

Treatment of Contaminated Water, Air and Soil With UV Flashlamps

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A new and effective method has been developed for the treatment of VOC's, PCB's and other toxic organics. Direct UV photolysis of organics is achieved with this new method with the use of high intensity ultraviolet light of a broad UV spectrum. Standard and novel UV flashlamps can be used for generation of this broad UV spectrum. The pulsing nature of such spectrum helps to increase the efficiency of destruction of toxics. The final products of this destruction process are non-toxic simple compounds. The energy efficiency of this new process exceeds that of traditional UV aided processes with medium pressure mercury lamps. This article reviews the Direct UV Photolysis Process, gives experimental results, and provides recommendations for applications in the treatment of groundwater, wastewater, contaminated air and soil.

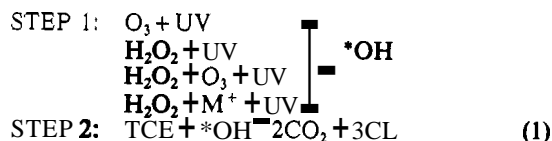
INTRODUCTION

Treatment of aqueous solutions containing toxic organics is of widespread concern in industry. Enormous quantities of groundwater are contaminated with volatile organic compounds (VOC's) such as trichlorethylene (TCE), benzene, toluene, xylene, etc. Additionally, many manufacturing facilities produce wastewater containing polynucleoaromatics (PNA), PCB's etc., which, if not properly contained, contaminate surface water, air and/or soil. Established methods of toxic treatment have to be re-evaluated under increasingly restrictive regulations.

Ultraviolet technologies offer the advantage of being very effective when compared to other processes because the UV-aided process totally destroys the contaminants leaving no residue. Other traditional technologies, such as filtration of contaminated water or the use of air stripping towers simply transfer toxic contaminants from one environmental medium to another, e.g. from water to air. Each traditional UV technology has its advantages and limitations, reviewed in [1] and briefly described in two sections below as first and second generation UV systems.

First Generation UV Systems

The basis of these first generation UV technologies is the use of 254 nm light emitted by conventional mercury vapor lamps. This line generates active radicals from peroxide or from ozone which are added during treatment to contaminated water. Some established systems, such as those produced by Peroxidation Systems (PSI) and ULTROX, require that the peroxide or ozone be thoroughly mixed with the water being treated [1,2,3]. The mixture must also be kept under UV light until the oxidants are converted into free radicals, which subsequently destroy toxic organics. This is a conventional advanced oxidation process (AOP) which, for example, for destruction of TCE is known to be as follows:



Where STEP 1 has one of 4 choices.

The traditional UV assisted process shown above has three drawbacks [1]:

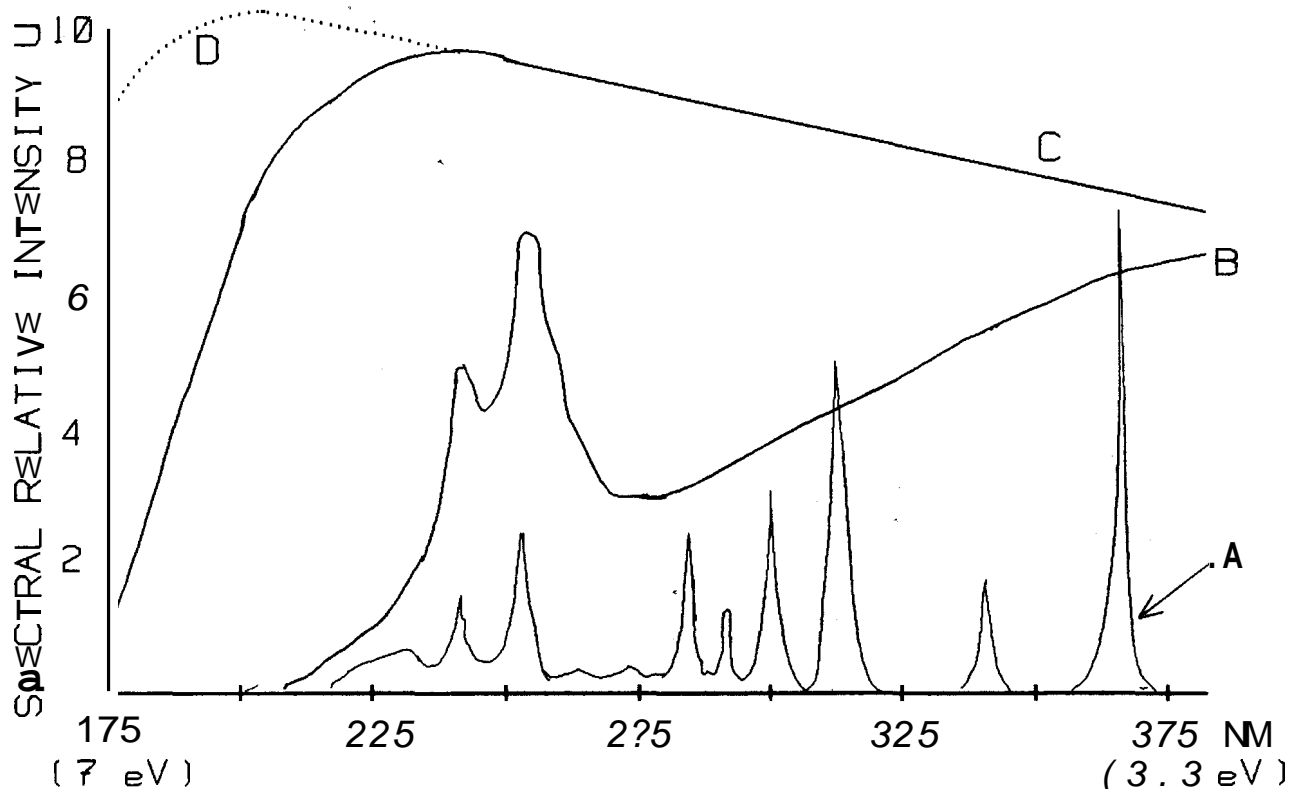


FIGURE 1. Spectral distributions in the region from 175 nm to 375 nm for four UV sources (A, B, C and D) in relative units U . Corresponding maximum and minimum photon energies for the region are given in eV ($1 \text{ eV} = 1.6 \cdot 10^{-19}$ Joules, $1 \text{ nm} = 10^{-9} \text{ m}$).

A. Medium pressure mercury lamp at the electrical load of 60 watt per lamp cm.

B. Xenon flashlamp, 450 Torr, arc length 5 cm, current density 8700 A/cm^2 , bore diameter 4 mm, energy 45 Joules, pulse duration $125 \mu\text{sec}$ [9, part 2]. The UV output at these power conditions is close to the maximum one can get from a xenon flashlamp.

C. Optimal spectra of a UV pulsed lamp. This curve is a fair approximation of the output from the WEKHOF lamp [10] at 60 watts per lamp cm.

D. Black body radiation at the same conditions as C. This is the maximum radiation for a plasma temperature achieved during tests and contains photons with energies which are absorbed by quartz.

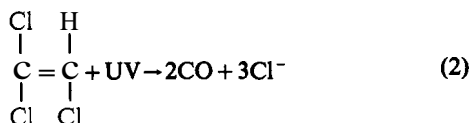
1) An excess of oxidants added in the treated stream can interfere with process flow or materials.

2) Reaction times in the processing chamber are prolonged, allowing for precipitates to form on the lamps and reduce the light supply.

3) These processes require large units. Another drawback of such an approach is its limitation to contaminants in water. There are only limited data on its use for soils and air.

Second Generation UV Systems

UV photons are also capable of destroying organic toxics directly without the use of additive oxidants by breaking chemical bonds in organics through photodissociation. Such process requires photon energies from 4 eV to 7 eV (their wavelengths from 300 nm to 175 nm respectively, where $1 \text{ eV} = 1.6 \cdot 10^{-19}$ Joules). For example, a direct UV photolysis of TCE is shown as follows:



For dissociating to occur, the UV wavelength must match up with the absorption band of the target contaminants. An absorption band can be as narrow as 1 nm or as wide as 20 nm. Each toxic contaminant has an optimal wavelength for photodissociation where its effectiveness, described by the molar extinction coefficient ϵ , is the largest [4]. For example, benzene absorbs strongly at 184 nm ($\epsilon = 47,000$) and at 202 nm ($\epsilon = 7,000$) plus has series of weak absorption bands between 230 nm and 270 nm ($\epsilon \approx 300$). Acetone has absorption bands at 220 nm ($\epsilon = 16,000$) and 318 nm ($\epsilon = 30$), while TCE has a strong band around 230 nm.

If a complex organic undergoes photodissociation, it may have byproducts which can also be toxic while its absorption bands are most likely differ from ones of the original organic. For that reason a further photodissociation is necessary until only non-toxic byproducts are left. This condition, as well as a presence of many different toxics in media, requires a dense structure of UV emission lines to support effectively the direct photolysis.

There are very limited choices of UV line sources which can do this job effectively. In fact, first generation UV sources generate only a very few lines in the shortwave UV region, and the strongest is the 254 nm line from mercury vapor lamps [1, 5]. Traditional medium and high pressure mercury vapor lamps having input powers over 200 watt/inch [80 watt/cm]

generate few other lines including 248, 265, 280, 297 and 302 nm, Figure 1a. Thus even high power medium pressure mercury vapor lamps cannot break most chemical bonds directly due to the limited available wavelengths not matching absorption bands of the targeted organics.

The number of UV lines in the deep UV region can be somewhat increased with dopants like iodide³ and magnesium placed into medium or high pressure mercury lamps [5]. Such lamps are known as metal halide lamps. Dopants in such lamps can be selected to fill wavelength gaps between mercury lines. Systems which employ lamps with dopants (SOLARCHEM systems is the best example [6]) are more effective than the first generation UV systems [7]. These systems are able to treat organic toxics both with and without adding an oxidant, i.e. they destroy toxics either in accordance with reaction (1) or with (2) or both. Adding peroxide combined with the adding a photocatalyst to increase its efficiency helps to double the overall process efficiency of such systems. That is because UV lines which dissociate peroxide are different from UV lines which dissociate targeted organic toxics. Thus, when an oxidant is used, mercury lamps with dopants have more efficient use of UV energy as well as better oxidizing byproducts, which cannot be broken further due to the lack of necessary emission lines in the lamp spectra.

Wekhof Process—The Third Generation UV Systems

The use of dopants in UV lamps has its limitation for creating additional UV lines to match absorption bands of selected toxics. In fact, any UV lamp with line emission does not have a sufficient number of UV lines which will effectively support direct photolysis in a media where many toxic compounds are present.

The alternative to the lamp with a line emission is the source of the **UV continuum** which overlaps absorption bands of all toxics present. If the UV continuum has sufficient intensity it can destroy all organics in a medium through the direct photolysis (2). The process can achieve a complete disintegration of toxics into non-toxic byproducts. Byproducts can be oxidized since oxygen is usually dissolved in water and is abundant in both air and soil. In the case of water treatment a peroxide can be added to increase the process efficiency.

The following sections describe the process, experimental results and recommendations for applications in groundwater, wastewater, contaminated air and soil.

EXPERIMENTAL

Sources of UV continuum

A broad UV spectrum similar to UV continuum and having a sufficient intensity can be generated by various pulsed devices [5]. Out of all such devices xenon and custom build flashlamps are the most simple and cost-effective for destruction of toxic organics. Standard xenon flashlamps generate a close to the required spectrum. Flashlamps are pulsed devices where xenon gas is converted to a plasma and heated by a short pulse of electric current. In order for a lamp to operate properly, one has to run it at nominal parameters where the lamp current density j and the pulse duration τ fall into ranges such as $1 \text{ kA/cm}^2 < j < 5 \text{ kA/cm}^2$ and $150 \text{ psec} < \tau < 1 \text{ msec}$. In this case, xenon plasma temperature ranges from $6,000^\circ \text{K}$ to $9,000^\circ \text{K}$ and emit from 5% to 8% of all radiation below 300 nm respectively [5, 8, 9].

A dramatic increase in UV output for all wavelengths below 300 nm occurs if a xenon flashlamp is operated under a severe stress with a current density j in the range from 6 kA/cm^2 to 14 kA/cm^2 [8,9]. A corresponding spectrum (for $j = 8.8$

kA/cm^2) is presented on Figure 1b. However, such operating conditions shorten the life of the lamp (reduces the total number of flashes) by up to 100-fold or more. A trade-off can be achieved between the UV output, the lamp lifetime and operating costs for toxic treatment. The desirable and in principle achievable UV spectrum of a flashlamp is presented on Figure 1c [10].

Description of the test apparatus

The block diagram of the experimental apparatus is presented on Figure 2. In our initial tests, we used a standard xenon flashlamp with a bore diameter of 7 mm and with a discharge gap of 6 inches (15 cm). The lamp was loaded from a pulse forming network (PFN) where a capacitor C (5 or 10 μF) was charged to voltage of $V = 3 \text{ kV}$ and then discharged into the lamp through an electronic switch (silicon controlled rectifier, SCR). In later tests we used a custom designed UV flashlamp with a spectra similar to the one on Figure 1c [10].

Our circuit provided the rate of current rise dI/dt up to 300 $\text{A}/\mu\text{sec}$, peak currents I up to 3 kA and the current density from 6 kA/cm^2 to 12 kA/cm^2 . Another capacitor C and a charging voltage V can be used to achieve the same current density as well. However, smaller peak currents and smaller dI/dt will result in a lesser UV output.

Treated water (or air) was moved through a quartz processing chamber (3 cm in diameter, 20 cm long) placed alongside the lamp. The UV flashlamp and the quartz processing chamber were encircled (optically coupled) by an elliptical UV reflector. The processing chamber was connected to a batch vessel (1.5 L) through forward and return lines, and a pump was placed on a forward line. The flow rate through the system could be adjusted. The system could also treat water or air flowing only through the processing chamber. In a number of tests, the lamp was placed along the vertical axis of a 6-L processing chamber made from a stainless steel. Samples were taken through a short drain line with a valve so that there was no exposure to the ambient air. All tests were taken and analyzed by an independent customer or a laboratory.

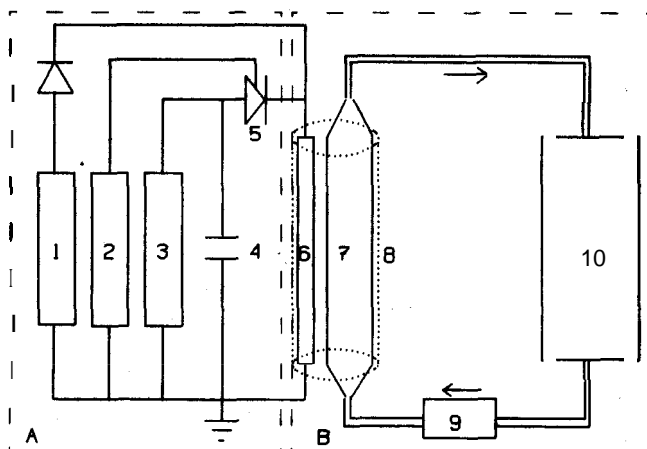


FIGURE 2. Experimental apparatus for a small scale testing at UVERG facilities.

A. Electrical diagram: (1)—simmer power supply (200 V, 3 A); (2)—control unit; (3)—capacitor charging power supply (2 kV to 5 kV); (4)—capacitor (5 μF to 100 μF); (5)—silicon controlled rectifier (SCR); (6)—xenon (or custom) UV flashlamp. When a medium pressure mercury vapor lamp was used, it had its own power supply.

B. Wafer treatment unit: (7)—quartz processing chamber; (8)—UV elliptical reflector; (9)—pump; (10)—batch volume.

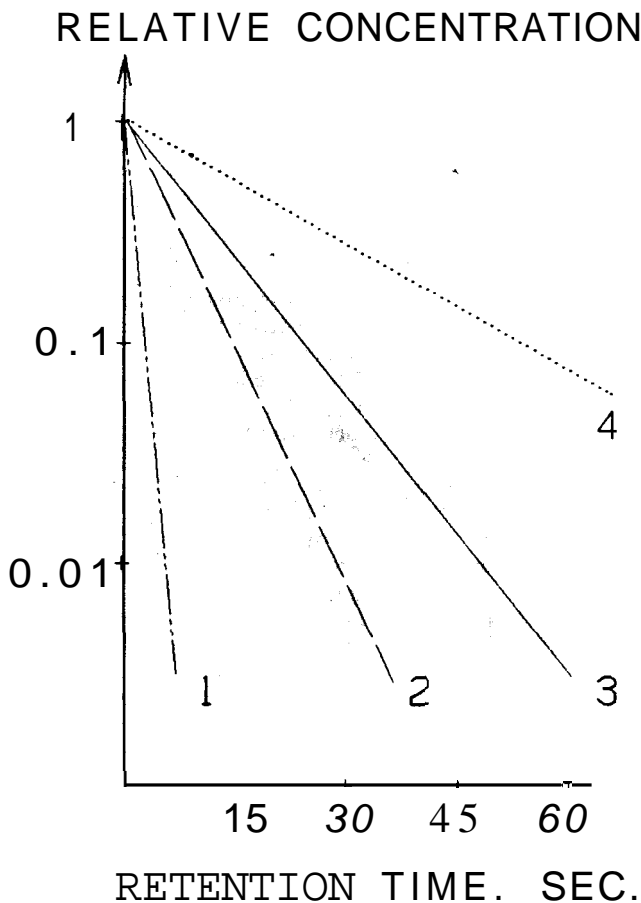


FIGURE 3. Retention times for toxics in media. Data obtained with UV from a 15 cm xenon flashlamp at the load of 60 watt per lamp cm; (1)—TCE in air; (2)—TCE in water; (3)—Benzene in water, Data obtained with 15 cm long medium pressure mercury vapor lamp at 60 watts/cm, peroxide was added: (4)—TCE in water.

Tests with water

We compared the effectiveness of direct photolysis supported by a xenon flashlamp and the traditional UV/oxidation process with peroxide supported by the 254 nm UV line from a medium pressure mercury lamp. The electrical consumption was the same for both lamps and equal 100 and 150 watts per lamp inch [40 and 60 watt/cm]. For some of these tests, tap water was spiked with different compounds (one for each series of tests) and some tests were done with real waste water or with site groundwater. A qualified third party provided either spiked samples or field samples and their analysis. The following toxins were treated in our tests: TCA, TCE, benzene, PNA, saturated oil and grease also bacteria and others. In some tests we added peroxide to the treated water. Some of the results of these tests are presented in Figures 3, 4, 5, and 6.

As can be seen from Figures 3 and 4, the effectiveness of direct photolysis achieved for TCE and for saturated oil and grease exceeds up to a few times the traditional Advanced Oxidation Process (AOP). The process has an impressive effect on bacteria (Figure 5); each UV pulse decreased a population of bacteria in water about 100 times. The results with bacteria were later confirmed by Maxwell Laboratories, Inc., San Diego, CA.

Tests with air

We used the same apparatus for tests in which air was spiked with TCE or with benzene vapors and then passed through the

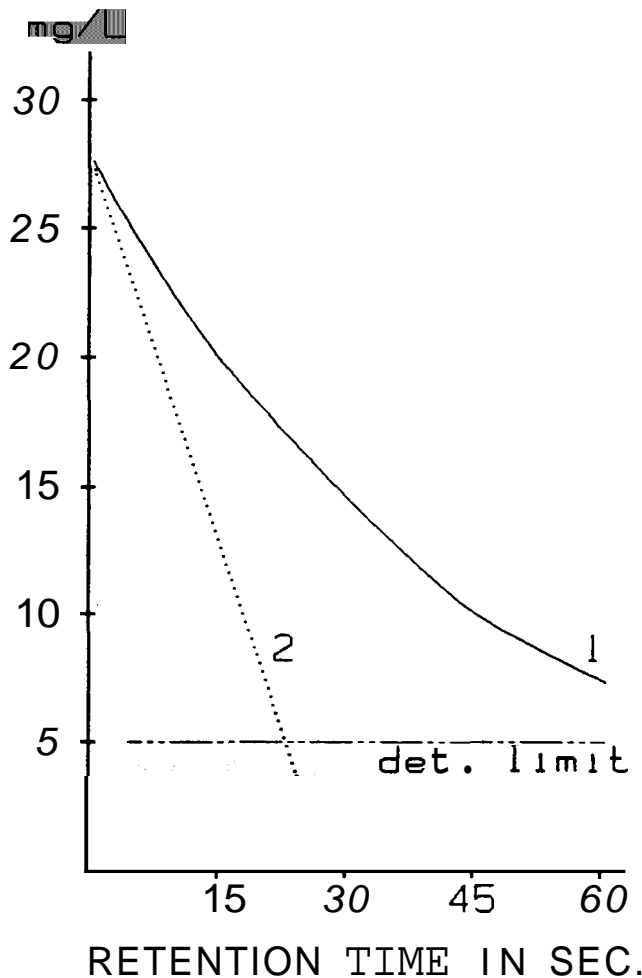


FIGURE 4. Retention times for reduction of saturated oil and grease in a field sample brought by a representative of Pacific Gas & Electric Company from a power plant at Hunters Point, San Francisco, CA. The same test conditions as for Fig. 3: (1)—medium pressure mercury lamp; (2)—pulsed xenon flashlamp.

processing chamber. There was no recycle for the air. Our preliminary data showed that the organics destruction in a gas flow was about five times faster than in water, Figure 3.

Soil tests

We performed these tests on soil spiked with approximately 800 mg/kg of PCB's, 650 mg/kg of DDT and 550 mg/kg PNA's. Since UV does not penetrate the soil matrix, one has to use a surfactant to extract the contaminants from within the soil up to its surface and then to rake the solids continually. We used a standard surfactant, Sodium Lauryl Sulfate ($C_{12}H_{25}O_4SNa$) in 1% solution. It was sprayed at the rate of about 0.5 g/cm² min while raking the soil every 2 minutes. Sample sizes were 200 g and were placed in a shallow and wide container (2 cm x 7 cm x 18 cm). The distance between soil and a flashlamp was 5 cm. The flashlamp had a parabolic UV reflector for a uniform distribution of UV light over the soil sample.

Two series of soil tests were performed: one with a 15 cm long flashlamp and another one with a 15 cm long medium pressure mercury lamp. In each case, the lamps had the same power consumption of 60 watt per lamp cm. We found that the pulsed UV lamp was much more effective than a medium-

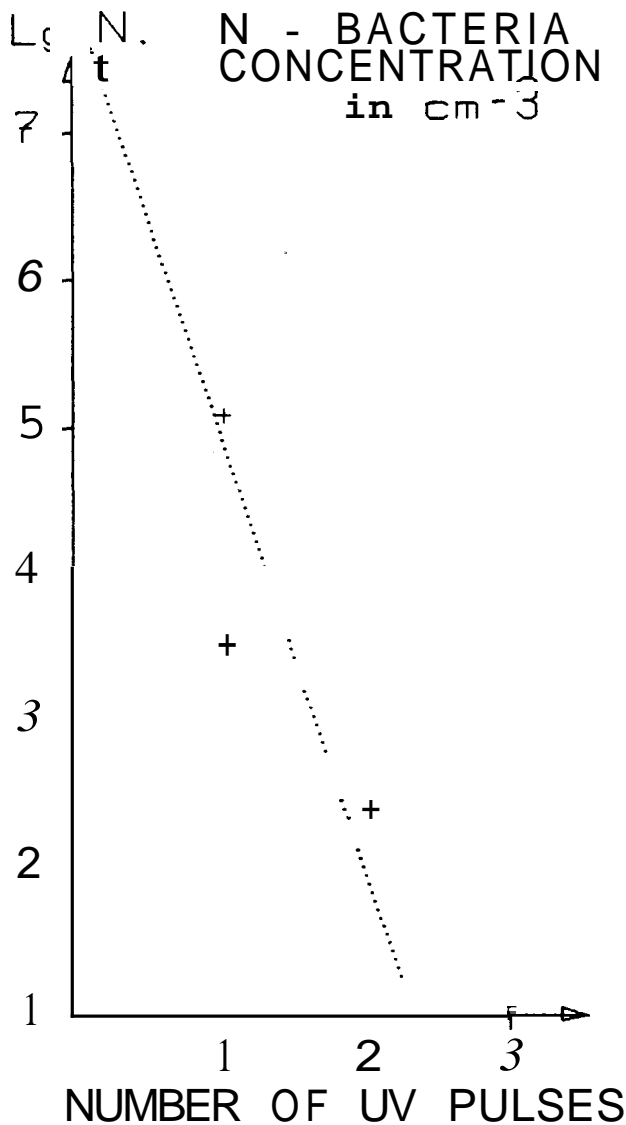


FIGURE 5. Disinfection test with a pulsed Xenon flash-lamp. Pulse energy 20 Joules, Water volume 1 L with injected E-coli bacteria.

pressure lamp for destruction of chemicals in soil. The 30-min. exposure from a pulsed lamp reduced PCB, DDT and PNA concentrations by 85 +/- 5% (Fig. 7). On the other hand, the presence of chlorine compounds in the soil did not increase.

Data Analysis

In various tests the following organic toxics were disintegrated with a pulsing UV continuum (Wekhof Process):

1. Petroleum Compounds such as benzene, gasoline, toluene, MTBE, oil and grease, etc.
2. Polynuclear Aromatics such as naphthalene, perene, etc.
3. Double-bonded organics such as TCE, etc.
4. Saturated organics such as TCA, carbon tetrachloride, chloroform.
5. Pesticides such as DDT, DEE.
6. Cyanides.
7. PCB's, dioxins.
8. Nitrites and nitrates.
9. Pink water (TNT).
10. Bacteria.

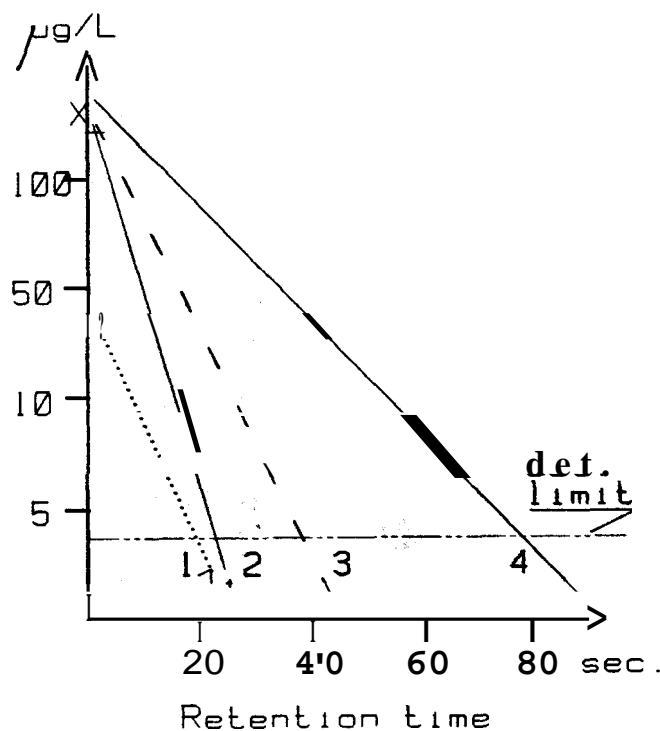


FIGURE 6. Retention times for PNA compounds destroyed with pulsing UV from a 15 cm xenon lamp at 60 watts/cm: (1)—Perene; (2)—Acenaphthene; (3)—Naphthalene; (4)—Fluorine.

The variety of organics disintegrated by a pulsing UV continuum shows that the process has a universal application. The destruction efficiency depended on a type of the organic; for example, it was higher for TCE and xylene and lesser for benzene and TCA. In most cases of water treatment, except for TCE, the addition of peroxide increased the process efficiency two or more times. The reason for that is the same as for the second generation UV systems—a better use of UV energy since peroxide absorb its own part of the UV spectra and toxic organics absorb different parts of the UV spectra.

The rate Γ of the photodissociation process can be simply calculated with the following correlation:

$$\Gamma = \Phi \cdot \sigma \cdot n [\text{cm}^{-3} \text{sec}^{-1}] \quad (3)$$

where

- Φ —UV flux within an absorption band (photons/cm²·sec)
- σ —cross-section for a photodissociation of an undesirable compound; a typical peak value is from 10⁻¹⁷ cm² to 10⁻¹⁶ cm² and has to be measured or calculated for each absorption band.
- n —concentration of toxics per cm³ of the carrier medium.

Our estimates showed that our lamps provided sufficient UV fluxes Φ within absorption bands, at least 0.1 watt/cm²/nm within the treated media. Thus, commercially acceptable rates of toxic destruction such as $\Gamma = 1 \text{ mg/L/sec}$ were achieved. Similar fluxes were generated in tests with mercury medium pressure lamps, but their few UV lines didn't have sufficient matching with absorption bands of treated toxins. That is one of the reasons for their poor performance comparatively with UV flashlamps of the same power.

The more effective action of the direct UV photolysis with pulsing UV vs. the 254 nm line + peroxide process (Figures 3 and 4) can be explained in terms of equation (3). Although both lamps consumed the same electrical power, the values of UV fluxes Φ emitted within absorption bands and respective

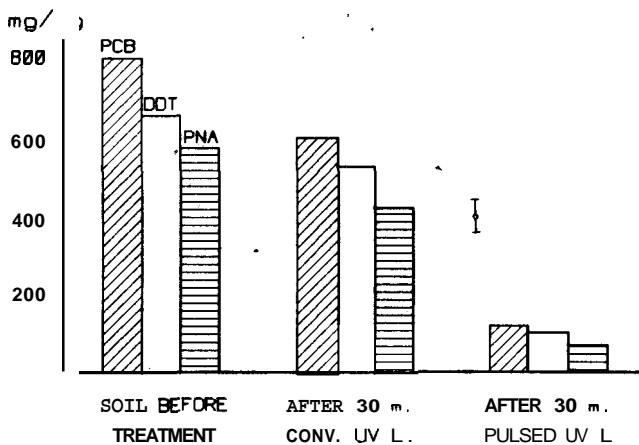


FIGURE 7. Reduction of PNA's, PCB's and DDT from the soil, placed into a 18 cm by 5 cm tray in 1.5 cm thick layer. The lamp was 5 cm from the soil and had a parabolic UV reflector. (1)—Initial concentrations. (2)—Reduction after 30-min. treatment with a medium pressure mercury lamp at 60wt/cm load. (3)—reduction after 30 min treatment with UV pulsed lamp at the same loading.

dissociation cross-sections σ were higher for the pulsed process than those for the UV flux of 254 nm line and σ for creating active radicals from peroxide [Equation (1)].

There is also another important advantage in using a pulsed UV source. It is its ability to produce very high photon fluxes, which are thousands of times higher than the same energy per second emitted continuously. This changes the kinetics of photochemistry in a way which speeds up targeted reactions. These higher photon fluxes have three distinct characteristics: peak power, RMS power and average power.

Peak power $P(p)$ is defined as ratio between the energy of a single pulse $E(p)$ and a time duration τ of a pulse:

$$P(p) = E(p)/\tau. \quad (4)$$

The **RMS power $P(rms)$** defines the effectiveness of the periodically repeated pulsed action of the peak power $P(p)$ at the repetition rate R :

$$P(rms) = 0.5 \cdot P(p) \cdot \sqrt{\tau \cdot R} \quad (5)$$

Average power $P(a)$ is the combined energy of all pulses delivered in 1 second at the repetition rate R :

$$P(a) = E(p) \cdot R \quad (6)$$

The peak power is thousands of times as much as the average power emitted (and consumed) by a pulsed lamp. We found [11] that with the same spectral interval of the UV source the effective destruction achieved by the process was attained when the ratio of rms power $P(rms)$ to average power $P(a)$ falls in the characteristic range of 1:10 to 1:100. The ratio of peak power $P(p)$ to average power $P(a)$ falls in the characteristic range of 1000:1 to 10,000:1; and the average power density is maintained at least at a value of about 0, 1 Watt/cm²/nm within the treated medium.

Within these ranges, one has to determine experimentally the best ratio for the destruction of each particular toxic and its concentration, α for a combination of toxics. The ratio of RMS to average power does not have to be selected if the ratio of the peak to average power is found for particular toxics: it will be present within the specified range anyway.

The existence of effective power ratios for this process can be explained by the fact that the ratio of the peak power to the average power is indirectly related to the plasma temperature, and, by this, shifts the peak of UV generation to a region with targeted absorption bands.

A faster destruction of organics in air than in water can be explained by a combination of three factors:

1. Lower UV absorption by air than by water.
2. Higher mobility of dissociated species which prevents the reverse process of toxics recombination.
3. Presence of oxygen in the air, so that UV converts a small part of the oxygen into ozone which contributes to the UV-aided photolysis, [Equation (1)].

The presence of air also helped to oxidize byproducts in soil. This means that destruction of organics was followed by a full mineralization of the process byproducts and by their escape from the soil. This explains why there was no increase in chloride compounds in the treated soil.

TABLE 1. ECONOMIC COMPARISONS FOR GROUNDWATER TREATMENT SYSTEMS

projected at the following assumptions:

Contaminant: 20 mg/L benzene plus 20 mg/L TCE;
 Target reduction: 100-fold each;
 Flow rate: 100 gal/min (0.38 m³/min);
 Operating costs are given for 1 year roundclock operation.

ITEM	AIR/CARBON	PSI LV60	UVERG 20
EQUIPMENT	\$ 100,000	\$ 115,000	\$ 115,000
INSTALLATION	20,000	20,000	15,000
CAPITAL COST	\$ 120,000	\$ 135,000	\$ 120,000
EL. POWER	\$ 5,120	\$ 34,500	\$ 11,400
CARBON COST	\$ 274,300	\$ 0	\$ 0
CHEM. COST	\$ 0	\$ 12,000	\$ 6,000
LAMPS COST	\$ 0	\$ 38,400	\$ 17,800
MAINTENANCE	\$ 15,600	\$ 6,750	\$ 6,000
AMORTIZATION	\$ 24,000	\$ 27,000	\$ 25,000
TOTAL OPER. COSTS	\$ 319,020	\$ 118,650	\$ 66,200
TREAT. COST \$/m ³ (\$/1,000 gal)	\$1.60 (\$ 6.07)	\$ 0.59 (\$ 2.24)	\$ 0.33 (\$ 1.26)

Processing Costs and Engineering Recommendations

Estimates are made for wastewater containing 20 mg/L TCE plus 20 mg/L benzene. The target reduction was 100-fold for each compound. Two established methods of treatment such as air stripper with off-gas vapor phase carbon, based on data from Westates Carbon Inc., (Los Angeles, CA), and a conventional UV/peroxide method based on LV60 system from PSI (Tucson, Arizona) are compared with the treatment projected for 20 kW UVERG system. A detailed costs breakdown for each of three cases is presented in TABLE 1. The results show a considerable advantage for the Wekhof process.

Operational costs for soil treatment with Wekhof Process, (such as on Fig. 7), were estimated to be between \$120/m³ and \$250/m³. This treatment can be performed at the rate of 1 m³ per 24 hours with a 100 kW system mounted on a trailer. For comparison, treatment of such grossly contaminated soil by bioremediation may take a few years at double the cost while treatment by incineration creates a strong air pollution and

makes the cleaned soil useless for vegetation. The soil treated with pulsing UV retained its vegetation properties.

An environmental engineer should consider the following applications of this new technology:

1. Groundwater treatment

- a) Direct treatment providing that water is filtered from solid compounds and has no coloration.
- b) Water can be treated by air stripping towers where the pulsed UV process cleanse its exhaust.

2. Wastewater treatment

- a) The recycling of the wastewater at plants which use water for product washing.
- b) The recycling of water at power plants.
- c) Water regeneration at refineries.

3. Air treatment

- a) Emission control at plants.
- b) Bacteria' control in large air conditioning systems, i.e. hospitals.

4. Soil remediation

- a) Remediation firms may consider to acquiring transportable soil UV processing units to treat small amounts of highly contaminated soil on customer sites.
- b) Treatment of a soil which has to retain its vegetation properties.

CONCLUSIONS

Our data allows us to conclude that the direct photolysis with intense pulsing deep UV continuum (Wekhof Process) is both the most efficient and clean method of organics destruction in water, gas and in soil. Adding peroxide in wastewater will further increase the process efficiency.

The requirements on pulsing UV sources exceed that of other commercially available (however, a limited use of xenon flashlamps is possible). A new custom-built source—WEKHOFUV flashlamp is recommended.

Each group of organics has the most efficient destruction if UV continuum is delivered with specific ratios between peak and average powers providing that the average UV power within the targeted toxic absorption band equal at least $0.1 \text{ wt/cm}^2/\text{nm}$ in the bulk of the treated medium.

The standard oxidation process with peroxide plus 254 nm UV line from a medium pressure mercury lamp has at least a three-fold less efficiency than the process with a lamp generating a pulsing UV continuum and consuming the same electrical energy.

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