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Department of Energy
Richland Field Office
P.O. Box 550
Richland, Washington 99352

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93-RPB-036

Mr. David B. Jansen, P.E.
Hanford Project Manager
State of Washington
Department of Ecology
P.O. Box 47600
Olympia, Washington 98504-7600

Dear Mr. Jansen:

SUPPORTING DOCUMENTS FOR USE OF ULTRAVIOLET OXIDATION FOR DESTRUCTION OF ORGANIC COMPOUNDS IN THE 242-A EVAPORATOR AND PUREX PLANT CONDENSATE TREATMENT FACILITY (PROJECT C-018H)

Enclosed are supporting documents for use of ultraviolet oxidation for destruction of organic compounds in the 242-A Evaporator and Plutonium-Uranium Extraction Plant Condensate Treatment Facility (CTF). The supporting documents are being submitted to the State of Washington Department of Ecology (Ecology) following a request by Mr. Robert King, of your staff, in a Unit Managers Meeting held on September 17, 1992. The information supports the U.S. Department of Energy, Richland Field Office's selection of ultraviolet oxidation as Best Available Technology and All Known, Available, and Reasonable Technology for destruction of organic compounds in the CTF. The list of documents are as follows:

- "UV Oxidation Feasibility Test Report in Support of C-018H Effluent Treatment Facility," WHC-SD-C018H-TRP-002, Westinghouse Hanford Company, Richland, Washington, August 1991
- "Treatment of Contaminated Water, Air and Soil with UV Flashlamps," Ultraviolet Energy Generators, Inc., Oakland, California, November 1991
- "Treatability Study of Enhanced Oxidation for Groundwater Contaminated with Chlorinated Organics," Halliburton NUS Corporation, Pittsburgh, Pennsylvania
- "Simultaneous Air Stripping and Advanced Oxidation Processes (AOP) for Process Water Treatment," Texas Tech University, Lubbock, Texas

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- "The perox-pure™ Oxidation System, A Comparative Summary," Peroxidation Systems, Inc., Tucson, Arizona
- "Advanced Oxidation Technologies for the Treatment of Contaminated Groundwater," U.S. Environmental Protection Agency (EPA), Reduction Engineering Laboratory, Cincinnati, Ohio, PRC Environmental Management, Inc., Chicago, Illinois
- "RAYOX® - A Second Generation Enhanced Oxidation Process for the Destruction of Waterborne Organic Contaminants," Solarchem Environmental Systems, Richmond Hill, Ontario, Canada
- "Demonstration Bulletin, Ultraviolet Radiation and Oxidation," EPA/540/M5-89/012, EPA, Center for Environmental Research Information, Cincinnati, Ohio
- "Applicability of UV/Oxidation Technologies to Treat Contaminated Groundwater," EPA/600/D-91/278, EPA, Cincinnati, Ohio, EPA, Region III, Philadelphia, Pennsylvania, PRC Environmental Management, Inc., Chicago, Illinois
- "Application of RAYOX® for the Remediation of Contaminated Groundwater," Solarchem Environmental Systems, Richmond Hill, Ontario, Canada
- "Treatment of Dissolved Organics with UV/Hydrogen Peroxide," Peroxidation Systems, Inc., Tucson, Arizona
- "Destruction of Water Contaminants," North Carolina State University, Raleigh, North Carolina, University of Turin, Turin, Italy, Concordia, University, Montreal, Canada.

One copy of each document has been provided to the Kennewick Office of Ecology.

Should you have any questions regarding this transmittal, please contact me or Mr. D. C. Bryson of my staff on (509) 372-0738.

Sincerely,

June M. Hennig, Director
Waste Management Division

EAP:RNK

Enclosures:
1. Ultraviolet Oxidation Test Report
2. Treatment of Contaminated Water, Air, and Soil with UV flashlamps
3. Treatability Study
4. Simultaneous Air Stripping and Advanced Oxidation Processes
5. The PEROX-PURE Oxidation System
6. Advanced Oxidation technologies
7. RAYOX
8. EPA Demonstration Bulletin
9. Applicability of Ultraviolet Oxidation Technologies
10. Application of RAYOX
11. Treatment of Dissolved Organics
12. Destruction of Water Contaminants

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Subject: SUPPORTING DOCUMENTS FOR USE OF ULTRAVIOLET OXIDATION FOR DESTRUCTION OF ORGANIC COMPOUNDS IN THE 242-A EVAPORATOR AND PUREX PLANT CONDENSATE TREATMENT FACILITY (PROJECT C-018H)

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Enclosure 2

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Treatment of Contaminated Water, Air and Soil With UV Flashlamps

Alex Wekhof

Ultraviolet Energy Generators, Inc. (UVERG) 285 Fifth Street, Oakland, CA 94607

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 polynuecleoaromatics (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:

$$\begin{array}{ll} \text{STEP 1:} & \left.\begin{array}{l} O_3 + UV \\ H_2O_2 + UV \\ H_2O_2 + O_3 + UV \\ H_2O_2 + M^{*} + UV \end{array}\right\} \rightarrow {}^{\bullet}OH \\ \text{STEP 2:} & TCE + {}^{\bullet}OH \rightarrow 2CO_2 + 3CL \end{array} \qquad (1)$$

Where STEP 1 has one of 4 choices.

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

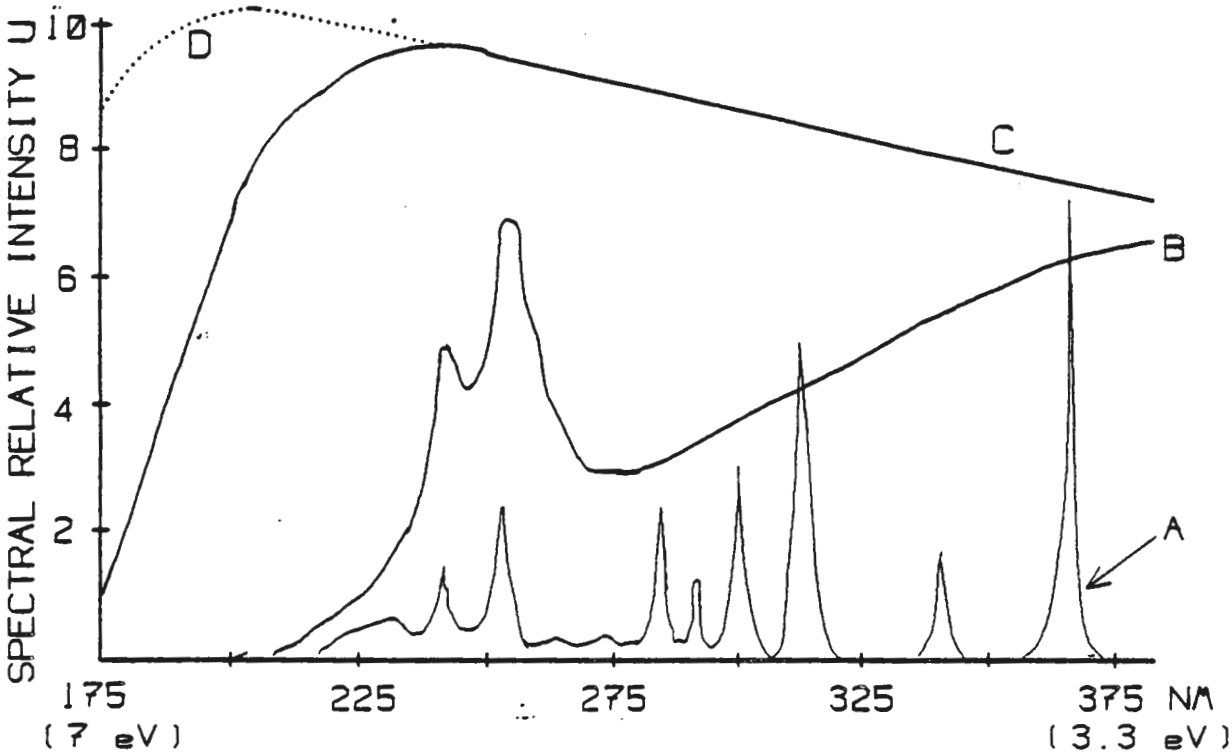

FIGURE 1. Spectral distributions in the region from 175 nm to 375 nm for four UV sources (A, B, C and D) in relative units U. Corresponding maximum and minimum photon energies for the region are given in eV (1 eV = 1.6 10^{-19} Joules, 1 nm = 10^{-9} m).

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/cm², bore diameter 4 mm, energy 45 Joules, pulse duration 125 μsec [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 eV = $1.6 \cdot 10^{-19}$ Joules). For example, a direct UV photolysis of TCE is shown as follows:

$$\begin{array}{ccc} Cl & & H \\ | & & | \\ C & = & C \\ | & & | \\ Cl & & Cl \end{array} + UV \rightarrow 2CO + 3Cl^- \qquad (2)$$

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 (ϵ = 47,000) and at 202 nm (ϵ = 7,000) plus has series of weak absorption bands between 230 nm and 270 nm (ϵ = 300). Acetone has absorption bands at 220 nm (ϵ = 16,000) and 318 nm (ϵ = 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 iodides 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 $1 kA/cm^2 < j > 5 kA/cm^2$ and $150\ \mu sec < \tau > 1$ msec. In this case, xenon plasma temperature ranges from 6,000°K to 9,000°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 $V = 3$ 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 $A/\mu sec$, 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.

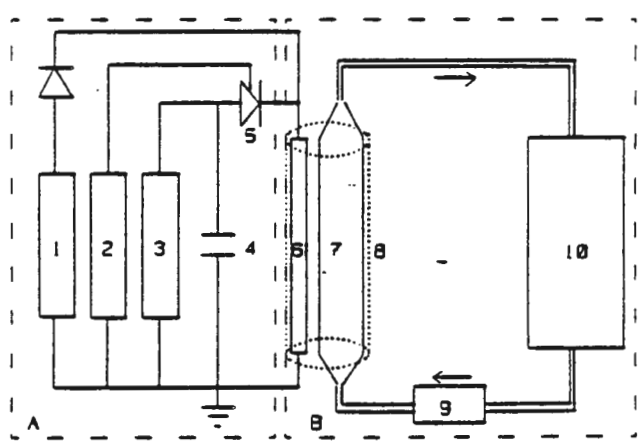

FIGURE 2. Experimental apparatus for a small scale testing at UVERG facilities.

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 it's own power supply.**

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

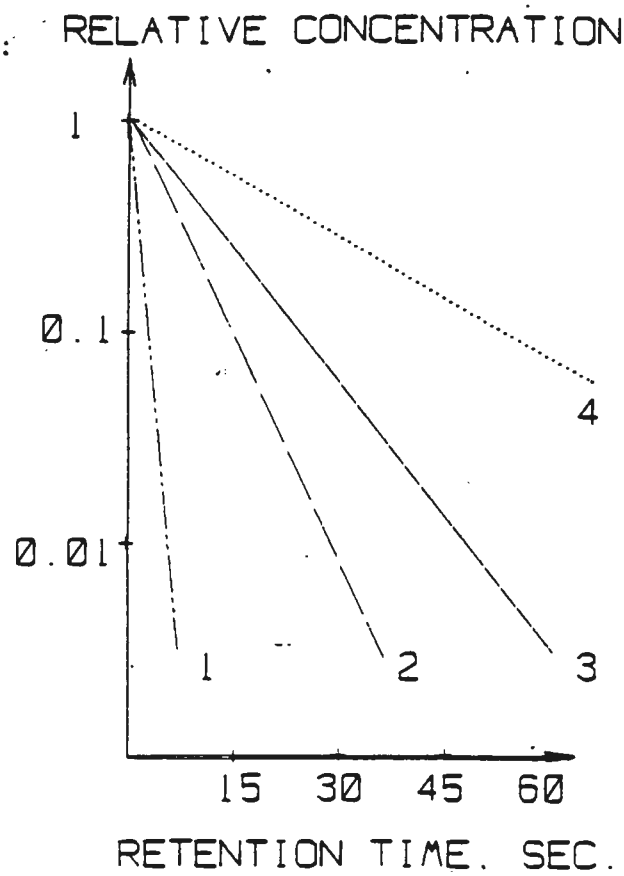

FIGURE 3. Retention times for toxics in media. Data obtained with UV from a 15 cm xenon flashlamp at the load of 60 watt per lamp cm; (1)—TCE in air; (2)—TCE in water; (3)—Benzene in water, Data obtained with 15 cm long medium pressure mercury vapor lamp at 60 watts/cm, peroxide was added: (4)—TCE in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

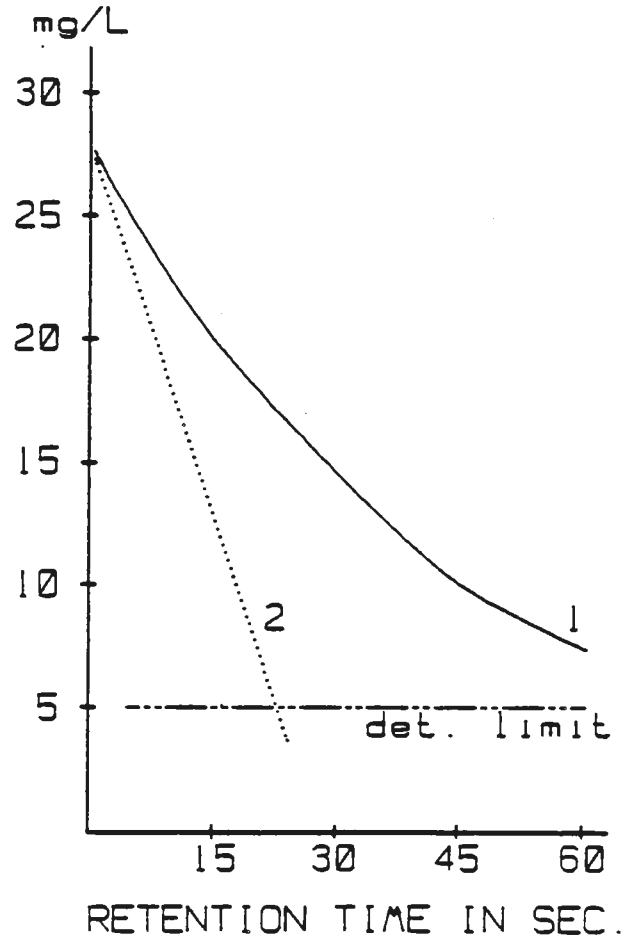

FIGURE 4. Retention times for reduction of saturated oil and grease in a field sample brought by a representative of Pacific Gas & Electric Company from a power plant at Hunters Point, San Francisco, CA. The same test conditions as for Fig. 3: (1)—medium pressure mercury lamp; (2)—pulsed xenon flashlamp.

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 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/cm^2 min while raking the soil every 2 minutes. Sample sizes were 200 g and were placed in a shallow and wide container (2 cm × 7 cm × 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-

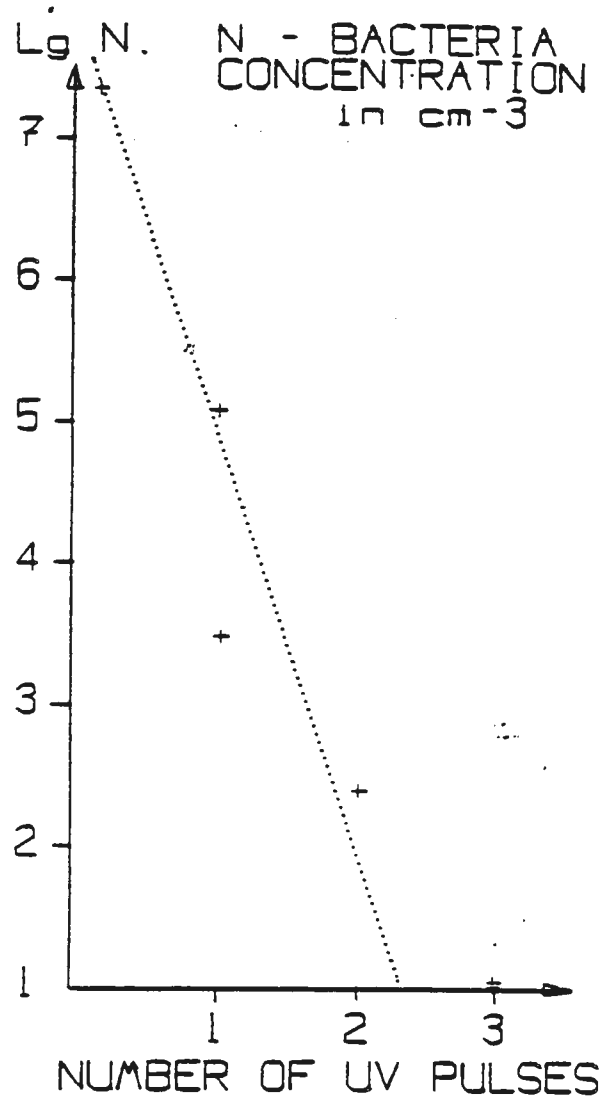

FIGURE 5. Disinfection test with a pulsed Xenon flashlamp. Pulse energy 20 Joules, Water volume 1 L with injected E-coli bacteria.

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.

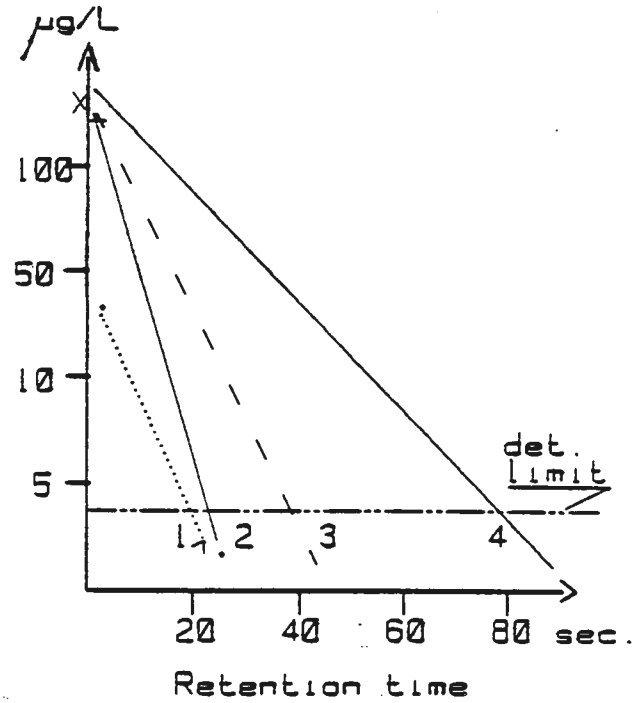

FIGURE 6. Retention times for PNA compounds destroyed with pulsing UV from a 15 cm xenon lamp at 60 watts/cm: (1)—Perene; (2)—Acenaphthene; (3)—Naphthaline; (4)—Fluorine.

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:

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

where

Φ—UV flux within an absorption band (photons/$cm^2 \cdot$sec)
σ—cross-section for a photodissociation of an undesirable compound; a typical peak σ value is from 10^{-17} cm^2 to 10^{-16} cm^2 and has to be measured or calculated for each absorption band.
n—concentration of toxics per cm^3 of the carrier medium.

Our estimates showed that our lamps provided sufficient UV fluxes Φ within absorption bands, at least 0.1 watt/cm^2/nm within the treated media. Thus, commercially acceptable rates of toxic destruction such as $\Gamma = 1$ 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

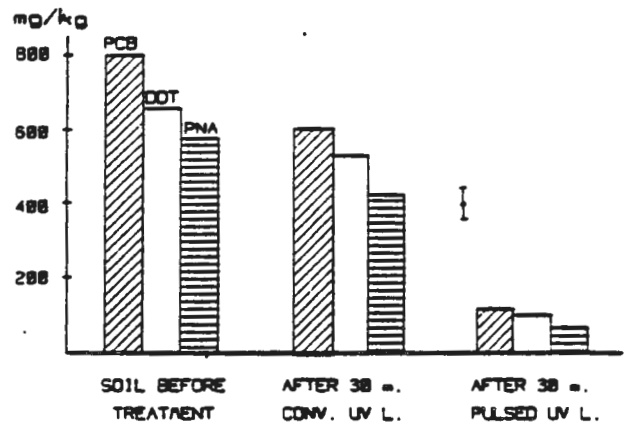

FIGURE 7. Reduction of PNA's, PCB's and DDT from the soil, placed into a 18 cm by 5 cm tray in 1.5 cm thick layer. The lamp was 5 cm from the soil and had a parabolic UV reflector. (1)—Initial concentrations. (2)—Reduction after 30-min. treatment with a medium pressure mercury lamp at 60wt/cm load. (3)—reduction 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/cm^2/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, or 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 m^3/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/m^3 and $250/m^3. This treatment can be performed at the rate of 1 m^3 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—WEKHOF UV 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 wt/cm^2/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.

ACKNOWLEDGEMENTS

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HALLIBURTON NUS
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C-49-01-92-119

January 13, 1992

Mr. Fred Bernardin
Peroxidation Systems, Inc.
5151 East Broadway
Suite 600
Tucson, Arizona 85711

Dear Mr. Bernardin:

Enclosed please find one courtesy copy of the manuscript entitled Treatability Testing of Enhanced Oxidation for Groundwater Contaminated with Chlorinated Organics. The paper is to be presented on February 21, 1992 at the Chemical Oxidation Second International Symposium at Vanderbilt University, Nashville, Tennessee.

Please call me at (412) 921-8650 if you have any questions.

Very truly yours,

Linda Klink

Linda Klink
Process Engineer

LEK/pam

Enclosure

cc: Michael Campbell (HALLIBURTON NUS)
Michael Albert (HALLIBURTON NUS)
Doug Hodson (HALLIBURTON NUS)

Enclosure 3

9 3 1 2 9 0 1 1 8 8 0

TREATABILITY STUDY OF ENHANCED OXIDATION FOR GROUNDWATER CONTAMINATED WITH CHLORINATED ORGANICS

Title: Treatability Study of Enhanced Oxidation for Groundwater Contaminated with Chlorinated Organics

Author: Linda Klink
Michael Campbell
Captain John Coho

ABSTRACT

NUS Corporation (now HALLIBURTON NUS Environmental Corporation) supervised a bench-scale treatability study conducted by Peroxidation Systems, Inc. (PSI) for Kelly Air Force Base (Kelly AFB) in Texas to determine the feasibility of employing enhanced oxidation to remediate groundwater contaminated primarily with chlorinated organics. Groundwater in an area of the base (designated Zone 2) was selected for the treatability test, since chlorinated organics were significant contaminants in that area. Groundwater samples from two of the most highly contaminated sites (designated E-1 and E-3) within Zone 2 were collected for the treatability test.

Site E-1 groundwater was contaminated mainly with trichloroethene (TCE) tetrachloroethene (PCE), vinyl chloride (VC), and 1,2-dichloroethene (1,2-DCE) whereas Site E-3 groundwater was contaminated with 1,1- and 1,2-dichloroethane (DCA), 1,2-dichloroethene (DCE), chlorobenzene (CB), dichlorobenzene (DCB) and VC. Following preliminary screening of contaminant concentrations and groundwater quality parameters, five test runs of enhanced oxidation were conducted per site, consisting of two test runs using hydrogen peroxide/ultraviolet light (H_2O_2/UV); one test run using ozone/ultraviolet light (O_3/UV); one test run using ozone/hydrogen peroxide/ultraviolet light (O_3/H_2O_2/UV); and one confirmatory test run each to replicate the most promising test run of the foregoing four test runs. In addition, a control test was conducted to determine contaminant losses due to causes other than enhanced oxidation. Results indicated that enhanced oxidation using H_2O_2/UV was a strong, effective process capable of achieving the removal of the chlorinated organic contaminants of concern. Test results indicated residual concentrations at less than detection limits, in most cases, and less than Maximum Contaminant Levels (MCLs) in others.

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INTRODUCTION

Groundwater contaminated with chlorinated organics can pose serious environmental and human-health risks. Although several conventional wastewater treatment technologies can be employed to effectively remediate contaminated groundwaters there are severe limitations in achieving the ultimate destruction of chlorinated organic contaminants.

Aerobic biological treatment cannot readily achieve the degradation of chlorinated alkanes and alkenes under typical conditions. Anaerobic biological degradation of TCE and PCE leads to the production of vinyl chloride, which is more toxic and less biodegradable than its parent compounds. Air stripping and activated carbon adsorption serve merely to transfer the contaminants into another media, which would require further treatment. Furthermore, vinyl chloride is not amenable to cost-effective removal from the aqueous phase (or gaseous phase) by granular activated carbon adsorption. Air stripping then would require thermal off-gas treatment. Reverse Osmosis, which concentrates the contaminants into smaller volumes would produce a concentrated waste stream that requires treatment; membrane degradation is an additional concern.

Chemical oxidation as opposed to physical and biological methods, has the potential to transform organic contaminants into relatively innocuous end products. Ozone (O_3) and hydrogen peroxide (H_2O_2) are powerful oxidants which have been used both for disinfection in water treatment, as well as for various industrial applications.

Oxidation using O_3 and/or H_2O_2 enhanced by ultraviolet light has been reported to be a cost effective treatment process for a wide array of organic compounds found in contaminated groundwater.(1) The use of O_3/UV or H_2O_2/UV or O_3/H_2O_2/UV as an enhanced oxidation process can achieve the destruction of many organic contaminants to relatively innocuous end products. Furthermore, vinyl chloride, which is not amenable to cost-effective treatment by conventional means, is expected to undergo enhanced oxidation into innocuous end-products.

During this process, UV light splits (by photolysis) the oxidant into highly reactive radicals and "activates" many of the organic molecules to make them more amenable to oxidation.(1) The photolytic reaction for the splitting of hydrogen/peroxide into radicals is known to be as follows(2):

$$H_2O_2 \xrightarrow{UV} 2HO^{\bullet} \qquad (1)$$

Organic molecules may be activated by direct UV absorption and either directly oxidize, or dissociate to form organic radicals and other reactive intermediates which would undergo oxidation more easily. By providing enough contact time and oxidants, molecules may be completely destroyed to CO_2, H_2O, and, if present, the appropriate inorganic salts(1).

Factors that affect the effectiveness of enhanced oxidation using O_3/H_2O_2/UV are both matrix specific as well as process design and operation dependent. These factors are mainly:

- Matrix specific:
  - (1) Type and concentration of organic contaminants and other interfering contaminants.
  - (2) Light transmittance of the water (color/suspended solids/turbidity)

- Process Design and Operation Dependent:
  (1) UV intensity, oxidant dosages
  (2) pH and Temperature
  (3) Use of catalyst

Therefore, a treatability study is useful to obtain data on the effectiveness of the process and its implementability, and to determine optimum process operating conditions for cost-effective remediation of the contaminated groundwater.

SPECIFIC OBJECTIVES OF THE TREATABILITY TEST

The overall objective of the treatability test was to determine the feasibility of using enhanced oxidation to reduce organic contaminant concentrations in Zone 2 groundwater at Kelly AFB. Representative samples from Sites E-1 and E-3 which have the highest concentrations of contaminants within Zone 2 were used for the testing. Although remediation goals for the final remedial system will vary, depending on the selected discharge option, drinking water standards were selected as the target remediation goals for purposes of evaluating treatability test effectiveness. Although a representative composite of Zone 2 groundwater was not used for testing, results from Site E-1 and Site E-3 tests were extrapolated to provide expected overall Zone 2 remediation efficiency.

The following specific testing objectives were identified:

- Investigate the effectiveness of enhanced oxidation to attain the target remediation goals for organics, without exceeding test dosages of oxidants considered economical or implementable for a full scale groundwater system.
- Conduct pretreatment, only as necessary, so that primary contaminants will not be significantly removed prior to the enhanced oxidation process.
- Test and evaluate various combinations and ratios of oxidants, as well as operating conditions (e.g., hydrogen peroxide, UV, pH) so that, based on the most effective parameters, a preliminary conceptual design can be established for a full-scale system.
- Provide preliminary costing information for the conceptual design of a full-scale system (-30 percent to +50 percent accuracy). Include capital cost information, as well as operating and maintenance costs (e.g., electricity to generate ozone, hydrogen peroxide, UV lamp replacements).

SITE BACKGROUND INFORMATION

SITE E-1

This site was originally used as an unlined disposal pit for chromium plating sludge and waste from 1940 to 1955. The pit was closed in 1955. A second pit with a clay liner was constructed at the same location in the early 1960s and was used as a chemical disposal and evaporation pit until 1966. An asphalt cap now covers the closed pit.

The main contaminants in the underlying ground water include benzene, CB, DCAs, DCEs, TCE, PCE, and VC, as well as bis(2-ethylhexyl)phthalate.

SITE E-3

An open evaporation pit was operated at Site E-3 beginning in 1966. Over the operating life of the pit, solvents, Industrial Waste Treatment Plant (IWTP) sludge, insecticides and other wastes, including Polychlorinated Biphenyls (PCBs), were disposed of in the pit. Disposal operations at Site E-3 were discontinued in 1980, except for the disposal of IWTP sludge in 1982. In 1985, all liquid materials, the clay liner, and all visibly contaminated soil were removed from the pit and disposed of off base. Subsequent investigation at the site indicated that groundwater underlying the site contained benzene, trichloroethanes (TCAs,) VC, DCEs, DCAs, CB and methylphenols, as well as DCBs, bis(2-ethylhexyl)phthalate, and napthalene. Elevated levels of iron and manganese were also present.

EQUIPMENT AND MATERIALS

A typical, continuous-flow, $O_3/H_2O_2/UV$ system consists of a H_2O_2 feed system, an oxygen or air source, an O_3 generator and feed system, a UV irradiation/oxidation reactor, and an ozone decomposer. The flow path and the configuration of UV lamps within the UV irradiation/oxidation reactor are designed to maximize O_3/H_2O_2 blending and exposure of the water to UV radiation. Typical reactor designs range from mechanically agitated reactors to spray, packed, and tray-type towers. Reactor exhaust gases are passed through a catalytic decomposer, which converts the remaining O_3 to oxygen. H_2O_2 may be substituted partly or completely for O_3, eliminating or reducing the need for an O_3 generator and decomposer.

Refer to Figure 1 for a schematic of the PSI testing apparatus used for the treatability study. The test unit is charged by placing an aliquot of water into the reservoir. A pump circulates the solution through the reactor and back into the reservoir, providing continual mixing in the closed system. (Note that, due to the use of this recycle loop, the overall system retention time is greater than the actual reactor vessel residence time.) The high intensity UV lamp is lit and hydrogen peroxide added as required to maintain a constant concentration in solution. For some of the tests, ozone was fed into the system using pure oxygen and an ozone generator. For the bench scale apparatus, solution temperature was controlled through the use of a cooling coil mounted inside the reservoir.

TREATABILITY TEST PROCEDURE

The treatability study for Kelly AFB consisted of the following stages:

- Pretreatment
- Preliminary screening of parameters (chemical dosage, pH)
- Confirmatory test of selected parameters; control test

Although Sites E-1 and E-3 groundwaters contain a variety of contaminants as identified earlier, the treatability test focused on the removal of only certain VOCs of concern.

For Site E-1 the VOCs of concern were:

- Vinyl chloride
- TCE
- PCE
- 1,1-DCA
- 1,1-DCE
- cis-1,2-DCE
- Benzene

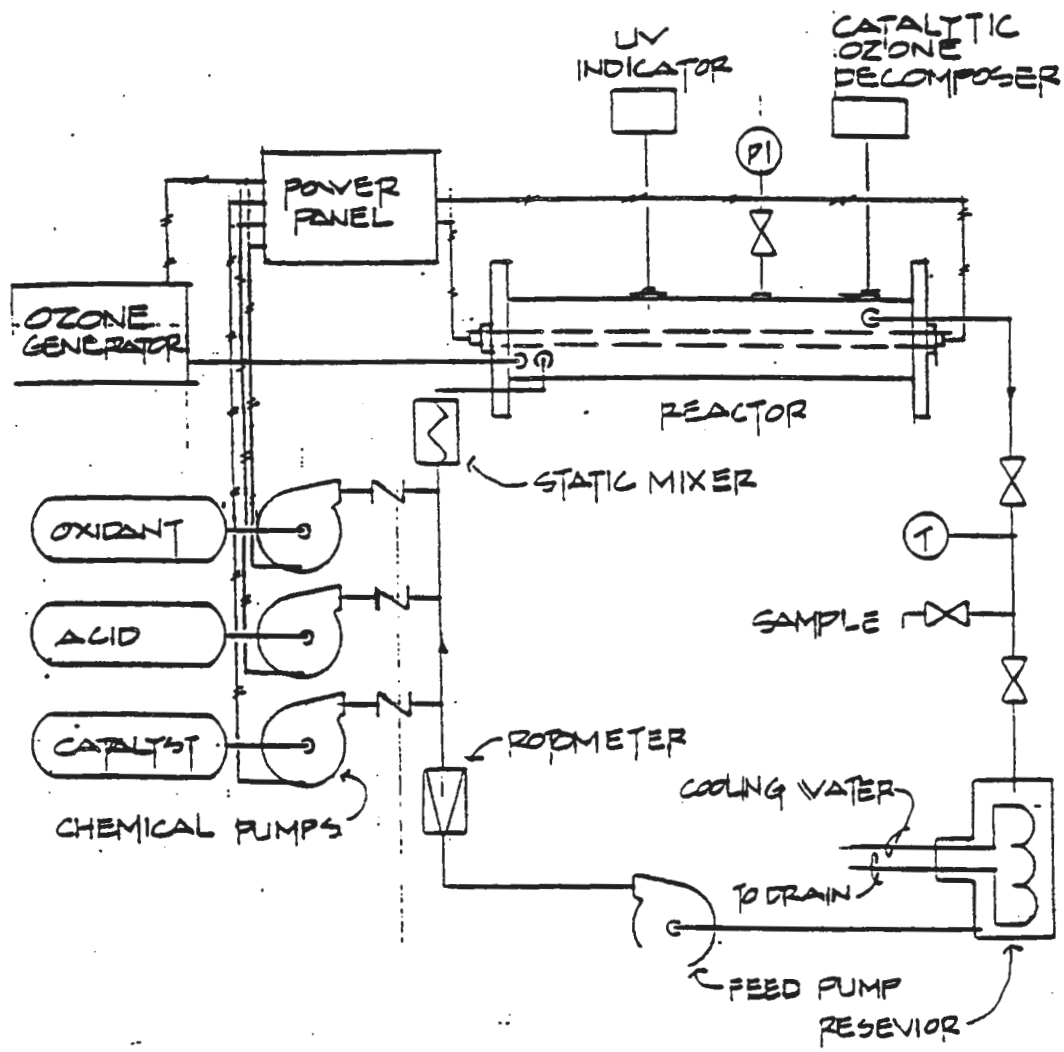


FIGURE 1
SCHEMATIC PROCESS FLOW DIAGRAM OF ENHANCED OXIDATION SYSTEM, P.S.I., INC.

For Site E-3 the VOCs of concern were:

- Vinyl chloride
- 1,1-DCA
- 1,2-DCA
- 1,1-DCE
- cis-1,2-DCE
- Benzene
- Chlorobenzene
- 1,4-DCB

PRETREATMENT

Pretreatment was performed to the minimal extent necessary to remove contaminants that would interfere with effectiveness of enhanced oxidation. The main contaminants most likely to adversely affect enhanced oxidation are: (1) suspended solids/turbidity which reduce the transmission of UV light and/or become preferentially oxidized; and (2) dissolved contaminants such as iron and manganese, which may not only become preferentially oxidized, but also would coat the UV lamp surfaces, and thus reduce the transmission of UV light.

Pretreatment for Site E-1 groundwater consisted of filtration through a 3μm filter. Pretreatment for Site E-3 groundwater consisted of pre-oxidation with H_2O_2 followed by filtration through a 3 μm filter.

Table I shows the effect of pretreatment on groundwater samples from Site E-1 and Site E-3. For the E-1 sample, it was observed that removal of approximately 8 to 20 percent was achieved for some of the VOCs present in significant concentrations such as Vinyl Chloride, cis-1,2-DCE, TCE, and PCE. This removal is expected to have occurred mainly as a result of physical causes such as turbulence/agitation and volatilization during the process of filtration, as well as adsorption onto filter media. For the E-3 sample it was observed that removal of 18 to 50 percent was achieved of VOCs present in significant concentrations such as VC, cis-1,2-DCE, and chlorobenzenes.

TABLE I: TYPICAL REMOVAL OF VOCs DURING PRETREATMENT

VOC of Concern	Site E-1			Site E-3		
	As Received (μg/L)	Pretreated (μg/L)	Percent Removal	As Received (μg/L)	Pretreated (μg/L)	Percent Removal
Vinyl Chloride	3,000	2,700	10%	300	150	50%
cis-1,2-DCE	8,775	8,030	8.5%	395	314	20.5%
1,1-DCA	28	30.5	—	388	315	18.8%
TCE	1,950	1,700	12.8%	4.2	5.6	—
PCE	3,230	2,570	20.4%	<2	2.4	—
Chlorobenzene	32	58	—	3,110	2,490	19.9%
1,4-DCB	42	36	14.3%	427	319	25.3%

In conclusion, because the concentrations of all VOCs of concern were of the same order of magnitude in the raw and pretreated groundwater samples, losses due to pretreatment were considered minimal.

PRELIMINARY SCREENING OF OPERATING PARAMETERS

Operating parameters that can be used to optimize the efficiency of enhanced oxidation are: 1) type of oxidant (H_2O_2/O_3); 2) oxidant dosage, 3) oxidation/UV irradiation contact time; and 4) use of chemical catalysts/and/or pH adjustment. When expressing oxidant dosage, it should be noted that the O_3 is applied as a gas, whereas H_2O_2 is applied as an aqueous solution for enhanced oxidation.

For the preliminary screening of these parameters, an intermediate set of test runs was conducted using selected combinations and dosages of oxidants, at two different pH levels. The oxidation/UV irradiation contact time required to achieve adequate removal of the VOCs of concern was determined from the test results. Also, the most effective operating conditions were established. The contact time was controlled by varying the number of cycles through the treatment system.

For Site E-1, the intermediate test run parameters were as follows:

Test Run	Oxidant Dosage	pH	Catalyst*
1	45 mg/L H_2O_2 in solution	5.0	none
2	45 mg/L H_2O_2 in solution	5.5	none
3	110 mg/L O_3 applied	5.1	none
4	11 mg/L H_2O_2 in solution + 110 mg/L O_3 applied	5.5	none

For Site E-3, the intermediate test run parameters were as follows:

Test Run	Oxidant Dosage	pH	Catalyst*
1	100 mg/L H_2O_2 in solution	5.1	none
2	100 mg/L H_2O_2 in solution	5.1	1.5 mg/L
3	70.8 mg/L O_3 applied	5.1	none
4	7 mg/L H_2O_2 in solution + 70.8 mg/L O_3 applied	5.0	none

The selection of the above combination of parameters for each test run was based on the experience of personnel of PSI. Tables II and III give the results of the intermediate test runs for Sites E-1 and E-3.

*Proprietary iron compound.

TABLE II: INTERMEDIATE TESTING ANALYTICAL RESULTS
SITE E-1

Organic Contaminants of Concern	Test 1 - H_2O_2/UV 45 mg/L H_2O_2 in solution pH = 5.0					Test 2 - H_2O_2/UV 50 mg/L H_2O_2 in solution pH = 5.5				Test 3 - Ozone/UV 110 mg/L ozone applied pH = 6.1					Test 4 - H_2O_2/Ozone/UV 11 mg/L H_2O_2 in solution 110 mg/L ozone applied pH = 5.5				
	Oxidation Time (minutes)					Oxidation Time (minutes)				Oxidation Time (minutes)					Oxidation Time (minutes)				
	0	2	4	8	12	0	1	2	4	0	2.5	7	14	28	0	2.5	7	14	28
Vinyl Chloride	<500	<50	<50	<50	<50	1,290	<50	<50	<50	4,150	<50	<50	<50	<50	2,720	<50	<50	<50	<50
1,2-Dichloroethene (total)	7,500	<4	<4	<4	<4	11,170	<4	<4	<4	15,200	1,220	10.4	<2	<2	15,580	1,965	<2	<2	<2
Benzene	<10	<2	<2	<2	<2	14.9	<2	<2	<2	16.6	<2	<2	<2	<2	17.9	<2	<2	<2	<2
1,1-Dichloroethane	22	<2	<2	<2	<2	37.7	5.6	<2	<2	114	37.2	18.7	2.7	<2	130	37.1	17.0	<2	<2
1,1-Dichloroethene	<10	<2	<2	<2	<2	18.6	<2	<2	<2	42.5	13.7	<2	<2	<2	56.1	12.4	<2	<2	<2
Tetrachloroethene	1,580	6.90(1)	<2	<2	<2	2,450	2.7(1)	<2	<2	1,720	4.2	<2	<2	<2	1,600	3.4	<2	<2	<2
Trichloroethene	1,430	<2	<2	<2	<2	1,550	<2	<2	<2	1,230	14	<2	<2	<2	1,630	18.1	<2	<2	<2
Ozone Dose (mg/L)	NA	NA	NA	NA	NA	NA	NA	NA	NA	0	12.7	27.5	55	110	0	12.7	27.5	55	110

(1) These values are due to sampling errors, not incomplete oxidation. An insufficient volume of water was used to rinse the sample port, in an attempt to achieve maximum volatilization of contaminants.
NA Not applicable.

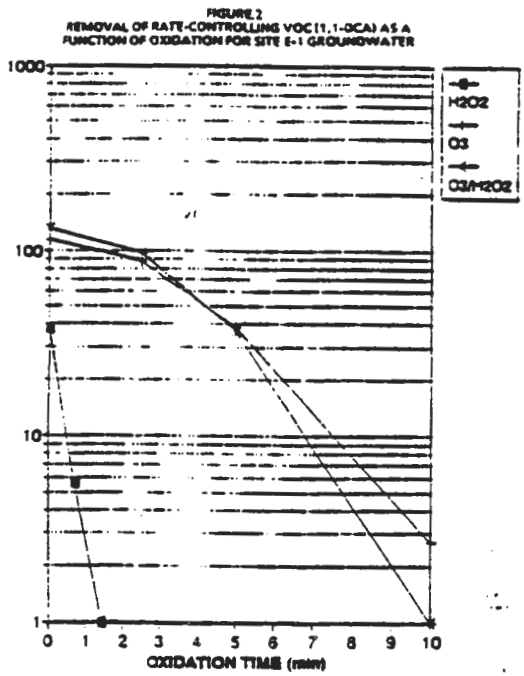
TABLE III: INTERMEDIATE TESTING ANALYTICAL RESULTS
SITE E-3

Organic Contaminants of Concern	Test 1 - H_2O_2/UV 100 mg/L H_2O_2 in solution pH = 5.1					Test 2 - H_2O_2/UV 100 mg/L H_2O_2 in solution pH = 5.1 1.5 mg/L catalyst					Test 3 - Ozone/UV 70.8 mg/L ozone applied pH = 5.1					Test 4 - H_2O_2/Ozone/UV 7 mg/L H_2O_2 in solution 70.8 mg/L ozone applied pH = 5.0				
	Oxidation Time (minutes)					Oxidation Time (minutes)					Oxidation Time (minutes)					Oxidation Time (minutes)				
	0	2	4	8	12	0	1	2	4	8	0	3	6	12	18	0	3	6	12	18
1,1-DCA	401	178	<2	<2	<2	387	333	92.4	<2	<2	380	313	268	164	72.5	397	226	190	2.7	<2
1,2-DCA	58.7	22.9	<2	<2	<2	54.3	37.5	7.4	<2	<2	50.1	47.9	41.9	33.2	30.3	58.6	46.5	23.6	<2	<2
1,1-DCE	5.6	<2	<2	<2	<2	4	3.2(1)	<2	<2	<2	4.7	2.3	<2	<2	<2	<2	<2	<2	<2	<2
1,2-DCE (cis + trans)	128	<4	<4	<2	<2	257	4	<2	<2	<2	296	43.2	18.5	<4	<4	334	26	<4	<4	<4
Vinyl Chloride	1,720	<50	<50	<50	<50	213	<50	<50	<50	<50	681	110	<50	<50	<50	419	13.5	<5	<5	<5
Benzene	16.6	<2	<2	<2	<2	29.5	<2	<2	<2	<2	14.9	11.7	5.0	<2	<2	14.5	5.1	<2	<2	<2
Chloroform	1,130	<2	<2	<2	<2	2,780	27(1)	<2	<2	<2	2,300	433	72.3	2.2	<2	2,350	138	<2	<2	<2
1,4-DCB	418	<2	<2	<2	<2	304	6.2(1)	<2	<2	<2	266	50.6	6.4	<2	<2	415	25.5	<2	<2	<2
Ozone Dose (mg/L)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0	11.8	23.6	47.2	70.8	0	11.8	23.6	47.2	70.8

(1) These values are due to sampling errors, not incomplete oxidation. An insufficient volume of water was used to rinse the sample port, in an attempt to achieve maximum volatilization of contaminants.
NA Not applicable

The oxidation times as reported in Tables II and III are the overall residence times of the groundwater in the treatment system (including the recycle loop) as recorded during testing. Based on the oxidation times required to achieve a reduction in concentrations of various VOCs of concern, 1,1-DCA was determined to be the least efficiently removed (and hence, the enhanced oxidation rate controlling) compound for both Site E-1 and E-3 groundwater samples.

Figures 2 and 3 (provided by PSI) show the variation in concentration of 1,1-DCA over time using the oxidants: O_3, H_2O_2 and a O_3/H_2O_2 combination. It was observed that enhanced oxidation using H_2O_2 was more efficient than O_3 or a O_3/H_2O_2 combination, since a greater reduction in concentration of 1,1-DCA was achieved in a given time using H_2O_2, than the other oxidants. Note that the oxidation times in Figures 2 and 3 have been corrected to reflect actual reactor residence times (excluding the recycle loop).



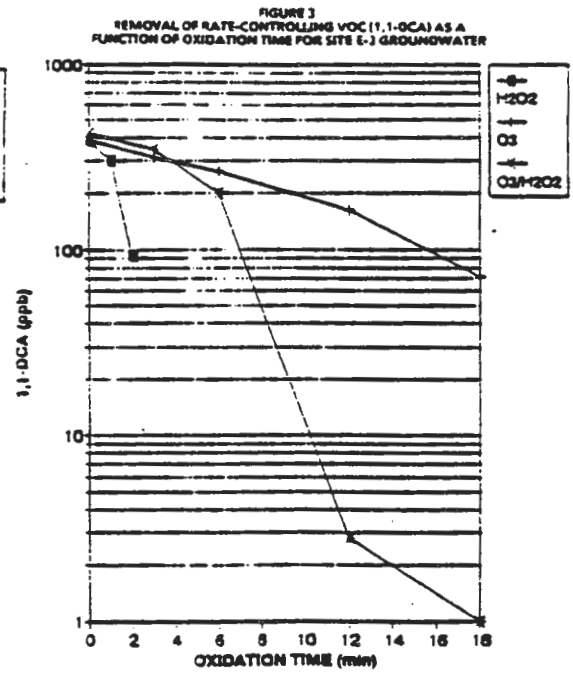
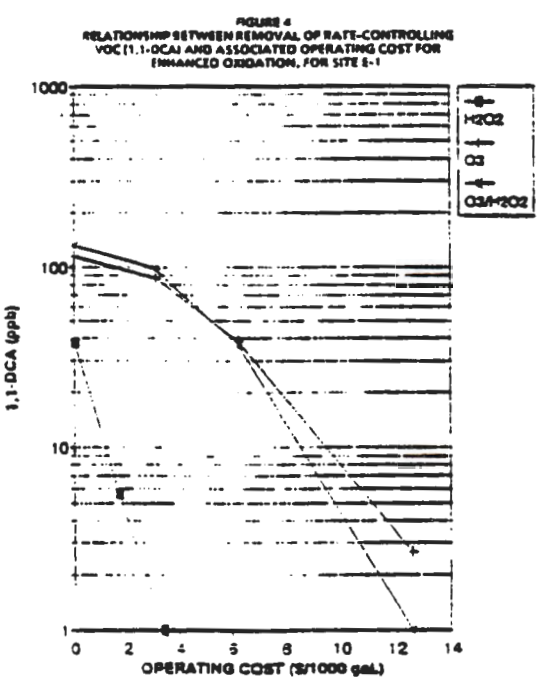
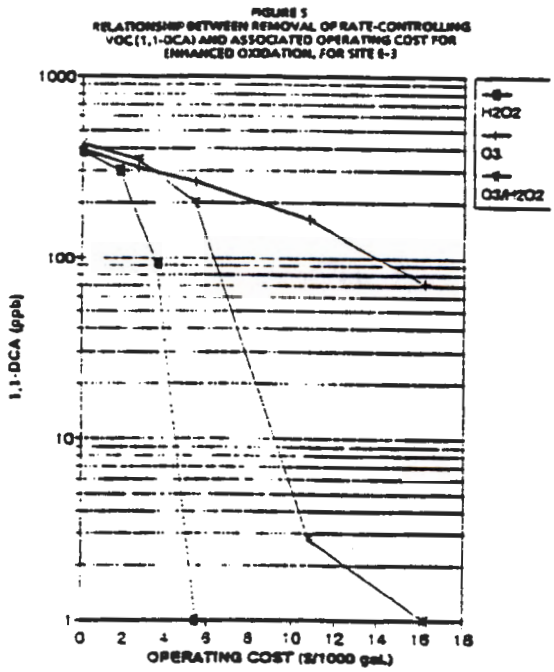


Figure 4 and Figure 5 (provided by PSI) show the relationship between removal of the rate-controlling VOC (1,1-DCA) and the associated estimated operating costs for enhanced oxidation for groundwater from Sites E-1 and E-3 respectively. The use of H_2O_2 as the oxidant leads to lower operating costs than the use of O_3 or a combination of O_3/H_2O_2 for achieving adequate removal of 1,1-DCA (the enhanced oxidation rate-controlling VOC of concern at both sites).





Based on the relative efficiencies of oxidation in the intermediate test runs, the combination of parameters chosen to be most effective for Site E-1 groundwater was: 50 mg/L H_2O_2 in solution and a pH of 5.5. This combination achieved adequate removal of VOCs of concern within an overall residence time of 2 minutes (i.e., 1.1 minutes reactor residence time). Similarly, the combination of parameters chosen to be most effective for Site E-3 groundwater was 100 mg/L H_2O_2 in solution and a pH of 5.1, a combination which achieved adequate removal of VOCs of concern within an overall residence time of 4 minutes (i.e., 3.5 minutes reactor residence time). Table IV shows the removal of VOCs achieved in the selected intermediate test run. The removal efficiencies achievable by the most efficient combination of parameters for Sites E-1 and E-3 were confirmed by repeating the chosen intermediate test runs using fresh samples of groundwater.

TABLE IV: REMOVAL OF VOCs OF CONCERN ACHIEVED IN THE SELECTED INTERMEDIATE TEST RUN

VOC of Concern	Site E-1 (1)			Site E-3 (2)		
	Initial Conc. (µg/L	Final Conc. (µg/L	Percent Removal	Initial Conc. (µg/L)	Final Conc. (µg/L)	Percent Removal
Vinyl chloride	1,200	<50	>95.83%	1,700	<50	>97%
1,1-DCA	37.7	<2	>94.7%	401	<2	>99.5%
1,2-DCA	NC	NC	-	68.7	<2	>97.1%
1,1-DCE	18.8	<2	>89.4%	5.6	<2	>64%
1,2-DCE	11,170	<4	>99.96%	428	<4	>99.1%
PCE	2,450	<2	>99.92%	NA	NA	NA
TCE	1,650	<2	>99.88%	NC	NC	-
Benzene	14.9	<2	>86.6%	18.8	<2	>89%
Chlorobenzene	NC	NC	-	3,100	<2	>99.9%
1,4-DCB	NC	NC	-	418	<2	>99.5%

(1) 45 mg/L H_2O_2 in solution/UV @pH 5.5.
(2) 100 mg/L H_2O_2 in solution/UV @pH 5.1.
NC VOC not of concern at this site.
NA Not detected during analysis.

CONFIRMATION TEST

The confirmation test for Site E-1 groundwater was conducted using 45 mg/L H_2O_2; UV; pH 5.5; and overall residence time of 2 minutes (i.e., 1.1 minutes reactor residence time. The confirmation test Site E-3 groundwater was conducted using 100 mg/L H_2O_2; UV; pH 5.1; and an overall residence time of 4 minutes (i.e., 3.5 minutes reactor residence time).

Table V provides the results of the confirmation test for Site E-1 groundwater samples along with the target remediation goals.

TABLE V: CONFIRMATION OF REMOVAL EFFICIENCY OF VOCs OF CONCERN, SITE E-1

VOC of Concern	Influent Concentration (µg/L)	Effluent Concentration (µg/L)	Percent Removal	Target Remediation Goal (µg/L)
Vinyl Chloride	628	<5	>99.2%	2
cis-1,2-DCE	12,700	17.7	99.86%	70
1,1-DCA	40.5	<2	>95.1%	3.5
TCE	2,200	4.2	99.8%	5
PCE	2,230	15.5(1)	99.3%	5
Benzene	11.3	<2	>82.3%	5
1,1-DCE	18.8	<2	>89.4%	7
trans-1,2-DCE	38.8	<2	>94.8%	100
Total VOCs	17,867.4	50.4	>99.72%	N.A.

(1) These values are due to sampling errors, not incomplete oxidation. An insufficient volume of water was used to rinse the sample port, in an attempt to assure minimum volatilization of contaminants.

NA Not applicable.

All the significant VOCs of concern were removed at efficiencies exceeding 90 percent. Only 1,1-DCE and benzene, which were present at relatively low concentrations (close to detection limits) were removed at lower efficiencies. The rate-limiting VOC, 1,1-DCA was removed at an efficiency exceeding 95.1 percent. In any case, residual concentrations of VOCs were below MCLs or detection limits.

Table VI shows the results of the confirmation test on the E-3 groundwater sample along with the target remediation goals. All the significant VOCs of concern were removed at efficiencies exceeding 90 percent. The rate-limiting VOC (1,1-DCA) was removed at an efficiency exceeding 99.2 percent In any case, residual concentrations of all VOCs of concern were below MCLs or detection limits.

TABLE VI: CONFIRMATION OF REMOVAL EFFICIENCY OF VOCs OF CONCERN, SITE E-3

VOC of Concern	Influent Concentration (µg/L)	Effluent Concentration (µg/L)	Percent Removal	Target Remediation Goal (µg/L)
Vinyl chloride	690	<5	>99%	2
cis-1,2-DCE	475	<2	>99.6%	70
1,1-DCA	412	3.1	99.2%	3.5
1,1-DCE	15.9	<2	>87%	7
trans-1,2-DCE	29.9	<2	>93.3%	100
1,2-DCA	77.6	<2	>97.4%	5
Chlorobenzene	3,390	8.1	99.76%	100
Benzene	18.2	<2	>89%	5
1,4-DCB	312	<2	>99.36%	75
Total VOCs	5420.6	<56.5	>99.96%	N.A.

N.A. - Not applicable.

In both confirmation tests, the removal efficiencies of VOCs of concern were at least as high as in the original intermediate test runs. The removal efficiencies of VOCs of low concentration appear lower than the VOCs of higher concentrations because effluent concentrations were taken as the detection limit whenever the reported concentrations were less than a given detection limit.

CONTROL TEST

A control test was performed for each sample to evaluate the loss of VOCs due to volatilization, photodegradation, and absorption. The control test simulated all the procedures of the enhanced oxidation process (including pretreatment) except for the treatment with hydrogen peroxide/UV. The control tests were conducted in parallel with the confirmation tests.

Table VII gives the results of the control tests for Site E-1 groundwater sample. The concentrations of VOCs in the effluent differed from the concentration in the influent by less than 5 percent in most cases. Only in the case of benzene, was the difference between effluent concentrations and influent concentrations significantly greater than 5 percent.

TABLE VII: LOSS OF VOCs OF CONCERN DURING CONTROL TEST RUN, SITE E-1

VOC of Concern	Influent Conc. (µg/L)	Effluent Conc. (µg/L)	Percent Loss in Conc.
Vinyl chloride	1,330	1,290	3%
cis-1,2-DCE	14,300	14,000	2.1%
trans-1,2-DCE	54.1	52.8	2.4%
1,1-DCA	56.1	55.5	1.1%
TCE	2,520	2,490	1.2%
PCE	2,060	2,080	--
Benzene	46.6	16.7	64.1%
1,1-DCE	31.9	32.7	--
Total VOCs	20,398.7	20,017.7	1.87%

Table VIII gives the results of the control test on Site E-3 groundwater sample. The concentrations of all VOCs of concern in the effluent except for vinyl chloride, differed from the influent concentrations by less than 5 percent.

TABLE VIII: LOSS OF VOCs OF CONCERN DURING CONTROL TEST RUN, SITE E-3

VOC of Concern	Influent Conc. (µg/L)	Effluent Conc. (µg/L)	Percent Loss in Conc. (µg/L)
Vinyl chloride	1,700	1,540	9.4%
cis-1,2-DCE	919	880	4.2%
1,1-DCA	459	446	2.8%
Chlorobenzene	3,450	3,390	1.7%
Benzene	19.7	19.4	1.5%
1,4-DCB	299	292	2.3%
1,1-DCE	21.1	20.3	3.8%
trans-1,2-DCE	52.5	52.5	0%
1,2-DCA	116	118	--
Total VOCs	7,036.3	6,758.3	3.95%

The PSI equipment (bench-scale, pilot-scale, and full-scale) is completely enclosed, and does not allow head-space for volatilization. Hence, the minimal loss of VOCs in the control test can be attributable mainly to adsorption and photodegradation. Additional causes for losses may be attributable to volatilization during sample injection, or variation during analysis. However, VOC losses due to causes other than enhanced oxidation were minimal. Hence enhanced oxidation achieved most of the removal, as seen in Figures 6 and 7, which compare the removal of VOCs in the confirmation test to the loss of VOCs during the control tests, for Sites E-1 and E-3 respectively.

Figure 6: REMOVAL OF VOCs OF CONCERN IN CONFIRMATION TEST vs CONTROL TEST :E-1

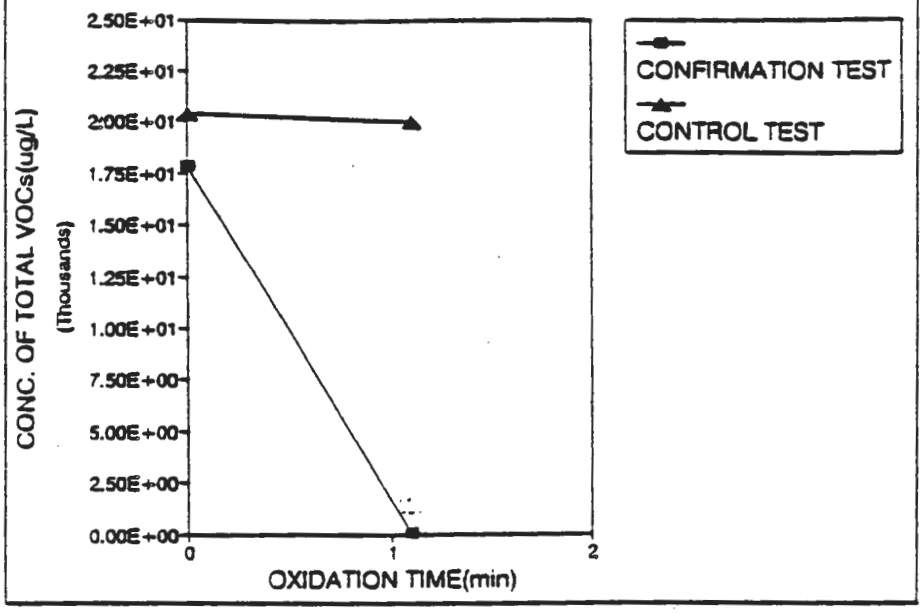
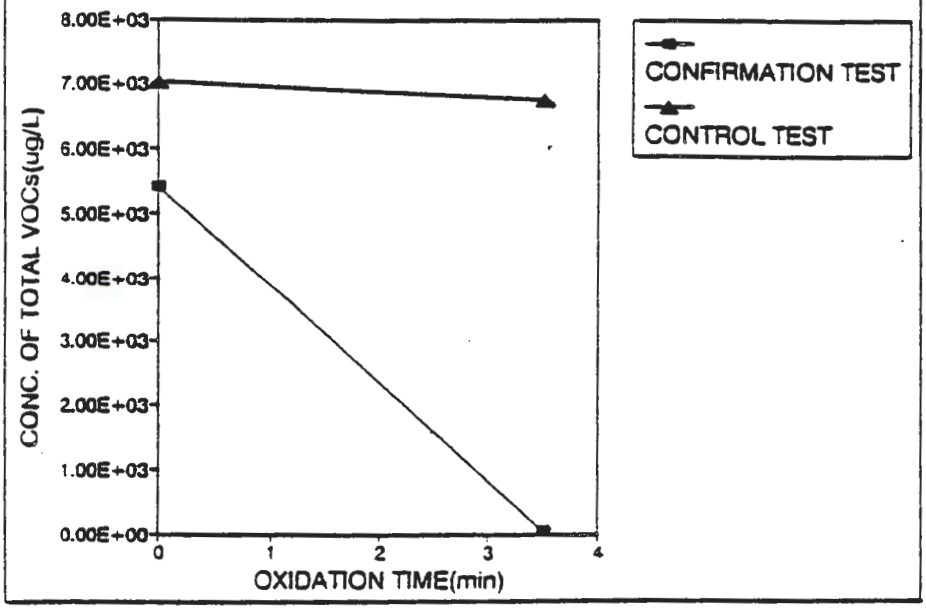


Figure 7: REMOVAL OF VOCs OF CONCERN IN CONFIRMATION TEST vs CONTROL TEST :E-3



COST

Budgetary cost estimates of groundwater treatment to achieve Target Remediation Goals (Drinking Water Standards) for Sites E-1, E-3 as well as the entire Zone 2 are presented in Table IX. These costs include all required controls and pretreatment chemicals, but do not include pretreatment and groundwater extraction systems, which have not yet been designed. The costs are expected to vary depending on the choice of equipment manufacturer. Table X provides the cost estimates for groundwater treatment to achieve 90 percent of Target Remediation Goals. The costs presented in Tables IX and X assume that Kelly AFB purchases the equipment from PSI, and has the option of either operating on its own or using PSI's services for operation. Table X provides the cost estimates for groundwater treatment to achieve 90 percent of Target Remedial Goals.

TABLE IX: BUDGETARY COST ESTIMATES FOR TREATMENT SYSTEM DESIGNED TO ACHIEVE TARGET REMEDIATION GOALS FOR A PURCHASED SYSTEM

Location	Flow Rate (gallons per minute)	Kelly AFB Operated System		PSI Operated System	
		Capital Costs ($1,000)[a]	Operating & Maintenance Costs ($1,000/ Month)[b]	Optional Maintenance & Technician Services Agreement ($1,000/month)[c]	Electrical Cost ($1,000/ month)
Site E-1	20	104.5	2.6	3.2	1.7
Site E-3	35	220.1	11.6	7.0	9.3
Zone 2	250	322.5	15.9	8.9	11.7

(a) Includes startup and training, enhanced oxidation unit, hydrogen peroxide storage/feed system.
(b) Includes maintenance, electricity, and hydrogen peroxide. Does not include amortization of capital. Does not incude replacement costs which are typicaly 2 percent of capital costs.
(c) Includes hydrogen peroxide supply, maintenance, replacement parts, emergency service and monthly maintenance visits.

TABLE X: BUDGETARY COST ESTIMATES FOR TREATMENT SYSTEM DESIGNED TO ACHIEVE 90% OF TARGET REMEDIATION GOALS FOR A PURCHASED SYSTEM

Location	Flow Rate (gallons per minute)	Kelly AFB Operated System		PSI Operated System	
		Capital Costs ($1,000)[a]	Operating & Maintenance Costs ($1,000/ Month)[b]	Optional Maintenance & Technician Services Agreement ($1,000/month)[c]	Electrical Cost ($1,000/ month)
Site E-1	20	67.5	2.0	2.7	1.2
Site E-3	35	157.5	5.9	5.0	4.0
Zone 2	250	—	—	—	—

(a) Includes startup and training, enhanced oxidation unit, hydrogen perioxide storage/feed system.
(b) Includes maintenance, electricity, and hydrogen peroxide. Does not include amortization of capital. Does not incude replacement costs which are typicaly 2 percent of capital costs.
(c) Includes hydrogen peroxide supply, maintenance, replacement parts, emergency service and monthly maintenance visits.

Tables XI and XII provide cost estimates for groundwater treatment to achieve Drinking Water Standards and 90 percent of Target Remediation Goals, respectively, but assuming that Kelly AFB leases the equipment and has the options of either operating on its own or by using PSI's services for operation.

TABLE XI: BUDGETARY COST ESTIMATES FOR GROUNDWATER TREATMENT TO TARGET REMEDIATION GOALS FOR A LEASED SYSTEM

Location	Flow Rate (gallons per minute)	Full Service Agreement ($1,000/Month)[a]	Electrical Cost ($1,000/Month)[b]
Site E-1	20	4.5	1.7
Site E-3	35	9.9	9.3
Zone 2	250	13.3	11.7

(a) Include hydrogen peroxide supply, maintenance, replacement parts, emergency service and monthly maintenance visits.
(c) Note that equipment replacement is included if necessary due to changing flow or organic contamination level.

TABLE XII: BUDGETARY COST ESTIMATES FOR TREATMENT SYSTEM DESIGNED TO ACHIEVE 90% OF TARGET REMEDIATION GOALS FOR A LEASED SYSTEM

Location	Flow Rate (gpm)	Full Service Agreement ($1,000/Month)[a]	Electrical Cost ($1,000/Month)[b]
Site E-1	20	3.0	1.2
Site E-3	35	7.1	4.0
Zone 2	250	—	—

(a) Include hydrogen peroxide supply, maintenance, replacement parts, emergency service and monthly maintenance visits.

(b) Note that equipment replacement is included if necessary due to changing flow or organic contamination level.

CONCLUSIONS

Based on the results of the treatability study, the following conclusions may be drawn about the effectiveness of enhanced oxidation for the removal of VOCs for the contaminated groundwater under consideration:

- Enhanced oxidation using H_2O_2/UV in the pH range of 5.0-5.5 is effective in achieving the removal of VOCs of concern to below MCLs or detection limits. Destruction by oxidation is the primary mode of removal.
- Although enhanced oxidation using O_3/UV achieves significant removal of the VOCs of concern, H_2O_2/UV is more effective.
- Pretreatment would be required for the oxidation or conventional precipitation of iron if present at concentrations exceeding 1 mg/L; and filtration for the removal of suspended solids exceeding 5 to 10 mg/L or turbidity exceeding 5 FTU.

CONCLUSIONS/RECOMMENDATIONS

Enhanced oxidation with H_2O_2/UV can be effectively used for the removal of the VOCs of concern from the contaminated groundwaters at Sites E-1 and E-3. The contaminants of concern in the zone wide groundwater at Zone 2 are similar to those at Sites E-1 and E-3; further, groundwater contaminants at Zone 2 are present at lower concentrations than those at these two sites. Hence, enhanced oxidation can be evaluated favorably for the feasibility of remediating the groundwater in the entire zone, based on the positive results obtained from the treatability tests for groundwaters at Sites E-1 and E-3.

Treatment by enhanced oxidation to achieve 90 percent of target remediation goals (drinking water standards) followed by post-treatment at the Individual Wastewater Treatment Plant (IWTP) would likely be more cost effective than treating to achieve drinking water standards followed by reinjection or discharge to surface waters.

During pilot-scale testing, the final products of enhanced oxidation must be analyzed and ensured to be innocuous. Pilot-scale testing is in the planning stage. Additional analytical parameters such as residual H_2O_2 and TDS will be evaluated during the pilot-scale test to ensure that the effluent does not exceed other discharge permit criteria in place for the IWTP.

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Enclosure 4

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SIMULTANEOUS AIR STRIPPING AND ADVANCED OXIDATION PROCESSES (AOP)

FOR

PROCESS WATER TREATMENT

BY

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SIMULTANEOUS AERATION AND ADVANCED OXIDATION PROCESSES (AOP) FOR PROCESS WATER TREATMENT

ABSTRACT

The oxidation of hydrocarbons to produce oxygenated organics also generates byproduct water. This water usually appears as distillation "tower bottoms" which contains trace amounts of the oxygenated organics. Such aqueous streams have no mineral content and have potential use as cooling tower water or boiler feed water. To do the latter, however, requires that the dissolved organics be removed or otherwise destroyed. This paper describes the use of several advanced oxidation processes (AOP) which were investigated as a means of reducing dissolved organics in such a process water stream. The raw process water contained six identifiable organic compounds and several $C/_5$ alcohols. The TOC level was 2500 ppm ($\pm$ 250) and the COD $\approx$ 13500 ppm. A ninety percent reduction in the COD level was sought.

Based on the experimental results obtained from a Taguchi statistical approach for design of experiments, temperature was found to have the greatest impact on TOC reduction. Hydrogen peroxide was the most effective chemical oxidizer. The organic acids, acetic and formic, were present in the water and could not be removed by air stripping techniques alone. They were also resistant to oxidation. For this particular waste process water stream, our results indicated that the desired 90% reduction in the dissolved TOC could be achieved in time periods of less than sixty minutes, but only under a conditions of 1.0 MPa (10 atm.), 180°C (350°F) and thirty percent peroxide. At these conditions, the projected reagent (oxidizer) costs were high, i.e. in excess of $100 per 1000 gallons of water.

Introduction

Advanced oxidation process, or AOP, is the acronym used to describe chemical oxidation in which oxidizing reagents other than molecular oxygen are used (1)(2)(3). Most frequently such processes utilize ozone, hydrogen peroxide, halogens and halogen oxides, either alone or in combination with catalysts. In general AOP can be viewed as a broad based technology developed for the treatment of waste water streams burdened with dissolved organics or pathogenic microorganisms. In theory, complete oxidation of the organics with AOP should occur rapidly and produce only carbon dioxide and water as products. However, even in the most successful applications of AOP, this is not always the case. Moreover, many of the reagents used with AOP are expensive and require demonstration of cost effectiveness if a particular AOP is to represent a true alternative process. AOP is still a technology in evolution, spurred on by environmental concerns and the need by industry to be in compliance with ever stricter regulatory constraints.

In this particular instance, the investigation of AOP began as a means for recovery and recycle of a process water stream. Approximately 30 m^3/hr (8000 gal/hr) as distillation bottoms were available for treatment (Table 1). Its temperature and pressure were 100°C and 122 kPa (3 psig). Because it represented the byproduct of an oxygenated organic synthesis process, the process stream contained trace oxygenated organics with a combined TOC level of 2500 ppm. Constituents contributing to this TOC level were low molecular weight, volatile compounds such as methanol and formaldehyde, along with the less volatile compounds of formic and acetic acids. The latter components are known to form

oligomers in both the liquid and vapor phases and to dissociate in water to form ions. Hence, removal of low molecular weight acids by deaeration is almost impossible. Biological treatment of soluble acids is possible, but would require additional pond capacity. The question was, therefore, could AOP be used to reduce the TOC level by 90% to 250 ppm (municipal water has a TOC of 3 to 15 ppm). If so, then the treated process water could be reused on site as cooling tower water or boiler feed water. Both applications were attractive, since the process water was mineral free and, therefore, should significantly reduce problems with scaling in such applications. However, due to the dissolved organic acids, the pH of the raw process water was approximately 3.0. Without additional pH adjustment after AOP, serious corrosion problems could arise. Finally, even if AOP provided the desired reduction in TOC levels, it would still have to be cost effective. With these constraints, the investigation into the use of AOPs was begun.

Experimental Design: **Process Water Variations**

The process water stream was found to have some variations in composition over time. Table 1 shows the composition ranges as determined by GC/MS for samples taken over intervals of several months. Based on these analyses, a theoretical TOC level was calculated. However, GC/MS analysis was not available for the many experimental runs planned for AOP. Hence, the more common COD level of the process water was used as the dependent variable by which the success or failure of a given AOP procedure could be measured. When a given procedure appeared to show promise, then the more sensitive GC/MS procedure was again

employed in order to determine actual changes in specific component concentration levels during and following an AOP treatment.

Other Experimental Variables

The use of AOP presents a wide range of possible scenarios. Temperature and degree of contact time are two obvious variables for consideration with any chemical kinetic system. The type or combination of oxidizers employed, as well as the use of a catalyst, are also potential variables which can play important roles. Because of this large number of potential variables, some early screening experiments were carried out to better define the final design of experiments.

For example, ozone is an oft touted, effective oxidizing reagent. However, the ozone generator available for this study could produce only one mole percent O_3 in with a total flow of 2L/min (STP). At this level of concentration O_3 was found to have an insignificant impact on COD reduction, while the air flow itself with O_3 excluded, produced significant COD reductions due to deaeration of the more volatile compounds. Hence, because of its low water solubility, ozone was dropped from further experimental study in favor of more concentrated and condensed oxidizing species such as hydrogen peroxide and ammonium nitrate. Both of these compounds are highly water soluble and could be introduced as liquid solutions into the experimental apparatus.

Catalysts were also screened for effectiveness in the initial tests. Of those tested, only platinum gauze was found to be effective. Heavy metal salts such as ferric chloride and molybdenum trioxide, as well as traces of inorganic sulfuric acid were found to produce only minimal changes in the reduction of COD by oxidation.

In addition these inorganics added to the dissolved solids level of the process water which was considered to be an undesirable feature. UV light was also tested, but the low wattage lamp available for testing probably limited COD reduction by UV interaction. Hence, UV was also abandoned in subsequent tests.

The final mix of variables ultimately selected for testing included the following;

(1) Air, as a means of providing deaeration and as a supply of molecular oxygen for chemical oxidation to reduce COD levels.
(2) Hydrogen peroxide and ammonium nitrate as potential condensed phase chemical oxidizers.
(3) Platinum gauze as a heterogeneous catalytic surface
(4) Temperature variations from 25°C (ambient) to 100°C (process stream conditions)
(5) Contact times of less that one hour in which to achieve the 90% COD reduction.
However, longer times were to be used in experimental studies in order to investigate mechanisms and establish kinetic rate constants.

Because of the large number of process variables, a statistical approach to the design of experiments was utilized. This approach is outline by Taguchi (4) and utilizes an AOV approach to determine the percentage contribution of each experimental variable to the change in the dependent variable, i.e. COD reduction. Although this approach was of invaluable assistance in the design of our experiments, space does not permit a full discussion of its application in this paper.

Experimental Apparatus

Because of the exploratory nature of this project, a batch reactor was utilized for experimentation. The low pressure studies were conducted in a three-arm 0.5 liter flask with the arrangement shown in Figure 1. This system allowed isothermal operation at selected temperatures between ambient and the boiling point of the process water. Liquid oxidizer solutions could be added continuously and air, when

used, was passed through the platinum gauze to encourage deaeration and provide mixing and liquid contact. The condenser helped minimize water vapor losses. Although deaeration or stripping was used in some isntances, no sampling was performed on the vented gases. However, samples of the treated process water could be withdrawn at regular intervals for COD or GC/MS analyses.

For higher pressure experiments, a modified PARR® reactor was used. This unit could hold a liter of process water and had the same features of temperature control and multiple access ports as did the glass flask which was used in the ambient pressure experiments.

Experimental Results: ***Overall Temperature Effect***

Based on the experimental results and the Taguchi approach to AOV, it was evident that temperature more than any other process variable controlled the rate and extent of COD reduction for this process water stream. Figure 2 presents this effect graphically for ammonium nitrate as the oxidizer. Similar results were achieved with hydrogen peroxide as the oxidizer. The temperature effects are manifested in several ways. First, an increase in temperature enhances deaeration of the more volatile components in the contaminated water by increasing their vapor pressures. Nearly 90% of the reduction in COD during the first thirty minutes was due to deaeration effects. Secondly, increases in temperature accelerates the rate of chemical reaction by oxidation. In these experiments we were able to show that gradual additions of hydrogen peroxide gave better COD reductions than did the same amount of hydrogen peroxide added on a one time basis. This indicated that temperature can also have a counter productive effect. That is, it can accelerate self destruction of the oxidizer

at the same time it enhances the organic chemical oxidation process. Hence, for contact times which extend to hours rather than minutes, serious consideration must be given to the loss of oxidizer by self or spurious reactions.

By developing a model of the combined deaeration and chemical reaction process from three isotherms, 25°C, 50°C and 100°C, it was possible extrapolate to conditions of higher temperature in order to estimate COD reductions. This as done for conditions at 1.01 MPa (160 psig) and a saturated boiling temperature of 180°C. The semitheoretical model predicted greater than 90% reduction in COD levels for a time period of less than one hour. This prediction was later confirmed experimentally, but only after an increase in total peroxide usage.

Oxidizer

The statistical approach indicated that for the conditions of this experiment, the hydrogen peroxide was a superior oxidizer to ammonium nitrate or to ozone. The latter had the distinct advantage of not being concentrated. Moreover, the cost for O_3 generation is higher than hydrogen peroxide or ammonium nitrate. Nor is it a storable reagent. Hence even if it were available at higher concentrations, there were no indications from this study that O_3 would be cost effective for this application. Ozone is most effective in gas phase reactions, as a biocide, and in the treatment of unstaurate organics.

The ammonium nitrate solutions had the distinction of being relatively cheap and easy to manage. However, decomposition does not always favor activated oxidizing fragments which lead to COD reduction. There is also some evidence to suggest that a threshold temperature is required with ammonium nitrate in order to

achieve high levels of oxidation (5).

The use of catalysts of various types has already been discussed in part. However, only the platinum gauze was found to have a statistical effect for the experimental conditions studied. This should change at elevated temperatures. Even so, platinum is an expensive metal and inventory costs would impact on cost effectiveness in this application.

Destruction of Specific Compounds

Although the COD level was the key dependent variable upon which the success of failure of the AOP was determined, several experimental runs were made in which specific compounds were monitored as a function of time. The GC/MS unit was used for this purpose and provided reliable data to within 5ppm. These data are shown in Tables 2 and 3. In general, low molecular weight compounds such as formaldehyde and acetone (DMK) go through a minimum concentration with elapsed time (Figure 3). This is interpreted as being due to an initial loss due to aeration followed by a slow increase in concentration as they are produced by the chemical oxidation process faster than they are stripped from solution. The C_5 compounds show a steady decline in concentration with elapsed time. Apparently the major mechanism is scission of one of two carbons at a time from the ends of the larger molecules. However, in one instance when a trace amount of sulfuric acid was used as a potential catalyst, the heavier C_5 fraction actually increased with time (Table 3). This suggested that a degree of polymerization may have occurred, i.e. aldehyde condensation to form acetals or ringed structures. Finally, the low molecular weight acids, formic and acetic, either remained at a constant concentration or showed a

gradual rise with elapsed time (Table 2). This would suggest that they are either stable products of the overall AOP process, and/or they are being produced by the degradation process. There is some evidence to suggest that formic and acetic peroxo compounds are formed. Certainly these two simple acids represent a major intermediate between the larger alcohols and their complete oxidation to produce carbon dioxide and water. Two other aspects of the small organic acids must be considered. They form dimmers and trimens in both the liquid and vapor phase, and they also ionize in water. Both of these tendencies make their solutions highly nonideal and retard or prevent their loss by simple deaeration. Consequently, these compounds (acids) along with formaldehyde, acetone, and methanol represent the final organic species for any AOP process. This is true no matter what the initial hydrocarbon contaminant is. If chlorinated compounds are present, however, chloroform will most probably also be generated as a final small molecule.

Reagent Cost

The final manipulation of the experimental data involved estimates of reagent costs per 1000 gallons of process waste water. Hydrogen peroxide was assessed a cost factor of $0.70 per pound and ammonium nitrate $0.06 per pound based on quotations in the Chemical Marketing Reporter. On this basis, the information shown in Figure 3 is indicative of the projected reagent costs for AOP with this particular process water. Obviously a 90% COD reduction by AOP starting with a contaminant level of 10000 ppm is a rather expensive approach (> $400/1000 gal). On the other hand 60% reductions can be achieved at a more reasonable cost; (< $10/1000 gal.)

Conclusions

The advanced oxidation processes can indeed be utilized to reduce or eliminate dissolved organics in aqueous waste or process streams. However, reagent and process costs will be high for these relatively heavily loaded streams. This suggests that AOP, in the condensed phase, may find more applications as a polishing operation rather than as a stand alone system for heavily contaminated water. Whenever the reagent costs exceed $100 - $300/1000 gal of water, then there are probably more cost effect alternatives to AOP. In the example of the process stream used for this study, it would appear feasible to use deration (6) and limited AOP to reduce the TOC about 60 percent. The system could then by neutralized with lime or caustic to a pH of 8 to 9, and then used to supplement cooling tower water.

Acknowledgement: The authors wish to acknowledge Hoechst Celanese for their assistance with GC/MS analytical work on this project.

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TABLE 1. PROCESS WATER CHARACTERISTICS

A. Stream Specifications:

(1) Flow rate 3×10^4 kg/hr (8×10^3 gal/hr)
(2) Temperature 100°C (212°F)
(3) Column base pressure 122 kPa (3 psig)
(4) Gross TOC level 2500 ppm
Municipal water has a TOC level of 3 to 15 ppm

B. Typical Component Analysis by GC/MS

Component	Weight Percent Range
*Formaldehyde	0.032 - 0.051
Acetaldehyde	0.002 - 0.003
*Dimethyl ketone	0.021 - 0.042
*Methyl alcohol	0.085 - 0.095
Methyl ethyl ketone	0.004 - 0.006
*Isopropyl alcohol	0.021 - 0.048
Biacetyl	0.003 - 0.051
*Acetonitrile	0.020 - 0.046
Sec-butanol	0.002 - 0.006
n-propanol	0.001 - 0.002
*Acetic acid	0.050 - 0.241
*Formic acid	0.024 - 0.149
*Unknown (est. C_5H_1,OH)	0.030 - 0.153
	0.033 0.900
Water	99.67 99.100

*Components making up > 90% of the dissolved organics.

TABLE 2: Concentration in (ppm) of Components in Process Water During AOP at Time (t).

	Time (t) minutes				
Component	0	30	60	90	120
Formaldehyde	573	214	14	10	205
Dimethyl Ketone	238	50	0	10	25
Methyl Alcohol	595	103	42	10	0
Methyl Ethyl Ketone	20	0	0	0	0
Isopropyl Alcohol	180	30	0	0	0
Ethyl Alcohol	70	10	0	0	0
Acetonitrile	364	10	0	0	0
Acetic Acid	1200	900	1100	1000	1300
Formic Acid	200	3900	7700	7400	6800

This run was for 450 ml of process water of composition shown at time (t) equal zero. Temperature = 98C. Air at 2L/min. was passed through Pt gauze catalyst. A 3% solution of hydrogen peroxide was added at a rate of 50 ml/hr.

TABLE 3: Concentration in (ppm) of Components in Process Water During AOP at Time (t).

Component	Time (t) minutes 0	30	60
Formaldehyde	814	688	523
Dimethyl Ketone	303	0	0
Methyl Alcohol	665	104	0
Methyl Ethyl Ketone	40	0	0
Isopropyl Alcohol	160	0	0
Ethyl Alcohol	80	10	0
Acetonitrile	446	10	0
Acetic Acid	1700	1100	1500
Formic Acid	500	700	1000
Heavies*	842	294	530

* Heavies were >C5's

This run was for 450 ml of process water of initial composition shown for time (t) equal zero. Temperature = 98C. A Pt gauze catayst was submerged in the boiling solution and three drops of 92% H2SO4 were added.

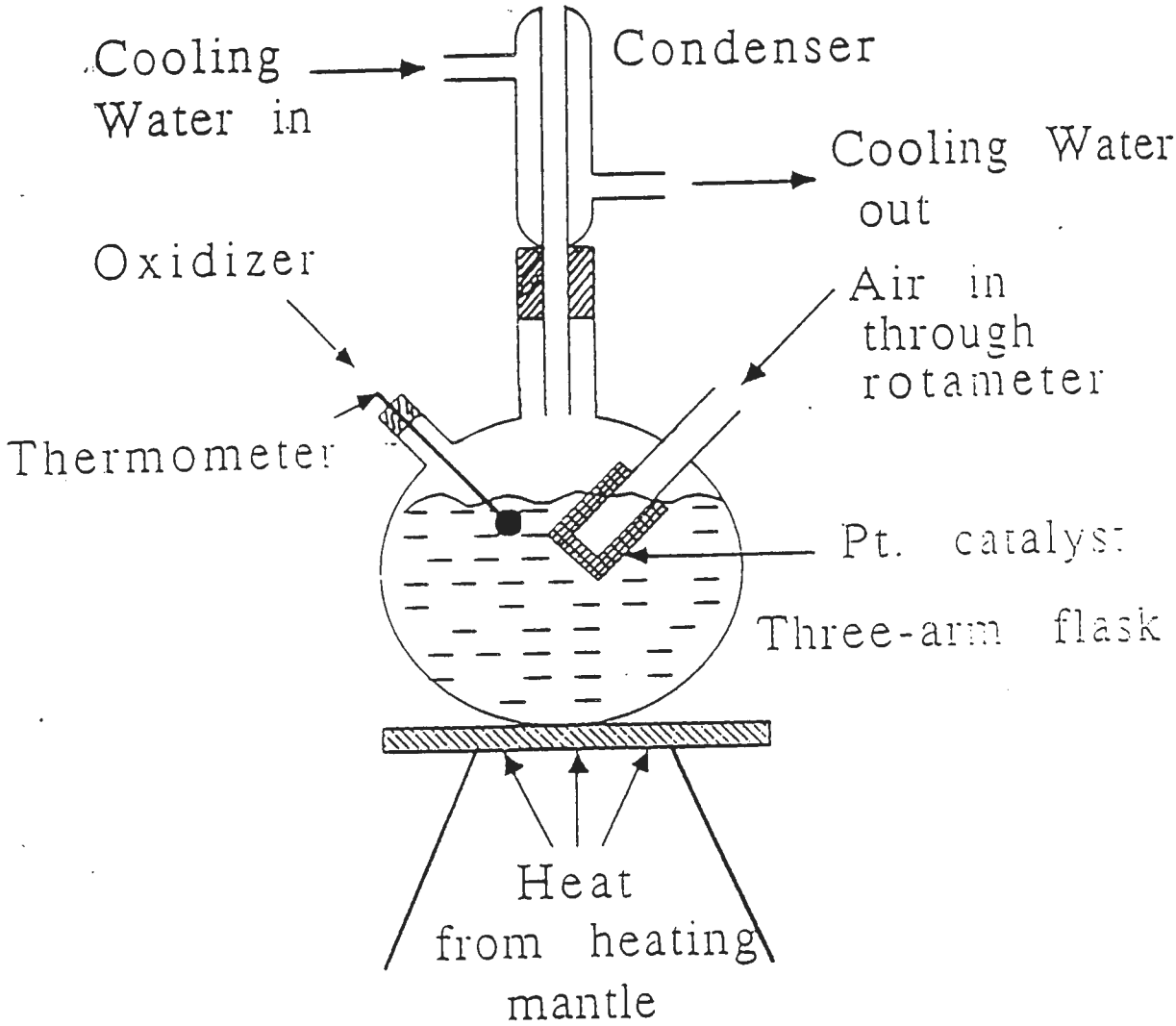

Fig. 1: Experimental set-up used in the design of experiments to destroy dissolved organics in process water

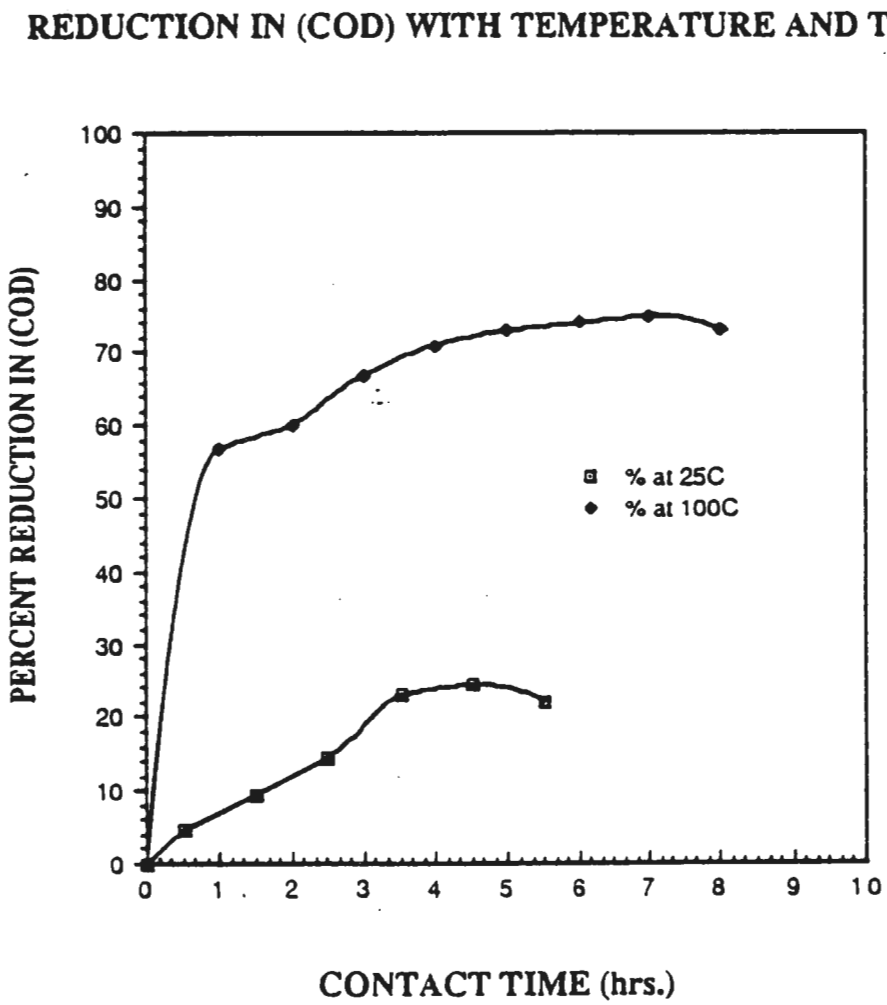

Figure 2. Reduction of Process Water (COD) as a Function of Temperature and Contact Time for Ammonium Nitrate Based AOP

COST of REAGENT OXIDIZER for (COD) REDUCTION

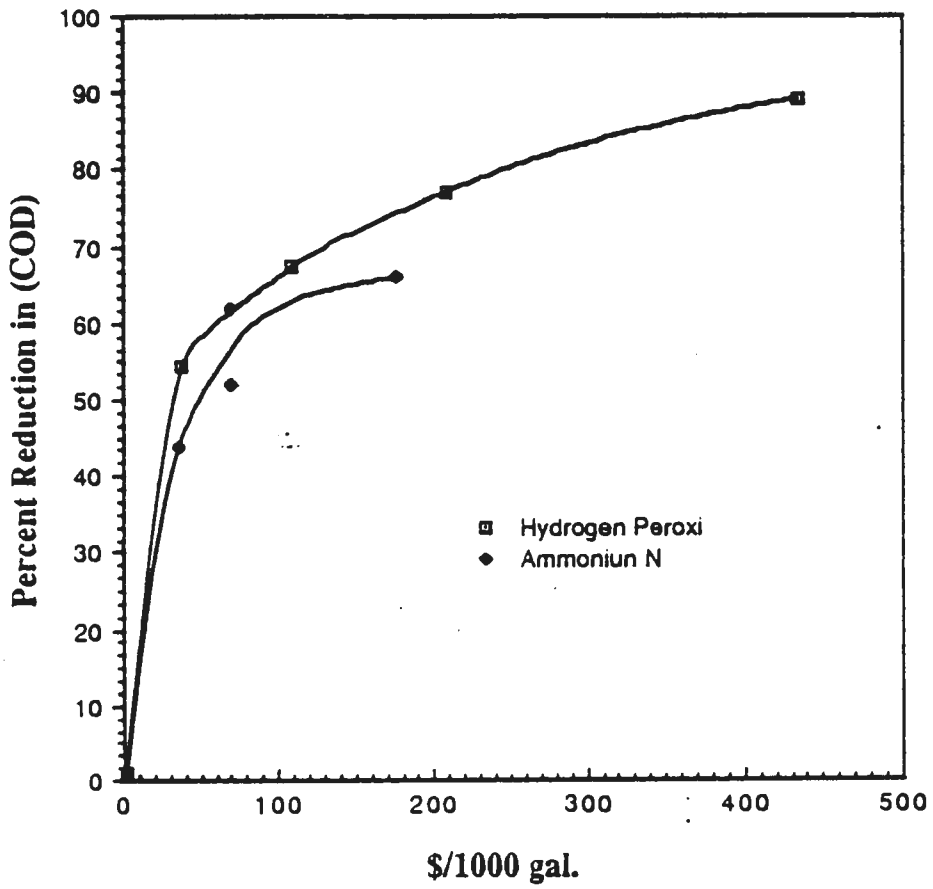

Figure 4. Hydrogen Peroxide and Ammonium Nitrate Costs for AOP Treatment of 1000 gallons (3.785m³) of Process Water

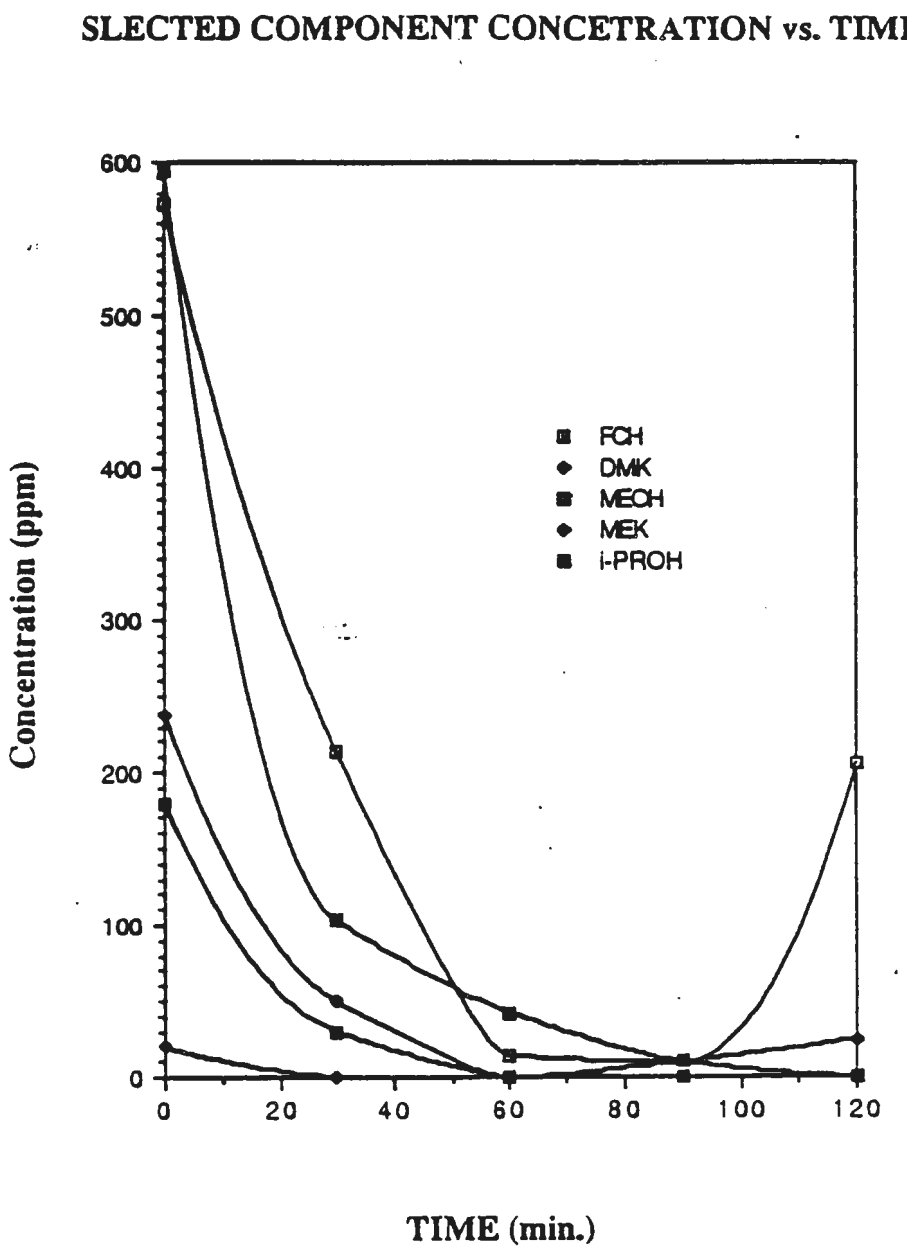

Figure 3. Selected Component Concentration Versus Time for AOP Treatment of Process Water

Enclosure 5

9 3 1 2 9 0 1 1 9 2 1

THE perox-pure™ OXIDATION SYSTEM
A COMPARATIVE SUMMARY

by

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Presented at

The American Institute of Chemical Engineers
1990 Summer National Meeting
San Diego, California
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THE perox-pure™ OXIDATION SYSTEM

A COMPARATIVE SUMMARY

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ABSTRACT:

During the 1980's, the pollution control industry was pressed to reevaluate available technologies for removing organic contaminants from water and wastewater. This was especially true of "transfer" technologies such as stripping and adsorption that merely transfer the contaminant from one phase to another. In the 1990's "transfer" technologies will give way to more acceptable on-site destruction processes such as chemical oxidation.

This paper will present data from laboratory tests, field demonstrations and full-scale operating systems utilizing the perox-pure™ Treatment Process. In addition to economic and performance data, process improvements and advantages of this unique UV light catalyzed oxidation system will be highlighted. Comparisons to other advanced oxidation processes will include a discussion of basic process principals as well as equipment and operational considerations.

INTRODUCTION:

The development of the **perox-pure™** UV peroxidation process was started in the late 1970's. Today, there are over thirty (30) full-scale treatment units that are in operation or in the final stages of design and installation, but the development and improvement of the process is continuing. This advanced oxidation

process, using ultraviolet (UV) light catalyzed hydrogen peroxide has been shown to be a cost-effective treatment for a wide array of organic compounds found in contaminated groundwater, toxic waste leachates and industrial wastewaters. Recent improvements in the **perox-pure**™ Process have reduced the operating cost for total destruction of these toxic organics by up to 50%. In addition, the oxidation rate of many of the "difficult to oxidize" compounds such as 1,1,1-trichloroethane (TCA), 1,1-dichloroethane (DCA), chloroform (CHCL3) and methylene chloride (MeCl) have been increased up to three fold. These advances increase the cost effectiveness of on-site destruction processes versus "transfer technologies" and broaden the applicability of chemical oxidation as the technology of choice.

perox-pure™ PROCESS

In this process, UV light converts the hydrogen peroxide (H202) in solution to hydroxyl radicals (HO·) and "activates" many of the organic molecules to make them easier to oxidize. The photolysis reaction which forms HO· can be shown as follows:

$$H202 \xrightarrow{UV} 2\ HO\cdot$$

The activation of the organic molecules can range from direct oxidation by absorption and disassociation to the formation of organic radicals or other reactive intermediates. With enough time and reactants, organic compounds can be completely destroyed to CO2, H2O and, if present, the appropriate inorganic salt.

Most early UV oxidation processes used low pressure mercury vapor lamps combined with ozone (O3). The **perox-pure**™ Process utilizes a proprietary high intensity UV lamp combined with H202. This provides a number of advantages for chemical oxidation of aqueous solutions.

Three process considerations which manifest advantages include:

- o <u>UV Intensity</u> - The higher intensity allows for a more compact equipment design as well as lower capital cost. In addition, the higher UV intensity gives better penetration in wastewater or high concentration waters and allows for treatment of a wider range of applications.

- o <u>UV Spectra</u> - Since activation of organic compounds plays a key role in the destruction process, the broad spectra of the high intensity lamps is better suited for most applications than the narrow spectrum low pressure mercury lamps.

- o <u>H202</u> - Because H202 is completely miscible with water, it can be easily added in any desired concentration. This wide range of concentrations combined with high intensity lamps allows for simplicity of reactor design, and short reaction times for both groundwater and wastewater applications. In addition, there are no toxic gas emissions or stripping of volatile organics into the air.

BENCH-SCALE TESTING:

Over the last five (5) years Peroxidation Systems, Inc. (PSI) has tested hundreds of water and wastewater samples from clients using bench-scale equipment. In addition, an on-going research and development program has contributed to the large body of information available on the oxidation of organic compounds by UV peroxidation. This data is stored in a computerized data base that can be used to generate preliminary process design and cost estimates for a given set of influent and effluent specifications. Table 1 is a partial listing of the compounds in the database.

Table 1

perox-pure™ Database
Organic Compounds Listing

Acenaphthene
Acenaphtylene
Acetic Acid
Acetone
Acetonitrile
Acrolein (Propenal)
Acrylic Acid
Acrylonitrile
Alachlor
Alcohols
Aldicarb
Aldrin
Aniline
Anthracene
Benzene
Benzoic Acid
Benzyl butyl phthalate
Bis (2-chloroisopropyl) ether
Bis (2-ethylhexyl) phthalate
Bromodichloromethane
Butyric Acid
Butyl Acrylate
Butylbenzene
Carbon tetrachloride
Chloroaniline
Chlorobenzene
Chlorodane
Chloroethane
Chloroform
Chloromethane
2-Chloronaphthalene
Chlorophenol
Cresol
Chlorotoluene
Cyanide
Cyclohenanone
1,2-Dibromo-3-chloropropane
Dibromochloromethane
1,2-Dibromoethane
Dichlorobenzene
Dichlorobenzidine
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
1,2-Dichloroethene
2,4-Dichlorophenol
Dichloropropane
Dichloropropene
Dinitrophenol
Dieldrin
EDTA
Endrin
Ethylbenzene
Ethylene Diamine
Fluoranthene
Fluorene
Formaldehyde
Formic Acid
Hexachlorobenzene
Hydrazines
Isophorone
Methyl ethyl ketone (MEK)
Methyl isobutyl ketone (MIBK)
Methylene chloride
MTBE
Napthalene
Nitroglycerine
Nitrophenol
Nitrosamine
PCBs
Pentachlorophenol
Phenanthrene
Phenol
Tetrachloroethane
Tetrachloroethene
Tetrahydrofuran
Toluene
Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
2,4,6-Trichlorophenol
Trichlorophenols
Vinyl chloride
Xylene

Some of the important process variables affecting performance and costs are shown in Table 2.

Table 2

perox-pure™ Process Variables

- UV and H202 Dosage
- Reactor Design
- Type and Concentration of Organics
- Type and Concentration of Inorganics
- pH
- Catalyst

One of the unique differences of the **perox-pure**™ Process relates to the reactor design. Since most of the oxidation of organics occurs via a chemical reaction with hydroxyl radicals, the reactor is designed to optimize this process. A more detailed discussion of the benefits of **perox-pure**™ reactor design is presented under PROCESS IMPROVEMENTS.

Another advantage of the **perox-pure**™ design is the ability of the high intensity lamps to mitigate the negative effects of some inorganic compounds present in the water. There is significant data present in the literature indicating that alkalinity, due to bicarbonate ions, reduces the rate of HO· attack. The data shown in Figures 1-3 compare low pressure and high intensity lamps for oxidation of TCA and MeCl at different levels of alkalinity. Analysis of Figures 1 and 2, using low pressure lamps, illustrate that the oxidation rate for TCA or MeCl is about 6-10 times slower in Tucson, Arizona tap water or in distilled water with 200 mg/l alkalinity added than in distilled water only. This same lowering of oxidation rate is seen in Figure 3 using high intensity lamps, but the difference is less than two (2) times slower. A similar effect using low pressure lamps can be seen with easy to oxidize compounds such as TCE and benzene, but the negative effect is only

2-3 times slower. With high intensity lamps, no significant lowering is seen in tap water for TCE or benzene.

The overall effect of high intensity lamps combined with H202 is to provide, for lower capital and maintenance costs, more flexibility in treating a broad range of organic compounds, and less problems with high concentrations of organics or interfering inorganic ions.

FULL-SCALE OXIDATION

Of the thirty (30) full-scale **perox-pure**™ systems in operation or final construction/installation, about 30% are treating wastewaters with organic concentrations between 10 mg/l and about 1%. The remainder are treating groundwater. Table 3 shows a partial list of the organic compounds being treated by these installations. Operating costs for these treatment systems range from about $0.50/1000 gallons for low concentration groundwater containing TCE and DCE to about $0.12/gallon for the highest concentration wastewaters.

Table 3

perox-pure™ Operating Systems
Organic Chemicals List

Acrylic Acid	Ethyl Benzene
Aniline	Hydrazines
Benzene	Isopropanol
Bis 2-ethylhexyl phthalate	MeCl
Butyl Acrylate	PCE
Chlorinated phenols	Pentachlorophenol
Chlorobenzene	1,1,1-TCA
Chloroform	TCE
1,1-DCA	Total Toxic Organics
1,1-DCE	Vinyl Chloride
1,2-DCE	Xylene
Dimethyl Nitrosamine	

The following three examples illustrate the range of treatment achievable with the perox-pure™ Process. This first example shown in Table 4 uses a combination air stripper and perox-pure™ treatment system.

Table 4

Full-Scale perox-pure™ Treatment Data
Site 1

Contaminant	Influent (µg/l)*	Effluent (µg/l)
MeCl	1.0	BDL
1,1-DCA	5.0	BDL
1,2-DCE	187	BDL
1,1,1-TCA	116	65
TCE	71	BDL
PCE	272	BDL
Toluene	7	BDL

Residence Time: 2 min.
H202: 40 mg/l

* Effluent from Air Stripper.

While the treatment system performed well there was only partial removal of the difficult to oxidize TCA. In addition, the bulk of the volatile organics were being stripped into the air rather than being destroyed. Recently, the two treatment systems were reversed to evaluate the performance of the perox-pure™ unit on the more concentrated influent. The data shown in Table 5 is the average of samples taken over a three month period.

Table 5

Full-Scale **perox-pure**™ Treatment Data
Site 1 - Ahead of Air Stripper

Contaminant	Influent (µg/l)	Effluent (µg/l)	Air Stripper (µg/l)
MeCl	30	1.5	BDL
1,1-DCA	42	BDL	---
1,2-DCE	2466	BDL	---
1,1,1-TCA	1606	1218	<5
TCE	1060	BDL	---
PCE	3160	BDL	---

With about the same operating cost this treatment arrangement was able to destroy over 85% of the total volatiles, produce a cleaner effluent and eliminate about 90% of the air emissions. Operating cost for the **perox-pure**™ system is about $2.00/1000 gallon.

The second example is a batch treatment operation on a concentrated wastewater containing hydrazines and other toxic organics. Table 6 shows typical results of the optimized treatment system.

Table 6

Full-Scale **perox-pure**™ Treatment Data
Site 2

Contaminant	Influent (mg/l)	Effluent (µg/l)
Hydrazine	1200	<1
Monomethyl Hydrazine	100	<10
Unsym. dimethyl Hydrazine	1500	<10
Nitrosodimethylamine	1.5	<0.02
Chlorinated Organics	75	<1
Pesticides/Herbicides	0.5	<1

While the operating cost for this extremely hazardous waste is high ($0.12/gallon) in comparison to the other examples shown in this paper, it demonstrates the ability of the UV peroxidation process to handle concentrated wastes that can't be effectively or safely

treated by other technologies. Total on-site destruction of the toxic organics without any air emissions was one of the major factors in choosing the **perox-pure**™ system.

In this last example, the **perox-pure**™ treatment system is used to treat a high flow low concentration groundwater stream. The flow rate at this site ranges up to 400 gpm, with low µg/l levels of TCE, 1,2-DCE and CHCl3 present in the influent.

Table 7

Full-Scale **perox-pure**™ Treatment Data
Site 3

Contaminant	Influent (µg/l)	Effluent (µg/l)
1,2-DCE	6.2	BDL*
TCE	66.3	BDL
Chloroform	2.1	BDL

* BDL = <0.1 µg/l.

The operating cost for this site is about $0.40/1000 gallons. Again, one of the main factors in choosing the **perox-pure**™ system was complete destruction of the organics with no by-products and no air emissions.

PROCESS IMPROVEMENTS

The **perox-pure**™ Process has proved to be a cost-effective treatment system for many groundwater and wastewater streams. On-going development work has focused on improving the process design with particular emphasis on the "difficult to oxidize" compounds such as 1,1,1-TCA, 1,1-DCA, MeCl and CHCl3. Recently, Peroxidation Systems, Inc. (PSI) announced a significant breakthrough that can reduce the operating cost for the **perox-pure**™ process by 30-50%. This new proprietary design is incorporated in all new equipment

and can be retrofitted to existing perox-pure™ equipment. While the details of this new second generation design will not be presented in this paper, it is important to note that the improvement comes from advances in both reactor design and electrical/lamp system performance.

The improvement in oxidation rate of some selected compounds is shown on bench-scale equipment in Figures 4-6. This data was generated using spiked tap water solutions containing mixtures of 3-5 volatile organic chemicals at an initial total organic concentration of 5-15 mg/l. In all cases the oxidation rate increased by 2-3 times with the new B design. Similar testing done on clients groundwater and wastewater samples show the same range of oxidation rate improvement with these "difficult to oxidize" chemicals.

Although only limited full-scale operational data is available with the new design, Tables 8 and 9 show two examples of the cost reduction and/or performance increase achieved.

Table 8

Full-Scale perox-pure™ Treatment Data
Old vs New (B) Design
Site 4

Contaminant	Inf. (µg/l)	Eff. (µg/l)	Operating Cost ($/1000 gal)* Old	New
TCE	8.4	<0.001	$ 1.22	---
	11.1	<0.001	---	$0.54
1,1,1-TCA	0.1	<0.02	14.58	---
	0.15	<0.03	---	3.86

* Costs based on $0.07/KWH and $0.50/lb. H202 as 50%.

Note that there was a significant cost reduction for TCE removal as well as TCA.

Table 9

Full-Scale **perox-pure**™ Treatment Data
Old vs New (B) Design
Site 5

Contaminant	Influent (µg/l)	Effluent (µg/l) Old	Effluent (µg/l) New
MeCl	600-800	245	33
1,1,1-TCA	200-400	145	26
1,2-DCE	50-250	<1	<1

The effluent requirements for Site were lowered to meet new discharge standards. By retrofitting the new design to the existing unit, the new effluent standards were met with no increase in cost.

SUMMARY

In the 1990's "transfer technologies" will give way to more acceptable on-site destruction processes such as chemical oxidation. The **perox-pure**™ Oxidation System has proven to be a cost-effective treatment process for the on-site destruction of toxic organic chemicals in groundwater and wastewater. Continuing improvements in the technology and costs will enable the **perox-pure**™ Process to be one of the technologies of choice for the 1990's.

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FIGURE 3

HIGH INTENSITY LAMP
UV/H2O2

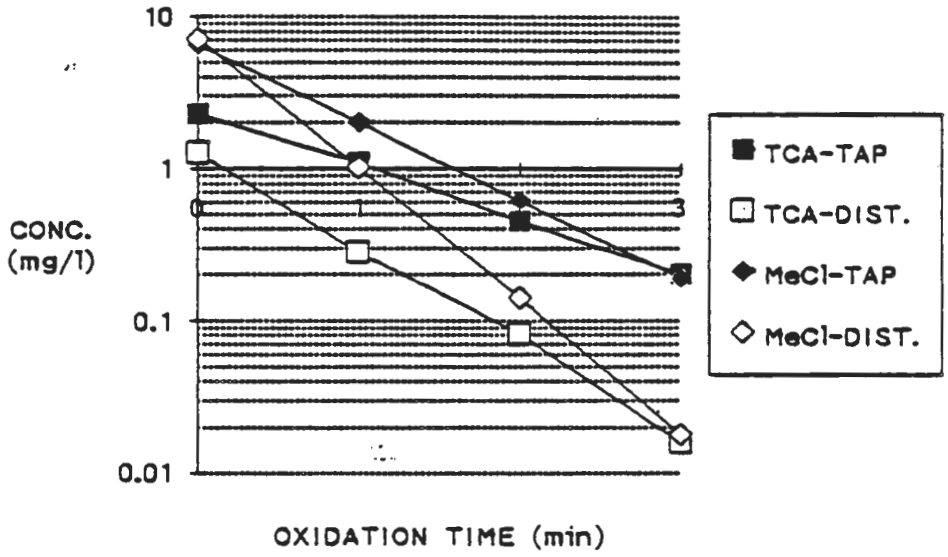


FIGURE 4

BENCH-SCALE PEROX-PURE TESTS
OLD vs NEW (B) DESIGN

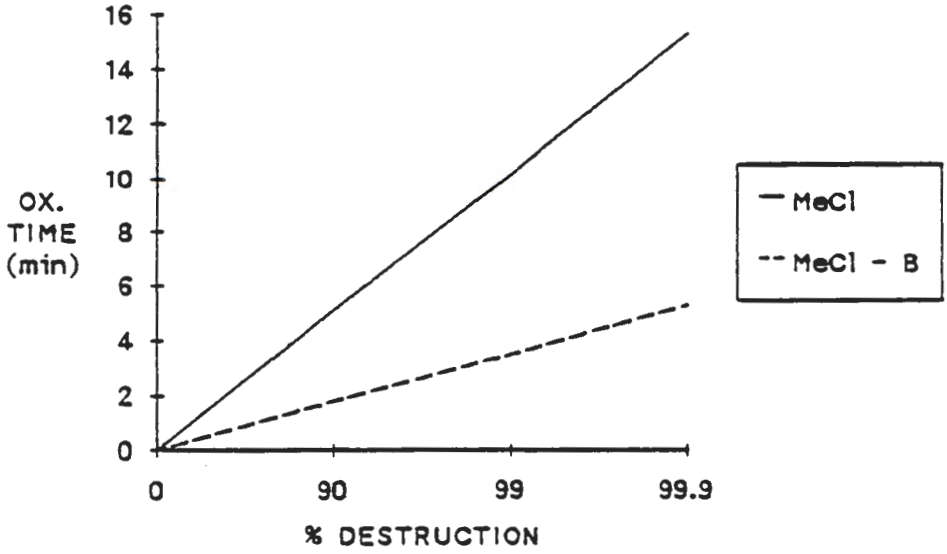


FIGURE 5

BENCH-SCALE PEROX-PURE TESTS
OLD vs NEW (B) DESIGN

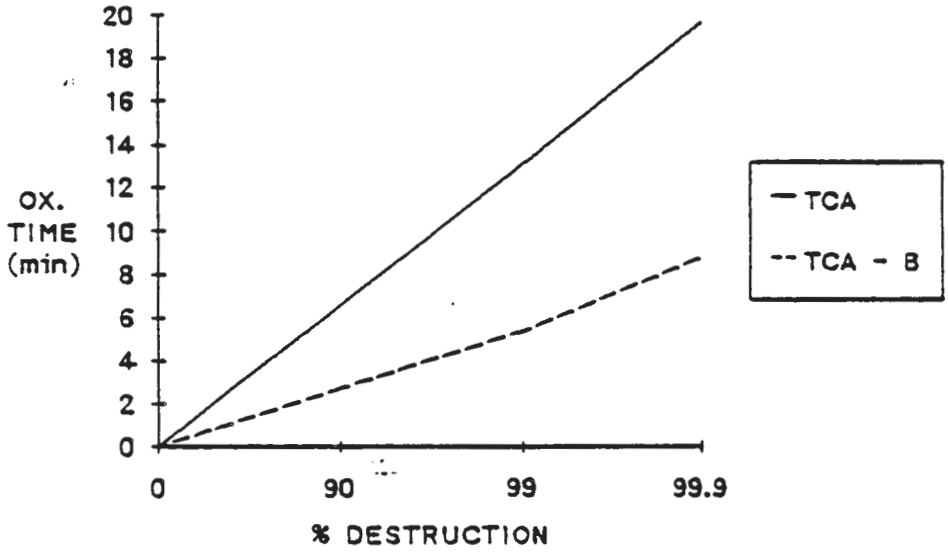


FIGURE 6

BENCH-SCALE PEROX-PURE TESTS
OLD vs NEW (B) DESIGN

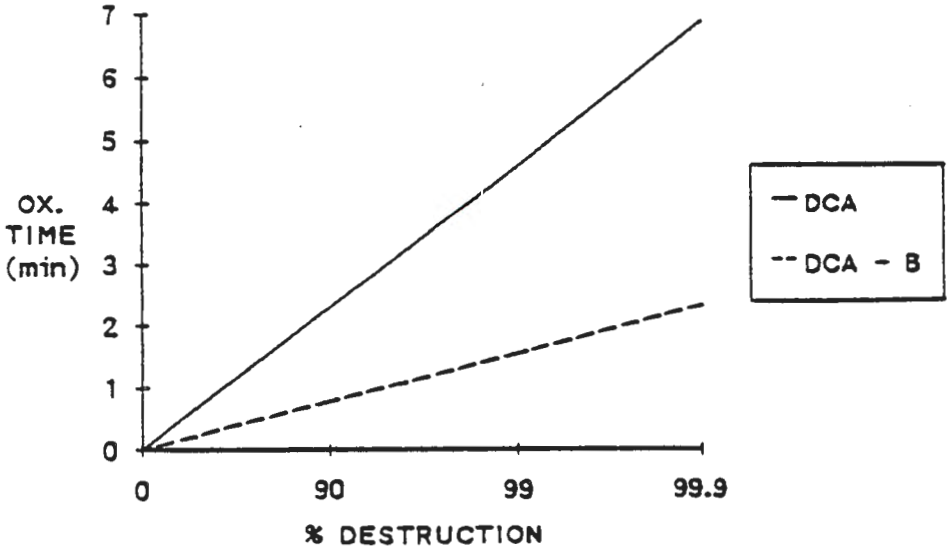


FIGURE 1

LOW PRESSURE LAMP
TCA OXIDATION
UV/H2O2

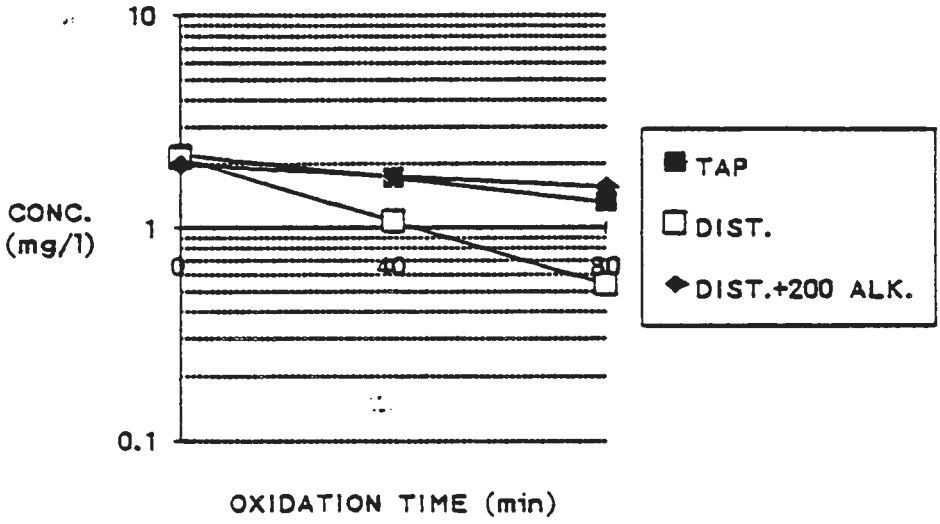
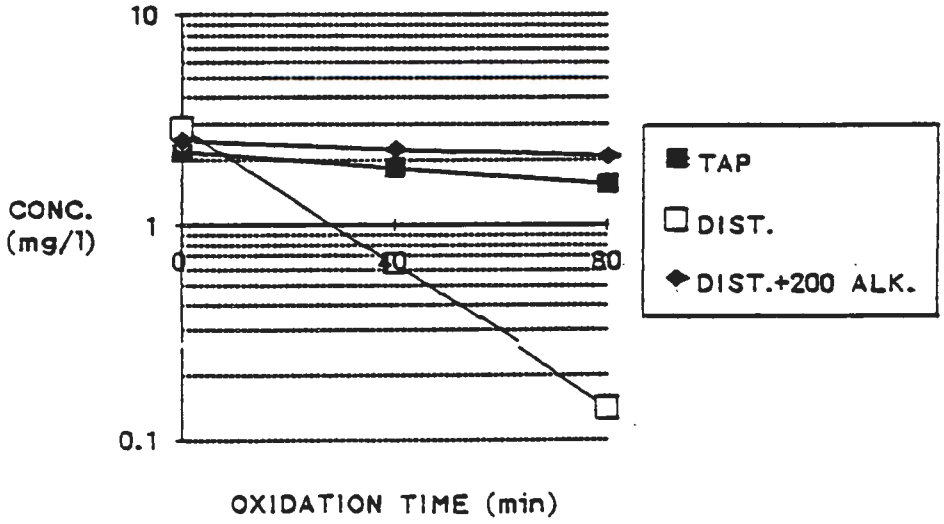


FIGURE 2

LOW PRESSURE LAMP
MeCl OXIDATION
UV/H2O2



Enclosure 6

9 3 1 2 9 0 1 1 9 3 8

ADVANCED OXIDATION TECHNOLOGIES FOR THE TREATMENT OF CONTAMINATED GROUNDWATER

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ABSTRACT

This paper presents information on two pilot-field applications of advanced oxidation technologies for contaminated groundwater with organics. The two UV/oxidation technologies were developed by Ultrox International of Santa Ana, California and Peroxidation Systems, Inc. of Tucson, Arizona. The Ultrox technology was demonstrated in 1989 with the U.S. Environmental Protection Agency's Superfund Innovative Technology Evaluation (SITE) program at the Lorentz Barrel and Drum (LB&D) site in San Jose, California. Peroxidation Systems technology was applied at the Old O-Field site located within the Aberdeen Proving Ground, in Maryland.

The Ultrox system was evaluated for its effectiveness in treating the volatile organic compounds (VOCs) present in groundwater at the LB&D site. Achievement of VOC removals were greater than 90 percent under best operating conditions at that time. Most VOCs were removed through Chemical oxidation, however, for a few VOCs, stripping also contributed toward removal. The treated groundwater met the applicable discharge standards at 95 percent confidence level for discharge into a local waterway. There were no harmful air emissions to the atmosphere from the Ultrox system, which is equipped with an off-gas treatment unit.

The Peroxidation Systems technology, achieved contaminant removal efficiencies of about 96 percent, and the treated water met the federal maximum contaminant levels for drinking water.

The information presented includes a description of the technologies, factors affecting the technologies, and results from the two pilot-scale studies of the UV/oxidation treatment system applications.

INTRODUCTION

The Superfund Innovative Technology Evaluation (SITE) program was created in 1986 to provide information on alternative and innovative technologies. The SITE program also generates reliable performance and cost data for these technologies from each demonstration, as well as a broader range of data on each process from non-SITE activities. Therefore, technologies to destroy, treat, detoxify, reduce mobility, volume or recycle hazardous waste materials are being developed and demonstrated within the Environmental Protection Agency (EPA).

Most conventional treatment processes, such as air stripping, steam stripping, carbon adsorption, and biological treatment, are quite effective in treating water contaminated with organics, but have certain limitations. These limitations include transfer of contaminants from one medium (water) to another (air or carbon) when using stripping and adsorption. In addition biological treatment processes generate sludge that may require further treatment and disposal.

Most of these limitations can be eliminated by chemical oxidation processes using ozone, hydrogen peroxide or some other conventional oxidant. However, because of kinetic limitations chemical oxidation by conventional oxidants has yet to become a competitive treatment option. Several studies have shown that the kinetic limitations could be overcome by using hydroxyl radicals to carry out the oxidation reactions (1-3). The hydroxyl radicals are known to be less selective in carrying out oxidation reactions and have much higher rate constants compared to ozone, hydrogen peroxide, or ultraviolet (UV) radiation.

Hydroxyl radicals are generated by the combined use of (1) UV radiation and hydrogen peroxide, (2) UV radiation and ozone, or (3) ozone and hydrogen peroxide. These processes are commonly referred to as "advanced oxidation processes" or, when UV radiation is used to generate hydroxyl radicals, "UV/oxidation technologies."

This paper briefly describes (1) the chemistry of UV/oxidation technologies and factors affecting these technologies and (2) the results from pilot-field scale operations of two UV/oxidation systems. These technologies differ in design and application, and therefore present unique features that demonstrate the efficiencies of both processes under different conditions. It is noted that Ultrox International has already been demonstrated under the EPA's SITE program in 1989 and has successfully been in the market for several years. Likewise, the Peroxidation Systems technology has been available in the market for a number of years, the technology, however, will be in the SITE demonstration program in 1992 at the Lawrence Livermore National Laboratory, in Livermore, California.

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UV/OXIDATION PROCESS CHEMISTRY

The generation of hydroxyl radicals is the key principle of UV/oxidation technologies through UV photolysis of hydrogen peroxide and/or ozone. When UV radiation is used to photolyze hydrogen peroxide or ozone, the UV radiation may also photolyze some organic contaminants. A summary of the chemistry of UV/oxidation technologies is given below. More information of the chemical reactions that occur during these applications is available elsewhere (4).

UV Photolysis of Hydrogen Peroxide

Generation of hydroxyl radicals by UV photolysis of hydrogen peroxide may be described by the following equation:

$$H_2O_2 + h\nu \rightarrow 2\ OH^{\bullet}$$

Most commercial applications are using low-pressure mercury vapor UV lamps to produce UV radiation. The maximum absorbance of UV radiation by hydrogen peroxide occurs at about 220 nanometers (nm). However, the dominant emission wavelength of low-pressure mercury vapor UV lamps is at about 254 nm. Also, the molar extinction coefficient of hydrogen peroxide at 254 nm is low, 19.6 liters per mole-centimeter ($M^{-1}\ cm^{-1}$). Because of the low molar extinction coefficient, a high concentration of hydrogen peroxide is needed in the medium to generate sufficient hydroxyl radicals.

UV Photolysis of Ozone

UV photolysis of ozone in water yields hydrogen peroxide, which in turn reacts with UV radiation or ozone to form hydroxyl radicals as shown below.

$$O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2$$
$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet}$$
$$2\ O_3 + H_2O_2 \rightarrow 2\ OH^{\bullet} + 3\ O_2$$

Because the molar extinction coefficient of ozone is 3,300 $M^{-1}\ cm^{-1}$ at 254 nm, the UV photolysis of ozone is not expected to have the same limitation as that of hydrogen peroxide when low-pressure mercury vapor UV lamps are used.

FACTORS INFLUENCING PERFORMANCE

Factors influencing the performance of a UV/oxidation technology can be grouped into three categories: (1) waste characteristics, (2) operating parameters, and (3) maintenance requirements. Following is a brief discussion of these factors.

Waste Characteristics

The type of contaminants to be treated influence the removal efficiencies of the UV/oxidation processes. For example, organics with double bonds, such as trichloroethene (TCE), tetrachloroethene (PCE), and vinyl chloride, and aromatic compounds, such as phenol, toluene, benzene, and xylene, are easily removed because they are readily oxidized. In systems that use ozone, organics without double bonds and with high Henry's law constants, such as 1,1-dichloroethane (1,1-DCA) and 1,1,1-trichloroethane (1,1,1-TCA), are also removed. However, because they are difficult to oxidize their removal is primarily due to stripping. Organics without double bonds and with low Henry's law constants, such as diethylamine and 1,4-dioxane, would be difficult to remove because they are not easily oxidized or stripped.

UV/oxidation technologies are intended for the destruction of organic contaminants, other species that consume oxidants are considered an additional load for the system. These species are called scavengers and include anions such as bicarbonate, carbonate, sulfide, nitrite, bromide, and cyanide. Metals present in their reduced states, such as trivalent chromium, ferrous iron, manganous ion, and several others, are likely to be oxidized. These reduced metals, in addition to acting as scavengers, cause additional concerns. For example, trivalent chromium is oxidized to more toxic hexavalent chromium, and ferrous iron and manganous ions are oxidized to less soluble forms, which precipitate in the reactor and can cause UV lamp scaling and suspended solids formation. Nontarget organics (for example, humic compounds) could also act as scavengers. Other parameters such as suspended solids and oil and grease would reduce UV transmission, thereby decreasing the treatment efficiency. For these reasons, pretreatment may be required for proper functioning of UV/oxidation units depending on the waste characteristics.

Operating Parameters

Operating parameters are those parameters that are varied during the treatment process to achieve the desired treatment efficiencies. Such parameters include hydraulic retention time, ozone dose, hydrogen peroxide dose, UV lamp intensity, influent pH level, and gas-to-liquid flow rate ratio.

In general, increasing the hydraulic retention time will increase treatment efficiency up to a certain point. At this point, the system tends to proceed toward equilibrium, and increasing the hydraulic retention time no longer increases treatment efficiency.

The higher the dose of oxidants, the better the treatment rate. However, the molar ratio of the oxidant doses must be considered. For example, when treating water containing TCE and PCE, maximum removals were observed when the molar ratio of ozone dose to hydrogen peroxide dose was equal to two, and the removals were significantly less when the ratio was not equal to two. In this

case, the expected stiochiometry for pure water agreed with the molar ratio at which optimum removal was observed; however, several factors may influence the molar ratio (1). These factors are summarized as follows:

> Hydrogen peroxide can act as a free radical scavenger itself, thereby decreasing the hydroxyl radical concentration if it is present in excess.
>
> Ozone can react directly with hydroxyl radicals, consuming both ozone and hydroxyl radicals.
>
> Ozone and hydroxyl radicals may be consumed by scavengers present in the water being treated.

Therefore, the optimum proportion of the oxidants for maximum removals cannot be predetermined. Instead, the proportion needs to be determined for the waste under consideration using pilot- or bench-scale treatability tests.

In addition to photolyzing hydrogen peroxide and ozone to generate hydroxyl radicals, the UV radiation may also photolyze some organic contaminants, such as PCE, aromatic halides, and pesticides, increasing the contaminant removal.

If water has bicarbonate and carbonate alkalinity at a level greater that 400 milligrams per liter (mg/L) as calcium carbonate, lowering the pH to a range of 4 to 6 should improve the treatment efficiency. Low pH decreases the concentration of these scavengers by shifting the equilibrium toward carbonic acid. If the carbonate and bicarbonate alkalinity is low, then a high pH should improve the treatment efficiency. High pH favors hydroxyl radical formation because of the reaction between ozone and the hydroxyl ion.

The ozone gas flow rate can also influence treatment rate. In practice, once the ozone dose is selected, several combinations of ozone gas phase concentration and ozone gas flow rate can be applied. According to Venosa and Opatken (5), the ratio of gas flow rate to liquid flow rate will dictate the hydraulic characteristics of the reactor, as shown in Figure 1. This figure shows that, at low gas-to-liquid flow rate ratios, the mixing regime in a reactor is close to that of a plug flow reactor (shown as Curve A); whereas at high ratios, the reactor mixing regime is close to that of a mixed reactor (shown as Curve C). For reactions with a positive reaction order, plug flow mixing characteristics offer higher treatment rate than mixed reactor mixing characteristics (6). Since most reactions have a positive reaction order, low gas-to-liquid flow rate ratios should be considered. In addition to increasing the treatment rate, low gas-to-liquid flow rate ratios reduce stripping of volatile organics.

Maintenance Requirements

Regular maintenance by trained personnel is essential for a successful treatment operation. The following components require maintenance: (1) ozonation system, (2) UV lamp assembly, (3) ozone decomposer unit, and (4) miscellaneous components. A brief summary of the maintenance requirements for these components is presented in Table 1.

PILOT-FIELD STUDY ONE

The Ultrox technology demonstration occurred in February, 1989 at the Lorentz Barrel and Drum (LB&D) site in San Jose, California, through an agreement between EPA's Region IX, Ultrox International, and the EPA's SITE program. The LB&D site was used primarily for drum recycling operations from about 1947 to 1987. The drums contained residual aqueous wastes, organic solvents, acids, metal oxides, and oils. The preliminary site assessment report for the LB&D site showed that the groundwater and soil were contaminated with organics and metals.

The upper aquifer at the LB&D site was selected as the waste stream for evaluation of the UV/oxidation technology. Samples from the shallow aquifer were collected in December 1988 which indicated that volatile organic compounds (VOCs) were present in the groundwater. VOCs detected at high levels included TCE (280 to 920μ/L), vinyl chloride (51 to 146 μg/L), and 1,2-trans-dichloroethylene (42 to 68 μg/L). The pH and alkalinity of the groundwater were about 7.2 and 600 mg/L as $CaCO_3$, respectively. These measurements indicated that the bicarbonate ion (HCO_3), which acts as an oxidant scavenger, was present at high levels. Other oxidant scavengers, such a bromide, cyanide, and sulfide were not detected. Iron and manganese were present at low levels (less than 1 mg/L). Detailed information is available (7) to describe the parameters and design of the SITE demonstration.

Ultrox System

The Ultrox UV/oxidation treatment system uses UV radiation, ozone, and hydrogen peroxide to oxidize organics in water. The major components of the Ultrox system are the UV/oxidation reactor module, air compressor/ozone generator module, hydrogen peroxide feed system and the catalytic ozone decomposition (Decompozon) unit (Figure 2).

The UV/oxidation reactor used has a volume of 150 gallons and is 3 feet long by 1.5 feet wide by 5 feet high. The reactor is divided by five vertical baffels into six chambers and contains 24 65-watt UV lamps in quartz sheaths. The UV lamps are installed vertically and are evenly distributed throughout the reactor (four lamps per chamber). Each chamber also has one stainless steel sparger that extends along the width of the reactor. These spargers uniformly diffuse ozone gas from the base of the reactor into the water. Hydrogen peroxide is added to the influent line to the reactor. An

in-line static mixer is used to disperse the hydrogen peroxide into the contaminated water in the influent feed line.

The Decompozon unit (Model 3014 FF) uses a nickel-based proprietary catalyst to convert reactor off-gas ozone to oxygen. The Decompozon unit can accommodate flows of up to 10 standard cubic feet per minute and can destroy ozone concentrations in ranges of 1 to 20,000 ppm (by weight) to less than 0.1 ppm.

Testing Approach

The study was designed to evaluate the Ultrox system by adjusting the levels of five operating parameters: (1) influent pH, (2) hydraulic retention time, (3) ozone dose, (4) hydrogen peroxide dose, and (5) UV radiation intensity. Eleven test runs were performed to evaluate the Ultrox system under various operating conditions. After these Runs, two additional runs were performed to verify that the system's performance was reproducible. The verification Runs (Runs 12 & 13) were at the best operating conditions which were determined to be those of Run 9, pH 7.2; hydraulic retention time 40 minutes; ozone dose 110 mg/L; hydrogen peroxide dose 13 mg/L; and all UV lamps operating.

During the study, a preliminary estimate of Ultrox system's performance in each run was obtained from the effluent concentrations of three indicator VOCs. The VOCs selected for this purpose were TCE, 1,1-DCA, and 1,1,1-TCA. TCE was selected because it is a major volatile contaminant at the site, and 1,1-DCA and 1,1,1-TCA were selected because they are relatively difficult to oxidize. At the end of the study, data from all samples was used to evaluate the system's effectiveness.

Results and Conclusions

Results of the Ultrox system are summarized to present the overall effectiveness of the UV/oxidation technology in removing VOCs from the groundwater at the LB&D site. The removal efficiencies and concentration profiles of all VOCs are not presented in this paper, but additional information can be obtained from the Technical Evaluation Report and the Application Analysis Report published by EPA (8).

Summary of Results for VOCs

Based on overnight analysis performed during the demonstration (when two of the six replicates determined the average effluent concentrations for each indicator VOC), Runs 8 and 9 showed that the effluent met the discharge standard at either set of conditions. Since a lower hydrogen peroxide dose was used in Run 9, compared to Run 8, Run 9 was chosen as the preferred operating run. However, based on a complete analysis of the four remaining replicates for Run 9 performed after the demonstration, the mean concentration of 1,1-DCA was found to be slightly higher than 5 µg/L, the discharge standard for the VOC. Since Run 9 had the

preferred operating conditions during the demonstration, the verification runs (12 and 13) were also performed at those conditions.

Figure 3 shows that the total VOC removals were about 90 percent, while removal efficiencies for TCE were about 98 percent and those for 1,1-DCA and 1,1,1-TCA were about 60 and 85 percent, respectively. Higher removal efficiencies for TCE than for 1,1-DCA and 1,1,1-TCA support the rationale used in selecting the indicator VOCs.

Figure 4 compares the 95 percent upper confidence limits (UCLs) for the effluent VOCs with the National Pollutant Discharge Elimination System (NPDES) limits. The UCLs were calculated using the one-tailed Student's t-test. The effluent met the discharge limits for all regulated VOCs at the 95 percent confidence level in Runs 12 and 13; in Run 9, the mean concentrations for 1,1-DCA and 1,2-DCA exceeded the discharge limits.

The gas chromatography (GC) and GC/mass spectrometry analyses performed for VOCs, semivolatile organics, polychlorinated biphenyls, and pesticides did not indicate the formation of new compounds in the treated water. Because VOCs made up less than 2 percent of the total organic carbon, the general claim that UV/oxidation technologies convert VOCs to carbon dioxide and water could not be verified.

Because the Ultrox system treated the groundwater by bubbling ozone gas through it, some VOC removal could be attributed to stripping in addition to oxidation. To determine the extent of stripping within the treatment system, VOC samples were collected from the reactor off-gas and emission rates for four VOCs were compared to the VOC removal rates from groundwater. The results are summarized in Table 2. Because the extent of stripping for any particular VOC is expected to be proportional to the ratio of air flow rate to water flow rate, this ratio is also presented in the table. The ratio for Runs 1 to 5 is approximately 2; for Run 6 and Runs 8 to 13, it is about 4.5; and for Run 7, it is 1. If stripping contributed to the total removal of the four VOCs, the extent of stripping would be expected to be least in Run-7, and most in Runs 6 and 8 to 13. The data presented in the table follow this trend for three of the four VOCs (except for the vinyl chloride in Runs 6,7, and 9). A quantitative correlation of the extent of stripping cannot be made, because the operating conditions were different in each run. For example, at a given air to water flow ratio, when oxidant doses are varied, the extent of oxidation also varies. Therefore, the extent of stripping will be indirectly affected.

Table 2 presents Henry's law constants for the four VOCs (9). By comparing these constants for the VOCs, their volatility is expected to increase from left to right as shown below:

1,1-DCA - TCE - 1,1,1-TCA - vinyl chloride

However, significant removal fractions for 1,1,1-TCA and 1,1-DCA were observed to be due to stripping. Conversely, the extent of stripping was low for vinyl chloride and TCE. This is because it is easier to oxidize vinyl chloride and TCE than 1,1-DCA and 1,1,1-TCA because of the double bonds between the carbon atoms in TCE and vinyl chloride. Therefore, UV/oxidation processes using ozone, stripping is a significant removal pathway for compounds that are difficult to oxidize.

Performance of the Decompozon Unit

The ozone concentrations in the influent to and the effluent from the Decompozon unit were analyzed in each run. Ozone destruction efficiencies greater than 99.99 percent were achieved in Runs 1 to 10. The effluent ozone concentrations were low (less than 0.1 ppm) for Runs 1 to 8, approximately 1 ppm in Runs 9 and 10, and greater that 10 ppm in Runs 11, 12, and 13. The high ozone levels (greater than 1 ppm) in the effluent are attributed to the malfunctioning heater in the Decompozon unit. The temperature in the Decompozon unit should have been 140° F for the unit to properly function, whereas the temperature for Runs 11 to 13 was only about 80° F.

Although the primary function of the Decompozon unit is to remove ozone, significant VOC removal also occurred when the unit functioned as designed (Runs 1 to 8). For example, the Decompozon unit removed TCE, 1,1-DCA, 1,1,1-TCA and vinyl chloride (present in the gas phase in the reactor at levels of approximately 0.1 to 0.5 ppm) to below detection levels.

PILOT-FIELD SCALE STUDY TWO

This pilot-field scale study was performed at the Old O-Field site located in the Edgewood Area of the Aberdeen Proving Ground, Maryland by the Peroxidation Systems, Inc. (PSI). The site was used for disposal of the chemical-warfare agents, munitions, contaminated equipment, and various other hazardous materials during the 1940s and early 1950s. The disposal of these hazardous materials contaminated several media at the Old O-Field site, including groundwater, surface water, and sediments.

During the pilot-field study, groundwater samples were collected which indicated that several organics, including VOCs, organosulfur compounds, and explosives, were present at the site in concentrations of 10 µg/L to 500 µg/L. Iron and manganese were present at levels of 120 mg/L and 2.5 mg/L, respectively (10). Trace levels of arsenic were also observed in some locations which were sampled before the pilot-field scale study.

Treatability studies were performed in April and May 1991 as part of the remediation process. A total of 37,000 gallons of groundwater from three wells was used to perform the treatability studies. The contaminated groundwater was pumped to two holding tanks and then treated by a metals precipitation system. The

metals precipitation was performed at pH 11, primarily to remove arsenic observed in samples collected before the pilot study began; however, the pilot study samples showed no arsenic contamination. Iron and manganese were removed to levels of 0.2 mg/L and 0.02 mg/L, respectively. The pH of the metals precipitation system effluent was adjusted to 7 and then treated using two parallel systems: (1) an air stripping system followed by carbon adsorption for both liquid and vapor phase effluents from the air stripper and (2) a UV/oxidation system. The air stripping/carbon adsorption system was developed by Carbonair and the UV/oxidation system was developed by Peroxidation Systems, Inc.

Peroxidation Systems Process

Figure 5 shows a schematic of the PSI UV/oxidation system. The system used at the Old O-Field site consisted of two parallel cartridge filters rated at 10 micrometers (μm) followed by the UV/oxidation reactor. The UV/oxidation reactor had a volume of 80 gallons and was divided by three horizontal baffles into four chambers. Each chamber contained one high intensity, broad band, mercury-arc-type 15-kw UV lamp. A splitter was used so that hydrogen peroxide could be added at multiple points, such as the influent line and at several locations inside the reactor, making hydrogen peroxide available for hydroxyl radical formation throughout the reactor. The effluent from the reactor was passed through an optional manganese-greensand filter to remove any residual hydrogen peroxide, followed by a pH adjustment to raise the pH to an acceptable level.

Testing Approach

Four tests were conducted at a flow rate of 15 gpm (hydraulic retention time of about 5.3 minutes). In Tests 1,2, and 3, hydrogen peroxide doses were 45 mg/L, 90 mg/L and 180 mg/L, respectively, with the splitter in operation; and in Test 4, hydrogen peroxide dose was 45 mg/L with the splitter not in operation. When the splitter was used, the total hydrogen peroxide dose was split into three equal parts, which were added at (1) the influent line to the reactor, (2) the effluent line from the first chamber, and (3) the effluent line from the second chamber. In Test 4, when the splitter was not used, all hydrogen peroxide was added at the influent line to the reactor. Treated and untreated water samples were collected for (1) chemical analyses to estimate removal efficiencies and compare them with federal maximum contaminant levels (MCLs) for drinking water, and (2) bioassay to evaluate whether the water was acutely toxic to fathead minnows, daphnia magna, sheepshead minnows, and mysid shrimp.

Results and Conclusions

A discussion of the optimum operating conditions of Test 3 is presented here, a more detailed description on the PSI system performance is available in an unpublished report by the U.S. Army Corps of Engineers Toxic and Hazardous Materials Agency (10). Also, Table 3 summarizes the influent and effluent contaminant levels and the removal efficiencies of several contaminants. These results show that for most compounds the effluent levels were below detection levels, and the removal efficiencies for these compounds were greater than 82 to 99 percent. The effluent levels of chloroform and 1,3,5-trinitrobenzene were 1.2 µg/L and .53 µg/L, respectively. The removal efficiencies for these compounds were in the range of 96 to 97 percent.

The treated effluent met the federal MCLs for all compounds. The influent to and the effluent from the PSI system passed the bioassay tests. The pH decreased by about one unit, indicating that some of the oxidation byproducts were acidic. Although the manganese-greensand filter was effective in removing residual hydrogen peroxide, it increased the manganese levels in treated water from about 0.02 mg/L to 1.4 mg/L, which is above the National Secondary Drinking Water Standard (50 µg/L). Therefore, the use of manganese-greensand filter is not recommended. Instead, other methods should be considered to neutralize any residual hydrogen peroxide in the treated water samples (for example, addition of ascorbic acid, thiosulfate, or catalase-D). If the residual oxidant level is greater than 1 mg/L and is not neutralized, it would continue to react with the contaminants in the sample bottles until analysis could be performed. This continued reaction may introduce a bias in the treatment system evaluation.

CONCLUSIONS ON THE UV/OXIDATION TECHNOLOGIES

The UV/oxidation technologies present an efficient and competitive alternative treatment, especially for the removal of organics present in water at low concentrations (less than about 100 mg/L). For higher concentration levels of contaminants, these technologies may prove cost-effective when used in combination with biological or adsorption processes. The UV/oxidation technologies are often preferred over adsorption or biological processes, because in the UV/oxidation technologies (1) contaminants are destroyed rather than transferred to some other medium and (2) no residuals requiring further handling, such as sludge or spent carbon, are generated. Due to the contaminants present it may be necessary to implement pretreatment processes to minimize shut down or delays.

Operation and maintenance data are currently being documented, and this information is instrumental in moving the technology to more efficient design and application techniques.

A greater understanding of the actual chemistry needs to be researched further, especially to understand the byproducts of the UV/oxidation of organics. Several technology developers claim that byproducts are carbon dioxide, water, and halides, but little published data are available to support these claims when UV/oxidation is used to treat the contaminants present in groundwater. Research is also being established in the area of using the UV/oxidation technologies for the destruction of organics in the air phase. Promising results are being generated for this application.

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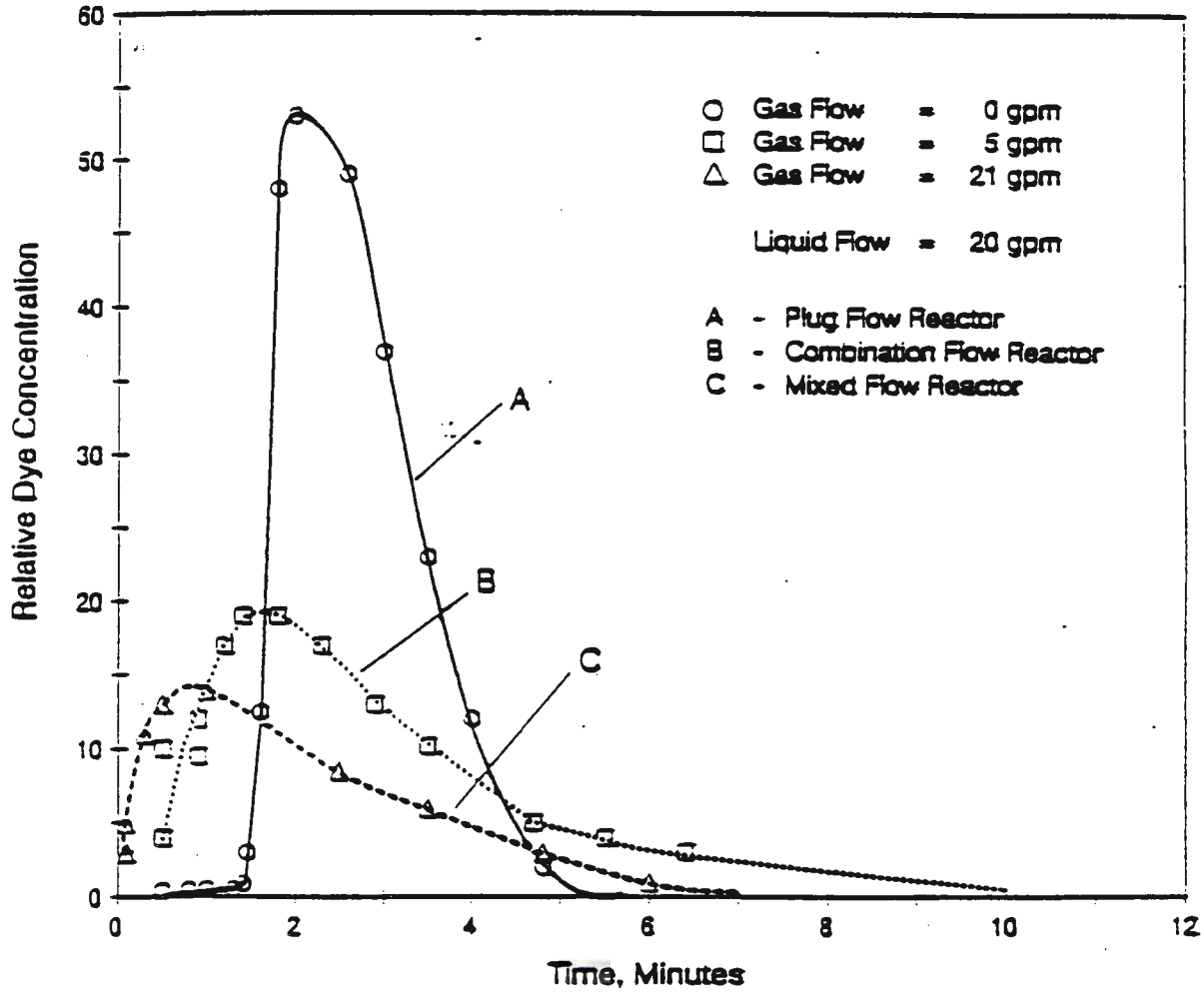

Figure 1. Dye tests showing effects of gas flow rates on the mixing characteristics of a bubble diffuser ozone contact basin.

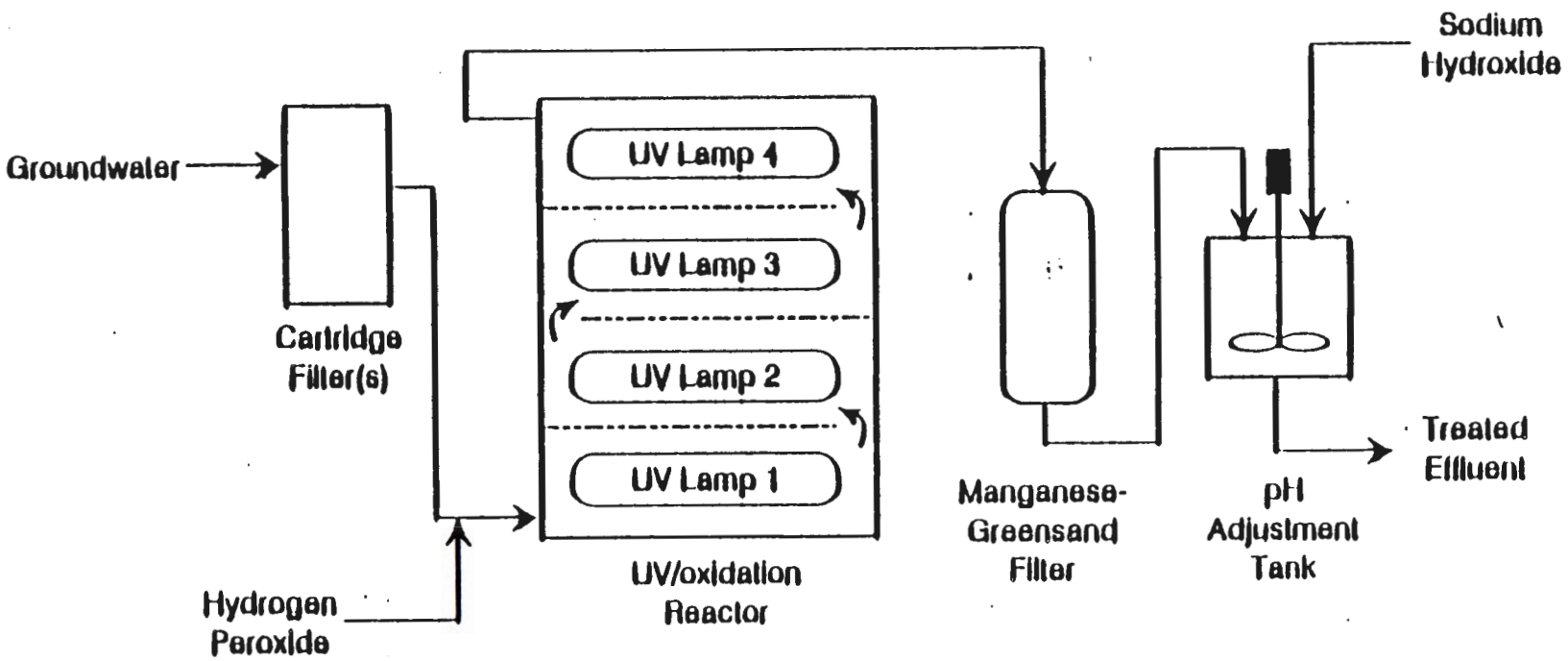

Figure 5. Schematic of PSI UV/oxidation system.

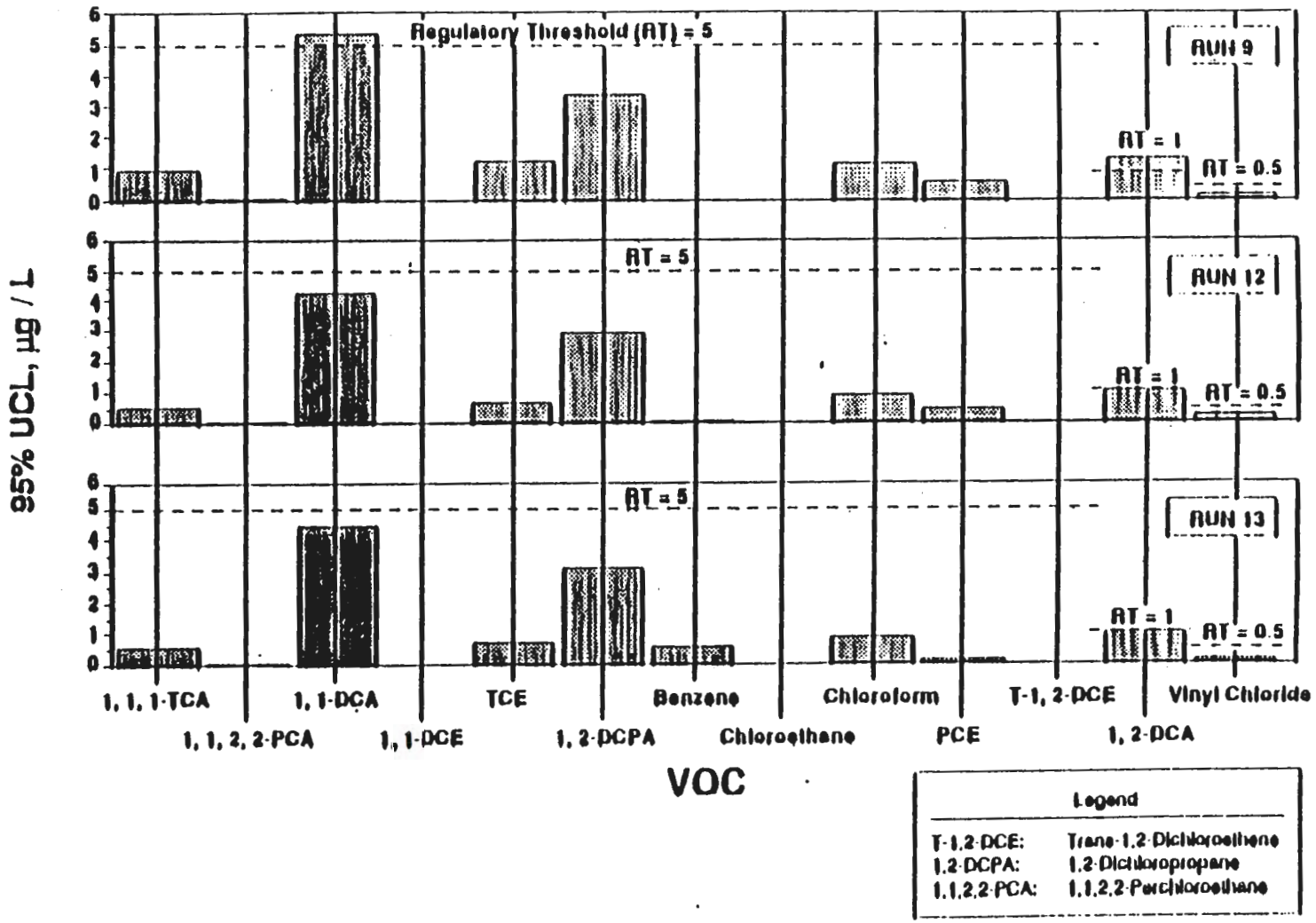

Figure 4. Comparison of effluent VOC concentrations.

Table 1. Maintenance Requirements for UV/oxidation Systems

Component	Maintenance	Comments
1. UV Lamp Assembly	Clean the UV lamps periodically (once every month to once every 3 months) using dilute acid (for example, acetic acid) wash, mechanical wipers, or ultrasonic equipment.	Frequency of cleaning varies depending on the type of suspended solids present in the influent or formed during treatment (for example, precipitation of iron and manganese). This can be minimized by providing proper pretreatment.
	Replace the UV lamps as necessary (due to lamp failure or significant reduction in UV radiation output with time).	Low pressure mercury vapor UV lamps are rated to last 7,500 hours and xenon UV lamps are rated to last about 500 hours, based on a use cycle of 8 hours.
		Some manufacturers recycle most of the lamp construction materials to minimize waste disposal.
2. Ozonation System		
(a) Air Preparation System	Replace the air filter at least once every 3 months.	Replacement frequency may vary based on air purity and flow rate.
	Check the air compressor, as recommended by the manufacturer, once every month to minimize feed air contamination by the compressor parts.	None.
	Inspect cooling water lines annually for scaling and deterioration. If a water chiller is used, inspect refrigerant dryer at least once every 3 months.	Tap water (potable water, suitable process water, or treated water) may be used as a cooling water source.
	Inspect desiccant dryer weekly to ensure proper operation. Disassemble the unit and inspect the desiccant annually, as recommended by the manufacturer, to prevent fire accidents. Replace the media once every 10 years.	Heatless absorption dryers may be used to prevent fire accidents. The media may have to be replaced sooner if the dryer has been overloaded or poorly maintained.
(b) Ozone Generator	Clean the dielectric tubes one year after startup and determine the future cleaning frequency at the end of first year depending on the condition of the tubes.	Trained personnel should perform the cleaning to minimize breakage or damage to the tubes. Proper maintenance of the tubes helps lower electrical energy costs.

Table 1. Maintenance Requirements for UV/oxidation Systems (Continued)

COMPONENT	MAINTENANCE	COMMENTS
2. Ozonation System (continued)		
(c) Ozone Contacting Equipment	Check pipings, valves, fittings, supports, brackets, and ozone gas spargers at least once every 3 months for deterioration resulting from a highly oxidizing environment.	Check spargers for plugging due to solids accumulation if a change in gas bubble diffusion pattern is noted. Clean the spargers to minimize cracking of joints and excessive electrical power costs.
3. Ozone Decomposer	Check the unit's temperature once a day for proper operation. Maintain the ozone decomposer as recommended by the manufacturer.	Ozone decomposer normally contains heating elements and a catalyst. The decomposer must be operated at the proper temperature to destroy ozone present in the reactor off-gas.
4. Miscellaneous	Check miscellaneous components of the treatment system, such as valves, flow meters, pipelines, and wastewater and chemical feed tanks (for example hydrogen peroxide and acid) once a week for leaks. Also check pumps and any other components once a week for proper operation.	None.

Table 2. Extent of VOC Stripping in Ultrox System

Run No:	Air Flow Rate ÷ Water Flow Rate	Percent Stripping Contributions			
		1,1-DCA 0.00043 *	TCE 0.0091 *	1,1,1-TCA 0.014 *	Vinyl Chloride 0.082 *
1	2.1	7.4	2.0	43	0.01
2	2.3	9.1	3.4	34	0.95
3	2.1	9.9	2.7	31	0.01
4	2.0	7.4	3.0	29	0.01
5	2.1	17.0	3.5	29	1.7
6	4.5	16.0	1.2	65	0.07
7	1.0	4.9	1.2	12	3.1
8	4.5	23.0	7.5	85	1.2
9	4.5	16.0	6.6	58	0.04
10	4.3	27.0	9.4	73	1.1
11	4.6	44.0	24.0	>99	13.0
12	4.4	34.0	7.0	76	8.9
13	4.3	37.0	26.0	75	1.8

* Henry's law constant of the VOC, atm-m³/mol.

Table 3. Performance Data for the PSI System at the Optimum Operating Conditions (Test 3)

Compound	Influent µg/L	Effluent µg/L	Percent Removal
Chloroform	41	1.2	97
1,2-DCA	22	<1.6	>92
1,2-DCE	195	<1.6	>99
Methylene Chloride	8	<1.1	>86
TCE	21	<1.4	>93
Benzene	52	<2.0	>96
Thiodiglycol	477	<10.0	>97
1,4-Dithiane	200	<2.2	>98
1,4-Oxathiane	82	<2.14	>97
Benzathiazole	20	<3.47	>82
1,3,5-Trinitrobenzene	15	0.53	96

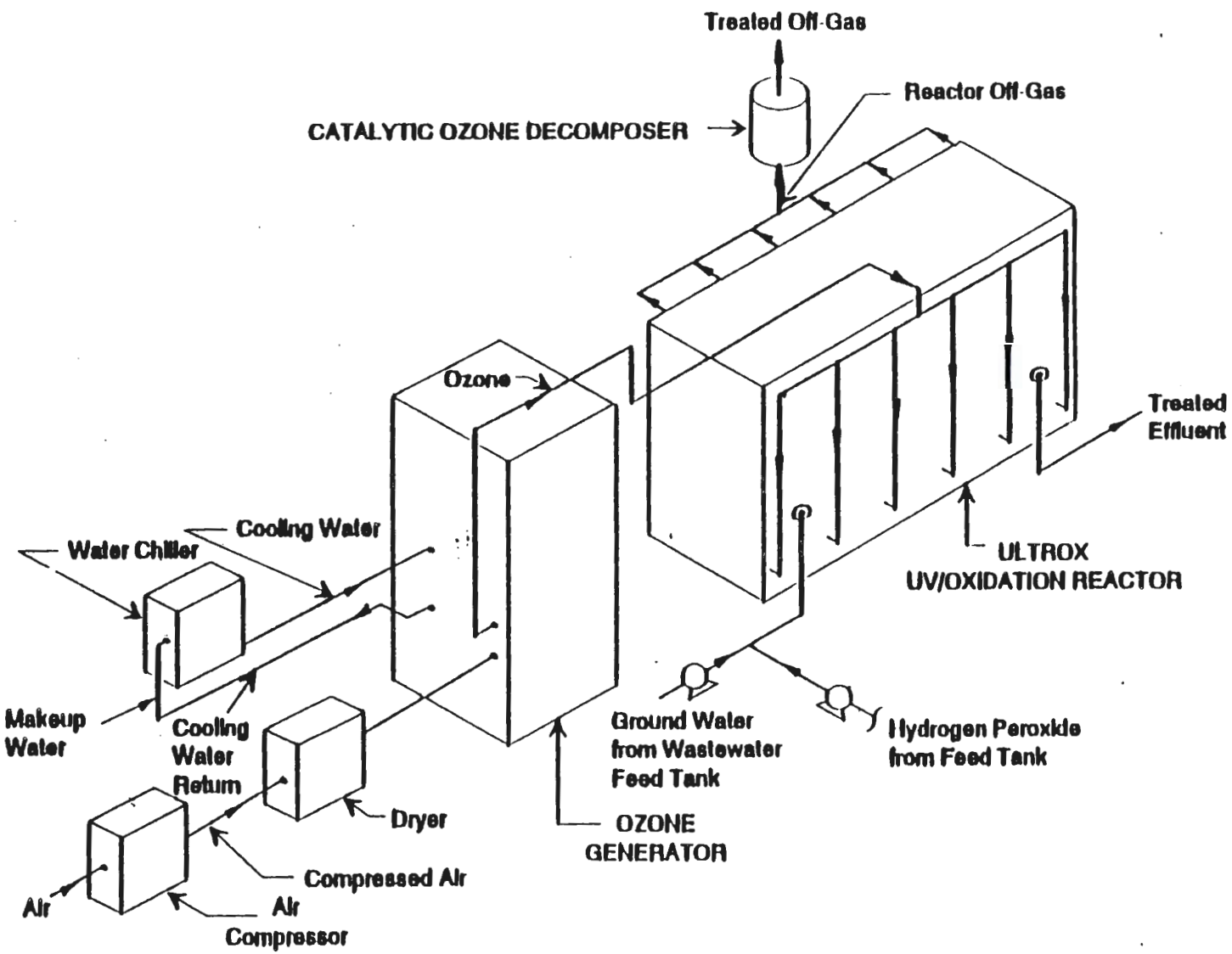

Figure 2. Isometric view of Ultrox system.

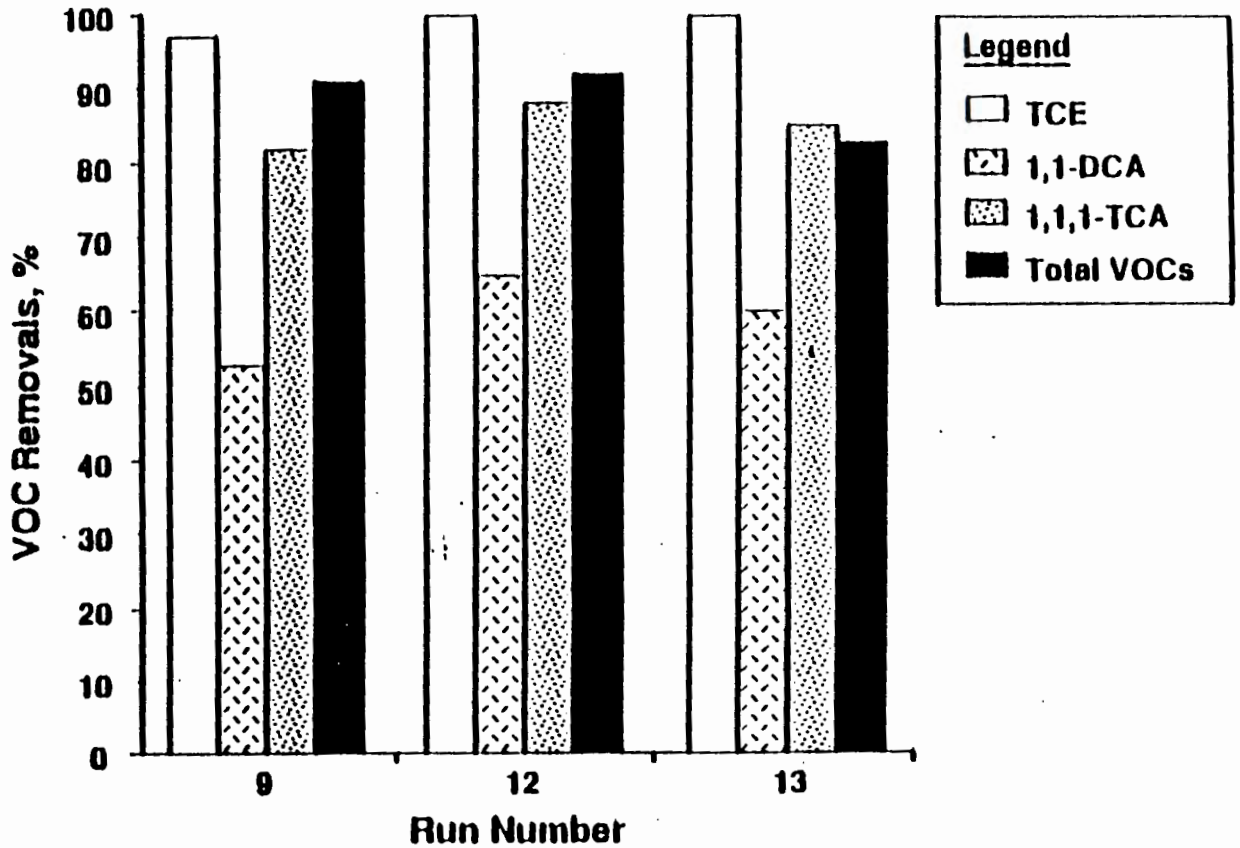

Figure 3. VOC removals at optimum conditions.

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RAYOX®

Second Generation Enhanced Oxidation Process for the Destruction of Waterborne Contaminants

RAYOX®- A SECOND GENERATION ENHANCED OXIDATION PROCESS FOR THE DESTRUCTION OF WATERBORNE ORGANIC CONTAMINANTS

This paper was presented by P.W. Smith at the Haz Mat South Conference in Atlanta, 1991.

INTRODUCTION

Over the past few years, the use of ultraviolet light enhanced oxidation processes (EOP) to treat groundwater contaminated with toxic or hazardous organics, has become more widely accepted by both the regulatory community and those seeking a cost effective solution to their remediation requirements. Apart from the generally attractive economic imperative, enhanced oxidation is a destruction technology. As such, there are no secondary disposal/liability issues surrounding its use compared to the more traditional treatment options such as biological processing, air stripping or carbon adsorption all of which essentially transfer the problem from one medium to another.

While earlier manifestations of enhanced oxidation processing have almost exclusively relied on hydroxyl radical driven destruction, and have suffered from lamp fouling in numerous applications, the advent of the now well -proven **Rayox®** second generation EOP technology has significantly improved the applications versatility, the economics, and the performance capability of this inherently attractive treatment alternative for removing toxic organics from water.

This paper outlines the reasons for, the nature of, and the benefits to be derived from, second generation enhanced oxidation treatment. Specific examples, drawn from actual system designs, have been chosen to highlight the rationale behind the significant advantages of **Rayox®** processing.

FIRST GENERATION EOP: THE MECHANISM AND THE LIMITATIONS

There are several methods of generating hydroxyl radicals ($OH^{\bullet}$) from ozone and/or hydrogen peroxide and ultraviolet (UV) light, all of which have been described by several authors. These approaches can be summarized by the following simplified equations:

$$H_2O_2 + UV \rightarrow 2OH^{\bullet}$$
$$2O_3 + H_2O_2 \rightarrow 2OH^{\bullet} + 3O_2$$
$$Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + Fe^{3+} + OH^{-}$$

Because hydroxyl radical attack of the target organic is one million to one billion times faster than the corresponding attack by ozone alone, this "enhanced oxidation" mechanism has essentially been the simple and sole basis for first generation EOP systems. Furthermore, because only a relatively select group of common waterborne toxic organics (perchloroethylene, benzene, phenol, several PAH's etc.) have a high rate constant with $OH^{\bullet}$, (approximately 10^{10} litres mole $^{-1}$ sec $^{-1}$), the range of applications for these systems has been more or less concentrated on these fast reacting compounds. Nonetheless, a reasonably strong base of these applications has now been established.

Compromising this general success story has been the inability of first generation systems to address, as successfully, compounds whose rate constants are in the 10^7 - 10^9 range ie. chlorinated aromatics, saturated compounds, ketones etc. Furthermore, because the hydroxyl radical is an indiscriminate species, attacking all

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organics present in a given water, first generation EOP systems generally have difficulty in economically treating toxic organics coincidentally present in high concentrations of other non-target organics. In addition, the presence of dissolved metals such as iron and manganese commonly found in groundwater, as well as the presence of oils and greases in wastewater from various industries, has generally acted as a further constraint on the breadth of application of first generation EOP systems due to fouling, or coating, of the UV lamps during operation. This phenomenon has generally required additional (and sometimes unexpected) investment by system purchasers for appropriate pretreatment equipment, or regular and costly maintenance shutdowns for lamp cleaning.

Clearly, improvements in the state of the art were needed in order to enhance the efficiency of destruction of a broader range of target compounds, while at the same time overcoming some of the chemical and mechanical limitations present in many applications.

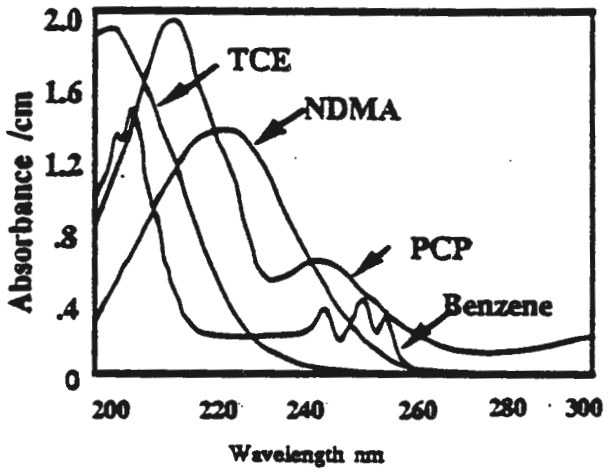
SECOND GENERATION EOP: "OUTSHINING" THE FIRST GENERATION ALTERNATIVE

The implementation of four major system design and operational improvements has permitted second generation **Rayox®** EOP systems to overcome the inherent limitations identified above. These are:

- significantly improved UV light sources
- the use of rate enhancing and selectivity catalysts
- an annular, multi reactor design concept, and
- incorporation of an automated lamp cleaning mechanism

The proprietary **Rayox®** ultraviolet lamp sources have significantly enhanced output in that region of the UV spectrum where virtually all priority pollutants are photochemically most active ie. below 250 nanometers wavelength. Figure 1 shows the wavelength absorption spectra for several compounds discussed later in this paper. The importance of the obvious skew to the left of the graph becomes evident when one realizes that the availability of low wavelength photons opens a second track of destruction, called photolysis, thereby allowing effective treatment of a broader range of compounds including those that do not respond as well to hydroxyl radical attack. Furthermore, when it is fully understood that the **Rayox®** ultraviolet lamps have at least twice the output per watt in this critical UV-C portion of the spectrum compared to first generation system lamps, and when this is combined with the greater than 90% efficiency of the **Rayox®** power supplies driving the lamps, inherently lower operating costs are the inevitable user benefit. By the same photolysis mechanism, the generation of hydroxyl radicals from hydrogen peroxide is similarly enhanced. This powerful, complementary destruction and rate enhancement mechanism is uniquely available in second generation systems like **Rayox®**.

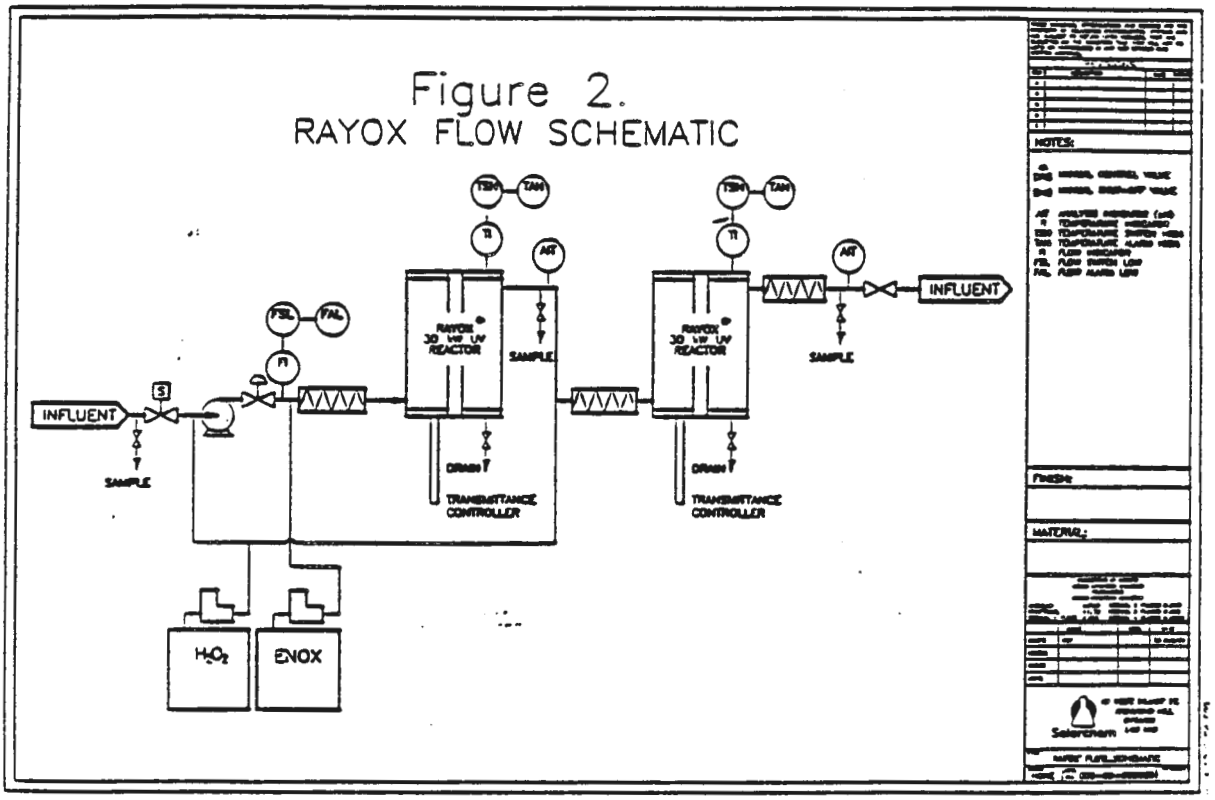
Figure 1
UV Absorption Spectrum



Several patented and proprietary ENOX additives, or "catalysts", have also been identified which can dramatically reduce the UV light input required in the design of a given treatment system through enhancement of the rate of radical formation and the efficiency of their use. Because second generation systems are sized by the amount of light required per order of magnitude of contaminant reduction per thousand gallons treated, rather than by the residence time which is typical of first generation systems, these additives, which are consumed during the **Rayox®** treatment, can effect a significant capital cost savings-often in the range of 20-30%.. The use of such additives is highlighted in the examples section of this paper.

The major benefit of the vertical **Rayox®** reactor design is its flexibility in optimizing treatment design thereby minimizing operating costs. Because each reactor is a separate entity, the type of treatment can be altered, or staged, in each reactor. Size, lamp type and additives can each be varied depending on water characteristics. Chemical usage reductions of up to thirty percent have been experienced as a result of this unique second generation reactor configuration.

The vertical reactor configuration also makes easily possible the incorporation of the fourth improvement in the state of the art inherent in second generation systems, automated UV lamp cleaning. This feature is portrayed in the **Rayox®** schematic provided as Figure 2. The obvious user benefits are the significant reduction in maintenance costs and system downtime, as well as the ability of the **Rayox®** system to handle groundwaters and process waters containing reasonable levels of soluble metals and oils and greases.



EXAMPLES MAKE THE CASE FOR SECOND GENERATION EOP

In a deliberate attempt to highlight the diverse applications straightforwardly being addressed by **Rayox®**, as well as the application of its second generation features in specific situations, five examples have been selected as follows:

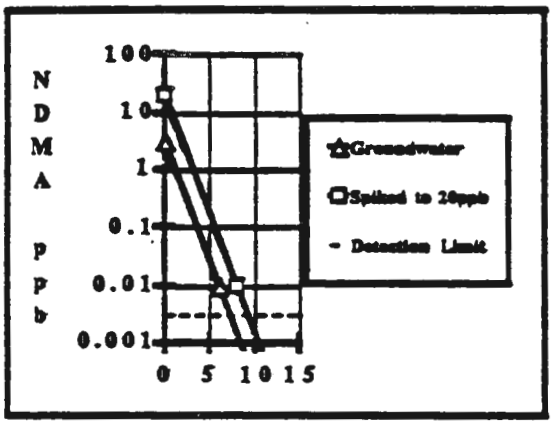
- groundwater treatment of dimethylnitrosamine (NDMA) using UV light (photolysis) alone
- high concentration (3+%) process wastewater containing normally tough-to-treat ketones
- photolysis/catalysis/oxidation of a process water specifically targeting pentachlorophenol
- BTEX/MTBE contaminated service station groundwater from LUST
- catalytic treatment of process water containing BTEX/MTBE along with competing non-target organics

Each of these system designs has benefited from second generation **Rayox®** processing capability as follows:

NDMA IN GROUNDWATER

Because NDMA is an extremely efficient absorber of UV light at 228 nm as shown in Figure 1, and one of the **Rayox®** UV lamps is a particularly strong emitter in the 200-240 nm range, only 2 kwh/ 1000 gallons/order of magnitude destruction is needed in order to reduce 40 ppb of NDMA to the drinking water standard of <9ppt virtually instantaneously. This system, which treats groundwater from a well that has been sunk to protect adjacent drinking water wells down gradient from becoming contaminated, treats 600 GPM using UV photolysis alone i.e. no peroxide or ozone is needed. Figure 3 shows the destruction curve for this installation, one of several such installations benefitting from the excellent direct photolysis characteristics of NDMA and the unique **Rayox®** ultraviolet lamps. With four orders of magnitude reduction being achieved, the direct operating costs are only $0.40/1000 gallons treated for this inherently simple system. Not incidentally, first generation systems considered for this application cost 2-3 times as much as **Rayox®** because they could not access the direct photolysis destruction mechanism.

Figure 3
Destruction of NDMA in Groundwater

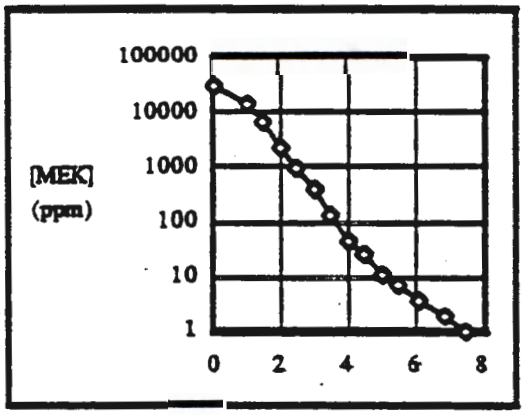


Rayox® Dose

METHYL ETHYL KETONE

In a rather unique **Rayox®** application, decanted steam stripping condensate containing up to 35000 ppm of MEK (80%) and as well as toluene/heptane/xylene (20%) is treated to less than 1 ppm of total toxic organics at 0.5 GPM using one 30kW **Rayox®** reactor. The second generation capabilities which make this treatment possible at a 25% lower capital cost than he next best alternative include a staged and catalyzed UV/peroxide treatment regimen together with strict pH control which varies with the staging of this batch treatment process. Figure 4 provides a destruction curve for this unusual application which clearly demonstrates the versatility of second generation EOP treatment on relatively refractory compounds. ($\sim 10^8$ litres mol $^{-1}$ sec $^{-1}$)

Figure 4
Rayox® Treatment of a High Concentration MEK Stream

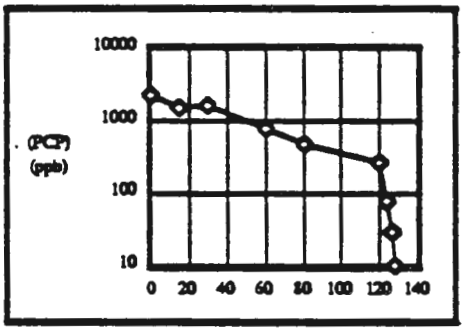


Rayox® Dose

PENTACHLOROPHENOL (PCP)

Figure 1 shows the peak absorption wavelength for PCP at 220 nm. With a very high extinction coefficient, a modest quantum yield and a good hydroxyl radical rate constant ($\sim 10^9$L mole $^{-1}$ sec^{-1}), PCP and similar compounds lend themselves very well to a combined direct photolysis/oxidation destruction mechanism typical of second generation EOP. In one among several installations treating chlorinated phenolics, an ENOX catalyzed **Rayox®** system is able to selectively treat 5 ppm of PCP to non detectable levels despite the strong presence of other organics (20,000 ppm COD) in a wood preserving industry process wastewater stream. Figure 5 shows the destruction curve for this 2 x 30 kW reactor system treating 8 GPM of process wastewater which is subsequently mixed before discharge with a PCP/PAH/cresol contaminated groundwater which itself has been **Rayox®** treated to non detectable levels (<1ppb) of all compounds.

Figure 5
Rayox® Treatment of PCP Contaminated Process Water



Rayox® Dose

TCE/DCE/HIGH Fe

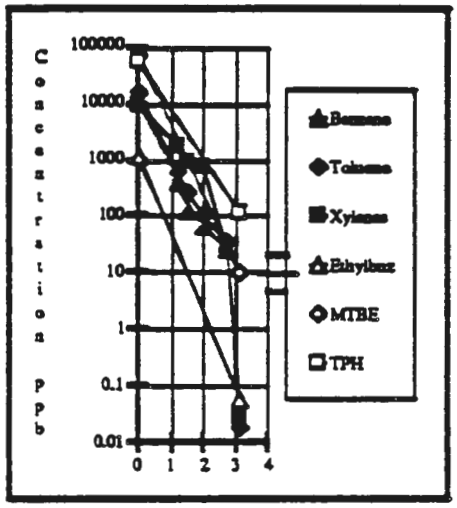
In an application more typical of those addressed by first generation technology, TCE,DCE and vinyl chloride are being treated from 35 ppm to <0.1ppm by **Rayox®** in a Northeastern state. The unique characteristics of this installation which make **Rayox®** the only practical solution to the requirement are the high hardness and iron (100ppm) concentrations. The high photodegradation efficiency of TCE at 215nm combined with the automated lamp cleaning feature inherent in second generation EOP systems, allows **Rayox®** to consistently achieve >99.999% destruction with no need for iron pretreatment.

BTEX/MTBE

A major oil company considered using activated carbon to treat BTEX contaminated water generated by barge ballast, site run-off and tank bottoms at one of its large light product distribution terminals. Treatment costs at one fifth those of carbon, combined with the coincident ability to easily treat MTBE to low ppb levels, prompted a clear decision in favour of **Rayox•**. Second generation system features which make this treatment possible when first generation technology failed, include the good UV absorption characteristics of BTEX at low wavelengths (see Figure 1) as well as the staged and catalyzed UV/H_2O_2 addition sequence in the modular **Rayox•** design. As in the PCP example cited above, it should be noted that the staged catalyzed treatment regimen allowed selective treatment of the BTEX/MTBE despite the presence of other non-target organics which tended to unduly load the carbon making it a much more costly treatment alternative. Figure 6 shows the destruction curves for a 3x 30kW reactor system which treats up to 350 ppm BTEX/MTBE to <10ppb of each compound at 150 GPM. Typical operating costs for this system are $5-6/1000 gallons treated.

While yet other examples of the versatility, and the benefits, of second generation EOP treatment with **Rayox•** could be cited, from the largest system in the world treating explosive compounds for the military, to the highly successful treatment of herbicide/pesticide containing wastewaters for the Environmental Response Team of the US EPA, it is clear that second generation EOP systems like **Rayox•** can offer significant cost and performance advantages over earlier EOP systems which are available in the market.

Figure 6
Rayox• Destruction of Gasoline Compomnents in Barge Ballast Water



Rayox• Dose

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United States
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EPA/540/M5-89/012
November 1989

EPA

SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Demonstration Bulletin

Ultraviolet Radiation and Oxidation

Ultrox International

TECHNOLOGY DESCRIPTION: The ultraviolet (UV) radiation/oxidation treatment technology developed by Ultrox International uses a combination of UV radiation, ozone, and hydrogen peroxide to oxidize organic compounds in water. Various operating parameters can be adjusted in the Ultrox® system to enhance the oxidation of organic contaminants. These parameters include hydrauiic retention time, oxidant dose, UV radiation intensity, and influent pH level.

schematic of the Ultrox system is shown in Figure 1. The treatment system is delivered on four skid-mounted modules, and includes the following major components:

- UV radiation/oxidation reactor module
- Ozone generator module
- Hydrogen peroxide feed system
- Catalytic ozone decomposer (Decompozon) unit for treating reactor off-gas

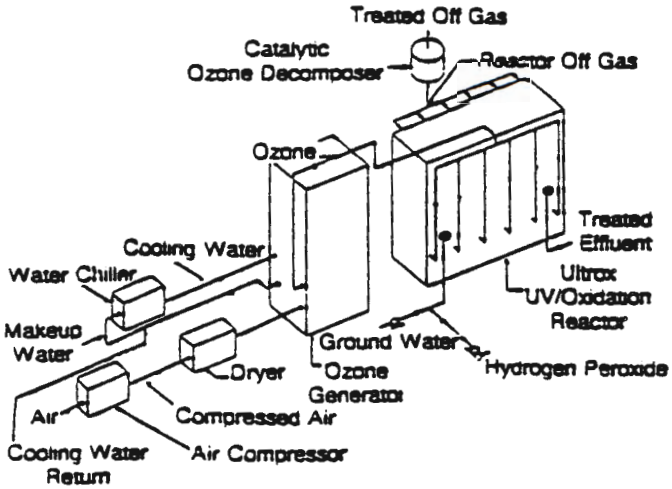

Figure 1. Isometric view of Ultrox System.

The commercial-size reactor used for the SITE Demonstration is 3 feet long by 1.5 feet wide by 5.5 feet high. The reactor is divided by five vertical baffles into six chambers. Each chamber contains four UV lamps as well as a diffuser which uniformly bubbles and distributes ozone gas into the groundwater being treated.

WASTE APPLICABILITY: This treatment technology is intended to destroy dissolved organic contaminants, including chlorinated hydrocarbons and aromatic compounds, that are present in wastewater or groundwater with low levels of suspended solids, oils, and grease.

DEMONSTRATION RESULTS: The SITE Demonstration was conducted at a former drum recycling facility in San Jose, California, over a 2-week period in February and March 1989. Approximately 13,000 gallons of groundwater contaminated with volatile organic compounds (VOC) from the site were treated in the Ultrox system during 13 test runs. During the first 11 runs, the 5 operating parameters were adjusted to evaluate the system. The last 2 runs were conducted under the same conditions as Run 9 to verify the reproducibility of the system's performance.

To evaluate the performance of each run, the concentrations of indicator VOCs in the effluent were analyzed overnight. Three of the 44 VOCs identified in the groundwater at the site were selected as indicator VOCs. These indicator VOCs were trichloroethylene (TCE); 1,1 dichloroethane (1,1-DCA); and 1,1,1-trichloroethane (1,1,1-TCA). TCE was selected because it is a major volatile contaminant at the site, and the latter two VOCs were selected because they are relatively difficult to oxidize.

Key findings from the Ultrox demonstration are ummarized as follows:

- The groundwater treated by the Ultrox system met the applicable National Pollutant Discharge Elimination System (NPDES) standards at the 95 percent confidence level. Success was obtained by using a hydraulic retention time of 40 minutes; ozone dose of 110 mg/L; hydrogen peroxide dose of 13 mg/L; all 24 UV lamps operating; and influent pH at 7.2 (unadjusted).
- There were no volatile organics detected in the exhaust from the Decompozon unit.
- The Decompozon unit destroyed ozone in the reactor off-gas to levels less than 0.1 ppm (OSHA Standards). The ozone destruction efficiencies were observed to be greater than 99.99 percent.
- The Ultrox system achieved removal efficiencies as high as 90 percent for the total VOCs present in the groundwater at the site. The removal efficiencies for TCE were greater than 99 percent. However, the maximum removal efficiencies for 1,1-DCA and 1,1,1-TCA were about 65 and 85 percent, respectively (Table 1).

Table 1. Performance Data During Reproducible Runs

	Mean Influent (µg/L)	Mean Effluent (µg/L)	Percent Removal
Run Number: 9			
TCE	65	1.2	98
1,1-DCA	11	5.3	54
1,1,1-TCA	4.3	0.75	83
Total VOCs	170	16	91
Run Number: 12			
TCE	52	0.55	99
1,1-DCA	11	3.8	65
1,1,1-TCA	3.3	0.43	87
Total VOCs	150	12	92
Run Number: 13			
TCE	49	0.63	99
1,1-DCA	10	4.2	60
1,1,1-TCA	3.2	0.49	85
Total VOCs	120	20	83

- Within the treatment system, the removals of 1,1-DCA and 1,1,1-TCA appear to be due to both chemical oxidation and stripping. Specifically, stripping accounted for 12 to 75 percent of the total removals for 1,1,1-TCA, vinyl chloride, and other VOCs.
- No semivolatiles, PCBs, or pesticides were found in the groundwater at the site. Among the VOCs, the contaminant present at the highest concentration range (48 to 85 µg/L) was TCE. The groundwater also had contaminants such as 1,1-DCA and 1,1,1-TCA in the concentration ranges of 10 to 13 µg/L and 3 to 5 µg/L, respectively.
- The organics analyzed by Gas Chromatography (GC) methods represent less than 2 percent of the total organic carbon (TOC) present in the water. Very low TOC removal occurred, which implies that partial oxidation of organics (and not complete conversion to carbon dioxide and water) took place in the system.

A Technology Evaluation Report and an Application Analysis Report describing the complete demonstration will be available in the Spring of 1990.

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Enclosure 9

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PB92-126853

APPLICABILITY OF UV/OXIDATION TECHNOLOGIES TO TREAT CONTAMINATED GROUNDWATER

(U.S.) Environmental Protection Agency
Cincinnati, OH

1991

U.S. DEPARTMENT OF COMMERCE
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16. ABSTRACT

This paper presents information useful in evaluating the applicability of UV/Oxidation treatment technologies for groundwater contaminated with organics. The information presented includes a description of the technologies, factors affecting the technologies, and results from two pilot-scale studies of UV/Oxidation treatment system applications. The first pilot-scale study describes the performance of a UV/Oxidation system, developed by Ultrox International of Santa Ana, California, in treating groundwater contaminated with volatile organic compounds (VOCs). At the optimum operating conditions, the Ultrox system achieved total VOC removals of greater than 90 percent. Most VOCs were removed through oxidation and stripping. The treated groundwater met the applicable limits for discharge into a local waterway. No harmful emissions were released to the atmosphere from the Ultrox system, which is equipped with an off-gas treatment unit. The second pilot-scale study describes the performance of another UV/Oxidation system, developed by Peroxidation Systems, Inc., of Tucson, Arizona, in treating groundwater contaminated with VOCs and chemical-warfare agent degradation products. At the optimum operating conditions, the system achieved contaminant removal efficiencies of about 96 percent, and the treated water met the federal maximum contaminant levels for drinking water.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Hazardous Materials Groundwater	Superfund Advanced Oxidation	

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THE APPLICABILITY OF UV/OXIDATION TECHNOLOGIES TO TREAT CONTAMINATED GROUNDWATER

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ABSTRACT

This paper presents information useful in evaluating the applicability of UV/oxidation treatment technologies for groundwater contaminated with organics. The information presented includes a description of the technologies, factors affecting the technologies, and results from two pilot-scale studies of UV/oxidation treatment system applications. The first pilot-scale study describes the performance of a UV/oxidation system, developed by Ultrox International of Santa Ana, California, in treating groundwater contaminated with volatile organic compounds (VOCs). At the optimum operating conditions, the Ultrox system achieved total VOC removals of greater than 90 percent. Most VOCs were removed through chemical oxidation. However, a few VOCs were removed through oxidation and stripping. The treated groundwater met the applicable limits for discharge into a local waterway. No harmful emissions were released to the atmosphere from the Ultrox system, which is equipped with an off-gas treatment unit. The second pilot-scale study describes the performance of another UV/oxidation system, developed by Peroxidation Systems, Inc. of Tucson, Arizona, in treating groundwater contaminated with VOCs and chemical-warfare agent degradation products. At the optimum operating conditions, the system achieved contaminant removal efficiencies of about 96 percent, and the treated water met the federal maximum contaminant levels for drinking water.

INTRODUCTION

Most conventional treatment processes, such as air stripping, steam stripping, carbon adsorption, and biological treatment, although quite effective in treating water contaminated with organics, have certain limitations. For example, stripping and adsorption merely transfer the contaminants from one medium (water) to another (air or carbon), whereas biological treatment processes generate sludge that requires further treatment and disposal. In addition, biological treatment processes have low contaminant removal rates.

Chemical oxidation by ozone, hydrogen peroxide, or some other conventional oxidant could overcome most of the limitations posed by the other conventional processes (for example, merely transferring contaminants from one medium to another). However, because of kinetic limitations chemical oxidation by conventional oxidants has yet to become a competitive treatment option. Several studies have shown that the kinetic limitations could be overcome by using hydroxyl radicals to carry out the oxidation reactions (1-3). The hydroxyl radicals are known to be less selective in carrying out oxidation reactions and have much higher rate constants compared to ozone, hydrogen peroxide, or ultraviolet (UV) radiation.

In commercial applications, hydroxyl radicals are generated by the combined use of (1) UV radiation and hydrogen peroxide, (2) UV radiation and ozone, or (3) ozone and hydrogen peroxide. These processes are commonly referred to as "advanced oxidation processes" or, when UV radiation is used to generate hydroxyl radicals, "UV/oxidation technologies."

This paper briefly describes (1) the chemistry of UV/oxidation technologies and factors affecting these technologies and (2) the results from pilot-scale operations of two UV/oxidation systems.

UV/OXIDATION TECHNOLOGIES: PROCESS CHEMISTRY

The key principle of UV/oxidation technologies is the generation of hydroxyl radicals through UV photolysis of hydrogen peroxide or ozone. When UV radiation is used to photolyze hydrogen peroxide or ozone, the UV radiation may also photolyze some organic contaminants, such as tetrachloroethene (PCE), aromatic halides, and pesticides, increasing their removal. A brief summary of the chemistry of UV/oxidation technologies is given below. More information on this can be found elsewhere (4).

UV Photolysis of Hydrogen Peroxide

Generation of hydroxyl radicals by UV photolysis of hydrogen peroxide may be described by the following equation:

$$H_2O_2 + h\nu \rightarrow 2\ OH\cdot$$

In commercial applications, low-pressure mercury vapor UV lamps are typically used to produce UV radiation, but these lamps may not be the best choice. The maximum absorbance of UV radiation by hydrogen peroxide occurs at about 220 nanometers (nm). However, the dominant emission wavelength of low-pressure mercury vapor UV lamps is at about 254 nm. Also, the molar extinction coefficient of hydrogen peroxide at 254 nm is low, 19.6 liters per mole-centimeter ($M^{-1}cm^{-1}$). Because of the low molar extinction coefficient, a high concentration of hydrogen peroxide is needed in the medium to generate sufficient hydroxyl radicals. To overcome this limitation, some technology

developers (for example, Purus, Inc. of San Jose, California) use xenon UV lamps and adjust the spectral output to match the absorption characteristics of hydrogen peroxide or any other photolytic target.

UV Photolysis of Ozone

UV photolysis of ozone in water yields hydrogen peroxide, which in turn reacts with UV radiation or ozone to form hydroxyl radicals as shown below.

$$O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + h\nu \rightarrow 2\ OH\cdot$$

or

$$2\ O_3 + H_2O_2 \rightarrow 2\ OH\cdot + 3\ O_2$$

Because the molar extinction coefficient of ozone is 3,300 $M^{-1}cm^{-1}$ at 254 nm, the UV photolysis of ozone is not expected to have the same limitation as that of hydrogen peroxide when low-pressure mercury vapor UV lamps are used.

FACTORS INFLUENCING PERFORMANCE

Factors influencing the performance of a UV/oxidation technology can be grouped into three categories: (1) waste characteristics, (2) operating parameters, and (3) maintenance requirements. Each of these is discussed below.

Waste Characteristics

The contaminant removal efficiencies depend on the type of contaminants to be treated. For example, organics with double bonds, such as trichloroethene (TCE), PCE, and vinyl chloride, and aromatic compounds, such as phenol, toluene, benzene, and xylene, are easily removed because they are readily oxidized. In systems that use ozone,

organics without double bonds and with high Henry's law constants, such as 1,1-dichloroethane (1,1-DCA) and 1,1,1-trichloroethane (1,1,1-TCA), are also removed. However, because they are difficult to oxidize their removal is primarily due to stripping. Organics without double bonds and with low Henry's law constants, such as diethylamine and 1,4-dioxane, would be difficult to remove because they are not easily oxidized or stripped.

Since UV/oxidation technologies are intended for the destruction of organic contaminants, any other species that consume oxidants are considered an additional load for the system. These species are called scavengers and include anions such as bicarbonate, carbonate, sulfide, nitrite, bromide, and cyanide. Metals present in their reduced states, such as trivalent chromium, ferrous iron, manganous ion, and several others, are likely to be oxidized. These reduced metals, in addition to acting as scavengers, cause additional concerns. For example, trivalent chromium is oxidized to more toxic hexavalent chromium, and ferrous iron and manganous ions are oxidized to less soluble forms, which precipitate in the reactor and can cause UV lamp scaling and suspended solids formation. Nontarget organics (for example, humic compounds) could also act as scavengers. Other parameters such as suspended solids and oil and grease would reduce UV transmission, thereby decreasing the treatment efficiency. For these reasons, pretreatment may be required for proper functioning of UV/oxidation units depending on the waste characteristics.

Operating Parameters

Operating parameters are those parameters that are varied during the treatment process to achieve the desired treatment efficiencies. Such parameters include hydraulic retention time, ozone dose, hydrogen peroxide dose, UV lamp intensity, influent pH level, and gas-to-liquid flow rate ratio.

In general, increasing the hydraulic retention time will increase treatment efficiency up to a certain point. At this point, the system tends to proceed toward equilibrium, and increasing the hydraulic retention time no longer increases treatment efficiency.

The higher the dose of oxidants, the better the treatment rate. However, the molar ratio of the oxidant doses must be considered. For example, when treating water containing TCE and PCE, maximum removals were observed when the molar ratio of ozone dose to hydrogen peroxide dose was equal to two, and the removals were significantly less when the ratio was not equal to two. In this case, the expected stoichiometry for pure water agreed with the molar ratio at which optimum removal was observed; however, several factors may influence the molar ratio (1). These factors are summarized as follows:

- Hydrogen peroxide can act as a free radical scavenger itself, thereby decreasing the hydroxyl radical concentration if it is present in excess.
- Ozone can react directly with hydroxyl radicals, consuming both ozone and hydroxyl radicals.
- Ozone and hydroxyl radicals may be consumed by scavengers present in the water being treated.

Therefore, the optimum proportion of the oxidants for maximum removals cannot be predetermined. Instead, the proportion needs to be

determined for the waste under consideration using pilot- or bench-scale treatability tests.

In addition to photolyzing hydrogen peroxide and ozone to generate hydroxyl radicals, the UV radiation may also photolyze some organic contaminants, such as PCE, aromatic halides, and pesticides, increasing the contaminant removal.

If water has bicarbonate and carbonate alkalinity at a level greater than 400 milligrams per liter (mg/L) as calcium carbonate, lowering the pH to a range of 4 to 6 should improve the treatment efficiency. Low pH decreases the concentration of these scavengers by shifting the equilibrium toward carbonic acid. If the carbonate and bicarbonate alkalinity is low, then a high pH should improve the treatment efficiency. High pH favors hydroxyl radical formation because of the reaction between ozone and hydroxyl ion.

The ozone gas flow rate can also influence treatment rate. In practice, once the ozone dose is selected, several combinations of ozone gas phase concentration and ozone gas flow rate can be applied. According to Venosa and Opatken (5), the ratio of gas flow rate to liquid flow rate will dictate the hydraulic characteristics of the reactor, as shown in Figure 1. This figure shows that, at low gas-to-liquid flow rate ratios, the mixing regime in a reactor is close to that of a plug flow reactor (shown as Curve A); whereas at high ratios, the reactor mixing regime is close to that of a mixed reactor (shown as Curve C). For reactions with a positive reaction order, plug flow mixing characteristics offer higher treatment rate than mixed reactor mixing characteristics (6). Since most reactions have a

positive reaction order, low gas-to-liquid flow rate ratios should be considered. In addition to increasing the treatment rate, low gas-to-liquid flow rate ratios reduce stripping of volatile organics.

Maintenance Requirements

Regular maintenance by trained personnel is essential for a successful treatment operation. The following components require maintenance: (1) ozonation system, (2) UV lamp assembly, (3) ozone decomposer unit, and (4) miscellaneous components. A brief summary of the maintenance requirements for these components is presented in Table 1.

PILOT-SCALE STUDY 1

This pilot-scale study was performed at the Lorentz Barrel and Drum (LB&D) site in San Jose, California. The LB&D site was used for drum recycling operations from about 1947 to 1987. The drums contained residual aqueous wastes, organic solvents, acids, metal oxides, and oils. Groundwater samples collected before the pilot-scale study indicated that several volatile organic compounds (VOCs) were present in the shallow aquifer. VOCs detected at high levels included TCE (280 to 920 micrograms per liter [μg/L]), vinyl chloride (51 to 146 μg/L), and 1,2-trans-dichloroethene (42 to 68 μg/L). The pH of the groundwater was about 7.2; and the alkalinity was about 600 mg/L as calcium carbonate. These measurements indicated that bicarbonate ion (HCO_3^-), an oxidant scavenger, was present at high levels. Other oxidant scavengers such as bromide, cyanide, and sulfide were not detected. Iron and manganese were present at low levels (less than 1 mg/L).

The pilot-scale study used a UV/oxidation system developed by Ultrox International of Santa Ana, California, and evaluated its effectiveness in treating the groundwater at the LB&D site (7). A brief description of the Ultrox system, the testing approach, and a summary of results is presented below.

Ultrox System

The Ultrox UV/oxidation treatment system uses UV radiation, ozone, and hydrogen peroxide to oxidize organics in water. The major components of the Ultrox system are the UV/oxidation reactor module, air compressor/ozone generator module, hydrogen peroxide feed system, and catalytic ozone decomposition (Decompzon) unit (see Figure 2).

The UV/oxidation reactor used has a volume of 150 gallons and is 3 feet long by 1.5 feet wide by 5 feet high. The reactor is divided by five vertical baffles into six chambers and contains 24 65-watt UV lamps in quartz sheaths. The UV lamps are installed vertically and are evenly distributed throughout the reactor (four lamps per chamber). Each chamber also has one stainless steel sparger that extends along the width of the reactor. These spargers uniformly diffuse ozone gas from the base of the reactor into the water. Hydrogen peroxide is added to the influent line to the reactor. An in-line static mixer is used to disperse the hydrogen peroxide into the contaminated water in the influent feed line.

The Decompzon unit uses a nickel-based proprietary catalyst to decompose reactor off-gas ozone to oxygen. The Decompzon unit can accommodate flows of up to 10 standard cubic feet per minute and can

destroy ozone concentrations in ranges of 1 to 20,000 parts per million (ppm) to less than 0.1 ppm by weight.

Testing Approach

The study was designed to evaluate the Ultrox system by adjusting the levels of five operating parameters: (1) influent pH, (2) hydraulic retention time, (3) ozone dose, (4) hydrogen peroxide dose, and (5) UV radiation intensity. Eleven test runs were performed to evaluate the Ultrox system under various operating conditions. After these runs, two additional runs were performed to verify that the system's performance was reproducible. The verification runs (Runs 12 and 13) were performed at the optimum operating conditions (Run 9 -- influent pH of 7.2; hydraulic retention time of 40 minutes; ozone dose of 110 mg/L; hydrogen peroxide dose of 13 mg/L; and all UV lamps operating).

During the study, a preliminary estimate of the Ultrox system's performance in each run was obtained from the effluent concentrations of three indicator VOCs. The VOCs selected for this purpose were TCE, 1,1-DCA, and 1,1,1-TCA. TCE was selected because it is a major volatile contaminant at the site, and 1,1-DCA and 1,1,1-TCA were selected because they are relatively difficult to oxidize. At the end of the study, data from all samples was used to evaluate the system's effectiveness.

Results and Discussion

This section summarizes the performance of the Ultrox system in verification runs and presents an evaluation of the UV/oxidation technology's effectiveness in removing VOCs from the groundwater at

the LB&D site. A detailed summary of the demonstration results, case studies, an economic analysis, and the applicability of the Ultrox UV/oxidation technology is presented elsewhere (8).

Summary of Results for VOCs

Percent removals for the indicator VOCs and total VOCs at optimum operating conditions (Runs 9, 12, and 13) are presented in Figure 3. The figure shows that the total VOC removals were about 90 percent, while removal efficiencies for TCE were about 98 percent and those for 1,1-DCA and 1,1,1-TCA were about 60 and 85 percent, respectively. Higher removal efficiencies for TCE than for 1,1-DCA and 1,1,1-TCA supports the rationale used in selecting the indicator VOCs.

Figure 4 compares the 95 percent upper confidence limits (UCLs) for the effluent VOCs with the National Pollutant Discharge Elimination System (NPDES) limits. The UCLs were calculated using the one-tailed Student's t-test. The effluent met the discharge limits for all regulated VOCs at the 95 percent confidence level in Runs 12 and 13; in Run 9, the mean concentrations for 1,1-DCA and 1,2-DCA exceeded the discharge limits.

The gas chromatography (GC) and GC/mass spectrometry analyses performed for VOCs, semivolatile organics, polychlorinated biphenyls, and pesticides did not indicate the formation of new compounds in the treated water. Because VOCs made up less than 2 percent of the total organic carbon, the general claim that UV/oxidation technologies convert VOCs to carbon dioxide and water could not be verified.

Because the Ultrox system treated the groundwater by bubbling ozone gas through it, some VOC removal could be attributed to

stripping in addition to oxidation. To determine the extent of stripping within the treatment system, VOC samples were collected from the reactor off-gas, and emission rates for four VOCs were compared to the VOC removal rates from groundwater. The results are summarized in Table 2. Because the extent of stripping for any particular VOC is expected to be proportional to the ratio of air flow rate to water flow rate, this ratio is also presented in the table. The ratio for Runs 1 to 5 is approximately 2; for Run 6 and Runs 8 to 13, it is about 4.5; and for Run 7, it is 1. If stripping contributed to the total removal of the four VOCs, the extent of stripping would be expected to be least in Run 7, and most in Runs 6 and 8 to 13. The data presented in the table follow this trend for three of the four VOCs (except for the vinyl chloride in Runs 6, 7, and 9). A quantitative correlation of the extent of stripping cannot be made, because the operating conditions were different in each run. For example, at a given air to water flow ratio, when oxidant doses are varied, the extent of oxidation also varies. Therefore, the extent of stripping will be indirectly affected.

Table 2 presents Henry's law constants for the four VOCs (9). By comparing these constants for the VOCs, their volatility is expected to increase from left to right as shown below:

1,1-DCA – TCE – 1,1,1-TCA – vinyl chloride

However, significant removal fractions for 1,1,1-TCA and 1,1-DCA were observed to be due to stripping. Conversely, the extent of stripping was low for vinyl chloride and TCE. This is because it is easier to oxidize vinyl chloride and TCE than 1,1-DCA and 1,1,1-TCA because of

the double bonds between the carbon atoms in TCE and vinyl chloride. In other words, in the UV/oxidation process using ozone, stripping is a significant removal pathway for compounds that are difficult to oxidize.

Performance of the Decompzon Unit

The ozone concentrations in the influent to and the effluent from the Decompzon unit were analyzed in each run. Ozone destruction efficiencies greater than 99.99 percent were achieved in Runs 1 to 10. The effluent ozone concentrations were low (less than 0.1 ppm) for Runs 1 to 8, approximately 1 ppm in Runs 9 and 10, and greater than 10 ppm in Runs 11, 12, and 13. The high ozone levels (greater than 1 ppm) in the effluent are attributed to the malfunctioning heater in the Decompzon unit. The temperature in the Decompzon unit should have been 140°F for the unit to properly function, whereas the temperature for Runs 11 to 13 was only about 80°F.

Although the primary function of the Decompzon unit is to remove ozone, significant VOC removal also occurred when the unit functioned as designed (Runs 1 to 8). For example, the Decompzon unit removed TCE, 1,1-DCA, 1,1,1-TCA and vinyl chloride (present in the gas phase in the reactor at levels of approximately 0.1 to 0.5 ppm) to below detection levels.

The Ultrox system's average electrical energy consumption was about 11 kilowatt-hours per hour (kwh/h) of operation at a flow rate of 3.75 gallons per minute (gpm).

PILOT-SCALE STUDY 2

This pilot-scale study was performed at the Old O-Field site located in the Edgewood Area of the Aberdeen Proving Ground, Maryland. The site was used for disposal of chemical-warfare agents, munitions, contaminated equipment, and various other hazardous materials during the 1940s and early 1950s. The disposal of these hazardous materials contaminated several media at the Old O-Field site, including groundwater, surface water, and sediments.

Groundwater samples collected during the pilot-scale study indicated that several organics, including VOCs, organosulfur compounds, and explosives, were present at the site in the range of 10 µg/L to 500 µg/L. Iron and manganese were present at levels of 120 mg/L and 2.5 mg/L, respectively (10). Trace levels of arsenic contamination was also observed in some locations sampled before the pilot-scale studies.

As part of the remediation efforts, pilot-scale treatability studies were performed in April and May 1991. A total of 37,000 gallons of groundwater from three wells was used to perform the treatability studies. Contaminated groundwater was pumped to two holding tanks and then treated by a metals precipitation system. The metals precipitation was performed at pH 11, primarily to remove arsenic observed in samples collected before the pilot-scale studies began; however, the pilot-scale study samples showed no arsenic contamination. Iron and manganese were removed to levels of 0.2 mg/L and 0.02 mg/L, respectively. The pH of the metals precipitation system effluent was adjusted to 7 and then treated using two parallel

systems: (1) an air stripping system followed by carbon adsorption for both liquid- and vapor-phase effluents from the air stripper and (2) a UV/oxidation system. The air stripping/carbon adsorption system was developed by Carbonair and the UV/oxidation system was developed by Peroxidation Systems, Inc. (PSI). A brief description of PSI UV/oxidation system, testing approach, and summary of results is presented below.

PSI UV/oxidation System

Figure 5 shows a schematic of the PSI UV/oxidation system. The system used at the Old O-Field site consisted of two parallel cartridge filters rated at 10 micrometers (μm) followed by the UV/oxidation reactor. The UV/oxidation reactor had a volume of 80 gallons and was divided by three horizontal baffles into four chambers. Each chamber contained one high intensity, broad band, mercury-arc-type 15-kw UV lamp. A splitter was used so that hydrogen peroxide could be added at multiple points, such as the influent line and at several locations inside the reactor, making hydrogen peroxide available for hydroxyl radical formation throughout the reactor. The effluent from the reactor was passed through an optional manganese-greensand filter to remove any residual hydrogen peroxide, followed by a pH adjustment tank to raise the pH to an acceptable level.

Testing Approach

Four tests were conducted at a flow rate of 15 gpm (hydraulic retention time of about 5.3 minutes). In Tests 1, 2, and 3, hydrogen peroxide doses were 45 mg/L, 90 mg/L, and 180 mg/L, respectively, with the splitter in operation; and in Test 4, hydrogen peroxide dose was

45 mg/L with the splitter not in operation. When the splitter was used, the total hydrogen peroxide dose was split into three equal parts, which were added at (1) the influent line to the reactor, (2) the effluent line from the first chamber, and (3) the effluent line from the second chamber. In Test 4, when the splitter was not used, all hydrogen peroxide was added at the influent line to the reactor. Treated and untreated water samples were collected for (1) chemical analyses to estimate removal efficiencies and compare them with federal maximum contaminant levels (MCLs) for drinking water, and (2) bioassay to evaluate whether the water was acutely toxic to fathead minnows, daphnia magna, sheepshead minnows, and mysid shrimp.

Results and Discussion

A summary of results at the optimum operating conditions (Test 3) is presented below. More details on the PSI system performance is available elsewhere (10). Table 3 summarizes the influent and effluent contaminant levels and the removal efficiencies of several contaminants. These results show that for most compounds the effluent levels were below detection levels, and the removal efficiencies for these compounds were greater than 82 to 99 percent. The effluent levels of chloroform and 1,3,5-trinitrobenzene were 1.2 µg/L and 0.53 µg/L, respectively. The removal efficiencies for these compounds were in the range of 96 to 97 percent.

Treated effluent met federal MCLs for all compounds. The influent to and effluent from the PSI system passed the bioassay tests. The pH decreased by about one unit, indicating that some of the oxidation byproducts were acidic. Although the manganese-

greensand filter was effective in removing residual hydrogen peroxide, it increased the manganese levels in treated water from about 0.02 mg/L to 1.4 mg/L, which is above National Secondary Drinking Water standard (50 µg/L). Therefore, the use of manganese-greensand filter is not recommended. Instead, other methods should be considered to neutralize any residual hydrogen peroxide in the treated water samples (for example, addition of ascorbic acid, thiosulfate, or catalase-D). If the residual oxidant level is greater than 1 mg/L and is not neutralized, it would continue to react with the contaminants in the sample bottles until analysis could be performed. This continued reaction may introduce a bias in the treatment system evaluation.

The PSI system's average electricity consumption was about 65 kwh/h of operation at a flow rate of 15 gpm.

CONCLUSIONS

UV/oxidation technologies appear to be efficient and competitive treatment alternatives for removing organics present in water at low levels (less than about 100 mg/L). For high strength wastes, these technologies may prove cost-effective when used in combination with biological or adsorption processes. In some cases, the UV/oxidation technologies are preferred over adsorption or biological processes, mainly because in the UV/oxidation technologies (1) contaminants are destroyed rather than being transferred to some other medium and (2) no residuals requiring further handling, such as sludge or spent carbon, are generated.

Since the UV/oxidation technologies have been used for only about 5 years long-term operation and maintenance data are currently being

developed for several applications. Based on the available data, in some cases, proper pretreatment is essential to minimize frequent shut downs.

More research is needed to identify the byproducts of UV/oxidation of organics. Several technology developers claim that the byproducts of UV/oxidation of organics are carbon dioxide, water, and halides, but little published data are available to support these claims when UV/oxidation is used to treat a multitude of contaminants present in groundwater. Despite this situation, UV/oxidation technologies can continue to be used as long as appropriate physicochemical analyses and toxicity tests are carried out on the effluent, and these analyses and tests indicate that the effluent meets the discharge criteria. In some cases, the economics may favor the effluent's use as process water or sanitary water in industries depending on access and suitability.

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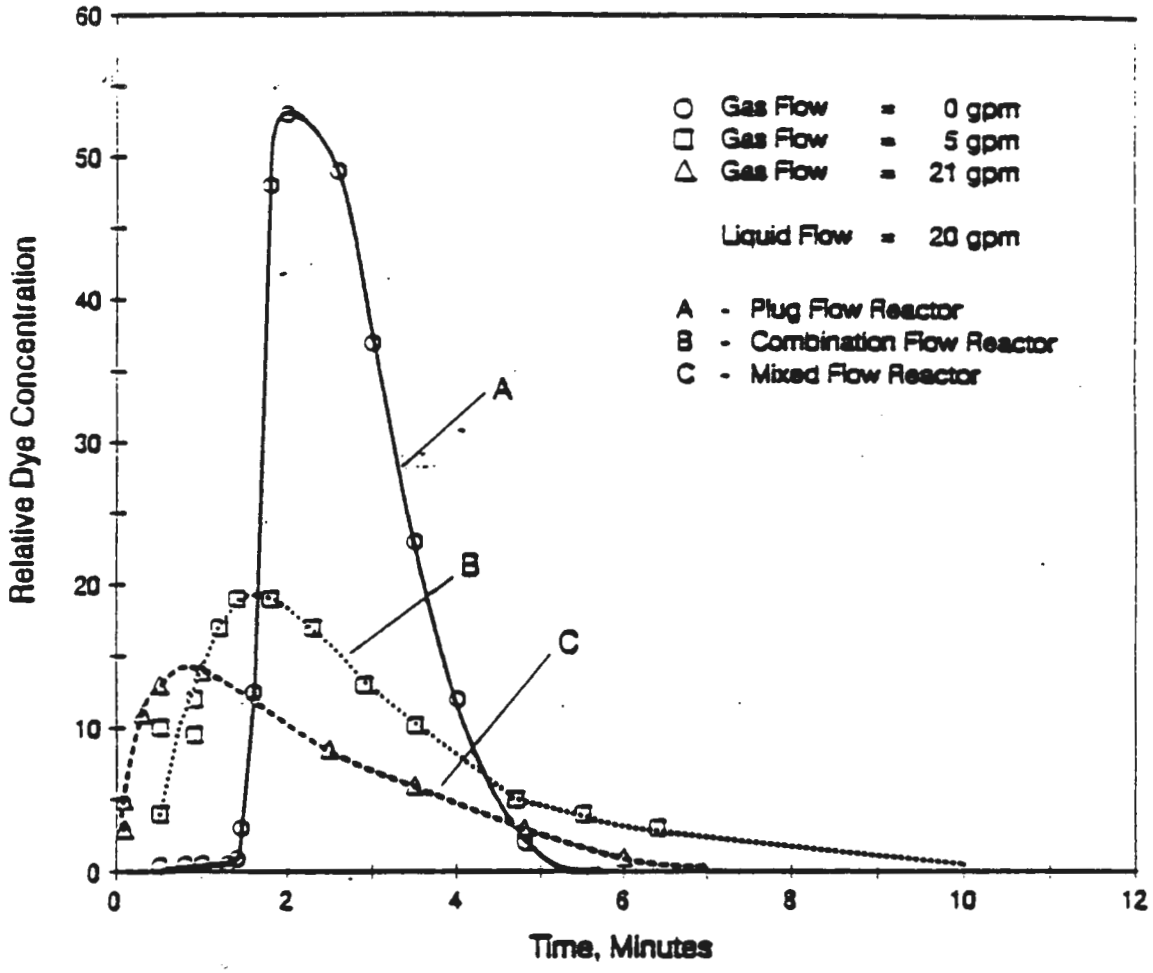

Figure 1. Dye tests showing effects of gas flow rates on the mixing characteristics of a bubble diffuser ozone contact basin.

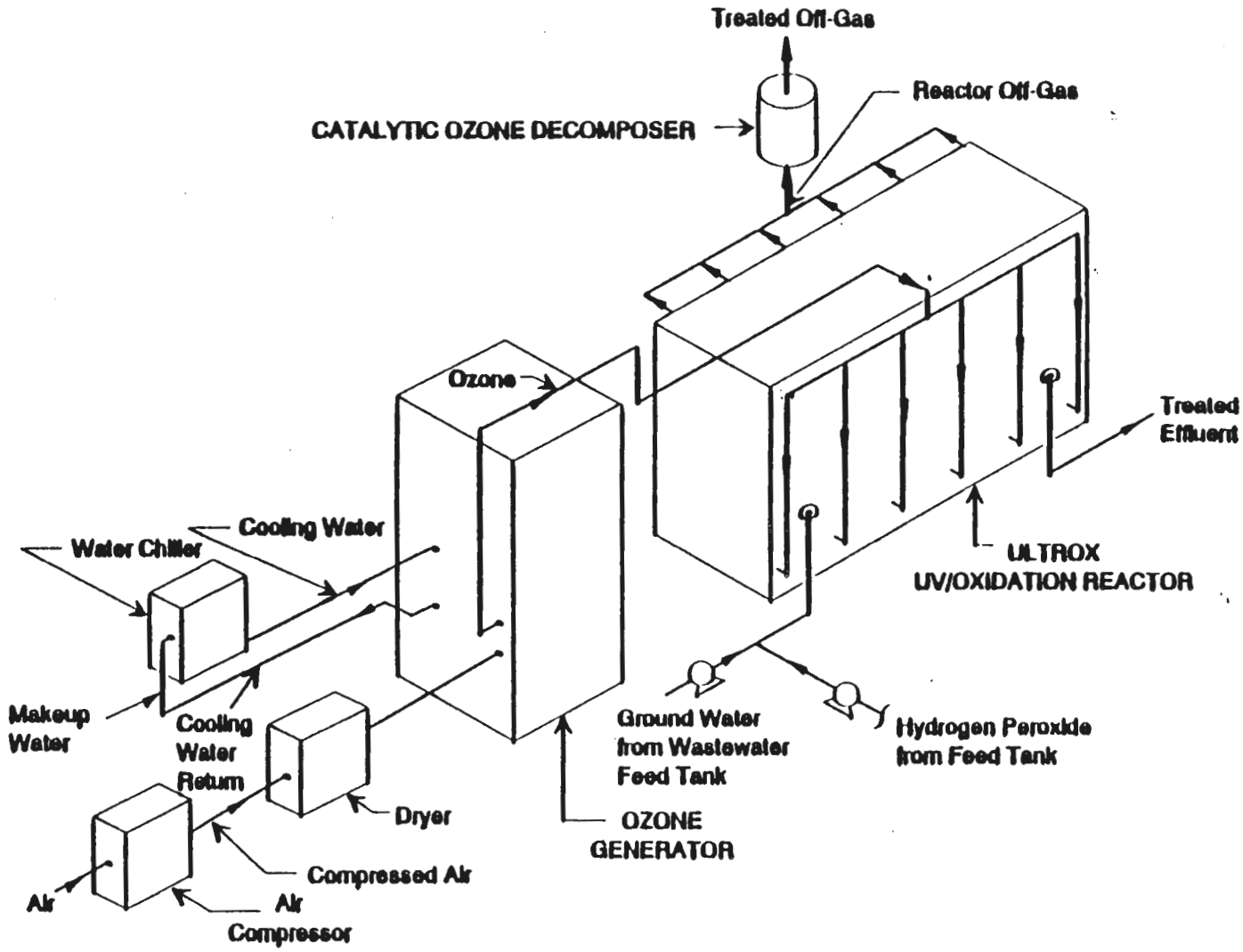

Figure 2. Isometric view of Ultrox system.

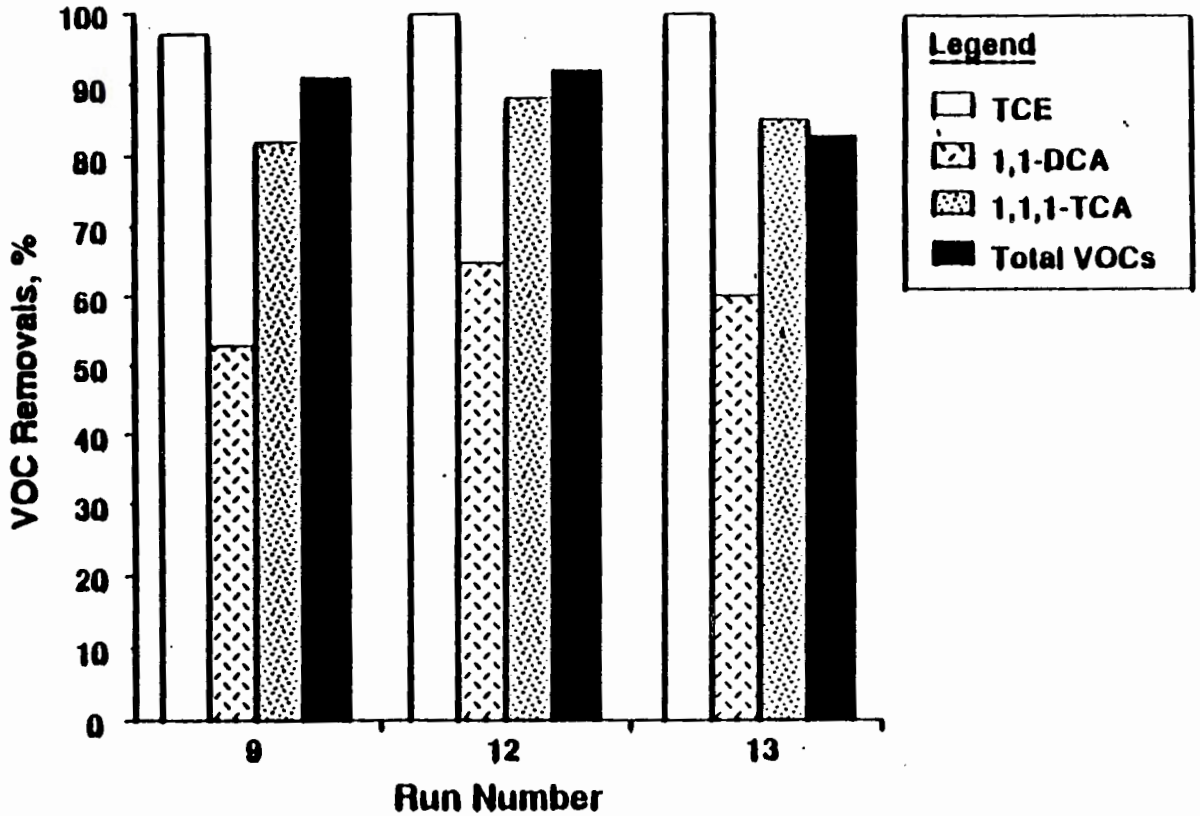

Figure 3. VOC removals at optimum conditions.

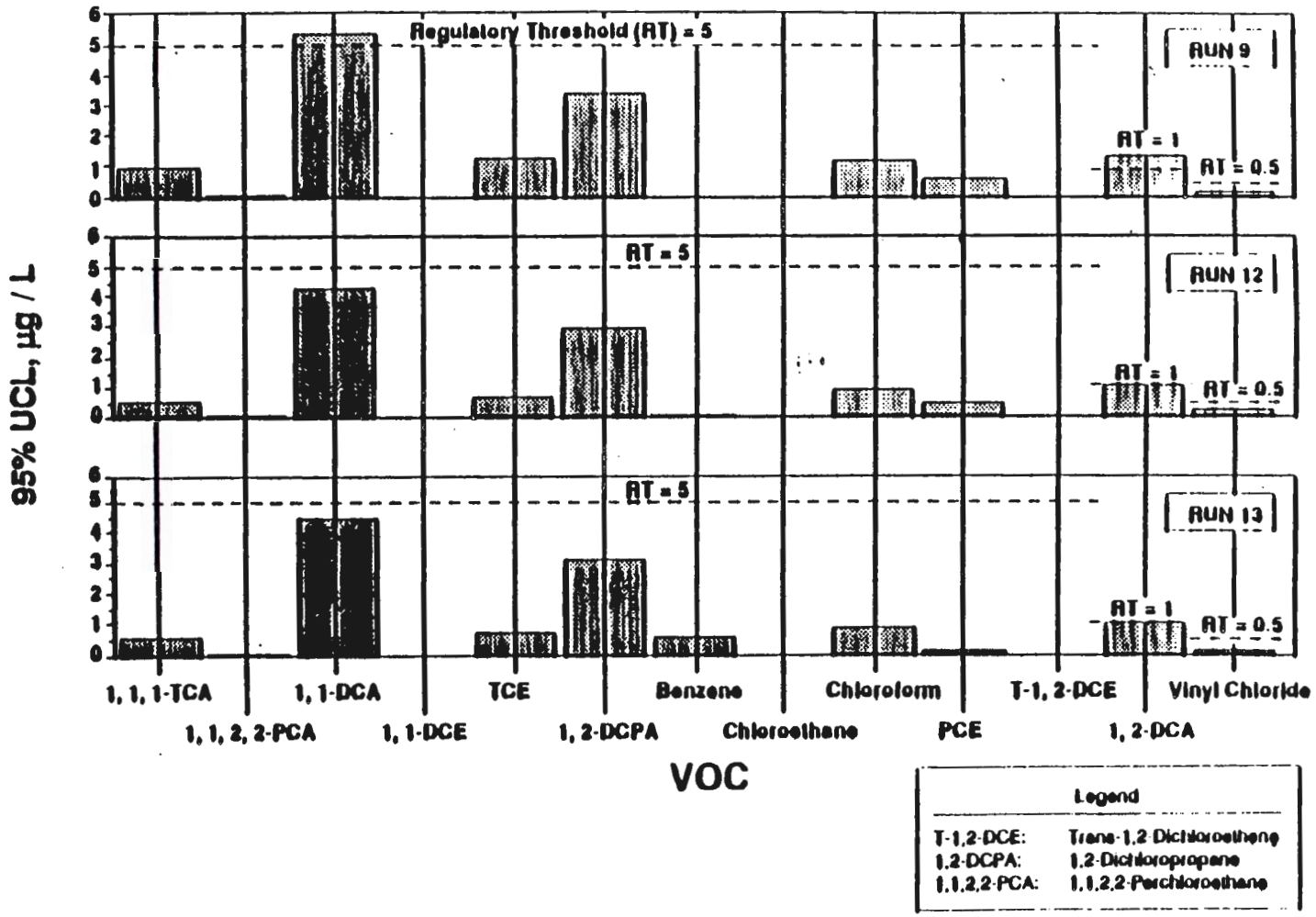

Figure 4. Comparison of effluent VOC concentrations.

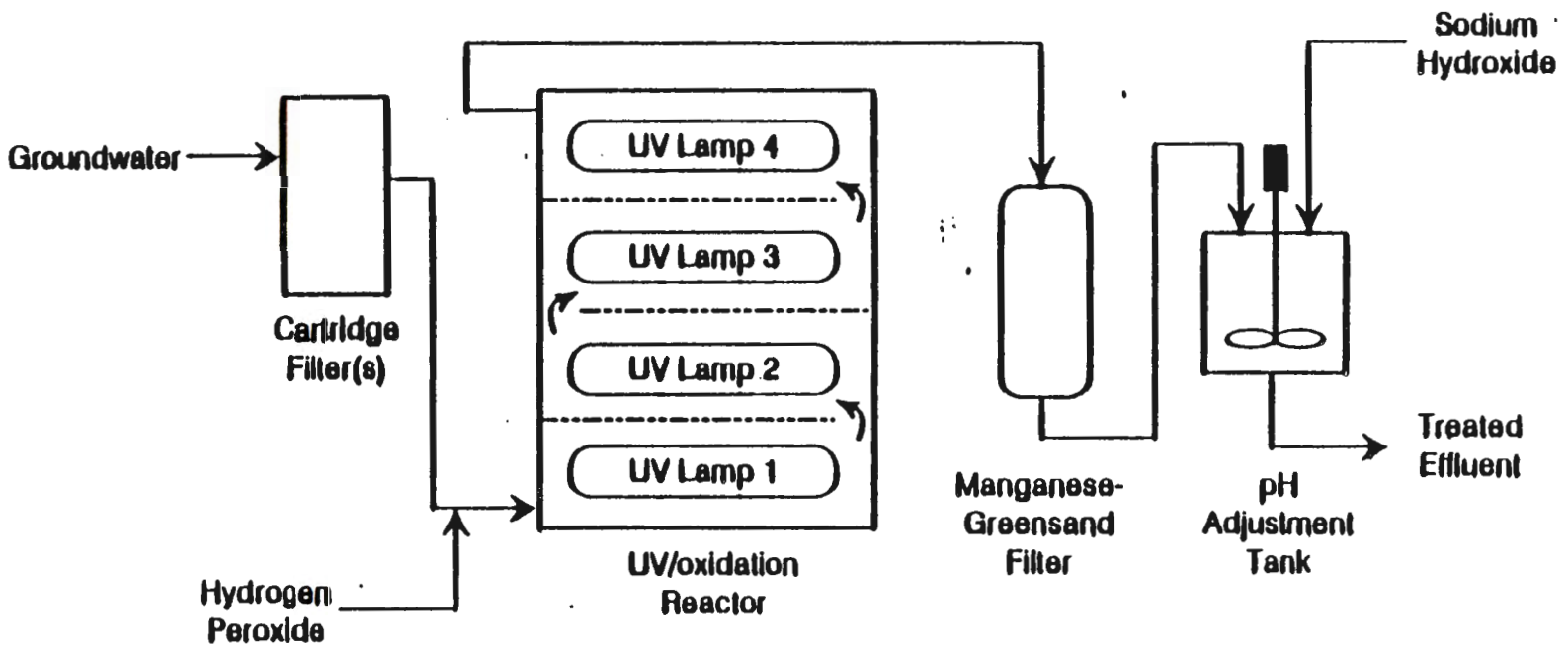

Figure 5. Schematic of PSI UV/oxidation system.

Table 1. Maintenance Requirements for UV/oxidation Systems

COMPONENT	MAINTENANCE	COMMENTS
1. UV Lamp Assembly	Clean the UV lamps periodically (once every month to once every 3 months) using dilute acid (for example, acetic acid) wash, mechanical wipers, or ultrasonic equipment.	Frequency of cleaning varies depending on the type of suspended solids present in the influent or formed during treatment (for example, precipitation of iron and manganese). This can be minimized by providing proper pretreatment.
	Replace the UV lamps as necessary (due to lamp failure or significant reduction in UV radiation output with time).	Low pressure mercury vapor UV lamps are rated to last 7,500 hours and xenon UV lamps are rated to last about 500 hours, based on a use cycle of 8 hours. Some manufacturers recycle most of the lamp construction materials to minimize waste disposal.
2. Ozonation System		
(a) Air Preparation System	Replace the air filter at least once every 3 months.	Replacement frequency may vary based on air purity and flow rate.
	Check the air compressor, as recommended by the manufacturer, once every month to minimize feed air contamination by the compressor parts.	None.
	Inspect cooling water lines annually for scaling and deterioration. If a water chiller is used, inspect refrigerant dryer at least once every 3 months.	Tap water (potable water, suitable process water, or treated water) may be used as a cooling water source.
	Inspect desiccant dryer weekly to ensure proper operation. Disassemble the unit and inspect the desiccant annually, as recommended by the manufacturer, to prevent fire accidents. Replace the media once every 10 years.	Heatless absorption dryers may be used to prevent fire accidents. The media may have to be replaced sooner if the dryer has been overloaded or poorly maintained.
(b) Ozone Generator	Clean the dielectric tubes one year after startup and determine the future cleaning frequency at the end of first year depending on the condition of the tubes.	Trained personnel should perform the cleaning to minimize breakage or damage to the tubes. Proper maintenance of the tubes helps lower electrical energy costs.

Table 1. Maintenance Requirements for UV/oxidation Systems
(Continued)

COMPONENT	MAINTENANCE	COMMENTS
2. Ozonation System (continued) (c) Ozone Contacting Equipment	Check pipings, valves, fittings, supports, brackets, and ozone gas spargers at least once every 3 months for deterioration resulting from a highly oxidizing environment.	Check spargers for plugging due to solids accumulation if a change in gas bubble diffusion pattern is noted. Clean the spargers to minimize cracking of joints and excessive electrical power costs.
3. Ozone Decomposer	Check the unit's temperature once a day for proper operation. Maintain the ozone decomposer as recommended by the manufacturer.	Ozone decomposer normally contains heating elements and a catalyst. The decomposer must be operated at the proper temperature to destroy ozone present in the reactor off-gas.
4. Miscellaneous	Check miscellaneous components of the treatment system, such as valves, flow meters, pipelines, and wastewater and chemical feed tanks (for example hydrogen peroxide and acid) once a week for leaks. Also check pumps and any other components once a week for proper operation.	None.

Table 2. Extent of VOC Stripping in Ultrox System

Run No.	Air Flow Rate ÷ Water Flow Rate	Percent Stripping Contributions			
		1,1-DCA 0.00043 *	TCE 0.0091 *	1,1,1-TCA 0.014 *	Vinyl Chloride 0.082 *
1	2.1	7.4	2.0	43	0.01
2	2.3	9.1	3.4	34	0.95
3	2.1	9.9	2.7	31	0.01
4	2.0	7.4	3.0	29	0.01
5	2.1	17.0	3.5	29	1.7
6	4.5	16.0	1.2	65	0.07
7	1.0	4.9	1.2	12	3.1
8	4.5	23.0	7.5	85	1.2
9	4.5	16.0	6.6	58	0.04
10	4.3	27.0	9.4	73	1.1
11	4.6	44.0	24.0	>99	13.0
12	4.4	34.0	7.0	76	8.9
13	4.3	37.0	26.0	75	1.8

* Henry's law constant of the VOC, atm-m³/mol.

Table 3. Performance Data for the PSI System at the Optimum Operating Conditions (Test 3)

Compound	Influent µg/L	Effluent µg/L	Percent Removal
Chloroform	41	1.2	97
1,2-DCA	22	<1.6	>92
1,2-DCE	195	<1.6	>99
Methylene Chloride	8	<1.1	>86
TCE	21	<1.4	>93
Benzene	52	<2.0	>96
Thiodiglycol	477	<10.0	>97
1,4-Dithiane	200	<2.2	>98
1,4-Oxathiane	82	<2.14	>97
Benzathiazole	20	<3.47	>82
1,3,5-Trinitrobenzene	15	0.53	96

Enclosure 10

9 3 1 2 9 0 1 2 0 0 2

RAYOX®

Second Generation Enhanced Oxidation Process for the Destruction of Waterborne Contaminants

APPLICATION OF RAYOX FOR THE REMEDIATION OF CONTAMINATED GROUNDWATER

INTRODUCTION

Until recently, the remediation of groundwater contaminated with chlorinated organic compounds, (e.g. TCE, TCA, PCB, $CHCl_3$, PCP, etc.), or petroleum derived hydrocarbons (e.g. benzene, ethyl benzene, toluene, xylene or BETX) has, in large measure, been undertaken using either air stripping or activated carbon or a combination of both technologies.

Recent regulatory developments such as the San Francisco Bay Area Air Quality Regulations and the RCRA Land Bans have resulted in a greater interest in enhanced ("advanced") oxidation processes which carry no secondary pollution or disposal requirements.

This paper describes enhanced oxidation processes (EOP) generally and some of the features which account for the superior performance of second generation systems like **Rayox**. It concludes with a discussion of results obtained in the remediation of a number of actual contaminated groundwaters.

THE ENHANCED ("ADVANCED") OXIDATION PROCESS

In the mid-seventies, a number of reports appeared describing the greatly enhanced rate of oxidation that was obtained when contaminated water with either dissolved O_3 or H_2O_2 was irradiated with ultraviolet (UV) light. One of the first reports was given by Prengle and co-workers *(1)*. The principles of this synergy are now understood and agreed upon in broad terms by researchers in this field. Recent discussions of the topic are given by Peyton *(2)*, Dore *(3)* and Hoigne et al *(4)*.

The results of these and other investigations have shown that the greatly increased rate of oxidation of waterborne contaminants obtained with an EOP was the result of the participation of powerful oxidizing radical agents such as the hydroxyl radical (HO•) and the perhydroxyl radical (HO_2•).

REACTION RATES OF OZONE AND HYDROXYL RADICALS WITH CLASSES OF ORGANIC COMPOUNDS (5)

COMPOUND	k, in L mole^{-1} s^{-1} O_3	OH
Olefins	1 to 450 x 10^3	10^9 to 10^{11}
S-containing organics	10 to 1.6 x 10^3	10^9 to 10^{10}
Phenols	10^3	10^9
N-containing organics	10 to 10^2	10^8 to 10^{10}
Aromatics	1 to 10^2	10^8 to 10^{10}
Acetylenes	50	10^8 to 10^9
Aldehydes	10	10^9
Ketones	1	10^9 to 10^{10}
Alcohols	10^{-2} to 1	10^8 to 10^9
Alkanes	10^{-2}	10^6 to 10^9
Carboxylic acids	10^{-3} to 10^{-2}	10^7 to 10^9

Table 1

SOLARCHEM ENVIRONMENTAL SYSTEMS

40 West Wilmot St., Unit 5
Richmond Hill, Ontario
Canada L4B 1H8
Telephone: (416) 764-9666
Fax: (416) 764-9669

16496 Bernardo Centre Drive, Suite 203
San Diego, California 92128
U.S.A.
Telephone: (619) 673-0285
Fax: (619) 485-9716

POSTULATED DESTRUCTION MECHANISM FOR CHLOROFORM (6)

$$CHCL_3 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}CCL_3 \xrightarrow{O_2} CCL_3O_2{}^{\bullet} \xrightarrow{AH^-} CCL_3O_2{}^-$$

$$\downarrow H_2O_2 \qquad\qquad \downarrow H_2O$$

$$HCL + {}^{\bullet}OH + [COCL_2] \qquad [COCL_2]$$

$$\downarrow H_2O \qquad\qquad \downarrow H_2O$$

$$HCL + CO_2 \qquad\qquad HCL + CO_2$$

Figure 1

These radicals, once formed, aggressively attack a waterborne contaminant and initiate a typically rapid, oxidative cascade of reactions, which, in the case of a hydrocarbon or an oxygenated hydrocarbon, results ultimately in CO_2 and H_2O. If the contaminant is a chlorinated organic compound, the mineralization process will also result in the formation of chloride (Cl^-) ions.

An appreciation of the reason for the increased rate of decontamination obtainable by enhanced oxidation can be obtained by reviewing the data in Table 1, which lists the rate constant, k, for the reaction of O_3 and HO• with a number of different classes of organic compounds. These data show that the rate constant for HO• attack on organic compounds is typically a million (10^6) to a billion (10^9) times faster than molecular ozone.

Mechanism of Mineralization

There have been a number of investigations into the details of the chemistry involved in the enhanced oxidation process. The detailed, step by step chemical processes involved in the mineralization (i.e. conversion to CO_2, H_2O and Cl^-) of a contaminant depends upon of a number of factors such as the presence and concentration of other organic and inorganic species and the pH. Thus, the degradation pathway to CO_2, H_2O and Cl^- followed by a given contaminant can vary from stream to stream, depending upon the prevailing conditions in each stream. However, the mechanism typically involves several steps and intermediate species, even for relatively simple systems such those containing a single, low molecular weight contaminant. The reaction mechanism proposed in a recent paper by Getoff *(6)* for the mineralization of chloroform is presented in Figure (1).

From this representation one can see that even in the relatively simple situation where the contaminant molecule contains only one carbon, there are several steps involved in mineralization.

Intermediates or By Products

Since the mineralization process is multistep involving intermediates, the question of converting one contaminant into another (and potentially more undesirable) contaminant sometimes arises, particularly in first generation EOP systems.

Fortunately, this is not a problem with second generation EOP Systems . Although intermediates (including non radical ones) can and are produced, they are, under the conditions prevailing in an enhanced oxidation reactor, thermodynamically unstable with respect to CO_2 and H_2O. In other words the difference in free energy, ΔG, between any possible intermediate and CO_2, H_2O (and Cl-), is always negative.

Expressed in Equation form:

$$\text{Intermediate(s)} \xrightarrow{HO\bullet/O_2/H_2O} CO_2, H_2O, Cl^- \quad \Delta G \text{ is -ve}$$

This, of course, means that given adequate contact time, <u>any and all</u> intermediates will themselves be converted to CO_2, H_2O (and Cl^- if chlorine was present in the original contaminant) The question then arises as to what are the typical lifetimes of the

intermediate species produced under the prevailing conditions found in a second generation enhanced oxidation system like Rayox.

Typically the lifetimes of many of the intermediates involved in an enhanced oxidation process would be very short, generally less than a millisecond (10^{-3}s). This is particularly true of the radical species, many of which would have a lifetime less than a microsecond (10^{-6}s)

The lifetime of any non-radical by-products or intermediates would be a function of the concentration of the various oxidizing species in solution (e.g. HO•, HO_2•, O_3 etc.) and the rate constant for the reaction between the oxidant and the compound in question. Mathematically this can be expressed as :

$$\tau_x = k_x^{-1} = (\Sigma k_i[R_i])^{-1}$$

where:
τ_x = lifetime of contaminant x

kx= pseudo first order rate constant for the decay of x

k_i = rate constant for the reaction between X and radical oxidizing species Ri

[R] = concentration of the radical oxidizing species present (e.g. HO•)

For example, even if the by product was relatively refractory such as a carboxylic acid (e.g. formic acid) then

$$\tau = \left[10^8 \frac{L}{mole.s} \times 10^{-9} \frac{moles}{L}\right]^{-1} = 10s$$

where the following assumptions have been made:

- $k_i = 10^7 \frac{L}{mole \cdot s}$ (from Table 1)
- [HO•] = steady state concentration of the hydroxyl radical $= (10^{-9} \frac{moles}{L})$
- that the HO• radical is the only oxidant reacting with the carboxylic acid in question

In the above example, the concentration of the carboxylic acid would decrease by a factor of (1/e) (~0.37) every lifetime, or every 10 seconds. If the byproduct reacted more quickly (i.e. had a larger rate constant,k) with the oxidants in solution, or the concentration of the oxidizing species were higher, then the lifetime of the intermediate would be further reduced.

From the foregoing discussion, it can be seen that the concentration of any intermediates or by-products that might be formed as a result of the HO• attack on the original compound, can be reduced to whatever levels desired by simply ensuring that the contact or residence time is sufficiently long to achieve the target discharge criteria What is usually observed in practice, however, given the highly reactive nature of the radical oxidizing species generated in the enhanced oxidation process, is that the contact times needed to reduce the concentration of the initial contaminants to target discharge values, also results in a satisfactorily complete destruction of any intermediates or by-products.

As a result of this near complete mineralization ("destruction") of any waterborne organic contaminants, the use of enhanced oxidation for groundwater remediation means that there is virtually never a secondary or downstream disposal or handling problem.

Rayox - A Second Generation Enhanced Oxidation Process

Although enhanced oxidation has been found to be a highly effective method of remediating a broad range of contaminated groundwaters, earlier embodiments of the technology have had limited success in cost effectively destroying several of the more refractory waterborne contaminants such as CCl_4, $CHCl_3$, TCA, DCA, fixed cyanides, Freon, etc.

The reason for this relatively limited success is rooted in the fact that the rate constant for HO• attack of these compounds is relatively small. Examples of some more refractory compounds are given in Table 2.

REACTION RATE CONSTANTS OF HYDROXYL RADICALS WITH SELECTED REFRACTORY COMPOUNDS

Compound	k (L mole^{-1}s^{-1})
CCl_4	1.5×10^6
$CHCl_3$	8.8×10^6
TCA	7×10^6
DCA	1.6×10^8
Freon 113	~6×10^5

Table 2

From Table 2 it can be seen that "k" for the reaction of HO• with TCA is ~10^7L mole^{-1}s^{-1} which is approximately 10^{-2} that for TCE. Thus, all other things being equal, it would take 100 times the contact time to achieve the same level of TCA destruction vs. that needed for TCE.

This likely explains, in large measure, why first generation enhanced oxidation systems have had limited success in achieving satisfactory rates of destruction of these more refractory compounds *(7)* i.e. these systems rely almost exclusively on radical (OH•) driven destruction. With Rayox, however the contact times required to treat refractories like TCA are typically only 3-5 times that needed for TCE.

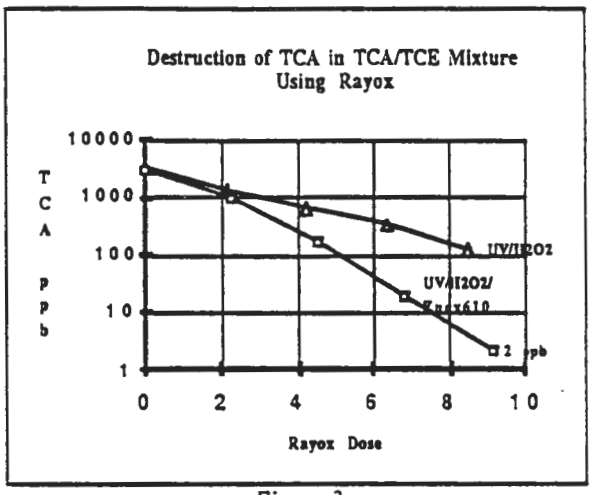

Figure 3

Destruction of Refractory Compounds with Rayox

To illustrate the powerful decontamination capability of Rayox, some typical results for the destruction of several refractory contaminants are given below:

Figure (2) shows the results for the reduction of the chloroform from about 30 ppm to less than 0.1 ppm.

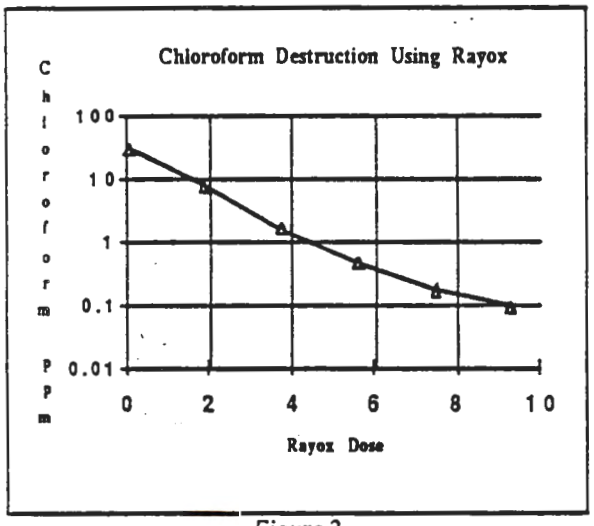

Figure 2

Figure (3) gives some results for the reduction of the TCA concentration from about 2000 ppb to less than 5 ppb.

Figure (4) presents results showing the reduction of Freon from about 100 ppb to less than 10 ppb.

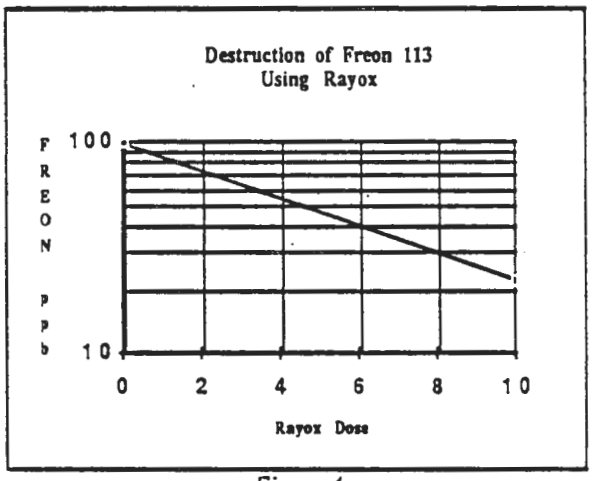

Figure 4

For each of the above examples, even lower discharge criteria could easily be achieved by simply increasing the Rayox dose.

Rayox Dose

The term "dose" is defined as the summation of remediating inputs into the contaminated water such as: the amount of light, peroxide, or proprietary additives per unit volume of water treated. This dose is proportional to cost, however, it should be noted that the results given in the above figures have not been standardized to the same basis, so that a unit of Rayox dose in a given figure is not necessarily equal to a dose unit in another figure. This is because the cost of the different inputs (photons, peroxide,

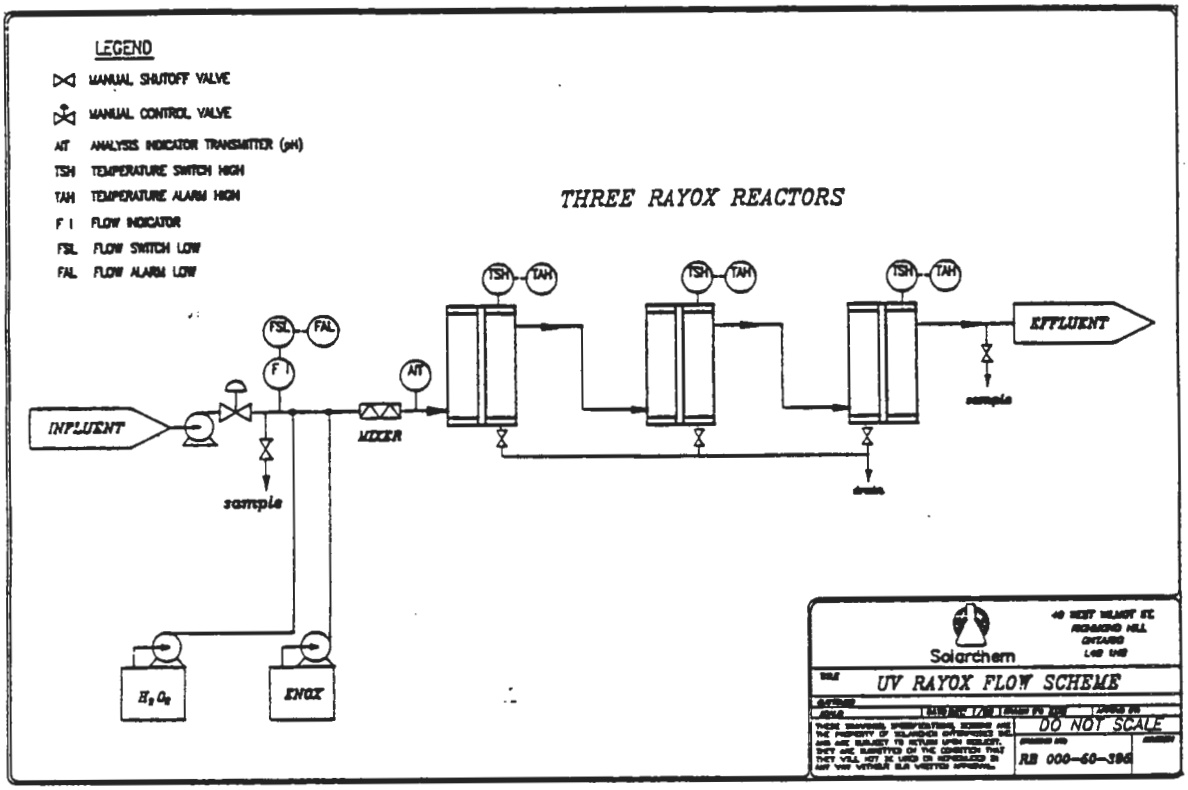

Figure 5

additives) is different and the optimum configuration of inputs varies from one type of contaminated stream to the other.

What the above results do unequivocally demonstrate is that Rayox can destroy even the most refractory waterborne contaminants and can achieve virtually any discharge criteria that might be set.

Reasons for Rayox's Superior Performance

- A System Design that allows for Variable, Multi-stage Treatment.
- A Unique Reactor Design Which Enhances Mass and Radiation Transfer.
- The Proprietary Solarchem Lamps, and
- The ENOX Additives.

Figure (5) shows that , the basic Rayox water decontamination system typically consists of a series of annular reactor(s) complete with a lamp, a quartz sleeve to protect the lamp, a transmittance controller to keep the quartz sleeve clean, a variable length annulus for water flow, and a stainless steel outer wall. This design facilitates variable, multistep treatment and efficient mass and radiation transfer. The important bearing reactor design has on performance can be seen from the results shown in Figure 6A. From actual treatment results, the dioxane concentration remaining after a dose of three in reactor B is roughly one half that remaining in reactor A. Since dose is proportional to cost, it can be seen that the operational costs involved with achieving the discharge concentration obtained with 3 dose units ~0.2 ppm with reactor B would be approximately 33% more with reactor A (i.e. 4 dose units with A vs 3 units with B)

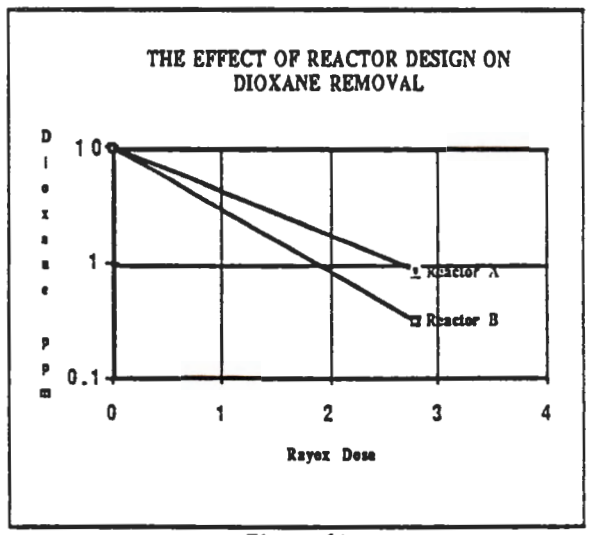

Figure 6A

The Solarchem lamps are high intensity UV light sources which have particularly strong output in the photo-active absorption bands of most waterborne contaminants. Powers 100-200 times those obtainable with low pressure mercury arcs, typical of first generation enhanced oxidation systems, are attainable with the Solarchem Lamps.

This substantial enhancement in effective power with the Solarchem lamps translates into smaller, simpler **Rayox** systems for a given throughput capacity. This, of course, becomes critically important for larger throughputs, e.g. > 100 gpm, or for more refractory contaminants such as TCA which require higher UV dosages.

The importance of the choice of UV lamp can be seen by reviewing the results given in Figure (6B). In this figure, results are shown for the destruction of waterborne dioxane as a function of dose using two different Solarchem lamps. These data show that the cost of achieving a discharge concentration of 1-ppm with lamp B would be roughly 50% that for lamp A with this particular compound.

Generally then, it is important to achieve a judicious match between the lamp emission spectrum and the photo-active absorption bands of the target contaminant(s), as this can create a significant new contaminant destruction channel i.e. photolysis or photodecomposition of the contaminant.

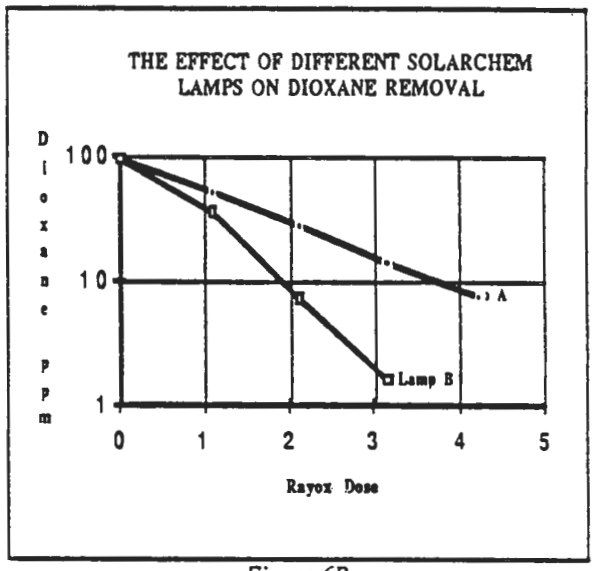

Figure 6B

A step by step reaction mechanism for the photo initiated destruction of waterborne CHC_3 is given in Figure (7). As with HO• attack on $CHCl_3$, photolysis results in the formation of a radical species ($\cdot CHCl_2$) which is transformed via a multistep process into CO_2, H_2O and Cl^-.

POSTULATED PHOTOCHEMICAL DEGRADTION MECHANISM OF CHLOROFORM(6)

$$CHCL_3 \xrightarrow{hu} {}^{\bullet}CL + {}^{\bullet}CHCL_2 \xrightarrow{O_2} CL_2CHO_2^{\bullet} \xrightarrow{AH^-} CL_2CHO_2^-$$

$$\downarrow H_2O/O_2 \qquad\qquad \downarrow H_2O$$

$$HCL + HCOOH \qquad\qquad CLCHO + HCL + {}^{\bullet}OH$$

$$\downarrow {}^{\bullet}OH/O_2 \qquad\qquad \downarrow H_2O_2$$

$$CO_2 + H_2O \xleftarrow{{}^{\bullet}OH/O2} HCOOH$$

Figure 7

The final factor contributing to **Rayox**'s superior performance is the use of Solarchem's proprietary ENOX additives. These additives enhance the rate of contaminant destruction by enhancing the rate of radical formation or the efficiency of radical utilization.

The extraordinary enhancement in decontamination efficiency obtained by using ENOX can be seen from

the data in Figure (8), wherein the concentration of benzene in water is plotted on a function of Rayox dose. From Figure (8), it can be seen that the use of ENOX 510 results in a cost one quarter (1/4) of that required for UV/peroxide alone to achieve a final benzene concentration of 1 ppb from an initial value of about 9000 ppb.

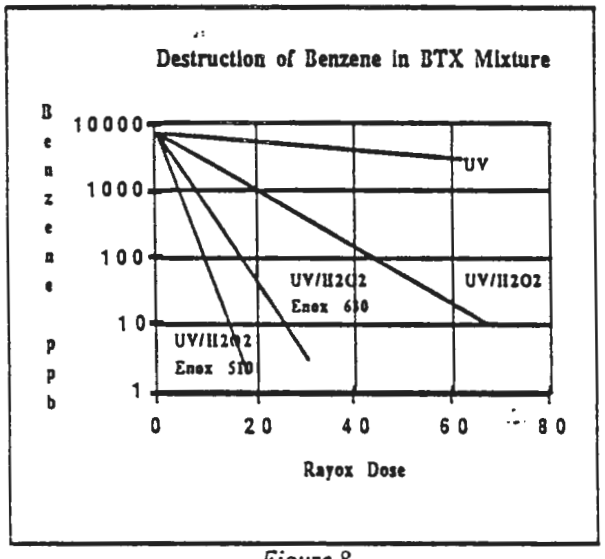

Figure 8

Groundwater Remediation Using Rayox

Figure (9) shows a typical transportable Rayox unit. This unit is capable of processing up to 30 gpm with the actual treatment capacity being dependent on factors such as influent contaminant concentrations, alkalinity, discharge criteria, etc. In most of the customer situations described below, a unit similar to this was used to develop the preferred treatment approach and final system design.

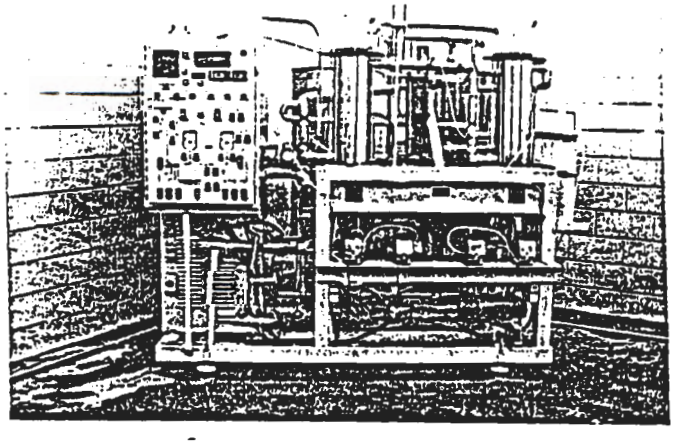

Figure 9

The chemical analysis in the work cited below were usually performed by either the customer's in house laboratory or by an independent, external laboratory hired by the customer. The analytical methodologies used were typically GC or GC/MS based with work up and operating conditions tailored to the analysis being undertaken.

1,4 Dioxane

Dioxane is an excellent, water miscible organic solvent, with a wide range of industrial applications. Unfortunately past process wastewater management practices i.e. lagoons have resulted in the contamination of some groundwater aquifers. For example, a Michigan manufacturer inadvertently contaminated an aquifer beneath one of its facilities with up to 130 ppm of dioxane.

The results shown in Figure (10) demonstrate that discharge concentrations of <2 ppb (99.999+% destruction) are readily achievable with Rayox.

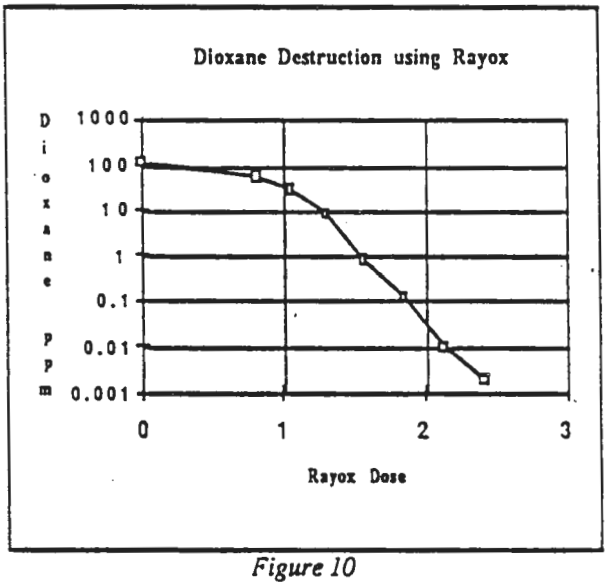

Figure 10

PCBs

Inadequate waste handling practices have resulted in the contamination of soil as well as the aquifers under a major PCB storage facility in Smithville, Ontario. The Ontario Ministry of the Environment wanted to achieve if a discharge concentration of less than 20 ppt (method detection limit). The treatment results shown in Figure (11) demonstrate that the <20 ppt target was readily attained.

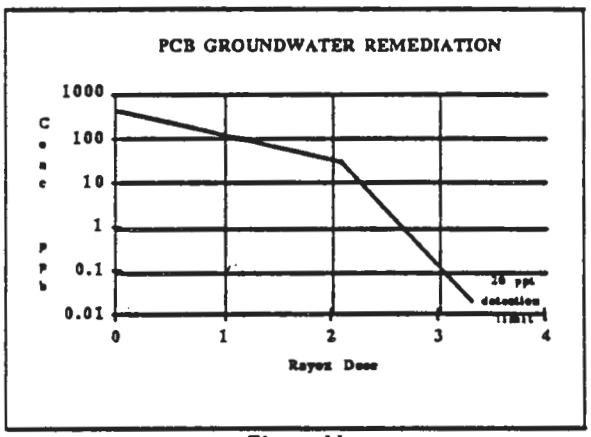

Figure 11

Benzene

The groundwater under a New Brunswick Department of Transport fueling station in New Brunswick had become contaminated over the years with BETX. As can be seen from the data in Figure (12), benzene was reduced from about 80 ppm to 1 ppb. As benzene is the most refractory of the BETX fraction, the other contaminants (ETX) were reduced to even lower concentrations.

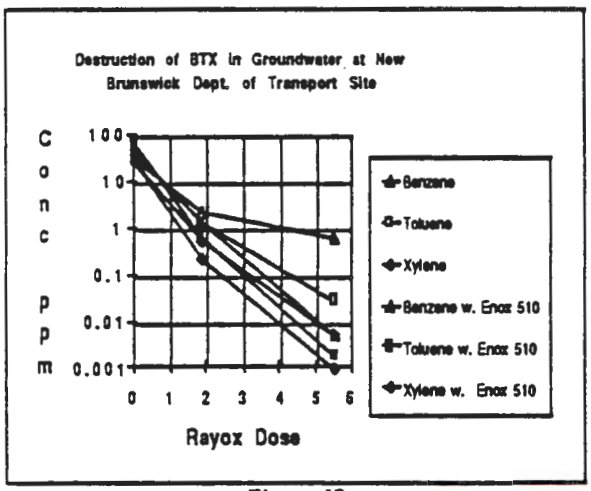

Figure 12

Another point worth noting was that no ozone was used, so there was no off gas with stripped BETX to treat. In some first generation enhanced oxidation systems, O_3 is used as a HO• source, with the result that a significant quantity of any volatile contaminant will be air stripped due to the large gas-liquid ratio involved with such systems.

Trichloroethane (TCA)

In Figure (13), results are shown for the destruction of TCA in contaminated groundwater at a site in Sunnyvale, California. The contaminated groundwater also contains other chlorinated paraffins and olefins but the customer and their consultant were especially interested in **Rayox's** ability to decontaminate groundwater containing TCA at a concentration of a few ppm. Although TCA is refractory, the results shown in Figure (13) clearly demonstrate **Rayox's** ability to destroy waterborne TCA and achieve the design discharge criteria of less than 5 ppb.

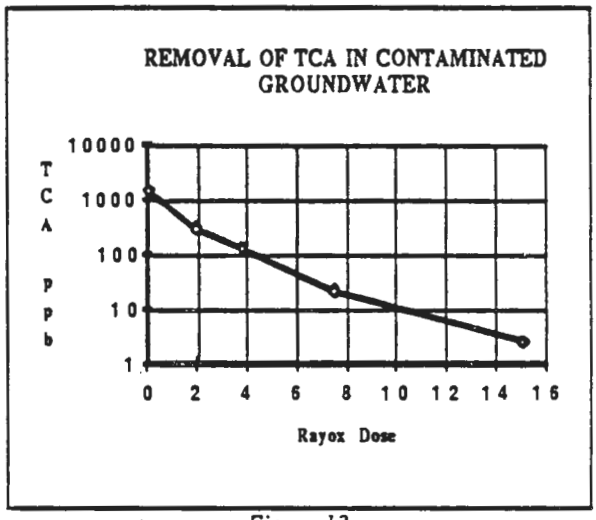

Figure 13

Pentachlorophenol (PCP)

A major Canadian wood treating firm has PCP contaminated groundwater at one of its plants in New Brunswick, Canada. The concentration of the PCP in the groundwater is about 5 ppm and the discharge criteria was set at less than 10 ppb. The results shown in Figure (14) prove that this target was easily achieved.

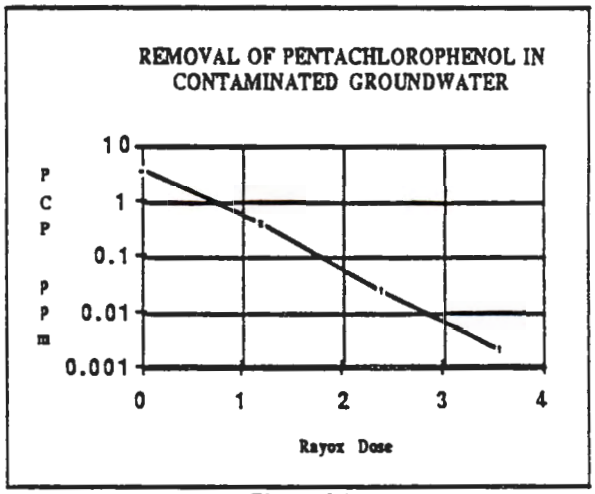

Figure 14

After processing by **Rayox**, the treated groundwater can be directly discharged to a nearby river. Even more stringent discharge criteria could easily be met by simply increasing the **Rayox** dose applied to the contaminated groundwater.

A noteworthy benefit of using **Rayox** to decontaminate groundwater containing PCP, is that there is no secondary disposal or handling problem to deal with as a result of this treatment. This, of course, is especially important for contaminants like PCP which often contain small amounts of dioxins or furans and represent a serious disposal problem if sorbed onto carbon. Also regeneration of PCP laden carbon is becoming increasingly difficult. Thus, the use of a destruction technology like **Rayox** offers considerable advantages for the remediation of PCP contaminated groundwater.

A number of other examples could be cited where **Rayox** is becoming the treatment system of choice for on site remediation of groundwater. The data presented here are meant to be only illustrative of the breadth of application and the powerful remediation capacity of the **Rayox** technology.

With its significant performance advantages over earlier enhanced oxidation equipment, and over traditional non-destruction techniques, it is suggested that those with a contaminated groundwater problem consider its many benefits which include:

- Virtual zero discharge attainable at reasonable cost
  99.999+% contaminant destruction
- No secondary disposal problems
  "in stream" contaminant destruction
- De-toxifies toxic effluent streams
  Rayox-treated output passes biological toxicity tests & HPLC/GC toxicity scans
- Broad spectrum applicability
  virtually all organic compounds including refractories such as CCl_4, TCA, $CHCl_3$ DCA, etc. as well as fixed cyanides, hydrazines and nitrosamines
- Highly automated system
  requires essentially no operator time
- Very versatile system
  capacity can readily be turned up or down

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Enclosure 11

9 3 1 2 9 0 1 2 0 1 2

TREATMENT OF DISSOLVED ORGANICS WITH UV/HYDROGEN PEROXIDE

By

Frederick E. Bernardin, Jr.
Peroxidation Systems, Inc.

Presented at

NWWA
FOCUS CONFERENCE ON EASTERN REGIONAL GROUND WATER ISSUES

Kitchener, Ontario, Canada

October 17-19, 1989

Organic chemicals are a very diverse group of chemicals and vary widely in structure, content, size and occurrance. The properties of organic molecules which are contaminating our groundwater resources and relate to both their presence and our ability to remove them from the water include:

- Solubility
- Toxicity
- Volatility (vapor pressure)
- Biodegradability

Solubility is important since highly soluble materials will disperse more rapidly through the subsurface water. Highly soluble organic materials are likewise more difficult to treat since their solubility makes them resistant to processes such as air stripping, steam stripping and carbon adsorption. Examples of such organics include alcohols, low molecular weight ketones and glycols. Toxicity obviously dictates the urgency to which treatment is necessary and the degree of treatment required. While some organics such as benzene, TCE and dioxin may signal immediate and low ppb treatment levels others such as alcohols, acetone and TCA may require less stringent reactions.

Volatility or vapor pressure of an organic species will usually result in lower solubility and a greater degree of transfer into the Vadose zone above the contaminated water. A volatile material also lends itself to stripping operations

such as air or steam although subsequent recovery and ultimate treatment will be necessary.

Biodegradability generally, although not necessarilly, relates to the less toxic materials. Biological organisms can adapt themselves to utilize many different organic materials in their metabolism and so can be employed for clean up of subsurface contamination. This approach may allow less than total removal of contamination by artificial means and reliance on the natural biological process for final cleanup of small residuals. The biological process even with enhancements is a relatively slow process, however.

Treatment Processes

Organic removal treatment processes are based on forementioned priniciples and each process has strong points and shortcomings related to its application and the properties of the organic material. Most of the processes, however involve phase separation, i.e., removal of the contaminant from the water without changing the properties of the molecule itself. These type processes include air stripping, steam stripping, vacuum extraction, carbon adsorption and others. The notable but limited exception is

biological treatment which changes the organic but may produce relatively large quantities of sludge for disposal. (This would not occur with insitu treatment but this process will be slow and can potentially plug the aquifer)

What I will present here is a new and innovative approach to treatment of dissolved organic materials in water--photochemical ultraviolet light catalyzed oxidation utilizing hydrogen peroxide (the UV-Peroxidation Process). One of the unique aspects of this process is the fact that it has a wider application across the organic spectrum and is less limited than other processes.

The UV-Peroxidation Process

The use of chemical oxidizing agents for organic oxidation is not a new process. Various oxidants such as potassium permanganate, chlorine, chlorine dioxide, ozone and hydrogen peroxide have been employed. What is new about the process I will describe -- the perox-pureTM Process * -- is the use of very high energy ultraviolet lamps to produce hydroxyl radicals, a very powerful oxidizing agent, from the very safe and easy to handle hydrogen peroxide.

Ultraviolet light catalyzes the chemical oxidation of organic contaminants in water by its combined effect upon the organic

contaminant and its reaction with hydrogen peroxide. Many organic contaminants absorb UV light and may undergo a change in their chemical structure or simply become more reactive to chemical oxidants.

More importantly, UV light, at less than 400nm wave length, reacts with hydrogen peroxide molecules to form hydroxyl radicals. These very powerful chemical oxidants then react with the organic contaminants in the water. If carried to completion, the end products of hydrocarbon

* Peroxidation Systems Inc., Tucson, Arizona

oxidation with the UV/Peroxidation Process are carbon dioxide and water.

The reaction of formic acid with UV catalyzed hydrogen peroxide illustrates this photochemical oxidation process:

$$H_2O_2 \xrightarrow[(<400nm)]{UV} 2\ OH^{\bullet}$$

$$HCOOH + OH^{\bullet} \longrightarrow H_2O + HCOO^{\bullet}$$

$$HCOO^{\bullet} + OH^{\bullet} \longrightarrow H_2O + CO_2$$

In the case of oxidation of chlorinated organics, dissolved chloride will also be a reaction product.

The oxidation potentials for common oxidants are listed in Table 1. As shown, the hydroxyl radical is second only to fluorine in oxidative power.

TABLE 1

OXIDATION POTENTIAL OF OXIDANTS

RELATIVE OXIDATION POWER (CLEL01)	SPECIES	OXIDATIVE POTENTIAL (VOLTS)
2.23	Fluorine	3.03
2.06	Hydroxyl Radical	2.80
1.78	Atomic Oxygen (singlet)	2.42
1.52	Ozone	2.07
1.31	Hydrogen Peroxide	1.78
1.25	Perhydroxyl Radical	1.70
1.24	Permanganate	1.68
1.17	Hypochlorous Acid	1.59
1.15	Chlorine Dioxide	1.57
1.10	Hypochlorous Acid	1.49
1.07	Hypoiodous Acid	1.45
1.00	Chlorine	1.36
0.80	Bromine	1.09
0.39	Iodine	0.54

Ozone (O3) also forms hydroxyl radicals under UV light catalysis. However, H2O2 is a more cost/effective reactant as each molecule of hydrogen peroxide forms two hydroxyl radicals. Furthermore, the other common oxidants either contain halogens or metals which may cause undesirable by-products if the oxidation reaction is incomplete. In

addition, there are other properties of H_2O_2 which make it inherently safer, easier to apply and more environmently acceptable than alternate oxidants. These advantages of H_2O_2 as a preferred reactant are summarized in Table 2.

TABLE 2

HYDROGEN PEROXIDE ADVANTAGES AS A CHEMICAL OXIDANT

- A safe, readily available chemical
- No toxic fumes or gases
- Easily stored and pumped
- Infinite solubility in water
  - No mass transfer problems associated with gases
  - Unlimited dosing capability
- Contains no halogens or metals
- Degradation products are O_2 and H_2O
- The most cost effective source of hydroxl radicals

Like most other chemical oxidations, the UV/Peroxidation process is dependent upon a number of reaction conditions which can affect both performance and cost. Some process variables are inherent to the properties of the contaminated water while other process variables can be controlled by the treatment system design and operation. Some of the more important process variables are summarized in Table 3.

TABLE 3

UV/PEROXIDATION PROCESS VARIABLES

- Variables related to the contaminated wataer:
  - type and concentration of organic contaminant
  - light transmittance of the water (color/suspended solids)
  - type and concentration of dissolved solids
- Variables related to treatment process design and operation:
  - UV and H2O2 dosages
  - pH and temperature conditions
  - use of catalysts

PROCESS PERFORMANCE

Over the past 5 years the UV/Peroxidation process has been applied to over 100 individual waters and wastewaters. I will present here some data showing the process alone and also in comparison to other technologies.

Tables 4 through 8 present data from field operated perox-pureTM systems while Table 9 data were generated on bench-scale equipment. The system in Table 4 is operating with 2 minutes contact time on a water pretreated by air stripping. The data show essentially 100% removal of the volatile organic contaminants with the exception of 1,1,1-trichloroethane (TCA). In most cases allowable effluent levels of TCA are much higher than other chlorinated

solvents. For example, the State of California drinking water action levels are 5 ppb for TCE and 200 ppb for TCA.

TABLE 4

Contaminant ug/L	INF	EFF
1.1 - DCA	4.5	BDL
1.2 - DCE	162	BDL
1,1,1 -TCA	105	74
TCE	68	BDL
PCE	272	BDL

Contact time: 2.0 min.

H2O2: 40 mg/L

Table 5 shows treatment of a more contaminated water and also shows the effect of increasing oxidation time within a very narrow range (1.0 to 1.6 minutes). In this case it is evident that there is a very rapid rate of destruction of the initial concentration of contaminant (up to 99.8%) in one minute with slower destruction thereafter.

TABLE 5

Contaminant ug/L	INF	Effluent 1.0 min.	Effluent 1.6 min.
Vinyl chloride	198	ND	ND
1,1 - DCA	184	43.9	31.2
1,2 - DCE	1834	15.9	6.9
1,1,1 - TCA	101.6	75.7	85.7
TCE	5622	27.2	23.9
Tolulene	651	1.2	ND

H_2O_2: 80 mg/L

Table 6 shows that the UV/Peroxidation process can be very effective in achieving complete or non-detectable levels of three fairly common contaminants, vinyl chloride, 1,2 - DCE and TCE. It is important to note that utilizing the perox-pureTM approach very low effluent levels can be achieved more simply and economically than by other processes since the process is not as concentration limited.

TABLE 6

Contaminant ug/L	INF	EFF
Vinyl chloride	14	ND
1,2 - DCE	101	<1
TCE	7.8	ND

Contact time: 3.2 min.

H_2O_2: 50 mg/L

Table 7 shows treatment of a water principally contaminated with hydrazine with other trace organics present. While it is notable that all treatment objectives were met it is also interesting to note that the total organic carbon (TOC) content of the water was also reduced over 93% indicating that most of the organics have been converted to CO_2.

TABLE 7

Contaminant ug/L	INF	EFF
Hydrazine	180,000	<10
Acetone	41	BDL
Phenol	14	BDL
Aniline	730	BDL
Bis, 2-ethyl hexyl phthalate	170	BDL
TOC	31,000	2,000

Oxidation time: 18 min.
H_2O_2:

Table 8 is comparison data on a site which operated both a granular activated carbon (GAC) and a UV/Peroxidation system. The principal difference in the operation was that while the GAC system was operated on a 200 gpm production well, the UV/Peroxidation system operated on a monitoring well with nearly 6 times higher concentration. Twelve months of operating data showed the UV/Peroxidation system capable of producing a significantly better effluent a cost one-third to one-half that of GAC.

TABLE 8

Contaminant	GAC 1. INF	GAC 1. EFF	UV/H2O2 2. INF	UV/H2O2 2. EFF
TCE	756	3.8	4016	<1

1. GAC usage 1.2 lbs./1000 gal., Contact time 50 min.
2. H2O2 usage 50 mg/L Oxidation time <1 min.

Table 9 presents an interesting demonstration of three technologies compared on the same water. In all cases the air stripping, GAC and UV/Peroxidation were applied to stringent, not necessarilly economical levels in order to determine the maximum capability of each. The data show predictable results for air stripping where volatile components are completely removed while soluble organics remain. For GAC as well, removal is predictable based on solubility and adsorption affinity with removal of the aromatics preferential over the acetone, however, low residuals of even the aromatics were noted. As the results show, only the UV/Peroxidation process was capable of removing all the organics present.

TABLE 9

Comparison Test

Contaminant ug/L	INF	A/S 1.	GAC 2.	UV/H2O2 3.
Acetone	370	66	110	<10
Toluene	400	<1	4	<1
Ethyl Benzene	250	<1	4	<1
Total Xylenes	740	<1	12	<1
Phenol	1800	550	<10	<10
Bis 2-ethyl hexyl-Phthalate	1200	66	<10	<10

1. 8 hours aeration
2. 50.4 g GAC/L (418 lbs/1000 gal.)
3. 30 minutes oxidation, 200 mg/L H_2O_2.

SUMMARY

Data are beginning to build showing the UV/Peroxidation Process to be a viable and cost effective means of destroying organic materials in water. The process is attractive due to its simplicity, small area required and lack of air, sludge or adsorbent byproducts. The process has proven its application and should be included in any evaluation of treatment technology alternatives.

Enclosure 12

9 3 1 2 9 0 1 2 0 2 6

DESTRUCTION OF WATER CONTAMINANTS

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Heterogeneous photocatalysis is a process in which the illumination of an oxide semiconductor, usually the anatase form of titanium dioxide, produces photoexcited electrons (e^-) and holes (h^+). These can migrate to the oxide surface and participate in half-cell reactions that are part of a closed, catalytic cycle. In the aqueous phase, the illuminated surface is widely regarded as a producer of hydroxyl radicals (e.g., $h^+ + OH^- \rightarrow \cdot OH$), and these and other highly oxidizing initial products of this indirect photochemistry go on to attack oxidizable contaminants.

In the six years since a 1985 *ES&T* review on photocatalysis applied to water purification (*1*), two NATO conferences (*2, 3*) and a NATO Advanced Study Institute course have been held (*4*), and one monograph (*5*) and more than 100 papers have been published on this topic. Like closely related photooxidation processes employing light plus ozone, light plus hydrogen peroxide (H_2O_2), or light/O_3/H_2O_2, photocatalysis research is driven by legislation in industrialized countries that encourages water purification (decontamination, detoxification, decolorization, deodorization) and simultaneous contaminant destruction. Although light alone or oxidant alone (H_2O_2, O_3) produces contaminant partial destruction, only the simultaneous use of either light and an oxidant [O_3, H_2O_2, or O_2 (with photocatalyst)] or of the dual oxidants ($O_3 + H_2O_2$) has often been shown to yield complete mineralization of organic carbon to carbon dioxide; this is the principal advantage of these advanced oxidation approaches to water treatment.

This article highlights recent developments in photocatalysis that are applicable to water treatment. Topics discussed include the generality of photocatalysis for complete contaminant destruction (mineralization); some specific contaminant classes of interest (chlorinated aromatics, surfactants, herbicides, and pesticides); the use of solar versus artificial illumination; the influence of additional oxidants such as H_2O_2; catalyst forms (suspended vs. immobilized); and related potential applications of photocatalysis [metal recovery and total organic carbon (TOC) analyses].

Generality

The complete mineralization of simple and complex chlorinated derivatives of alkanes, carboxylic acids, alkenes, and aromatics has been demonstrated repeatedly (*6, 7*). So far, the only chlorinated molecule found to be resistant to initial photocatalytic attack is the saturated molecule of carbon tetrachloride, which contains no abstractable hydrogen (*1*). [Even trichloroacetic acid can be dechlorinated photocatalytically (*7*)]. Although chlorinated hydrocarbons have been the example contaminants most studied via photocatalysis, the complete destruction of brominated compounds [bromoform (*8*) and ethylene dibromide (*9*)] and fluorinated compounds [fluorophenols (*10*)] also has been achieved.

Actual water treatment challenges characteristically will be multicomponent in several senses. First, multiple organic contaminants are routinely expected from materials such as gasoline [benzene (B), toluene (T), xylenes (X)] or from leaks in halogenated solvent tanks [perchloroethylene (PCE), trichloroethylene (TCE)] into underground or surface waters. Second, in the course of mineralization of any organic contaminant, oxidation will logically involve a series of intermediates of progressively higher oxygen-to-carbon ratios on the way to CO_2. Such intermediates make the conversion process multicomponent, even if only a single contaminant exists in the feed. Hence demonstration of the formation and elimination of intermediates also is important for showing complete removal of undesirable compounds. The same point has become a focus in homogeneous photooxidation (*11*).

Demonstrated mineralization

All advanced oxidation processes have the potential to carry the original organic contaminant through a series of increasingly oxidized intermediates to carbon dioxide. Because complete mineralization usually is desirable in a water-polishing operation, increased attention has been drawn to demonstrating not only reactant disappearance but also carbon dioxide appearance kinetics. For example, with PCE, reactant disappearance and CO_2 appearance are complementary (*12*), which indicates a virtual lack of kinetically stable important intermediates (Figure 1a). In contrast, benzene clearly passes through several stable intermediates; at least two are required to fit the CO_2 evolution data of Figure 1b.

Matthews has demonstrated that organic compounds containing phosphorus, sulfur, and halogen heteroatoms may be oxidized quantitatively, yielding phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), and halide (X^-), respectively (*13*). Oxidations of nitrogen-containing compounds present the most complex results (*14*). The photocatalyzed conversion of rings containing a single nitrogen atom results in the early appearance of inorganic nitrogen in the form of ammonia, and later as nitrate (*14*). Nitrate, a presumed secondary product, appears last but eventually dominates the product spectra.

The ring structure of *s*-triazine herbicides contains three nitrogens and is very stable; only partial degradation to cyanuric acid is achieved (*15*).

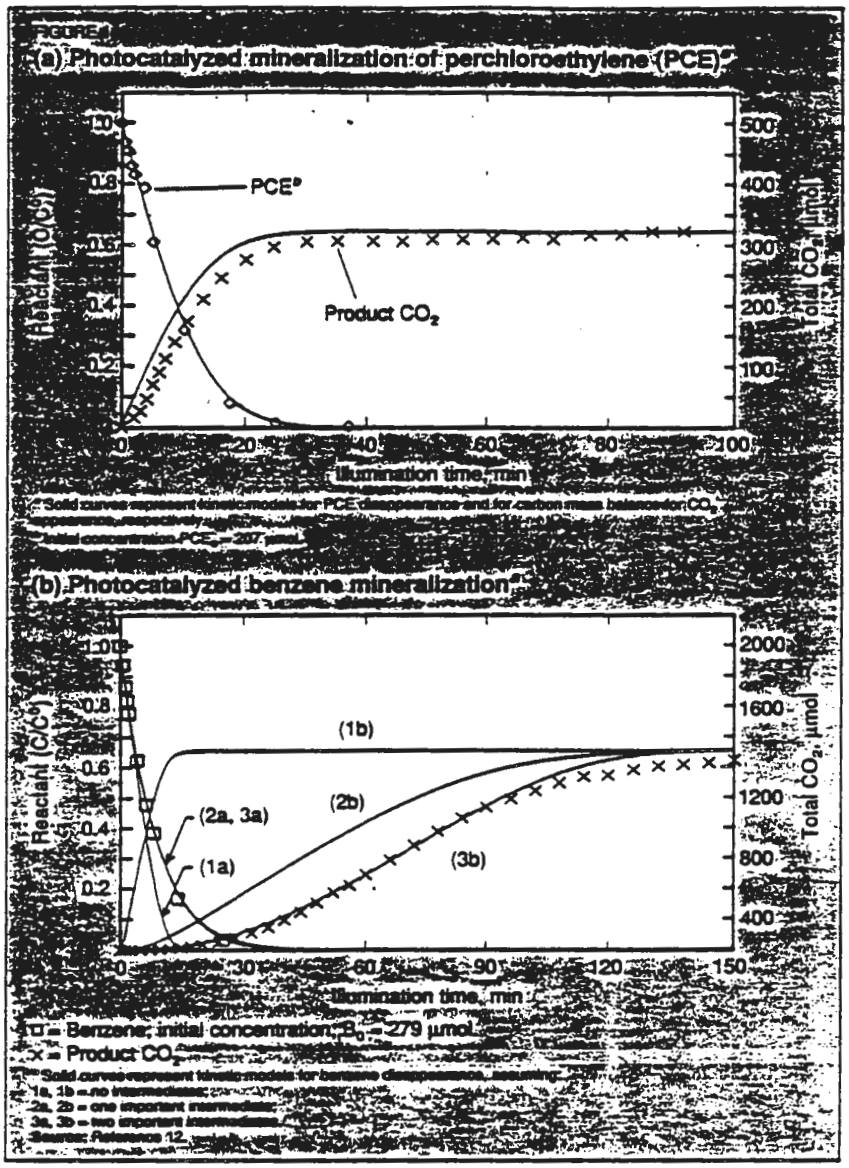
Pelizzetti et al. (*16*) have demonstrated complete mineralization of such long-chain alkanes as dodecane, dodecyl sulfate, 1-bromododecane, 1-decanol, and decanoic acid. Stoichiometric recovery of sulfate and bromide also was claimed when anion adsorption on the titanium dioxide photocatalyst was included.

Chlorinated aromatics

Since our 1985 summary of photocatalysis (*1*), spectacular progress has been made in demonstrating the complete photocatalyzed mineralization of chloroaromatics, including chlorophenols, chlorobenzenes, chlorinated biphenyl, chlorinated dioxins, and DDT. A sample of such compounds appears in Figure 2 (*17, 18*).

Dioxins are so water-insoluble that they can be examined only by loading them onto the catalyst via dissolution in hexane, contact with the catalyst, and solvent evaporation. Interestingly, this approach may allow direct hole (h^+) attack of adsorbed organics, and only by this solvent-loading approach are other oxides such as WO_3 and ZnO shown to be nearly as effective as TiO_2 for the decomposition of the chloroaromatic 3,3'-dichlorobiphenyl (DCB) (*19*).

Photocatalyzed destruction of DDT proceeds without evidence of significant formation of the more toxic DDE [1,1-dichloro-2,2-*bis*(*p*-chlorophenyl)ethylene] which forms by OH^- attack or biodegradation. This absence of DDE suggests a photocatalyzed ·OH radical attack on the aromatic ring, followed by ring opening; chlorine appears to be released only after ring opening, in contrast with most results with single-ring chloroaromatics (*20*).

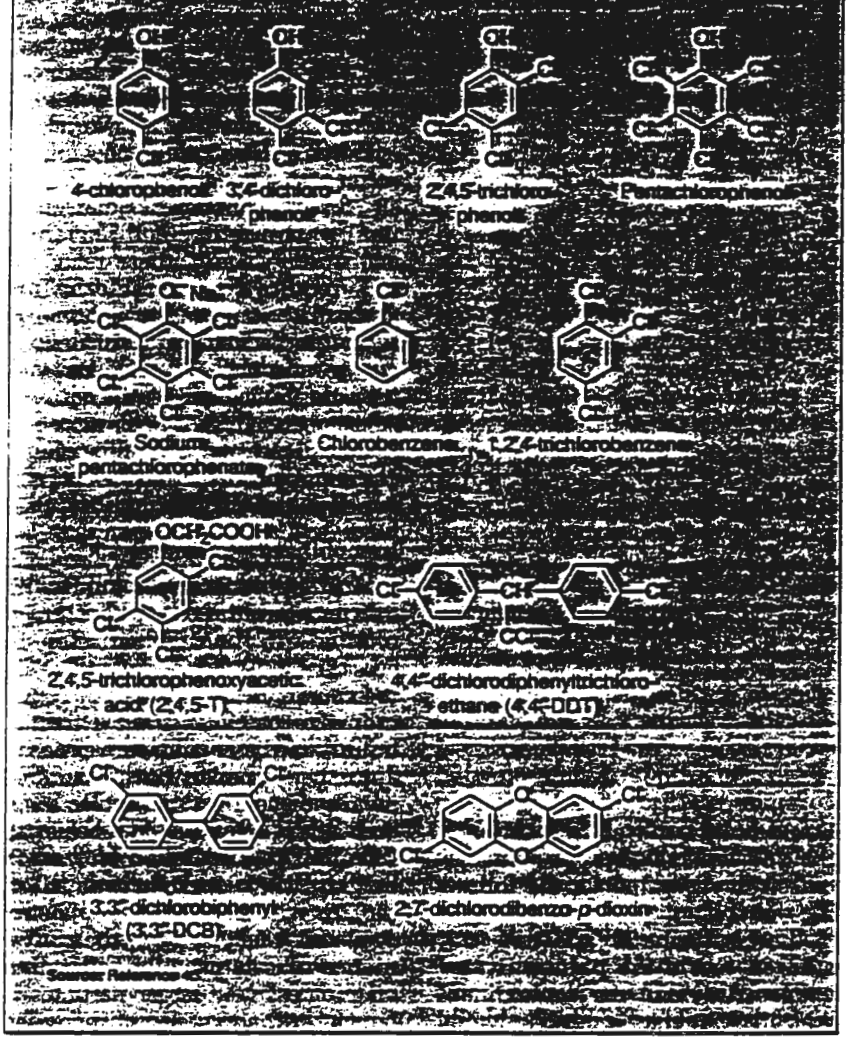


The use of photocatalysis in series with conventional chlorination also may be envisioned, because the rates of 2-chlorophenol or of atrazine disappearance have been shown to be largely unaffected by 3×10^{-4} to 10^{-3} M chlorine (*21*).

Surfactants

Earlier studies (*22–25*) of anionic, cationic, and non-ionic surfactants indicated that aromatic (benzyl) and hydrophilic moieties (e.g., $C-SO_3Na$) are relatively easily attacked and, for benzyl groups, fully mineralized, whereas the long hydrocarbon chain is converted slowly. Significantly, virtually complete loss of surface active behavior was demonstrated in parallel with loss of benzyl groups, a rare example in photocatalysis in which the elimination of the nuisance or hazard value of the reactant did not require complete reactant mineralization.

FIGURE 2.
Structural formulas of chloroaromatics degraded photocatalytically



Recently, the photocatalyzed degradation of alkyl phenols and the non-ionic nonylphenol ethoxylate were examined (*25*). The surfactant and alkyl phenols were susceptible to complete mineralization, as indicated by the demonstration of a carbon balance all the way to carbon dioxide for polyethoxylated 4-nonyl-phenols with average numbers of 2, 5, and 12 ethoxy units (*26*). The related solvents 2-ethoxy- and 2-butoxyethanol also were easily mineralized (*27*).

Herbicides and pesticides

The complete disappearance of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2,4,5-trichlorophenol (TCP) as well as ~ 100% recovery of initial chlorine as free chloride ion in the final state (reaction time of 30–90 min) was demonstrated (*28*). The ratio of free chloride to TCP converted was always 3:1, suggesting a very rapid mineralization and absence of appreciable accumulated intermediates. In contrast, the photocatalytic destruction of 2,4,5-T yielded smaller chloride-to-reactant converted ratios prior to complete mineralization, and major intermediates detected were 2,4,5-TCP and 2,4,5-trichlorophenylformate (*28*). These and other results indicate slow to moderate attack of ring compounds, followed by rapid mineralization once simple phenolics or opened rings have been achieved.

DDT is one of the most complicated chlorocarbons examined in photocatalysis: the complete dechlorination of 1-ppm solutions is reported (*29*) with a half life of ~ 40 min. An initially rapid DDT disappearance was followed by much slower final disappearance and chloride recovery, as would be expected for a reactant with a number of important kinetic intermediates.

The herbicide bentazon (3-isopropyl-2, 1,3-benzo-thiadiazin-4-one-2, 2-dioxide) is efficiently converted to give nearly quantitative yields of sulfur as sulfate ion and carbon as carbon dioxide (*30*).

The *s*-triazine herbicides (atrazine, simazine, trietazine, prometone, and prometryne) are degradable but are singularly resistant to complete mineralization. In all cases, the starting material is degraded to the very stable six-membered ring cyanuric acid $(-N{=}C(OH)-)_3$; virtually stoichiometric recovery of nitrogen, sulfur, and chlorine in ring side groups as nitrate, sulfate, and chloride ions has been demonstrated (*15*). Pathways for atrazine may include dehalogenation, dealkylation, and deamination (*15*) as summarized in Figure 3. Because cyanuric acid has a very low toxicity, these partial mineralization results are encouraging. Complete atrazine disappearance has been demonstrated even at parts-per-billion levels.

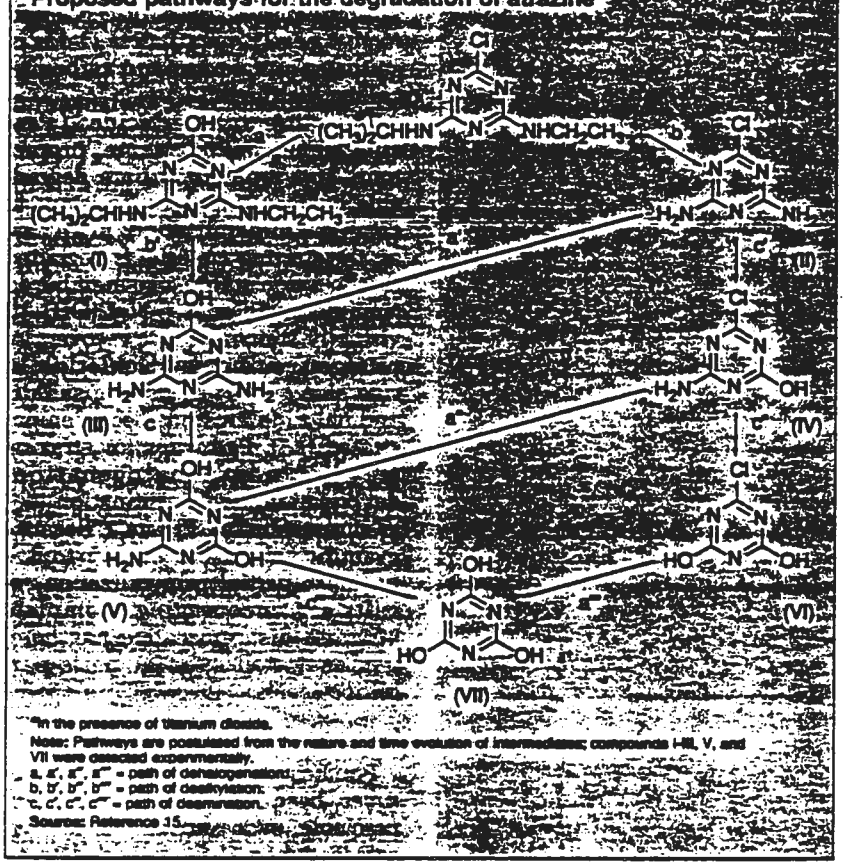
Rate enhancement by H_2O_2

Photocatalyzed reactions have, at times, been reported to exhibit appreciable, even substantial, rate increases when H_2O_2 is added to an aqueous photocatalyst slurry. Degradations showing increased rates include trichloroethylene and perchloroethylene (*31*), chloral hydrate (*32*), and phenol (*33*). The last study found that the photocatalyzed oxidation rates increase according to $O_2 < H_2O_2 < (H_2O_2 + O_2)$. Such enhancements are potentially very important for water treatment. The explanations for the observed enhancements may be several, depending on the following reaction conditions.

First, hydrogen peroxide is a better electron acceptor than molecular oxygen; hence it may increase the photocatalyzed rate by removing surface-trapped electrons, thereby lowering the electron-hole recombination rate and increasing the efficiency of hole utilization for reactions such as $OH^- + h^+ \rightarrow \cdot OH$ (*34*). This is a desired reaction because the hydroxyl radical is widely thought to be required to initiate photocatalyzed degradation.

Second, hydrogen peroxide may be split photolytically to produce $\cdot OH$ directly, as cited in studies of homogeneous photooxidation using $UV/(H_2O_2 + O_2)$ (*35*). Because many lamp sources, including solar simulators, have 300-nm and shorter wavelengths, this contribution will depend strongly on the individual

FIGURE 3
Proposed pathways for the degradation of atrazine[a]



[a]In the presence of titanium dioxide.
Note: Pathways are postulated from the nature and time evolution of intermediates; components I-III, V, and VII were detected experimentally.
a, a', a'', a''' = path of dehalogenation;
b, b', b'', b''' = path of dealkylation;
c, c', c'', c''' = path of deamination.
Source: Reference 15.

lamp and reactor wall material.

Third, the solution phase may at times be oxygen starved, because of either oxygen consumption or slow oxygen mass transfer; peroxide addition thereby increases the rate toward what it would have been had an adequate oxygen supply been provided.

These and other possibilities will require further examination before the influence of hydrogen peroxide "enhancement" is clearly established and understood.

Other oxidants, such as peroxydisulfate and periodate, also have been shown to enhance the overall reaction rate (*36*). As with H_2O_2, these may either trap surface electrons (rate enhancement by prevention of recombination of electrons and holes) or participate directly in an oxidative step. The resolution of the various possible heterogeneous steps, as well as the inclusion of any homogeneous phase chemistry, remains to be accomplished, as does an economic analysis of optimal oxidant addition levels.

Heterogeneous photocatalysis

Although it is widely presumed that titanium dioxide-mediated photocatalysis is initiated at the liquid–solid surface, the location of the subsequent steps is being intensely investigated for the following reasons.

A recent kinetic analysis (*37*) showed that if the photoactivated oxygen (O^*) and the contaminant reactant R interact according to any of the following rate-limiting elementary steps, the global rate of reaction, usually modeled as a Langmuir–Hinshelwood form, will have the same general dependence on reactant concentration R:

$$O^*_{ads} + R_{ads} \rightarrow \text{products}$$
$$O^*_{ads} + R_{sol'n} \rightarrow \text{products}$$
$$O^*_{sol'n} + R_{ads} \rightarrow \text{products}$$
$$O^*_{sol'n} + R_{sol'n} \rightarrow \text{products}$$

Thus, the widely observed fit of rate initial data to Langmuir–Hinshelwood equations of the form

$$r = \frac{k \cdot K \cdot R}{1 + K \cdot R}$$

offers no direct insight or verification of a given mechanism of O^* attack on R. (Here k = rate constant and K = binding constant.)

Recent experimental studies have identified active oxygen at the titanium dioxide surface (*38, 39*) and in solution (*40*). The reaction therefore may proceed at either or both locations. Moreover, the various light sources used may allow the simultaneous presence of homogeneous and heterogeneous photochemistry.

Where homogeneous photo-initiated chemistry also may occur, the situation is not unlike that suggested by Peyton et al. (*41*) for homogeneous photooxidation involving ozone. In that case, a four-term rate equation was written to account for reactant disappearance via photolysis, direct ozone attack (dark reaction), volatilization, and photolytic ozonation. Clearly, these reactions will require considerable further study. The contribution of homogeneous photochemistry will depend strongly on the optical density of the solution as well as the catalyst. A reactor analysis of this homogeneous plus heterogeneous photochemical problem has been published (*42, 43*).

Immobilized photocatalysts

Most photocatalysis studies to date have used ~ 0.1 wt% slurries of titanium dioxide particles, of gross size 0.1–30 mm depending on the source. Because recovery of micron-size particles from a treated liquid may be an awkward process, a number of papers have examined means of catalyst immobilization on beads (*44*), on inside tubes of either glass (*45*) or Teflon (*46*), on fiberglass (*47*), or on woven mesh (*48*). As with all other areas of heterogeneous catalysis (*49*), the convenience of catalyst immobilization on progressively larger particles is bought at the expense of increased average convective-diffusion distance from fluid to catalyst surface. This circumstance invites reactant mass transfer influence because, at pseudo-steady state, the mass transfer rate to the surface, r_m, must equal the surface catalyzed rate, r_c. Thus,

$$r_m = k_m (C_b - C_s)$$
$$r_c = k_c f(C_s)$$

where C_b and C_s are the bulk solution and surface concentrations of reactant, $f(C_s)$ represents the concentration dependence of the surface photocatalyzed rate, and k_m and k_c are the mass transfer coefficient and the reaction rate constant, respectively.

In 0.1 wt% slurries, the average interparticle distance is so small that the measured rate of TCE conversion is much less than the potential mass transfer limit (*50*). In contrast, with the catalyst immobilized on walls of tubes several millime-

ters diameter, mass transfer influence may exist and has been demonstrated with data for salicylic acid conversion in a coiled tube (*51*). Here, a clear variation of reaction rate with flow rate exists, and a reactor analysis (*50*) indicates that the data is strongly influenced by mass transfer. A similar influence of fluid flow rate on the first-order rate constant has been noted in the degradation of chlorophenol on photocatalyst-coated glass tubes (*52*).

Intensity: Optimal power question

Almost all of the few studies of photocatalyzed rate versus illumination intensity in systems that are not transport limited indicate that at illumination levels appreciably above 1 sun equivalent, the reaction rate increases with the square root of intensity. At sufficiently weaker levels of illumination (catalyst dependent), on the other hand, the rate is first-order in intensity (*53–58*). Because absorption of photons is first-order in intensity, it follows that at low intensity, the quantum efficiency (the number of molecules transformed per absorbed photon) is a constant, and at higher levels it decreases as $I^{-0.5}$, indicating an efficiency penalty for sufficiently intense lamps or concentrated solar sources. To be sure, increased intensity always results in an increase in volumetric reaction rate, until the mass transfer limit is encountered.

Thus, the quantum efficiency Φ varies with intensity as follows:

Low I:
rate varies as I
Φ = constant
Intermediate I:
rate varies as $I^{0.5}$
Φ varies as $I^{-0.5}$
High I (mass transfer limit):
rate varies as $I^{0.0}$ (const)
Φ varies as $I^{-1.0}$

When reactor cost is the most expensive part of the process, increased intensity increases the rate per volume (below the mass transfer limit) and is worthwhile, whereas if photon collection or generation is a major cost, a lower intensity will provide cheaper treatment. Because the $I^{1.0}$ to $I^{0.5}$ rate transition depends on catalyst material (*46*), and because the $I^{0.5}$ to $I^{0.0}$ rate transition depends on immobilized catalyst configuration and on flow-influenced mass transfer (*58*), the transition points between these regimes will vary with each application. Extension of the first-order regime to higher intensities may be possible by addition of better electron acceptors, such as H_2O_2, Cu^{2+}, and Ag^+, but much work in this area is needed to maximize the efficiency of the overall process.

A similar application-specific circumstance exists in photolytic ozonation (*59*), in which laboratory and field sample reaction rates varied with intensity as follows:

rate α $I^{1.0}$ (distilled water)
and
rate α $I^{0.4}$ (lake water)

These dependencies occurred in the dominant photolytic ozonation terms in the rate kinetics. Thus, the latter fractional order dependence of rate on intensity may be found commonly in environmental applications of homogeneous or heterogeneous photolytic oxidations in general. Such a circumstance is not surprising, because increased intensity should increase recombination processes (second-order) faster than oxidation processes (first-order in excited oxidant), regardless of the photochemistry involved.

Illumination: Artificial vs. solar

The spectral distribution of solar illumination versus that of some solar simulators that have been used in photocatalysis studies differs appreciably in the critical range of 280–300 nm, in which solar radiation itself is negligible (*57*). Because these wavelengths may initiate homogeneous photochemistry, care must be taken in assigning equivalency to solar illumination (*58*). Nonetheless, such studies using suitable filters have been fruitful in suggesting solar action, because compounds photocatalytically degraded by true solar illumination include trichloroethylene and trichloromethane (*60*), surfactants (*61*), salicylic acid (*62*), and dioxins and biphenyls (*19*).

Experiments with a Solarbox simulator (Xe lamp) and a 340-nm cutoff filter provide a unit air mass (AM1) spectral distribution to the photocatalyst. The broad range of contaminant structures that has been mineralized via this simulated solar illumination includes chlorophenols, chlorobenzene, and multi-ring structures (DDT, dioxins) (*63, 64*).

Metals stripping and recovery

A number of heavy metals have been demonstrated to be recoverable via photocatalyzed metal deposition on the illuminated catalyst (*65*). The selective, nearly sequential removal of platinum, gold, and rhodium from a mixed solute solution is achievable (Figure 4); a finite dissolved oxygen level is important to prevent rhodium reduction (*66*).

Gold is easily recovered from aqueous chloride media (*67*), and its recovery from gold–cyanide solutions has been demonstrated via sequential photooxidation processes such as UV/H_2O_2 oxidation of CN^- to OCN^-, followed by removal of excess H_2O_2 and photocatalyzed gold deposition in the presence of TiO_2 and added methanol (*68*).

Mercury (Hg[II]) chloride and methylmercury(II) chloride solutions can be treated photocatalytically to deposit elemental mercury. Conditions differ substantially, however; mercury is removed at the natural pH of $HgCl_2$ air-equilibrated solutions, whereas methylmercury solutions yield mercury metal deposition only when oxygen is removed and a substantial amount of methanol (20% v/v) is added (*69*). Also, platinized anatase TiO_2 can remove lead (Pb^{2+}) photocatalytically to give Pb^0 on platinum and PbO_2 on the metal oxide (*70*).

Analysis of organic carbon

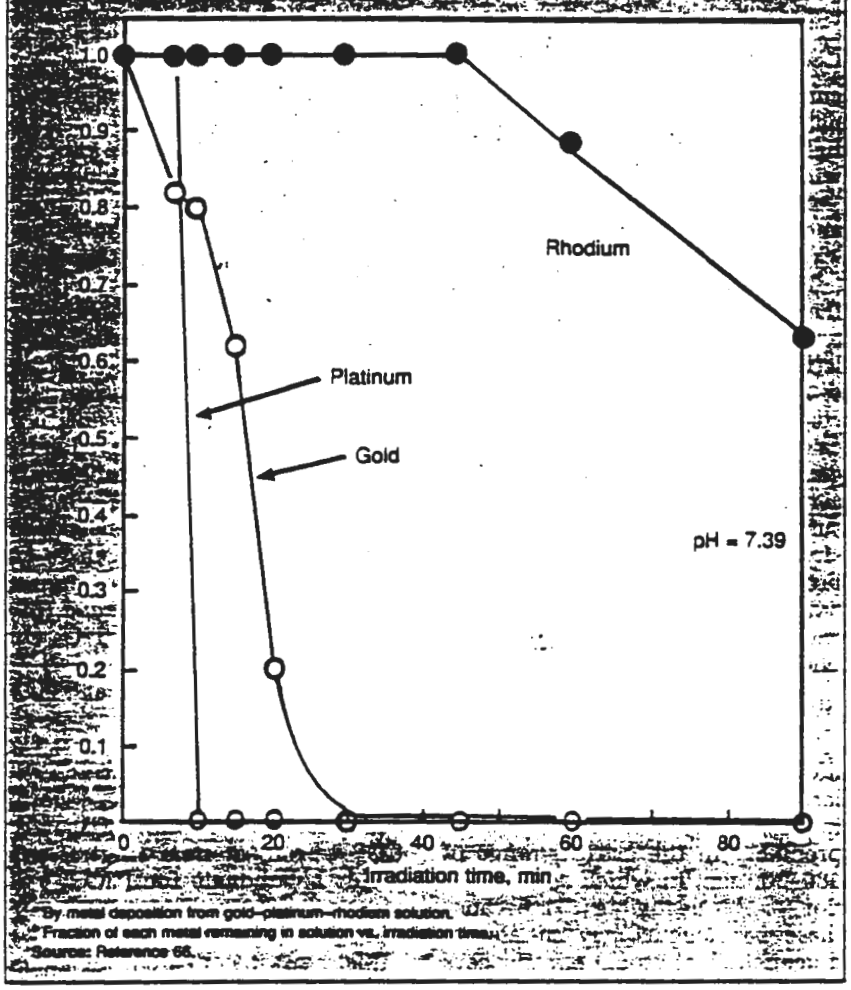
The mineralization of organic contaminants produces dissolved CO_2 which, at near neutral pH, yields bicarbonate ion (HCO_3^-) almost quantitatively:

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$$

Matthews has demonstrated that carrying out photocatalyzed sample mineralization, followed by equilibrating the dissolved CO_2 between the product sample and a separate conductivity loop, allows the loop to be used as a total organic carbon (TOC) analyzer (*71, 72*). This method is claimed to be suitable for the direct analysis of 0.1–30 ppm organic carbon and sample volumes of 1–40 mL. Higher level TOC samples can be diluted before analysis. Complete photocatalyzed mineralization (> 99% oxidation to CO_2) usually is accomplished in 5–10 min.

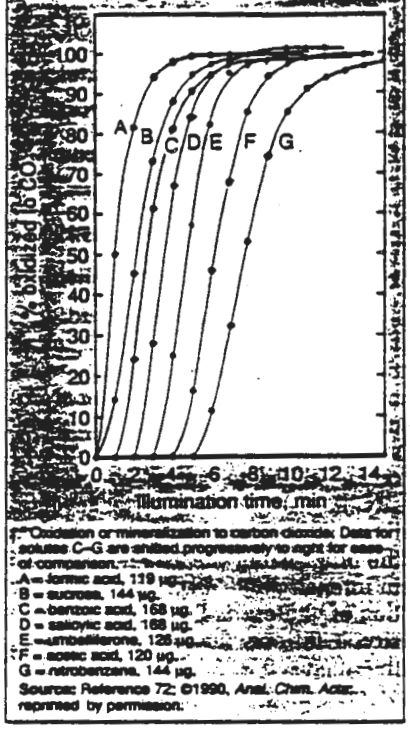
This approach represents a possible basis for an analytical device. Example data for CO_2 generation versus time in a device prototype are shown in Figure 5, which indicates total oxidation times of 5 min for formic acid, 8 min (acetic acid), and 15 min (estimated) for nitrobenzene. Also important from a sample analysis viewpoint is that the mineralization time for benzoic acid appears to be slowed most by HCl and less by phosphoric and sulfuric acids; perchloric and nitric acid have little effect.

FIGURE 4
Selective photocatalyzed separation of gold and platinum[a]



[a] By metal deposition from gold–platinum–rhodium solution.
[b] Fraction of each metal remaining in solution vs. irradiation time.
Source: Reference 66.

FIGURE 5
Time for total oxidation of various organic solutes[a]



[a] Oxidation or mineralization to carbon dioxide. Data for solutes C–G are shifted progressively to right for ease of comparison.
A = formic acid, 119 μg.
B = sucrose, 144 μg.
C = benzoic acid, 168 μg.
D = salicylic acid, 168 μg.
E = umbelliferone, 126 μg.
F = acetic acid, 120 μg.
G = nitrobenzene, 144 μg.
Source: Reference 72; ©1990, Anal. Chem. Acta; reprinted by permission.

A total organic carbon analyzer based on a photocatalytic device has been patented (*73*), in which the active titanium dioxide is coated inside a borosilicate glass spiral within which is set a 20-W near-UV light source. A flow injection configuration also has been demonstrated that uses an internally coated Teflon tubing wrapped around a 20-W near-UV tube (*74*). Complete oxidation of an appropriately diluted sample is attainable, provided there is sufficient dissolved oxygen.

The next decade's challenges

The literature has by now largely succeeded in establishing the general ability of photocatalysis to mineralize a host of water contaminants and to serve as a photochemical process basis for metals recovery and total organic carbon analysis. Over the next decade researchers who wish to use and commercialize photocatalysis will need to design reactors that increase the efficiencies of photon utilization and to demonstrate economic feasibility beyond that cited in the initial reports (*75*).

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