



Engineering Bulletin

Pyrolysis Treatment

Purpose

Section 121(b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) mandates the Environmental Protection Agency (EPA) to select remedies that "utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants, and contaminants as a principal element." The Engineering Bulletins are a series of documents that summarize the latest information available on selected treatment and site remediation technologies and related issues. They provide summaries of and references for the latest information to help remedial project managers, on-scene coordinators, contractors, and other site cleanup managers understand the type of data and site characteristics needed to evaluate a technology for potential applicability to their Superfund or other hazardous waste site. Those documents that describe individual treatment technologies focus on remedial investigation scoping needs. Addenda will be issued periodically to update the original bulletins.

Abstract

Pyrolysis is formally defined as chemical decomposition induced in organic materials by heat in the absence of oxygen. In practice, it is not possible to achieve a completely oxygen-free atmosphere; actual pyrolytic systems are operated with less than stoichiometric quantities of oxygen. Because some oxygen will be present in any pyrolytic system, nominal oxidation will occur. If volatile or semivolatile materials are present in the waste, thermal desorption will also occur.

Pyrolysis is a thermal process that transforms hazardous organic materials into gaseous components and a solid residue (coke) containing fixed carbon and ash. Upon cooling, the gaseous components condense, leaving an oil/tar residue. Pyrolysis typically occurs at operating temperatures above 800°F [1, pp. 165, 167] [2, p. 5].* This bulletin does not address other thermal processes that operate at lower temperatures or those that operate at very high temperatures, such as a plasma arc. Pyrolysis is applicable to a wide range of organic wastes and is generally not used in treating wastes consisting primarily of inorganics and metals.

Pyrolysis should be considered an emerging technology. (An emerging technology is a technology for which performance data have not been evaluated according to methods approved by EPA and adhering to EPA quality assurance/quality control standards, although the basic concepts of the process have been validated [3, pp. 1-2].) Performance data are currently available only from vendors. In addition, existing data are limited in scope and quantity and frequently of a proprietary nature.

This bulletin provides information on the technology applicability, the types of residuals resulting from the use of the technology, the latest performance data, site requirements, the status of the technology, and where to go for further information.

Technology Applicability

Pyrolysis systems may be applicable to a number of organic materials that "crack" or undergo a chemical decomposition in the presence of heat. Pyrolysis has shown promise in treating organic contaminants in soils and oily sludges. Chemical contaminants for which treatment data exist include polychlorinated biphenyls (PCBs), dioxins, polycyclic aromatic hydrocarbons, and many other organics. Treatment data discussed in this bulletin were taken from treatability studies conducted by three vendors.

Pyrolysis is not effective in either destroying or physically separating inorganics from the contaminated medium. Volatile metals may be desorbed as a result of the higher temperatures associated with the process but are similarly not destroyed.

The probable effectiveness of pyrolysis on general contaminant groups for various matrices is shown in Table 1. Examples of constituents within contaminant groups are provided in "Technology Screening Guide for Treatment of CERCLA Soils and Sludges" [4, pp. 10-12]. Table 1 is based on current available information or professional judgment where no information was available [1, pp. 165, 168] [2, pp. 9-14] [5, pp. 10-15] [6, p. 9]. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiencies achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatment results indicated that the technology was effective for

* [reference number, page number]

Table 1
Effectiveness of Pyrolysis on General Contaminant Groups for Soil and Sediment/Sludge

Contaminant Groups		Effectiveness	
		Soil	Sediment/ Sludge
Organic	Halogenated volatiles	▼	▼
	Halogenated semivolatiles	▼	▼
	Nonhalogenated volatiles	▼	■
	Nonhalogenated semivolatiles	■	■
	PCBs	■	■
	Pesticides (halogenated)	▼	▼
	Dioxins/Furans	▼	■
	Organic cyanides	▼	▼
	Organic corrosives	□	□
Inorganic	Volatile metals	□	□
	Nonvolatile metals	□	□
	Asbestos	□	□
	Radioactive materials	□	□
	Inorganic corrosives	□	□
	Inorganic cyanides	□	□
Reactive	Oxidizers	□	□
	Reducers	□	□
■ Demonstrated Effectiveness: Successful treatability test at some scale completed. ▼ Potential Effectiveness: Expert opinion that technology will work. □ No Expected Effectiveness: Expert opinion that technology will not work.			

that particular contaminant and medium. The ratings of potential effectiveness or no expected effectiveness are both based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular medium. When the technology is not applicable or will probably not work for a particular combination of contaminant group and medium, a no-expected-effectiveness rating is given.

Limitations

The primary technical factors affecting pyrolytic performance are the temperature, residence time, and heat transfer rate to the material. There are also several practical limitations which should be considered.

As the medium is heated and passes through a pyrolytic system, energy is consumed in heating moisture contained in the contaminated medium. A very high moisture content would result in lower throughput. High moisture content, therefore, causes increased treatment costs. For some wastes, dewatering prior to pyrolysis may be desirable.

The treated medium will typically contain less than one percent moisture. Dust can easily form in the transfer of the treated medium from the treatment unit, but this problem can be mitigated by water sprays.

A very high pH (greater than 11) or very low pH (less than 5) may corrode the system components. The pyrolysis of halogenated organics will yield hydrogen halides; the pyrolysis of sulfur-containing organics will yield various sulfur compounds including hydrogen sulfide (H₂S). Because hydrogen halides and hydrogen sulfide are corrosive chemicals, corrosion control measures should be taken for any pyrolytic system which will be processing wastes with high concentrations of halogenated or sulfur-containing organics.

Technology Description

Pyrolysis is formally defined as chemical decomposition induced in organic materials by heat in the absence of oxygen. Pyrolysis is a thermal process that transforms organic materials into gaseous components and a solid residue (coke) containing fixed carbon and ash. The pyrolysis of organics yields combustible gases including carbon monoxide, hydrogen, methane, and other low molecular weight hydrocarbons [7, pp. 252-253]. Pyrolysis occurs to some degree whenever heat is applied to an organic material. The rate at which pyrolysis occurs increases with temperature. At low temperatures and in the presence of oxygen, the rates are typically negligible. In addition, the final percent weight loss for the treated material is directly proportional to the operating temperature. Similarly, the hydrogen fraction in the treated material is inversely proportional to the temperature.

The primary cleanup mechanisms in pyrolytic systems are destruction and removal. Destruction occurs when organics are broken down into lower molecular weight compounds. Removal occurs when pollutants are desorbed from the contaminated material and leave the pyrolysis portion of the system without being destroyed.

Pyrolysis systems typically generate solid, liquid, and gaseous products. Solid products include the treated (and dried) medium and the carbon residue (coke) formed from hydrocarbon decomposition. Various gases are produced during pyrolysis, and certain low-boiling compounds may volatilize rather than decompose. This is not typically a problem. Gases may be condensed, treated, incinerated in an afterburner, flared, or a combination of the above. Depending on the specific components, organic condensate may be reusable. Other liquid streams will include process water used throughout the system. A general schematic of a pyrolytic process is shown in Figure 1.

As shown in Figure 1, the first step in the treatment process is the excavation of the contaminated soil, sludge, or sediment. Oversized rejects such as large rocks or branches are removed and the material is transferred to the pyrolysis unit. The treatment system may include a desorption stage prior to pyrolysis. If so, the desorbed gases flow to the gas treatment system for treatment and/or recovery, and the contaminated matrix (minus any desorbed chemicals) is transferred to the pyrolysis chamber [1, p. 166] [2, pp. 3-6].

The temperature in the pyrolysis chamber is typically between 800 and 2,100° F, and the quantity of the oxygen present is not sufficient for the complete oxidation of all contaminants. In pyrolysis, organic materials are transformed into coke and gaseous components. Gas treatment options include: 1) condensation plus gas cleaning and 2) incineration plus gas cleaning.

Pyrolysis forms new compounds whose presence could impact the design of the offgas management system. For example, compounds such as hydrogen halides and sulfur-containing compounds may be formed. These must be accounted for within the design of the Air Pollution Control (APC) system.

There are three pyrolytic systems which will be discussed in this bulletin. These systems are: the HT-V system marketed by TDI Thermal Dynamics (formerly Southdown Thermal Dynamics), a process developed by Deutsche Babcock Anlagen AG, and an "anaerobic thermal processor" (ATP) marketed by SoilTech, Inc.

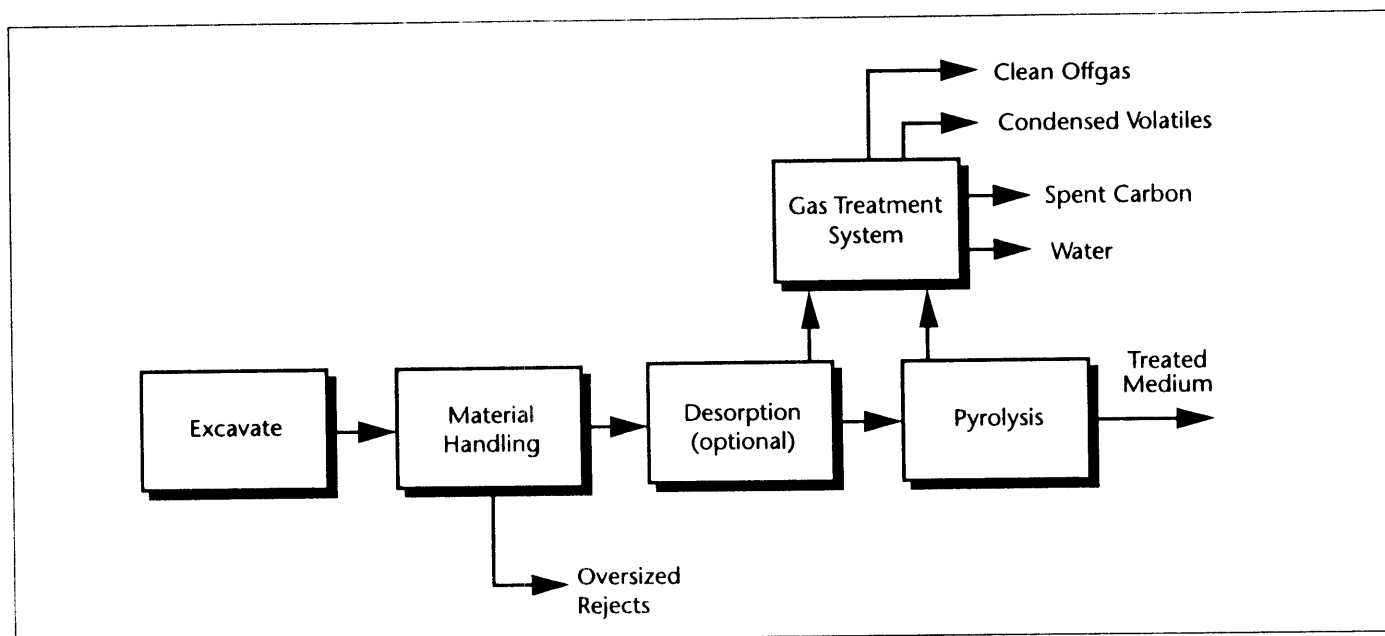
The HT-V Thermal Distillation System is a mobile thermal desorption system which may be operated in a pyrolytic mode. The Thermal Distillation System processes waste by applying heat in a nitrogen atmosphere. Gravity and a system of annular augers are used to transfer waste through a series of three electrically heated distillation chambers. The temperature is ambient at the entrance to the distillation chambers and increases to full operating temperature (up to 2,100°F) as the waste progresses through the chambers. The continuous introduction of a nitrogen sweep gas removes and separates the volatile contaminants [8, p. 3]. The sweep gas must be periodically sent to a flare to reduce the noncondensable combustible portion.

TDI is currently conducting bench-scale tests on the Thermal Degradation System, which was developed for use in conjunction with the Thermal Distillation System. The full-scale design of the system is currently theoretical, but TDI envisions that Thermal Degradation will follow Thermal Distillation and will be used primarily for pyrolysis. In recent bench-scale tests, the Thermal Degradation System was operated at approximately 2,000°F and a copper catalyst was used to enhance the pyrolysis of halogenated organics [2, pp. 3-6] [5, pp. 3-7].

A German company, Deutsche Babcock Anlagen AG, developed a pyrolytic process which utilizes an indirectly heated rotary kiln. In the first step of the Deutsche Babcock system, pyrolysis occurs at a temperature of 1,100 to 1,200°F. If volatile or semivolatile organics are present, they will be desorbed in this step. In the second step, the gases produced by pyrolysis (as well as other volatilized organics) are combusted in an afterburner at a high temperature (1,800 to 2,400°F). Heat produced during the second step may provide at least a portion of the energy for the first step, which is endothermic. Prior to discharge, effluent gases from the second step are scrubbed to remove various pollutants including hydrogen halides and sulfur oxides [1, p. 166].

The pyrolysis systems marketed by Deutsche Babcock are not currently available in mobile or transportable configurations and are therefore not directly applicable to onsite remediation of Superfund sites. These systems were included in this discussion to provide additional data and to indicate the potential viability of pyrolysis. In addition, full-scale applications and testing of the Deutsche Babcock system have included the cleanup of contaminated soils [1, pp. 165-168].

Figure 1. Schematic Diagram of Pyrolysis



Finally, SoilTech, Inc. (Canonie Environmental) markets an anaerobic thermal processor (ATP) which may be operated in a pyrolytic mode. The ATP is also known as the AO STRA-Taciuk process and is essentially an indirectly-heated rotary kiln. A transportable ATP with a nominal processing rate of 10 tons per hour is available for onsite demonstrations and remediation [9, p. 3].

The ATP unit includes four chambers: preheat, reaction, combustion, and cooling. In the preheat chamber, volatile materials are desorbed at temperatures up to 500°F. Pyrolytic conditions and temperatures between 700 and 1,150°F are maintained in the reaction chamber. The desorption and/or pyrolysis of heavier organics will occur in this chamber. Coke and noncombustible hydrocarbons produced by pyrolysis are transferred to the combustion chamber and burned [9, pp. A-1 to A-2]. Additional fuels such as gas or oil must be available for start-up, for control, and to supplement the pyrolysis products when they do not provide adequate fuel. Solids and gases from the combustion chamber proceed into the cooling zone. The cooling zone and the preheat zone function as a heat exchanger in which heat is transferred from the combustion residuals to the feed [10, p. 3].

Process Residuals

The effluents generated by pyrolytic systems typically include solid, liquid, and gaseous residuals. Solid products include debris, oversized rejects, dust, ash, and the treated medium. Dust collected from particulate control devices may be combined with the treated medium or, depending on analyses for carryover contamination, recycled through the treatment unit.

Depending on the individual system, the flue gases from the pyrolysis unit will generally be treated by wet or dry APC systems before discharge through a stack. In the Deutsche Babcock System, offgases are treated by incineration [1, p. 166].

Ash and treated soil/solids from pyrolysis may be contaminated with heavy metals. APC system solids, such as fly ash, may contain high concentrations of volatile metals. If these residues fail required leachate toxicity tests, they can be treated by a process such as solidification/stabilization and disposed of onsite or in an approved landfill [11, p. 8.97]. If the treated medium and ash pass all required tests, they may be disposed of onsite without further treatment.

Depending on the specific pyrolysis system, liquid streams may include condensed organics or water from the APC system. After organics are removed, condensed water may be used as a dust suppressant for the treated medium. Scrubber purge water can be purified and returned to the site wastewater treatment facility (if available), discharged to the sewer, or used for rehumidification and cooling of the hot, dusty media.

Liquid waste from the APC system may contain excess alkali, high chlorides, volatile metals, organics, metals particulates, and inorganic particulates. Treatment may require neu-

tralization, chemical precipitation, settling, filtration, or carbon adsorption before discharge.

Site Requirements

Pyrolytic treatment processes are not expected to have significantly different site requirements than those for thermal desorption or incineration processes.

Note that the pyrolytic systems marketed by Deutsche Babcock are not currently available in mobile or transportable configurations. The HT-V system and the ATP are transportable, and vendors claim that they can be set up in a matter of days.

Standard site requirements include electric power (440 or 480 V, 3-phase) and water. The quantity of water required is design- and site-specific.

Treatment of contaminated soils or other waste materials require that a site safety plan be developed to provide for personnel protection and special handling measures. Storage should be provided to hold the process product streams until they have been tested to determine their acceptability for disposal or release. Depending upon the site, a method to store waste that has been prepared for treatment may be necessary. Storage capacity will depend on waste volume.

Onsite analytical equipment capable of monitoring site-specific organic compounds for performance assessment make the operation more efficient and provide better information for process control.

Performance Data

Limited performance data are available for pyrolytic systems treating hazardous wastes containing PCBs, dioxins, and other organics [1, pp. 165, 168] [2, pp. 9-14] [5, pp. 10-15] [6, p. 9]. The quality of this information has not been determined. These data are included as a general indication of the performance of pyrolysis equipment and may not be directly transferable to a specific Superfund site. Good site characterization and treatability studies are essential in further refining and screening the pyrolysis technology.

The HT-V system's performance on oily sludges contaminated with dioxins and PCBs was evaluated in bench-scale treatability tests conducted by Law Environmental on April 25, 1991 [2, pp. 9-14] [5, pp. 10-15]. The simulated waste used in the dioxin test was contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). A decontamination efficiency of over 99.99% was calculated, as no 2,3,7,8-TCDD was detected in the treated residue, offgases, or condensate. In addition, the test report claims that no significant quantities of new toxic compounds were synthesized by the process [2, pp. 9-14].

A second bench-scale treatability study was conducted on a mixture of PCB-contaminated soil, PCB-contaminated oil, and

water. All process streams were sampled and analyses indicated a decontamination efficiency of over 99.99%. PCB levels were below the detection limits in all effluent streams and the test report claims that no significant quantities of new toxic compounds were synthesized by the process [5, pp. 10-15]. Although these results appear promising, complete closures of mass balances are not possible with the information collected during the HT-V treatability tests.

The Deutsche Babcock system was tested in an industrial-scale demonstration in May and June 1988. Prior to this demonstration, the same system was used to treat 35,000 tons of soil. The plant is located in Unna-Bonen, West Germany, at a former coke oven site. The unit had a design rate of 7 tons/hour with a soil moisture content of 21 percent and 5 percent volatile compounds. The destruction of 17 polycyclic aromatics was measured. A system decontamination efficiency of 99.77 percent was achieved. The results are summarized in Table 2 [1, p. 168]. Note that this test was conducted in

Table 2
Deutsche Babcock Pyrolytic Rotary Kiln
Contaminated Soil Results

Date	March 8, 1989		January 27, 1989	
	Input mg/kg	Output mg/kg	Input mg/kg	Output mg/kg
Naphthalene	101.00	1.7	161.60	0.5
2-methylnaphthalene	40.20	0.5	73.80	0.1
1-methylnaphthalene	23.40	0.3	42.90	0.1
Dimethylnaphthalene	n.d.	n.d.	93.20	0.3
Acenaphthylene	n.d.	n.d.	68.20	0.1
Acenaphthene	n.d.	n.d.	42.30	0.1
Fluorene	156.00	0.1	238.00	0.1
Phenanthrene	686.00	0.6	1055.30	1.4
Anthracene	281.00	0.1	226.00	0.3
Fluoranthene	n.d.	n.d.	688.60	1.3
Pyrene	236.00	0.1	398.20	0.6
Benz[a]anthracene	155.00	0.2	2259.20	0.3
Chrysene	214.00	0.5	134.60	0.9
Benzo[e]pyrene	66.60	0.4	111.50	1.1
Benzo[b]fluoranthene	112.00	0.1	168.50	5.2
Benzo[k]fluoranthene	43.70	0.1	81.90	0.3
Benzo[a]pyrene	86.60	0.2	138.10	0.4
Dibenz[a, h]anthracene	16.80	0.1	23.20	0.1
Benzo[g, h, i]perylene	14.00	0.1	60.20	0.1
Indeno[1, 2, 3-cd]pyrene	33.80	0.1	69.50	0.1
Sum	2266.10	5.2	6134.80	13.4
n.d. = not detectable				
Decontamination efficiency in %	99.77		99.78	

Germany and that the majority of the applications of the Deutsche Babcock system have been in Germany. German requirements regarding incineration were not researched and may differ significantly from US requirements.

The Soiltech ATP is being used in conjunction with chemical dehalogenation to remediate the Wide Beach Superfund site. Much of the soil in the small community of Wide Beach, New York is contaminated with PCBs from road oils. PCB levels range from approximately 10 ppm to over 5,000 ppm; the primary cleanup requirement is to reduce PCB concentrations to less than 2 ppm [6, pp. 2-3].

The system used at Wide Beach is similar to the ATP described previously but also includes a reagent mix system. The reagent mix system adds dechlorination chemicals (potassium hydroxide and polyethylene glycol) to a stream of oils recycled from the system effluent [6, p. 4] [12, p. 45].

PCB concentrations in the treated soil were below the reporting limit of 70 ppb, which is significantly below the required level. In addition, the process water contained no more than 1 ppb PCBs, stack gas PCB levels were less than 33 percent of the New York State Department of Environmental Conservation (NYDEC) limits, fugitive emissions were within NYDEC limits, and treated soils passed the toxicity characteristic leaching procedure (TCLP) [6, pp. 2,9]. At the beginning of the cleanup effort, treated soil was returned to local sites. The treated soil, however, does not have the same consistency as untreated soil, and current plans are to landfill the soil rather than returning it to the original sites [12, p. 45].

Technology Status

Pyrolysis has been used to treat various hazardous wastes as documented in the Performance Data section of this bulletin. In particular, pyrolysis has been applied to the remediation of the Wide Beach Superfund site (in conjunction with chemical dehalogenation) [6, pp. 1-2] and to the cleanup of contaminated soils in Germany [1, pp. 165-168].

EPA Contact

Technology-specific questions regarding pyrolysis may be directed to:

Mr. Donald Oberacker
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
Telephone: (513) 569-7510.

Acknowledgments

This bulletin was prepared for the U.S. Environmental Protection Agency, Office of Research and Development (ORD), Risk Reduction Engineering Laboratory (RREL), Cincinnati, Ohio,

by Science Applications International Corporation (SAIC) under contract no. 68-C8-0062. Mr. Eugene Harris served as the EPA Technical Project Monitor. Mr. Gary Baker (SAIC) was the Work Assignment Manager, and Ms. Sharon Krietemeyer and Mr. Richard Gardner (SAIC) were co-authors of this bulletin. The authors are especially grateful to Mr. Donald Oberacker and Mr. Paul de Percin of EPA, RREL, who have contributed significantly by serving as technical consultants during the develop-

ment of this document.

The following other contractor personnel have contributed their time and comments by participating in the expert review meetings and/or peer reviewing the document:

Mr. James Cudahy
Dr. Steve Lanier

Focus Environmental, Inc.
Energy and Environmental
Research Corp.

REFERENCES

1. Schneider, D., and B.D. Beckstrom. Cleanup of Contaminated Soils by Pyrolysis in an Indirectly Heated Rotary Kiln. *Environmental Progress* (Volume 9, No. 3), pp. 165-168. August 1990.
2. Test Report of Bench Scale Unit (BSU) Treatability Test for Dioxin Contaminated Oily Sludge. Test Date: April 25, 1991. Prepared by Law Environmental, Inc. for Southdown Thermal Dynamics. June 1991.
3. The Superfund Innovative Technology Evaluation Program: Technology Profiles. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response and Office of Research and Development, Washington, D.C. EPA/540/5-90/006. November 1990.
4. Technology Screening Guide for Treatment of CERCLA Soils and Sludges. EPA/540/2-88/004, U.S. Environmental Protection Agency, 1988.
5. Test Report of Bench Scale Unit (BSU) Treatability Test for PCB Contaminated Oily Sludge. Test Date: April 25, 1991. Prepared by Law Environmental, Inc. for Southdown Thermal Dynamics. June 1991.
6. Vorum, M. PCB-Soil Dechlorination at the Wide Beach Superfund Site: The Commercial Experience of SoilTech, Inc. May 1991.
7. Incinerating Hazardous Wastes, H. M. Freeman, Editor. Technomic Publishing Co., Lancaster, PA 1988.
8. Southdown Thermal Dynamics, Marketing Brochures, circa 1990.
9. The Taciuk Process Technology: Thermal Remediation of Solid Wastes and Sludges. Technical Information. Submitted by SoilTech, Inc.
10. Ritcey, R. and F. Schwartz. Anaerobic Pyrolysis of Waste Solids and Sludges: The AO STRA Taciuk Process System. Presented to the Environmental Hazards Conference & Exposition, Environmental Hazards Management Institute, Seattle. May 1990.
11. Standard Handbook of Hazardous Waste Treatment and Disposal. H. M. Freeman, Editor. U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory. McGraw-Hill Book Company, New York, pp. 8.91-8.104.
12. Turning "Dirty" Soil into "Clean" Mush. *Soils*. September-October 1991.

United States
Environmental Protection Agency
Center for Environmental Research Information
Cincinnati, OH 45268

Official Business
Penalty for Private Use
\$300

EPA/540/S-92/010

BULK RATE
POSTAGE & FEES PAID
EPA
PERMIT No. G-35