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SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Emerging Technology Summary

Development of a Photothermal Detoxification Unit

There has long been interest in utilizing photochemical methods for destroying hazardous organic materials. Unfortunately, the direct application of classic, low temperature photochemical processes to hazardous waste detoxification is often too slow to be practical for wide spread use. Furthermore, low-temperature photochemical processes often fail to completely convert the targeted wastes to mineral products which are either harmless to the environment or easily scrubbed from the system effluent. Researchers at the University of Dayton Research Institute (UDRI) have developed a unique photothermal process that overcomes many of problems. Specifically, it has been found that there are numerous advantages to conducting photochemical detoxification at relatively high temperatures. Under the conditions of simultaneous exposure to heat and ultraviolet (UV) radiation the rate of destructive photothermal reactions can be greatly increased with complete mineralization of the waste feed. Furthermore, it has been demonstrated that at the elevated temperatures used in this process the efficiency of UV radiation absorption also increases resulting in an overall improvement in process efficiency. These features (i.e., fast, efficient, and complete destruction of organic wastes) make this a promising technique for destroying hazardous organic wastes in the gas-phase. The authors present the theoretical foundation for the photothermal detoxification process along with a summary of the results from a bench-scale flow reactor system. The basic design, capital cost, and operating cost for a full-scale flow reactor system using currently available industrial illumination equipment is also presented.

This Project Summary was developed by the EPA's National Risk Management Research Laboratory, Cincinnati, OH, to announce key findings of the SITE Emerging Technology that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

One approach to destroying hazardous organic wastes which has received considerable attention over the years is the use of photochemical reactions in place of conventional thermochemical or combustion reactions. Photochemical techniques have been of interest because photochemistry, the use of light to induce a chemical

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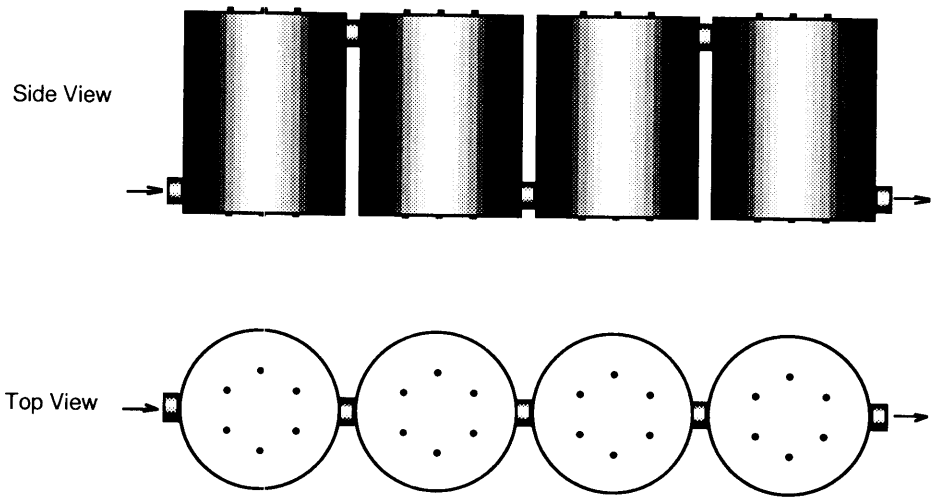
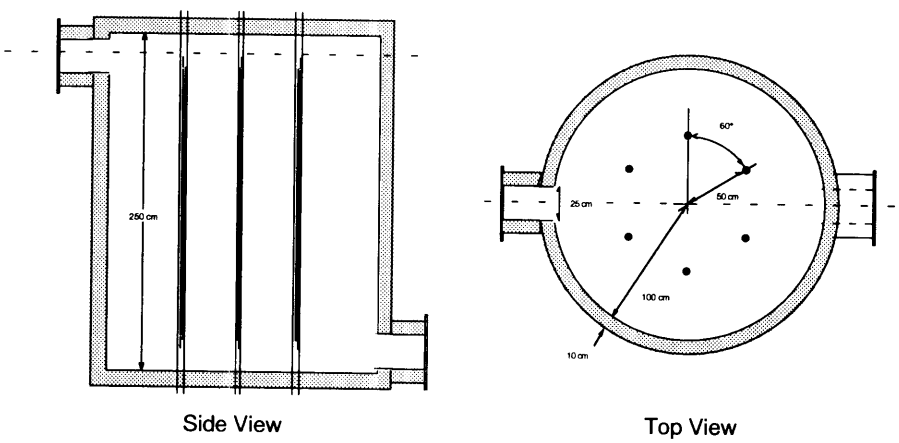
reaction, can be conducted at relatively low temperatures, often at or near room temperature. Unfortunately, most attempts to exploit photochemistry as a waste destruction technology have been frustrated by slow reaction rates and the inability to completely convert waste materials to mineral products. Specifically, conducting photochemistry at low temperatures often requires exposure times of minutes, hours, and even days to achieve meaningful levels of conversion. Furthermore, the products of the reactions are often other organic compounds rather than inorganic mineral compounds such as carbon dioxide, water, and hydrogen chloride. The University of Dayton Research Institute (UDRI) has developed a novel photochemical process, embodied in a device called a Photothermal Detoxification Unit (PDU), which overcomes these problems and offers an efficient means of destroying hazardous organic materials.

The PDU, illustrated in Figure 1, is a relatively simple device consisting of a thermally insulated vessel enclosing a set of large, medium-pressure, mercury vapor lamps. The purpose of the lamps is to provide an efficient source of near-UV radiation as well as heat for the process. Additional heat may be provided by unit operations upstream of the PDU, such as a thermal desorption unit, combustor, a dedicated preheater, or other operations. The basis for the PDU's operation is to use the near-UV radiation from the mercury vapor lamps to induce destructive photochemical reactions and to conduct these reactions at moderate temperatures (i.e., 200-600°C) so they proceed to complete mineralization quickly and efficiently. Since this process requires both light, as with conventional photochemical processes, and heat, it is referred to as a photothermal detoxification process. The



General Layout of a Four Chamber PDU



Chamber Details

Figure 1. *Conceptual schematic of a prototype Photothermal Detoxification Unit (PDU) based on a mercury arc lamp illumination system.*

result is a technology capable of destroying organic materials at temperatures much lower than thermal processing alone and at temperatures easily achievable through non-combustion means. Indeed, the temperature requirements for the system may already exist for many processes such as the thermal desorption of contaminants from soils.

Procedure

The specific exposure conditions of time, temperature, and radiant intensity will be largely dependent on the materials of interest and the required level of destruction. In general, these aspects of the PDU design and operation are brought together through a reactor performance model such as

$$f_r = \exp[-(k_{gnd} + k_{ab}\phi)t] \qquad (1)$$

where fr is the fraction remaining in the process stream exiting the PDU, kgnd is the rate of thermal reactions, k_{ab} is the rate of light absorption, ϕ is an efficiency term for the photothermal reactions referred to as the quantum yield, and t is the mean exposure time. In the PDU, the rate of thermal reactions should be relatively small, but it is important to explicitly include it for those cases where the system may be operated at higher temperatures and thermal reactions can become important. The rate of light absorption reflects the extent of overlap between the emission spectrum of the light source and the absorption spectrum of the waste. This term is also dependent on the intensity of the light source and the number of lamps used. The quantum yield is an efficiency term describing what fraction of the light absorbed actually results in destruction of the waste feed. Finally, the mean exposure time reflects the size of the PDU and the rate of flow through the system. Note that all of these terms lie in the exponent of Equation 1 and therefore can have a powerful influence on the performance of the PDU.

Other reactor performance models may be used to describe the PDU, but all share the same basic features of Equation 1. Specifically, to predict the performance of the PDU, and hence define a system for a given application, it is necessary to have knowledge of the thermal chemistry (k_{gnd}), the photochemistry (ϕ), and the UV absorption behavior (k_{ab}) of the system. Furthermore, all of these aspects of the PDU are expected to be functions of temperature. Unfortunately, since the PDU operates under unique circumstances, none of the required high-temperature spectroscopic and photochemical data is available from the literature. Therefore, researchers at UDRI designed and built a High Temperature Absorption Spectrophotometer (HTAS) to obtain the necessary spectroscopic data, and a Laboratory Scale-Photothermal Detoxification Unit (LS-PDU) for the basic thermal and photothermal information. The latter was particularly useful for demonstrating the effectiveness of the photothermal process.

The HTAS, shown in Figure 2, is a custom built, single-beam spectrophotometer capable of operating at temperatures as high as 1,000°C. Since the organic molecules for which the HTAS was designed to study tend to decompose with prolonged exposures at elevated temperatures, the system is fitted with a flow cell rather than a static cell found in most commercial spectrophotometers. Furthermore, an inert carrier gas (i.e., nitrogen) is used for sample transport to eliminate the possibility of sample oxidation. By flowing a carrier gas laden with the sample of interest through the cell the length of exposure to elevated temperatures can be kept short (typically 1 sec) to limit destruction of the sample at very high temperatures.

The LS-PDU, shown in Figure 3, is a dedicated flow reactor system capable of obtaining thermal and photothermal decomposition data on a great variety of compounds. Structurally, the LS-PDU shares many features with the HTAS. For example, the LS-PDU includes dual sample inlets connected to a cylindrical vessel through a single sample transfer line. However, whereas the HTAS was design to prevent reactions from taking place in the system, the LS-PDU was designed to conduct reactions under carefully defined conditions and analyze the products of those reactions. For this purpose the vessel connected to the inlet line

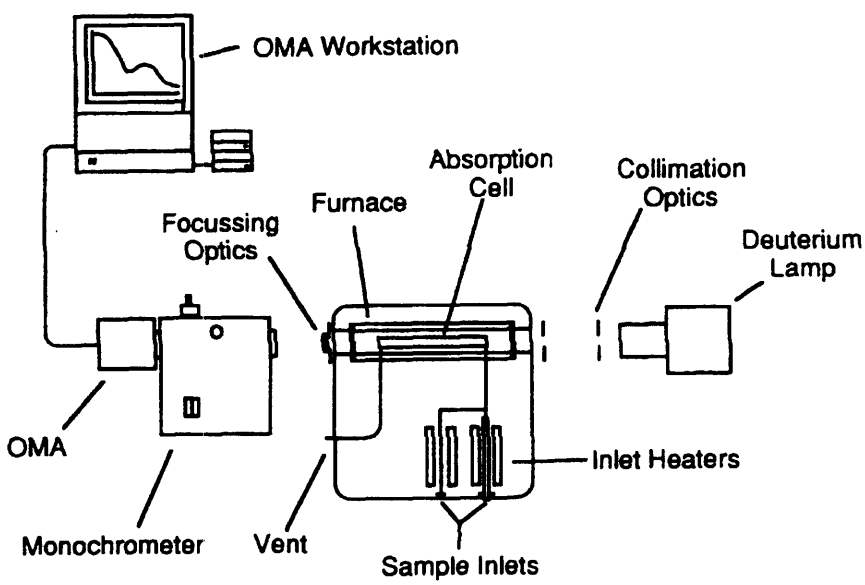


Figure 2. *General schematic of the High Temperature Absorption Spectrophotometer (HTAS) showing the principal elements of this system.*

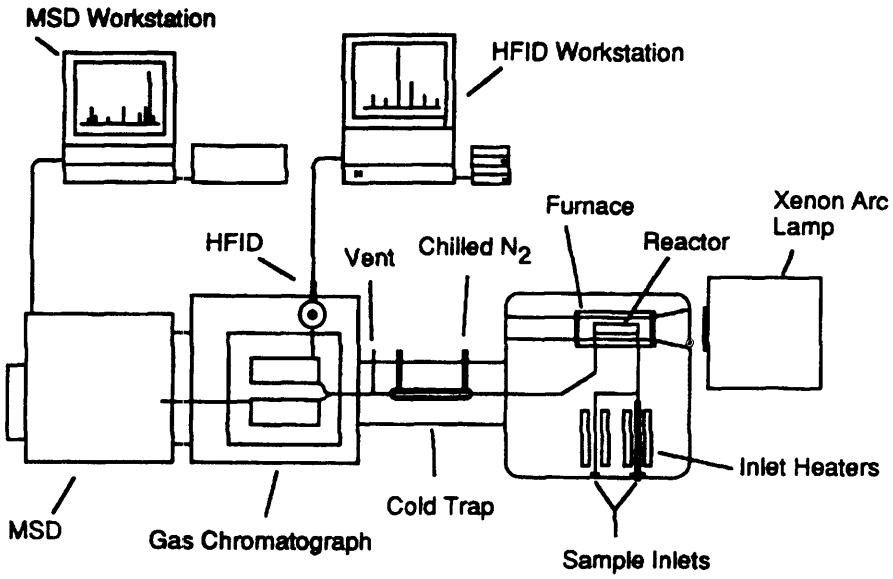


Figure 3. *General schematic of the Laboratory Scale-Photothermal Detoxification Unit (LS-PDU) showing the principal elements of this system.*

is a small cylindrical reactor measuring 1.2 cm in diameter by 8.4 cm long. The exhaust from the reactor flows through a heated transfer line to a trapping system which collects all of the condensable materials from the flowing gas. This trap is a single tube-in-shell design similar to a laboratory condenser. The shell side is cooled with nitrogen gas which has in turn been cooled by a liquid nitrogen bath. This allows the trap to operate at temperatures as low as -180°C, though -160°C is routinely used. During the effluent collection phase of operation the exhaust from the trap is vented to a fume hood. In preparation to analyze the collected material, this vent is closed which directs the flow of gas to an inline analytical system consisting of a programmed temperature, capillary column gas chromatograph (GC) fitted with dual columns and an inlet splitter. One of the columns is connected to a scanning quadrapole mass spectrometer (MS), the other to a hydrogen flame ionization detector (FID). The LS-PDU may be operated at temperatures as high as 1,000°C and used with nearly any UV radiation source. It is currently configured with a pulsed dye laser, solar simulator, and a high pressure xenon arc lamp.

All samples used in the tests described below were high purity standards (typically 99+%) obtained from commercial suppliers.

Results and Discussion

Conducting photochemical detoxification at elevated temperatures improves the overall efficiency of the process in three important areas; the spectroscopy, the rate of destruction, and the completeness of the destruction.

The impact of temperature on the spectroscopy is illustrated by the high temperature absorption spectra for trichloroethylene (TCE) shown in Figure 4. For comparison, the emission spectra for high-pressure, xenon arc (which was used on the LS-PDU) and medium-pressure, mercury vapor lamp (proposed for the PDU) are shown in Figure 5. The data summarized in Figure 4 show that as the temperature increases, the absorption spectrum shifts to longer wavelengths and increases in overall intensity. The net result is that the overlap between the emission spectrum of the light source and the absorption spectrum of the sample increases with temperature. In the case of TCE, the rate of photon absorption with xenon arc as the radiation source, increases over 8-fold as the temperature increases from 100 to 600°C. Recalling that the reactor performance model suggests an exponential dependence on the rate of absorption, this is a very significant feature of the photothermal process.

The most important aspect of the photothermal process is whether the light absorbed by the waste feed results in the destruction of the waste feed. The LS-PDU data for TCE exposed to 18.1 W/cm^2 of xenon arc radiation for 10 sec in air (summarized in Figure 6) show that is indeed what happens. Specifically, this example clearly shows the photothermal process is capable of destroying a significant portion of the TCE under conditions where no thermal destruction is occurring. For example, at 500°C the thermal decomposition has not yet begun, while the photothermal process has destroyed approximately 60% of the sample.

The data presented in Figure 6 seem to suggest that the thermal and photothermal processes become equally efficient at high temperatures (i.e., above 600°C). However, this is in fact an artifact of how the data is presented. If we compare the ratio of the fraction remaining undestroyed from a thermal exposure to the fraction remaining from a photothermal exposure (a value referred to as the photothermal enhancement ratio), we find the photothermal process actually continues to improve over the comparable thermal process throughout the temperature range (cf. Figure 7).

The results for TCE illustrate that it is important to utilize a reactor model that explicitly includes the thermal component of the photothermal process so that the two components may be separated in the course of interpreting data from the bench-

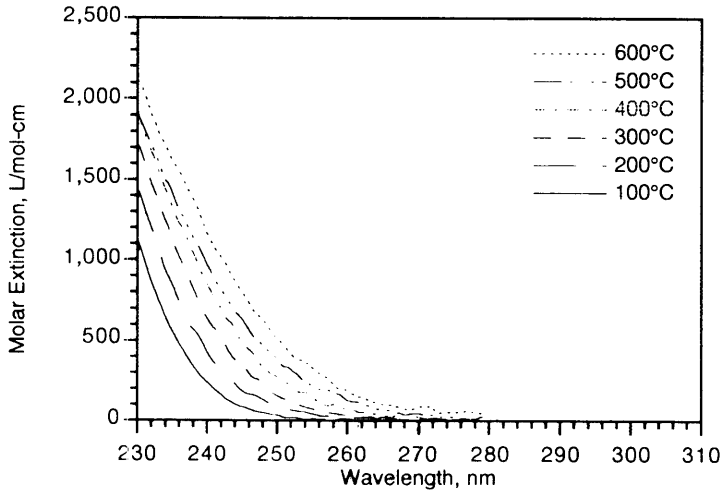


Figure 4. *The absorption spectra for trichloroethylene at 100, 200, 300, 400, 500, and 600°C showing that the absorption shifts to longer wavelengths and increases in intensity as the temperature increases.*

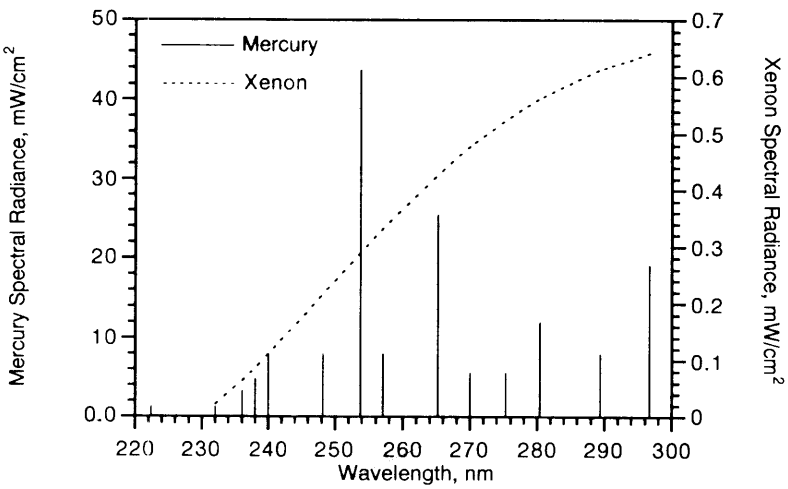


Figure 5. *The spectral radiance of 1W/cm² of medium pressure mercury and high pressure xenon arc emission showing the xenon arc spectrum (approximately 2.5% of which is at wavelengths less than 300 nm) is spread out as broad-band emission, while the mercury arc spectrum (of which approximately 15% is at wavelengths less than 300 nm) is concentrated in narrow emission lines.*

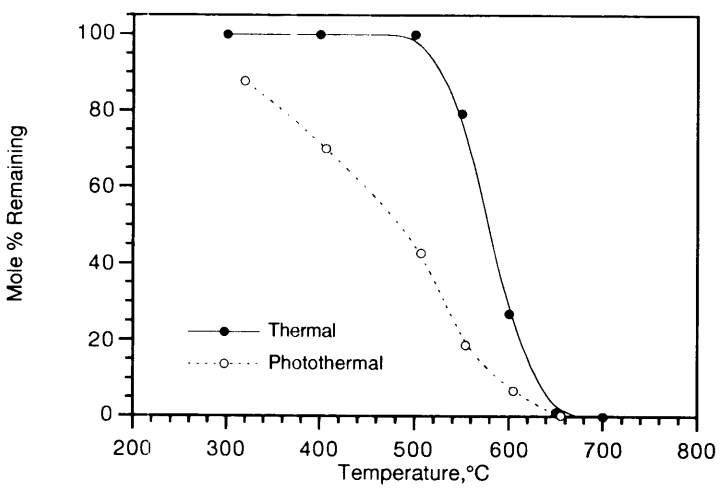


Figure 6. *Conversion as a function of temperature for trichloroethylene exposed to 0 (thermal) and 18.1 W/cm² (photothermal) of xenon arc radiation for 10 sec in air showing that the photothermal process can induce destructive photochemical reactions at relatively low temperatures.*

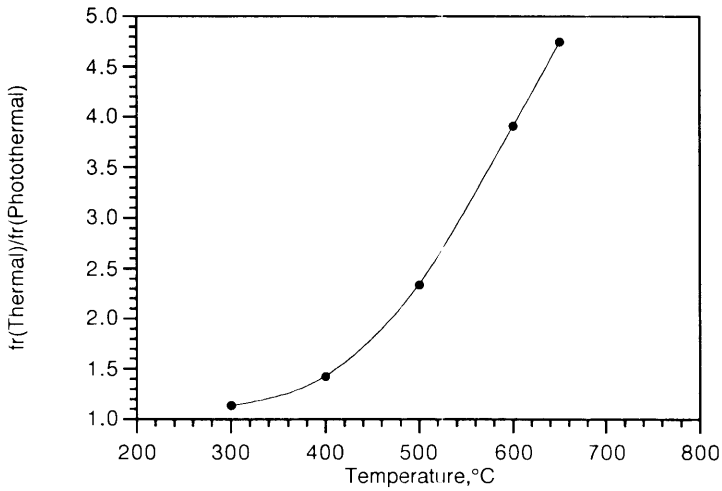


Figure 7. *The ratio of the fraction remaining following thermal and photothermal exposures for trichloroethylene exposed to 0 (thermal) and 18.1 W/cm² (photothermal) of xenon arc radiation for 10 sec in air showing that the photothermal process steadily increases in efficiency compared to the thermal process as the temperature increases.*

scale system. In this way, fundamental information can be obtained to predict the performance of full-scale systems. Although the results for TCE demonstrate that the exposure conditions used in the bench-scale system are probably inappropriate for a full-scale system, the data are still valuable for the fundamental information contained. The thermal data yield information about the thermal decomposition needed for the PDU model, and the spectroscopy (ca. Figures 4 and 5) gives the light absorption rate information. When this information is combined with the photothermal destruction data, the quantum yield can be extracted as shown in Figure 8. These results illustrate that the rate of destructive photochemical reactions is increasing with temperature (the decrease in quantum yield between 550 and 600°C is thought to result from competing thermal reactions which become significant in this temperature region). Recalling that the rate of photon absorption also increases with temperature, the data clearly show the importance of high temperature in the photothermal process.

The last important aspect of the photothermal process is its ability to completely mineralize the waste feed (i.e., convert to mineral products of complete conversion such as carbon dioxide, water, hydrogen chloride, etc.). The data for 1,2,3,4-tetrachlorodibenzo-p-dioxin (TCDD) shown in Figure 9 demonstrate that the photothermal process can easily destroy this type of hazardous material which has traditionally challenged conventional waste destruction techniques. The efficiency of the photothermal process is clearly shown in the enhancement ratio data summarized in Figure 10. As in the case of TCE, the photothermal enhancement increases throughout the temperature range and by 600°C it reaches a value of nearly 1,300. In addition to demonstrating the high efficiency in destroying TCDD, this data set allows direct observation of how a photothermal reactor behaves when operating in a predominantly photo mode (as compared to a combined photo/thermal mode as in the case of the LS-PDU data for TCE). It is instructional to examine the chromatograms from these tests.

LS-PDU GC/FID traces from thermal exposures at 300°C (100% remaining) and 600°C (35.4% remaining), and a photothermal exposure at 600°C (0.0285% remaining) for TCDD are summarized in Figure 11. The 600°C thermal data illustrate the production of numerous PICs that often accompany the thermal decomposition of organic compounds. The photothermal trace clearly shows that not only is the parent TCDD destroyed under these conditions, but nearly all of the associated products as well. Furthermore, the data shown here include all products that were condensable at -160°C (the temperature at which the LS-PDU's effluent trap was operated), so that all but the lightest organic products (such as methane and ethane) are recovered. This emphasizes that the photothermal process differs significantly from conventional direct photochemical processes in that photothermal decomposition reactions lead to the complete mineralization of the waste feed.

With the available laboratory- and bench-scale reactor data, it is now possible to predict the performance of a full-scale PDU, given the geometry of the reactor and the emission characteristics of the illumination system. In the PDU in Figure 1, the basic reactor vessel is shown as a cylinder measuring 2.5 m (8.2 ft) tall and 2m (6.6 ft) in diameter giving an internal volume of 7.85 m³ (277 ft³). The illumination system consists of six medium pressure mercury lamps delivering 15 kW of radiant energy each with a nominal arc length of 2 m (6.6 ft). This gives a mean radiant intensity of 1.23 W/cm² with a near-UV spectral distribution (cf. Figure 5). Performance estimation using a tanks-in-series model suggests that a complete PDU system should consist of four such vessels connected in series. In this arrangement the system performance would approach that of a plug flow reactor, which would offer the highest theoretical destruction efficiency. Therefore, the PDU system would have an internal volume of 31.4 m³, or approximately 1,100 ft³. Larger capacity can be achieved by operating additional chambers in series, or sets of chambers in parallel.

The performance of a four-chamber PDU expressed in terms of the estimated capacity achieving 99% destruction in actual ft³/min for selected compounds is summarized in Table 1. These results indicate that for volatile organic compounds, the PDU should be operated at temperatures greater than 500°C and throughputs on the order of 1,000-3,000 cfm can be expected. The performance for semi-volatiles may be much greater, both in the allowable temperature range (greater than 300°C) and capacity (2,000 to 6,000 cfm). This illustrates that the PDU is capable of processing VOCs at high temperatures and is particularly well suited for semi-volatile compounds where it can be operated at lower temperatures. Furthermore, there are other types of lamps which may be used (i.e., low pressure mercury, xenon excimer, etc.) which could give better performance for volatile compounds.

The overall capital and operating costs for the PDU chamber illustrated in Figure 1 were calculated as summarized in Table 2. In this table the costs for the shell and insulating firebrick where taken to be similar to that reported for a hazardous waste incinerator afterburner and corrected to 1995 costs. The cost for the lamps, lamp wells, and lamp ballasts were taken from the manufacturer's literature. These esti-

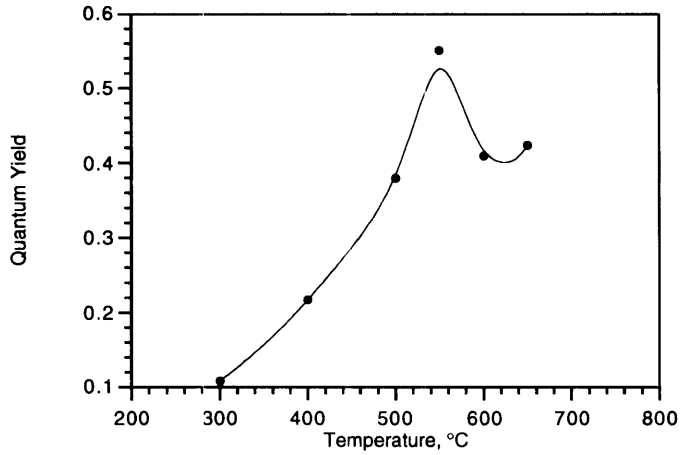


Figure 8. *The photothermal quantum yield for trichloroethylene illustrating the rate of the photochemical reactions increasing with temperature. The observed increase in the overall efficiency of the photothermal process is a result of this increase in the reaction rate and the increase in the efficiency of near-UV light absorption.*

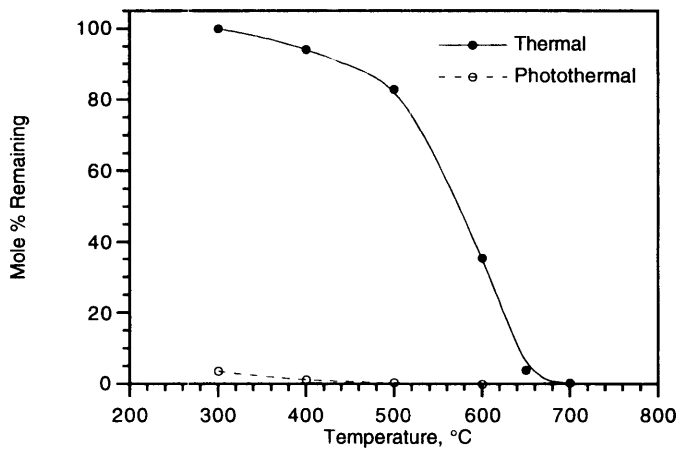


Figure 9. *Conversion as a function of temperature for 1,2,3,4-tetrachlorodibenzo-p-dioxin exposed to 0 (thermal) and 18.1 W/cm2 (photothermal) of xenon arc radiation for 10 sec in air showing that the photothermal process can destroy this compound to very high levels at relatively low temperatures.*

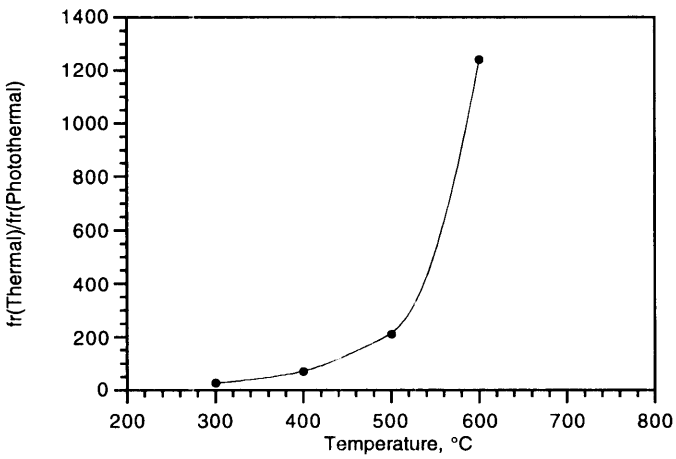


Figure 10. *The ratio of the fraction remaining following thermal and photothermal exposures for 1,2,3,4-tetrachlorodibenzo-p-dioxin exposed to 0 (thermal) and 18.1 W/cm^2 (photothermal) of xenon arc radiation for 10 sec in air showing that the photothermal process steadily increases in efficiency compared to the thermal process as the temperature increases.*

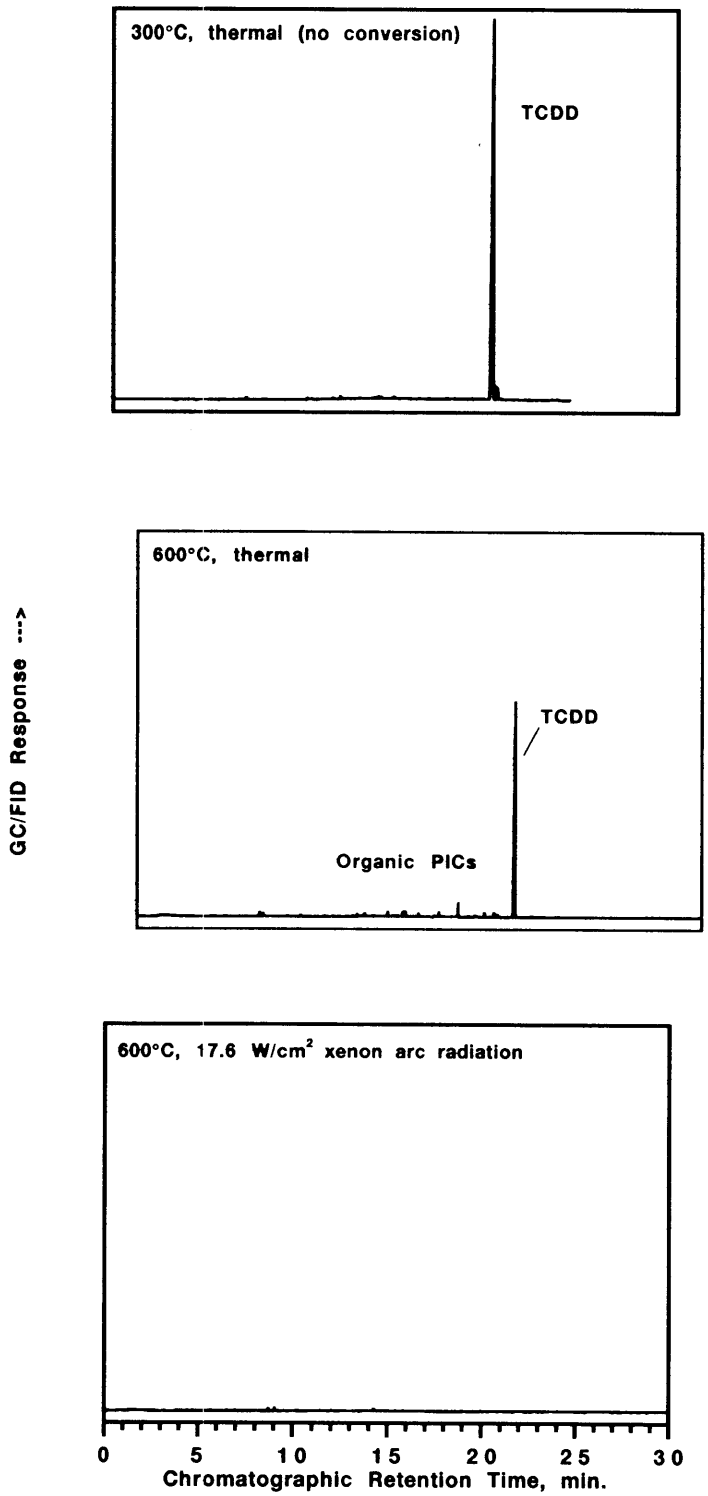


Figure 11. *Example GC/FID chromatograms from TCDD exposed to 300 thermal, 600 thermal, and 600°C photothermal (17.6 W/cm²) for 10 sec in air showing that the photothermal process destroys the complex mixture of PICs (or prevents their formation) as well as the parent compound.*

Table 1. *Estimated PDU[1] Capacity[2] for Selected Compounds*

Compound	Temperature (°C)			
	300	400	500	600
Trichloroethylene	131	384	937	2,590
m-Xylene	53	60	158	1,900
Chlorobenzene	98	131	427	1,730
1,2,3,4-Tetrachlorodibenzo-p-dioxin	2,190	2,504	3,300	5,780

[1] Four 2.5 x 2 m chambers fitted with six 15 kW medium pressure mercury lamps.
[2] Expressed as actual cubic feet per minute achieving 99% destruction.

Table 2. *Estimated Costs for a Single PDU Chamber Fitted with Six 15 kW Medium Pressure Mercury Lamps*

Item	Cost	Expected Life	Annual Cost
Carbon Steel Shell	$20,800 [1]	20 years	$1,040
Firebrick Insulation	$1,370 [2]	5 years	$274
Lamp Wells	$8,400	2 years[3]	$4,200
Lamp Ballasts	$8,500	4 years[4]	$2,125
Support Structure	$8,500 [5]	20 years	$425
Sub Total	$47,570		$8,064
Lamps	$3,000	6 months[6]	$6,000
Sub Total	$50,570		$14,064
Electrical Service[7]			$22,500
Grand Total			$36,564
Hourly Cost[8]			$7.31

[1] Assuming $86/ft^2
[2] Assuming $1.44/ft^2-in.
[3] Assuming 10,000 hr life and 5,000 hr of operation/yr.
[4] Assuming 20,000 hr life and 5,000 hr of operation/yr.
[5] Assuming support structure and equipment is 20% of the chamber cost less support.
[6] Assuming 2,500 hr life and 5,000 hr of operation/yr.
[1] Assuming $0.05/kW-hr and 5,000 hr of operation/yr.
[8] Assuming 5,000 hr of operation/yr.

mates suggest the majority of the capital costs will be in fabricating the reactor shell, followed by the lamp wells, ballasts, and the system support structure and equipment.

With respect to the amortized costs (using a simple linear depreciation model), Table 2 suggests the most expensive component will be the lamps and the lamp wells. The 2,500 hr used for the lamp life was based on the manufactuer's estimate assuming 5 hr of operation for every lamp start. Discussions with lamp manufacturers indicate that since the lamps will likely see continuous service in the PDU, significantly longer service life is likely. This should reduce overall cost of the lamps and, hence, the operating costs of the PDU. The second highest amortized cost is the lamp wells which are expected to degrade from attack from dust and water vapor. The cost estimates assume the lamp wells are replaced with new wells for every 10,000 hr of operation. If the wells can be replaced with refurbished units, this cost could be reduced.

With respect to consumable materials only electricity for the lamps is considered here. As Table 2 illustrates, electricity is the largest single contributor to the overall cost of the PDU. The relatively high electrical energy requirement comes from the fact that only about 15% of the electrical energy is converted to useful near-UV radiation. If other lamps are made available, such as low pressure mercury or xenon excimer, this cost could be considerably reduced by the thermal contribution to the system from the lamps. Specifically, in a well insulated vessel the 90 kW supplied to the chamber by the six 15 kW lamps is sufficient to heat approximately 600 cfm of air saturated with water vapor (as from a soil vapor extraction unit) from 15°C to 500°C. Therefore, depending on the specific site requirements, the heat from the lamps should reduce the size of a preheater, or even eliminate one entirely. The estimate summarized in Table 2 suggests the overall operating cost for a PDU based on the design presented in Figure 1 should be approximately $8/hr-chamber including the depreciation of the equipment, replacement lamps, and required electrical service.

Conclusions and Recommendations

In summary, the photothermal detoxification process offers a technologically simple and effective means of destroying organic materials in gaseous process streams. It is a non-combustion process, so additional fuel and gases (e.g., combustion air) are not required, though in some cases (e.g., low temperature processes such as soil vapor extraction) a preheater may be needed. Furthermore, the process efficiency is not dependent on initial concentration making it ideally suited for dilute waste streams. Results from bench-scale tests show that the process is exceptionally efficient in destroying semi-volatile wastes such as dioxins which suggests similar results may be expected for related compounds such as polychlorinated biphenyls and dibenzofurans. Estimated capital and operating costs suggest the photothermal process should be relatively economical to implement using currently available industrial illumination systems and hardware, and that future advances in near-UV illumination systems should reduce the overall cost even further. Given these results it is recommended that the PDU be advanced to the level of a pilot-scale demonstration at an appropriate Superfund site.

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***Chien T. Chen** is the EPA Project Officer (see below).*
The complete report, entitled "Development of a Photothermal Detoxification Unit," (Order No. PB95-255733; Cost: $27.00, subject to change) will be available only from:

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The EPA Project Officer can be contacted at:

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