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# **SUPERFUND TREATABILITY CLEARINGHOUSE**

## **Document Reference:**

**International Technology Corp., AFESC, EG&G Idaho, Inc. "Technology Demonstration of a Thermal Desorption/UV Photolysis Process for Decontaminating Soils Containing Herbicide Orange." Prepared for EG&G Idaho. 14 pp. Technical report.**

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## SUPERFUND TREATABILITY CLEARINGHOUSE ABSTRACT

Treatment Process: Physical/Chemical - UV Photolysis

Media: Soil/Generic

Document Reference: International Technology Corp., AFESC, EG&G Idaho, Inc. "Technology Demonstration of a Thermal Desorption/UV Photolysis Process for Decontaminating Soils Containing Herbicide Orange." Prepared for EG&G Idaho. 14 pp. Technical report.

Document Type: Contractor/Vendor Treatability Study

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Site Name: NCBC Gulfport, MS; Johnston Island; and Guam (Non-NPL)

Location of Test: Gulfport, MS and Guam

**BACKGROUND:** This treatability study report presents the results of laboratory and field tests on the effectiveness of a new decontamination process for soils containing 2,4-D/2,4,5-T and traces of dioxin. The process employs three operations, thermal desorption, condensation and absorption of contaminants into a solvent and photo decomposition. Bench-scale tests were conducted to establish the relationships between time and temperature and treatment efficiency. A pilot-scale (100 lbs/hr) system evaluation was conducted at two sites to evaluate system performance and develop scale-up information.

**OPERATIONAL INFORMATION:** The intent of the laboratory and pilot-scale tests was to reduce the combined dibenzo dioxin and furan constituents, which originate from Herbicide Orange (HO), to less than 1 ng/g. This level represents the anticipated soil cleanup criteria. The soils used had similar concentrations of HO contaminants, but were different types of soil. In the laboratory the contaminated soil is passed through thermal desorber and the off gases from the soils, including the contaminants, are passed through a scrubber that uses a hydrocarbon solvent. Contaminants dissolve in the solvent and the solvents are passed through a flow reactor which subjects the contaminant to UV radiation to decompose the contaminant molecules. Testing was conducted on soil samples from three HO contaminated sites; Johnson Island, Eglin AFB and NCBC in Biloxi, MS. The soils tested had 2,3,7,8-TCDD concentrations greater than 100 ng/g of soil and 2,4,-D/2,4,5-T levels greater than 1000 ng/g soil. Tests were run at three different temperatures and two different power levels using high intensity UV quartz mercury vapor lamps.

Pilot tests were conducted at the NCBC site using a rotary indirect calciner as the desorber, an off gas transfer and scrubber system and a

photo chemical reactor to irradiate the contaminants contained in the scrubber solution. A 1200-watt high intensity mercury vapor lamp was used to irradiate the contaminated scrubber solution. No QA/QC plan was contained in the document. No discussion of analytical techniques utilized to detect HO and associated compounds is contained in the paper. A detailed list of soil properties (particle size distribution, surface area, organic matter, etc.) from the three different sites is contained in the document.

**PERFORMANCE:** Laboratory studies revealed that thermal desorption/UV photolysis destroyed all compounds to below their analytical detection limit (which was generally less than 0.1 ng/g). The concentration of 2,3,7,8-TCDD was reduced from 200 ng/g to less than 1 ng/g. Insoluble brown tars (presumably phenolic tars) were deposited on the surfaces of the reactor vessel and lamp well. Reaction kinetics quantum yields' and rate constants were determined. Pilot tests also produced soil containing less than 1 ng/g of 2,3,7,8-TCDD. Table 1 shows the results of the tests.

**CONTAMINANTS:**

Analytical data is provided in the treatability study report. The breakdown of the contaminants by treatability group is:

<u>Treatability Group</u>	<u>CAS Number</u>	<u>Contaminants</u>
W02-Dioxins/Furans/PCBs	1746-01-6	2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

**TABLE 1**

**EFFECT OF TREATMENT CONDITIONS ON RESIDUAL 2,3,7,8-TCDD DURING NCBC PILOT THERMAL DESORPTION TESTS**

Test No.	Soil Feed Rate (kg/hr)	Residence Time <sup>a</sup> (min)	Soil Temperature (°C)	2,3,7,8-TCDD <sup>b</sup> (ng/g)	
				Initial	Residual
1	13.6	40	560	260	ND
2	13.6	40	560	272	ND
3	25	19	560	236	ND
4	44	10.5	560	266	ND
5	20	24	460	233	0.5

- Notes: a) Soil residence time in heated zone.  
 b) Detection level for 2,3,7,8-TCDD was generally less than 0.1 ng/g with a range of 0.018 to 0.51 ng/g.  
 c) This is a partial listing of data. Refer to the document for more information.

June 1987

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Technology Demonstration of a Thermal Desorption/UV Photolysis  
Process for Decontaminating Soils Containing Herbicide Orange

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Laboratory and field testing determined the effectiveness of a new decontamination process for soils containing 2,4-D/2,4,5-T and traces of dioxin. The process employs three primary operations - thermal desorption to volatilize the contaminants, condensation and absorption of the contaminants in a solvent, and photochemical decomposition of the contaminants. Bench-scale experiments established the relationship between desorption conditions (time and temperature) and treatment efficiency. Laboratory tests using a batch photochemical reactor defined the kinetics of 2,3,7,8-TCDD disappearance. A pilot-scale system was assembled to process up to 100 pounds per hour of soil. Tests were conducted at two sites to evaluate treatment performance and develop scale-up information. Soil was successfully decontaminated to less than 1 ng/g 2,3,7,8-TCDD at temperatures above 460°C.

As part of a major program being conducted by the U.S. Air Force to restore to normal use several Department of Defense sites where soils have been contaminated with low levels of Herbicide Orange (HO), International Technology Corporation (IT), under subcontract to EG&G Idaho, has been conducting a project involving laboratory bench-scale and field pilot-scale tests to demonstrate a new soil treatment process - thermal desorption/UV photolysis (TD/UV). The intent of the demonstration was to reduce the combined tetra-, penta-, and hexa-chlorinated dibenzodioxin (CDD) and furan (CDF) congeners, which originated from the HO, to less than 1 ng/g, which represented the anticipated soil clean-up criteria. Treatment should also effectively remove the primary HO constituents, 2,4-D

and 2,4,5-T. Two sites were included in the field demonstration project for the TD/UV process, each having substantially different types of soil but reasonably similar concentrations of the HO constituents. Testing at the Naval Construction Battallion Center (NCBC) at Gulfport, Mississippi was conducted by IT during May 1985; testing at Johnston Island (JI) in the Pacific Ocean occurred in July 1986. Based on the results of these field pilot demonstrations, an engineering and cost evaluation is being performed for applying TD/UV technology using large, mobile systems for these two sites or other sites having similar contaminated soil problems. This paper describes the technology, highlights the results of the initial laboratory test phase, and summarizes the field demonstration results.

### Process Description

The thermal desorption/UV photolysis process developed by IT accomplishes substantial volume reduction and toxicity reduction by concentrating the hazardous constituents contained in the soil into a small volume which is easier to treat than large quantities of soil. The process incorporates three steps:

- Desorption - heating the soil to volatilize the organic contaminants
- Scrubbing - collecting the volatilized organics in a suitable solvent
- Photolysis - converting the contaminants to relatively non-hazardous residues through photochemical reactions.

A schematic block-flow diagram is presented as Figure 1. Contaminated soil is passed continuously through an indirectly heated desorber which can be one of many types of conventional equipment applicable for thermal processing of solids. The treatment performance of the desorber is controlled by the residence time and temperature of the soil. Treatment requirements (i.e., operating conditions) are determined by the volatility of the soil contaminants and the required contaminant removal efficiency (final versus initial concentration).

The off-gas leaving the desorber contains organic vapors, water vapor originating as initial soil moisture, and small quantities of air which enter with the soil. Scrubbing using a high boiling hydrocarbon solvent is used to treat the off-gas to remove the organic contaminants and water vapor by cooling, condensation, and absorption. Particulates (e.g., fine soil) which may be entrained by the off-gas are also collected by the scrubbing solvent. Scrubbed off-gas is passed through a conventional emission control system, such as carbon adsorption, to ensure that no organic contaminants or solvent vapors are released. Scrubber solvent is recirculated to the scrubber after being processed through a system of phase separation, filtration, and cooling. Condensed water, which is immiscible with the solvent, is separated and either directly treated using conventional techniques, such as filtration and carbon adsorption, or discharged to an existing

wastewater treatment facility. Filtered solids are recycled to the desorber or packaged as process waste for off-site disposal, depending on the relative quantity and composition.

A small portion of the recirculated solvent stream is diverted to a UV photolysis system to treat (detoxify) and remove the organic contaminants, with the treated solvent purge recycled to the scrubbing system. The equilibrium concentration of the contaminants in the scrubber solvent is maintained as high as practical to minimize the purge stream and afford higher photolysis reaction rates, thereby decreasing the size of the photolysis treatment system. The concentration limitation is dependent on the solubility properties and partial pressure of the contaminants in the solvent, and the resultant effect on scrubber efficiency and emission potential. The photolysis system contains a specially designed flow reactor which subjects the contaminant-laden solvent to UV radiation to induce molecular decomposition. High intensity mercury vapor lamps produce a band of wavelengths, some of which match the absorption energy of the specific organic molecules being treated. Cooling is provided to the reactor to remove the thermal output of the lamp. The photolyzed solvent is treated by using selected conventional physical or thermal separation processes, such as distillation, to remove the reaction product residue. Alternatively, a purge of the photolyzed solvent can be discarded as waste to control the levels of reaction products in the recirculated solvent system.

Other configurations of treatment processes using thermal desorption as the primary separation technique can be applied to organically contaminated soils. Alternative physical/chemical processes can be used to treat the desorber off-gas and the contaminants. To achieve complete contaminant destruction, the off-gas can be treated by using conventional fume incineration or other thermal treatment technology. The choice of the type of desorber and off-gas treatment system depends on the concentration and properties of the chemical contaminants, soil characteristics, quantity of contaminated material, site characteristics, availability of off-site disposal, and regulatory and related requirements.

#### Laboratory Testing and Results - Thermal Desorption

Thermal desorption is a physical separation process, although chemical transformation of the organic contaminants may occur depending on the thermal stability and the operating temperatures required to achieve adequate decontamination efficiency. Thermal desorption has been used only in a limited number of cases (1-4) for treating contaminated soil, and these applications have involved relatively volatile organic compounds, such as solvents. Because of the extremely low volatility of CCD and CDFs, the development of basic treatability data was essential to confirm that 1 ng/g levels in soil could be achieved and that the required desorption conditions were practical, considering the design features and operating rates of equipment available for performing such treatment.

Desorption treatability testing was conducted on samples of contaminated soil from three HO contaminated sites - NCBC, JI, and

Eglin Air Force Base. The goals of the test effort were to evaluate the effect of time and temperature on 2,3,7,8-TCDD removal efficiency and to establish the importance of soil type. The samples were selected by the Air Force based on results of site surveys to yield high contamination levels in order to investigate a broad range of treatability. This testing was an extension of earlier testing performed for the EPA on two dioxin-contaminated soil samples from Missouri to support EPA's mobile incinerator trial burn in 1985 (5).

After each soil sample was blended, air dried, and screened (2 mm sieve opening) triplicate aliquots were taken and analyzed for 2,3,7,8-TCDD, CDD and CDF congeners, and 2,4-D and 2,4,5-T. The three prepared soils had 2,3,7,8-TCDD levels greater than 100 ng/g and 2,4-D/2,4,5-T levels of about 1000 µg/g. The JI soil had significant concentrations of hepta and octa CDD compared with the other two samples. In addition, selected physical and chemical properties presented in Table I, were measured (6). The EPA test program (5) had indicated that soil properties had only a minor influence on removal efficiencies for 2,3,7,8-TCDD.

Table I. Physical-Chemical Analysis of Prepared Soil Samples Used for Laboratory Thermal Desorption Tests

Parameter	JI	Eglin	NCBC
pH	8.4	3.8	8.6
Conductivity (millimhos/cm)	5.0	0.15	0.21
Organic matter (percent)	4.2	1.2	2.3
Cation exchange capacity milliequivalents/100g)	0.73	0.77	2.4
Oil and grease content (grams/100g)	0.19	0.41	0.34
Surface area (m <sup>2</sup> /g)	6.7	2.5	12.3
Particle size distribution (percent)			
Medium sand	41	41	26
Fine sand	37	52	59
Silt	19	5	12
Clay (<5 microns)	3	2	3
Moisture	2.3	0.79	1.1

A series of 10 individual tests was performed using temperatures between 430 and 560°C and treatment times of 8 to 30 minutes. Table II presents the test results, which are comparable to the earlier results for Missouri soils. The objective of 1 ng/g 2,3,7,8-TCDD residual in soil was achieved for all three soils subjected to the highest temperature. There was some difference in treatability observed between the three soils at the lower temperatures. Also, longer treatment times were required for the NCBC soil because of the higher initial 2,3,7,8-TCDD level (500 ng/g vs. 100 ng/g). One set of treated test samples which contained less than 1 ng/g 2,3,7,8-TCDD was also analyzed for the other CDD and CDF congeners and 2,4-D/2,4,5-T. These results, shown in Table III, indicate greater than 99.999 percent removal of the initial

2,4-D/2,4,5-T and the effective removal of higher chlorinated CDDs and CDFs.

Table II. Effect of Treatment Conditions on Residual 2,3,7,8-TCDD in Soil During Laboratory Thermal Desorption Tests

Nominal Test Temperature (°C)	Soil Identification	Time at Test Temperature (min)	2,3,7,8-TCDD Concentration (ng/g)	
			Initial	Final
430	JI	20	106	38.5
	Eglin	20	101	4.4
	NCBC	30	494	26.6 <sup>a</sup>
481	JI	15	106	4.5
	JI	30	106	1.6
	Eglin	15	101	1.1 <sup>a</sup>
	Eglin	30	101	0.45
	NCBC	15	494	10.1
	NCBC	30	494	4.6
558	JI	8	106	0.56 <sup>a</sup>
	Eglin	8	101	0.71
	NCBC	15	494	0.76 <sup>a</sup>

<sup>a</sup>Average of duplicate tests or duplicate analyses.

Table III. Residual 2,4-D, 2,4,5-T, and CDD/CDF in Soil Samples Treated at 558°C in Laboratory Thermal Desorption Tests

Compound	Concentration (ng/g)		
	JI	Eglin	NCBC
2,4-D	ND <sup>a</sup>	ND	ND
2,4,5-T	16	0.8	3
TCDF	0.6	0.4	ND
OCDF <sup>b</sup>	0.3	ND	ND

<sup>a</sup>ND = Not detected.

<sup>b</sup>No other CDD and CDF congeners were detected.

#### Laboratory Testing and Results - Photolysis

Photolysis has had limited application for treatment of hazardous waste or detoxification of chemically contaminated materials. The susceptibility of chlorinated aromatics, including herbicides such as 2,4-D and 2,4,5-T, to UV-induced decomposition is well established (7,8). Photodecomposition of such compounds leads to successive dechlorination followed by condensation reactions to form phenolic polymers (7,8). Other research has demonstrated that CDD and CDF decompose in the presence of UV light (8,9,10). Development of a photochemical process for destroying 2,3,7,8-TCDD in a waste tar indicated similar dechlorination and condensation reactions and products (8). The high-molecular weight end products, which are similar in structure to humic acids, would be expected to have low toxicity and mobility. Therefore, essentially complete



conversion of toxic constituents could produce a potentially non-hazardous (according to RCRA), easily disposable residue.

Laboratory photolysis experiments were designed to confirm that 2,3,7,8-TCDD contained in the selected scrubber solvent could be reduced to 1 ng/g and to determine the reaction rates of the primary HO constituents and 2,3,7,8-TCDD in that solvent matrix. A previous photolysis process for 2,3,7,8-TCDD used hexane as a solvent (8). The solvent selected for use in the TD/UV process was different - a high boiling (kerosene-like) mixture of isoparaffins. This hydrocarbon solvent was selected because of its very low vapor pressure and water solubility, nontoxic and nonflammable characteristics, relatively low cost, chemical stability, and good solvent properties for HO constituents. A second major difference from earlier IT photolysis studies was the presence in the scrubber solution of significant concentrations of other chlorinated organic reactants (2,4-D and 2,4,5-T) which were also subject to photolysis. In fact, the typical concentration ratio between 2,4-D or 2,4,5-T and 2,3,7,8-TCDD in the soil samples used in the desorption treatability testing was 2000:1.

The three steps of the laboratory program included generation of scrubber solution, bench-scale batch photolysis reactions, and a pilot system trial. In order to generate a representative sample of scrubber solution for photolysis tests, a small desorption and scrubbing system was assembled. A portion of the prepared samples of both NCBC and JI soil used for the thermal desorption tests was used to generate scrubber solution. Contaminated soil (~100 g) was placed in a standard tube furnace apparatus which was heated to about 500°C for 15 to 30 minutes. A nitrogen purge swept the vapors into the scrubbing system, which consisted of several solvent-filled impingers. Analysis of the prepared scrubber solutions indicated thermochemical conversion of the 2,4-D and 2,4,5-T in the contaminated soil to the corresponding chlorophenols at molar equivalents. In addition to using prepared scrubber solutions, solvent spiked with 2,4-D and 2,4,5-T, the corresponding chlorophenols, or 2,3,7,8-TCDD was used for baseline photolysis tests.

Most photolysis experiments were conducted in a 0.5 liter capacity standard quartz photochemical reactor using either recirculation or bottom agitation for heat and mass transfer. Both 100- and 450-watt high pressure quartz mercury vapor lamps (Canrad-Hanovia, Inc., Catalog Nos. 608A and 679A) were used, depending on the initial reactant concentration in the particular solvent solution being tested. The wavelengths of interest based on spectrophotometric absorbance measurements of 2,3,7,8-TCDD, 2,4-D and 2,4,5-T were in the 280 to 320 nm region. Isopropyl alcohol (~0.05 g/g solvent solution) was used as a proton donor to minimize formation of polymeric reaction by-products which tend to foul the light transmission surfaces (8). The bench-scale photolysis tests gave the following results:

1. All compounds disappeared to below the analytical detection limits.
2. The concentration of 2,3,7,8-TCDD was reduced to less than 1 ng/g from initial concentrations as high as 200 ng/g.

3. For a given reactor configuration and lamp wattage, the reaction rates of 2,3,7,8-TCDD and 2,4,5-trichlorophenol were proportional to the concentration, indicating pseudo-first order kinetics in agreement with previous work (8).
4. Absorbance of UV energy by the solvent, which increased during irradiation, resulted in low quantum yields and low rate constants.
5. Insoluble brown reaction products (presumably phenolic tars) were deposited on the surfaces of the reactor vessel and lamp well. This expected phenomenon plus the high solvent absorbance demanded a careful reactor selection and photolysis system design.

Trials using a pilot reactor system described in the following section were performed in the laboratory to establish reactor efficiencies and operating characteristics prior to transport to the field. A synthetic scrubber solution was prepared containing 2,4,5-trichlorophenol at a concentration (~2,000 µg/g) projected to be representative of the planned field tests. Kinetics were determined to be first-order with a rate constant of  $0.07 \text{ sec}^{-1}$ .

#### On-site Pilot Testing and Results

Based on the information developed from the laboratory test program, a pilot-scale TD/UV system was designed and assembled. Three skids were used to mount the desorber, scrubber, and photolysis systems; the largest skid was 1.5 meters by 4.3 meters. A conventional pilot-scale, rotary, indirect-fired calciner was used as the desorber. The calciner consisted of a 3.3 meter long by 16 cm internal diameter rotating tube through which the soil was transferred, and a gas-fired furnace which surrounded the middle 2.0 meters of the tube length. The initial and final tube sections were used for soil feeding and cooling. The flow rate and residence time of soils traveling through the desorber were controlled by varying the tube inclination and rotational speed. Temperature of the soil was measured at different locations by a thermowell probe extending inside the tube. Soil was fed to the desorber from a small hopper using a variable speed screw conveyor. Soil leaving the tube was collected in a sealed metal can.

The off-gas transfer and scrubbing system was designed to enable recirculation of scrubbed off-gas through the desorber. The entire off-gas treatment and recirculation system, including the desorber and scrubber, was operated at a slightly negative pressure to prevent potential fugitive emissions. A small amount of air entered the system with the soil feed or through seal leakage. Nitrogen was added to the recirculated gas stream to maintain the oxygen concentration below the level necessary to support combustion. This was an extra safety feature since the vapor pressure of the solvent at normal scrubber operating conditions is very low. A portion of the scrubbed off-gas was vented from the recirculation system to maintain proper pressure in the system. This purge stream was passed through a small HEPA filter and carbon adsorber before being discharged to the atmosphere. The solvent system

consisted of a scrubber, receiving and separation tank, storage tank, recirculation pump, filters for removing suspended solids, and solvent cooler.

The photolysis system was independent of the desorber and scrubber systems; its design capacity was lower than necessary to match the desorber's soil-processing rate. A portion (about 40 kg) of contaminant-laden solvent was taken from the scrubber system after completion of one or more desorption tests and transferred to the photolysis system. This system consisted of an agitated storage tank, solvent recirculation pump, and photochemical reactor with associated cooling, DC power supply, and controls. The selected type reactor was a standard quartz falling-film unit, approximately 10 cm in diameter and 50 cm long (Ace Glass, Inc., Part No. 7898). A 1200 watt high intensity mercury vapor lamp was inserted through a central quartz tube within the reactor to irradiate the solvent as it flowed by gravity down the circumference of the reactor body. The solvent was recirculated through the reactor for many cycles to achieve sufficient irradiation (e.g., reaction) time.

Five desorption tests were carried out at NCBC at various treatment conditions. A total of 800 kg of soil was processed; soil was prepared by drying and crushing to less than 1/2 inch to allow proper flow in the desorber feed mechanism, and blending for uniformity. Each test lasted 5 to 10 hours, including the heat-up and cool-down cycle. Samples of feed soil and treated soil were taken during steady-state operation, and samples of the scrubber solvent and vent carbon were taken at the conclusion of each run. Samples were analyzed for 2,4-D, 2,4,5-T, other HO indigenous compounds, priority pollutant organics and metals, and tetra-hexa congeners of CDD and CDF. In addition, 2,3,7,8-TCDD concentrations of treated soil and photolyzed solvent samples were determined on a quick-response basis to enable adjustment of the operating conditions in subsequent tests. Fresh solvent and carbon were used for each test, and the entire desorber and scrubber network was cleaned out between tests. This cleaning enabled thorough inspection of the condition of the equipment and provided several different compositions of contaminated solvent to use in the photolysis tests.

Table IV shows the effect of different soil temperatures and residence times on residual 2,3,7,8-TCDD for NCBC pilot tests. Table V presents the analytical results for 2,4-D, 2,4,5-T, and total CDD and CDF. Analytical detection levels for 2,3,7,8-TCDD and the various congeners were generally less than 0.1 ng/g but varied from sample to sample, ranging from 0.018 ng/g to 0.51 ng/g.

Table IV. Effect of Treatment Conditions on Residual 2,3,7,8-TCDD During NCBC Pilot Thermal Desorption Tests

Test No.	Soil Feed Rate (kg/hr)	Residence Time <sup>a</sup> (min)	Soil Temperature (°C)	2,3,7,8-TCDD (ng/g)	
				Initial	Residual
1	13.6	40	560	260	ND
2	13.6	40	560	272	ND
3	25	19	560	236	ND
4	44	10.5	560	266	ND
5	20	24	460	233	0.5

<sup>a</sup>Soil residence time in heated zone.

Table V. Residual 2,4-D, 2,4,5-T, and CDD/CDF in NCBC Pilot Thermal Desorption Test

Compound	Concentration (ng/g)				
	Test 1	Test 2	Test 3	Test 4	Test 5
2,4-D	180	150	20	-	170
2,4,5-T	500	270	60	-	1240
TCDD	ND <sup>a</sup>	0.23	0.11	0.61	0.75
PCDD	ND	ND	ND	ND	ND
HCDD	ND	ND	ND	ND	ND
TCDF	ND	ND	ND	0.13	0.95
PCDF	ND	0.14	ND	0.54	1.0
HCDF	ND	ND	ND	ND	ND
CDD and CDF <sup>b</sup>	ND	0.37	0.11	1.28	2.70

<sup>a</sup>ND = not detected.

<sup>b</sup>Total of quantified values for detected congeners.

All test conditions produced soil containing less than 1 ng/g 2,3,7,8-TCDD. The total quantified tetra-hexa congeners were less than the treatment goal of 1 ng/g for the first three tests, which were performed at the lower feed rates. Test 4, made at the highest feed rate, nearly met this value, whereas the much lower soil temperature used for the final test resulted in almost 3 ng/g combined residual CDD and CDF. A longer residence time could have improved this performance. Residual 2,4-D and 2,4,5-T concentrations were less than 1 µg/g for all but the final test. This reduction represents greater than 99.97 percent removal efficiency for these primary HO constituents.

Because of the very low moisture content of the prepared soil feed, an insufficient volume of aqueous condensate was collected from the tests to perform analysis or treatability tests. A vent gas sample was taken, but no valid analytical results were generated because of delays in sample processing. However, analysis of the carbon used in the emission control adsorbers enabled some evaluation of scrubber performance and process emission potential. Only the front (upstream) portion of carbon from one of the

tests showed detectable levels of any CDD or CDF. No HO constituents were detected in the downstream portion of carbon. Calculated scrubber removal efficiencies exceeded 99.9 percent for CDD, CDF, 2,4-D, and 2,4,5-T. Vent gas volume was about 0.05 m<sup>3</sup>/minute for all tests.

Results of the photolysis tests are presented in Table VI. The total solvent volume (-10.5 l) was recirculated through the reactor at 0.75 l/min for 6.5 hr, resulting in 28 cycles with an irradiation time of about 1.5 sec/cycle. The photolysis system operating time was selected based on the laboratory trials to achieve less than 1 ng/g 2,3,7,8-TCDD; the actual residual level of 0.36 ng/g represented greater than 99 percent conversion. The reaction conversion of the other CDD and CDF congeners varied from 85 to 99 percent. Photolysis reduced the concentrations of 2,4-dichlorophenol (2,4-DP) and 2,4,5-trichlorophenol (2,4,5-DP), (corresponding to the 2,4-D and 2,4,5-T present in the initial soil) by 85 and 97 percent respectively. Figure 2 shows the rate of disappearance of 2,3,7,8-TCDD, 2,4-DP, and 2,4,5-TP. As demonstrated during the laboratory tests, the reaction kinetics were pseudo-first order over the given range of concentrations. The reaction rate constants were similar for the three species (0.11 sec<sup>-1</sup>, 0.04 sec<sup>-1</sup>, and 0.08 sec<sup>-1</sup>, respectively); the rate constant for 2,4,5-TP was comparable to that determined in the laboratory trials of the pilot system.

Table VI. Initial vs Final Concentration of Selected Compounds in Scrubber Solution from NCBC Pilot Photolysis Tests

Compound	Concentration (ng/g)	
	Initial	Final
2,4-Dichlorophenol	490,000	82,000
2,4,5-Trichlorophenol	977,000	31,000
2,3,7,8-TCDD	43.3	0.36
Total TCDD	46.3	0.92
Total PCDD	15.7	2.3
Total HCDD	0.84	0.037
Total TCDF	31.0	3.8
Total PCDF	3.7	1.1
Total HCDF	1.7	0.0031

Three desorption tests and one photolysis test were conducted at JI to compare the effects of different soil characteristics and investigate higher processing rates. The coral-like soil used for the tests contained lower levels of HO contamination than NCBC (about 50 ng/g versus 250 ng/g). As much as 95 kg/hr of soil was successfully decontaminated to less than 1 ng/g 2,3,7,8-TCDD using desorption temperatures of 550°C. Treated soil from all three desorption tests had nondetectable residual tetra-hexa CDD and CDF congeners, 2,4-D and 2,4,5-T, and corresponding chlorophenols. Analysis of carbon removed from the desorber-scrubber system vent showed no detectable concentration of CDD or CDF. Gas samples taken downstream of the carbon adsorber showed nondetectable concentrations of CDD and CDF, 2,4-D and 2,4,5-T, and chloro-

phenols. Photolysis test results were comparable with NCBC tests. Initial concentrations of HO contaminants were much higher in the scrubber solvent due to processing of considerably more soil and use of less solvent. The concentration of 2,3,7,8-TCDD was reduced from 780 ng/g to less than 0.7 ng/g during 12 hours of system operation (representing about 80 sec reaction or irradiation time). Total chlorophenols were reduced from 430 µg/g to less than 6 µg/g, and tetra-hexa CDD and CDF congeners were effectively treated. Reaction rate constants for specific compounds were essentially the same between the NCBC and JI photolysis tests. At JI as at NCBC, brown residues were deposited on the reactor surfaces, and solvent discoloration was obvious, but there was no evidence of rate retardation.

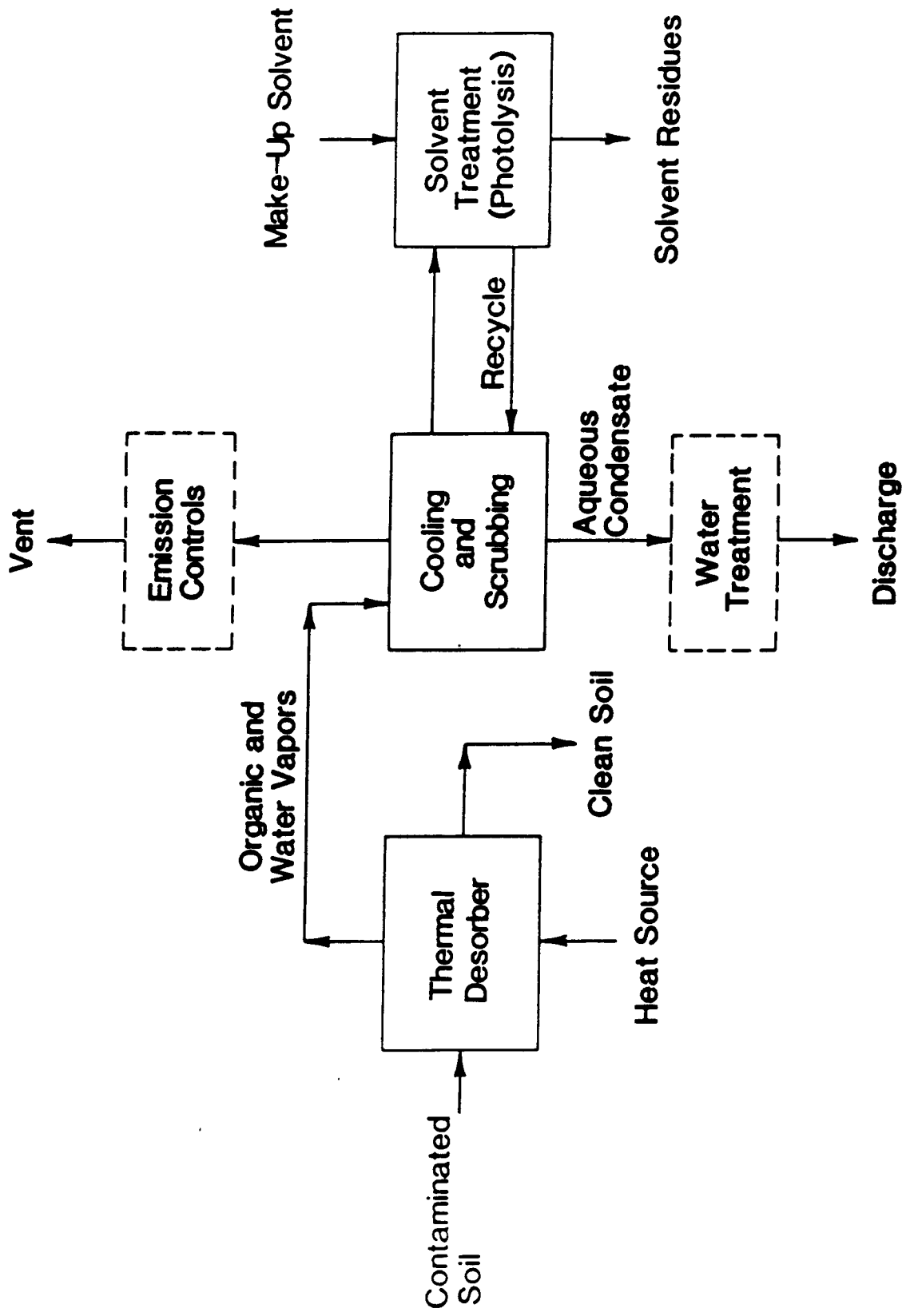
### Conclusions

The effectiveness of thermal desorption to decontaminate soil containing HO and of UV photolysis to destroy HO toxic constituents has been demonstrated in bench- and pilot-scale tests. Some additional technical information is 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. This project illustrates the requirements for developing and implementing new process technology for solving contaminated-soil environmental problems. Only through such demonstration efforts can more cost-effective and environmentally sound remedial action alternatives be made available.

### Literature Cited

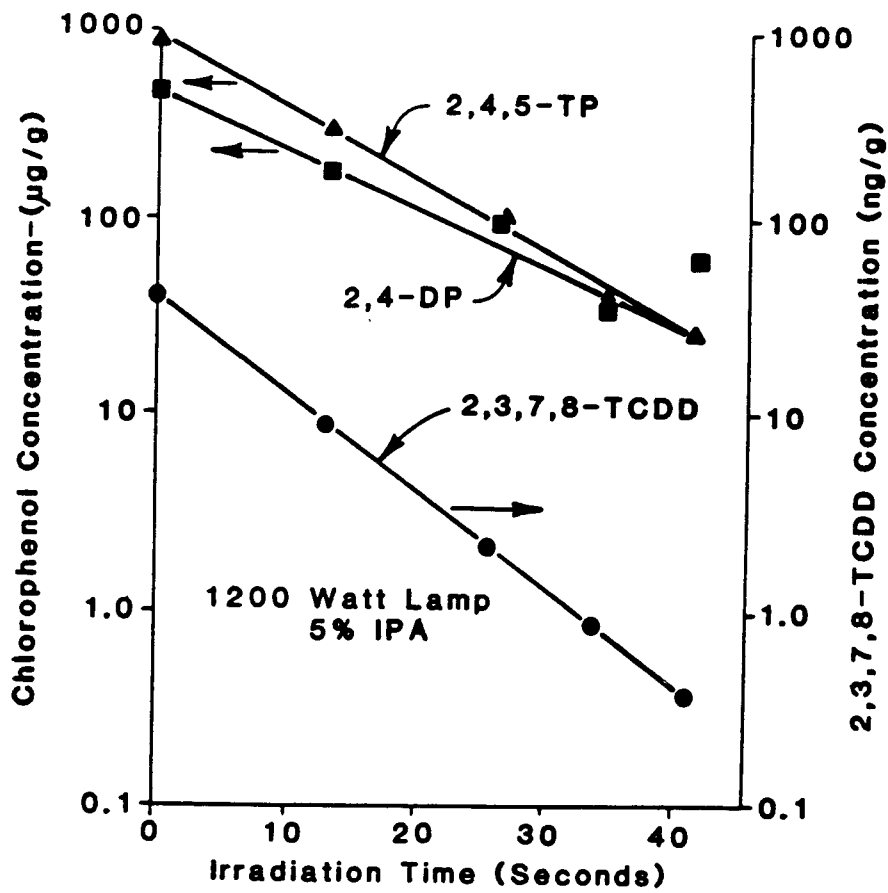
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**Thermal Desorption/UV Photolysis Process Concept**





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