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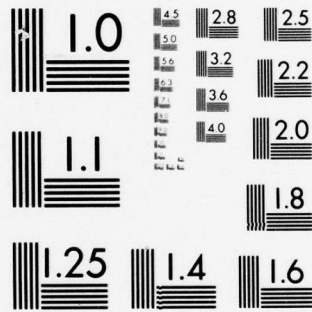
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EFFECTS OF ULTRASOUND ON MUST HOSPITAL COMPOSITE WASTEWATERS.

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by

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Kinetic mathematical models were derived to express the rate of COD and TOC destruction as a function of ozone concentration, VVM and organic concentration. These models can be used for design and scale-up of similar ozone-sound reactors.

Insonation was found to increase system overall oxygen mass transfer coefficients ($K_L a$) in the range of 1% to 36% over the no sound condition. The value of K_L obtained was directly related to position above the gas sparger and VVM.

Improvements in air-stripping rates of organics in UF permeates were noted when sound waves were employed over previously reported plain air-stripping experiments.

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1.0 INTRODUCTION

This report is a summary of the work performed under USAMRDC Contract DAMD-17-77-C-7031 entitled "Effects of Ultrasound on MUST Hospital Composite Wastewaters." The experimental portion of this contract was completed during the time period May to August 1977.

Previously, the viability of the concept that the presence of sound waves in an ozone reactor enhanced both oxidation and reaction rates was established during Contract DAMD-17-76-C-6057 entitled "Mass Transfer and Reaction Rate Studies of Ozonated MUST Wastewaters in the Presence of Sound Waves" [1]. Further, it was demonstrated that the auto-decomposition rate of ozone to nascent oxygen with the subsequent production of other oxygen free-radical species was increased when ultrasound was present. These conclusions were drawn from experimentation with MUST hospital composite and clinical laboratory wastewaters, both of which were synthetically produced reverse osmosis permeates. The major effort was expended on wastewaters produced by laboratory activities within the MUST hospital complex. The rationale for this emphasis was that the water processing element (WPE) was required to treat each non-sanitary wastewater stream emanating from the MUST hospital individually and the laboratory wastewaters were shown to be the most refractory of the six major input streams which included the operating room, kitchen, x-ray laboratory, shower, and laundry flows. Since this work was performed however, the design specifications on the ozone reaction portion of the MUST WPE treatment system has been modified. For instance, it is

no longer a requirement to treat a complete stream of individual wastewaters. However, a second modification now requires that before discharge to the environment, all ultrafiltration (UF) permeates must be treated by the full ozonation system [2].

2.0 OBJECTIVES

Basically, this contract was to investigate three potential application areas of sonic and ultrasonic sound waves. The first task was to examine the effect that sound waves would have during the ozone oxidation of UF and RO synthetic hospital composite permeates utilizing low (i.e., 0.75 and 1.00 weight percent) ozone concentrations in air at low volumetric gas flow rates (i.e., volume of gas per minute [measured at the inlet pressure to the ozonator] volume of liquid (VVM) of 0.1, 0.2, and 0.4). The second task was primarily concerned with delineating the effects of sonic and ultrasonic sound waves on the mass transfer of oxygen into solution at the above-mentioned low VVM rates. Task three was to examine the effects of insonation on the stripping of UF synthetic permeates at 45°C.

3.0 EXPERIMENTAL

3.1 General

In this section of the report is described the synthetic MUST hospital composite UF and RO permeate formulations and their production, the experimental equipment and the analytical procedures utilized. Figure 1 is a flow diagram for the experimental system employed.

3.2 Formulations

Throughout the course of this experimentation synthetic UF and RO permeates were manufactured from the ingredients listed in Table 1. For each day's operation, analytical reagent-grade chemicals were mixed in 64.0 liter batches with City of Tucson tap water serving as the solvent. All chemical additions were made with either micro-liter syringes produced by the Hamilton Company, Model No. 80300 and Model 80500 which were respectively 100 micro-liter and 10 micro-liter pipettes or by volumetric pipettes. Solid chemical in the formulations was first dissolved in one-liter of tap water and then the desired quantity pipetted into the batch.

3.3 Equipment

3.3.1 Ozone Reactor. A six-inch internal diameter by 7.5 foot high reactor was fabricated from pyrex glass pipe. The bottom closure plate of the ozone reactor was constructed from 304 type stainless steel which served as the acceptor of the Biosonic IV ultrasonic system and was backed up with an aluminum plate. Two ports (0.25 inch diameter) served as

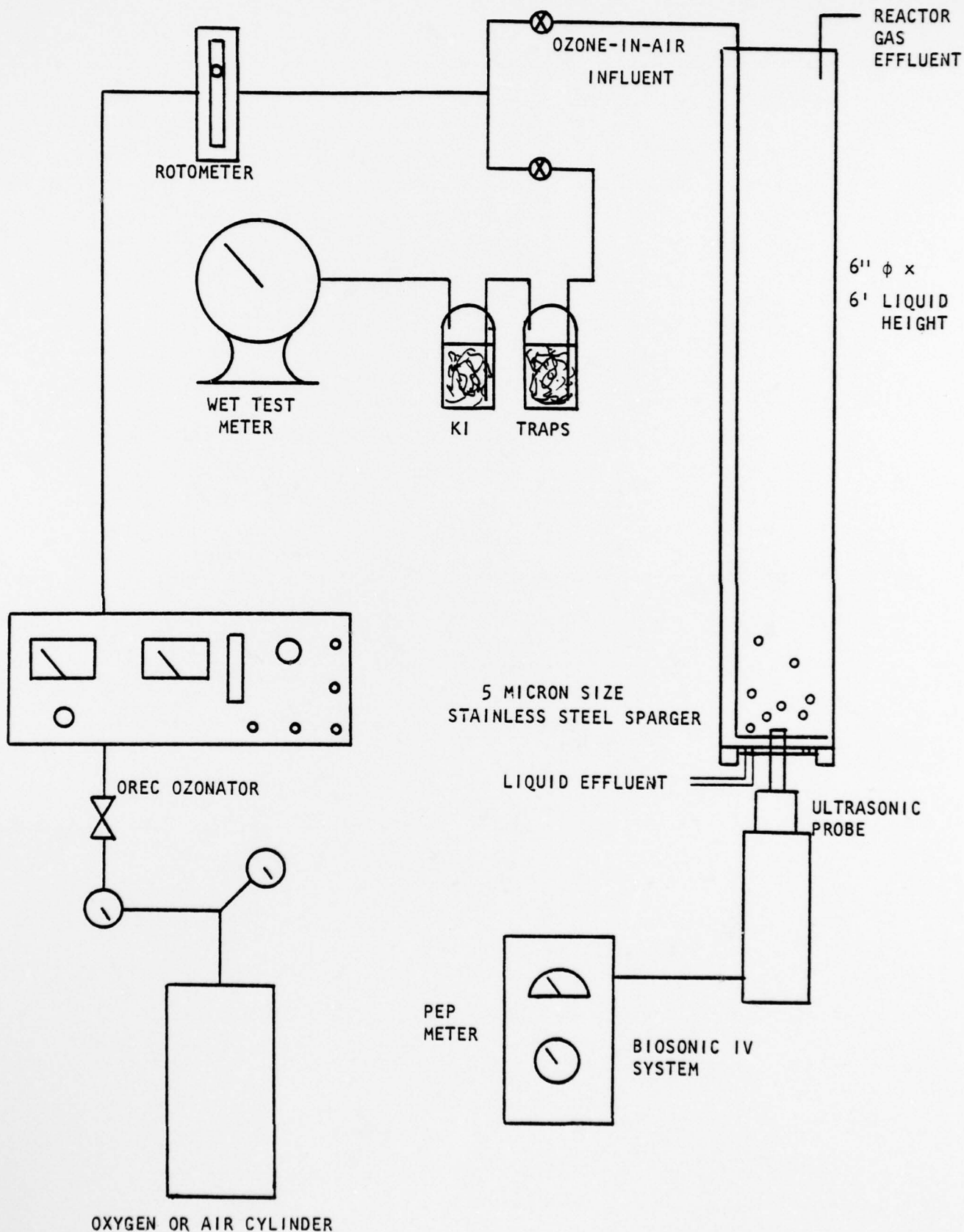


FIGURE 1. EXPERIMENTAL APPARATUS.

TABLE 1

ORGANIC CHEMICAL COMPOSITION OF HOSPITAL COMPOSITE
ULTRAFILTRATION PERMEATES AND REVERSE OSMOSIS PERMEATES

	UF PERMEATE	RO PERMEATE
methanol	29.8 μ l/l	16 μ l/l
acetone	6.3 μ l/l	5 μ l/l
acetic acid	3.4 μ l/l	2.8 μ l/l
diethyl ether	0.6 μ l/l	0.1 μ l/l
N,N-Diethyl-m-toleramide (Deet)	0.8 mg/l	0.2 μ l/l
ethanol	0.5 μ l/l	0.5 μ l/l
oleic acid	0.5 μ l/l	0.1 μ l/l
phenol	1.3 mg/l	0.4 mg/l
urea	18.0 mg/l	12.0 mg/l
Kodak X-Omat Developer	942 μ l/l	283 μ l/l*
Kodak X-Omat Fixer	942 μ l/l	283 μ l/l*

* Assumed R.O. membrane 70% rejection based on B-10 separation characteristics and an estimated 2:1 ratio for hydroquinone: acetic acid content which forms the major organic portion of the fixer/developer.

drain ports for the reactor which was always run in the semi-batch mode (i.e., continuous gas addition and fixed liquid volume, 6 feet). The top cover plate on the reactor likewise was produced from 304 stainless steel and had two 0.25 inch diameter ports. One port was used for admitting the ozone and air mixture through tygon tubing to a gas sparger located at the reactor bottom while the second port was used to permit residual gas to escape after it had been sparged through the reaction liquid. Liquid samples were taken from one of the bottom drain ports at the appropriate times. In each instance 2ℓ were removed, before the actual sample was taken, and returned through the top of the reactor. Pyrex conical pipe joints Model 72-0739 were used with the top and bottom plates. A complete set of drawings and description of the top and bottom plates has been reported by Sierka [1].

The gas sparger was of a doughnut design with an outside diameter of 5.0 inches while the inside hole diameter was 1.25 inches. The Biosonic IV ultrasonic probe tip was inserted through the hole in the gas sparger and therefore sound waves flowed concurrently with the gas bubbles coming from the 5-micron size 316 stainless steel sparger.

3.3.2 Ultrasonic System. For all experimentation, the Biosonic IV ultrasonic system was utilized. The unit had a lead zirconium titanate transducer which delivered up to 95% current efficiency at optimum performance. The unit had two ceramic discs in the transducer which provided a feedback from the probe to the generator and compensated for the required output assuring reproducibility in the reaction through constant power output. A power meter monitoring system was also used

which indicates peak envelope power (PEP) delivered from the generator to the head in the tip. This unit reflected any changes in the process due to generator output, voltage input, increased temperature of the generator, out-gassing of the solution, and increased temperatures resulting from energy input from the transducer. The unit was theoretically capable of delivering up to 300 watts of acoustical power to the reaction liquid. Control as to the amount of acoustical power was accomplished by a dial in the front of the system. Energy utilization for this unit has been reported by Sierka [1].

3.3.3 Ozonator. The ozonator used throughout the research was an Orec Model 03B1-0. For the majority of runs commercial air consisting of 20% oxygen and 80% nitrogen with negligible hydrocarbon content were fed to the ozonator at - 15 psig for ozone production. Pure oxygen at 10 psig served as the feed gas to the ozonator for two reverse osmosis and two ultrafiltration permeate runs. Tygon tubing was used to carry ozone-in-air or oxygen to the reactors. Tap water served as the cooling medium for the generator. The ozonator incorporated a water pressure limit switch which shut down the unit if the water pressure was below 3 psi or above 45 psi.

A powerstat permitted operation at the desired voltage. A watt meter and volt meter indicated primary operating values of the ozone generator. Increasing current increased ozone output. Increasing gas flow increased ozone output with attendant decrease in weight concentration ratio to air.

It was noted that a variation in ozone concentration occurred over each two-hour experimental run. The variation was apparently due to changes in cooling water pressure and operating temperature in the unit. Therefore, at the end of each run, the ozone production rate out of the ozonator was monitored and this concentration reported as the average ozone concentration admitted to the reactor.

3.4 Analytics

3.4.1 Chemical-Oxygen Demand (COD). COD tests were run on all samples utilizing standard methods procedures [3]. A normality of 0.10 was used for the potassium dichromate solution and the ferrous ammonium sulfate was 0.05 and 0.25 normality. A sample size of 10 ml was always employed for this test.

3.4.2 Total Organic Carbon (TOC). TOC data were obtained on a Beckman Model 915 Total Organic Carbon Analyzer using direct liquid injection of samples and standards. The samples were stripped of inorganic carbon by acidifying with concentrated hydrochloric acid to approximately pH 2.0, followed by bubbling pure oxygen through the sample for a period of one minute. All injections were performed with a Hamilton CR700-200 constant rate syringe in triplicate.

Total carbon standards were made by dilutions of a 1000 mg/l carbon standard containing 2.125 gms of potassium acid phthalate per l. All analyses were performed in the range 0 to 120 mg/l of total carbon for the synthetic UF permeate and 0 to 60 mg/l range of total carbon in the case of the hospital composite RO permeates.

3.4.3 Temperature and pH. The temperature of the batch was measured by sampling from the reactor bottom at 30 minute intervals and manually inserting a thermometer into the reaction liquid. A portion of the sample was retained for organic analysis and the remainder used to measure pH on a Beckman Expandomatic pH meter.

3.4.4 Oxygen Mass Transfer Procedures. A series of oxygen uptake runs were performed in the 6-inch diameter reactor. Laboratory distilled water was placed in the column to a depth of 6.0 feet. Sodium bisulfite (for deoxygenation) and cobalt chloride (for catalysis) were added according to the Thirteenth Edition of Standard Methods [3]. The water was discarded after companion runs were conducted (i.e., with and without sound) to prevent spurious results due to the build-up of salts or catalyst. Dissolved oxygen measurements were made with a Yellow Spring Dissolved Oxygen Meter Model 57 placed at depths of 6-inches, 12-inches and 55-inches above the gas sparger. The time to reach each 0.5 m/l change in dissolved oxygen of the reactor contents was recorded and used to calculate the overall oxygen gas transfer coefficient ($K_L a$).

4.0 RESULTS AND DISCUSSION

4.1 Task 1 - The Effect of Sound Waves on the Ozone Oxidation of MUST UF and RO Permeates at Low VVM's

4.1.1 General. In a preliminary design meeting the U.S. Army Medical Bioengineering Research and Development Laboratory (USAMBRDL) modified the design basis for the ozone reactors of the WPE process [2]. The primary design change is that all UF permeates must now traverse all stages of the ozone reactor before discharge to the environment. The discharge quality requirements are a TOC of 80 mg/l and a COD of 128 mg/l. Also, the synthetic formulations used to derive the reactor design relationships have been changed. Comparison of synthetic formulations previously employed can be made by consulting with past experimental work [1].

Examination of Table 1 reveals that the current synthetic formulation for the UF permeate contains the identical substrates as that proposed for the synthetic RO permeate, however in the former case they are present in a higher concentration with the exception of ethanol. The presence of high organic concentrations in the wastewaters to be treated requires high ozone mass transfer rates initially. This is particularly true of the UF permeate oxidation if it is to be carried out in the reaction-rate control mode.

To date, there does not exist information relative to the oxidation of the present UF permeate formulation. Sierka [3] previously reported on the oxidation of individual UF-MUST wastewater streams including the operating room, kitchen, laundry, x-ray, and shower wastes as well as

the total hospital composite. In the latter case, the actual UF processed hospital composite was pretreated with 1000 mg/l of Filtrabsorb-400 before ozonation for 120 minutes. This powdered activated carbon reduced the initial TOC from 81.3 to 43.0 mg/l while the ozone oxidized an additional 22 mg/l of TOC.

Of the five UF treated individual waste streams, only the shower wastes were reduced in TOC to 5 mg/l; the target quality, after the two-hour period of ozonation.

To provide data to derive design kinetic equations, a series of semi-batch experiments were carried out using the current MUST UF permeate formulation in the ozone-ultrasound system. Three experiments each were performed at constant VVM and variable ozone inlet gas concentrations and three experiments with variable VVM and constant ozone inlet gas concentrations with UF and RO permeates serving as the substrate.

Although the MUST ward containers limit the maximum liquid height to six feet for each state of the ozone reactor system, this parameter has not been optimized. Therefore, experiments with UF permeate were also performed at various liquid heights to obtain scale-up data with respect to ozone utilization and organic oxidation in the presence of ultrasound.

4.1.2. Kinetic Equation Development for UF Permeate Ozone Sound Oxidation. Six semi-batch runs (continuous addition of ozone-in-air) in the presence of ultrasound were carried out with the following operating conditions: (1) a starting pH of 9.0 and uncontrolled during the reaction,

(2) ambient temperature operation (approximately $26 \pm 1^\circ\text{C}$), (3) a 6.0 foot water depth in the reactor, and (4) a batch reaction time of 2.0 hours.

During the first three runs, an approximately constant ozone concentration of 1.0 weight percent (0.96% - 1.03%) in air was employed. The reaction gas was applied at three different VVM's (0.1, 0.2, and 0.4).

Figure 2 is a semi-log plot showing the ratio of TOC/TOC_0 as a function of batch ozonation time, while Figure 3 displays the run data on a COD basis. In Figure 4 is graphed the ratio of ozone leaving the reactor to that entering at various batch reaction times.

From Figure 2 it is evident that, as VVM is increased, the rate and extent of the organic destruction is enhanced. After two hours of ozonation, the TOC remaining for the 0.1, 0.2, and 0.4 VVM runs was 88%, 70%, and 48% respectively. On a COD basis (Figure 3), the extent of oxidation is greater than with TOC. These results basically reflect the difference in the nature of the TOC and COD tests. Where the TOC test quantifies the loss of organic carbon by total oxidation to carbon dioxide, the COD test indicates the change in molecular chemistry of the dissolved substrate and measures the oxygen demand of the substance remaining. The COD test, in other words, gives indication of the partial oxidation of the dissolved organics in solution.

For runs carried out at 0.1, 0.2, and 0.4 VVM, the percentage of COD remaining at the end of the run was 72%, 48%, and 22%.

The ozone concentrations of the gas leaving the reactor was monitored at irregular times throughout the run. In Figure 4, it can be seen that all of the ozone applied to the reactor was utilized when the UF

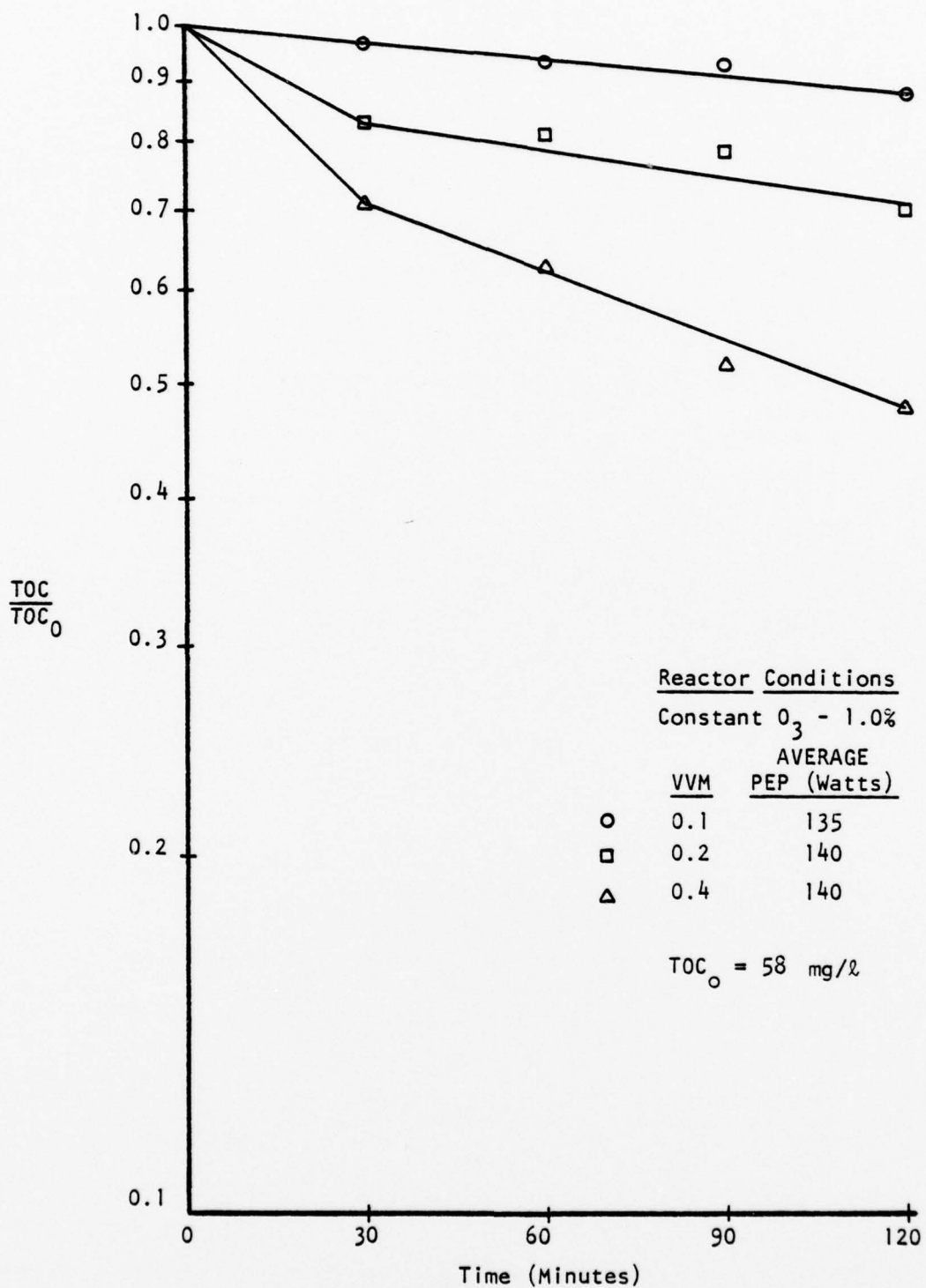


FIGURE 2. EFFECT OF GAS FLOW RATE ON TOC REMOVAL FROM ULTRAFILTRATION PERMEATES AT CONSTANT OZONE CONCENTRATION AND VARIABLE VVM.

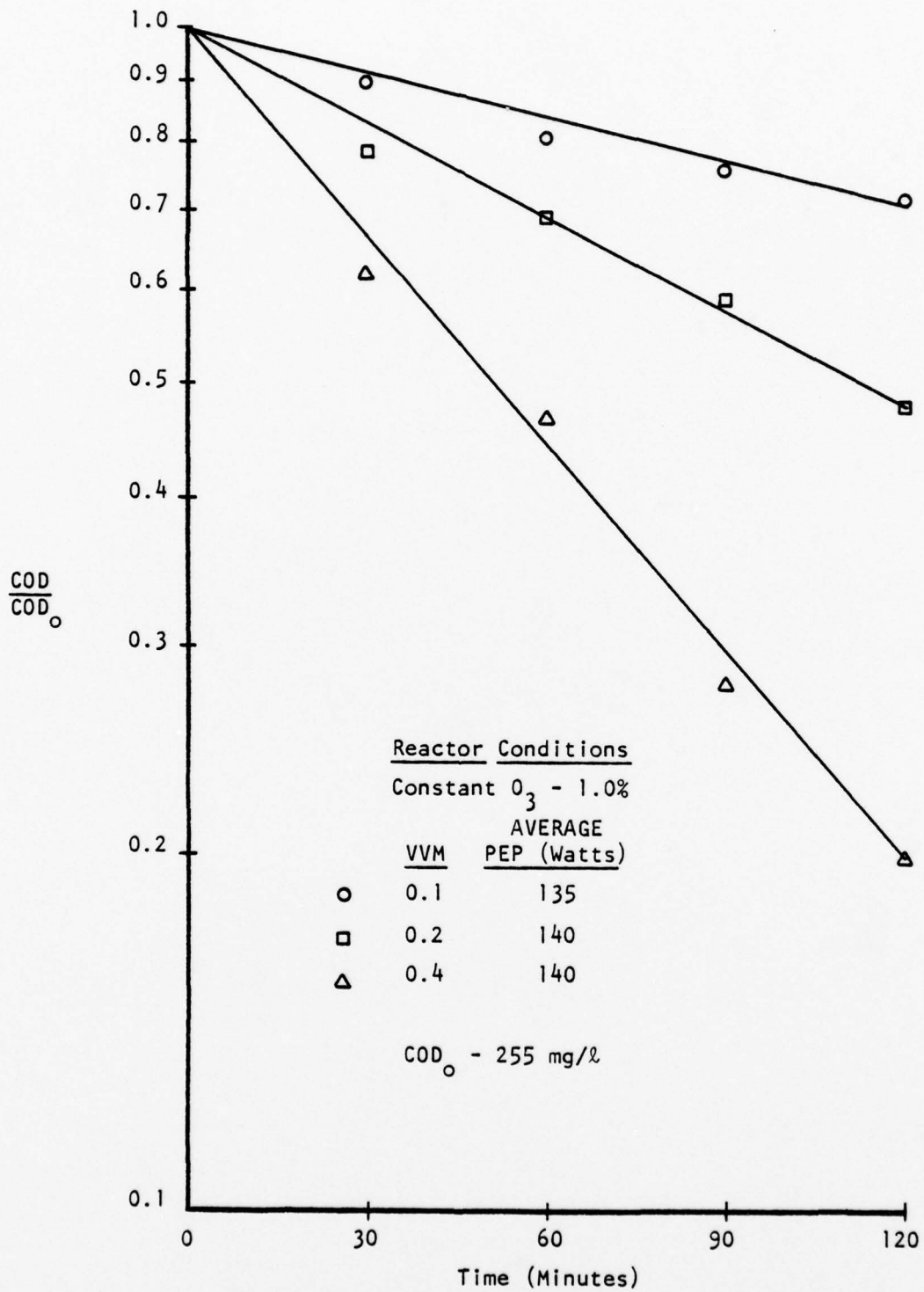


FIGURE 3. EFFECT OF GAS FLOW RATE ON COD REMOVAL FROM ULTRAFILTRATION PERMEATES AT CONSTANT OZONE CONCENTRATION AND VARIABLE VVM.

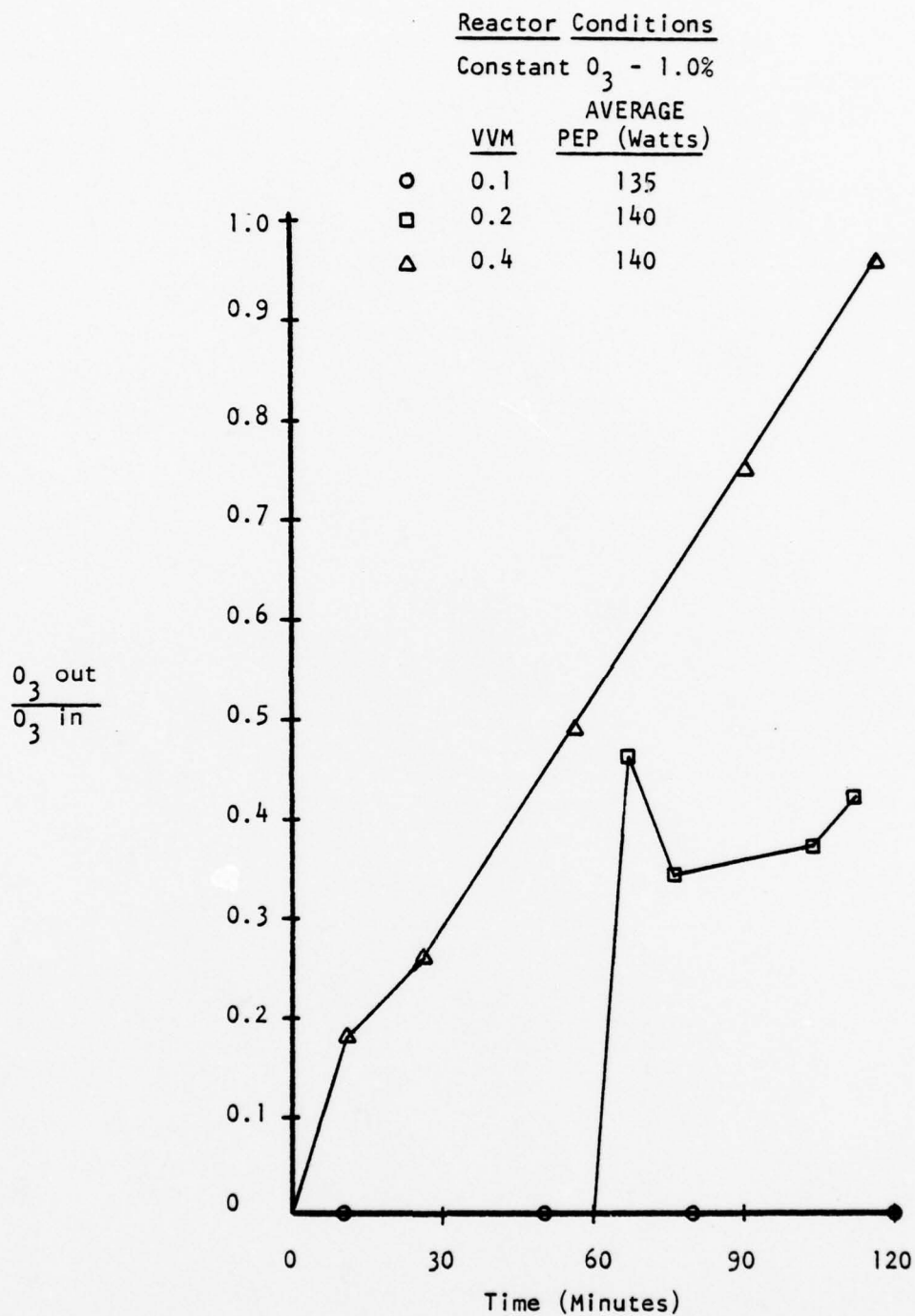


FIGURE 4. THE RATIO OF REACTOR OUTLET TO INLET OZONE CONCENTRATION AT VARIOUS REACTION TIMES DURING THE OXIDATION OF ULTRA-FILTRATION PERMEATES AT CONSTANT OZONE CONCENTRATION AND VARIABLE VVM.

permeate was being oxidized by ozone at the 0.1 VVM condition. Thus, the run was totally mass transfer controlled and represents the major reason that only 12% of the TOC and 28% of the COD was oxidized. The average ultrasound PEP level for the experiment was 135 watts. When the VVM was increased to 0.2, again approximately at the 1.0 weight per cent ozone-in-air concentration, no residual ozone was found in the gas coming from the top of the reactor until 60 minutes of the run had been completed. From that time on, to the end of the run at 120 minutes, the effluent ozone gas concentration ranged between 34% and 46%. As discussed above, the corresponding response was an increase in COD and TOC removals (i.e., 30% TOC and 52% COD).

Finally, when the VVM was increased to 0.4, ozone was first noted in the effluent gas stream from the column at 10 minutes into the run. The increase in ozone gas concentration from 10 to 120 minutes was linear with batch reaction time, until at the termination of the run, 96% of the ozone gas admitted was found to be exiting the reactor.

The next series of three runs were performed at constant VVM (0.4) and variable ozone gas concentration. Ozone gas concentrations were 0.86%, 0.96%, and 2.21% by weight in air. The first two ozone concentrations were produced from air while the 2.21% ozone by weight was prepared from pure oxygen. The use of oxygen was necessitated by the fact that the OREC ozonator could not produce an ozone concentration greater than 1.0% by weight when air was used as the feed stream to the OREC unit, for the utilized VVM operating conditions. The object of these last three runs was to obtain a portion of the data required to derive a kinetic relationship and quantify the ozone partial pressure effect.

Figures 5 and 6 show that as the inlet ozone concentration was raised from 0.86% to 0.96% and then to 2.12%, the TOC destroyed, at the end of two hours of oxidation, was 34%, 52%, and 61% respectively, while 70%, 80%, and 90% of the COD was destroyed. These figures point out that the partial pressure effect is highly significant in reducing the time required to produce a given organic quality effluent. Sierka [1], Gollan et al. [5], and See et al. [6] previously likewise demonstrated this effect.

Consideration of Figure 7 however, shows that as ozone concentration is increased, the amount of ozone leaving the reactor likewise increases, thus operating and energy cost penalties are incurred unless this ozone can be utilized in the precontactor or collected and readmitted to subsequent reactor stages. Further, it should be noted that ultrasound at PEP levels ranging from 140 to 180 PEP were employed. These sound levels represented the maximum obtainable PEP at the start of the run with this particular configuration. Since the sound energy was converted to heat in the reactor, the batch temperature generally rose between 0.25 and 2.0°C during the run depending on the PEP level. As batch temperature increased, PEP increased between 10 to 20 units. The number and size of bubbles also affected the PEP obtainable; normally PEP decreased with increases in superficial gas velocity.

Chian et al. [7] have studied ozone oxidation pathways in the presence and absence of ultraviolet light for compounds found in the synthetic reverse osmosis permeates. Since methanol, acetone and acetic acid make up the largest organic fraction of these wastewaters, these three

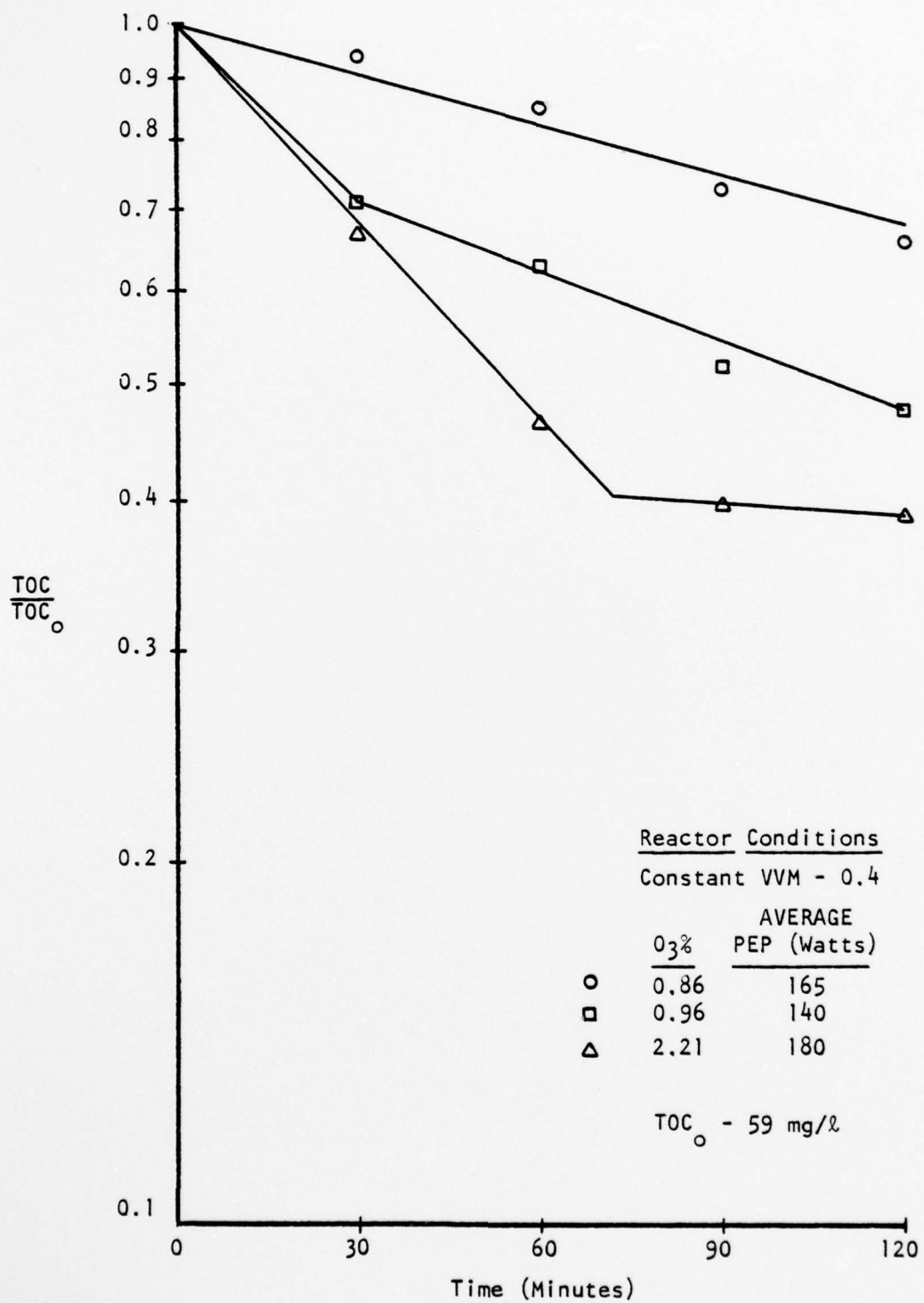


FIGURE 5. EFFECT OF OZONE CONCENTRATION ON TOC REMOVAL FROM ULTRAFILTRATION PERMEATES AT CONSTANT VVM AND VARIABLE OZONE CONCENTRATION.

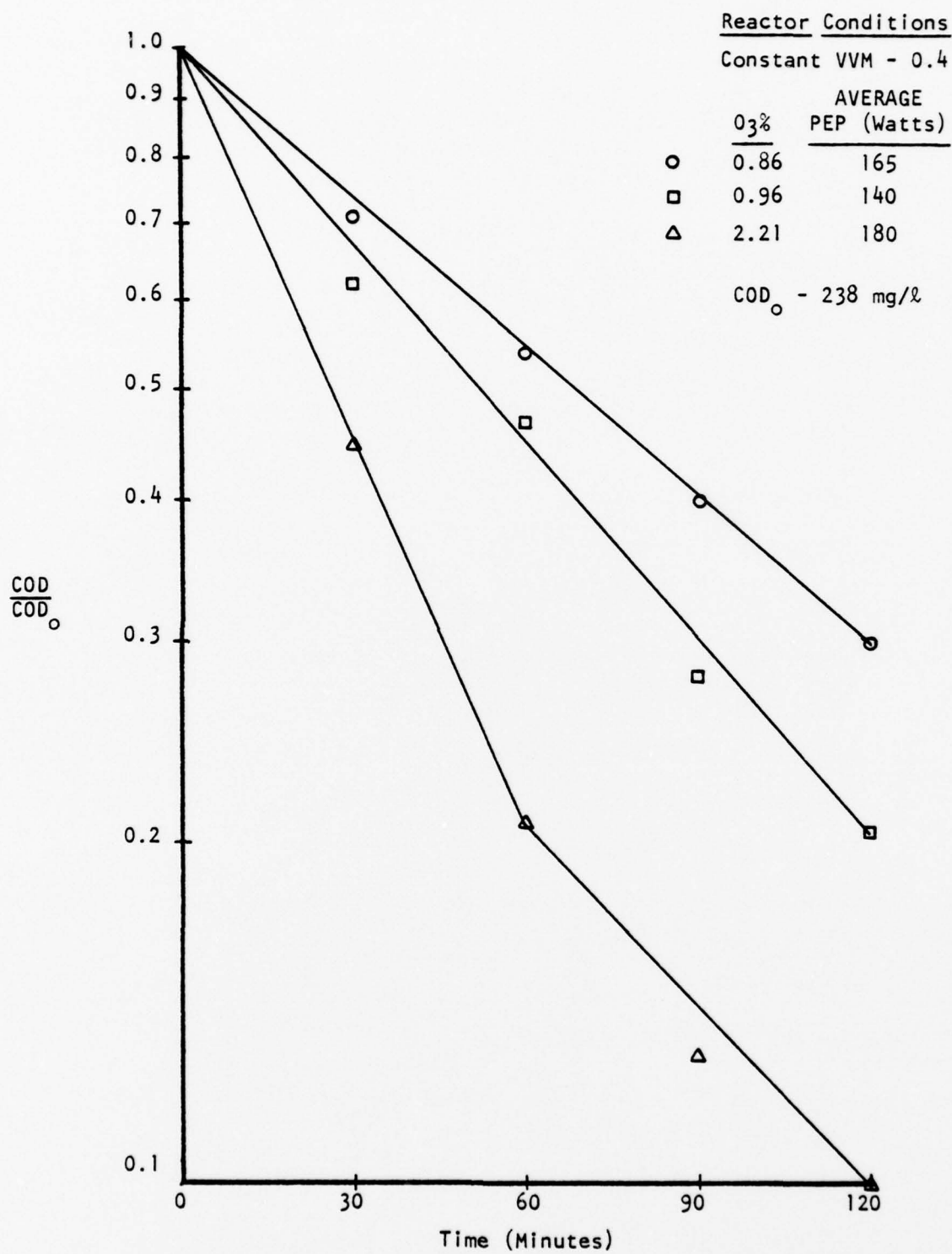


FIGURE 6. EFFECT OF OZONE CONCENTRATION ON COD REMOVAL FROM ULTRAFILTRATION PERMEATES AT CONSTANT VVM AND VARIABLE OZONE CONCENTRATION.

Reactor Conditions

Constant VVM - 0.4

	<u>O₃%</u>	<u>AVERAGE PEP (Watts)</u>
○	0.86	165
□	0.96	140
△	2.21	180

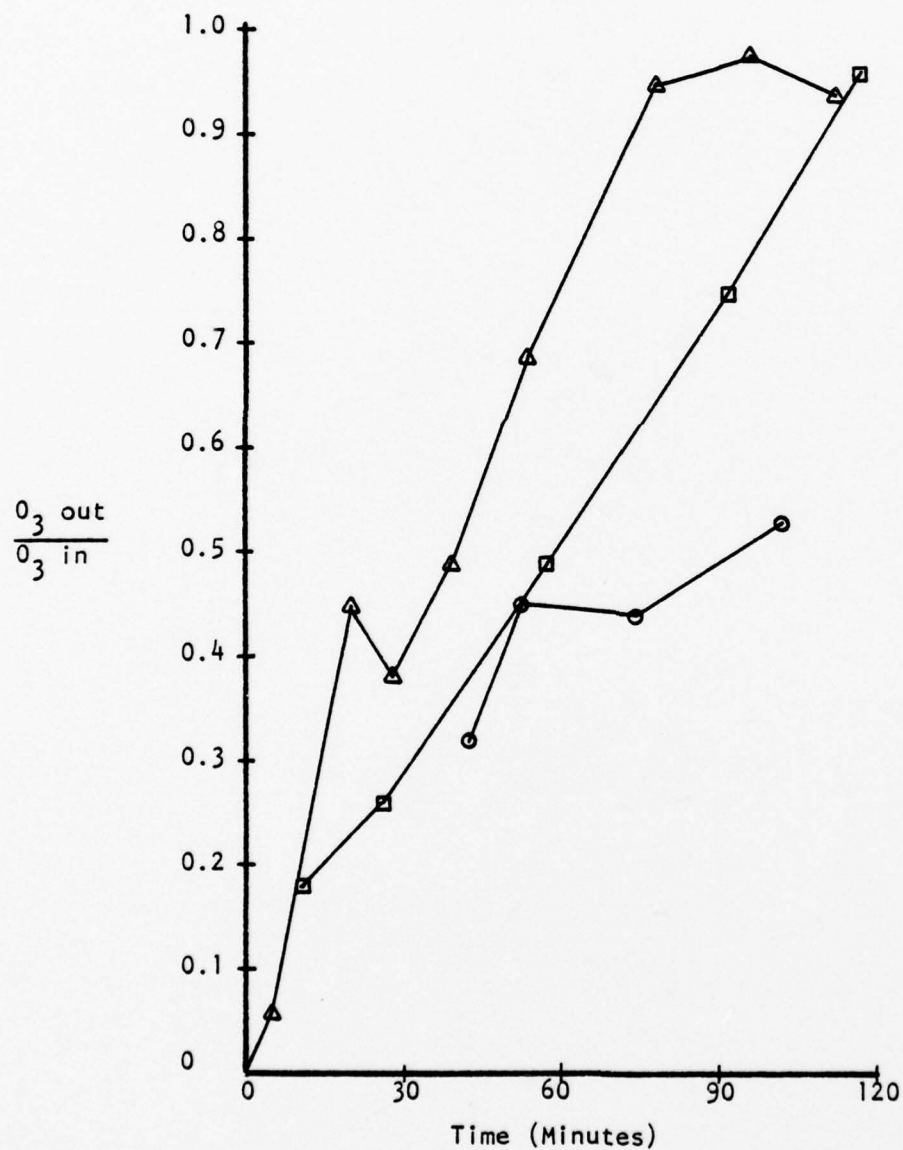


FIGURE 7. THE RATIO OF REACTOR OUTLET TO INLET OZONE CONCENTRATION AT VARIOUS REACTION TIMES DURING THE OXIDATION OF ULTRA-FILTRATION PERMEATES.

substrates and their oxidation products were of major interest. Chian et al., have shown that for methanol, the partial oxidation products include formaldehyde and formic acid, before the final oxidation to carbon dioxide. The TOC/COD ratio for this reaction would range from 4.0 to 1.33. For acetone, the identified partial oxidation products include acetic acid, glyoxilic and oxalic acid [8] with corresponding COD/TOC ratios of 2.66, 1.33, and 0.67.

In Figure 8 are shown the COD/TOC ratios for a portion of the data presented in Figures 5 and 6. These data show in a given batch reaction time that the COD/TOC ratio is lower as the ozone partial pressure increases. Thus, the COD/TOC trend seen by Chian [7] for single substrate oxidations and McCarthy et al. [10] for laboratory permeates is mirrored here. When the COD/TOC data are plotted against the TOC remaining in the batch (Figure 9), it can be seen that this ratio is approaching a value of less than one, which is expected since Chian has shown formic acid, glyoxilic acid, and oxalic acid are the final partial oxidation products prior to CO_2 production. These compounds have a COD/TOC ratio of 1.33, 1.33, 0.67 respectively. Sierka [1] has shown that oxidation of sodium acetate with and without insonation yielded different oxidation pathways. For instance, when sound was used, the COD/TOC ratio after two hours of ozone oxidation was 1.19 while the ratio was 1.88 for plain ozonation of sodium acetate.

Utilizing the data plotted in Figures 2 through 7, a kinetic equation of the form:

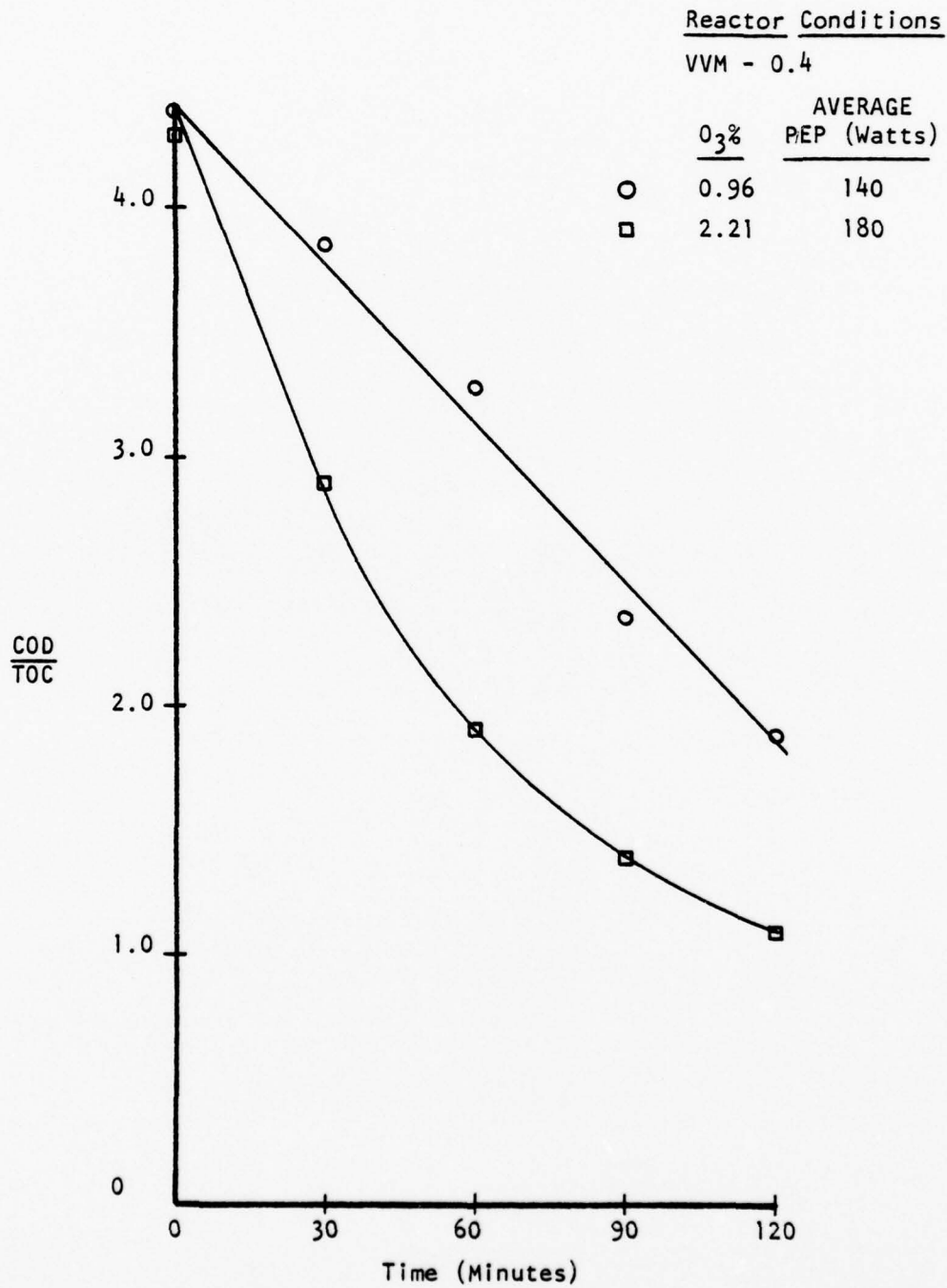


FIGURE 8. COD/TOC RATIO CHANGES WITH REACTION TIME AT TWO OZONE CONCENTRATIONS DURING THE OXIDATION OF UF PERMEATE.

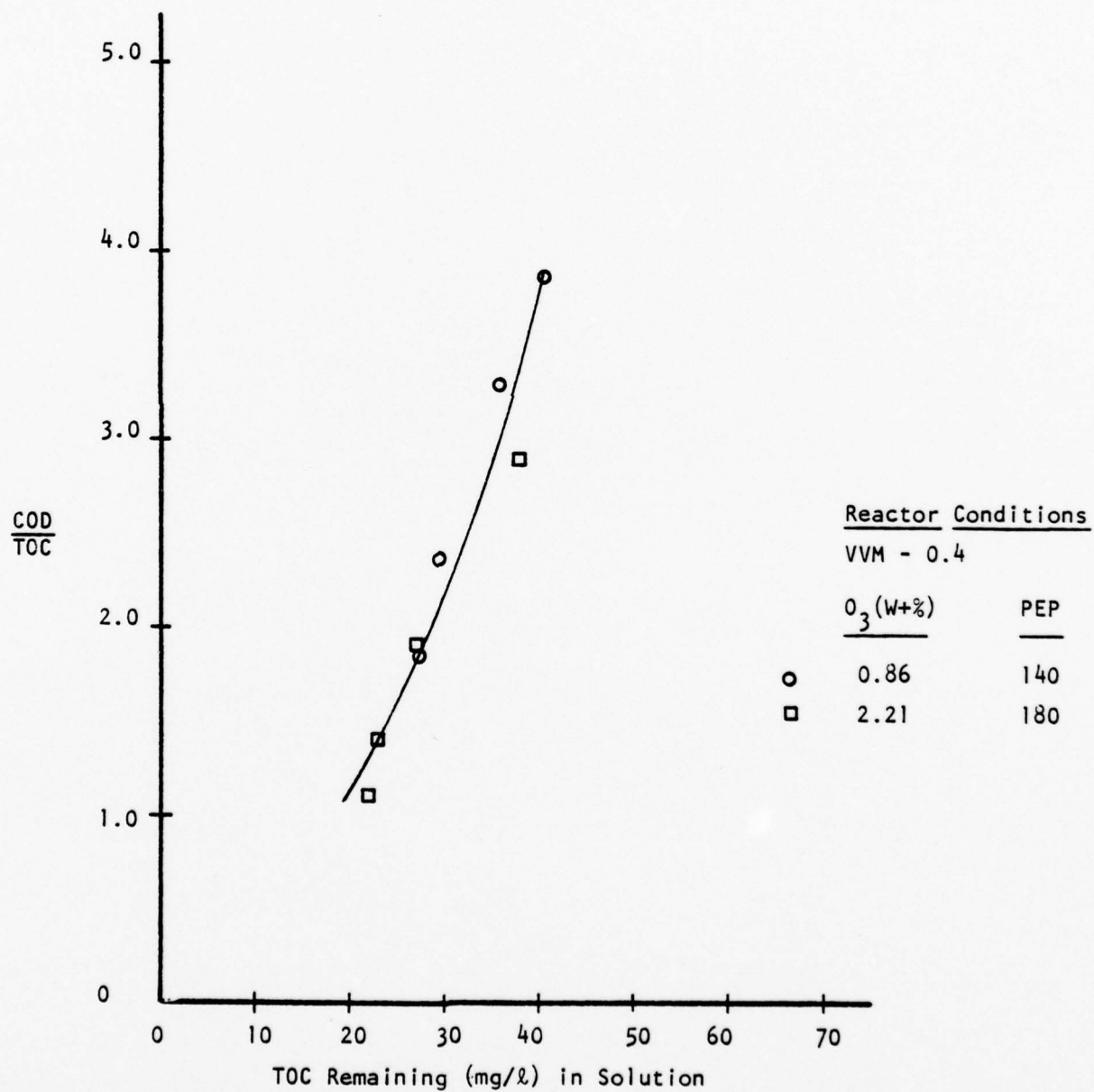


FIGURE 9. COD/TOC RATIO CHANGES AS A FUNCTION OF TOC REMAINING SOLUTION DURING THE OXIDATION OF UF PERMEATE.

$$-\frac{d(\text{TOC})}{dt} = K_1 (\text{VVM})^{R_1} (\text{Inlet Ozone Concentration})^{S_1} \quad (1)$$

(Organic Concentration, TOC)

$$-\frac{d(\text{COD})}{dt} = K_2 (\text{VVM})^{R_2} (\text{Inlet Ozone Concentration})^{S_2} \quad (2)$$

(Organic Concentration, COD)

where

$R_1, R_2, S_1, S_2 =$ exponents

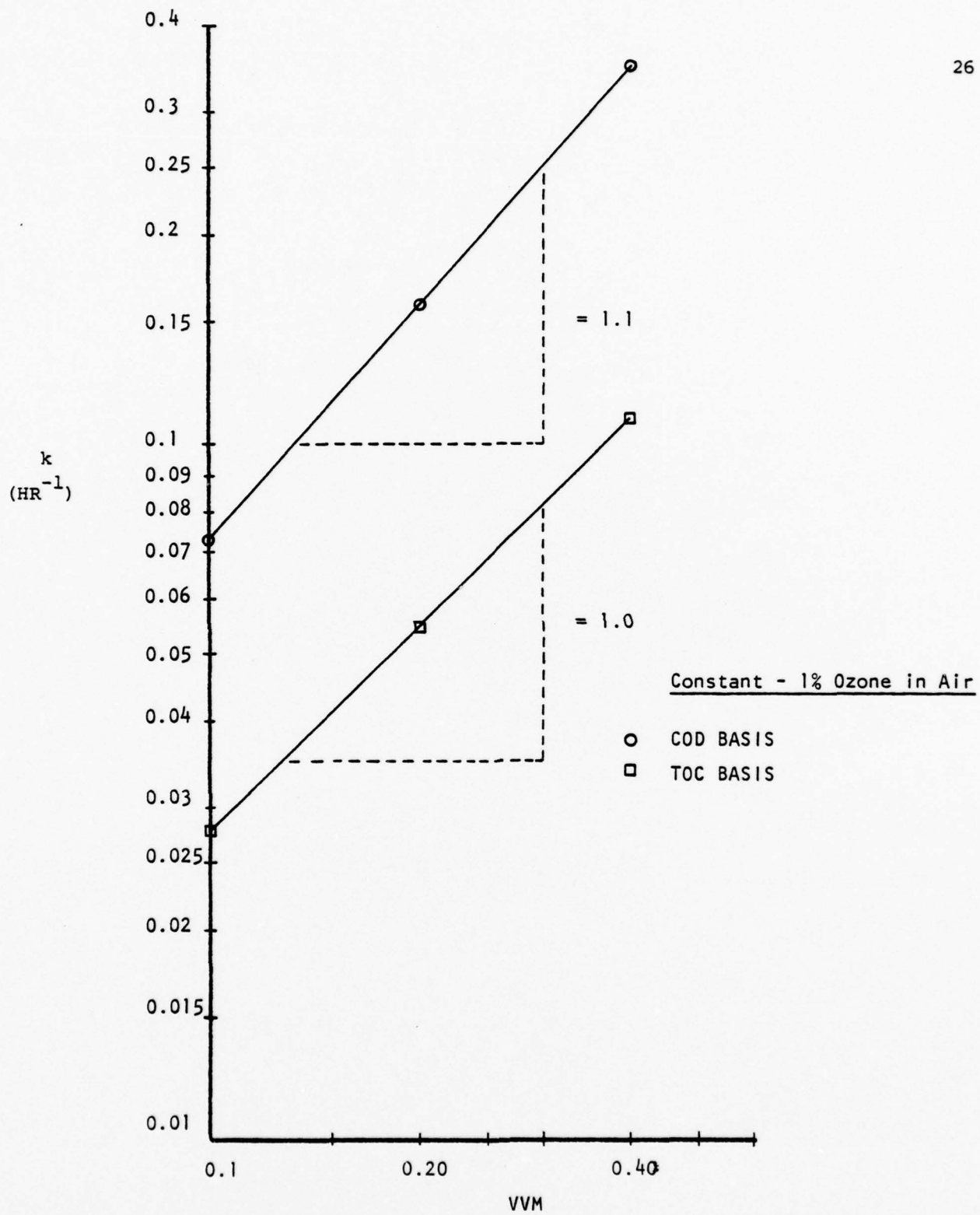
$K_{1,2} =$ proportionality constant which is a function of system operating variables

VVM = volume gas applied/minute/volume reaction liquid

Inlet Ozone Concentration = weight percent ozone in air

was developed for the oxidation of UF permeates by ozone in the presence of ultrasound.

The exponents R and S were obtained in the following manner. First, from Figures 2 and 3, the slopes of the TOC and COD destruction curves were obtained from runs performed at an approximately constant weight percent ozone-in-air and were plotted on log-log coordinates (Fig. 10) against VVM. The slopes of these lines are numerically equal to the exponents R_1 and R_2 , respectively. Similarly, the slopes of the organic destruction rate curves at variable O_3 inlet concentration and constant 0.4 VVM from Figures 5 and 6 on a TOC and COD basis were plotted against inlet ozone concentration (Figure 11) on log-log coordinates. The slopes of these lines are numerically equal to the exponents S_1 and S_2 , respectively. The final forms for Equations 1 and 2 are:

FIGURE 10. ESTIMATE OF R_1, R_2 .

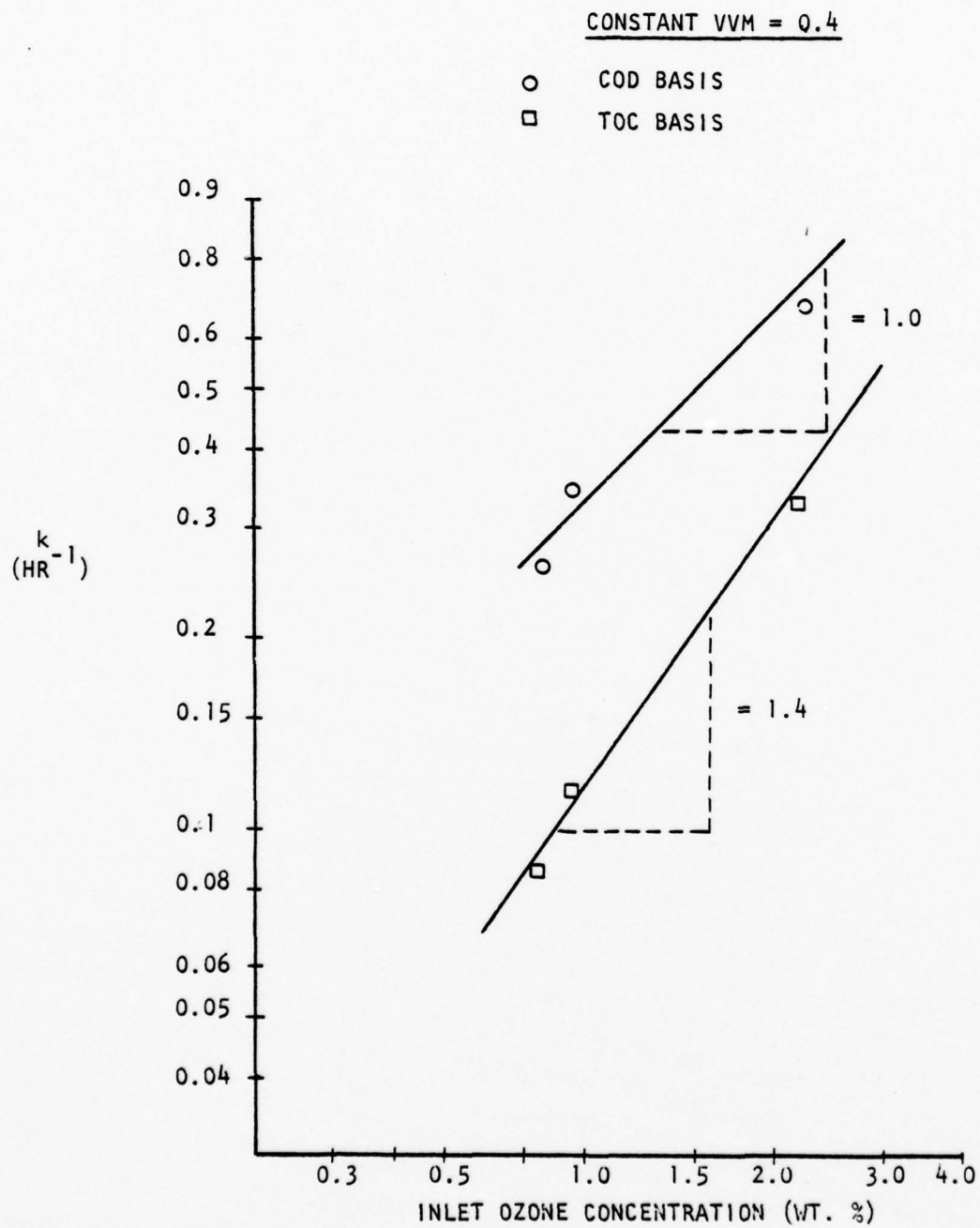


FIGURE 11. ESTIMATE OF S_1, S_2 .

$$-\frac{d(\text{TOC})}{dt} = K_1 (\text{inlet ozone concentration})^{1.4} (\text{VVM})^{1.0} \text{TOC} \quad (3)$$

$$-\frac{d(\text{COD})}{dt} = K_2 (\text{inlet ozone concentration})^{1.0} (\text{VVM})^{1.1} \text{COD} \quad (4)$$

where

$K_{1,2}$ = Proportionality constant which is a function of system operating variables

VVM = Volume gas applied/minute/volume reaction liquid

Ozone Concentration = weight % ozone

4.1.3 Ultrasound Scale-Up Experiments with UF Permeate. The benefits of sound inclusion into any ozone reactor are expected to come from improvement in gas transfer and decomposition of ozone to various free radicals. Sierka [1] has demonstrated with small laboratory size equipment that these benefits do exist.

For larger systems, the question of scale-up procedure must be addressed. Today, there does not exist a sufficient body of technical expertise for reactor design employing ultrasonics to permit scale-up based on well defined scientific principles and therefore, an empirical approach must be used. Since the experiments performed during this research were limited to the use of a Biosonic IV sound generator, operating basically at one frequency (20 Hz.), liquid height in the reactor was varied and maximum achievable sound power was employed in an attempt to characterize this effect.

For these experimental runs, four liquid heights (1.0, 2.0, 3.0, and 6.0 feet), which on a liquid volume basis corresponded to 5.55, 11.1, 16.0, and 33.3 liters of synthetic UF permeate, were ozonated at essentially constant ozone gas concentration (approximately 1.1 percent by weight ozone in air) and a constant superficial gas velocity* of 2.39 feet per minute. Even though the superficial gas velocity was constant, the VVM's were variable because VVM is calculated to be the volume of gas per unit minute admitted to the reaction mass per volume of liquid. This calculation points out the insufficiency of using VVM as a design concept.

The results of these experiments plotted in Figure 12 indicate a direct proportional increase in the mass of TOC removed with liquid height. Also, it can be seen in Figure 13 that ozone utilization increases with liquid height in the reactor. Since the ozone mass flow rate ($\text{mg O}_3/\text{minute}$) was the same in all four runs, it can be concluded from these data that sound is effective throughout the entire range of liquid heights up to 6.0 feet, the maximum liquid height permissible in the WPE.

In Table 2 is summarized the ozone utilization efficiency for the above discussed reactions. Column 7 in this table, which is the ozone decomposed and reacted divided by the ozone theoretically required in the reactor, shows that as liquid height is increased, at a fixed superficial gas velocity and inlet ozone concentration, that the ozone utilization efficiency increases. This response is expected since the amount of ozone transferred is proportional to the ozone partial pressure and gas residence time in the reactor, given fixed areas for gas transfer.

*Superficial gas velocity--gas flow rate at ozonator outlet pressure per cross sectional area of the reactor.

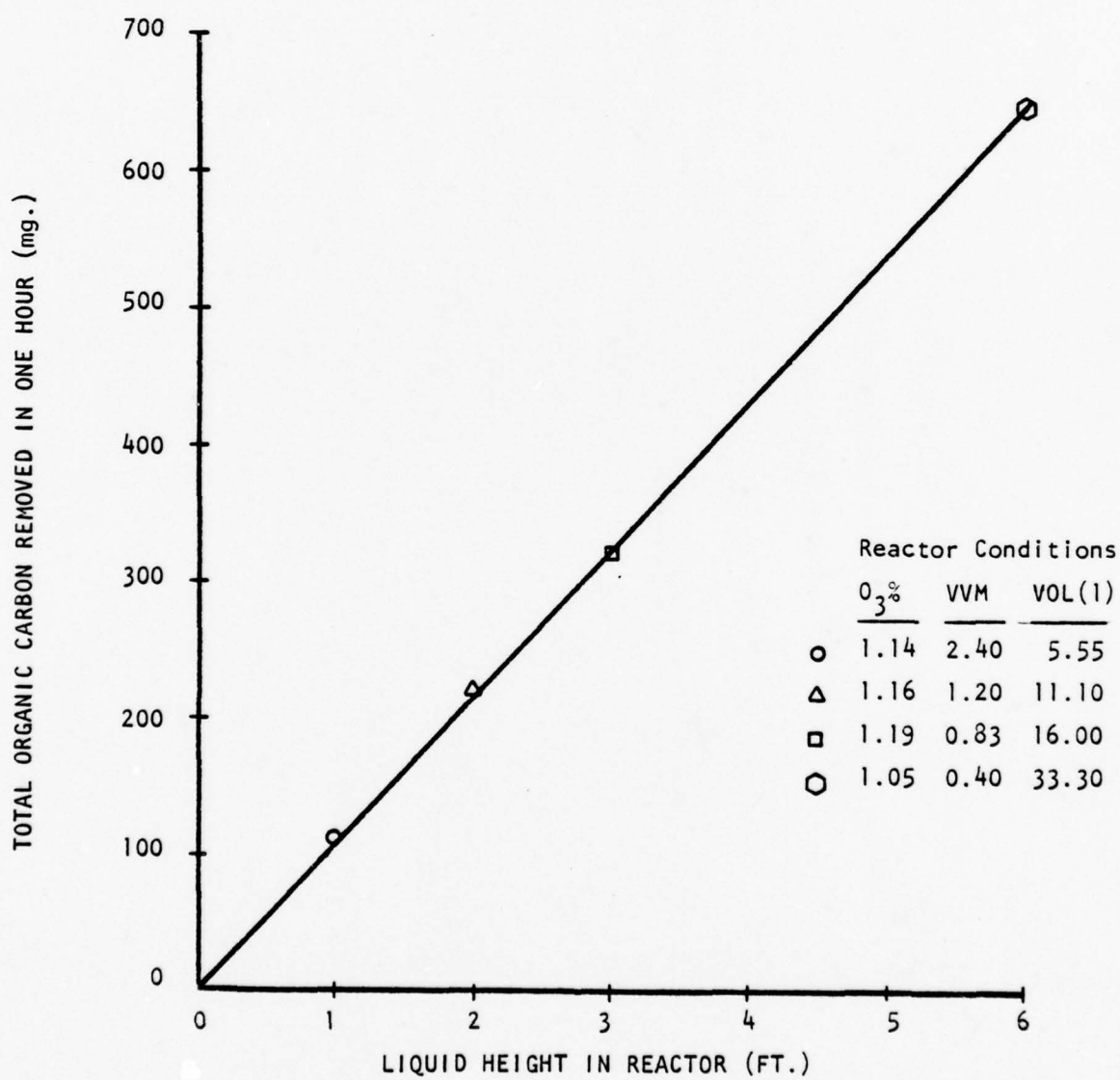


FIGURE 12. OXIDATION OF ULTRAFILTRATION PERMEATES AT VARIABLE LIQUID HEIGHTS IN THE OZONE REACTOR

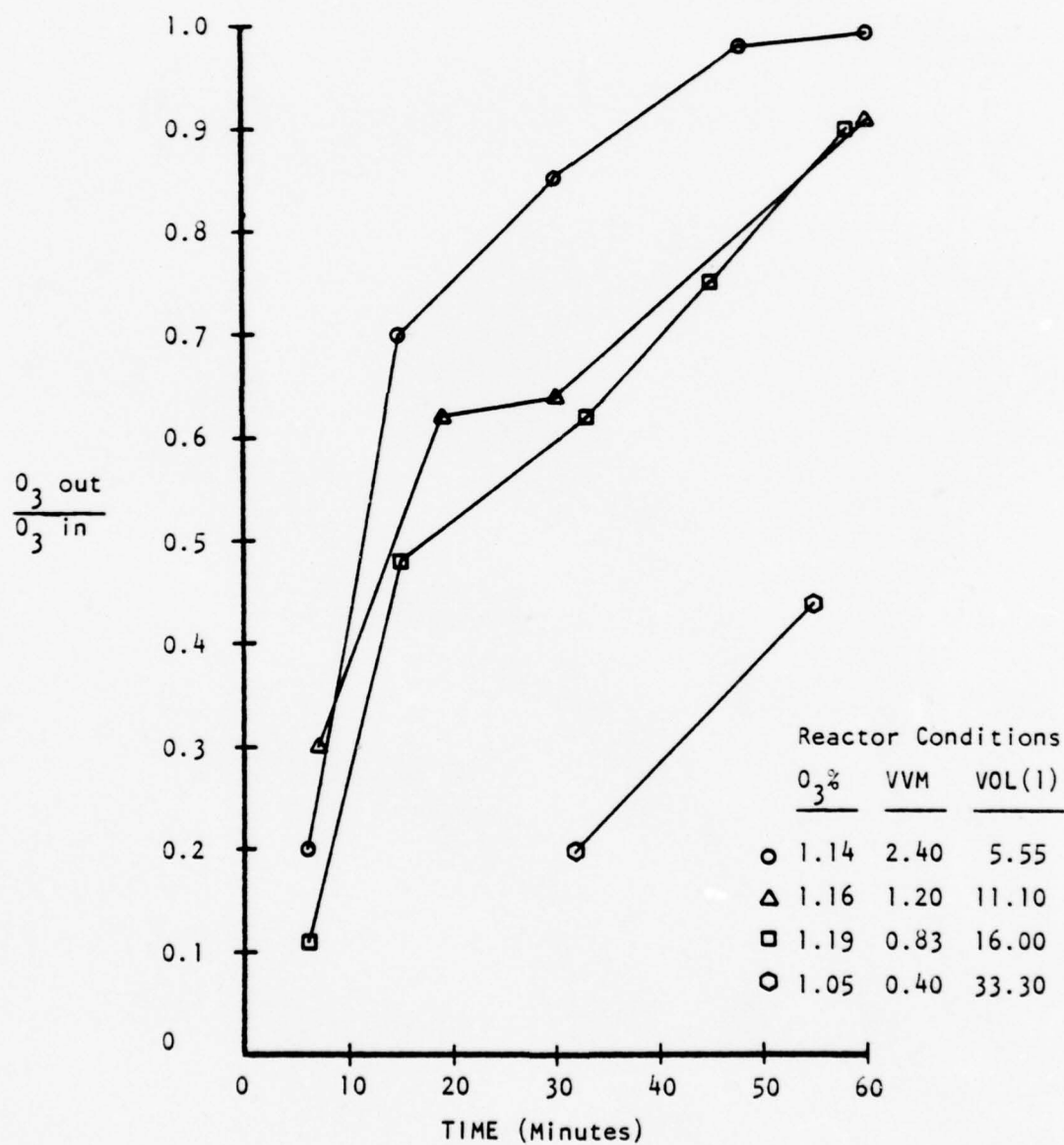


FIGURE 13. THE RATIO OF OZONE INLET TO OUTLET GAS CONCENTRATION AS A FUNCTION OF BATCH REACTION TIME DURING THE OXIDATION OF UF PERMEATE AT VARYING LIQUID HEIGHTS.

TABLE 2

OZONE UTILIZATION IN VARIABLE HEIGHT EXPERIMENT
WITH SYNTHETIC UF PERMEATE

[1]	[2]	[3]	[4]	[5]	[6]	[7]
Reactor Liquid Volume (l)	TOC Removed in 1 Hr (mg) ^a	Theoretical O ₃ Required (mg) ^b	Total O ₃ Applied (mg) ^c	Total O ₃ Unreacted ^d (mg) ^d	Total O ₃ Utilized in Reaction (mg) ^e	O ₃ Utilized Theoretical O ₃ Required (mg/mg) ^f
5.55	111	888.0	11,767	8,781	2,986	3.36
11.10	222	1,760.0	12,037	7,459	4,578	2.60
16.00	320	2,560.0	12,308	6,510	5,798	2.26
33.33	649	5,196.0	10,955	2,366	8,589	1.65

Note:

- a. TOC in (mg/l) - TOC_{60 minutes} (mg/l) x volume (l) in Column 1
- b. Theoretical ozone demand is calculated to be 8 times the mass of TOC removed. This assumes that only nascent oxygen is capable of totally oxidizing the TOC to CO₂.
- c. Ozone mass flow rate (mg/min) from ozonator x 60 minutes
- d. Integrated average over the run based on reactor effluent gas analysis
- e. Column 4 - Column 5
- f. Column 6/Column 3

Data from Column 7 of Table 2 is plotted in Figure 14 versus batch liquid height. It demonstrates that with a 6.0 ft. liquid head, the system is approaching the theoretical limit of one. This is a moot point, however, since a maximum height of 6.5 ft. is available in the WPE ward container for the ozone reactor. However, this data could be applied to other ozone reactors not constrained in this manner.

4.1.4 Kinetic Equation Development for RO Permeate Ozone-Sound Oxidation. The objective of this portion of Task One was to ascertain the effect of sound waves on the oxidation of hospital composite RO permeate at low VVM (i.e., 0.1, 0.2 and 0.4) conditions.

Experimentation with MUST RO permeate was conducted to accomplish the following. First, data would be gathered to construct a mathematical model identical to that given by equations 1 and 2. Second, the organic destruction rate data would be compared with that generated by LSI* in a geometrically similar single stage ozone reactor employing ultra-violet (UV) light similar to the one used in this research. A description of the LSI reactor can be found in reference [10].

A set of six experiments was carried out with the identical operating conditions used for the UF experiments. These conditions were: (1) starting pH = 9.0 and uncontrolled during the reaction, (2) ambient temperature operation (approximately $26^{\circ}\text{C} \pm 1^{\circ}\text{C}$), (3) a 6.0 foot liquid depth in the reactor and (4) a batch reaction time of 2.0 hours.

* Life Systems Incorporated, Cleveland Ohio.

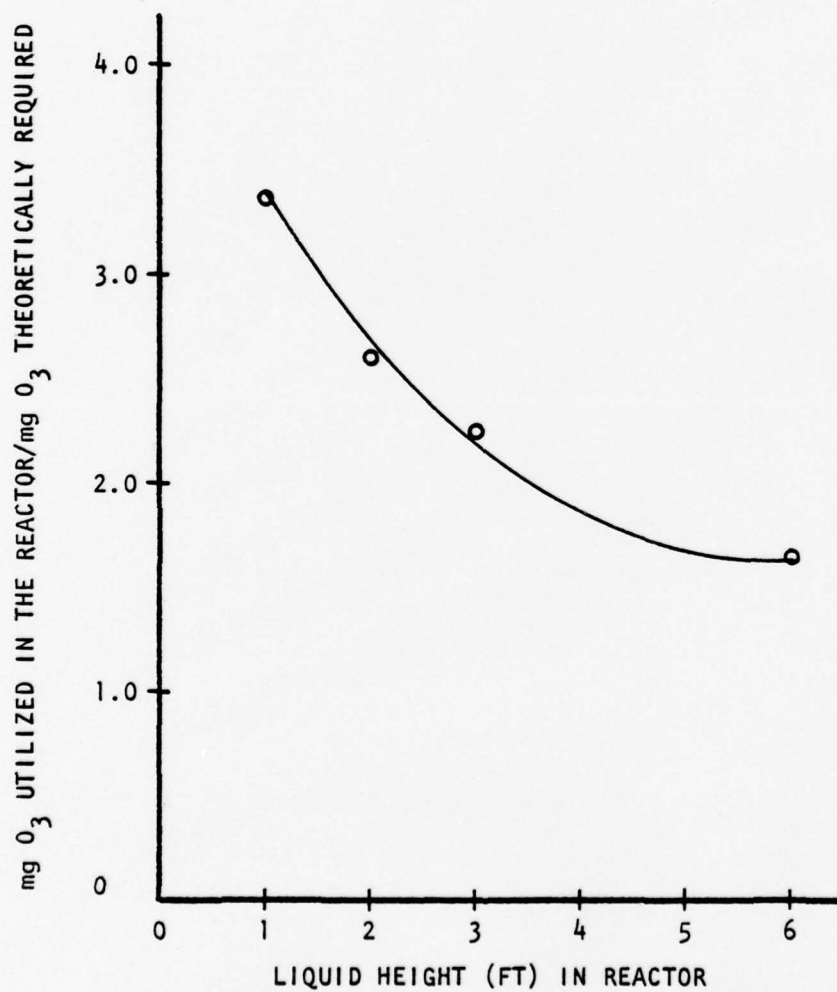


FIGURE 14. THE EFFECT OF LIQUID HEIGHT ON THE RATIO OF OZONE UTILIZED TO OZONE THEORETICALLY REQUIRED IN UF PERMEATE OXIDATION.

During the first three experiments an approximately constant ozone concentration of 1.0 weight % (1.0 - 1.09) in air was employed and was applied at three different VVM's (0.1, 0.2 and 0.4).

The destruction of TOC with batch reaction time is graphed in Figure 15. As VVM was increased, the amount of TOC oxidized to CO_2 was progressively increased from 54% to 62% to 78%. Figure 16 depicts the destruction of COD. Clearly the pattern is similar; that is, as VVM increases the amount of COD destroyed likewise increases. For the 0.1 VVM run, 45% of the initial COD was oxidized. However, after 120 minutes of ozonation, the effluent for the 0.2 and 0.4 VVM runs both contained only 13% of the original COD in the permeate, whereas the TOC concentration at the end of the run in these samples showed a larger difference.

Figure 17 shows the ratio of reactor outlet to inlet ozone, gas phase concentration for the three runs at constant ozone concentration (~1%) and variable VVM. The data show that improved ozone gas utilization is obtained as VVM is reduced; however, this results in an increase in reaction time, which is translatable to the reactor volume required, to meet the quality specifications with respect to TOC and COD (see Figures 15 and 16).

Comparison of the data in Figures 17 and 4 give an insight as to the effect that organic concentration has on ozone utilization. For instance, after 60 minutes of operation at 0.4 VVM and 1% O_3 , 52% of the ozone gas entering the reactor is found in the effluent gas stream when UF permeate is being oxidized (Figure 4), while approximately 84%

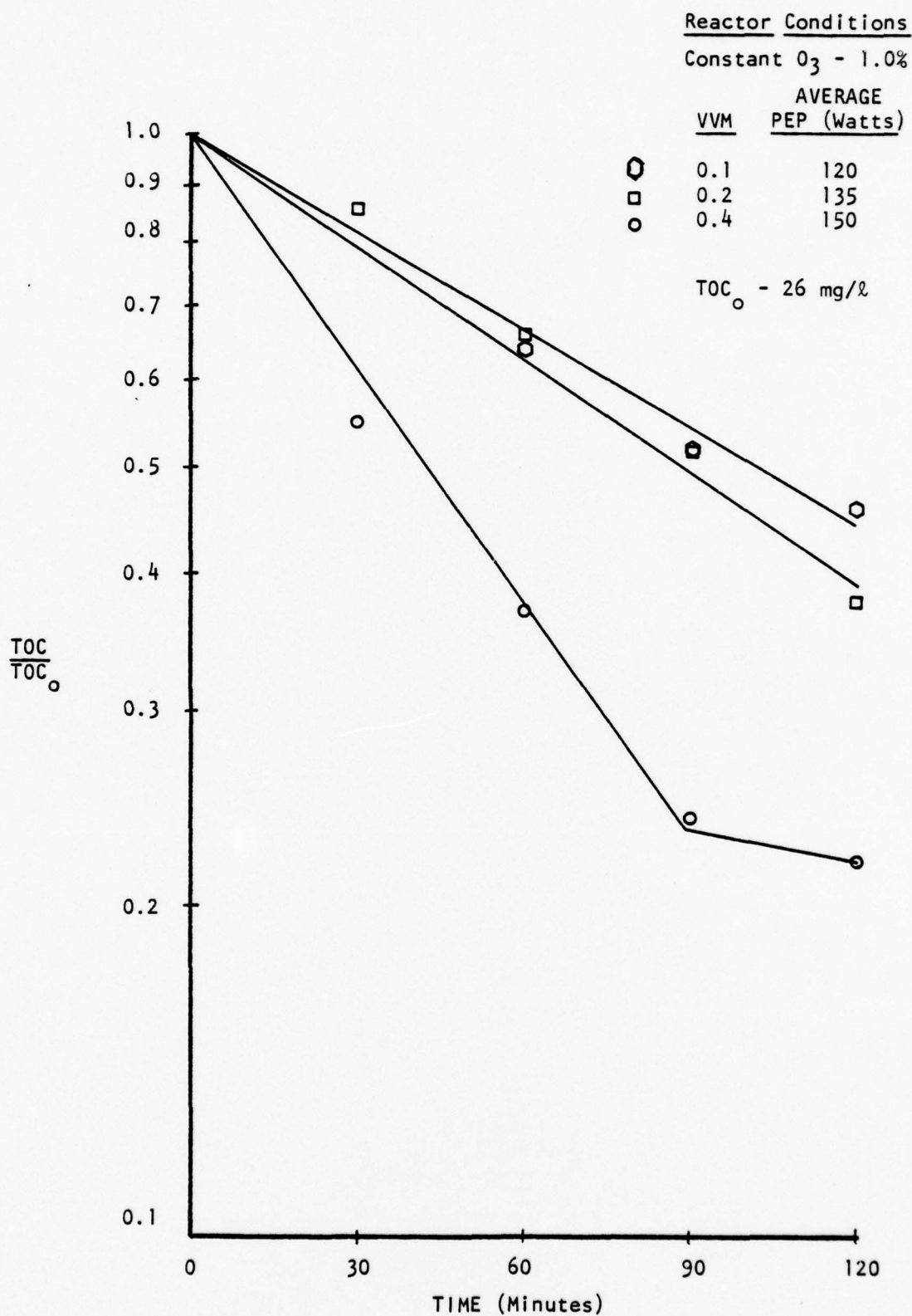


FIGURE 15. EFFECT OF GAS FLOW RATE ON TOC REMOVAL FROM REVERSE OSMOSIS PERMEATES AT CONSTANT OZONE CONCENTRATION AND VARIABLE VVM.

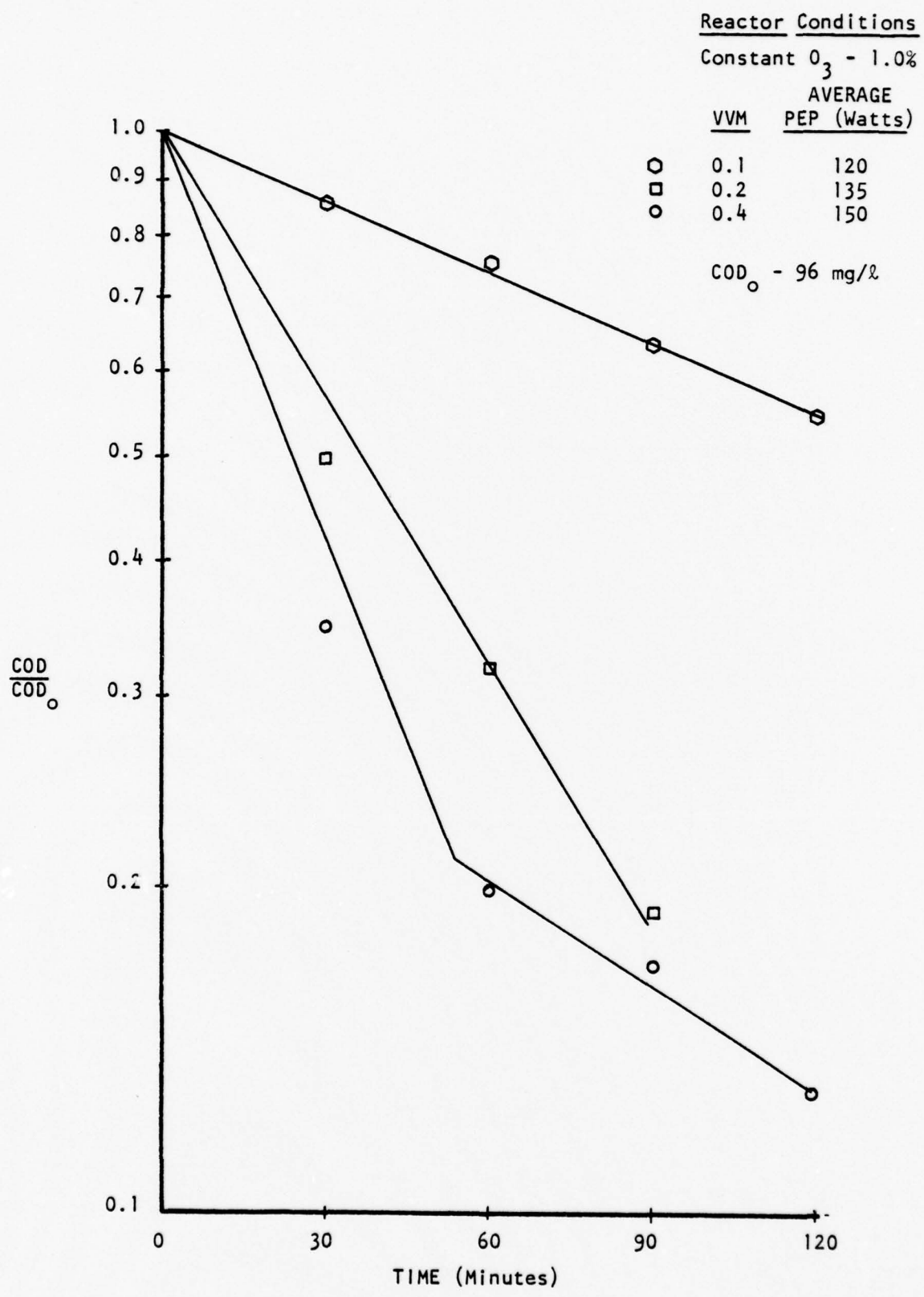


FIGURE 16. EFFECT OF GAS FLOW RATE ON COD REMOVAL FROM REVERSE OSMOSIS PERMEATES AT CONSTANT OZONE AND VARIABLE VVM.

Reactor ConditionsConstant O_3 - 1.0%

AVERAGE

VVM PEP (Watts)

○	0.1	120
□	0.2	135
○	0.4	150

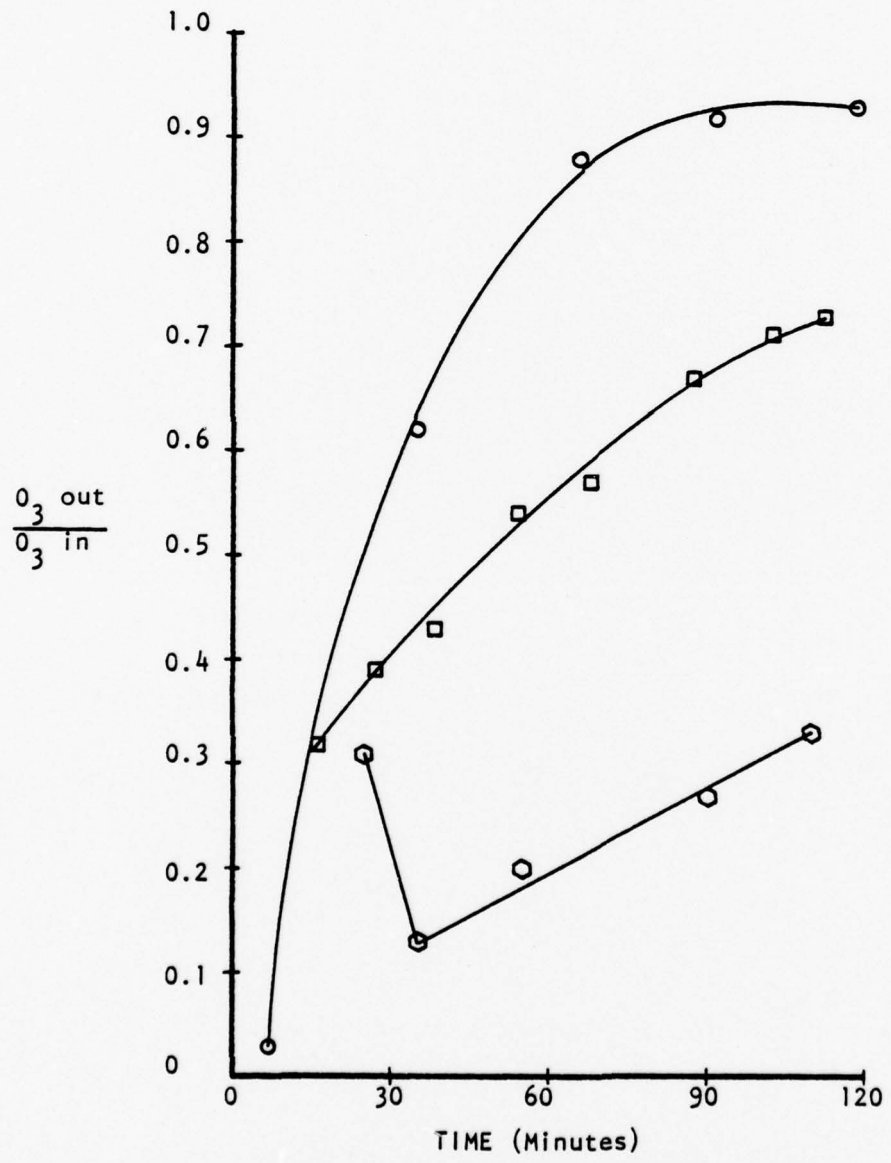


FIGURE 17. THE RATIO OF REACTOR OUTLET TO INLET OZONE CONCENTRATION AT VARIOUS REACTION TIMES DURING THE OXIDATION OF REVERSE OSMOSIS PERMEATES.

of the entering ozone exits the reactor when the substrate is RO permeate. The theoretical TOC for the UF and RO formulations are respectively 70 mg/l and 30 mg/l while for COD the concentrations are 274 mg/l and 108 mg/l. Comparisons of ozone concentration leaving the reactor as a function of batch reaction time for the 0.1 and 0.2 VVM experiments gives additional indication of the organic concentration effect.

The next series of three experiments were conducted at constant VVM (0.4) and variable ozone-gas concentration. Inlet ozone gas concentrations were 0.90, 1.10 and 2.40 weight. The highest ozone concentration (2.40%) was produced from a pure oxygen feed source in the Orec ozonator while the other two concentrations were produced from air.

In Figure 18 is plotted the TOC reduction data for the constant 0.4 VVM runs. The percent TOC remaining, after two hours of ozonation decreased from 25% to 2% as the ozone concentration increased. The COD destroyed for these runs as depicted in Figure 19 displays a similar pattern. In fact, the COD remaining after only 90 minutes of reaction was less than 2% for the 2.4% ozone-in-oxygen concentration run.

The major difference among these runs occurred when pure oxygen was used to produce ozone. It is quite obvious that the increased driving force to gas transport, which was due to the increased ozone partial pressure, was responsible for the increased reaction rates observed. Also the shape of the organic destruction curves should be noted. While the runs employing ozone produced in air show two distinct first order COD destruction rates, the ozone in oxygen run yields only

Constant VVM - 0.4

O_3 %	AVERAGE PEP (Watts)
---------	---------------------

○	0.90	120
□	1.10	150
△	2.40	185

$TOC_0 = 26 \text{ mg/l}$

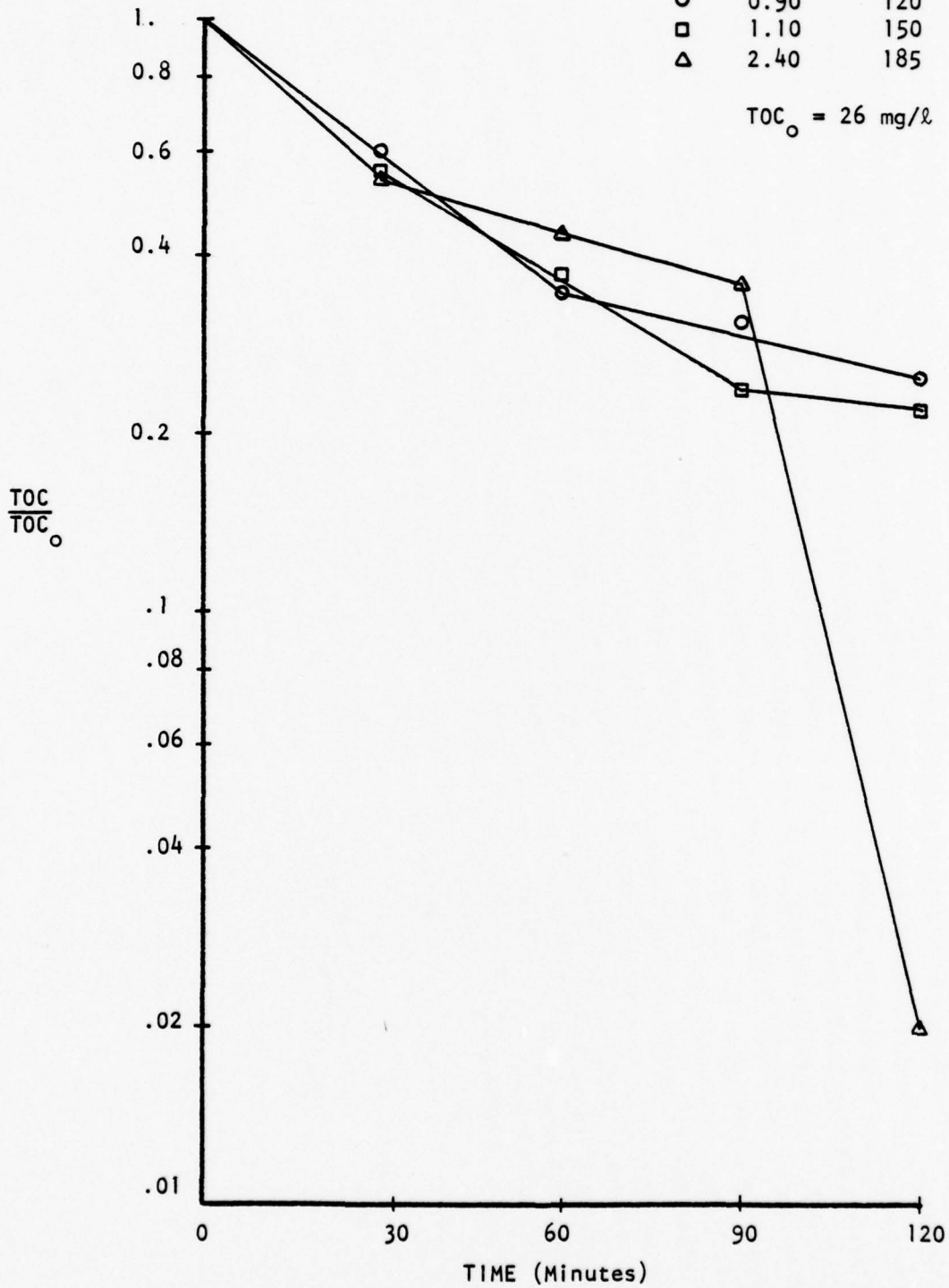


FIGURE 18. EFFECT OF OZONE CONCENTRATION ON TOC REMOVAL FROM REVERSE OSMOSIS PERMEATES AT CONSTANT VVM AND VARIABLE OZONE CONCENTRATION.

Reactor Conditions

Constant VVM - 0.4

AVERAGE	
$O_3\%$	PEP (Watts)

○	0.90	120
□	1.10	150
△	2.40	185

COD - 86 mg/l

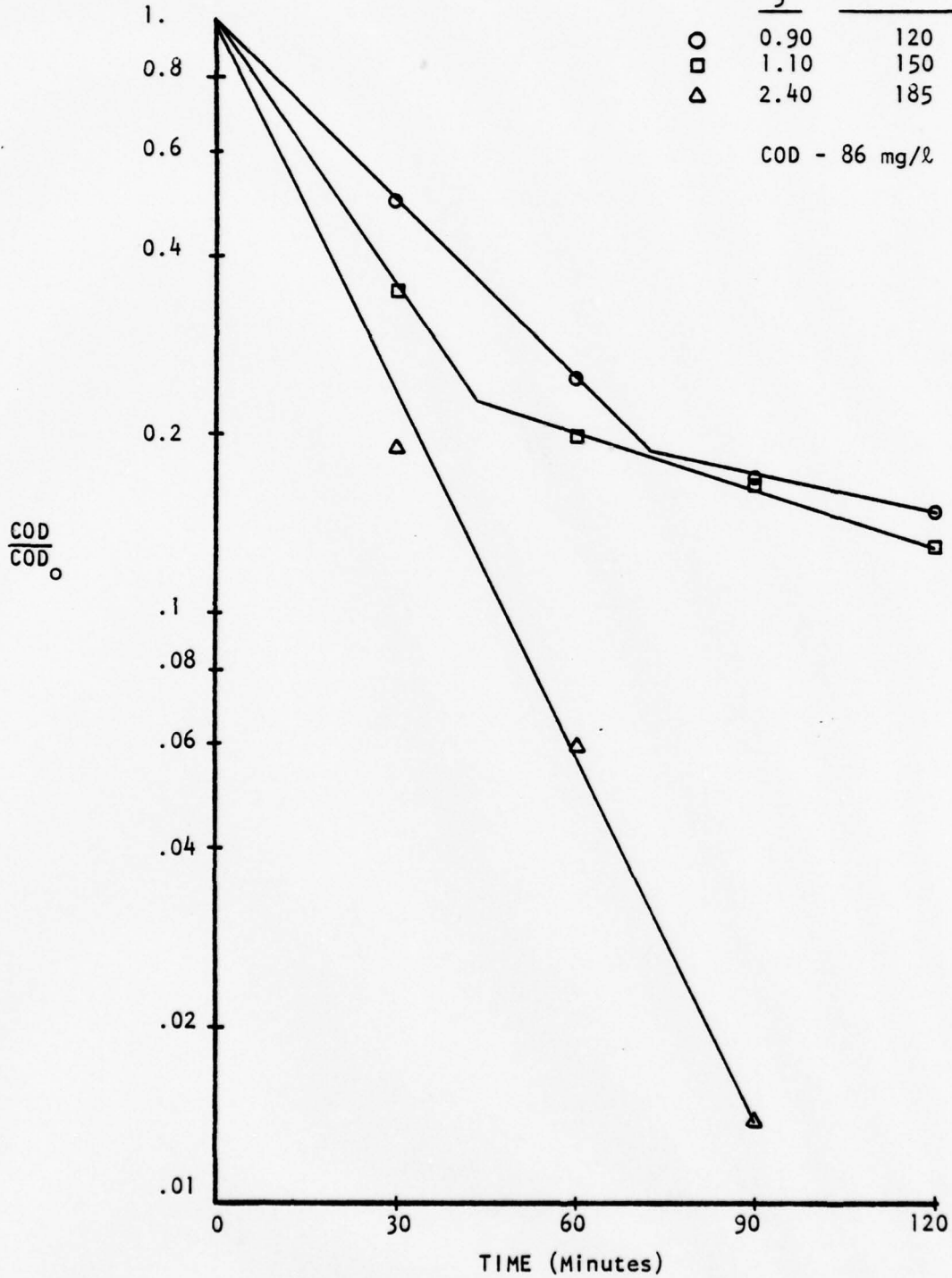


FIGURE 19. EFFECT OF OZONE CONCENTRATION ON COD REMOVAL FROM REVERSE OSMOSIS PERMEATES AT CONSTANT VVM AND VARIABLE OZONE CONCENTRATION.

a single first order rate over the first 90 minutes of the run at which time approximately 2% of the original COD and TOC remains in the reactor.

Correlating the behavior with the unreacted ozone gas passing out of the reactor (Figure 20) it is clear that for even the low ozone concentration (0.90 - 1.10%) runs the reaction was probably not mass transfer limited. For the ozone-in-oxygen run, ozone gas was found in the reaction effluent gas stream within less than five minutes of reaction time. This data are partially indicative of a reaction rate controlled system.

The data from these runs were fitted to the mathematical models given in Equations 1 and 2 in an identical manner to that described in Section 4.1.2 for the UF runs.

The resulting equations are:

$$-\frac{d(\text{TOC})}{dt} = K_3 (\text{inlet ozone concentration})^{3.0} (\text{VVM})^{0.7} \text{TOC} \quad (5)$$

and

$$-\frac{d(\text{COD})}{dt} = K_4 (\text{inlet ozone concentration})^{0.8} (\text{VVM})^{1.4} \text{COD} \quad (6)$$

where the parameters have the definitions previously described (see Section 4.1.2). LSI (11) obtained the following kinetic equation in an ozone reactor employing UV light at an intensity of 2 watts/l.

$$-d(\text{Ca})/dt = k_o (\bar{P}_{\text{Oz}})^{1.5} (\text{Vs})^{1.25} \text{Ca} \quad (7)$$

where: Ca = TOC concentration

\bar{P}_{Oz} = Ozone partial pressure, psi

Reactor Conditions

Constant VVM - 0.4

	<u>0₃%</u>	<u>AVERAGE PEP (Watts)</u>
○	0.90	120
□	1.10	150
△	2.40	185

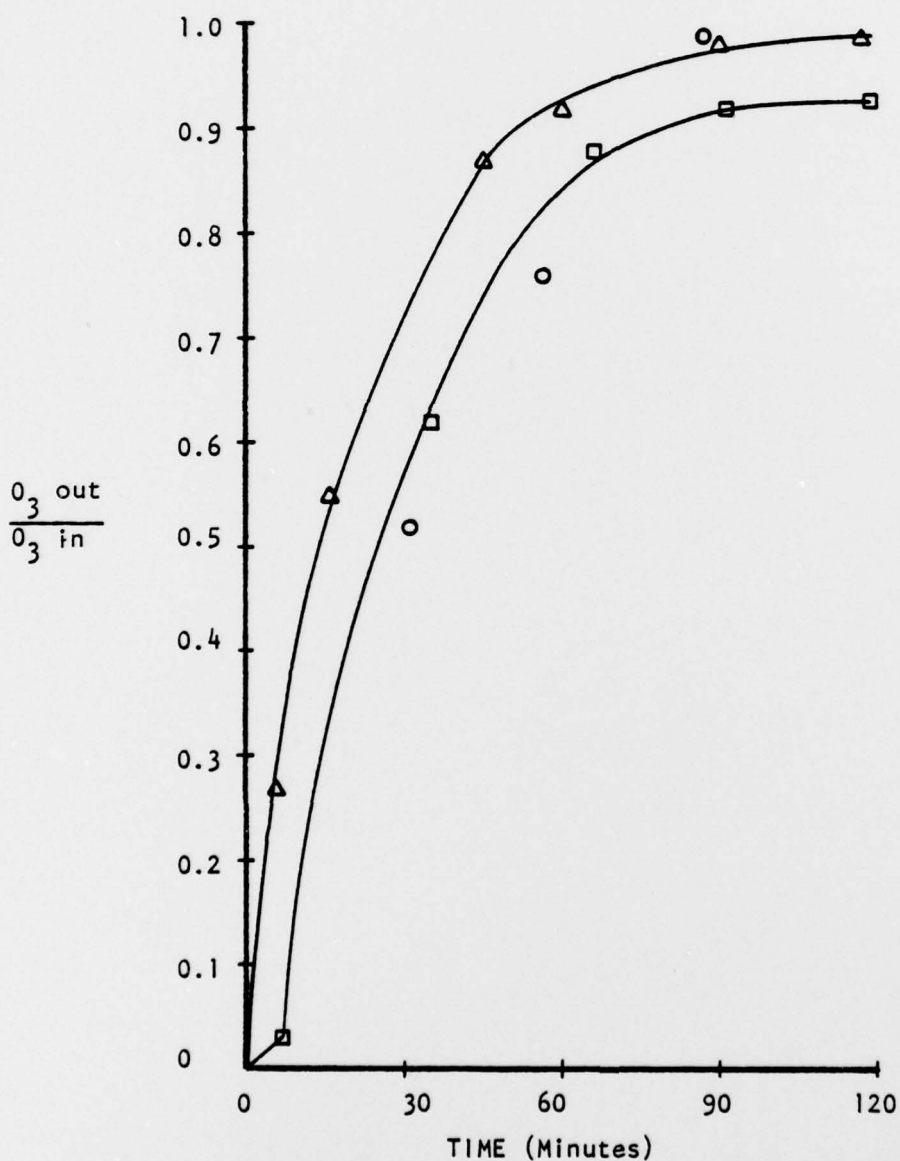


FIGURE 20. THE RATIO OF REACTOR OUTLET TO INLET OZONE CONCENTRATION AT VARIOUS REACTION TIMES DURING ONE OXIDATION OF REVERSE OSMOSIS PERMEATES.

V_s = air superficial gas velocity and

k_o = constant

An analysis of the LSI and the author's kinetic expression show that they are essentially equal. For instance, while LSI uses ozone partial pressure measured in psi, equation 1 and 2 employ weight percent ozone in air. Since a constant liquid depth of 6.0 feet was used in both reactors and since the reactor diameters were essentially equal, VVM is directly proportional to V_s . Thus, comparison of the exponents on the individual terms in the equation is valid.

The effect of ozone concentration on the destruction of TOC is substantially different as evidenced by the exponent (3.0 vs. 1.5; Eq. 5, 7) on this term in the two kinetic equations. This difference may be due in part to the presence or absence of UV light or ultra sound. It has been shown by past research [7] that not only are the oxidation pathways different with UV light, but the rates of TOC destruction are increased. Thus, the exponent on the ozone term should reflect this effect. Also, in the LSI experiment ozone was always produced from air while one run in this research used oxygen as a feed gas. The range of ozone concentrations used by LSI was 0.70% to 1.29% while in the study it was 0.90% to 2.40%. Finally, Figure 18 shows that over the first 90 minutes of reaction very little difference in the rate of TOC destruction is evident for the three runs with varying ozone feed gas concentrations. Thus, for the case of 2.40% ozone in oxygen only the last 30 minutes of the run were used in calculation for the mathematical model.

As for the experiments on V_g and VVM they, too, are essentially different by a factor of 2.0; however, the LSI data shows a much greater dependency on gas flow rate. This effect was predictable since sound waves should have enhanced gas mass transport, while the presence of UV light in the LSI reactor would not contribute to this function. Also, LSI data is based on a constant 0.2 VVM, while this research employed 0.4 VVM.

When equation (3) is compared with equation (7) a much closer agreement is seen in the exponents of the models. Basically, the UF formation is the same as the RO formulation except the organic concentrations are higher in the former. Therefore, comparisons between the RO of LSI and the UF model of this research is worth further consideration. It should be noted that, while the exponent on the ozone term are in good agreement (1.5 versus 1.4), the effect of gas flow rate for this research is less sensitive (1.0 versus 1.25) than for the LSI experiment. Again, this is attributable to a higher VVM operation (0.4 versus 0.2) and the presence of sound waves in the reaction. The major reason for the agreement on the exponent for the ozone term is that with UF, since the organic concentration (i.e., TOC) is high, initially ozone reactions - even if they are not UV catalyzed - could yield a response similar to the RO oxidations in the presence of UV light.

Model comparisons on a COD basis are not possible since LSI did not perform this analysis on treated effluent. Equation (6) is the kinetic model on a COD basis for the RO experiments conducted during this research.

4.2 Task 2 - Ultrasound and its Effect on Oxygen Mass Transfer at Low VVM Operation

4.2.1 General. The objective of this task was to quantize the degree to which ultrasound enhanced oxygen mass transfer at low (0.1, 0.2, and 0.4) VVM's. McCarthy et al (16) demonstrated that oxygen mass transfer in a 6.6 inch diameter pipe reactor was dependent on height in the column and VVM. They found that maximum overall mass transfer coefficients ($K_L a$) were obtained at between 8 and 18 inches from the 5 micron pore size sintered stainless steel gas sparger and that $K_L a$ increased with VVM in the range 0.29 to 0.89. These $K_L a$ values ranged between 138 and 260 hours⁻¹. Longitudinal dye dispersion tests [9] demonstrated that a minimum 0.26 VVM (20 scfh) condition was required in their gas sparged reactor to yield completely mixed reactor hydraulic behavior and further increases in VVM did not appreciably improve mixing.

It has been postulated by Lee & See [11] that in the initial stages of ozone oxidation of MUST RO permeates, the reaction is controlled by the transfer of ozone from the bulk gas to the bulk liquid stage. They maintain that mass transfer would be aided by decreasing bubble size, increasing superficial gas velocity and ozone partial pressure.

Bubble size for experiments performed by the U. S. Army and the author are already minimized since the pore sparger size is 5 microns. The ozone partial pressures are limited since the ozone must be produced from air in MUST field operations. The state of current technology is such that 1.0 weight % ozone-in-air is the upper

concentration limit of production capability. Superficial gas velocity in the ozone reactor is related to the ozone production capability. If the gas mass flow rate through the ozonator is increased, the ozone concentration will decrease and thus the driving force to gas transport will be reduced.

Because of the particular parameter association in the ozonator and reactor systems, other measures must be applied if gas mass transfer is to be enhanced. The application of sound waves to the reaction mass is one such available alternative.

Dahi [12] experimented with the effect of 20kHz ultrasonic waves on the transfer of oxygen to distilled water. Using a 38 mm ultrasonic probe and 160 watts of power, he reported increases in $K_L a$ of between 15--45% when oxygenating 1.0 liters of distilled water by means of 0.4 mm i.d. hypodermic needle.

Kapustina [13] points out that when a sound field is applied to bubbles in a liquid they vibrate. The solubility of the gas at the bubble surface varies periodically with the sound vibrations. Additionally, sound waves reduce the thickness of the hydrodynamic layer and, therefore, the gas diffusion boundary layer, producing microstreaming at the surface of the vibrating bubble. This, in turn, accelerates the transport of gas across the liquid boundary layer which is manifested in terms of a larger liquid film transfer coefficient (i.e., k_g). The overall effect is enhanced mass transfer until steady-state situation is reached.

4.2.2 Experimental Results. To evaluate the effect that ultrasound had on mass transfer, a series of oxygen uptake runs were performed in the 6-inch diameter column reactor at 0.1, 0.2, and 0.4 VVM. Overall oxygen transfer coefficients ($K_L a$) were measured at the 6.0, 12.0 and 55.0 inch levels from the gas sparger surface. Table 3 is a summary of the experimental results.

At the 6.0 inch level, $K_L a$ increased proportionately with increases in VVM. This is evident for runs carried out in the presence and absence of sound waves. For the no-sound condition, $K_L a$ increased from 15.8 to 35.4 hrs.⁻¹, while in runs with sound (PEP approximately 110 watts) $K_L a$ values increased from 20.9 to 42.7 hrs.⁻¹. It was also noted that for each VVM condition, there was an increase in the $K_L a$ value when sound was present over the no-sound condition.

For all three VVM levels tested, the bubble pattern changed abruptly near the 6-inch height level. The largest rate of bubble diameter increase was noted at this height. Also, the swarming tendency of these bubbles was very much decreased particularly when sound was applied. There appeared to be much greater oscillation of individual bubbles in the sound field.

Repetition of the oxygen uptake experiments with the dissolved oxygen probe at the 12-inch level yielded the same trend; that is, as VVM increased so did the $K_L a$ value. Likewise, dissolved oxygen probe at the 55-inch level yielded the same response.

Examination of the data in Table 3 also point out that at a fixed VVM, $K_L a$ increased with distance from the gas sparger.

TABLE 3

OVERALL MASS TRANSFER COEFFICIENT ($K_L a$) MEASUREMENTS FOR
DISTILLED WATER IN A 6" DIAMETER COLUMN REACTOR
IN THE PRESENCE AND ABSENCE OF SOUND WAVES

VVM	0.1	0.2	0.4
Dissolved Oxygen			
Probe Height (in.)	6	6	6
From Sparger			
$K_L a$ (HR. ⁻¹)			
PEP (0) Watts	15.8	26.9	35.4
PEP (110) Watts	20.9	29.5	42.7
VVM	0.1	0.2	0.4
Dissolved Oxygen			
Probe Height (in.)	12	12	12
From Sparger			
$K_L a$ (HR. ⁻¹)			
PEP (0) Watts	36.1	37.2	95.8
PEP (100) Watts	49.6	55.1	112.1
VVM	0.1	-	0.4
Dissolved Oxygen			
Probe Height (in.)	55	-	55
From Sparger			
$K_L a$ (HR. ⁻¹)			
PEP (0)	46.8	-	106.7
PEP (130)	47.1	-	121.6

Liquid Depth - 6.0 ft.

The improvement in oxygen mass transfer with VVM in a similar reactor has been reported by McCarthy et al [1976]. They found that the average overall oxygen transfer coefficient ranged from 138 to 260 hours⁻¹ as VVM increased from 0.29 to 0.89. While these values are considerably higher than those found in Table 3, the trend is identical. Further, it was reported by these investigators that the maximum $K_L a$ was obtained between 12 and 18 inches from the sparger.

4.3 Task 3 - The Effect of Ultrasound on the Stripping of UF Permeate

4.3.1 General. McCarthy [9] et al. had investigated the effect of stripping in a nominal one-quarter scale UV-ozone contractor system which included an ozone scrubber or precontactor. They studied the effectiveness of stripping MUST laboratory RO permeate. A correlation between a first order stripping rate constant and oxygen mass transfer coefficient was developed.

The success of this model led to further experimentation with MUST hospital U.F. permeate serving as the substrate. The experimental conditions and results for this work is listed in Table 4. From these experiments it was concluded that, air-stripping of U.F. permeates was of little value [14]. However, Task 3 was carried out to determine if air stripping aided by ultrasound could reverse this conclusion.

4.3.2 Experimental Results. One air stripping run was performed. A 33.3 l batch of UF permeate at pH-8.9 was preheated to 45°C and air stripped at a VVM of 0.69 for three hours. Table 5 lists the data collected during the run.

TABLE 4

U.S. ARMY MEDICAL BIOENGINEERING R & D LABORATORY UF STRIPPING RUN

REACTOR CONDITIONS

Gas stripping bottle in a constant temperature bath

Temperature - 49°C
 Wastewater volume - 500 ml
 VVM - 0.8
 Gas type - Air

TEST RESULTS

<u>TIME</u> <u>(MIN)</u>	<u>TOC</u> <u>(mg/l)</u>	<u>COD</u> <u>(mg/l)</u>
0	62.2	259
15	60.8	261
60	62.3	264
120	61.4	261
240	59.2	227

TABLE 5

ULTRAFILTRATION PERMEATE STRIPPING IN THE PRESSURE OF ULTRASOUND

<u>REACTION TIME</u> <u>(MIN.)</u>	<u>TEMP</u> <u>(°C)</u>	<u>COD</u> <u>(mg/l)</u>	<u>TOC</u> <u>(mg/l)</u>	<u>PEP</u> <u>(WATTS)</u>
0	45.0	254.	55	170
60	44.0	232.	53	170
120	39.0	229.	49	165
180	36.5	227.	48	170

From this data it is evident that air stripping was not particularly successful. However it can be stated that the rates of COD and TOC removal in the presence of ultrasound did exceed those obtained by the USAMBRDL. This increase can be attributed to the enhanced mass transport properties of the air-sound system.

The results indicated that practically speaking air-stripping even in the presence of sound would preclude the use of this concept in the field due to the unreasonably high hydraulic detention times required.

5.0 CONCLUSIONS

The following conclusions have been drawn from experiments where

UF permeates served as the substrate:

1. Increasing VVM (0.1, 0.2 and 0.4), at a fixed ozone concentration, (1% by weight), produced corresponding increases in organic oxidation rates.
2. Increasing inlet ozone gas concentrations (0.86, 0.96 and 2.21%), at a fixed (0.4) VVM produced corresponding increases in organic oxidation rates.
3. At an inlet concentration of 1.0 weight percent ozone the reaction is ozone mass transfer controlled for the entire run at 0.1 VVM, for one hour at 0.2 VVM at 0.4 VVM the reaction is essentially reaction rate controlled.
4. Ozone utilization increased with liquid height (1.0 to 6.0 feet) in the reactor. With a constant superficial gas velocity and a 1.1 weight percent ozone inlet concentration, the ratio of ozone utilized in the reactor to the theoretical amount required for the TOC destroyed decreased from 3.36 to 1.65 at liquid heights of 1.0 and 6.0 feet respectively. For this reactor and these reaction conditions the mass of TOC removed in the ozone-sound reactor was directly proportional to liquid height at a fixed superficial gas velocity (2.39 ft/min) and ozone concentration (~1.1%).
5. Insonation enhanced the air stripping over the no-sound condition but not to the degree where it would become a viable concept for organic removal within the MUST treatment process.

The following conclusions have been drawn from experiments where

RO permeates served as the substrate:

1. Increasing VVM (0.1, 0.2 and 0.4) at a fixed ozone concentration (1% by weight) produced corresponding increases in organic oxidation rates.
2. On a COD basis, increasing inlet ozone concentration (0.9, 1.10 and 2.40%) yielded corresponding increases in oxidation rates. At low ozone concentration (0.9, 1.1) two distinct first order rates were observed while at the

highest hybrid ozone inlet concentrates (2.40%) only one first order rate was noted over the entire course of reaction. On a TOC basis no appreciable ozone partial pressure effect was seen during the first 90 minutes of reaction, however at the 2.40% ozone concentration a large decrease in effluent TOC occurred over the 90 to 120 minute portion of the experiment.

The following conclusions have been derived from oxygen mass transfer experiments.

1. Overall mass transfer coefficient ($K_L a$) increase directly with VVM and position above the gas sparger.
2. For a fixed VVM and position above the gas sparger greater $K_L a$ values were obtained when ultrasound was employed over the no sound condition. The improvement ranged from 1% to 36%.

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