

4. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

4.1 PRODUCTION

CDFs are not manufactured commercially in the United States or any other country except on a laboratory scale for use in chemical laboratories or for toxicological studies. These compounds are produced as undesired by-products during the manufacture of PCBs, polychlorinated phenols, and herbicides, such as Agent Orange. They are also formed during the pyrolysis of PCBs, polychlorinated diphenyl ethers, polychlorinated phenols, polychlorinated benzenes, and phenoxy herbicides. Municipal and industrial incinerators also produce CDFs. These compounds can also be produced from the photolysis of PCBs, polychlorinated diphenyl ethers, and polychlorinated benzenes (Van den Berg et al. 1985). Chlorine bleaching at paper and pulp mills can also result in CDF formation (Campin et al. 1991; Näf et al. 1992). Detailed information on the sources of CDFs are given in Chapter 5.

Several methods are available for the synthesis of CDFs; all yield mixtures of isomers (EPA 1986a; Gara et al. 1981). Two methods that have been used to synthesize a number of structure-specific CDFs are cyclization of diazotized chlorophenoxy-o-aniline and cyclization of chlorinated diphenylethers, promoted by palladium(II) acetate (Gara et al. 1981; Gray 1976; Humppi 1986; Kuroki et al. 1984; Norstrom 1979). In the first process, chlorophenates and chloronitrobenzene react to form nitrochlorodiphenyl ethers. The later compounds are reduced to aminochlorodiphenyl ethers, diazotized, and cyclized with isoamyl nitrite to form the CDFs. In the second method, chlorinated diphenyl ethers are produced by refluxing chlorinated diphenyl iodonium salt with chlorophenolate. The chlorinated diphenyl ethers are cyclized with palladium acetate in the presence of acetic acid and methane sulfonic acid (Kuroki et al. 1984).

Another method that has been used to synthesize 22 high purity CDF isomers is the cyclization of o-hydroxy polychlorinated biphenyls by refluxing with dimethyl sulfoxide and potassium hydroxide (Safe and Safe 1984). The o-hydroxyl PCBs are produced either by a diazo coupling of chlorinated anisidines and symmetrical chlorinated benzenes or by diazo coupling of chlorinated anilines with chlorinated anisoles.

4. PRODUCTION, IMPORT, USE, AND DISPOSAL

The pyrolysis of PCBs, commercial chlorobenzenes, and chlorinated diphenyl ethers yields CDF mixtures. Although the pyrolysis method produces mixtures of isomeric CDFs, it has been used frequently to prepare qualitative CDF standards, because it is fast and safe (Buser and Rappe 1979; EPA 1986a; Grace et al. 1989). Similarly, qualitative standard mixtures of CDFs have also been produced by the ultraviolet and gamma irradiation of octachlorodibenzofuran (Buser 1976).

Since SARA Section 313 does not require that releases of CDFs be reported, there are no data on these compounds in the 1989 Toxics Release Inventory (TRI) (TRI89 1992).

4.2 IMPORT/EXPORT

No data were located on the import or export of CDFs.

4.3 USE

There is no commercial use of CDFs other than small amounts used in chemical and biochemical laboratories.

4.4 DISPOSAL

Several methods for disposing CDFs have been proposed; some of these have been put into field use to decontaminate wastes containing CDFs. The most commonly used methods for disposal or decontamination of CDF-containing wastes are photolysis, incineration, chemical destruction, microbial degradation, and landfilling. Each of these methods has limitations, but some may be preferable to others. The common methods for CDF waste disposal/decontamination are discussed below.

In the photolytic process, CDDs/CDFs are destroyed by dechlorination of the compounds by ultraviolet light most efficiently in the presence of hydrogen donors. The most commonly used hydrogen donor is isopropyl alcohol (des Rosiers 1983). TCDD-containing Seveso soil was decontaminated by ultraviolet treatment of the soil in the presence of olive oil emulsion as a hydrogen donor. A total reduction in excess of 60% was observed after 48 hours of irradiation. The decontamination efficiency of CDFs by ultraviolet radiation was reported to be 90% after 48 hours irradiation of the walls and ceiling of a building contaminated during a PCB fire (Borwitzky and Schramm 1991). When CDFs

4. PRODUCTION, IMPORT, USE, AND DISPOSAL

were extracted from a contaminated soil in hexane and irradiated with ultraviolet light in the presence of a hydrogen donating solvent (propanol), the decontamination efficiency reached 99.9% in 4 hours (Drechsler 1986). The destruction efficiencies of CDFs by liquid phase photolysis are faster than CDDs (Muto and Takizawa 1991). The advantage of photolytic destruction is that it poses only a small risk to workers. The notable disadvantages of the photolysis process are that it is time consuming (when a large area is involved or solvent extraction is performed) and may not be universally applicable to other contaminants (Borwitzky and Schramm 1991).

Incineration is a preferred method for disposing of CDF-containing wastes. In this process, the waste is burned in a stationary or rotary kiln incinerator at temperatures between 900 and 1,000°C and a minimum residence time of 1.8 seconds; however, the destruction of particle bound CDFs may require higher temperatures and longer retention times. Higher temperatures can be attained by adding a secondary combustion chamber to a rotary kiln incinerator. Land-based and at-sea incineration facilities are available. Investigators have postulated the following combustion criteria for land-based incineration of CDF wastes: a 2-second dwell time at 1,200°C or 15second dwell time at 1,600°C, a combustion efficiency in excess of 99.99%, and a scrubber system to control flue gas emission (Almemark et al. 1991; des Rosiers 1983). EPA considers CDFs Principal Organic Hazardous Constituents (POHCs) and requires them to be incinerated, in order to achieve a destruction and removal efficiency of 99.99% (EPA 1990b).

Some of the chemical methods available for the destruction of CDFs include alkaline dehydrochlorination; reduction with hydrogen in the presence of a palladium or platinum catalyst at 100°C; catalytic oxidation with ruthenium tetroxide, chlorolysis in the presence of chlorine gas at 600°C and a pressure of 170 atm; or micellar catalysis with either benzalkonium dichloroiodide or cetylpyridinium dichloroiodide. Disadvantages of these methods are generation of unwanted byproducts requiring high temperatures or pressures and, in some cases, cost. The preferable chemical method is dehydrochlorination in a mixture of alkaline polyethylene glycol and inorganic peroxide at a temperature <100°C (des Rosiers 1983; Drechsler 1986; Hagenmaier et al. 1987; Tiernan et al. 1989). A chemical method employing precipitation by the addition of alum or lime at a concentration of 9,000 mg/L removed >98% of CDDs/CDFs from bleach plant filtrates and combined treated mill effluents from pulp and paper industries (Barton et al. 1990). However, the sludge from this process contains the CDDs/CDFs and requires proper disposal. The destruction of CDFs in aqueous solution

4. PRODUCTION, IMPORT, USE, AND DISPOSAL

at a pH of 10 and temperature of 50°C by ozone was reported to be >90% in 4 hours (Palauschek and Scholz 1987).

Decontamination of CDF-containing wastes by a biodegradation method has also been attempted. *Phanerochaete chrysosporium*, a white rot fungus, which degraded TCDD in laboratory experiments (des Rosiers 1986), may be suitable for biodegrading CDFs. However, no successful biotreatment method exists that can satisfactorily decontaminate CDF wastes.

In the past, land disposal of waste materials contaminated with CDDs and CDFs was considered an option under strict technical conditions. Some of these conditions included use of soil with low water permeability, the use of synthetic membrane liners to cover the soil, compatibility with the hydrogeology of the site, maintenance of a leachate monitoring program, and acquisition of waivers from the appropriate EPA or state agency (des Rosiers 1983). However, land disposal of certain CDF wastes is presently prohibited. The Toxic Substances Control Act (TSCA) regulates the use, disposal, and distribution in commerce of process waste water treatment sludges intended for land application that are derived from pulp and paper industry employing chlorination processes (EPA 1991).