Chapter 3

Nonthermal Treatment Technologies

DECHLORINATION TECHNOLOGIES

The ultimate objective of all dechlorination methods is to destroy or detoxify hazardous chlorinated molecules through gradual, but progressive replacement of chlorine by other atoms (particularly hydrogen). The study and application of dechlorination dates back more than 70 years when it was first used in the commercial production of phenols. For the most part, chemical companies focused their efforts on searching for new reagents as well as for ways to reduce their dependence on dechlorination processes requiring high temperature and pressure. Only in the past decade did researchers begin to look at the potential applications of dechlorination technology to dioxin treatment.[1] One of the first U.S. Environmental Protection Agency (EPA) reports on the potential application of reagents for the destruction of polychlorinated biphenyls (PCBs) in soils was presented in 1983.[2]

Dechlorination processes are now designed to use glycols, alcohols, or water as their primary reagents. The degree of success of glycol- or alcohol-based methods in removing chlorinated compounds (e.g., PCBs, dioxins, and furans) from contaminated material at any given site varies among methods and among sites. The conditions that most commonly determine the efficacy of dechlorination methods employing glycols or alcohols (e.g., on contaminated soil) include:

- the organic carbon content of the soil,
- the size distribution of soil particles,
- the chemical forms (or isomers) of chlorinated compounds present in the soil,
- the soil moisture content,
- the temperature of the chemical reaction,
- the type of reagent formulation used, and
- the length of time during which contaminated soil is exposed to the reagents.

These factors, as well as the cleanup level required, also greatly affect total remediation costs.[3]

Unlike glycol- or alcohol-based methods, the water-based dechlorination treatment researched by EPA, called base-catalyzed decomposition (BCD), is not affected by the same factors. As an example, water is used in the BCD process to distribute reagents throughout the soil. This unique feature allows as little as 1 to 5 percent (wet weight) of reagent to be used to treat soil and eliminates the need to recover reagents for reuse.[4]

Early Dechlorination Methods

Early dechlorination techniques were used primarily for the destruction of PCBs and PCB-contaminated materials such as certain oily wastes. As a consequence, relatively little information exists on their potential to detoxify dioxins. The most relevant dechlorination processes in this group are those of the Goodyear Tire & Rubber Co., Acurex Corp., and Sun Ohio.

The Goodyear technique was designed primarily to dissociate PCB molecules from transformer fluids by using sodium naphthalene and sodium tetrahydrofuran. Although PCB concentrations up to 500 parts per million (ppm) could be reduced to 10 ppm in 1 hour of treatment, this practice was abandoned because of the presence of the primary pollutant naphthalene in treated residues. The effectiveness of the Goodyear system on dioxins is unknown.[5]

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[1] Kimberly A. Roy, "When Chemistry Is Right . . . A Fine-Tuned Dechlorination Process Destroys Dioxins, PCBs," *Hazmat World,* September 1990, p. 36; Robert L. Peterson and Stephen L. New, Galson Remediation Corp., "APEG-PLUS: Dechlorination of Dioxins, PCBs, and Pentachlorophenol in Soils and Sludges," undated paper, p. 1.

[2] C.J. Rogers, "Chemical Treatment of PCBs in the Environment" paper presented at the Eighth Annual Research Symposium, Cincinnati, OH, September 1983 (EPA-600/9-83-003), pp. 197-201.

[3] Paul E. des Rosiers, "Chemical Detoxification of Dioxin-Contaminated Wastes Using Potassium Polyethylene Glycolate," *Chemosphere, vol. 18, No. 1-6, 1989,* p. 351; and U.S. Environmental Protection Agency, Hazardous Waste Engineering Laboratory, ***Treatment Technologies for Dioxin-Containing Wastes,*** EPA/600/2-86/096 *(Cincinnati,* OH: October 1986), p. 5.12.

[4] Charles J. Rogers, Risk Reduction Engineering Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH, personal communication June 13, 1991.

[5] U.S. Environmental protection Agency, op. cit., footnote 3, pp. 5.2-5.3, 5.5.

The Acurex (Chemical Waste Management) technique involves mixing filtered PCB-contaminated oil with a sodium-based reagent in an inert nitrogen atmosphere to produce: 1) oil with no detectable PCBs, and 2) sodium hydroxide (NaOH) solution. This system, which is commercially available, is known to reduce dioxin levels in PCB 1 liquids ranging from 1,000 to 10,000 ppm to less than 1 ppm.[6]

Known as the PCBX process, the Sun Ohio (now ENSR, Canton, Ohio) process is a mobile, closed-loop system in which dewatered PCB-contaminated mineral/bulk oils are mixed with a reagent. After filtration, the end products include clean oil, PCBS, and salt residues that are solidified in a Toxic Substances Control Act (TSCA) PCB-permitted landfill. This process has been effective in reducing PCBs only in oils. Two to three passes through the closed-loop system are sufficient to reduce PCB concentrations from 3,500 to approximately 2 ppm. Treatment costs for the Sun Ohio PCBX process are estimated to be in the range of $3 per gallon of bulk oil[7]

Today, the methods developed by Acurex, Goodyear, and Sun Ohio are commercially available, but the reactivity of these primarily sodium-formulated reagents with water hampers their use on dioxin-contaminated soil, sediment, sludge, and dredging.[8] Although these dechlorination methods are marketed for a variety of uses, treatment of dioxin-contaminated soil is not one of them.

Recent Dechlorination Methods

Alkaline Polyethylene GIycolate (APEG or KPEG)[9]

In 1978, Franklin Research Institute began an attempt to identify a chemical reagent that would break down carbon-halogen bonds in the PCB molecule. Of the dehalogenation formulations tested, the most successful was composed of 60 grams of molten sodium and 1 liter of polyethylene glycol (PEG) with a molecular weight of about 400.[10][11] The effect of the PEG-based formulation on dioxin-contaminated soil was also studied by the EPA Risk Reduction Engineering Laboratory (RREL), Cincinnati, Ohio, and Wright State University, “Dayton, Ohio, in 1982.

Testing and Availability of APEG Treatment—In ***1985,*** under the auspices of EPA, the Galson Remediation Corp. (East Syracuse, New York) tested and compared two dechlorination reagent[12] on soil and slurry containing a dioxin isomer[13] at concentrations as high as 2,000 parts per billion (ppb). At the conclusion of the study, the PEG-based formulation (known as APEG) was found to reduce the dioxin level to less than 1 ppb in about 12 hours. Later that same year, EPA tested the APEG process on dioxin-contaminated soil at the Shenandoah Stables, Moscow Mills, Missouri, and learned that the moisture content of the soil tested (18 to 21 percent water) significantly reduced APEG’s effectiveness.[14] In light of these results, in 1986 EPA concluded that although APEG was highly efficient under laboratory conditions, more work was required in the field.[15]

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[6] Ibid., p. 5.5.

[7] Ibid., pp. s.3, 5.5, 5.12.

[8] Alfred Kornel, Charles J. Rogers, and Harold L. Sparks, ‘‘KPEG Application From the Laboratory to Guam, ’’ in U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, *Third International Conference on New Frontiers of Hazardous Waste Management,* EPA/600/9.89/072 (Cincinnati, OH: August 1989), p. 461.

[9] Throughout this section, APEG and KPEG are used interchangeable> because both processes employ a polyethylene glycol/potassium hydroxide solution to remove chlorine atoms from the dioxin molecule APEG is offered by Galson Remediation Corp., Syracuse, NY (patent covers dimethyl sulfoxide cosolvent/catalyst) and KPEG by remediation companies such as Canonie Environmental, Inc., in Colorado.

[10] A similar process using heavier PEGs (molecular weight between 1,500 and 6,000) in combination with a weak base (potassium carbonate) or an inorganic peroxide (sodium peroxide) ‘‘to form a clear solution’’ has been tested at bench scale in Europe for the destruction of dioxins such as those found at Seveso, Italy. However, this process, although investigated has never been used

[11] U.S. Environmental Protection Agency, Op cit., footnote 3, p 5.4

[12] The reagents tested were potassium hydroxide/polyethylene glycol 400/dimethyl sulfoxide (KOH/PEG/DMSO), and potassium hydroxide/2-(2-methoxyethoxy)ethanol/dimethyl sulfoxide

[13] 1,2,3,4-tetrachlorodibenzo-*p*-dioxin

[14] U.S. Environmental Protection Agency, Op cit., footnote 3, p 5.9

[15] Ibid., p. 5.12.

APEG and KPEG processes are extremely hygroscopic, and exposure to water readily deactivates the PEG-based reagent formulation.[16] EPA, in response to poor results obtained from tests on in situ treatment of soil in U.S. EPA Region II (Glenn Falls, New York; South Buffalo, New York) and Region VII (Moscow Mills, Missouri), has concluded that in situ chemical treatment of soil with APEG is not a viable option.[17]

Costs Estimates for APEG or KPEG Treatment— According to hypothetical scenarios developed by Galson Remediation Corp. and EPA's RREL, the costs incurred from APEG treatment are as follows: For in situ treatment, the cost is nearly $300 per ton of soil treated, with about two-thirds of this resulting from the purchase of reagents; setup and operational activities would be responsible for only about 22 percent of the total.

For slurry or batch treatment, theoretical calculations showed that costs could be about $91 per ton of soil treated. Of this total, 22 percent is for reagent purchase and 59 percent for setup and operation. Compared to in situ treatment, the slurry process was three times less costly due to the ability of the system to recycle the reagents used in treatment.[18]

More recently, actual costs of using dechlorination (KPEG process) have been reported by Canonie Environmental. According to a company official, the cost for treating 1 ton of PCB-contaminated soil at the Wide Beach, New York, site, is about $265. For dioxin-containing soil, costs are expected to range between $250 and $350 per ton.[19]

APEG-PLUS Treatment Process

From 1981 to 1986, Galson Remediation Corp. (GRC) conducted laboratory- and pilot-scale studies on its APEG process. These efforts were later implemented by the construction of a mobile treatment unit by Niagara-Mohawk Power Co. (then under contract with GRC) to provide the first full-scale application of GRC treatment. Until that time, application of the APEG process had been limited primarily to oil contaminated with chlorinated hydrocarbons; the new treatment facility made soil treatment possible.[20] This GRC dechlorination process for treating soil (shown in figure 3-1) is now patented in the United States, Canada, and Europe and is known as APEG-PLUS.[21]

APEG-PLUS detoxifies materials contaminated with dioxins, PCBs, pesticides, and other chlorinated hydrocarbons. The patented APEG-PLUS process consists of potassium hydroxide (KOH) in a mixture of polyethylene glycol and dimethyl sulfoxide (DMSO). According to company officials, the PEG-DMSO mixture is not toxic.[22]

Once the unit has been assembled, excavated soil or sludge is conveyed to a mixer, where it is combined with reagents to form a slurry. When proper mixing has been achieved and chlorinated organic compounds (PCBs, dioxins, furans) are extracted from the soil particles and incorporated into the mixture, the slurry is pumped into the reactor vessel and heated to 150 'C. During the reaction, chlorine atoms attached to the dioxin molecule are replaced by PEG to form a water-soluble substance (glycol ether) that can be degraded easily into nontoxic materials or washed from the soil.[23] [24]

After chemical analysis performed in the mobile laboratory unit indicates that the required treatment level has been reached, the slurry is sent to a centrifuge. The spinning motion of the centrifuge separates the reagent from treated soil. The soil is water-washed for decontamination and removed for redisposal on land. The wash water is passed through

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[16] Ibid., p. 5.9.

[17] Rogers, op. cit., footnote 4.

[18] U.S. Environmental protection Agency, op. cit., footnote 3, Pp. 5.12-5.13.

[19] Alister Montgomery, Canonie Environmental, Inc., personal communication, Mar. 20* 1991.

[20] Robert L. Peterson and Stephen L. New, op. cit., footnote 1, p. 2; Roy, op. cit., footnote 1, p. 38; and Brief review of APEG-PLUS by McLaren Associates for Syntex Corp., submitted to Missouri Department of Natural Resources, Oct. 10, 1990, p. 5.

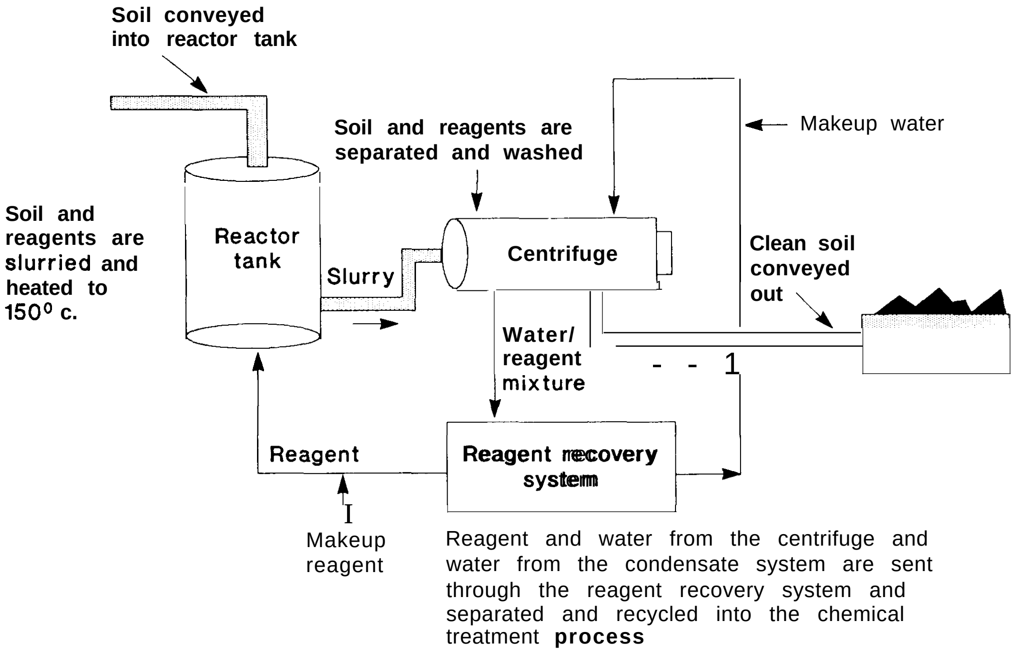
[21] Roy, op. cit., footnote 1, pp. 36-37.

[22] Galson Remediation Corp., ''GRC's APEG-PLUS: Dechlorination for the '90s," fact sheet, January 1991; Peterson and New, op. cit., footnote 1, p. 5.

[23] The high water solubility of this larger, stable glycol ether molecule facilitates its flushing from soil after treatment with PEG-PLUS. (Source: Brief review of APEG-PLUS, op. cit., footnote 20.)

[24] Robert L. Peterson and Stephen L. New, "Dioxin Destruction with APEG-PLUS Chemical Dechlorination" Galson Remediation Corp., paper undated; Peterson and New, op. cit., footnote 1, pp. 3-4.

Figure 3-1—Galson Remediation Corp.'s APEG-PLUS Chemical Treatment System



SOURCE: Galson Remediation Corp., "Galson's APEG-PLUS Treatment System-Equipment and Job Description," 1990.

a bed of activated carbon to remove dechlorinated products; the contaminated carbon is then treated. The collected reagent and wash water are sent to the reagent recovery system for recycling (soils with high clay content are known to consume reagents in significant quantities). This process may take 30 to 120 minutes.[25]

Dechlorination of oversized materials is generally accomplished by washing the soil particles and treating the washed soil. However, if the materials have concrete surfaces, they must be crushed and treated with the soil because concrete is known to absorb solvents that contain dioxins. The type and size of equipment needed to wash and crush such materials generally depend on specific site conditions.[26]

Testing and Availability of APEG-PLUS Process—The most complete demonstration of APEG-PLUS (on a pilot scale) was sponsored by EPA as part of the cleanup activities conducted at the PCB-contaminated site in Wide Beach, New York. Test results indicated that cleanup levels could be met; the pilot-scale test also showed that reagents could be recycled up to seven times without noticeable reduction in the ability of the treatment to meet the required cleanup level. Results of this and other tests have shown that dioxins are most susceptible to APEG-PLUS, followed by PCBs and pentachlorophenol (PCP).

Concerned about the toxicity of dechlorination byproducts from treated dioxin-contaminated soil, the EPA Risk Reduction Engineering Laboratory (Cincinnati, Ohio), asked scientists at the Health Effects Research Laboratory (HERL) in North Carolina to evaluate whether its residues or byproducts were toxic or mutagenic .27 At the end of the test, HERL concluded that:

- the alkaline polyethylene glycol mixture was neither toxic nor mutagenic to ***Salmonella strains*** studied,
- dechlorination byproducts resulting from the treatment of 2,3,7,8-tetrachlorodibenzo-p-

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[25] Peterson and New, op. cit., footnote 1, p. 8.; Kimberly A. Roy, op. cit., footnote 1.

[26] Galson Remediation Corp., "Galson's APEG-PLUS Treatment System: Equipment and Job Description," undated, p. 2.

[27] David M. DeMarini and Jane E. Simmons, "Toxicological Evaluation of By-Products From Chemically Dechlorinated 2,3,7,8 -TCDD," *Chemosphere*, vol. 18, No. 11-12, 1989, pp. 2293-2294.

dioxin (TCDD) were toxic but not mutagenic to guinea pigs, and
- no deaths occurred from exposure of guinea pigs to dechlorination residues.

Studies on fish (carp) led to similar conclusions. No effects on liver tissue and thymus gland were detected.[28] HERL stated at the end of the report that . . . the present study provides evidence for the efficacy and relative safety of KPEG for dechlorinating TCDD and helps to put KPEG in context with other clean-up technologies. ”[29] Other tests conducted by EPA at Research Triangle Park, North Carolina and Duluth, Minnesota on samples containing dechlorinated waste from the Butte, Missouri and Western Processing, Washington sites showed no toxic effects (including bioaccumulation, cell mutation, acute toxicity) from exposure to byproducts.[30]

APEG-PLUS technology has been applied at several contaminated sites in the United States. Some of these are:

- Montana Pole, Butte, Montana—This 20-acre site, formerly a wood-treating facility, is located in an abandoned mining site in which soil and groundwater were contaminated with dioxins and furans. In January 1986, research was conducted to determine if APEG-PLUS dechlorination could be used to treat nearly 9,000 gallons of dioxin- and furan-containing petroleum oil collected from groundwater over a 2-year period. The oil was estimated to contain 3.5 percent PCPs; dioxin and furan concentrations ranged from 422 to 83,923 ppb. Because of the success achieved, particularly with respect to the presence of dioxins and furans in the waste, EPA selected APEG-PLUS technology for treatment of the remaining 9,000 gallons of contaminated oil at the site. Complete decontamination was achieved in July 1986. Neither dioxin nor furan derivatives were detected in treated oils at limits of detection (part-per-trillion level).[31]
- Western Processing Site, Kent, Washington—The Western Processing site was remediated almost completely in 1984; the only remaining task involved treating more than 7,500 gallons of spent solvents contained in a storage tank. These materials were known to be contaminated with dioxins[32] at levels of about 120 ppb. Treatment with dechlorination was accomplished in September 1986, by using the reactor employed earlier at the Montana Pole, Montana site. No dioxin was found in the treated solvents at the detection limit of 0.3 ppb.[33]
- Signo Trading Site, New York—Remediation at the Signo Trading site involved dechlorination of about 7 gallons of dioxin-contaminated liquid waste retrieved from the Signo warehouse in Mount Vernon, New York. The liquid was treated in a 40-gallon drum for 50 minutes. No dioxin was found in the treated oil at a detection limit of 0.3 ppb; as a consequence, EPA's Dioxin Disposal Advisory Group declared the treated waste dioxin-flee and no longer subject to the Resource Conservation and Recovery Act (RCRA) dioxin-listing rule.[34]
- Wide Beach, New York—The Wide Beach site is a 55-acre residential community located in the Town of Brant, about 30 miles south of Buffalo, on the shores of Lake Erie. In 1980, State officials estimated that this site contained 30,000 to 40,000 cubic yards of PCB-contaminated soil resulting from the application of dust suppressants between 1968 and 1978. PCB levels, primarily Aroclor 1254, ranged from 10 to 1,000 ppm. In 1985, despite the fact that a large-scale dechlorination system was not commercially available, EPA selected

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[28] Ibid., pp. 2296-2297; Thomas O. Tiernan, “Treatment of Chemical and Contaminated Soils Containing Halogenated Compounds and Various Metals With Potassium-Polyethylene Glycol Reagent,” *Proceedings of the Oak Ridge Model Conference,* Oct. 13-16, 1987, Oak Ridge, TN, p. 126; David DeMarini, U.S. EPA, Health Effects Research Laboratory, personal Communication Jan. 9, 1991.

[29] DeMarini and Simmons, op. cit., footnote 27, p. 2299.

[30] Harmut S. Fuhr and J. Paul E. des Rosiers, “Methods of Degradation Destruction, Detoxification, and Disposal of Dioxins and Related Compounds,” *Pilot Study on International Information Exchange and Related Compounds (North* Atlantic Treaty Organization Committee on the Challenges of Modem Society, Report No. 174, August 1988), pp. 5-6.

[31] Kornel, Rogers, Sparks, op. cit., footnote 8, p. 462; Tiernan, op. cit., footnote 28, p, 114.

[32] Primarily 2,3,7,8-TCDD.

[33] des Rosiers, op. cit., footnote 3, pp. 343-345.

[34] Memorandum from Paul des Rosiers, Chairman, Dioxin Disposal Advisory Group, to Charles E. Fitzsimmons, On-Scene Coordinator, EPA Region II, Edison, NJ.

dechlorination (KPEG) as the specified technology for treating soil containing PCBs at concentrations higher than 10 ppm. From October 1990 to October 1991, the 200-ton-per-day unit located at the Wide Beach Superfund site successfully treated more than 42,000 tons of contaminated soil; equipment removal is now taking place.[35]

- U.S. Navy Base, Guam—The Guam site corresponds to a l/4-mile-long storm drainage ditch contaminated with PCBs from transformer repair operations and past hazardous waste disposal practices at the U.S. Naval Public Works Center. Remediation of the site is required by both CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) and RCRA.[36] Results of characterization studies estimate that PCBs (primarily Aroclor 1260) are present at levels ranging from 0 to 6,500 ppm; the total volume of soil contaminated with 25 ppm or more of PCBs is estimated to be 4,000 cubic yards (5,500 tons) .37 APEG[38] treatment of soil during two separate pilot-scale studies in 1988 showed PCB destruction efficiencies greater than 99.9 percent. Larger field-scale testing is under way at the site.[39]

In the past, critics have claimed that the APEG-PLUS process was too time-consuming and costly to treat certain soils. Reaction time does not seem to be a problem now, but APEG-PLUS's limited record on dioxin-contaminated soil, coupled with the risk that its liquid byproducts may require incineration—thus making it less cost-effective—may still be significant factors to consider.

In addition to the full-scale mobile treatment unit currently available, which is capable of treating 40 tons of contaminated soil daily, GRC officials expect to offer a 100-gallon reactor pilot unit soon. The construction of several truck-mounted units and of a "treatment train" that would include bioremediation, solidification, and metal extraction procedures is also planned.[40]

According to company officials, given 24-hour-a-day operation, 7 days a week, for 260 days a year, the cleanup of nearly 100,000 cubic yards of dioxin-contaminated soil (at a site such as Times Beach) could be accomplished in about **2-1/2 years** by using GRC's 200-ton-per-day facility.

Although APEG-PLUS has been tested at a number of sites, some public officials continue to view it as a highly experimental technology .41

Cost Estimates for APEG-PLUS Process—For PCB-contaminated soil, APEG-PLUS processing costs have ranged between $100 and $800 per ton, depending on factors such as the nature and volume of soil treated, characteristics of the site, and cleanup levels required. At the U.S. Naval Public Works Center in Guam, for example, the cost of dechlorinating PCB-contaminated soil with APEG-PLUS was anticipated to be about $270 per ton.[42]

The above figures, however, do not include the costs incurred by: 1) performance of treatability studies prior to actual treatment (about $25,000 to $30,000 for an average site), 2) excavation and handling of soil, and 3) final disposal of waste (RCRA incinerator or onsite if delisted).[43] Remediation costs can be further affected by the price of electricity, the cost of fuels and chemicals, the

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[35] Brief review of APEG-PLUS prepared by McLaren Associates for Syntex Corp., and submitted to Missouri Department of Natural Resources on Oct. 10, 1990, p. 5; Michael Andurer and Chofran Tsang, "Bench and Pilot Testing of the KPEG Process on PCB-Contaminated Soils," EBASCO Services, Inc., Oct. 10, 1990, pp. 1,2, 5; and Alister Montgomery, Canonie Environmental, personal communication, Mar. 20 and Oct. 31, 1991.

[36] Naval Civil Engineering Laboratory, Engineering Evaluation/Cost Analysis @E/CA) for the Removal and Treatment of PCB-Contaminated Soils at Building 3009 Site, Naval Civil Engineering Laboratory, Port Hueneme, CA, July 3, 1990, pp. 1-2.

[37] Ibid., p. 3.

[38] This reagent, developed in EPA's RREL, is composed only of polyethylene glycol and potassium hydroxide.

[39] Kornel, Rogers, and Sparks, op. cit.,footnote 8, PP. 462-464.

[40] Galson Remediation Corp., op. cit., footnote 22.

[41] Memorandum from David A. Shorr, Director, Division of Environmental Quality, to G. Tracy Mehan, III, Director, Missouri Department of Natural Resources, July 3, 1990, p. 3; Paul E. des Rosiers, Chairman, Dioxin Disposal Advisory Group, U.S. Environmental Protection Agency, personal communication, June 10, 1991.

[42] Naval Civil Engineering Laboratory, op. cit., footnote 36.

[43] Brief review of APEG-PLUS, op. cit., footnote 20.

efficiency of the centrifuge stage, and off-site transportation if required.[44]

For dioxin-contaminated sites, the costs incurred by APEG-PLUS treatment are expected to be higher than those for PCBs due to the more stringent cleanup level required. According to a public official, the cost of using APEG-PLUS at Times Beach, Missouri “will be about the same as thermal destruction.’ ’[45]

Base-Catalyzed Decomposition Process (Free-Radical Dehalogenation)

The base-catalyzed decomposition (BCD) process[46] developed by RREL in Cincinnati, Ohio, was initiated in 1989 after pilot-scale testing of APEG had been completed on Guam.[47] The BCD process was developed to eliminate processing problems experienced during the Guam field test of APEG.

Unlike APEG, the BCD process:

- reduces the processing requirements of soil (size reduction to 0.5 inch or less);
- employs lower-cost bases such as sodium bicarbonate or sodium hydroxide instead of the more costly potassium hydroxide;
- eliminates the need to use costly polyethylene glycol as a reagent component;
- treats soil or other matrices in minutes rather than hours;
- employs reagents in concentrations as low as 1 to 5 percent by weight of the matrix to be treated;
- eliminates the need to recover and recycle reagents;
- achieves complete dechlorination of pollutants in contaminated matrices; and
- reduces the volume of waste for disposal.

BCD processes employ hydrogen from hydrogen donor compounds[48] to effect the removal of halogens or chlorine from halogenated compounds. This is accomplished by treating the contaminated matrices in the presence of a hydrogen donor and base at higher temperature (250 to 350 ‘C) than in the APEG-PLUS method (150 to 180 ‘C).

Once heated to temperature in the presence of a base, the organically bound hydrogen is released as a nucleophile, to combine with and remove chlorine from chlorinated compounds (hydrogenation).

Testing and Availability of BCD Process—In treatability tests, the BCD process has been demonstrated on a laboratory scale to destroy PCBs (3,000 ppm) in soil to less than 0.4 ppm within 2 hours. Also, in recent treatability tests on the phenoxy herbicides 2,4-D-[49], 2,4,5-T-[50], Silvex-, and dioxin-contaminated soil from the Jacksonville and Rogers Landfills in Jacksonville, Arkansas, BCD destroyed the herbicides and reduced dioxins to the part-per-trillion (ppt) level.[51]

Currently, the EPA Region VII has approximately 25,000 gallons of herbicides (42 percent), 2,4,D-, and 2,4,5-T contaminated with up to 4,000 ppb of TCDD for disposal. In treatability tests, BCD has achieved complete destruction of the 42-percent herbicide and reduction of TCDD to an average of 100 ppt. Although the BCD process was developed to reduce chlorinated organics in contaminated matrices to ppm concentrations, it has also been demonstrated to destroy chlorinated organics at a concentration of 42 percent. Tests are going on to examine the use of BCD to treat 70,000 gallons of PCBs in transformer oil (60 percent) on a U.S. Department of Energy (DOE) site, as well as the 25,000 gallons of herbicide and 1.3 million pounds of 2,4-D/2,4,5-T vermiculite formulation contaminated with TCDD in EPA Region VII. Test results confirmed that BCD is a candidate technology for the cleanup of halo-carbon-contaminated liquids

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[44] Memorandum from Shorr, op. cit., footnote41, pp. 1-2; Galson Remediation Corp., op. cit., footnote 26,p. 3; Roy, op. cit., footnote 1, P. 38; and des Rosiers, op. cit., footnote 3, p. 343.

[45] Memorandum from Shorr, op. Cit., footnote 41, p. 2.

[46] C.J. Rogers, Alfred Kornel, and Harold Sparks, *Method for Destruction of Halogenared Compounds in Contaminated Medium*, patentNo. 5,019,175; May 1991.

[47] Naval Civil Engineering Laboratory, op. cit., footnote 36, p. 9; and Charles Rogers, U.S. EPA, Risk Reduction Engineering Laboratory, personal communication Dee. 17, 1990, Apr. 1, 1991, and Oct. 28, 1991.

[48] Charles J. Rogers et al., “Base Catalyzed Decomposition of Toxic and Hazardous Chemicals,” paper presented at the HazPac ’91 Conference, cairns, Australia, Apr. 17, 1991; U.S. EPA pending patent No. 07/515,892, April 1990.

[49] 2,4-dichlorophenoxyacetic acid.

[50] 2,4,5-trichlorophenoxyacetic acid.

[51] Rogers et al., op. Cit., footnote 48.

and soils in an environmentally acceptable manner (closed system).

BCD treatment has been selected over both incineration and APEG-PLUS as the preferred technology for cleanup of the U.S. Navy's PCB-contaminated sites. The first BCD process (1 ton per hour) has been constructed and is being used to treat approximately 90 tons of PCB-contaminated soil on a U.S. Navy site in Stockton, CA. The process will then be transported to Guam to treat an additional 5,550 tons of PCB-contaminated soil, starting in December 1991.[52]

Cost Estimates for BCD Process—The limited field application of this promising technology is the primary reason for the current lack of cost estimates for BCD treatment of dioxin-contaminated soil. However, the BCD process theoretically could achieve significant cost reductions over APEG-PLUS because of the much lower cost of the reagents required. Regarding the application of the BCD process to dioxin-contaminated soil, theoretical calculations by EPA suggest that the estimated projected cost would be about $245 per ton.[53]

Thermal Gas-Phase Reductive Dechlorination[54]

Thermal technologies make use of heat as the major agent in the destruction of waste. Typical glycol- and alcohol-based dechlorination processes detoxify hazardous waste through a progressive replacement of chlorine atoms by other atoms, notably hydrogen. One new process has incorporated the best of both of these existing methodologies to develop a patented thermochemical reduction technology. This new process could be suitable for a variety of matrices, particularly waste that is primarily aqueous in nature, such as harbor sediment, landfill leachate, lagoon sludge, and potentially soil.

For the past several years, ELI-Eco Logic International, Inc. (Rockport, Ontario and Ann Arbor, Michigan) has been conducting research on a bench scale, a laboratory scale, and a mobile pilot-scale field unit for the destruction of toxic waste. Several criteria have been used in developing the process technology, including maximization of destruction efficiency, absence of dioxin or furan formation, continuous process monitoring, process control suitability, suitability for aqueous waste, mobility as opposed to transportability, and reasonable waste processing costs.

Thermal gas-phase reductive dechlorination is based on the gas-phase thermochemical reaction of hydrogen with organic matter and chlorinated organic compounds at elevated temperature. At or above 850 °C, hydrogen reacts with organic compounds reductively to produce smaller, lighter hydrocarbons. For chlorinated organic compounds such as dioxins and PCBs, the reaction products include hydrogen chloride, methane, and ethylene. The reaction is enhanced by the presence of water, which also acts as a reducing agent. Bench-scale and laboratory-scale testing with compounds such as trichlorobenzene and chlorinated phenols have yielded destruction efficiencies in a range of 99.999 to 100.000 percent.

The Eco Logic process is not an incineration technology. Combustion and incineration processes destroy chlorinated organic waste by breaking down contaminant molecules at high temperature and then combining them with oxygen, usually from the atmosphere. The Eco Logic process uses hydrogen to produce a reducing atmosphere devoid of free oxygen and thus eliminates the possibility of dioxin or dibenzofuran formation.

Other nonchlorinated hazardous organic contaminants (e.g., polycyclic aromatic hydrocarbons (PAHs)), are also reduced to smaller, lighter hydrocarbons, primarily methane and ethylene. Because of the tendency of the reaction to produce lighter, more volatile gases, the process lends itself to continuous monitoring of the destruction efficiency. Incorporated into the Eco Logic technology is an online chemical ionization mass spectrometer, capable of measuring up to 36 toxic organic compounds every

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[52] Charles Rogers, U.S. EPA, op. cit., footnote 47; Department of the Navy, Naval Civil Engineering Laboratory, ***Chemical Dehalogenation Treatment: Based-Catalyzed Decomposition Process (BCDP)***, Technical Data Sheet (Port Hueneme, CA: Department of the Navy, August 1991).

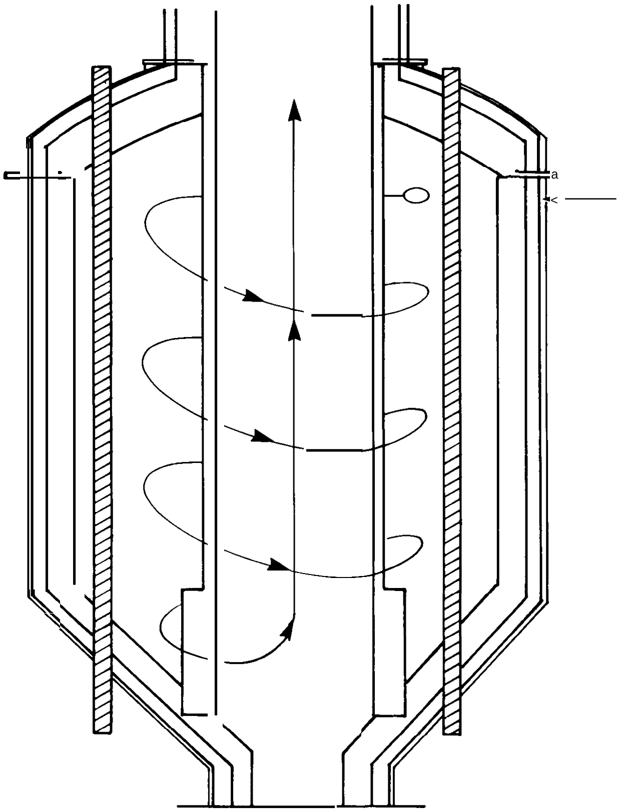
[53] Rogers, op. cit., footnote 47; and Department of the Navy, op. cit., footnote 52.

[54] D.J. Hallett, K.R. Campbell, and W.R. Swain, "Thermal Gas-Phase Reduction of Organic Hazardous Wastes in Aqueous Matrices," ***EPA Abstract Proceedings: Second Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International***, Philadelphia, PA, May 15-17,1990, EPA/500/2-09/009 (U.S. Environmental Protection Agency, 1990); D.J. Hallett and K.R. Campbell, "Demonstration Testing of a Thermal Gas Phase Reduction Process,' ***Proceedings of the Third Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International***, June 11-13, 1991, Dallas, TX (U.S. Environmental Protection Agency, in press); Wayland R Swain, Vice President, Eco Logic International, Inc., personal communication July 3, 1991 and Oct. 20, 1991; Paul W. Rodgers, Vice President, Limno Tech, Inc., personal communication, May 29, 1991.

0.1 second. Data from the mass spectrometer can be directed to the process controller so that any increase in undesirable organic compounds either alters the rate of waste or reaction gas input or, in the extreme case, halts the input of waste and alerts the operator that the system has been shut down.

Figure 3-2 is a schematic of the reactor vessel designed to accommodate thermochemical reduction. A mixture of preheated waste and hydrogen is injected through nozzles mounted tangentially near the top of the reactor. The mixture swirls around a central ceramic tube past glo-bar heaters, which heat the waste to 850 ‘C by the time it exits the ports at the bottom of the ceramic tube. Particulate matter up to 5 mm in diameter not entrained in the gas stream impacts the hot refractory walls of the vessel, thereby volatilizing any organic matter associated with the particulate. Larger particulate exit from the reactor bottom into a quench tank. Finer particulate entrained in the gas stream flow up the ceramic tube and through the retention zone. The reduction reaction takes place within the ceramic tube and requires less than 1 second to come to completion.

Figure 3-2—Reactor Used for Thermochemical Treatment in Eco Logic Process



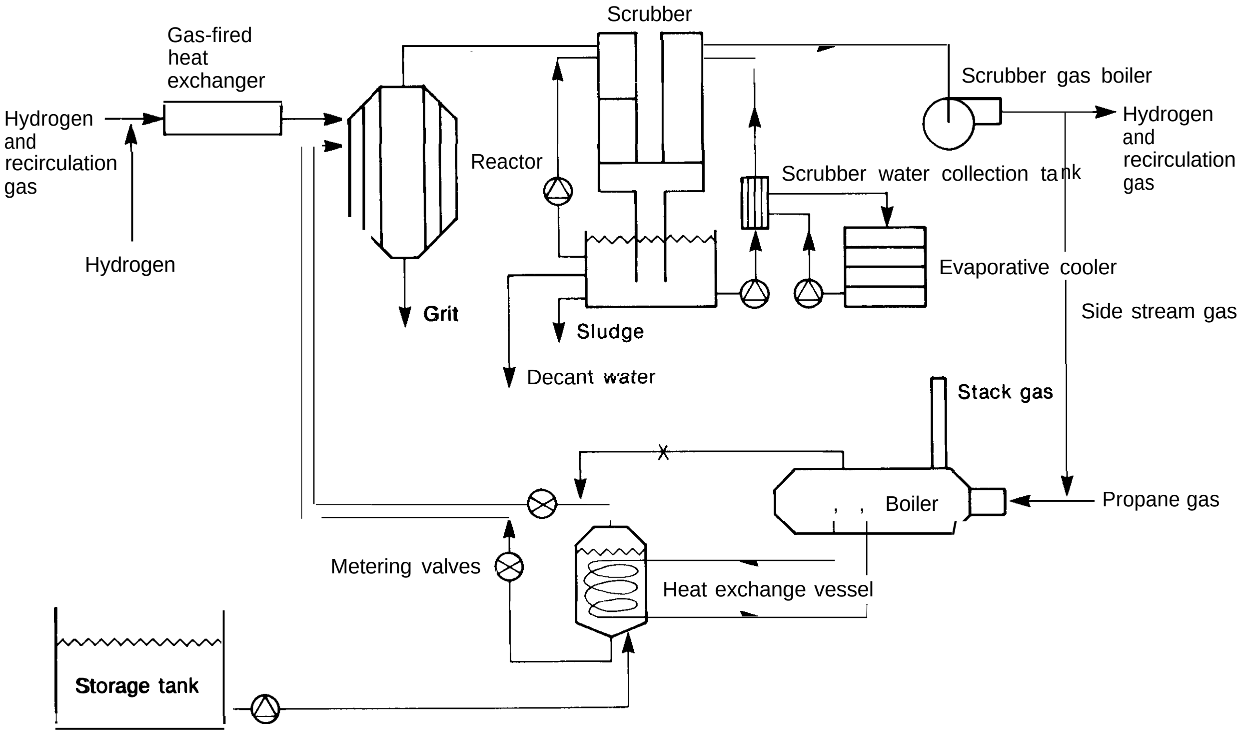
SOURCE: ELI-Eco Logic International, Inc., Ann Arbor, MI, 1991.

Figure 3-3 presents a complete process schematic of the field demonstration unit. In this unit, waste liquid and suspended solids are pumped from a small storage tank to a heat exchanger vessel for preheating to 150^{0}C by a small boiler. The hot liquid and steam from the watery waste are metered continuously by use of special metering valves and are injected into the reactor by use of atomizing nozzles. A mixture of hydrogen and recirculation gas also enters the reactor near the top after passage through a gas-fired heat exchanger. Heavy particulate exit as grit from the bottom to a quench tank. Fine particulate matter passes up the ceramic tube (shown in figure 3-2) where gas-phase reduction takes place. Additional residence time is provided by the retention zone elbow and extension pipe. On exiting the reaction zone, gases enter the scrubber where they are quenched by direct injection of scrubber water spray. Hydrogen chloride and fine particulate matter are removed by contact with scrubber water as the gases pass through carbon steel scrubber media on the down leg and polypropylene on the scrubber up leg. Scrubber water is collected in a tank by means of a large water-sealed vent, which also acts as an emergency pressure relief duct. Scrubber water is cooled to 35 ^{0}C by using a heat exchanger fed by cooling water from an evaporative cooler. Sludge and decant water represent the two effluent streams from the scrubber. Both of these effluents are held in tanks for batch analysis prior to disposal.

Gases that exit the scrubber consist of excess hydrogen, reduction products (e.g., methane and ethylene), and a small amount of water vapor. Approximately 95 percent of this gas is recirculated to the reactor after being reheated to 500 ‘C. The remaining 5 percent of the hydrocarbon-rich gas is used as supplementary fuel for the boiler. The boiler uses propane gas as its main fuel to produce steam for use in the heat exchanger. The only air emissions are from the boiler in the form of stack gas. Because the fuel going into the boiler is very clean (i.e., no chlorine content), emissions from the boiler to the air are insignificant.

In the event of a process upset in which total destruction of hazardous organic compounds is incomplete, the online mass spectrometer automatically diverts all gases into the recirculation mode. No sidestream gas is sent to the boiler, and the waste

Figure 3-3-Schematic Flow Diagram of the Thermal Gas-Phase Reductive Dechlorination Process



SOURCE: ELI-Eco Logic International, Inc., Ann Arbor, MI, 1991.

feed is stopped. Recirculation continues until analysis indicates that the reaction is again occurring optimally. Because 95 percent of the gas stream is recirculated under normal conditions, this procedure does not represent a drastic action.

The entire Eco Logic technology is contained on two 45-foot drop-deck flatbed trailers and thus is mobile. An additional trailer, housing the online mass spectrometer, the process control unit, and other analytical equipment, completes the array of equipment necessary for waste destruction. Onsite, the space required for processing waste is little more than the size of the three trailers. Setup time for this system is a matter of a few days, and the minimum run with this device may be less than a single unit's daily capacity. On the other end of the spectrum, the continuous throughput process is well suited to high-volume, long-run waste destruction. Throughput capacity can be varied at will by attaching additional reactor units to a single ancillary support and control system, thereby allowing flexibility of operation and redundancy of design.

Some of the largest and most serious contaminant remediation requirements involve soil and sediment having high water content. Incineration technologies consume very large amounts of energy to heat up the water component to combustion temperature. Additionally, because these technologies utilize air (79 percent nitrogen) for combustion and must combust all the organic matter, they often require 10 times the volume of the Eco Logic process for the same residence time of reaction. Other dechlorination technologies (e.g., APEG, KPEG, APEG-PLUS) are much less efficient in treating water-bearing waste because of consumption of the reagent by water, and a potential for explosive reaction exists. By contrast, in dealing with soil and sediment having a high water content, the Eco Logic process employs typical sediment/water mixtures in a range of 30 to 50 percent as optimal for this unit. Treatment material containing less than 30 percent solids is possible, but the economy of the destruction process begins to diminish below this level.

Testing and Availability of Thermal Gas-Phase Reductive Dechlorination Process—At the time of preparation of this paper, the Eco Logic technology has been successfully tested by the Canadian Federal Government and the government of the Province of Ontario in a site demonstration in Hamilton, Ontario, Canada. The site demonstration began on April 8, 1991 and took about 4 months to complete. The demonstration consisted of the destruction of contaminated sediments (not dioxin) from Hamilton Harbor in Lake Ontario under the auspices and supervision of Environment Canada's Contaminated Sediments Treatment Program and the Province of Ontario's Technologies Program. Preliminary results show thermal gas-phase reductive dechlorination to be highly effective in the treatment and volume reduction of contaminated harbor sediments.

A single full-scale reactor vessel has been designed to process 12 kilograms (26 pounds) of waste per minute under normal operating conditions. This throughput is, of course, dependent on the nature of the contaminant of concern, its degree of chlorination, and its water content. The range of throughput values lies between 15 and 20 tons per day. Present design planning calls for the construction of a 50-ton-per-day unit in early 1992. Because it is possible to use multiples of the reactor vessels with a single process control entity, treatment capacity can be increased easily. With the present configuration, as many as three reactors may be grouped per control unit, enabling 45 to 60 tons of waste to be treated daily. A new design would handle up to 150 tons per day.

Cost Estimates for Thermal Gas-Phase Reductive Dechlorination Process—The combination of equipment requirements and process characteristics suggests a relatively lower capital cost for the Eco Logic system compared to incineration. Operating economies to treat water-bearing waste are expected to be three to five times lower than incineration technologies of comparable capacities. Cost estimates for the destruction of waste are a function of both the chlorine content of the contaminant of concern and its concentration in the environmental matrix. For sedimentary materials containing resistant chlorine compounds (e.g., PCBs, polychlorinated dibenzofurans (PCDFs), and polychlorinated dibenzo-p-dioxins (PCDDs)) in a concentration up to 1,000 milligrams per kilogram, costs can be expected to fall in a price category of $350 to $500 per ton of waste processed. According to company officials, this range represents the total cost of processing the waste, because no residually contaminated materials remain to be transported or treated elsewhere.

Thermal Desorption/UV Destruction (Photolysis)

Thermal desorption/ultra violet (UV) radiation destruction technology consists of three main operations: 1) resorption, which involves heating the soil matrix to volatize the dioxin present; 2) scrubbing or collection of dioxin into a solvent suitable for subsequent treatment; and 3) UV treatment or exposure of the dioxin-solvent mixture to UV radiation to decompose the dioxin molecules through photochemical reactions (photolysis).[55]

Within a reactor system, dioxin-contaminated soils are continuously passed through a heating unit (rotary drum or desorber) and heated to temperatures up to 560‘C to volatize the dioxin molecules present in soil particles. Once removed, the dioxin vapors, along with soil moisture, small soil particles, and air, are scrubbed with a solvent, and subsequently cooled. Prior to its release into the atmosphere, the scrubbed off-gas is passed through pollution control equipment (e.g., carbon adsorption; scrubber) to remove solvent vapors and any dioxin that may have been left untreated.[56] Following separation or filtration, the scrubber solvent is cooled and recirculated to the scrubber. The water remaining is treated (e.g., filtration, carbon adsorption) and discharged. The faltered soil particles are either recycled to the rotary drum or desorber for additional treatment or packaged for disposal (see figure 3-4).[57]

The developers of this technology (International Technologies Corp., Knoxville, Tennessee) claim that it reduces the volume of soils requiring treat-

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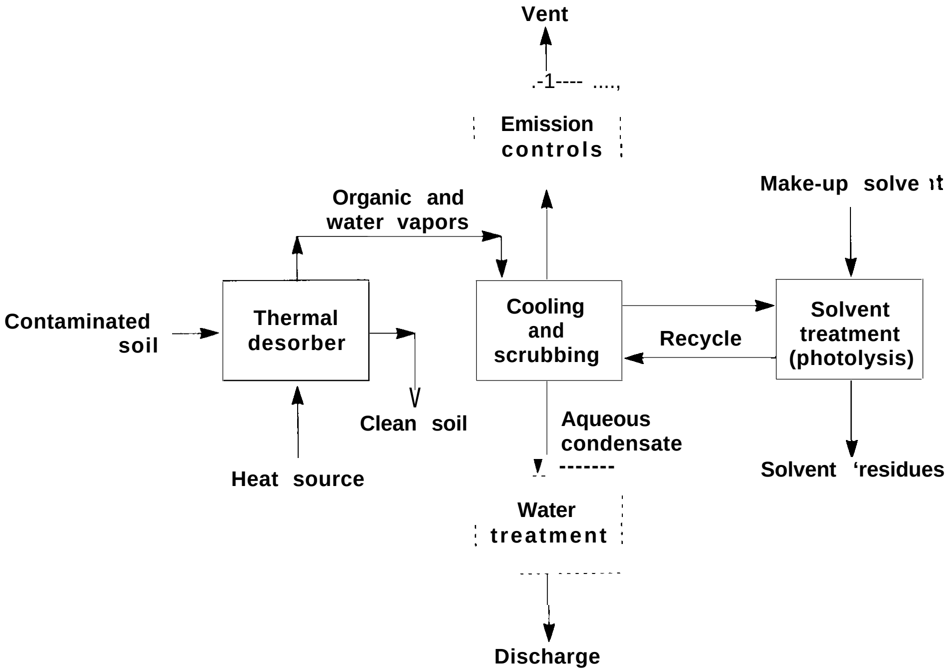
[55] **R. Helsel et al.,** "**Technology** Demonstration of a Thermal Resorption-W **Photolysis** Process for **Decontaminating** Soils Containing Herbicide Orange," **J.H. Exner,** ***Solving Hazardous Waste Problems: Learning From Dioxins***, American Chemical Society Symposium Series 338 **(Washington,** DC: American Chemical Society, **1987),** pp. 319-322.

[56] **Ibid.; R.D. Fox, International Technology Corp.,** "Experience With Treatment **Alternatives** fOr **Organohalogen Contamination,**" paper presented at Dioxin '90 Conference, **Bayreuth,** Germany, Sept. 14, 1990.

[57] **Helsel** et **al.,** op. cit., **footnote** 55, pp. 319-322.

Figure 3-4—Low-Temperature Thermal Resorption Process



SOURCE: International Technology Corp.

ment, producing a concentrate that is easier and more cost-effective to treat. They also claim that this process will achieve cleanup goals similar to those of thermal treatment but without a high-temperature incinerator.

Testing and Availability of Thermal Resorption/ UV Destruction

Although thermal resorption/UV destruction process has been tested on soils containing highly volatile solvents, testing on soils contaminated with low volatile chemicals, such as dioxins, is limited.

Of the tests performed by International Technology Corp., only those conducted at the Department of Defense's Naval Construction Batallion Center (Gulfport, Mississippi) in 1985 and at Johnston Island in 1986 are relevant to dioxin-contaminated soils.[58] [59] These pilot-scale tests resulted in reducing dioxin concentrations in soil from over 200 ppb to below detection limits (0.1 ppb).[60]

The researchers who participated in the two tests concluded that ". . . additional technical information [was] needed for a complete evaluation of the process and to provide the basis for design of a full-scale system for on-site remedial action."[61] Since 1986, however, little additional work related to dioxin-treatment has been done on this process. The developers claim that lack of funds and markets are the major factors inhibiting further development.[62]

This system, however, is being applied to remediate a PCB-contaminated site in Massachusetts.[63] Also, EPA has proposed this technology as a remedial option for cleaning up nearly 40,000 cubic

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[58] The contaminant of concern at these sites was Herbicide Orange known to contain 2,4-D, 2,4,5-T, and dioxin.

[59] Helsel et rd., op. cit., footnote 55, p. 320.

[60] Ibid., pp. 322-330; Paul E. des Rosiers, "Advances in Dioxin Risk Management and Control Technologies," Chemosphere, vol. 18, Nos. 1-6.1989, p, 41; Fuhr and des Rosiers, op. cit., footnote 30, p. 33.

[61] Helsel et al., op. cit., footnote 55, p. 336.

[62] Robert D. Fox, Director, Technology Development, International Technology Corp., personal communication, Sept. 17, 1991.

[63] Robert D. Fox, International Technology Corp., personal communication, Sept. 3, 1991.

yards of PCB-contaminated soil and debris at the Carter Industrial Superfund site in Detroit, Michigan.[64] One site With dioxin contamination at which thermal resorption/UV destruction is being considered for application is Baird & McGuire (Holbrook, Massachusetts).[65] Cost estimates for its application at any of these sites, however, are not available.

BIOREMEDIATION

The use of microorganisms to break down and metabolize organic pollutants has been studied for many years, particularly for treating industrial wastewater and domestic sewage. Since the early 1970s, several organisms have been identified as having the ability to break down chlorinated substances (including dioxin species such as 2,3,7,8-TCDD in soil and in water);[66] however, neither the level of decomposition nor the products that result are known precisely. Of the different strains studied to date, the white rot fungus *(Phanerochaete chrysosporium) is the* most promising because of its ability to degrade halocarbons such as lindane, DDT, 4,5,6-trichlorophenol, 2,4,6-trichlorophenol, and dichlorophenol.[67] [68] Encouraging results have also been reported in Germany on the biodegradation potential of the bacteria ***Pseudomonas*** sp.[69]

In general, bioremediation refers to the transformation of contaminants into less complex and probably less toxic molecules by naturally occurring microbes, by enzyme systems, or by genetically engineered microorganisms. This process can be carried out in situ or in a reaction vessel, under anaerobic or aerobic conditions, and alone or in combination with other treatment methods; several months or years may be required to achieve complete contaminant removal. Understanding the microbial population to be used, as well as the characteristics that ensure their survival, is key to any bioremediation project; these include, among other factors, moisture and oxygen levels, organic content, temperature, pH, food source availability, and possible degradation pathways. Although considerable laboratory and field work has been reported in each of these major areas,[70] few studies exist in which contaminants have been destroyed or removed at levels higher than 90 percent.[71]

Dioxins are known to degrade naturally in the presence of sunlight (ultraviolet radiation) or with the help of microorganisms. The time that dioxins

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“’Thermal DeSorption Fix Offered in Detroit,’’ *Superfund, May* 3, 1991, p. 5.

[65] U.S. Environmental Protection Agency, Region I, Superfund Program, “Fact Sheets-Treatment Technologies,’’ July 1991.

[66] M. Philippi et al., “A Microbial Metabolize of TCDD,” *Experiential,* vol. 38, 1982, p. 659; S. Banerjee, S. Duttagupta, and A.M. Chakrabarti, ‘‘Production of Emulsifying Agent During Growth of *Pseudomonas cepacia* With 2,4,5-Trichlorophenoxyacetic Acid,” *Arch. Microbiology, 1983 vol. 135,* p. 110; J.J. Kilbane, D.K. Chatterjee, and A.M. Chakrabarty, ‘‘Detoxification of 2,4,5-Trichlorophenoxyacetic Acid From Contaminated Soil by *Pseudomonas cepacia,* “ *Applied& Environmental Microbiology,* vol. 45, No. 5, March 1983, p. 169; D. Ghosal, L.S. You, D.K. Chatterjee, and A.M. Chakrabarty, ‘Microbial Degradation of Halogenated Compounds,’ *Science,* vol. 228, No. 4696, Apr. 12,1985, p. 135; Mary L. Krumme and Stephen A. Boyd, “Reductive Dechlorination of Chlorinated Phenols in Anaerobic Upflow Bioreactors,” *Water Resources,* vol. 22, No. 2, 1988, p. 171; and Gary M. Klecka and D.T. Gibson, “Metabolism of Dibenzo-*p*-dioxin and Chlorinated Dibenzo-*p*-dioxins by a *Beijenrinckia* Species, ” *Applied & Environmental Microbiology, vol. 39, No. 2,* February 1980, p. 288.

[67] U.S. Environmental protection Agency, op. cit., footnote 3, p. 5.38; des Rosiers, op. cit., footnote 60, p. 53.

‘Rudy Baum, “Degradation Path for Dichlorophenol Found,” *Chemical & Engineering News,* vol. 69, No. 1, Jan. 7,1991, pp. 22-23; Harry M. Freeman and R.A. Olexey, ‘‘A Review of Treatment Alternatives for Dioxin Wastes,” *Jnl. Air Pollution Control Assoc.,* vol. 36, No. 1, Jan. 1986, p. 74.

[69] Hauke Harms et al., ‘‘Transformation of Dibenzo-*p*-Dioxin by *Pseudomonas sp. Strain HH69,” Applied & Environmental Microbiology,* vol. *56, No. 4, 1990, pp. 1157-1159.*

[70] Sanjoy K. Bhattachayia, Tulane *University,* “Innovative Biological Processes for Treatment of Hazardous Wastes;” William R. Mahaffey and G. Compeau, ECOVA Corp., “Biodegradation of Aromatic Compounds;’’ Michael J.K. Nelson, J.A. Cioffi, and H.S. Borow, “In Situ Bioremediation of TCE and Other Solvents;’’ Proceedings of the HMCRI’s 1 1th Annual National Conference and Exhibition *SUPERFUND ’90 (Silver* Spring, MD: Hazardous Materials Control Research Institute, 1990), pp. 776-787; 800-806; 847-852. Harlan S. Borow and J.V. Kinsella, ECOVA Corp., “Bioremediation of Pesticides and Chlorinated Phenolic Herbicides—Above Ground and In Situ: Case Studies;’’ Richard A. Brown and J.R. Crosbie, “Oxygen Sources for In Situ Bioremediation,’’ Proceedings of the HMCRI’s 10th Annual National Conference and Exhibition *SUPERFUND* ’89 (Silver Spring, MD: Hazardous Materials Control ResearchInstitute, 1989), pp. 325-331; 338-344; C. Cernilia, ‘‘Microbial Metabolism of Polycyclic Aromatic Hydrocarbons,” Adv. *Appl. Microbic/.,* vol, 30, 1984, pp. 30-70; J.W. Falco, Pacific Northwest Laboratory, “Technologies to Remediate Hazardous Waste Sites” (PNL-SA-18030; DE90-011946), paper presented at the Mixed Waste Regulation Conference, Washington, DC, Apr. 17-18, 1990; D.T. Gibson and V. Subramanian, “Microbial Degradation of Hydrocarbons” D.T. Gibson (cd.), *Microbial Degradation of Organic Compounds (New* York, NY: Marcel Dekker, 1984); Harmut S. Fuhr and J. Paul E. des Rosiers, op. cit., footnote 30, p. 32; Ronald Sims, “Soil Remediation Techniques at Uncontrolled Hazardous Waste Sites-A Critical Review,” *Jnl. Air Waste Manag. Assoc., 1990,* pp. 720-722; Eugene L. Madsen, ‘‘Determining In Situ Biodegration: Facts and Challenges, *Environ. Sci. Technol.,* vol. 25, No. 10, 1991, pp. 1663-1673.

[71] Naval Civil Engineering Laboratory, op. cit., footnote 36, p. 10; U.S. Environmental Protection Agency, Op. cit., footnote 3, Pp. 5.3*5.35.

remain in soil, however, has been particularly difficult to assess because they are present in low concentrations (the lower the concentration, the more difficult it is for microorganisms to find and break down dioxins) and tightly bound to soil particles and organic matter. One laboratory study shows that even after a year of treatment, more than 50 percent of the dioxin remained in test soil.[72] Equally significant is the fact that researchers identified half-lives of more than 10 years for dioxins at the site in Seveso, Italy and at certain U.S. Air Force bases in which defoliant use has been reported.[73]

Although information from field work is limited, some potential advantages of future bioremediation methods at dioxin-contaminated sites include the following:

1. byproducts of biodegradation may be non-toxic;
2. bioremediation could be used in combination with other remedial methods (e.g., treatment trains); and
3. treatment of dioxins in subsurface soil and groundwater might not require extensive removal of overlying soil.[74]

One bioremediation technique being evaluated by EPA is in-situ microbial filters. This technology involves the injection of naturally occurring (indigenous) microbes, cultured bacteria, nutrients, and oxygen into the soil column or groundwater to form zones of microbial activity. These zones are established in close proximity to contaminant plumes to facilitate the availability of the latter to injected microbes. The bioremediation of chlorinated and nonchlorinated pollutants has as end products: carbon dioxide, water, and bacterial biomass.[75]

At present, in situ microbial technology has been tested only in the laboratory; consequently, its effectiveness in subsurface soil degradation is unknown (microbes may opt to metabolize injected nutrients instead of contaminants). Cost data are also nonexistent. A field demonstration planned at the Goose Farm Superfund site, Plumstead Township, New Jersey, was canceled in April 1990; efforts to select a new demonstration site are under way.[76] Prior to its utilization on dioxin-contaminated sites, researchers will be required to determine factors such as:

1. the level of chemical reaction that can be achieved,
2. the role of injected nutrients, and
3. the growth rate of microbes in the subsurface.

Testing and Availability of Bioremediation Technology

Although bioremediation is theoretically attractive for cleaning up dioxin-contaminated sites, its real applicability and effectiveness continue to be highly questionable. Comparisons of dioxin research efforts with 2,4,5-trichlorophenol and Agent Orange reveal that only a fraction of the vast amount of laboratory work has been targeted toward dioxin and demonstrated in the field.[77] Furthermore, the current bioremediation literature lacks any reports documenting the success of this technology in treating dioxin-contaminated soil, sludge, or sewage.[78]

Major obstacles in researching dioxin include:

1. its high acute toxicity and low volubility, such that it cannot be found in the aqueous environments in which most microorganisms live;
2. the high cost of treatment; and

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[72] Philip C. Kearney et al., "Persistence and Metabolism of Chlorodioxins in Soils," *Environ. Sci. Technol.*, vol. 6, No. 12, November 1972, p. 1017.

[73] U.S. Environmental Protection Agency, op. cit., footnote 3, p. 5.35; A. DiDominico et al., "AccidentalReleases of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) at Seveso, Italy," *Ecotoxicology & Environmental Safety*, vol. 4, No. 3,1980, pp. 282-356; Paul E. des Rosier% "Remedial Measures for Wastes Containing Polychlorinated Dibenzo-*p*-dioxins (PCDDs) and Dibenzofurans (PCDFs): Destruction, Containment or Process Modification," *Ann. Occup. Hyg*, vol. 27, No. 1, 1983, pp. 59-60; Ronald Sims, op. cit., footnote 70; Dermis J. Paustenbach, "Recent Developments on the Hazards Posed by 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in Soil: Implications for Setting Risk-Based Cleanup Levels at Residential and Industrial Sites," paper submitted for publication to *J. Toxicol. Environ. Health,* June 1991.

[74] U.S. Environmental Protection Agency, op. cit., footnote 3, p. 5.48; U.S. Environment Protection Agency, Office of Research and Development Risk Reduction Engineering Laboratory, Technology *Profiles*, EPA/540/5-90/006 (Cincinnati, OH: November 1990), p. 40.

[75] Ibid.

[76] Ibid., p. 41.

[77] U.S. Environmental Protection Agency, op. cit., footnote 3, p. 5.44; A.M. Chakrabarty, Department of Microbiology and Immunology, University of Illinois, Chicago, personal communication Jan. 9, 1991, and Aug. 23, 1991.

[78] Fuhr and des Rosiers, op. cit., footnote 30, p. 2.

3. its presence at concentrations so low that microorganisms in the natural environment do not consider it food (i.e., an important source of carbon).

The complex nature of the soil environment found at contaminated hazardous waste sites is also a major obstacle because it prevents researchers from developing models useful for predicting bioremediation results accurately.

Experts also criticize the fact that basic environmental research is not well funded. This is due primarily to the fact that the health effects of exposure often are not visible for a long time and companies do not consider environmental bioremediation research to have a market value. Another reason for the lack of research on dioxin at the academic level is that 4 years of biodegradation research produces very little information that could be used by a graduate student to fulfill dissertation requirements. According to A.M. Chakrabarty of the Department of Microbiology and Immunology, University of Illinois, Chicago, ''There is no credible report on bacterial removal of dioxin at the present time.''[79]

Judging from the review performed at the U.S. Navy site in Guam for the selection of a remedial technology, bioremediation techniques must be studied further before they can be applied.[80] The long time required by bioremediation processes, coupled with their undocumented ability to reduce risks to human health and the environment, were considered by technology reviewers as sufficient reasons for not recommending soil bioremediation at that site.

In the view of most experts, bioremediation processes for dioxin are not ready for field demonstration at this time. However, they may become cleanup options in the future, aided by scientific achievements in the fields of biochemistry and genetic engineering of microorganisms, and of the chemistry of TCDD surrogates (e.g., chlorophenols, chlorobenzenes, and the herbicides 2,4,D- and 2,4,5-T).

Cost Estimates for Bioremediation

Cost figures for bioremediation of dioxins do not exist at present. One reason is that treatment of chlorinated dibenzo-p-dioxin and chlorinated dibenzofurans has not been proved beyond the analysis performed on a bench scale in 1985; no field testing has been conducted to date. According to projections based on laboratory work, in situ bioremediation might be the most economical treatment because it does not require excavation of soil. Nevertheless, in the long term, the costs of in situ bioremediation could increase considerably because tilling, fertilizing, and irrigation practices may be required.[81] Current figures, however, do not illustrate the costs involved in actual bioremediation treatment.

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[79] Chakrabarty, op. cit., footnote 77.

[80] Naval Civil Engineering Laboratory, op. cit., footnote 36, p. 10.

[81] U.S. Environmental Protection Agency, op. cit., footnote 3, p. 5.46.