



# Project Summary

## Technical Resource Document: Treatment Technologies for Dioxin-Containing Wastes

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The 1984 Hazardous and Solid Waste Act Amendments to the Resource Conservation and Recovery Act (RCRA) directed EPA to ban certain dioxin-containing wastes from land disposal unless EPA determines that restrictions on land disposal of these wastes are not needed to protect human health and the environment. Congress, through the 1984 Amendments, fixed a deadline of 24 months from the enactment of the Amendments for EPA to regulate the land disposal of these identified wastes (with some exceptions). In the event that the Agency has not issued regulations by that time (November 1986), land disposal of all specified dioxin-containing waste streams automatically will be banned.

An important aspect of the land disposal restrictions is the identification and evaluation of alternative technologies that can be used to treat the listed wastes in such a way as to meet proposed treatment levels which EPA has determined are protective of human health and the environment. If alternatives to land disposal are not available by November 1986, it may be necessary to extend the deadline for the restrictions on land disposal. The full report identifies and evaluates alternative technologies that remove and/or destroy dioxin and related compounds from listed dioxin wastes in order to achieve constituent levels that allow the safe land disposal of the treated residues.

*This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Scope

A number of potential technologies exist for treating wastes containing dioxin. Because many of the technologies are currently in developmental stages, it is not possible to assess fully the effectiveness of these technologies at this time. Further testing of a technology in the future may, for example, indicate that a technology is or is not practical on a full scale. In addition, several new technologies for treating dioxin wastes may emerge for which information is not currently available. Consequently, it must be emphasized that the information discussed here represents that which was available in the spring of 1986.

Technologies under evaluation are those that destroy dioxin or somehow change its form so that it is less toxic. Temporary management methods, such as storage in mines, are not evaluated because these methods only involve moving the waste without changing the chemical form and characteristics of the waste. The majority of the technologies are those whose performance has been tested on dioxin-

containing wastes. Those that have not been tested on dioxin-containing wastes have, at least, been tested on PCB-containing wastes. Because of the similarity of PCBs and dioxins, these technologies should also be applicable to dioxin wastes. Technologies that have been developed to full scale as well as those only investigated in the laboratory are included. This is primarily because, as mentioned previously, this field is rapidly evolving. Many of the technologies that are now only in the laboratory stage may be standard technologies for treatment of these wastes in the future.

### Definition of Dioxin Waste

The term "dioxin waste" is meant to include those RCRA wastes listed as EPA hazardous waste Numbers F021, F022, F023, F026 and F027. As shown in Table 1, these waste codes are designated as "acute hazardous" and include wastes from the production and manufacturing use of tri-, tetra-, and pentachlorophenols, wastes from the manufacturing use of tetra-, penta-, and hexachlorobenzene under alkaline conditions, and also discarded, unused formulations containing tri-, tetra-, and pentachlorophenols. Soil that has been contaminated by improper management of these wastes is also encompassed by these waste codes. Residues from the incineration of this contaminated soil are designated as toxic instead of acute hazardous and are covered under waste code F028.

The wastes described by these waste codes are listed hazardous wastes primarily because they contain one of a number of forms of dioxin. The term "dioxin" has been used very loosely. It encompasses a family of aromatic compounds known chemically as dibenzo-p-dioxin. The forms of dioxin that are of most environmental concern are the chlorinated dioxins, in which a chlorine atom occupies one or more of the available eight positions on the double benzene ring structure. Thus, there are 75 possible chlorinated dioxin compounds, the most toxic of which is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Throughout the full report, various terms will be used to refer to certain types of dioxin. When only the word "dioxin" is used, it refers to chlorinated dioxin compounds in general. Other commonly used abbreviations are:

PCDDs = all isomers of chlorinated dibenzo-p-dioxins

**Table 1.** Dioxin Contaminated Wastes Listed as RCRA Hazardous Wastes, January 14, 1985, 50 FR 1978

Hazardous Waste From Nonspecific Source		
EPA hazardous waste no.	Hazardous waste	Hazard code
F020*	Wastes** from the production or manufacturing use of tri- or tetrachlorophenol, or of intermediates used to produce their derivatives.**	(H)
F021*	Wastes** from the production or manufacturing use of pentachlorophenol (PCP), or of intermediates used to produce its derivatives.	(H)
F022*	Wastes** from the manufacturing use of tetra-, penta-, or hexachlorobenzene under alkaline conditions.	(H)
F023*	Wastes** from the production of materials on equipment previously used for the production or manufacturing use of tri- or tetrachlorophenols.***	(H)
F026*	Wastes** from the production of materials on equipment previously used for the manufacturing of tetra-, penta-, or hexachlorobenzene under alkaline conditions.*	(H)
F027*	Discarded unused formulations containing tri-, tetra-, or pentachlorophenol or discarded unused formulations derived from these chlorophenols.****	(H)
F028	Residues resulting from the incineration or thermal treatment of soil contaminated with EPA hazardous waste F020, F021, F022, F023, F026, and F027.	(T)

\*A proposed regulation [50 FR 37338] would make residues from the incineration of these wastes (if the waste contained less than or equal to 10 ppm TCDD prior to incineration) toxic instead of acute hazardous.

\*\*Except wastewater and spent carbon from hydrogen chloride purification.

\*\*\*This listing does not include wastes from the production of hexachlorophene from highly purified 2,4,5-trichlorophenol.

\*\*\*\*This listing does not include formulations containing hexachlorophene synthesized from prepurified 2,4,5-trichlorophenol as the sole component.

(H) = Acute Hazardous Waste

(T) = Toxic Waste

CDDs = all isomers of tetra-, penta-, and hexachlorodibenzo-p-dioxins  
 TCDD } = the 2,3,7,8- isomer  
 PeCDD, }  
 HxCDD, } = the penta-, hexa-, and  
 and OCDD } octachloro compounds  
 Other toxic constituents that may be present in the listed dioxin wastes are chlorinated dibenzofurans (CDFs), chlorophenols, and chlorophenoxy compounds.

### Waste Sources, Characteristics, and Quantities

The waste codes included in the dioxin listing encompass process wastes from the production of various chlorophenols, primarily 2,4,5-trichlorophenol and pentachlorophe-

nol, and chlorophenoxy pesticides such as 2,4,5-T and Silvex. As indicated in a report prepared by Technical Resources, Inc. for the EPA Office of Solid Waste, the manufacture of most of these compounds has been stopped. For example, 2,4,5-trichlorophenol has not been manufactured for several years. As a result, the majority of the dioxin-bearing process wastes requiring treatment at this time are wastes such as still bottoms and reactor residues that were generated in the past and remain to be treated. The only process waste stream that is still being generated, and may continue to be generated in the future, is from the manufacture of pentachlorophenol (PCP). However, by far the largest quantity of dioxin-bearing wastes that have been identified are the contaminated soils

such as those at Times Beach, Missouri, and various other CERCLA sites throughout the country.

Table 2 shows estimated waste quantities for each of the waste codes. Several items associated with the information in the table should be noted. One is that no sources have yet been identified for waste codes F022 and F026. Another is that waste code F028 is not included because it is expected that residues from future incineration of contaminated soil will meet EPA delisting requirements. Finally, contaminated soils are placed in a separate category both because of their unique physical form relative to most process wastes, and also because a large fraction of the contaminated soils are at CERCLA sites

whose wastes will not be affected by the RCRA land disposal restrictions until November 1988.

The estimates of the quantities of wastes generated within each waste category in Table 2 could have a significant impact on future treatment practices. As shown in the table, there are more than 500,000 metric tons of dioxin-contaminated soil that may require treatment. This quantity is considerably greater than the estimated maximum 7500 MT of process wastes, such as still bottoms currently requiring treatment and the estimated 2500 MT of industrial process wastes that will be generated in future years. Consequently, it would appear that treatment technologies capable of treating soil

wastes are of most importance at this time, particularly those technologies, such as solvent extraction, that are capable of removing the toxic constituents from the soil and thereby reducing the total volume of waste requiring final detoxification/destruction.

### Technologies for Treating Dioxin Wastes

As mentioned previously, a number of technologies for treating dioxin waste are evaluated in this document. A summary of the status of these technologies is provided in Table 3. Because studies have shown that dioxin decomposes by heating or oxidation at tem-

**Table 2.** Summary of Dioxin Waste Sources and Quantities

Waste code	Waste source	Physical form	Quantity generated (metric tons)	
			Present (or stored)	Future
F020	Manufacture of herbicides such as 2,4,5-T, 2,4,5-trichlorophenol, hexachlorophene; disposal of wastes in uncontrolled landfills or storage areas	<ul style="list-style-type: none"> <li>- Still bottoms containing organic solvents and chlorophenols</li> <li>- Nonaqueous phase leachate (NAPL) containing solvents, chlorophenols, heavy metals</li> <li>- Carbon used to treat aqueous leachate</li> </ul>	Still bottoms-2,300 NAPL -1,450 Other - 550	0 0-200 Unknown
F021	Manufacture of pentachlorophenol: wastes from purification; wastes from formulation	<ul style="list-style-type: none"> <li>- Still bottoms or other concentrated materials containing nonvolatile organic solids and chlorinated solvents and phenols</li> <li>- Sludges from formulation</li> </ul>	Still bottoms-0 Formulation waste-700	750 Unknown
F022	No known sources at this time	- NA*	0	0
F023	Production of chemicals on equipment formerly used to manufacture F020 compounds, e.g., 2,4-D on 2,4,5-T equipment	- Similar to F020 wastes - still bottoms, reactor residues containing chlorophenols and organic solvents, and wash water sludges from formulation	0-600	0-600
F026	No known sources at this time	- NA	0	0
F027	Discarded formulation of tri-, tetra-, and pentachlorophenols and their derivatives	- Active ingredient in an emulsifiable concentrate, as a salt or an ester, or dissolved in an oil (such as in the case of pentachlorophenol)	1000-2000	0-1,000***
	Contaminated soil from improper disposal and spills of F020-F027**	- Soils containing low concentrations of dioxins and related compounds	500,000	Unknown

\*NA-Not applicable.

\*\*Not listed as a specific waste code.

\*\*\*Only from pentachlorophenol products.

**Table 3. Summary of Treatment Processes**

Process name	Applicable waste streams	Stage of development	Performance/ destruction achieved	Cost	Residuals generated
Stationary Rotary Kiln Incineration	Solids, liquids, sludges	Several approved and commercially available units for PCBs; not yet used for dioxins	Greater than six nines DRE for PCBs; greater than five nines DRE demonstrated on dioxin at combustion research facility	\$0.25-\$0.70/lb for PCB solids	Treated waste material (ash), scrubber wastewater, particulate from air filters, gaseous products of combustion
Mobile Rotary Kiln Incineration	Solids, liquids, sludges	EPA mobile unit is permitted to treat dioxin wastes; ENSCO unit has been demonstrated on PCB waste	Greater than six nines DRE for dioxin by EPA unit; process residuals delisted	NA*	Same as above.
Liquid Injection Incineration	Liquids or sludges with viscosity less than 10,000 ssu (i.e., pumpable)	Full scale land-based units permitted for PCBs; only ocean incinerators have handled dioxin wastes	Greater than six nines DRE on PCB wastes; ocean incinerators only demonstrated three nines on dioxin containing herbicide orange	\$200-\$500/ton	Same as above, but ash is usually minor because solid feeds are not treated
Fluidized-bed Incineration (Circulating Bed Combustor)	Solids, sludges	GA Technologies mobile circulating bed combustor has a TSCA permit to burn PCBs anywhere in the nation; not tested yet on dioxin	Greater than six nines DRE demonstrated by GA unit on PCBs	\$60-\$320/ton for GA unit	Treated waste (ash), particulates from air filters
High Temperature Fluid Wall (Huber AER)	Primarily for granular contaminated soils, but may also handle liquids	Huber stationary unit is permitted to do research on dioxin wastes; pilot scale mobile reactor has been tested at several locations on dioxin contaminated soils	Pilot scale mobile unit demonstrated greater than five nines DRE on TCDD - contaminated soil at Times Beach (79 ppb reduced to below detection)	\$300-\$600/ton	Treated waste solids (converted to glass beads), particulates from baghouse, gaseous effluent (primarily nitrogen)
Infrared Incinerator (Shirco)	Contaminated soils/sludges	Pilot scale, portable unit tested on waste containing dioxin; full scale units have been used in other applications; not yet permitted for TCDD	Greater than six nines DRE on TCDD-contaminated soil	Treatment costs are \$200-\$1,200 per ton	Treated material (ash) particulates captured by scrubber (separated from scrubber water)
Molten Salt (Rockwell Unit)	Solids, liquids, sludges; high ash content wastes may be troublesome	Pilot scale unit was tested on various wastes—further development is not known	Up to eleven nines DRE on hexachlorobenzene; greater than six nines DRE on PCB using bench scale reactor	NA	Spent molten salt containing ash, particulates from baghouse

**Table 3.** (continued)

Process name	Applicable waste streams	Stage of development	Performance/ destruction achieved	Cost	Residuals generated
Supercritical Water Oxidation	Aqueous solutions or slurries with less than 20 percent organics can be handled	Pilot scale unit tested on dioxin-containing wastes—results not yet published	Six nines DRE on dioxin-containing waste reported by developer, but not presented in literature; lab testing showed greater than 99.99% conversion of organic chloride for wastes containing PCB	\$0.32–\$2.00/gallon \$77–\$480/ton	High purity water, inorganic salts, carbon dioxide, nitrogen
Plasma Arc Pyrolysis	Liquid waste streams (possibly low viscosity sludges)	Prototype unit (same as full scale) currently being field tested	Greater than six nines destruction of PCBs and CCl <sub>4</sub>	\$300–\$1,400/ton	Exhaust gases (H <sub>2</sub> and CO) which are flared and scrubber water containing particulates
In Situ Vitrification	Contaminated soil - soil type is not expected to affect the process	Full scale on radioactive waste; pilot scale on organic contaminated wastes	Greater than 99.9% destruction efficiency (DE) (not offgas treatment system) on PCB-contaminated soil	\$120–\$250/m <sup>3</sup>	Stable/immobile molten glass; volatile organic combustion products (collected and treated)
Solvent Extraction	Soils, still bottoms	Full scale still bottoms extraction has been tested—pilot scale soils washer needs further investigation	Still bottom extraction: 340 ppm TCDD reduced to 0.2 ppm; 60-90% removal from soils, but reduction to below 1 ppb not achieved	NA	Treated waste material (soil, organic liquid); solvent extract with concentrated TCDD
Stabilization/Fixation	Contaminated soil	Laboratory scale using cement and emulsified asphalt; lab tests also using K-20	Tests using cement showed decreased leaching of TCDD, but up to 27% loss of stabilized material due to weathering followed by leaching	NA	Stabilized matrix (soil plus cement, asphalt, or other stabilization material); matrix will still contain TCDD
UV Photolysis	Liquids, still bottoms, and soils can be treated if dioxin is first extracted or desorbed into liquid	Full scale solvent extraction/UV process was used to treat 4,300 gallons of still bottoms in 1980; thermal desorption/UV process currently undergoing second field test	Greater than 98.7% reduction of TCDD using solvent extraction/UV process—residuals contained ppm concentrations of TCDD; thermal desorption/UV process demonstrated reduction of TCDD in soil to below 1 ppb	Cost of treating the 4,300 gallons of still bottoms using solvent extraction/UV was \$1 million; thermal desorption/UV estimated to cost \$250–\$1,250/ton	Solvent extraction/UV process generated treated still bottoms, a solvent extract stream, and an aqueous salt stream; thermal desorption/UV generates a treated soil stream and a solvent extract stream
Chemical Dechlorination-APEG processes	Contaminated soil (other variations of the process used to treat PCB-contaminated soils)	Slurry process currently being field tested at pilot scale; in situ process has been tested in the field	Laboratory research has demonstrated reduction of 2,000 ppb TCDD to below 1 ppb for slurry (batch process); laboratory and field testing of in situ process not as promising	\$296/ton for in situ APEG process; \$91/ton for slurry (batch) process	Treated soil containing chloride salts (reagent is recovered in the slurry process)

**Table 3.** (continued)

Process name	Applicable waste streams	Stage of development	Performance/ destruction achieved	Cost	Residuals generated
Biological Degradation- primarily in situ addition of microbes	Research has been directed toward in situ treatment of contaminated soils-liquids are also possible	Currently laboratory scale-field testing in next year or two	50-60% metabolism of 2,3,7,8-TCDD in a week long period under lab conditions using white rot fungus-reduction to below 1 ppb not achieved	NA	Treated waste medium such as soil or water with TCDD metabolites depending on microorganisms
Chemical Degradation using Ruthenium Tetroxide	Liquid or soil wastes-possible most effective in decontaminating furniture, other surfaces	Laboratory scale-no work reported since 1983	Reduction of 70 ppb TCDD to below 10 ppb in 1 hr (on soil sample)	NA	Treated medium plus the solvent which has been added (water, CCl <sub>4</sub> ); TCDD end products not known
Chemical Degradation using Chloroiodides	Liquid or soil-thought to be most applicable to decontaminating furniture and buildings	Laboratory scale-no work reported since 1983	Up to 92% degradation on solution of TCDD in benzene-reductions to below 1 ppb were not demonstrated	NA	Treated waste medium; degradation end products are chlorophenols
Gamma Ray Radiolysis	Liquid waste streams (has been applied to sewage sludge disinfection)	Laboratory research; no research currently being conducted	97% destruction of 2,3,7,8-TCDD in ethanol after 30 hours-100 ppb to 3 ppb	Cost for sewage disinfection facility treating 4 tons per day is \$40 per ton; TCDD treatment would be more expensive	Less chlorinated dioxin molecules are the degradation end products in addition to the treated waste medium

\*Not available

peratures greater than 1000°C, thermal methods for treating these wastes have received a large amount of attention. Thermal technologies evaluated in this document are those in which heat is the major agent of treatment or destruction. Technologies included in this category are:

- Stationary rotary kiln incineration
- Mobile rotary kiln incineration
- Liquid injection incineration
- Fluidized-bed incineration
- Infrared incineration
- High temperature fluid wall destruction
- Plasma arc pyrolysis
- Molten salt destruction
- In-situ vitrification
- Supercritical water oxidation

EPA has indicated that incineration is currently the only sufficiently demonstrated treatment technology for dioxin-containing waste (51 FR 1733). RCRA performance standards for incineration and other thermal treatment processes require the demonstration of 99.9999 percent destruction and removal efficiency (DRE) of the principal organic hazardous constituent (POHC). Several of the thermal technologies have

demonstrated this performance on chlorinated compounds of one type or another. However, only three, and perhaps four, thermal technologies have been demonstrated to achieve this level of performance on dioxin. These technologies are the EPA mobile rotary kiln incinerator, Huber's high temperature fluid wall reactor, Shirco's infrared incinerator, and possibly, Modar's supercritical water oxidation process. Modar has not yet released data conclusively showing six nines DRE, but they do claim to have achieved this performance. Thermal technologies that have achieved six nines DRE on PCBs include stationary rotary kiln incinerators, liquid injection incinerators, fluidized-bed incinerators (the circulating bed variation), the plasma arc process, and the molten salt process. The in situ vitrification process has not shown six nines DRE; however, it is as much a stabilization process as it is a destruction process. Therefore, the primary objective of this technology is to prevent the leaching of dioxin or other toxic constituents from the treated soil; whether the dioxin is driven out of the soil by volatilization or merely contained

within the vitrified material is a secondary concern (as long as volatilized dioxin is captured and subsequently destroyed).

Nonthermal technologies evaluated include the following:

- Chemical dechlorination
- Ultraviolet (UV) photolysis
- Solvent extraction
- Biodegradation
- Stabilization/fixation
- Chemical degradation using ruthenium tetroxide
- Chemical degradation using chloroiodides
- Gamma ray radiolysis

Of the nonthermal technologies, those that have shown the most promise and the highest level of recent investigation and testing are chemical dechlorination and UV photolysis. Both of these technologies are currently being field tested on dioxin-contaminated soil. As indicated in Table 3, preliminary field data on the thermal desorption/UV photolysis process indicate that dioxin was desorbed from soil to a level below 1 ppb, and then destroyed efficiently using ultraviolet radiation. The chemical dechlorination process has also

demonstrated a reduction of TCDD in soil to below 1 ppb, but only on a laboratory scale.

The other nonthermal processes have not shown as much promise with regard to treating dioxin waste. Solvent extraction is a potentially useful technology since it could, if successfully applied to soil treatment, reduce the volume of the waste stream that requires final treatment/destruction by several orders of magnitude. Unfortunately, this technology has not yet demonstrated the ability to reduce dioxin in contaminated soil to a level of 1 ppb. Biodegradation is also a potentially attractive approach since it presumably would not require the large energy inputs, sophisticated equipment, and the chemical additions that the other technologies require. However, biodegradation, particularly in situ, has not proven to be very effective as a dioxin destruction process. Stabilization and/or fixation would allow the treatment of contaminated soils in place. Since this method does not involve destruction of the dioxin there is always the possibility that the stabilized waste/soil matrix will break down and the dioxin will be released. Finally, the last three technologies listed (two chemical degradation processes and gamma ray radiolysis) are methods that have been studied in the laboratory but have not yet shown enough promise technically or economically to be developed on a larger scale. Investigation of these methods, at this time, appears to have stopped.

Of all the treatment technologies evaluated none is currently commercially available for the treatment of

dioxin wastes. The EPA mobile incinerator has been used to treat a variety of waste forms at the Denney Farm in Missouri, but this unit is intended to be used for research purposes and not as a commercial treatment process. The high temperature fluid wall process (AER) operated by Huber at its Borger, Texas facility is permitted to perform research on dioxin contaminated wastes and is also a research tool which is not intended to be used for actual waste treatment.

### Conclusions

Dioxin wastes, particularly those dioxin-contaminated soils which account for over 98 percent of the contaminated wastes identified in Table 2, contain low levels (10 to 100 ppb) of dioxins and/or dibenzofurans. Nonetheless, many technologies, particularly the thermal destruction technologies, require that the total quantity of the waste be treated to destroy the extremely low dioxin fraction resulting in very high energy usage for dioxin destruction. In addition, when incineration and other thermal destruction technologies are used, large quantities of exhaust gases are generally formed. These waste streams can contain toxic products of incomplete combustion (PICs) and other hazardous emissions. They and other associated waste streams are themselves subject to costly treatment processes. Therefore, technologies such as solvent extraction or desorption, which separate the toxic constituents from the waste matrix prior to final treatment should receive further investigation.

Most of the emerging technologies are being designed for operation at the waste source. This trend to portable or field-erected technologies reflects a reaction to public opposition to the transport of dioxin waste from source to waste treatment facilities, and should continue to be encouraged.

In addition, because of the large volume of soil contaminated by relatively low concentrations of dioxin, it is also important to investigate methods of in-situ treatment. These methods would limit the handling of the waste so that further dispersion of contaminated materials into the environment is minimized. Most of the technologies in this category, such as biodegradation, in situ vitrification, chemical dechlorination, and stabilization in the near future have not yet been sufficiently demonstrated. Use in the near future seems improbable without more intense development of these technologies. Steps should be taken to encourage these developments.

The treatment of dioxin contaminated liquids and low viscosity sludges does not appear to be as large a problem as is the treatment of contaminated soils. This is primarily because the quantity of liquids and sludges is much lower, and also because the liquid waste form generally calls for less extensive handling and pretreatment. Technologies, such as plasma arc pyrolysis and supercritical water oxidation, appear to be capable of treating these wastes, and their development should be fostered, as should other reasonable activities aimed at the development of emerging technologies.

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*The complete report, entitled "Technical Resource Document: Treatment Technologies for Dioxin-Containing Wastes," (Order No. PB 87-110 813/AS; Cost: \$24.95, subject to change) will be available only from:*

*National Technical Information Service*

*5285 Port Royal Road*

*Springfield, VA 22161*

*Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:*

*Hazardous Waste Engineering Research Laboratory*

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