To the Graduate Council:

I am submitting herewith a thesis written by Michael A. Miller entitled "The Destruction of Pentachlorophenol in Wood Preserving Plant Wastewater by UV/Ozonation." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

Dennis W. Weeter, Major Professor

We have read this thesis and recommend its acceptance:

Wayne J. Davis

Accepted for the Council:

Vice Chancellor
Graduate Studies and Research

THE DESTRUCTION OF PENTACHLOROPHENOL IN WOOD PRESERVING PLANT WASTEWATER BY UV/OZONATION

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Michael Allen Miller

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ABSTRACT

Pentachlorophenol (PCP) has been widely used in the wood preserving industry. PCP's use is controlled by both the "Clean Water Act" and the "Resource Conservation and Recovery Act." Plants which use PCP are now faced with a disposal problem. The treatability of PCP has had limited success, however nowhere in the literature has a treatment scheme been shown which will treat PCP to the limitations proposed in current regulations. This thesis investigates treating PCP by a process using UV/ozonation.

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I. INTRODUCTION

A. Background

The wood preserving industry in the United States comprises about 400 commercial treating plants and treats timbers for various uses to include telephone poles, railroad ties, and varied uses in the construction industry.[1] In their process, several chemicals must be used as preservatives and fire retardants. Creosote, pentachlorophenol, and various inorganic salts are the main preservatives used by the industry. Pentachlorophenol, (PCP), will be the topic of this paper. PCP has a relatively low solubility in water and is therefore normally applied with a carrier petroleum oil.[1]

The wood preserving process generates several wastewater streams to include steam condensate, boiler blowdown, surface condenser condensate, miscellaneous wash water and other leakage. All the above streams can be contaminated with preservatives except the boiler blowdown which could be contaminated with other various chemicals such as chromates and phosphates. For the purpose of this paper, all the above waste streams will be considered as one and will be referred to as wood preserving wastewater.

B. Federal Regulations

The forest products industry is regulated by two specific acts; (1) PL 92-500 (The Federal Water Pollution Control Act of 1972) as amended by PL 95-127 (The Clean Water Act of 1977)[2] and (2) PL 94-580 (The Resource Conservation and Recovery Act of 1976) as amended (RCRA).[3]

1. The Clean Water Act

The first regulations affecting the forest products industry appeared in the Federal Register in April 1974 and January 1975, with pretreatment regulations for existing sources appearing in the Federal Register in December 1976.[1] Effluent limitations resulting from these regulations, for the wood preserving segment of the industry, included chemical oxygen demand (COD), phenols, oil and grease, and pH. A civil action suit was brought about by the promulgation of these regulations which resulted in a Settlement Agreement made on June 7, 1976.[1] The Agreement charged the Environmental Protection Agency (EPA) with the task of developing and promulgating effluent limitations guidelines and standards for 65 toxic substances (Table 1) for 21 major industrial categories, of which timber products processing is first on the list.

On October 31, 1979, proposed rules for "Timber Products Processing Point Source Category Effluent Limitations Guidelines, Pretreatment Standards, and New Source Performance Standards" were published.[4] The wood preserving subparts of the proposed rules calls for zero (0) discharge of pentachlorophenol to publically owned treatment works (POTW's). This means that the individual wood preserving plant must either not discharge wastewater containing PCP at all, or they must treat their wastewater to below detection limits.

TABLE 1

SETTLEMENT AGREEMENT POLLUTANTS

Acenaphthene	Cyanides	Mercury & Compounds
Acrolein	DDT & Metabolites	Napthalene
Acrylonitrile	Dichlorobenzene	Nickel & Compounds
Aldrin/Dieldrin	Dichlorobenzidine	Nitrobenzene
Antimony & Compounds	Dichloroethylenes	Nitrophenols
Arsenic & Compounds	2,4-Dichlorophenol	Nitrosamines
Asbestos	Dichloropropane & Dichloropropene	Pentachlorophenol
Benzene	2,4-Dimethylphenol	Phenol
Benzidine	Dinitrotoluene	Phthalate Esters
Beryllium & Compounds	Diphenylhydrazine	Polychlorinated Biphenyls
Cadimium & Compounds	Endosulfan & Metabolites	Polynuclear Aromatic Hydrocarbons
Carbon Tetrachloride	Endrin	Selenium & Compounds
Chlordane	Ethylbenzene	Silver & Compounds
Chlorinated Benzenes	Fluoranthene	2,3,7,8-Tetrachlorodibenzo-P-Dioxin
Chlorinated Ethanes	Haloethers	Tetrachloroethylene
Chloralkyl Ethers	Halomethanes	Thallium & Compounds
Chlorinated Napthalene	Heptachlor & Metabolites	Toluene
Chlorinated Phenols	Hexachlorobutadiene	Toxaphene
Chloroform	Hexachlorocyclohexane	Trichloroethylene
2-Chlorophenol	Hexachlorocyclopentadiene	Vinyl Chloride
Chromium & Compounds	Isophorone	Zinc & Compounds
Copper & Compounds	Lead & Compounds	

Source: EPA Settlement Agreement (NRDC and EDF vs. EPA)

On January 26, 1981, EPA issued revised effluent regulations for the wood preserving industry. The new Federal regulations are significantly different than the proposed regulations in that existing plants will maintain current effluent standards with no PCP limitation. New sources however, will still be required to achieve no discharge of PCP whether they discharge directly into navigable waters or indirectly into a publically owned treatment work (POTW).

2. The Resource Conservation and Recovery Act

On May 19, 1980, final rules and regulations were published in the Federal Register under Subtitle C section 3001 of RCRA.[5] In Subpart D - List of Hazardous Wastes, bottom sediment sludge from the treatment of wastewaters from wood preserving processes that use creosote and/or pentachlorophenol was listed as a hazardous waste by reason of toxicity. On the same day, proposed rules were published in the Federal Register to amend the list of hazardous wastes under Section 3001 so as to include wastewater from wood preserving processes that use creosote and/or pentachlorophenol.[5] These proposed rules are of critical concern to the industry since they are already extremely limited from discharging wastewater under the Clean Water Act.

Now, (if the proposed rules become final) they will be generating, storing and/or disposing of a listed hazardous waste under Section 3001 of RCRA.

II. LITERATURE DEFICIENCIES AND OBJECTIVES

A review of the literature indicates a void concerning the treatment of wood preserving wastewater by means of ozonation or ultraviolet (UV) light and ozone in combination. EPA[6] states, "No example of the use of ozone to treat timber products wastewater appears in the literature." The literature does indicate that the UV/ozonation process has proved effective in the destruction of pentachlorophenol (PCP).

The objective of this study is to evaluate the UV/ozonation process as it relates to the destruction of PCP in wood preserving wastewater. The feasibility of this process will also be examined in regards to "real world" implementation by the timber industry.

III. LITERATURE REVIEW

A. Current Treatment Technology in the Wood Preserving Industry

Numerous treatment schemes have been employed by the industry.[1, 6, 7] Many types of treatment have been tried by the industry, most of which have not been effective regarding proposed discharge limitations.

1. Primary Treatment

Treatment plants using oily type preservatives (oil is usually used as a carrier fluid, especially for PCP) almost always have gravity oil-water separation, regardless of subsequent treatment steps or ultimate disposal of wastewater.[1, 6] Chemical flocculation is then needed since oil-water emulsions are not broken down by mechanical oil removal procedures. Lime, ferric chloride, various polyelectrolytes, and clays are used for this purpose. Chemical oxygen demand (COD) reductions can range from 30 to 80 percent or more, primarily due to oil removal.[1] Pentachlorophenol solutions cause more emulsion problems than do creosote or its solutions, especially those that employ open steaming. Significant reductions in pentachlorophenol are also achieved by flocculation. Table (2) shows the reduction of COD, oil and grease, and PCP after chemical flocculation.

TABLE 2

REDUCTION IN CONTENT OF SELECTED WASTEWATER PARAMETERS DUE TO FLOCCULATION TREATMENTS

Plant No.	Before Flocculation (mg/liter)			After Flocculation (mg/liter)			% Reduction		
	O&G	COD	PCP	O&G	COD	PCP	O&G	COD	PCP
1	2,640	12,627	47.8	165	6,645	5.2	94	47	89
6	24,450	147,555	860	90	4,645	134	99+	97	84
7	735	15,695	-	245	10,515	-	67	33	-
9	270	22,915	26.7	45	20,390	9.0	83	11	66
10	3,010	15,345	-	120	2,565	-	94	84	-
14	35	1,170	5.7	20	530	2.71	43	69	53

2. Biological Treatment

Biological Treatment has been used in various forms to include: trickling filters, activated sludge, aerated lagoons, and soil irrigation. Biological treatment has shown excellent removals of pollutants such as COD, oil and grease and total phenols. PCP reductions are substantial, however, they are well above detection limits in all cases, usually in the 1-10 parts per million range.[7] This range is well above the "no detection" limitation being proposed in the guideline standards.[4] Therefore, biological treatment (at least single-stage biological treatment) can be ruled out for consideration of

reducing PCP below detection limits. Multiphase biological treatment, in combination with appropriate primary treatment may be of consideration, however no data is available at this time to evaluate this alternative.

3. Membrane Systems

Ultrafiltration and reverse osmosis (which employ similar principles) have both been studied for use by the wood preserving industry. Although excellent volume reduction, COD, and oil removals were achieved, only 20 and 70 percent phenol removals were achieved with cellulose acetate membranes, and polyethylenimine membranes respectively.[4] These results all but rule out membrane systems for consideration of PCP removal.

4. Carbon Adsorption

Carbon adsorption does an excellent job in removing phenolics from wood preserving wastewater, however as with other systems it rarely treats below the 1 mg/L range.[4] Another problem is also experienced when using activated carbon. Other organics, principally water-soluble wood sugars, greatly increase carbon exhaustion rates. Therefore, high operation and maintenance costs, along with the fact that no evidence is available showing treatability below detection limits for PCP; carbon adsorption can be eliminated from consideration. It should be noted however, that carbon adsorption used as a tertiary treatment, following biological treatment to remove the wood sugars may be economically

viable and meet standards. No mention of this process was found in the literature, so it cannot be evaluated at this time.

5. Evaporation Process

Evaporation has been most widely accepted by the industry as the principal method of wastewater disposal.[1] There are several different applications of this process used by the industry, some of which are more economical than others. Evaporation methods, where process steam is used, are not considered economical because of the high energy costs involved. This application will become less and less attractive as energy costs continue to rise. Methods relying on simple surface evaporation are quite economical but usually are not effective, especially in areas where yearly rainfall equals or exceeds yearly evaporation.

The most effective method of evaporation is to equip the evaporation pond with mechanical spray equipment or atomizers. Even this system can lead to problems during rainy seasons especially where the plant is restricted in the pond sizing because of space requirements. Another problem associated with this process is the volatization of toxic organics into the air. The fate of these compounds is currently unknown, but EPA is initiating projects to measure these toxic constituents and their effects.

The sludges and bottom sediments resulting from all these processes will also be considered as a hazardous material under Section 261.32 of RCRA on the basis of toxicity.[5] Therefore, when the time came for cleaning of these ponds, all sludges would be a hazardous waste and would need to be disposed of accordingly. Likewise, these ponds would be considered hazardous waste storage facilities during the interim.

B. UV/Ozone Process

The UV/ozone process is a relatively new concept. The literature revealed several studies using the process. One of the earlier studies was by Zeff.[8] Zeff's process tested a synthetic wastewater consisting of equal parts of hydroquinone, pyrogallol, zylenol, urea, and sodium acetate. Zeff's bench scale set-up is shown in Figure 1.

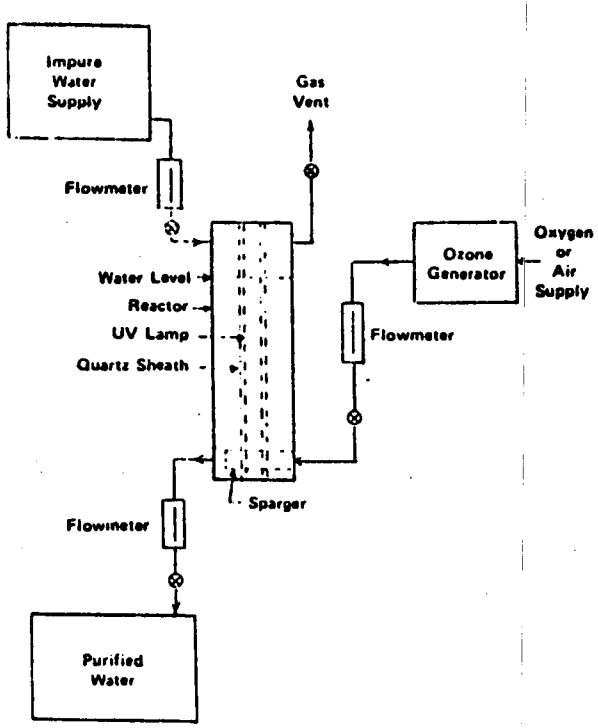


Figure 1. Schematic of Bench Reaction System

Source: J.S. Zeff, 68th Annual AlChE Mtg., November 1975.

To determine the amount of energy consumed to completely oxidize each milligram of carbon per liter, indices for oxidation efficiency and UV energy efficiency were established. TOC/O_3 was oxidized to the molecular equivalent of ozone fed into the process. The results of Zeff's work are shown in Table 3.

TABLE 3

SIMULATED TWO-STAGE CONTINUOUS OPERATION
THREE-PART SIMULATED WASTEWATER

1st STAGE									2nd STAGE							
Influent conc TOC mg/l	Flow Rate ml/min	Res Time min	Effluent conc TOC mg/l	O_3 Input mg/min	O_3 Output mg/min	$\frac{TOC}{O_3}$ Effic.(%) Supplied	Lamp Watts	UV Energy Demand $\frac{W\text{-}m}{mgC}$	Influent conc TOC mg/l	Flow Rate ml/min	Res Time (min)	Effluent conc TOC mg/l	O_3 Input mg/min	O_3 Output mg/min	$\frac{TOC}{O_3}$ Effic. (%)	Lamp Watts	UV Energy Demand $\frac{W\text{-}m}{mgC}$
84.2	100	30	23.8	70.8	23.0	68.2	43	7.2	23.8	100	30	8.4	70.8	32.1	17.4	29	17.5
56.3	100	30	16.0	70.8	25.1	45.5	43	10.7	16.1	100	30	4.5	70.8	31.7	13.1	29	25.0
86.0	100	30	47.3	70.8	21.8	43.7	43	11.1	46.0	100	30	9.1	70.8	43.9	41.7	29	8.8
65.0	100	30	33.7	75.6	21.6	33.1	43	13.7	33.1	100	30	7.5	75.6	29.0	27.1	29	12.5
40.4	200	15	22.9	70.8	27.1	39.5	43	12.3	22.9	200	15	5.4	70.8	37.4	39.5	43	12.3
43.3	200	15	20.0	70.8	27.8	52.6	43	9.2	19.0	200	15	5.4	70.8	35.5	30.7	29	10.7
19.5	200	15	7.1	70.8	26.4	28.0	43	17.3	7.5	200	15	4.5	70.8	70.6	6.8	0	0
19.5	200	15	9.3	75.6	32.4	21.6	29	14.2	8.0	200	15	4.9	75.6	67.9	6.6	0	0
19.5	200	15	7.1	75.6	31.2	26.2	29	11.7	6.3	200	15	5.8	54.7	46.3	1.7	0	0

Source: J.D. Zeff, 68th Annual AlChE Mtg., November 1975.

Zeff looked at variables such as residence time, O_3 concentration, UV intensity, and TOC concentration. UV intensity studies are shown in Figures 2 and 3. It is apparent from these figures that the intensity of UV light plays an important role in this process.

Figures 2 and 3 show the importance of UV as an apparent driving force or catalyst in the process. Zeff's work did not try to optimize operating variables, however, the importance of UV assistance was usually striking in all cases. Zeff oxidized ethanol and acetic acid with 72.5 milligrams of ozone per minute (2.7% O_3 concentration by weight) in a 12 liter reactor with one 43 watt lamp.

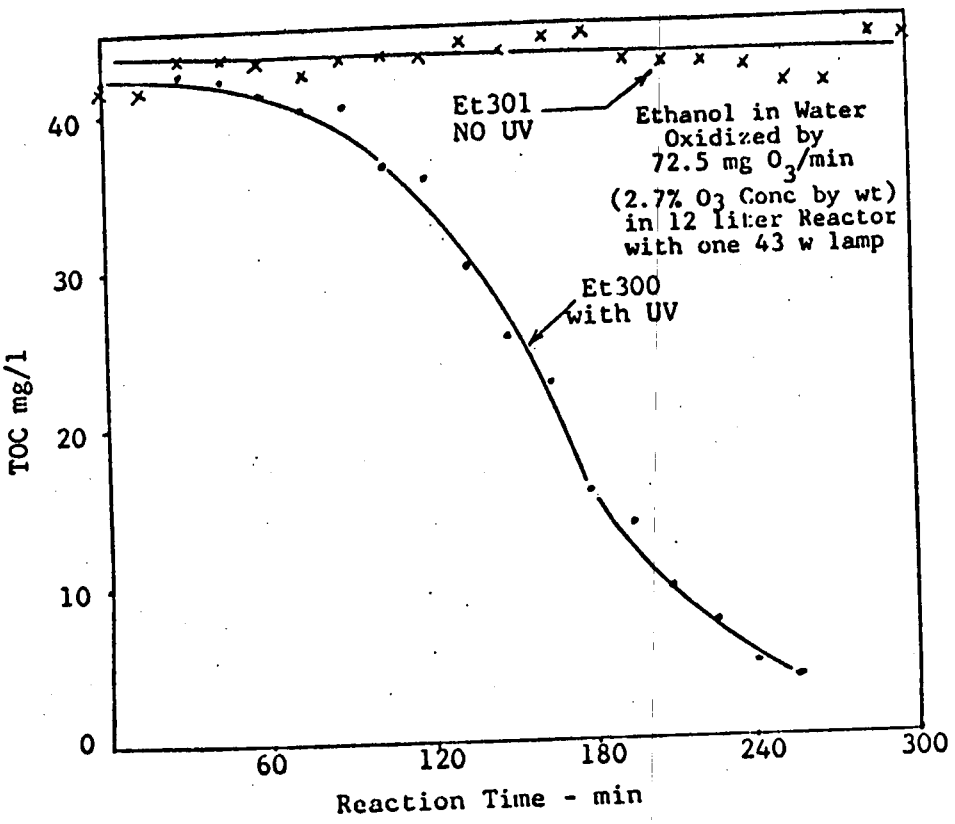


Figure 2. Ethanol Oxidation by O_3 With and Without UV

Source: J.D. Zeff, 68th Annual Meeting, AIChE, November 1975.

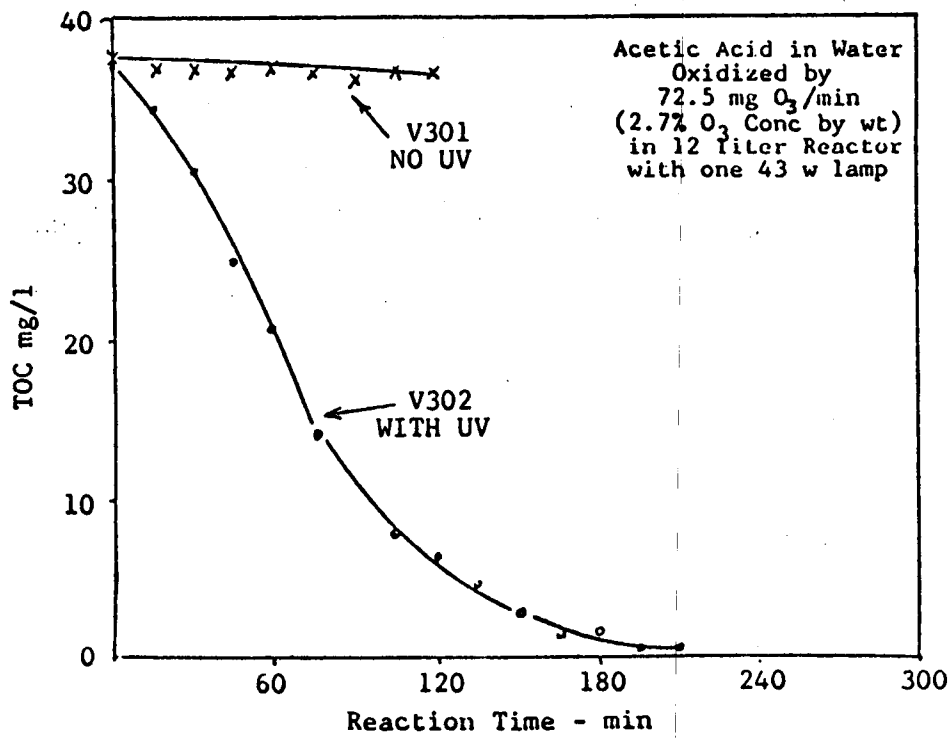


Figure 3. Acetic Acid Oxidation by O_3 With and Without UV

Source: J. D. Zeff, 68th Annual Meeting, AIChE, November 1975.

Prengle et al.[9] used the UV/ozonation process to treat many refractory compounds. Many of these compounds may be economically oxidized whose reaction rates would otherwise be too low to be processed in other systems. Ultraviolet radiation enhances and drives the reaction to completion to harmless materials such as carbon dioxide (CO_2) and water (H_2O).[9] Some compounds such as acetic acid which is essentially unoxidized by ozone alone proceed rapidly with the UV/ozonation process. Figure 4 shows some results of Prengle's work.

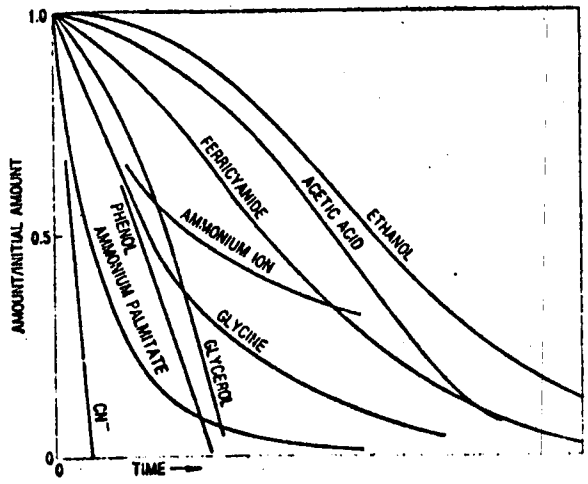


Figure 4. Typical Removal Curves for Refractory Compounds by Ozone with UV near 30° C.

Source: Prengle et al., Hydrocarbon Processing, October 1975.

Prengle et al. also looked at pH and temperature effects shown in Figures 5 and 6. As can be seen, temperature and pH can indeed have an effect on the process. The effect of pH however seems to vary with the compound and can sometimes be ignored. The author points out that a temperature rise will increase the reaction rate, however Figure 7 shows that increasing UV achieves the same results. It was also shown that increasing UV was much more effective than elevating temperature and required less energy, so therefore temperature controls can usually be eliminated from the system.

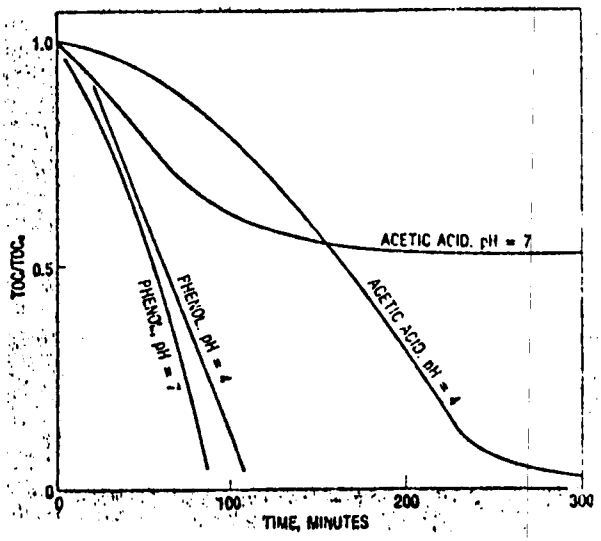


Figure 5. Effect of Initial pH on Oxidation of Ozone with UV near 30° C.

Source: Prengle et al., Hydrocarbon Processing, October 1975.

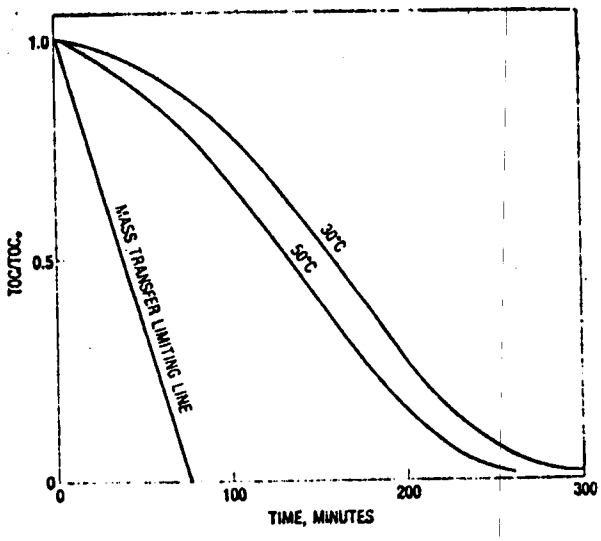


Figure 6. Ozone Oxidation of Acetic Acid, Effect of Temperature Low UV Intensity

Source: Prengle et al., Hydrocarbon Processing, October 1975.

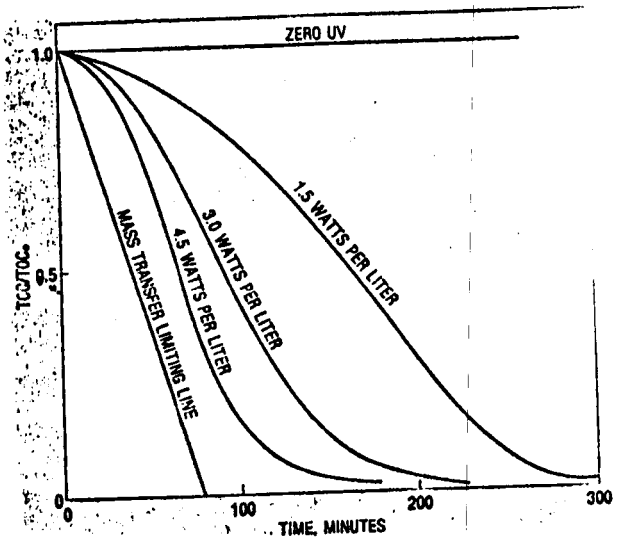


Figure 7. Ozone Oxidation of Acetic Acid, Effect of UV near 30°C.

Source: Prengle et al., Hydrocarbon Processing, October 1975.

Glaze et al.[10] conducted a three year study of the ozone/ultra-violet radiation process. The study examined the kinetics and to some extent, the by-products of the photolytic ozonation of chloroform, bromodichloromethane, tetrachloroethylene, and 2, 2', 4, 4', 6, 6' - hexachlorobiphenyl. The study also examined the effects of UV and ozone separately. The resulting data were then analyzed to determine kinetic rate expressions relating the dependence of the reaction rate on ozone dose rate, UV intensity, and substrate concentration.

Results of the study found the ozone/UV process to be 4-50 times faster than either ozone of UV alone, depending on the compound and matrix.[10] The apparatus used in the study is shown in Figure 8. This apparatus was made of quartz so as to allow UV light penetration. The entire quartz reactor could be lowered into a chamber surrounded by UV lamps. The UV light used in the study was a 2537 A lamp whose spectral energy distribution is shown in Figure 9.

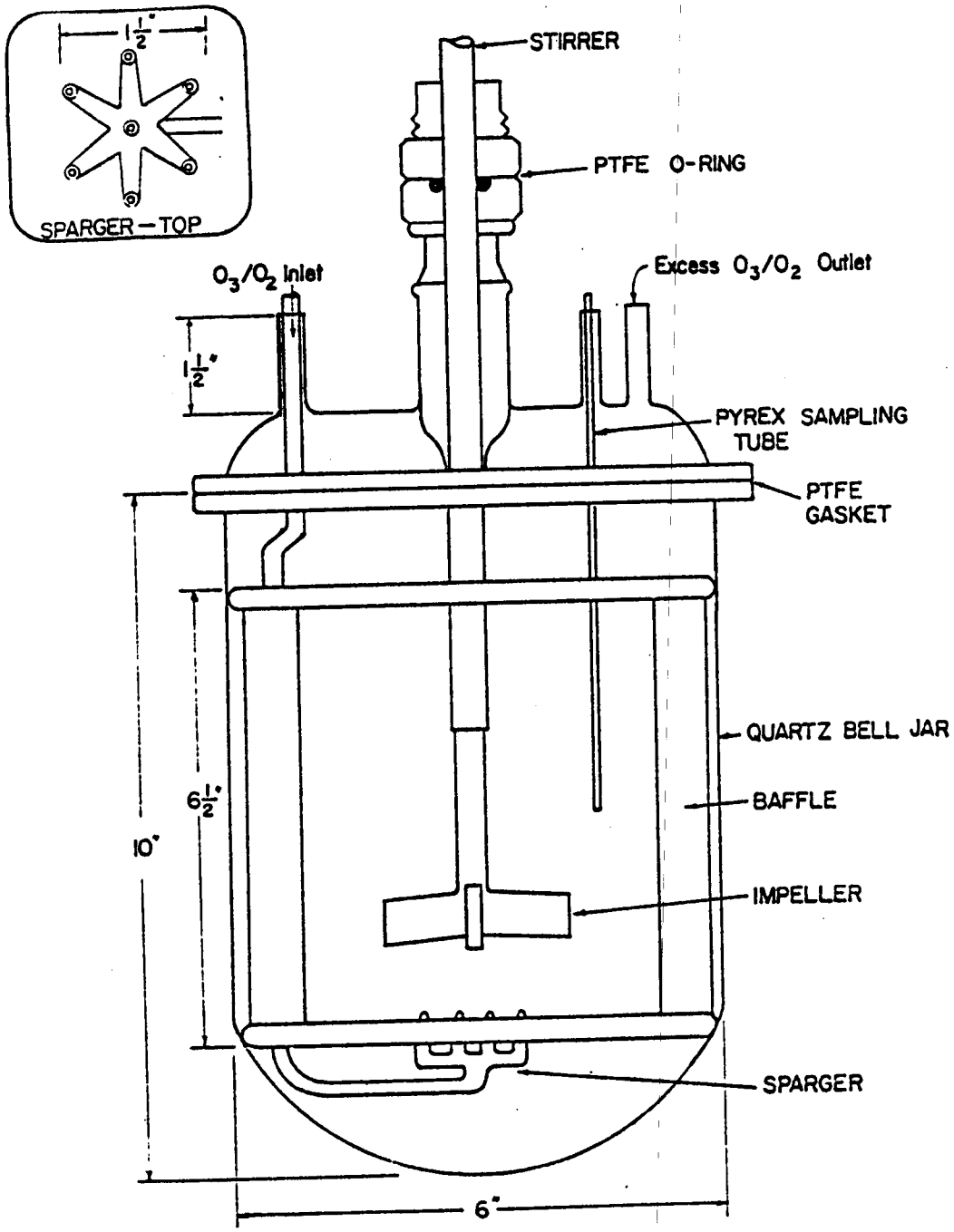
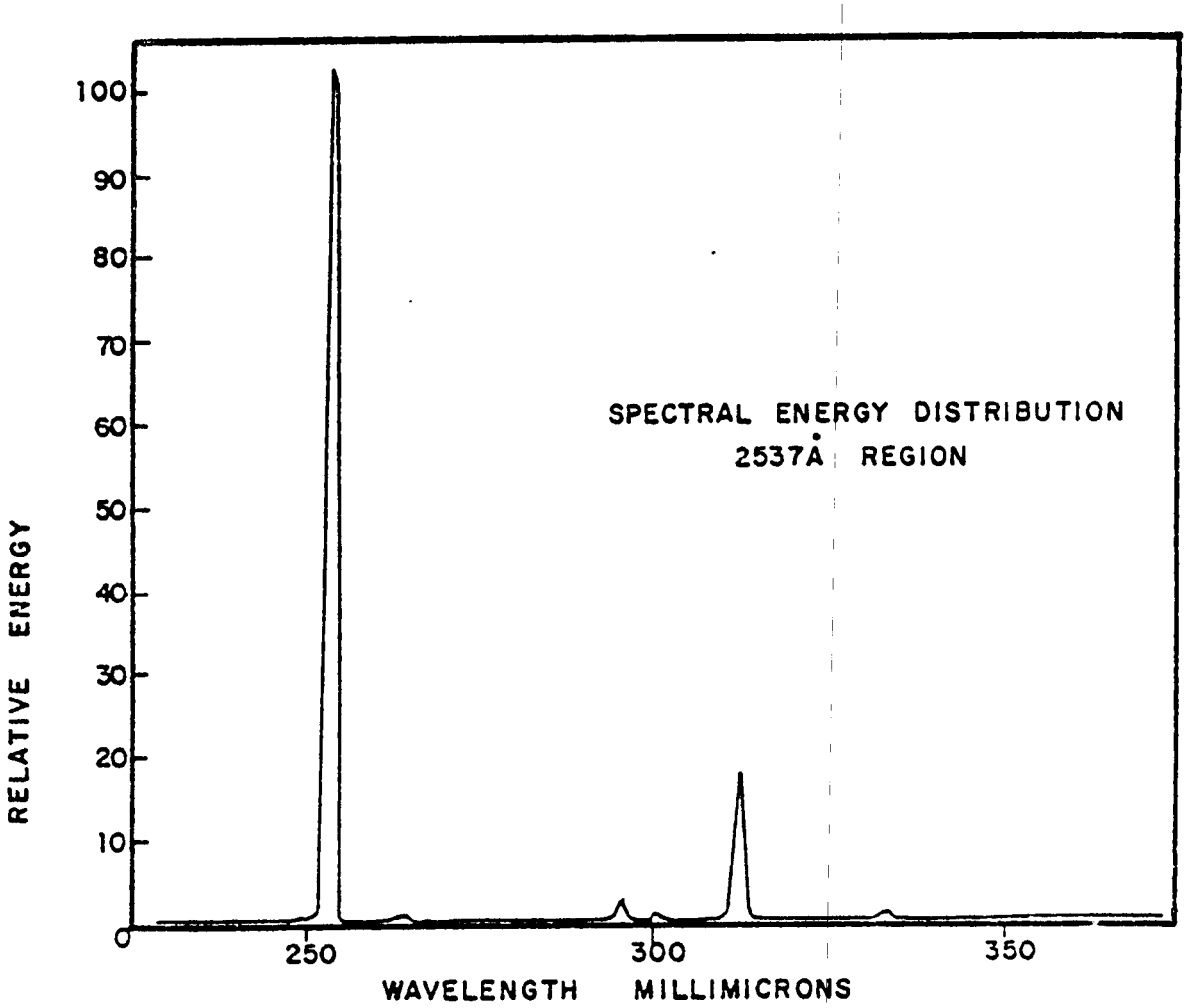


Figure 8. North Texas State University Photochemical Reactor

Source: Glaze et al, EPA "Draft Report".



WAVE LENGTH (A)	INTENSITY READINGS IN MICROWATTS/cm^2 AT: 2 INCHES FROM LAMPS
2537	16000
2652	488
2804	16
2894	22
2967	83
3022	40
3129	313
3654	267
4047	316
4359	960
5461	523
5780	113

Figure 9. Spectral Distribution from UV Lamp

Source: Glaze et al., EPA "Draft Report".

C. Pentachlorophenol Destruction by UV/Ozone

Houston Research, Inc., has utilized the UV/ozone process to destroy or detoxify hazardous chemicals in solution.[11] The technique involves a simple apparatus shown in Figure 10.

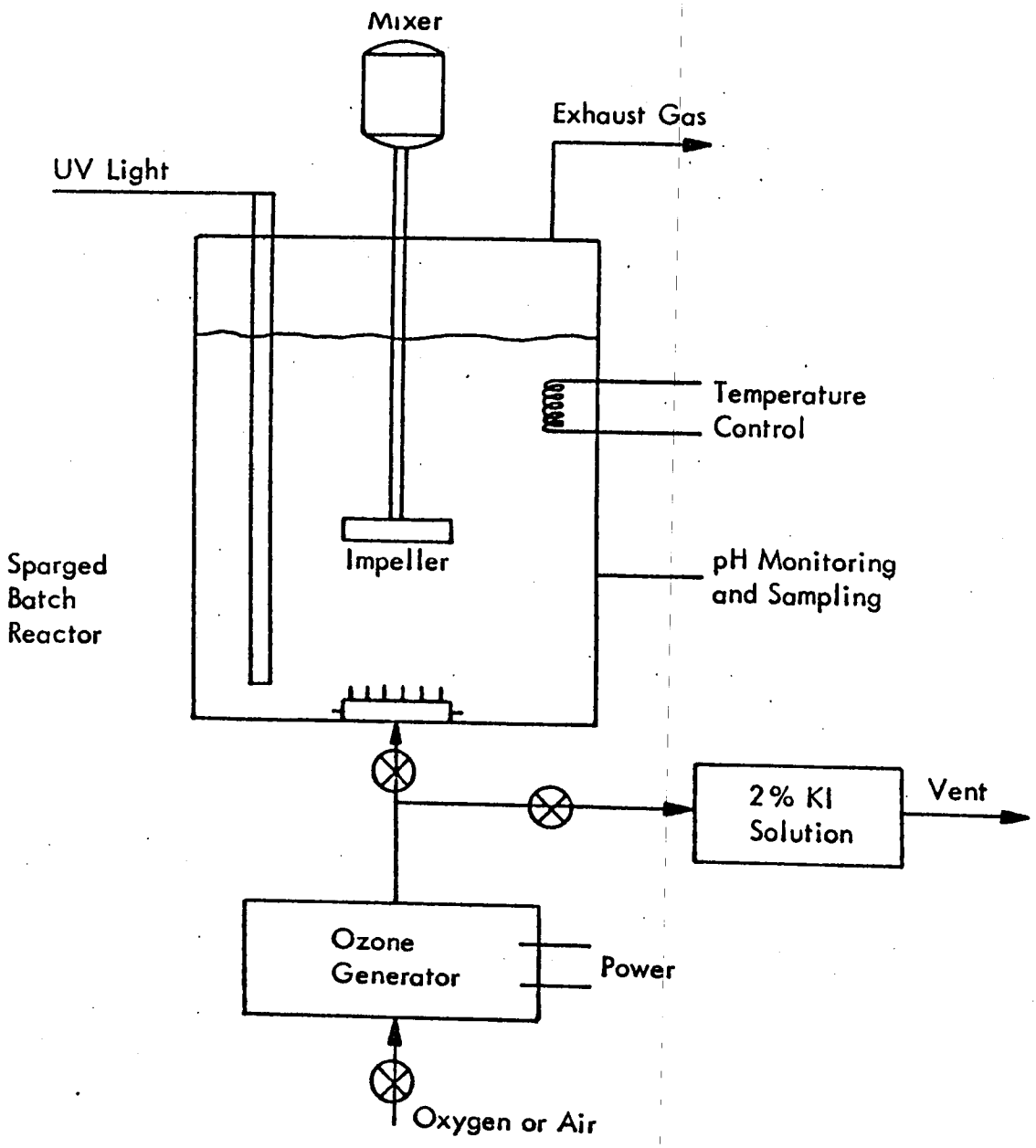


Figure 10. Schematic for Ozonation/UV Irradiation Apparatus

Source: Prengle et al., 2nd International Ozone Symposium, May 1975.

PCP has been reduced to levels below 0.5 parts per million (ppm) from initial concentrations of 70 ppm.[11]

The chemical reaction for PCP reduction although not completely verified appears to be similar to that of Figure 11. PCP may be initially dehalogenated followed by ring oxidation.

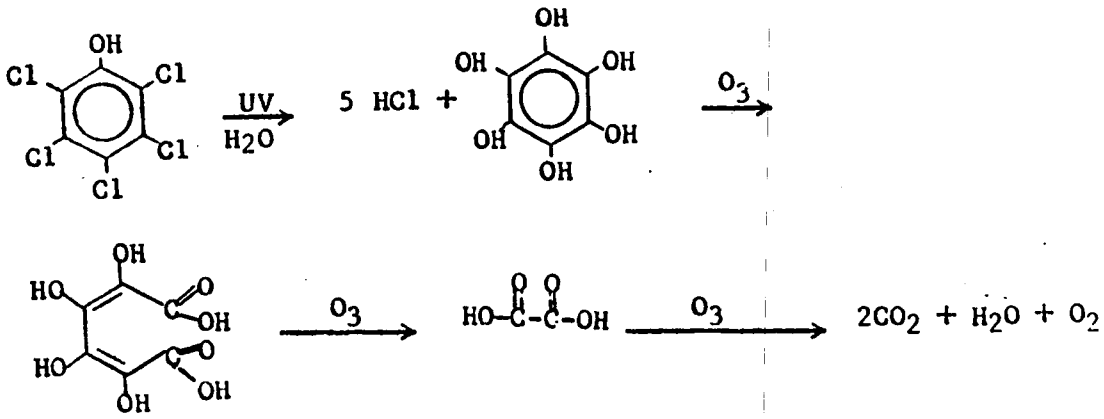


Figure 11. Chemical Reaction for PCP Reduction

Source: State-of-the-Art Report - EPA, August 1978.

Figure 12 shows results of different UV inputs and UV and ozone alone. It appears that 1.32 watts/L UV is as much as is useful. Results of PCP and other pesticide destruction are shown in Table 4.

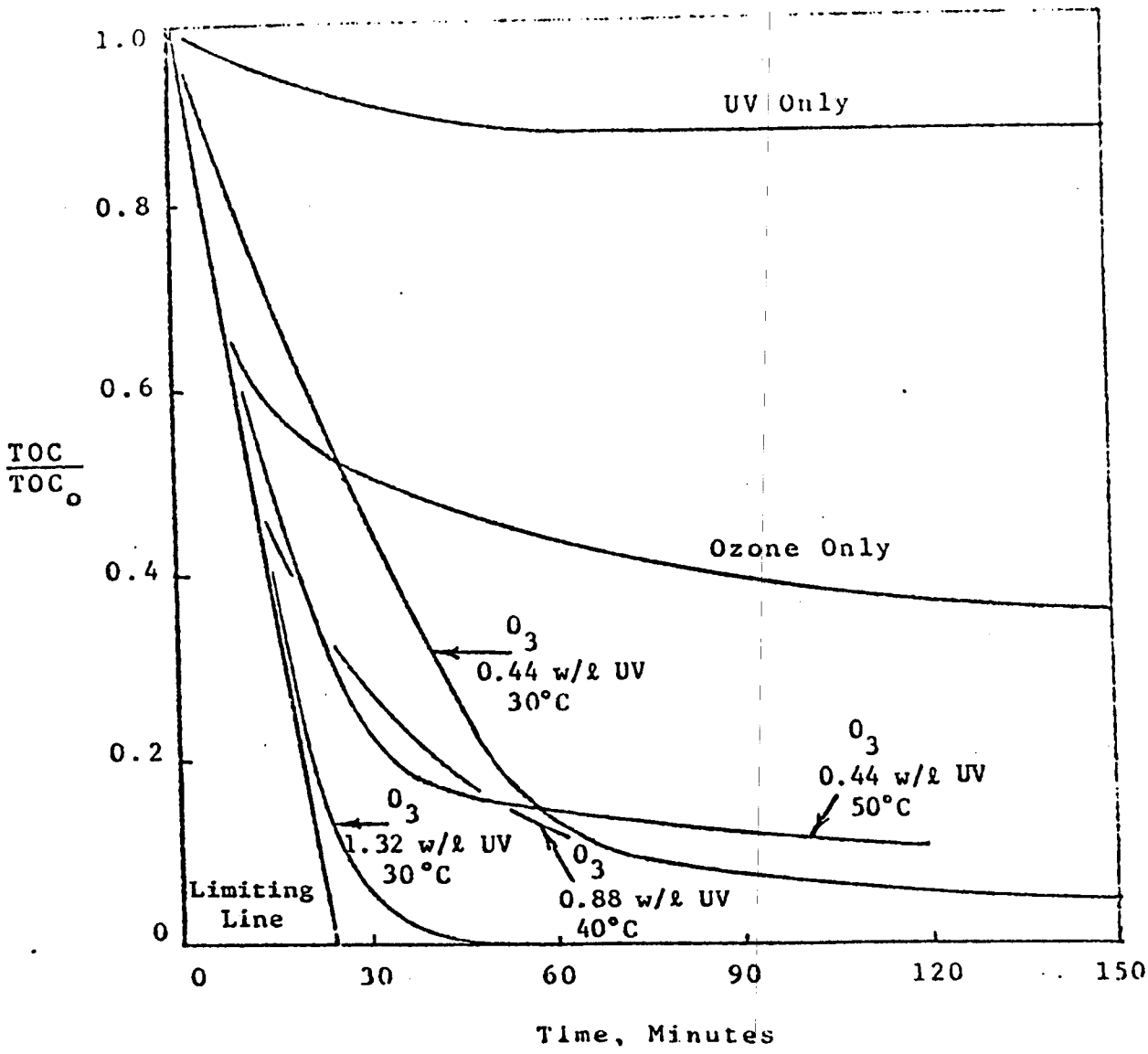


Figure 12. Destruction of Pentachlorophenol TOC (Initial PCP, 70 mg/L)

Source: U. S. Department of Commerce, July 1976.

TABLE 4

TYPICAL RESULTS OF OZONE/UV IRRADIATION OF PESTICIDES

Pesticide	Solution temperature (°C)	Ozone concentration (ppm)	UV light concentration (w/l)	Apparent percentage detoxification	Starting pesticide concentration (ppm)	Residual pesticide concentration (ppm)	Total time elapsed (min)
DDT	30	10	1.32	> 99.9	0.057	< 0.0005	30
PCP	30	10	1.32	> 99.3	71.0	< 0.5	15
Malathion	25	50	1.32	> 99.8	55.0	< 0.1	30
Baygon®	25	20	1.32	> 99.8	49.0	< 0.1	30
Vapam®	25	20	1.32	> 99.3	70.0	< 0.5	30

Source: Prengle et al., 2nd International Ozone Symposium, May 1975.

IV. TREATABILITY STUDY

A. Introduction

The pentachlorophenol samples used in this study were obtained from Langdale Company, Sweetwater, Tenenssee. Langdale discharges approximately 9,000 - 12,000 gallons of wastewater a day. It is laden with oils and PCP along with other wood tars, resins, and sugars. Langdale currently treats its waste by oil-water gravity separation followed by two ponds in series. The first pond acts as an additional oil-water separator, while the second pond is equipped with spray atomizers to enhance evaporation.

During periods of dry weather, Langdale was able to maintain its water balance without major difficulties. When needed, two evaporation tanks, heated by #2 diesel fuel were also available. Because of the rising costs associated with the diesel fuel, these evaporating tanks are not an ideal treatment system.

Permission had been granted by the Tennessee Division of Water Quality Control, for Langdale to discharge wastewater to the City of Sweetwater's municipal sewage treatment plant. Dilution was taken into account so as to allow Langdale to discharge PCP in quantities not to exceed 14 parts per billion (ppb) in Sweetwater's final effluent. The State's reasoning for this decision was based on fish tainting being associated with the 14 ppb limitation. Langdale knew that this was only a temporary solution since proposed pretreatment guidelines for the timber industry were zero (0) discharge.[4] A surprise came to Langdale however on May 19, 1980 when RCRA listed wastewater from the wood preserving industry as a hazardous waste. This meant that Langdale

would have to cease discharge to the municipal system on November 19, 1980 when RCRA went into effect. The situation gave Langdale several alternatives. First, they could evaporate all their wastewater, which would undoubtedly require use of the energy dependent evaporating tanks. Second, they could design a treatment system to treat their wastewater to below detection as required by the regulations and continue to discharge to the City of Sweetwater. A third alternative would be for Langdale to change its operation to a dry process using salts rather than PCP.

Several changes in regulations have occurred since Langdale originally initiated this study. The first change came on November 17, 1980 when wastewater treatment facilities were delisted as hazardous waste management facilities. This does not apply to Langdale however since earthen ponds are excluded. The next change came on January 29, 1981, when existing plants were excluded from PCP limitations. As a result, Langdale was no longer in need of a treatment scheme to remove PCP from their waste streams.

This study is still of importance to new sources as they will still have to meet zero (0) discharge limitations for PCP. Langdale also may benefit from this study since the State of Tennessee can still be more restrictive than the federal regulation if a water quality limited stream segment is involved as is the case with Langdale.

B. Methods and Materials

In this study an OREC Model 03B2-O/S (Ozone Research & Equipment Corporation of Phoenix, Arizona) was used as the ozone generation source. A small portable ultraviolet light, Model UVS-54 by Mineralight was used as the UV light source. The lab apparatus is shown in Figure 13.

The original mode of operation was to treat the waste with UV light and ozone simulataneously. Several problems arose to prevent this arrangement. The waste foamed during the process due to a combination of ozone being bubbled through the waste, and unknown reactions with tars, sugars, resins, and possible surfactants in the waste. For this reason the waste was treated in a two-stage method.

The chemistry of the reaction as shown in the literature[12] indicated that the UV light should be the first step followed by ozonation. The UV light was held constant at 254 nm since the literature[8] shows this to be the most effective range. The ozone concentrations were varied by increasing or decreasing the voltage through the generator. The ozone flow rate was held constant at a value which allowed maximum ozone contact with waste, yet minimum foaming action.

The contact time was varied merely by removing a sample from the reactor vessel at various times during each run. A short method COD (chemical oxygen demand) test was run throughout the experiment to verify possible trends occurring in the reaction vessel, indicating possible treatment of the waste.

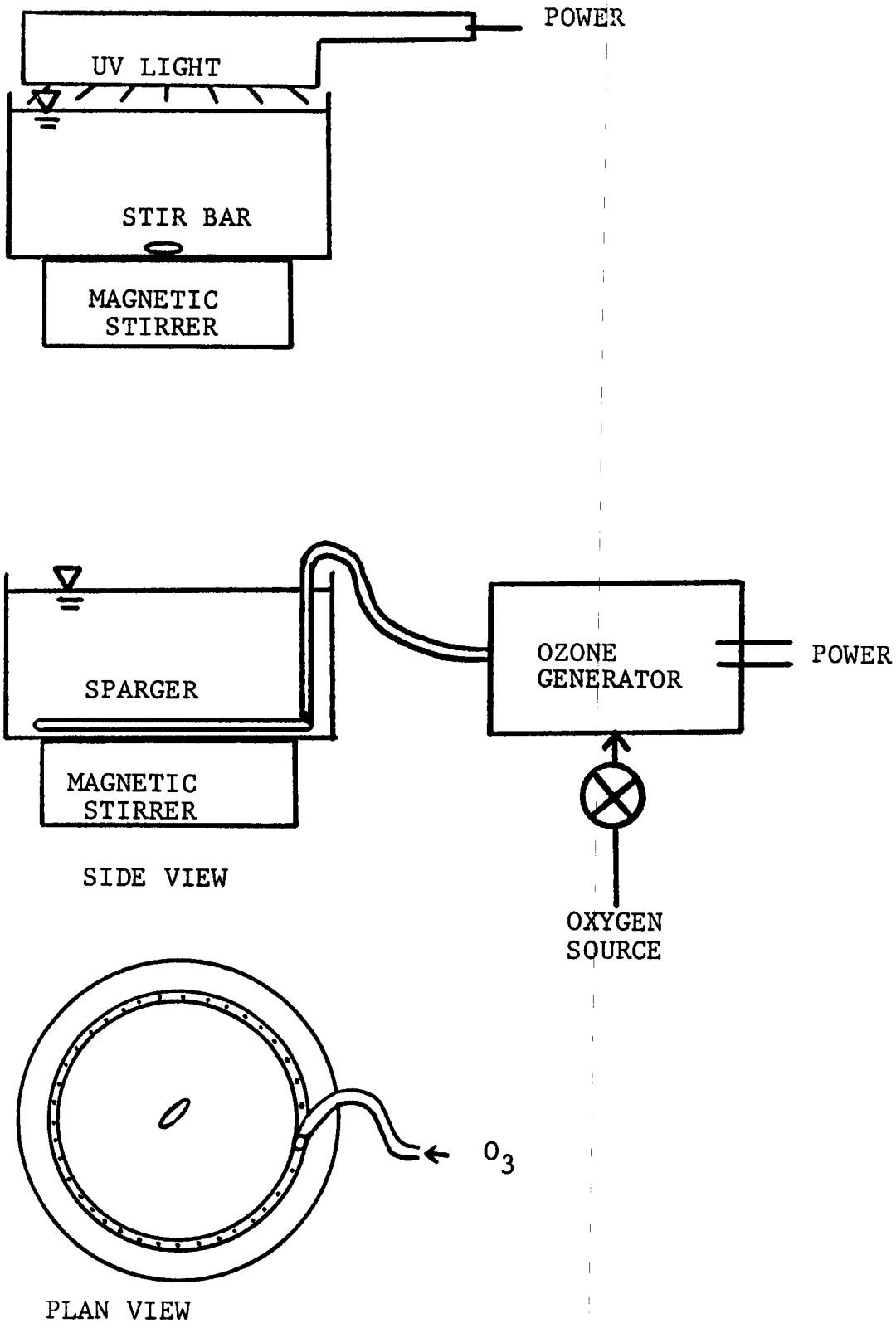


Figure 13. Laboratory Set-up

Three runs were performed at three separate ozone concentrations varying from approximately 3 ppm to as high as 21 ppm. Each reactor vessel started with 1.5 liters of waste and a temperature of 17°C.

All waste used in this study had first been treated at Langdale (primarily gravity oil separation and settling) and then chemically flocculated using surfactants. Chemical flocculation was employed for several reasons. The first reason was to help eliminate the foaming and the second being to remove as much of the oils as possible. This was to enhance the effectiveness of the UV light. UV penetration appeared to be minimal when using the raw waste which was quite opaque. Chemical flocculation provided a clear, slightly pale yellow colored liquid. Foaming was also reduced considerably.

V. RESULTS

Results of this study which includes short method COD results and PCP concentrations are presented in Table 5. Because of the expense related with PCP analyses, only five (5) samples were actually sent out to be analyzed. These five (5) samples were considered the critical samples which would indicate success or failure of the experiments.

TABLE 5

COD AND PCP RESULTS

		Run 1		Run 2		Run 3	
	time (min)	COD (mg/L)	PCP (ug/L)	COD (mg/L)	PCP (ug/L)	COD (mg/L)	PCP (ug/L)
UV	0	*	*	320	*	400	2400
	120	*	*	560	*	400	2700
O_3	0	1600	1300	560	*	400	2700
	30	*	*	280	*	320	*
	60	1400	*	280	*	360	*
	120	1200	*	360	*	240	*
	180	*	*	*	*	240	130
	240	1320	*	*	*	*	*
	300	1240	23	*	*	*	*

Note: * Denotes - no test performed.

See Table 6 for test conditions pertaining to run 1, 2, and 3.

TABLE 6

TEST CONDITIONS FOR RUNS 1, 2, AND 3

Reactor Volume	1.5 liters	1.5 liters	1.5 liters
UV Reaction Time	120 min.	120 min.	120 min.
Ozone Flow Rate	0.7 cfm	0.7 cfm	0.7 cfm
Ozonator Voltage	60 volts	90 volts	110 volts
Ozonator Amperage	.9 amps	4.1 amps	5.1 amps
Ozone Concentration	3.6 mg/L	18.2 mg/L	21.4 mg/L

The COD results are plotted on Figure 14 and show expected trends. In general the COD results show a gradual decrease in the waste. The COD's are still high which indicate that the wastewater still has a high pollutant level. It should be noted that the COD of run number one (1) is considerably higher in the raw sample. This is probably due to the fact that this sample was collected at a different time than were runs two (2) and three (3). They were also treated with surfactants at a different time and apparently not as well.

During the course of the experiment, a definite color reduction was noted in all three runs. Each run began as a deep straw yellow color. Even after ten (10) minutes of ozone, there was a slight color change. Each run produced a clear liquid during the course of the experiment. This color change would imply a destruction of organics. No color reduction was noticed after two hours of UV light which preceeded each ozone run.

PCP results showed a large reduction in concentration during the course of the experiment. PCP concentrations as low as 23 parts-per-billion (ppb) were exhibited in run one (1) after five (5) hours of ozone at a low concentration (3.56 mg/L). Run three (3) showed 130 ppb after only three (3) hours at a high concentration of ozone (21.376 mg/L). These results show a 98+ and 95+ percent reduction in PCP concentrations in runs one (1) and three (3) respectively.

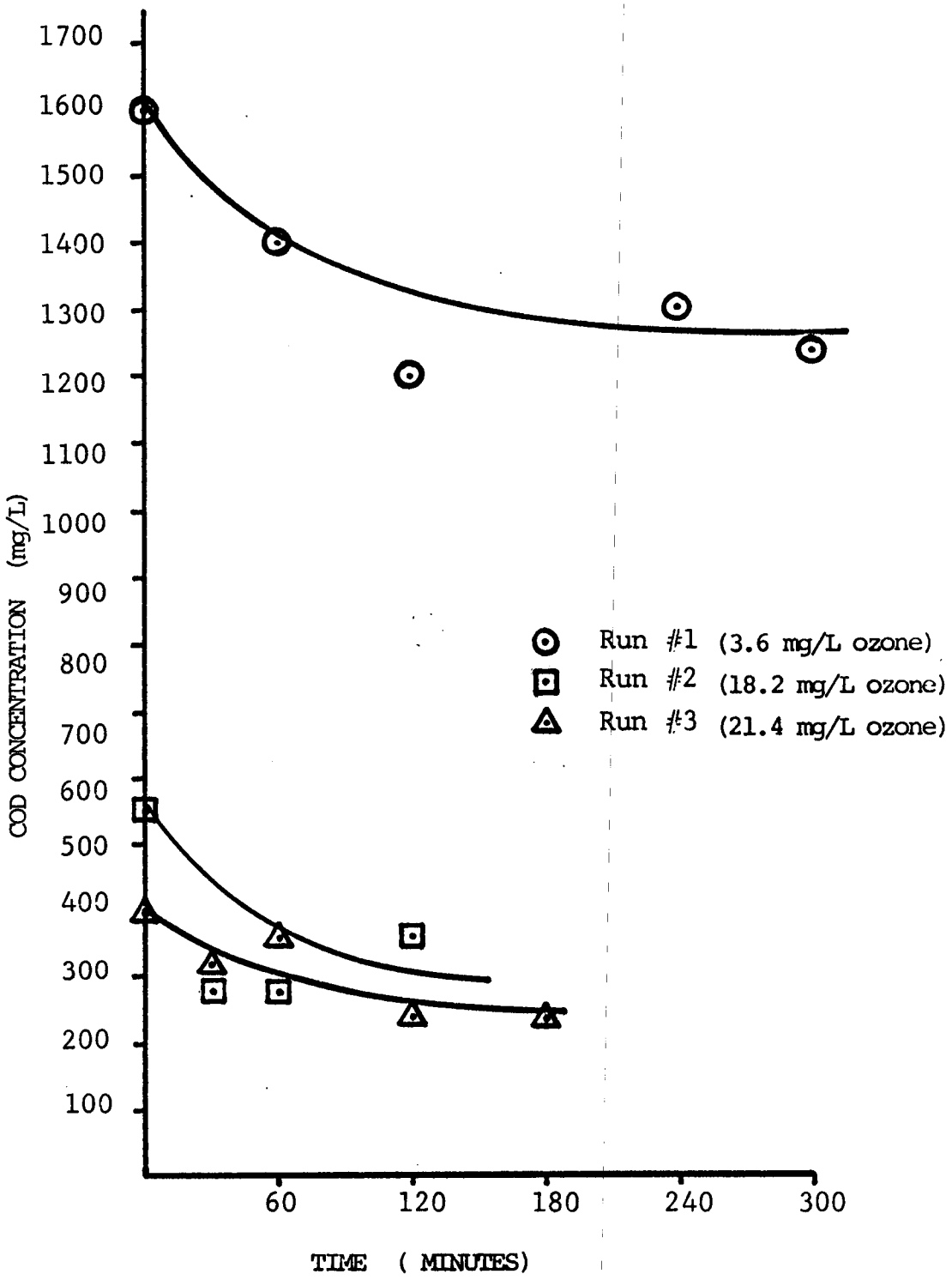


Figure 14. COD Test Results

VI. INTERPRETATION OF RESULTS AND SUMMARY

Although this study did not achieve a total destruction of PCP, it did succeed in reducing PCP concentration to near detectable limits. Detection limits for PCP is in the 1 to 2 ppb range using gas chromatograph/mass spectroscopy (GC/MS) as stated by the commercial laboratory used for PCP analysis in this study (Stewart Laboratory, Knoxville, Tennessee). The literature[11, 12] discusses treating PCP to the low parts-per-million (ppm) range from higher concentrations. This study shows that treating to the low ppb range is also feasible. The total destruction of PCP using UV/ozonation is highly possible.

This study had many setbacks and problems. The portable UV light used was not the best possible set up and was chosen because of limited funding for the project. There was no way to determine actual UV penetration or intensity. The foaming problem prohibited the use of UV and ozone simultaneously. The reaction vessels were not made of quartz which prohibited penetration by UV light therefore precluding mounting the light under the reactor vessel. Had there been a better technique employed with proper UV equipment the study might have reduced the PCP concentrations even more.

The contact time in this study was also a point of contention. Since UV light application was not properly monitored, the UV contact time used in this study was merely a chosen value.

The COD values remained high even though a general reduction trend was noted. The literature[9, 10, 13] reports destruction of most refractory organics to produce CO_2 and H_2O. However, even though

reaction time was sufficient to destroy most of the PCP and presumably other organics there is no reason to presume that this contact time was sufficient to reduce all organics.

VII. COST ANALYSIS OF UV/OZONATION PROCESS

A direct cost comparison between the UV/ozonation process and current "state-of-the-art" technology will be difficult since EPA[6] did not include UV/ozonation in the development document for the industry. EPA considers evaporation, preceded by oil-water separation, flocculation, and sand filtration to be the "state-of-the-art" and recommended treatment scheme for the steaming wood preserving industry. This would be a no discharge system.

Since the UV/ozonation process also needs primary oil separation and flocculation, these costs will carry over to both treatment schemes. EPA[6] states that almost one-half of the initial capital costs are involved in the spray evaporation equipment and the land required which are not needed with UV/ozonation.

Edwards, et al.[14], presents some cost data for a 40,000 gallon per day ULTROX plant which is a commercially built UV/ozone type package plant. This data is presented in Table 7 which shows equipment and operating and maintenance costs.

When looking at the overall cost picture for the treatment schemes, UV/ozonation appears quite attractive. It does not require the large amounts of land that spray irrigation does and it also destroys the PCP as opposed to atomizing it as an airborne pollutant or depositing it in the sludge as an evaporation system would tend to do.

TABLE 7

EQUIPMENT PLUS OPERATING AND MAINTENANCE COSTS
40,000 GPD ULTROX PLANT

Reactor	$94,500
Generator	30,000
	$124,500
O & M Costs/Day	
Ozone generator power	$ 4.25
UV lamp power	15.00
Maintenance (Lamp Replacement)	27.00
Equipment Amortization (10 years @ 10%)	41.90
Monitoring Labor	85.71
TOTAL/DAY	$173.86
Cost per 1,000 gals (3,785 liters) with monitoring labor	$4.35
Cost per 1,000 gals without monitoring labor	$2.20

Source: Arisman and Musick, General Electric Co., Hudson Falls, NY, Zeff and Crase Westgate Research Corp., West L.A., California.

Source: Edwards et al., Ebon Research Systems.

VIII. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

Many problems were encountered in this study. The foaming problem mentioned previously was the most significant since that prohibited treatment with UV and ozone simultaneously. Other problems included a poor choice of UV lamps, since it was not submersible; breakdown of ozone generator; lack of funds for sufficient analytical testing; and no measurement device to determine UV intensity or concentration. Considering these problems encountered in the study, and the marginal laboratory set-up, it is encouraging to see the results that were obtained. A proper set-up could conceivably obtain concentrations below detection limits and provide the industry with an alternative to their present dilema concerning new and proposed Federal regulations.

It is difficult to interpret whether this study truly examined the UV/ozonation process. Ozonation definitely played a major role in the PCP reductions, however there is no way of determining the role of the UV light. A separate ozonation study might have achieved similar results.

B. Recommendations for Future Studies

The ozonation aspect of these experiments appear to have been quite successful. Ozone concentrations seem quite reproducible by varying voltage on the machine. The UV light segment needs a complete change so as to provide reliable data. A quartz lamp which is submersible must be employed so as to provide UV light during the

ozonation phase. A reliable method of measuring UV intensity and concentrations must also be incorporated.

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VITA

Michael A. Miller was born in New Brunswick, New Jersey on April 27, 1955. He attended elementary school in Spotswood and graduated from South River High School, South River, New Jersey in 1973. He completed a Bachelor of Science Degree in Civil Engineering at Old Dominion University in Norfolk, Virginia in December 1977. He began work in pursuit of a Master of Science Degree from the University of Tennessee at Knoxville in March of 1978 while working as an Environmental Engineer for the State of Tennessee, Department of Public Health. He is currently a Process Engineer in the Environmental Control Group for General Electric Company in Mount Vernon, Indiana.