bacteria, may employ additional mechanisms.

Toxic substances in waste streams and polluted environments present complex and little studied problems affecting biological treatment of many waste and polluted environments. To approach this problem requires an initial assessment of the nature and abundance of the toxicants. Next, their availability to the microbe must be considered, since many toxicants may be sorbed, partitioned into nonaqueous phases or complexed. Degradation of a component of a polluted environment could release the toxicant, a potentially suicidal action from the microbe's perspective. Since the abundance, variety and disposition of microbiocides in polluted environments are often unique to each site, this factor is usually ignored until a normally efficacious microbial treatment fails. From the perspective of a molecular biologist, it would be useful to note that microbes differ substantially in their tolerance to general chemical biocides such as phenol, hypochlorite and various solvents, but the genetic basis for tolerance has not been explored systematically. It is also useful to note that bacteria employ a number of strategies to avoid heavy metal toxicity, some of them specified by genes on plasmid DNA and potentially transmissible to related strains. An example of the variety of possible actions are the Hg^{2+}-reducing and Hg^{2+}-methylating activities of bacteria. The success of these activities in the environment is suggested by the ease of isolation of mercury resistance functions from bacteria in mercury-contaminated sediments [23].

Other considerations for the molecular biologist designing new pollution treatments include the occurrence of pollutants in mixtures of other potential nutrients and the physical interactions of compounds. Mixtures may be advantageous to the genetically altered microbe if they contain a compound that can be used as a growth substrate to support the cometabolism of another, presumably recalcitrant, component of the mixture. Creation or extension of cometabolic capacity in bacteria through mutation and selection, especially site-specific mutation, is an endeavor of enormous practical importance. The same principle of enzyme and pathway alteration discussed in connection with extending adventitious dehalogenation reactions can be applied to the extension of cometabolic transformations. The genes for enzymes catalyzing the transformation of a utilizable compound may be mutated, and variant strains may be obtained that retain the enzyme's active sites but have acquired the ability to act on closely related substrates (cosubstrates) not metabolized by the parental strain. Since these mutant enzymes are likely to be selected one at a time and the organism will not derive benefit from

the transformation until the entire pathway has been altered, a growth substrate is necessary for the organism.

The principal difficulties created by occurrence of compounds in mixtures involve inhibitory interactions of components of the mixture with the microbe. Beyond components that are biocidal or that alter the nature of the physical environment, compounds may be competitive or dead-end inhibitors of essential enzyme reactions, thereby reducing metabolic rates. Compounds also may act as regulators of metabolism (coinducers and corepressors) that alter a metabolic pattern in an unfavorable way. Examples of such action from studies of pure cultures of eutrophic bacteria (and hence of unknown relevance to mixed flora and complex mixtures of compounds) include catabolite repression by glucose or succinate in *E. coli* and *P. putida*, respectively.

Both problems and opportunities are created for microbes by their interaction with interfaces, and by interfacial influences on xenobiotic compounds. Particularly important are the solid-liquid interfaces found in sludge, on the surfaces in trickling filters and rotating biological disc reactors, and in soils and sediments. Burns has discussed influences associated with interfaces affecting the microbial breakdown of pesticides [24]. These include potential increases and decreases in the rate of transformation of compounds sorbed to a surface, enhanced tolerance of sorbed microbial populations to transient changes in the aqueous environment (pH, temperature and shock loadings), sequestration of compounds and alteration in genetic exchange among microbes.

Adhesion of microbes to solid surfaces is an extremely common occurrence. Simple models suggest that surfaces wetted with a water film of thickness less than the minimum dimensions of a particle will develop capillary forces sufficient to bind the particle to the surface [25]. These conditions typically are found in soil and bind bacteria to surfaces. Such forces may severely restrict the movement of an introduced, engineered microbe into the soil column where its target compound resides. Adhesion of microbes to surfaces in aquatic environments and in treatment facilities usually involves a modification of the surface by deposition of a glycoprotein, conditioning and modifying the properties of the surface.

Effects specific to the structure of the glycoprotein and microbe, and general influences dependent on ionic strength, glycoprotein concentration and coverage of the surface all affect adhesion (for an excellent, detailed discussion see Berkeley et al. [26]). The importance of microbial adhesion to the success and spread of an introduced species is not known, nor has the opportunity to manipulate adhesion phenomena by genetic alterations of microbial glycoproteins been explored.

CONCLUSIONS

From the preceding sections it is evident that development of improved treatments for toxic wastes through genetic manipulations of microorganisms will require contributions from a number of disciplines and the successful integration of this knowledge in a goal-oriented fashion. The breadth of information needed to intelligently develop new treatments is itself an impediment, since it is difficult for specialists to communicate across such a broad range of knowledge. Newsletters, problem-focused symposia and short courses might be used to coordinate the activities of scientists in relevant disciplines.

The most pressing area of basic research is the need to evaluate the potential of engineered organisms to colonize polluted habitats or to spread new genetic information to indigenous microbes. Before genetic intervention can be used to enhance colonization or plasmid spread, it seems likely that further basic research will be needed to characterize microecosystems, especially those present in treatment facilities. Because the conditions in treatment facilities are better controlled than in open environments, it is plausible to expect that the first applications of genetic manipulation will come in this setting. Equally, the evaluation of colonization or plasmid spread should be easier in the microflora associated with a treatment facility than in the open environment. On the practical side, the costs of defining environmental factors (such as the presence and availability of microbial toxicants) can be justified more easily when viewed as a step toward improvement of the performance of a waste treatment facility.

Whether new treatment technologies can be developed expeditiously will depend on the outcome of these studies. The promise of incisive gene manipulation urges timely exploration of this approach.

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CHAPTER 20

POTENTIAL ROLE OF GENETICALLY ENGINEERED MICROORGANISMS TO DEGRADE TOXIC CHLORINATED HYDROCARBONS

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It is well known that microorganisms are capable of degrading a wide diversity of organic compounds. Microorganisms have been shown to degrade methane [1,2], fatty acids, benzene [3,4], naphthalene [5,6] and various petroleum fractions [7,8]. Many synthetic compounds, such as 2,4-dichlorophenoxyacetic acid (2,4-D) [9,10]; 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) [11]; DDT [12,13]; 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine (Atrazine) [14]; and some isomers of polychlorinated biphenyls (PCB) [15–17] are also degraded by microorganisms.

If environmental microorganisms are capable of degrading a diverse number of toxic chlorinated hydrocarbons, what is the purpose or reason for employing genetic engineering methods? Because of several inherent problems encountered when employing microorganisms to degrade toxic chlorinated hydrocarbons, genetic engineering may benefit microbial systems in four areas: stabilization, increased activity, multiple degradative activities, and health, safety and environmental concerns.

POTENTIAL BENEFIT OF GENETIC ENGINEERING TO MICROBIAL DEGRADATION

Stabilization

It has been shown that the ability to degrade some hydrocarbons is encoded on extrachromosomal DNA (plasmids) [18,21]. These plasmids and, thus, their encoded activities can be lost under certain conditions. Bacteria containing the TOL (toluene degradation) plasmid can lose the ability to degrade toluene if they are repeatedly subcultured on benzoate. The ability to degrade 2,4-D (Tfd plasmid) can be lost if strains are repeatedly cultured in the absence of 2,4-D [20,21]. In bacterial strains with unique degradative activities, these activities are best maintained if the compound degraded is also incorporated into the maintenance medium. However, sister cultures maintained on media devoid of the compound will often be cured of the plasmid (lose the plasmid-encoded trait permanently) after several transfers, without affecting culture viability.

The observation that environmental microorganisms can easily lose plasmid-encoded degradative traits without affecting the viability of the population (or culture) is important. Although these plasmid elements may confer a selective advantage to the microorganisms, their maintenance is not a requirement for the microorganism (i.e., they can live equally well without the plasmid). Selective pressure must therefore be placed on the host microorganism to maintain the plasmid-encoded trait.

There are several genetic engineering mechanisms that may be employed to stabilize a plasmid-encoded degradative trait. It has been shown [22,24] that hybrid plasmids can be constructed to stabilize an element. This could be accomplished by insertion of the desired element into a region where replication is under the control of a conserved element.

Increased Activity

The copy number of degradative plasmids is generally low (1–3 copies) [20], whereas the copy number of some other plasmids is higher [25,26] or can be amplified [26,27], resulting in increased protein synthesis and, ultimately, in increased activity. If the plasmid encoding the degradative trait is not amplifiable, then increased plasmid copy number could be obtained by inserting the degradative trait into a plasmid that is a high-

copy-number plasmid or can be amplified. It also may be possible to excise the segment of plasmid DNA that limits plasmid copy number and thus achieve an increase in plasmid copy number. Activity could also be increased by optimizing the promoter location of the degradative trait [28].

Multiple Degradative Activities

The fusion by Chakrabarty [29] of multiple degradative plasmids [camphor (CAM), TOL and octane (OCT)], which are incompatible plasmids, was the first demonstration of constructing a microorganism with multiple degradative traits. Recombinant DNA techniques could be similarly employed to insert elements representing multiple degradative traits into a single plasmid.

Health, Safety and Environmental Concerns

When a microorganism is considered for use in an industrial process, the potential for adverse effects should be examined and addressed. The potential for adverse effects applies equally to wild-type and engineered strains. Based on information concerning the hazards of recombinant DNA, it is unlikely that recombinant DNA techniques as applied to microbial degradation will result in any additional biohazard. In all probability, the host microorganism(s) will dictate the potential hazard.

Several techniques can be employed to minimize the potential for adverse effects. Nontransmissible plasmids are recommended, so that the potential for a plasmid to escape its host will be minimized. If the size of a plasmid can be reduced to the smallest size possible without adversely affecting the desired trait, superfluous genetic information and cryptic genes can be removed, thus reducing the possibility of transferring undesirable genetic information into the host. The host microorganism can also be enfeebled, so that it can only survive under defined conditions and is incapable of survival if it does escape. Lastly, containment systems can be constructed to limit the potential for escape of a microorganism into the environment. The additional advantages of containment devices will be discussed in further detail in the following section.

Figure 1 shows the schematic representation of an idealized degradative plasmid. In addition to those properties previously mentioned, the gene(s) of choice would be flanked by specific sequences so that additions or deletions to this region would be facilitated.

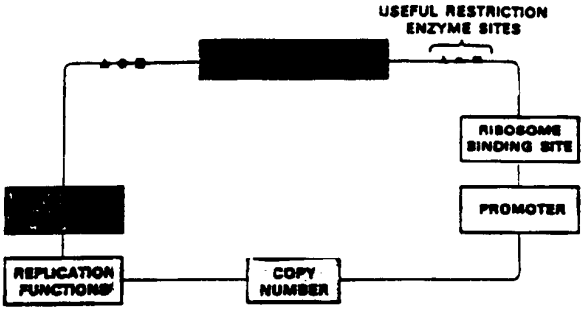

Figure 1. Schematic representation of an idealized degradative plasmid.

PROBLEMS THAT MAY LIMIT THE SUCCESS OF GENETIC ENGINEERING AS APPLIED TO MICROBIAL DEGRADATION

Although genetic engineering promises significant improvements, there are several factors that, if not taken into account, could jeopardize a genetic engineering program in the area of degradation. These are: compatibility and coordination, unfavorable environmental conditions, and adequate containment.

Compatibility and Coordination

Successful insertion of a plasmid into a pseudomonad host is no guarantee that the desired trait will be expressed. Plasmids in pseudomonads have been classified into incompatibility groups [24,29,30]. A cell containing a plasmid cannot accept a new plasmid if both plasmids belong to the same incompatibility group. The problem of dealing with incompatible plasmids can be solved by fusing the plasmids and then transferring them (as a single plasmid) to a suitable host (28). The problem may also be addressed by constructing hybrid plasmids using recombinant DNA techniques and then transferring the hybrid plasmid to the appropriate host.

However, other problems may now be encountered that result in unsuccessful cloning and no expression of the desired trait(s). It is

imperative that the pathway or reactions encoded by the inserted plasmid are compatible with the biochemical pathways encoded by the host chromosome. *Pseudomonas putida* MT-2, which harbors the TOL plasmid, can degrade toluene [31]. The TOL plasmid can be transferred to *E. coli*, but no toluene-degradative phenotype will be expressed. It has been shown in many cases that degradative plasmids are responsible for only the first several biochemical reactions of the degradative pathway [20], while the remainder of the pathway is encoded by chromosomal genes. Therefore *E. coli*, which do not have the chromosomal genes normally found in *Pseudomonas putida* MT-2 (TOL$^+$), are unable to degrade toluene even when the TOL plasmid is present.

Coordinating biochemical pathways and their regulation mechanisms is further complicated in pseudomonads because there are three documented pathways for the degradation of aromatic compounds (*ortho* and *meta* cleavage and gentisate pathways [32]). Successful strategies therefore must be based not only on selection of an appropriate host, but on sound genetic and physiological characterization of host and inserted element.

Environmental Conditions

A genetically engineered (or wild-type) microorganism that demonstrates a high degradative ability under laboratory conditions may not be successful when used in the field. Potential reasons for failure to degrade in the field exist. Even a microorganism with a unique degradative trait, which might be considered to confer some selective advantage, would have to compete with the resident microflora to establish a permanent position in the microbial community. If the assumption is made that there are 10^8–10^9 bacteria per gram of soil, it can then be seen that a very large number of bacteria would have to be added to this soil to achieve a reasonable probability of establishing a "new" bacterium in the community.

Assuming a "new" microorganism could be introduced and established in a given ecosystem, additional problems would also have to be addressed (e.g., temperature, pH, substrate concentration and oxygen tension). Most microorganisms have relatively well defined operating parameters. Since it is likely that at any given time one or more of these parameters are apt to be outside the optimal range for activity, the majority of the time the microorganism will have a reduced activity. (e.g., a bacterium that degrades *n*-alkanes optimally at 30°C in an aqueous medium would most likely perform poorly if exposed to an oil spill under North Sea conditions). Because of generally unfavorable operating

conditions and the difficulty that is likely to be encountered in establishing a "new" bacterium in an ecosystem, broadcast application of genetically engineered microorganisms to treat toxic chlorinated hydrocarbons is not likely to be widely successful given our current state of knowledge in this area.

Containment

It is probable that engineering systems can be fabricated to provide additional containment and a means whereby operating conditions could be controlled and optimized. Such a system could be developed and applied to aqueous treatment schemes (e.g., landfill leachate, plant effluent, holding ponds, collected runoff or municipal water). These treatment systems would most likely incorporate additional features, such as pretreatment to concentrate toxicants to levels that would support a higher microbial activity.

SUMMARY

There are considerable benefits to be derived from successful application of genetic engineering to the microbial degradation of hazardous compounds and pollutants. The benefits to this area will most likely include stabilization of activities, increased rate of activity, increased spectrum of activity and development of safe microbial systems. There presently are technical restraints or problems to achieving these goals. These restraints will be overcome as better cloning-vector systems for pseudomonads and other degradative bacteria become available. Also, with more information regarding the physiology, biochemistry and regulation of these degradative bacteria, the realization of these goals will come closer to reality. It must also be stated that before such successful "engineered" microorganisms are a reality, engineering information must also be integrated and developed where necessary.

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CHAPTER 21

MICROBIOLOGICAL SEPARATION FOR TRACE-ORGANICS REMOVAL

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Trace-level contamination by anthropogenic organic compounds is a newly discovered, but widespread phenomenon. Since surface, ground-, waste- and potable waters contain residuals of pesticides, solvents and other manmade contaminants that can have deleterious impact on human health and aquatic ecosystems, the concentrations may need to be reduced significantly. Microbiological separation is one possibility for removing trace-level organic compounds from water.

Two main mechanisms can bring about microbiological separation: biodegradation and sorption. Biodegradation is a particularly advantageous separation process, because the polluting compounds can be mineralized completely to harmless compounds, such as CO_2, H_2O and Cl^-. In addition, biodegradation is a self-perpetuating process that does not require use of expensive chemicals, intense energy or sophisticated technology. However, biodegradation requires appropriate microorganisms in sufficient numbers and an environment suitable for their growth and metabolism. The second mechanism, sorption, does not mineralize the organic compounds; instead, the compounds are separated from the water and sorbed into or onto the microorganisms. Ultimate removal of the sorbed organic compounds is brought about by harvesting or removing the microorganisms from the treatment system for subsequent disposal or treatment.

This chapter describes some of the key concepts that control microbiological biodegradation. Microbiological sorption is beyond the scope of the chapter. The approach is to use three examples that represent different trace-organic problems and that illustrate different concepts and treatment approaches. Use of examples should make the concepts and possible treatment approaches more substantive and relevant. The three examples are (1) a contaminated groundwater source, (2) a contaminanted wastewater effluent, and (3) a leachate from a hazardous-waste landfill.

CONTAMINATED GROUNDWATER

Groundwater, which serves as the supply of drinking water for about 50% of the U.S. population, can be contaminated from spills, leaching and injection of harmful pesticides, industrial solvents and other compounds [1]. Treatment to remove these compounds before the water is used as a water supply or before being reinjected into the ground may be necessary in some cases. The example considered here is a groundwater having mineral and esthetic quality suitable for use as a drinking water, but also having trace-level organics that need to be reduced in concentration.

Groundwater Quality

Table I [2-5] gives the quality of typical groundwater found in the Midwest. After softening, this water would satisfy conventional drinking-water standards [6] and normal water-supply practice. Because a ground water supply could become contaminated with pesticides, solvents, phenolics or other organic chemicals that are not mentioned in the drinking water standards [6], the U.S. Environmental Protection Agency (EPA) and the World Health Organization (WHO) have proposed for organic compounds the lower hazard limits listed in Table II [7]. The hazard limits are all quite low (<1 $\mu g/l$), and they may be reduced as more health-related information becomes available. Table II shows that contamination by hazardous organics can occur at such low concentrations that the aggregate organic parameters listed in Table I could be unaffected.

Table I. Inorganic and Organic Quality of Typical Midwestern Groundwater [2–5]

Constituent	Concentration (mg/l)
SiO_2	10
Fe(III)	0.09
Ca^{2+}	92
Mg^{2+}	34
Na^+	8.2
K^+	1.4
HCO_3^-	333
SO_4^{2-}	84
Cl^-	9.6
NO_3^-	13
Total Dissolved Solids	434
Total Hardness, as $CaCO_3$	369
Total Organic Carbon	1.5
Total Organic Matter	4.7
Chemical Oxygen Demand	6.0

Table II. Proposed Lower Hazard Limits for Selected Organic Compounds in Water [7]

Compound	Limit (μg/l) per Compound
Trihalomethanes and Tetrachloromethane	1
Chlorinated Pesticides (e.g., lindane, DDT and dieldrin)	0.1
Dichorobenzenes, Chloroethers	1
Pentachlorophenols	1
Polynuclear Aromatics	0.1
Phenolics	1
Dibutylphthalates, Diphenyl Ether, Nitrotoluene	1
Others	0.1

Concentrations in excess of the hazard limits can be found in otherwise good quality groundwater. For example, Roux and Althoff [8] reported that 1,1,1-trichloroethane, tetrachloroethylene and other related compounds contaminated groundwater, including the public water supply, at concentrations up to 1000 μg/l. Although the aquifer supplying drinking water was deep, windows in the aquacludes allowed these organic

contaminants to travel from industrial plants to the drinking water supply. Lang et al. [9] reported the following groundwater concentrations: vinyl chloride, 13.1 μg/l; *trans*-,2-dichloroethylene, 1.5 μg/l; *cis*-1,2-dichloroethylene, 29 μg/l; 1,1-dichloroethylene, 1.0 μg/l; trichloroethylene, 0.34 μg/l; and tetrachloroethylene, 1.2 μg/l. Clearly, otherwise acceptable groundwaters have become contaminated with hazardous organic chemicals present at 1- to 1000-μg/l concentrations.

Key Factors for Biological Separation

Many of the compounds that can contaminate groundwaters are biodegradable. Recent reports in the literature have presented evidence that the following industrial chemicals can be biodegraded: tetrachloroethylene, 1,1-dichloroethylene, 1,2-dichloroethylene, vinyl chloride, 1,1,1-trichloroethane, chloroform, methylene chloride, carbon tetrachloride, chlorobenzene, dichlorobenzene, naphthalene, styrene, bromo-and chloromethanes, 1,1,2-trichloroethane, 1,1,2-trichloroethylene, and 1,1,2,2-tetrachloroethane [9–13]. It is well known that most of the pesticides can be at least partially degraded [14]. Although many compounds are biodegradable, having been biodegraded under laboratory or field conditions does not guarantee that a compound will be biodegraded when present in groundwater.

Two interrelated factors control how well biological processes can achieve trace-organics separation in a groundwater. The first factor is the concentration of organic matter. Low concentrations limit the amount and type of biological activity that can occur. The second factor is the availability of solid surfaces. When organic substrate concentrations are low, the predominant form of microbial activity is found attached to solid surfaces as biofilms [15,16].

Table 1 shows that little organic matter is in typical groundwater supplies, and the readily biodegradable portion of that organic material is often only a small fraction of the total [17]. Thus, the potential for growing and sustaining microorganisms through organic-substrate utilization is not great. Rittmann and McCarty [18] developed a model of biofilm kinetics especially appropriate for cases like contaminated groundwater. The model simultaneously considers mass transfer of substrate from the bulk liquid to the surface of the biofilm, diffusion of substrate through the biofilm, utilization of substrate by the bacteria within the biofilm, growth of the biofilm due to substrate utilization, and biofilm losses due to decay. Figure 1 illustrates that the model of a steady-

state biofilm predicts that the biofilm mass and reaction rate decline rapidly to zero as the substrate concentration approaches a limiting value S_{min}, which can be predicted from fundamental kinetic parameters:

$$S_{min} = K_s \frac{b}{Yk - b} \qquad (1)$$

where K_s = Monod half maximum-velocity concentration (M_s/L^3)
Y = true yield (M_x/M_s)
k = maximum specific substrate utilization rate ($M_s/M_x - T$)
b = first-order decay or biomass-loss coefficient (T^{-1})

At substrate concentrations less than S_{min}, the biofilm loss rate is greater than the biofilm growth rate, and any biofilm present will decay away. Hence steady-state biofilms can not persist when substrate concentration is always less than S_{min}.

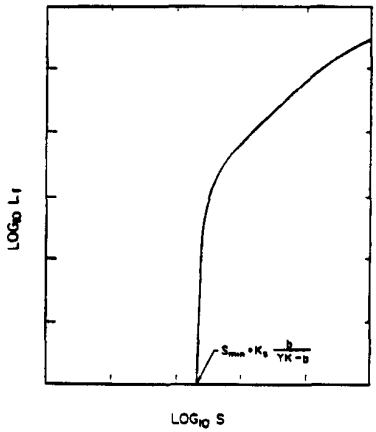

Figure 1. Example of relationship of steady-state biofilm thickness (L_f) to substrate concentration (S).

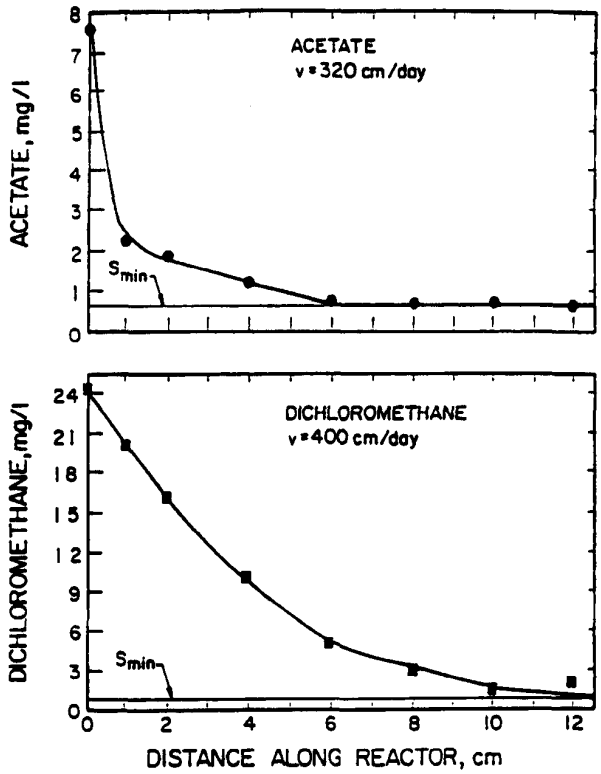

Figure 2. Removal of acetate and dichloromethane in steady-state biofilm reactors. Reactors were 12 cm long × 2.5 cm diam, and the biofilm support medium was 3-mm glass beads. T = 20°C.

Experiments with once-through biofilm reactors have demonstrated S_{min}. Figure 2, taken from the work of Rittmann and McCarty [10,19], shows that substrate concentrations leveled off at S_{min} values when acetate, a common metabolite, and dichloromethane, a widely used

industrial solvent, were used as substrates in separate reactors. Typical values for S_{min} obtained for aerobic biodegradation of various organics range from about 0.1 to 1.0 mg/l [10, 19, 20].

The limitation of S_{min} seems to suggest that compounds already present at concentrations less than typical S_{min} value may be impossible to biodegrade. However, two further concepts present ways in which biodegradation can occur. The first possibility is selection, enrichment and application of specially adapted oligotrophic bacteria, which have advantages and can survive in very low-concentration environments. Oligotrophic bacteria use an efficient metabolism and a high affinity for substrates, and these characteristics allow the oligotrophs to survive and function when other bacteria die or remain dormant. Although oligotrophs have been studied very little, some attributes of bacteria that have shown oligotrophic characteristics were recently compiled [21]. The outstanding features include extremely efficient utilization of multiple and varied compounds, constitutive production of transport enzymes with high affinity for catalyzed substrates, inducible enzymes for catabolic pathways and relatively slow maximum growth rates. The high affinity for substrates would be mostly detected as a very low K_s value. Equation 1 shows that oligotrophic, biofilm-forming bacteria could have S_{min} values in the 1-μg/l range if K_s were reduced sufficiently.

Since little work has been performed with freshwater oligotrophic bacteria, their potential usefulness in trace-organic removal is speculative. Basic questions have only begun to be asked. What strategies give oligotrophs their advantage at low concentration? Can bacteria with appropriate metabolic functions be adapted to oligotrophy? What is the minimum concentration of a given substrate to which oligotrophic bacteria are adapted? How can oligotrophic bacteria be best cultivated and used?

A second and better-studied possibility for trace-organics removal when substrate concentrations are already less than S_{min} is called secondary utilization. Secondary utilization is defined as the utilization of a substrate, called the secondary substrate, which does not supply sufficient energy or carbon for the cells' growth and maintenance [20,22,23]. Cometabolism, the partial transformation of substituted analogs of primary substrates, is a subclass of secondary utilization. A compound present at $\leq S_{min}$ concentration is an excellent example of a secondary substrate, since the reason that no biofilm exists for concentrations less than S_{min} is that the rate of energy capture through substrate utilization does not supply enough energy to meet even maintenance requirements. Secondary substrate utilization can and does occur, however, if the biofilm is grown and sustained through utilization

of a primary substrate, which is present at suitably high concentration to support the bacteria. The primary substrate can be one compound or an aggregate of many compounds. In fact, the primary substrate can be the composite of many secondary substrates, none of which could sustain the biofilm alone.

Figure 3 gives a relevant example of how secondary utilization can work. A biofilm was grown using a feed medium that consisted of laboratory deionized water plus mineral nutrients. No organic substrate was added, and a biofilm was sustained through utilization of about 0.17 mg C/l out of a feed total organic carbon (TOC) of 0.59 mg/l. When sodium acetate was added to the feed, it was removed to concentrations well below S_{min} (about 30 μg/l) as shown in Figure 3. The substrate was a mixture of many organics, and might be representative of the natural organics found in a clean groundwater.

For treatment of a contaminated groundwater through secondary utilization, the naturally occurring organic compounds may be able to serve as the primary substrate. On the other hand, it may be necessary in some cases to supplement the water with a primary substrate to ensure that sufficient bacterial growth occurs. When treating a contaminated groundwater that could be used as a potable source, added materials must be chosen carefully so that they are not harmful themselves and do not cause undesirable taste, odor or color. Simple metabolites seem most appropriate.

Although secondary utilization is a demonstrated and promising concept for trace-organics removal, it raises some questions and has some drawbacks. The first question concerns the availability of suitable primary substrate to allow growth of bacteria capable of biodegrading the hazardous pollutants. Experiments were carried out to ascertain if biofilm bacteria grown on a given primary substrate could also utilize other secondary substrates [20]. Figure 4 presents typical data from these experiments. The secondary substrates were fed for only a short time, while the biofilm had been grown for the long term on only the primary substrate, thymine. Although alanine and acetate, both common metabolites, were readily utilized by the thymine-grown biofilm, phenol and galactose were largely unutilized. Thus, not all compounds can serve as primary substrates for bacteria that can metabolize a potential secondary substrate. For the exotic, anthropogenic compounds, finding an appropriate primary substrate naturally occurring in the groundwater or to add to the water may be difficult; research along this line is continuing.

A second and closely related problem is that very low concentrations of anthropogenic compounds may not be as easily degraded by bacteria as

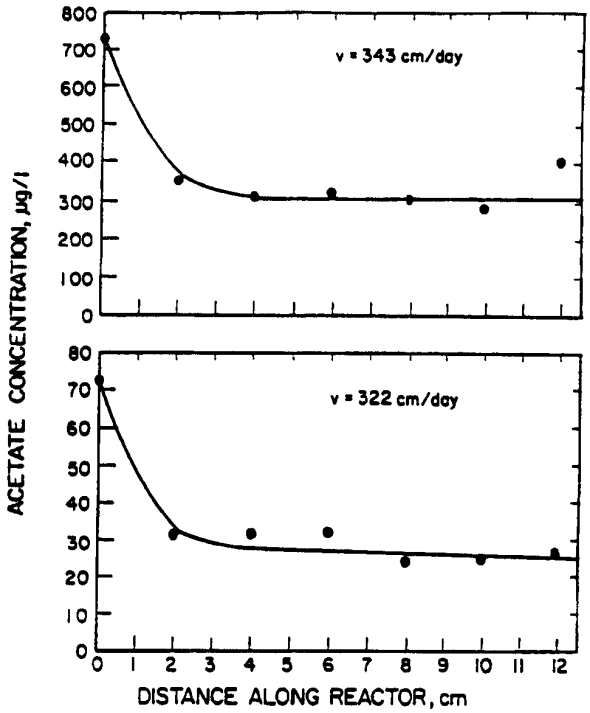

Figure 3. Secondary utilization of acetate by biofilm bacteria grown on residual organics in laboratory deionized water plus minerals. T = 20°C.

are high concentrations. Boethling and Alexander [24] reported that 2,4-D and 1-naphthyl-*N*-methylcarbamate plus 1-naphthol (Sevin®) were not biodegraded at concentrations below 2.2 and 30 μg/l, respectively, although they were degraded at higher concentrations. Rittmann et al. [11] showed a similar threshold effect for dichloro- and chlorobenzenes present below about 100 μg/l. These apparent threshold effects, which

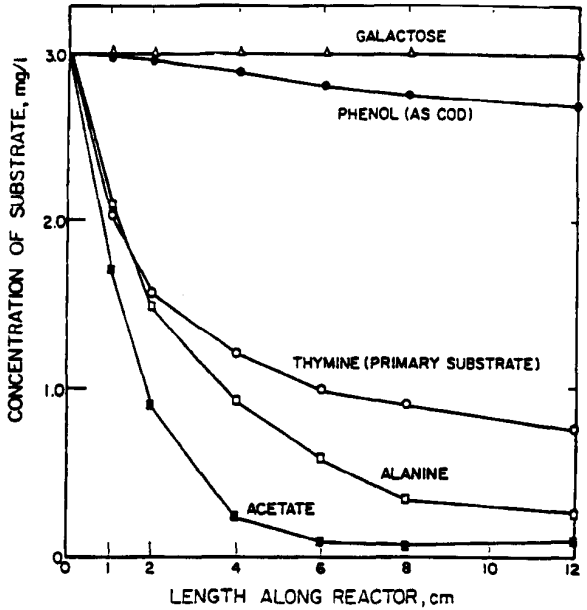

Figure 4. Removal of secondary substrates and primary substrate by biofilm grown with thymine as primary substrate. T = 22°C; ν = 610 cm/day.

show no degradation below some low concentration, may be caused by a lack of enzyme induction or activation when little substrate is available. Somewhat similar effects were reported for common metabolites, such as starch (25 μg/l), glycerol (20 μg/l), gluconate (10 μg/l), and mannitol (20 μg/l) [25]. The mechanisms for such thresholds are unknown, but existence of thresholds in the 1- to 100-μg/l range could severely hamper application of biodegradation by secondary utilization. Fortunately, work by Bouwer and McCarty [26] showed secondary utilization of chlorinated benzenes present at about 10 μg/l when a primary substrate, acetate, was also continuously present. Perhaps the presence of a primary substrate allows continued genetic expression and enzyme activity; more work is necessary in this area.

Two important engineering decision can affect process performances: selection of biofilm support media and reactor configuration. Biofilm growth can occur on many surfaces, including glass beads, sand, carbon, metal oxides and plastics. For removal of trace-level organics, activated carbon seems to offer numerous advantages over other surfaces. One key advantage seems to be an enhancement of bacterial surface attachment, especially for very thin biofilms that experience high shearing stresses [27–29]. The reasons for improved attachment are related to the creviced and hydrophobic nature of the activated carbon surface, but the quantitative extent of such an advantage remains unknown.

A second advantage of using activated carbon as biofilm support medium is that the activated carbon adsorbs and stores solutes that are not immediately biodegraded. This storage is probably advantageous to the formation of a biofilm, since more substrate is available to the organisms at the surface, and this can help reduce S_{min} limitations during biofilm inception and growth. Backdiffusion and biodegradation of sorbed organics (termed bioregeneration by those interested in the adsorption capacity of activated carbon) have been demonstrated to be important [30–32]. Adsorption of organic solutes by carbon is also advantageous in another way. A compound that escapes biodegradation because it is nonbiodegradable by the biofilm or because its mass loading exceeds the capacity of the removal kinetics of the biofilm can be adsorbed to the carbon. The adsorption reduces the concentration of the process effluent and sufficiently retards the compound's travel through the reactor (the chromatographic effect) so that the bacteria have an increased opportunity to degrade the compound.

Selection of process configuration is also an important choice that can affect overall process performance. In water and wastewater treatment practice, activated carbon reactors, which are not necessarily used for biodegradation, are operated in fixed- and fluidized-bed modes. From the viewpoint of biodegradation of low concentrations of organic compounds, the fluidized-bed reactor can offer numerous advantages over the fixed-bed reactor. Rittmann [33] has shown how fluidization of the biofilm support medium reduces the S_{min} restrictions on biofilm growth by uncoupling the steady-state mass of biofilm present at any point in the reactor from the substrate concentration at that point. The advantage of a fluidized bed comes about like this: in a fluidized bed reactor, the solid medium is expanded and well mixed throughout the reactor, which means that a particle of biofilm is sometimes near the inlet, where substrate concentration is high, and sometimes near the outlet, where substrate concentration is low. Rittmann [33] demonstrated that mixing and periodic exposure to the high substrate concentration near the

inlet allow the greatest total biofilm mass throughout the reactor and distribute the biofilm evenly, which increases the biofilm's effectiveness. In other words, fluidization allows biofilm to grow near the inlet and be transported near to the outlet, where it brings about substrate removal, even though the outlet substrate concentration is already less than S_{min}.

Figure 5 gives an example of how fluidization can improve process performance [33]. The feed concentration and detention time are the same

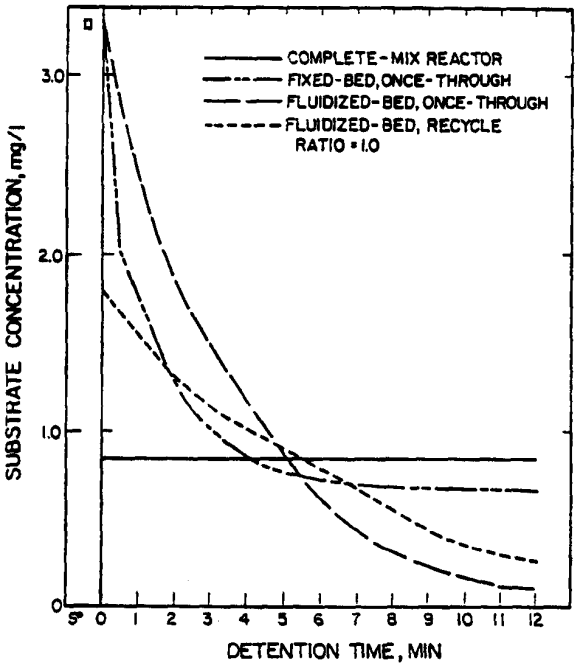

Figure 5. Comparison of predicted process performance for biofilm reactor configurations. S^o = 3.3 mg/l; ν^o = 500 cm/day; Y = 0.142 mg VSS/g; b = 0.205 day^{-1}; D = 1.09 cm^2/day; D_f = 0.87 cm^2/day; d_p = 3 mm; T = 20°C.

for each reactor, but the fluidized-bed reactor reduced the effluent concentration to about 0.1 mg/l, while the fixed-bed reactor reduced the concentration to S_{min}, about 0.7 mg/l. The improved performance of the fluidized-bed reactor occurred because the biofilm mass was spread out evenly throughout the reactor, while the liquid flowrate was still rather "plug flow." In this way, the best conditions—liquid plug flow, but uniform biofilm distribution—bring about the maximum substrate removal [33].

Figure 5 also shows that adding recycle, which may be necessary for fluidization in some cases, begins to transform the nature of the liquid flow from plug flow into complete mix. Since complete-mix (liquid flow) reactors give the smallest substrate removal, use of recycle should be minimized. A recycle ratio (Q^R/Q^O) of about 10 results in a nearly complete-mix regime and negates the benefits of fluidization [33]. Fortunately, activated carbon has a low mass density and often can be fluidized without using excess recycle, provided the detention times are less than a few hours.

Despite its advantages, fluidized-bed technology will not work if the S_{min} requirement is not met in the influent. Secondary utilization, possibly including primary substrate supplements, is necessary for fluidized bed removal of trace-level organic contaminants. If there is sufficient primary substrate in the influent, fluidized beds obtain the best performance. On the other hand, fluidization does not allow growth when there is no primary substrate.

WASTEWATER EFFLUENT

Effluent Quality

The effluents from municipal and industrial wastewater treatment processes can contain significant concentrations of hazardous organic chemicals. The sources of these chemicals include direct discharge into the sewers, accidental spills, leakage into the sewers through infiltration and production during chlorination. Although some of these compounds are removed by biodegradation, sorption or air stripping during conventional wastewater treatment, many compounds persist in the effluents.

Table III [34–37] lists some concentrations of anthropogenic compounds detected in wastewater effluents. All are less than 100 μg/l, but many compounds are well above the proposed hazard limits (see Table

Table III. Concentrations of Anthropogenic Compounds Detected in Municipal Wastewater-Treatment Effluents

Compound	Concentration (μg/l)	Reference
Chlorobenzene	4.1, 0.9	34,35
1,2-Dichlorobenzene	1.9, 2.0	34,35
1,3-Dichlorobenzene	0.6,0.3	34,35
1,4-Dichlorobenzene	0.5,2.0	34,35
Sum of Dichlorobenzenes	5.6	36
1,2,4-Trichlorobenzene	0.5,0.2	34,35
Sum of Trichlorobenzenes	57.	36
Naphthalene	0.9, 0.2	34,35
Styrene	4.7	34
Benzonitrile	12.	34
Chloroform	2.5, 7.1	35,36
Dichlorobromomethane	0.2	35
Chlorodibromomethane	2.2	35
Bromoform	0.5	35
Dichloromethane	2.4, 2.9, 2.5–8.4	35–37
Trichloroethylene	1.5	35
Tetrachloroethylene	1.3, 3.9	35,36
1,1,1-Trichloroethane	6.3, 9.0	35,36
1,1,2-Trichloroethylene	8.6	36
Lindane	0.05–0.08	37
p,p'-DDD	0.15	37

II). Although wastewaters are seldom reused directly for potable water, they frequently are indirectly reused after discharge to a surface receiving water or recharge of a groundwater aquifer. In addition to possible harmful effects from indirect human consumption, these compounds can damage aquatic ecosystems.

After secondary wastewater treatment, a wastewater effluent has quality characteristics that classify it as a low-concentration medium. The typical chemical oxygen demand (COD) and TOC of an effluent are about 30 and 10 mg/l, respectively. Although greater than those found in most groundwaters, the organic concentrations of wastewater effluents are still low, and biological growth is still limited. Some years ago, efforts were made to characterize the chemical constituents of sewage and sewage-treatment effluents. The results of the characterizations give an idea of what types of potential primary substrates are available.

Table IV. Concentration Ranges for Organic Classes Commonly Present in Effluents from Biological Wastewater Treatment

Class	Range (mg/l as COD)	References
Protein/Amino Acids	0–8	38–42
Fatty Acids	2–30	43–46
Detergents	1–5	38,41,42,45
Carbohydrates	1–3	41,42,46
Ether Extractables	1–3	41,42
Humic Acids	2–6	41,42,46
Fulvic Acids	6–9	41,42,46
Sum	13–64	

Table V. Chemical Breakdown of "Typical" Effluent After Biological Wastewater Treatment

Chemical Class	COD (mg/l)
Proteins/Amino Acids	3
Fatty Acids	9
Detergents	2
Carbohydrate	2
Ether Extractables	3
Humic Acids	5
Fulvic Acids	6
Sum	30

Table IV [38–46] summarizes the concentration ranges for the chemical classes normally found in wastewater treatment effluents. The wastewater effluents represented in Table IV had rather widely ranging total organic concentrations. Table V gives a breakdown of the organic classes for a "typical" effluent having a soluble COD of 30 mg/l. Table V was derived from the data in Figure 4 after adjustments were made for the different strengths. Most of organic material seems to be organic acids, which are common metabolic intermediates, and humic and fulvic acids, which are the biologically resistant products of natural decay. The values in Tables IV and V suggest that the most likely primary substrates naturally occurring in wastewater effluents are the organic acids, which amount to about 9 mg/l as COD in a "typical" effluent.

Biological Separation Processes

As long as the bacteria grown on the primary substrate can also utilize the anthropogenic compounds of interest, a typical sewage effluent should have sufficient biodegradable organic material to carry out secondary utilization in aerobic systems. Utilization of activated carbon media and/or a fluidized-bed configuration should enhance removals and reduce the hazardous compounds to sub-μg/l levels.

Natural organics seem to be adequate primary substrates for secondary utilization of many trace contaminants [20,23,26]. On the other hand, other compounds pass through the biological systems largely or completely undegraded. If, therefore, the contaminants of interest are not biodegraded by the naturally selected microorganisms, special consideration must be given to supplying a primary substrate. Perhaps in such cases the only workable primary substrate is the contaminant itself. For the groundwater example, it would be totally inappropriate, if not illegal, to add a hazardous compound to the water to promote biological growth, as a failure in the system could result in a seriously contaminated water supply. In some cases this restriction may not be necessary for wastewater treatment.

Adding a compound to the water for the purpose of promoting growth of bacteria able to degrade that compound can be effective for achieving very low effluent concentration only through use of a nonsteady-state technology. A nonsteady-state biofilm reactor is one in which the biofilm in the reactor undergoes net growth or decay, and it is different from the previously described steady-state reactors, in which biofilm growth is continuously balanced by losses. Operated in a nonsteady-state mode, a biofilm reactor is fed a high-concentration feed for a relatively short time, such as one week. During that time, the biofilm grows to a relatively large thickness. Subsequently, the normal, low-concentration feed is applied. Since the large biomass is already present and its decay and other losses are typically much slower than was the growth, the biofilm can utilize the input substrate for a relatively long time, even though the feed concentration is less than S_{min}. Once biofilm losses have reduced the biofilm's capacity to an unacceptable level, the cycle is repeated. A biofilm operated in this mode is nonsteady-state because it grows when the high concentration feed is applied and decays when the low-concentration feed is applied. To operate such a system, several parallel units would be required; while one unit would be in the growth mode, the other units would be treating the wastewater.

Figure 6 [47] illustrates how nonsteady-state operation was able to achieve effluent concentrations well below S_{min}. The biofilm was grown

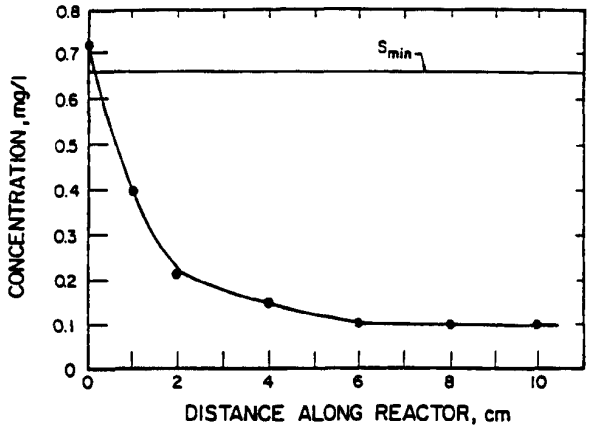

Figure 6. Nonsteady-state biofilm reduction of acetate concentration to below S_{min} when influent concentration is reduced from 7.6 to 0.76 mg/l of acetate. T = 20°C; v = 400 cm/day [47].

with a feed acetate concentration of 7.2 mg/l, which grew a biofilm capable of reducing the effluent concentration to S_{min}, about 0.66 mg/l. When the feed concentration was reduced to 0.72 mg/l, the biofilm, already present, was able to reduce the effluent concentration to 0.1 mg/l or only about 15% of S_{min}. Even lower concentrations could be achieved if the feed concentration were lower.

LANDFILL LEACHATE

Quality Characteristics

The quality of landfill leachate is as varied as the material that is disposed of in landfills. A noteworthy example is the leachate collected from the southern sector of the Love Canal landfill site at Niagara Falls, New York [48]. Table VI lists selected characteristics of the Love Canal leachate.

Compared to the groundwater and wastewater effluent examples, the Love Canal leachate is about 400–4000 times more concentrated in terms

Table VI. Selected Characteristics of Landfill Leachate from Love Canal [48]

Parameter	Value (mg/l)[a]
pH	5.6
TOC	4,300
COD	11,500
Total Dissolved Solids	15,700
Sulfate	240
Sulfide	0.1
Total Phosphate, as P	0.1
Sodium	1,000
Calcium	1,500
Iron	330
Methanol	19
Toluene	39
Chlorotoluene	26
Benzene	14.5
Chlorobenzene	12
Benzyl Alcohol	29
Chlorobenzyl Alcohol	26
Phenol	11
Chlorobenzaldehydes	26

[a]Except pH

of total and specific organics. Problems of trace levels would seem to be eliminated, since more than ample COD is available for growing bacteria. Even anthropogenic compounds are present at fairly high concentration. However, many trace-level compounds are present in the leachate, and the ultimate treatment goal is still to reduce the concentration to less-than-hazardous levels.

Biological Separation Processes

The first factor in treating leachate is that it must be contained and treated in a controlled reactor. First, the leachate cannot remain in the ground, because it may escape and seriously contaminate a groundwater aquifer. Second, a treatment reactor is necessary because successful treatment is very unlikely in situ. The problems with in situ treatment are numerous: (1) the microorganisms are not well distributed and will not adequately come into contact with leachate spread under many hectares of landfill; (2) gas production (CH_4, CO_2, H_2S) in the landfill can create

dangerous explosion and unstable land conditions; and (3) little or no process control over temperature, pH, and electron acceptor can be effected. Therefore, in situ treatment is an unreliable alternative.

The most promising biological treatment scheme for landfill leachate involves anaerobic methanogenesis. A methanogenic process is advantageous for five obvious reasons:

1. The leachate is already anaerobic.
2. Methanogenic processes require no aeration to supply oxygen. To supply enough oxygen to meet the oxygen requirements of aerobic activated sludge treatment of the Love Canal leachate would cost about $0.40/m^3 of leachate, not including capital recovery.
3. The anaerobic process produces 10-20 times less biological sludge than would an aerobic process. Low sludge production means major cost savings, since sludge handling and disposal for aerobic operations typically requires half of the operating budget.
4. The lack of sludge production during methanogenesis means that nutrient additions (N and P) can be relatively low. Table VI shows that the Love Canal leachate has no P and probably little inorganic N. Aerobic treatment would require addition of about 340 g N/m^3 and 70 g P/m^3, while the requirements with anaerobic treatment would be 10-20 times less.
5. Methanogenesis produces a valuable product, methane gas, which can easily be captured and used to run pumps or equipment, heat buildings, or generate electricity. The methane gas produced through anaerobic treatment of Love Canal leachate would generate about $0.60/m^3 of electrical power.

Besides the obvious benefits of methanogenesis, the anaerobic process can be the most appropriate for leachate decontamination because degradation of certain anthropogenic organics is enhanced in the anaerobic environment. For example, the breakdown of chlorinated hydrocarbons is greatly increased in an anaerobic environment [50,51], where the original organic matter, metabolic products (such as reduced flavins) and reduced inorganics (such as iron and sulfur) serve as electron donors and electron-transfer agents. The result is that chlorinated hydrocarbons are reductively dechlorinated, with hydrogen replacing the chlorine. Since the dechlorination step often limits biodegradation of chlorinated compounds, the anaerobic environment is often ideal for enhancing biodegradation of many of the most critical contaminants.

Numerous reports [13,50-53] have shown that degradation of halogenated hydrocarbons requires an anaerobic environment. Particularly pertinent is the work of Bouwer et al. [13], in which low concentrations (less than 1 mg/l) of halogenated one- and two-carbon hydrocarbons were degraded anaerobically, but not aerobically. Even without biological activity, the brominated compounds were dehalogenated, although not nearly as quickly as with methanogenic activity; others have also shown that strongly anaerobic conditions can bring

about reductive dehalogenation when microbial activity is not present [50,51], and dehalogenation is correlated to a negative E_H. Thus, the use of an anaerobic treatment process enhances microbiological and possibly chemical degradation of many of the contaminants of most concern.

It must be pointed out that halogen-substituted aromatic rings seem to be resistant to anaerobic attack, but require aerobic hydroxylation to dehalogenate them [50]. Recent work at very low concentrations [11,13] has reinforced this idea: halogenated hydrocarbons were degraded anaerobically, but not aerobically; chlorinated aromatics were degraded aerobically, but not anaerobically. Should anaerobic dehalogenation of aromatic compounds be found feasible in the future, the anaerobic system should be capable of completely degrading the resulting aromatic products [54].

Methanogenic processes have been used for treating high-strength industrial wastes, as well as sewage sludges. The anaerobic filter [49] has been gaining popularity because it offers the advantages of a fixed-film system: process stability and high loading rates. It has been used to treat wastewater resembling hazardous landfill leachate. DeWalle and Chian [55] used a fixed-bed, complete-mix anaerobic filter to treat a landfill leachate having a COD of 32,000–54,000 mg/l, and they reduced the COD to 1000 mg/l with a 7.5-day detention time at 25°C. Suidan et al [30] treated high strength phenolic wastewater with a fluidized-bed anaerobic filter at 35°C.

A most important factor for use of anaerobic filters is the chemical characteristics of the wastewater, since certain characteristics could cause operating problems. The first problem is toxicity. Numerous inorganic compounds that can be present in leachate are toxic to methanogens [56]. Among the most likely to be problems are sodium, sulfur and heavy metals. An excessive sodium concentration, such as 3500 mg/l or more, is inhibitory to methanogens, and more than 8000 mg/l can be strongly inhibitory or toxic. Reduced sulfur compounds in solution—H_2S, HS^- and S^{2-}—are toxic at 200 mg/l, while soluble heavy metals, such as Cd, Zn and Ni, are toxic at mg/l levels. If the metals and sulfur are reasonably well balanced in the feed, metal sulfides precipitate in the anaerobic system, rendering both types of toxics harmless. Too great a quantity of sulfur or metals, which could easily occur in a leachate, would create toxic conditions preventing the methane-producing bacteria from functioning properly.

Organic materials, such as found in leachate, can also be highly toxic, and their toxicity often occurs at low concentrations. For instance, chloroform is toxic at 2–100 mg/l, cyanide at 1–200 mg/l, methylene chloride at 20 mg/l, and ethylene dichloride at 32 mg/l [57,58]. In some

cases, the anaerobic systems seem to acclimate, but acclimation is not the rule.

The second problem with methanogenic treatment is pH control. In its essence, anaerobic treatment is a two-step process. In the first step, anaerobic bacteria break down complex organic compounds through fermentative pathways, producing mostly short-chain organic acids, CO_2 and H_2. In the second step, methanogens utilize the first-stage products and produce methane gas. Treatment, or COD removal, occurs because the electron equivalents of the original organic matter end up in methane, which is easily stripped from the water. If the methanogens are unable to utilize the acids produced during the first stage as fast as they are produced, the buffering capacity of the system is neutralized by the acids and the pH falls. Since methanogens are sensitive to low pH, a decrease below about pH 6.5 still further slows the methanogenic reaction and hastens the ultimate failure of the system.

The anaerobic process is appropriate for leachate treatment because (1) the leachate is already anaerobic and has enough organic material to sustain anaerobic conditions; (2) it enhances degradation of many contaminants; and (3) it can make treatment an energy-producing enterprise. On the other hand, anaerobic treatment may not be able to degrade certain aromatic compounds, and it may not produce an effluent with suitably low concentrations of total organics or specific compounds. A prudent approach is to follow anaerobic treatment with a simple aerobic process, such as a rotating biological contactor (RBC) [59,60]. The anaerobic unit provides most of the COD removal, while the aerobic system polishes the effluent and removes compounds unaffected by the anaerobic process. Costs of aerobic treatment are minimized because most of the COD is removed during anaerobic treatment.

SUMMARY

Biodegradation of anthropogenic organics present in waters is a complicated and not very well developed field. However, several factors are clear. When the contaminants are at very low concentration, special consideration must be given to providing enough energy for the bacteria to sustain themselves in the system. Biofilm processes seem most appropriate, since the bacteria are kept in the reactor by attachment, and biofilms predominate naturally with low concentrations. Secondary utilization, nonsteady-state operation, and activated carbon attachment are methods to promote bacterial growth when concentrations are very

low. In combination with these three methods, fluidized-bed treatment offers advantages for obtaining very low effluent concentrations.

For landfill leachate, which is often anaerobic and contains rather high organic strength, anaerobic methanogenic processes offer the benefits of decreased operating costs and enhanced degradation of many hazardous contaminants. Caution must be exercised to prevent toxicity to the anaerobic microorganisms, and posttreatment with a simple aerobic process may be necessary to polish the effluent and degrade halogenated aromatics.

Although some concepts and techniques are known today, much basic information about biodegradation of trace-level organics is lacking, such as:

- physiological response of bacteria to very low concentrations of substrates;
- relationship between primary and secondary substrates;
- toxicity of trace-level organics to biological processes;
- ability to apply treatment concepts to realworld applications;
- consequences of partial degradation; and
- interactions among communities of microorganisms necessary to completely degrade compounds.

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CHAPTER 22

PEROXIDASE FOR REMOVAL OF HAZARDOUS AROMATICS FROM INDUSTRIAL WASTEWATERS

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Most phenols and aromatic amines are toxic, and many are known or suspected human carcinogens [1–4]. They are inherent in the wastewaters of a variety of industries, including coal conversion, petroleum refining, resins, plastics, textiles, dyes, organic chemicals, paving, roofing, iron and steel. For instance, phenol, cresols and xylenols are produced by high-temperature carbonization of coal, a process that will increase in importance as alternative supplies of fossil fuels diminish.

There are a number of methods currently being used to remove these types of pollutants from wastewaters: microbial degradation, adsorption onto activated carbon, chemical oxidation, solvent extraction, membrane processes and irradiation [2,5–7]. Unfortunately, these methods, despite their usefulness, have some serious drawbacks, such as high cost, low efficiency, incompleteness of purification and formation of hazardous by-products [7]. Therefore, new approaches to the problem of wastewater treatment are necessary.

We have proposed the use of the enzyme horseradish peroxidase to treat wastewaters containing phenols and aromatic amines [8,9]. Our method is based on the enzyme's ability to catalyze, with hydrogen peroxide, the oxidation of a variety of phenols and aromatic amines

[10,11], thus generating the corresponding phenolic and aromatic amine free radicals [12].

These free radicals diffuse from the active center of the enzyme into solution [13] where they can polymerize to polyaromatic products [10-12]. These high-molecular-weight polymers (see Figure 1 as an example), unlike their monomeric precursors, are water-insoluble and can be separated with relative ease by filtration or sedimentation.

We have tested this approach on more than 40 phenols and aromatic amines [8,9]. In most cases, on addition of horseradish peroxidase and H_2O_2, a solution containing the pollutant immediately becomes colored, followed by gradual separation of a precipitate. To quantify the degree of enzymatic water purification, we use the parameter "removal efficiency" [11,14], which is defined as the percentage of chemical removed from solution under given conditions.

Table I shows the removal efficiencies for some of the phenols and aromatic amines we tested. While many of the removal efficiencies are very high (> 99%), some are significantly lower. Moreover, certain phenols and aromatic amines (e.g., nitrophenols) cannot be precipitated enzymatically. Fortunately, we have discovered an effect that helps to eliminate these problems.

If easy-to-remove pollutants are mixed with hard-to-remove ones, the former aid in the precipitation of the latter. Apparently, peroxidase oxidation of some compounds, such as phenol and aniline, yields products of relatively low molecular weight. These products are appreciably soluble in water, and therefore the pollutants have low removal efficiencies. However, if the same pollutants are mixed with compounds such as benzidine or 1-naphthol, which polymerize to high-molecular-weight products (and have high removal efficiencies), the free radicals from both types of pollutants react with each other to form high-molecular-weight mixed polymers that precipitate readily. This can be

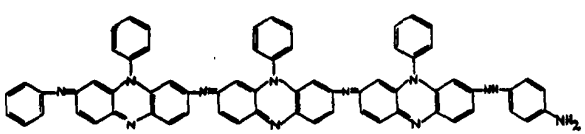

Figure 1. Structure of aniline black, the major product of peroxidase-catalyzed oxidation of aniline with H_2O_2 [10].

Table I. Removal of Aromatic Amines and Phenols from Water by Horseradish Peroxidase and H_2O_2[a]

Pollutant	Removal Efficiency[b] (%)	Reference
Benzidine	99.94	8
3,3'-Dimethoxybenzidine	99.9	8
3,3'-Diaminobenzidine	99.6	8
3,3'-Dichlorobenzidine	99.9	8
3,3'-Dimethylbenzidine	99.6	8
1-Naphthylamine	99.7[c]	8
2-Naphthylamine	98.3[c]	8
5-Nitro-1-naphthylamine	99.6[c]	8
N,N'-Dimethylnaphthylamine	93.2[c]	This work
Phenol	85.3[d]	9
2-Methoxyphenol	98.0[e]	9
3-Methoxyphenol	98.6[e]	9
4-Methoxyphenol	89.1[f]	9
2-Methylphenol	86.2[d]	9
3-Methylphenol	95.3[d]	9
4-Methylphenol	85.0[e]	9
2-Chlorophenol	99.8[f]	9
3-Chlorophenol	66.9[f]	9
4-Chlorophenol	98.7[e]	9
2,3-Dimethylphenol	99.7[d]	9
2,6-Dimethylphenol	82.3[e]	9
Aniline	72.9[f]	9
4-Chloroaniline	62.5[e]	9
4-Bromoaniline	84.5[e]	9
4-Fluoroaniline	86.4[f]	9
1,3-Diaminophenol	98.6[f]	9
Diphenylamine	80.5[f]	This work
1-Naphthol	99.6[d]	9
2-Nitroso-1-naphthol	98.9[d]	9
4-Phenylphenol	99.9[d]	9
8-Hydroxyquinoline	99.8[f]	9

[a] Conditions: 100-mg/l aqueous solution of a phenol or an aromatic amine; 3-hr treatment at room temperature; pH 5.5; 100 units/l peroxidase, 1 m*M* H_2O_2 (unless otherwise indicated).

[b] Aromatic amines and phenols were determined using the specific assays by Butt and

[c] 5 m*M* H_2O_2, 1000 units/l peroxidase.

[d] 1 m*M* H_2O_2, 1000 units/l peroxidase, pH 4.0.

[e] The same as in footnote d, but at pH 5.5.

[f] The same as in footnote d, but at pH 7.0.

[g] It should be pointed out that treatment with either peroxidase or H_2O_2 alone results in no precipitation and no removal of the chemicals from water under the conditions used.

illustrated by our finding [9] that, whereas the enzymatic removal efficiency for phenol is 74.6%, in the presence of 8-hydroxyquinoline, benzidine and 3,3-dimethoxybenzidine, the removal efficiency for phenol increases to 99.8, 99.5 and 99.7% respectively.

In fact, we found that this phenomenon could even be extended to the removal of nonphenolics and nonaromatic amines, which normally are not substrates for peroxidase. For instance, naphthalene does not react with peroxidase and H_2O_2 at all. However, in the presence of 100 mg/l of 2,3-dimethylphenol, more than 60% of the naphthalene precipitates. The results are even more spectacular with azobenzene, a common intermediate in the chemical industry and a suspected carcinogen [4]. Azobenzene does not react with horseradish peroxidase and H_2O_2. However, in the presence of 2,7-naphthalenediol and 1-naphthol, 99.9 and 99.3% of azobenzene, respectively, can be precipitated on peroxidase treatment (20 mg/l azobenzene, 100 mg/l naphthalenediol or naphthol, 4 mM H_2O_2, 300 units/l peroxidase, pH 4.0, 48-hr treatment).

The discovery of the enhanced enzymatic removal of poorly or nonremovable compounds in mixtures of pollutants has an important practical implication. Real industrial wastewaters always contain many different pollutants. Hence, even if only a few of them are easily precipitated by peroxidase, they will facilitate the removal of the others by the enzyme and hydrogen peroxide. The significance of this is documented by our experiments with wastewater from a chemical plant.

TREATMENT WITH A CRUDE ENZYME PREPARATION AND OTHER PEROXIDASES

Since our enzymatic treatment is designed to have a practical application, it is important to minimize the cost. In all of the experiments described above, a partially purified horseradish peroxidase obtained from a commercial supplier (Type II, Sigma Chemical Co., St. Louis, Missouri) was used. However, we also examined the possibility of using a crude enzyme preparation made from horseradish roots bought at a local supermarket. The roots were minced in a blender, suspended in water, stirred and pressed through cheesecloth. The juice was used as a peroxidase source and its enzymatic concentration determined using the standard guaiacol assay [17].

Table II compares the removal efficiencies of several different phenols precipitated by the crude enzyme preparation and the commercial

Table II. Removal of Phenols from Water by Purified and Crude Peroxidases[a]

Phenol	Removal Efficiency[b] (%)		pH
	Sigma Enzyme	Crude Enzyme	
Phenol	87.6	89.8	3.5
3-Methylphenol	85.3	99.6	4.0
4-Methylphenol	98.5	95.6	5.5
2-Chlorophenol	99.7	99.7	7.0
2,3-Dimethylphenol	99.6	99.3	4.0
1-Naphthol	97.4	99.6	4.0
2-Nitroso-1-naphthol	96.0	95.0	4.0
8-Hydroxyquinoline	99.9	99.7	7.0

[a] Conditions: 100-mg/l phenols; 1000 units/l peroxidase; 2.5 m*M* H_2O_2; 21-hr treatment at room temperature.

[b] The phenols were assayed by the method of Emerson [16] (except for 4-methylphenol, which was assayed in accordance with Arnow [18] as described by Klibanov et al. [9]).

peroxidase. In all cases, the results were comparable, demonstrating that the efficiency of this process does not depend on the purity of the enzyme.

We also studied whether peroxidases from sources other than the horseradish root can be used to precipitate phenols and aromatic amines. We examined two commercially available peroxidases (from Sigma), lactoperoxidase from cow's milk and chloroperoxidase from *Caldariomyces fumago*. Treatment by lactoperoxidase and H_2O_2 (800 units/ml enzyme, 2 mmol H_2O_2, pH 5.5, 24 hr) of 100 mg/l benzidine, 1-naphthylamine, phenol, aniline, 2-methoxyphenol, 1-naphthol, 4-phenylphenol, 3-methylphenol and 2-chlorophenol resulted in removal efficiencies of 90.8, 35.1, 0, 0, 31.6, 32.0, 38.3, 15.4, 13.7%, respectively. The only compound from the above list that can be precipitated enzymatically by chloroperoxidase is benzidine. Therefore, it appears that, although lactoperoxidase and chloroperoxidase are capable of precipitating certain phenols and aromatic amines, the efficiency of their removal is too low to be of practical value. However, since peroxidases are ubiquitous in microorganisms and plants, it seems likely that a bacterial peroxidase may be found that has a very broad substrate specificity similar to that of the horseradish enzyme. Such a peroxidase potentially would be even less expensive than horseradish (see cost analysis below) and be available in virtually unlimited quantities. The search for such an enzyme is currently underway in our laboratory.

TREATMENT OF WASTEWATER FROM A CHEMICAL PLANT

To demonstrate the practicability of our method, we used it to treat "real" aqueous effluent obtained from a chemical plant that produces triaryl phosphates (used as flame retardants). The waste sample contained more than 150 different chemicals, including various phenols, cresols, xylenols, isopropylphenol, *tert*-butylphenol and some nonphenolic compounds such as triaryl phosphates and inorganic phosphate. The total phenol concentration was 105 mg/l.

Usually this chemical plant treats its water by a two-step process. First, the water is subjected to bacterial degradation, which takes several days and reduces the phenol content by 85–90%. Then, the remaining phenols are removed by adsorption onto activated carbon. The initial step, bacterial treatment, is carried out in open ponds. Since bacteria do not degrade phenols at low temperatures, it is impossible to use such a method during the winter. For this reason, we carried out our treatment of the industrial sample in cold and room-temperature environments. Also from a practical standpoint, it was desirable to work in a pH range of 6–8, because lower pH tends to cause the corrosion of steel columns with activated carbon and other metal containers.

One liter of the wastewater was adjusted to pH 7 and put in a refrigerator. Then, 100 units of peroxidase and 2.5 mmol of H_2O_2 were added to the cold solution. After 40 hr in the refrigerator, the system was assayed for phenols [9]. As a result of our treatment, the phenol concentration decreased from 105 to 3.7 ppm, equivalent to a removal efficiency of 96.5%. Even at 25 units/l peroxidase and 2 mmol H_2O_2, the removal efficiency was approximately 85–90%. The crude peroxidase described above was as effective as the purified enzyme, and treatment at 4°C and room temperature yield about the same removal efficiency.

ECONOMIC CONSIDERATIONS

We have attempted to assess the economic feasibility of our method. A precise analysis is not possible at the present time, but a rough estimation can be made. The current wholesale price for horseradish is about 35¢/lb [19], and one pound contains about 15,000 units of peroxidase [20]. Treatment of 1000 liters of water (at 25 units/l peroxidase) will cost 58¢. The current price for H_2O_2 is 21¢/lb of 35% solution. Treatment of 1000 liters containing 105 ppm phenols (at 2 mmol H_2O_2) will cost 11¢. Therefore, the total cost of materials for the enzymatic treatment of 1000

liters of water is 69¢. It is interesting to note that since the growth productivity of horseradishes is about 8000 lb/ac (1 harvest/yr) [21] the area needed to provide enough peroxidase to treat 1000 liters of wastewater is 0.84 m^2.

For comparison, we also examined the chemical cost of the FMC process [22], an existing, commercially available method that uses H_2O_2 and an iron catalyst to remove phenol. This treatment oxidizes phenol to CO_2 and H_2O. However, it cannot be used with most substituted phenols nor with aromatic amines. Still it is interesting to estimate its cost as we did with our method. Since H_2O_2 and Fe^{2+} completely oxidize phenol, a 14-fold molar excess of H_2O_2 is required [22]. To treat 1000 liters of water containing 105 ppm phenol, approximately 4 lb of 35% H_2O_2 is needed at a cost of 84¢. Therefore, even without the cost of Fe^{2+}, the price of materials for our enzymatic treatment is comparable with that of the FMC process.

CONCLUSION

We have demonstrated that treatment of wastewaters with horseradish peroxidase and H_2O_2 causes the precipitation of phenols, anilines and some other organics. Our preliminary cost analysis indicates that this new enzymatic approach to water detoxication may be economically feasible and cost-competitive with conventional methods. (One should also note that the precipitate formed as a result of enzymatic polymerization of pollutants can, in principle, be burned and the energy obtained can be used for heating.) It is hoped that as industry continues to tackle the ever-growing problem of wastewater treatment, the enzymatic process described in this work will be seen as a feasible and attractive alternative.

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