

DEVELOPMENT OF A
PORTABLE OZONE
TEST UNIT

By

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ABSTRACT

A portable ozone test unit was designed for the continuous treatment of Kraft pulp mill waste with ozone, using a venturi as the gas-liquid contact method. The design specifications were the result of tests made with a batch process treatment of the waste water.

The EVOP process developed by G. E. P. Box was used to systematically determine the optimum operating conditions of the test unit. Chemical oxygen demand, color, and odor reduction were the criteria chosen to evaluate the performance of the test unit.

The specific pulp mill waste tested had a COD of 1200 mg/l, a light transmittance of 2% (at a wavelength of 420 Å), and a noxious odor. At the optimum operating conditions the portable test unit reduced the COD to 240 mg/l, increased the light transmittance to 49%, and reduced the odor until it was imperceptible. The ozone utilization rate at these operating conditions was 77%.

DEVELOPMENT OF A PORTABLE OZONE TEST UNIT

I. INTRODUCTION

The use of ozone is currently under study as a method of tertiary treatment of waste water. Ozone is a strong oxidizing agent and, as such, is effective in the reduction of chemical oxygen demand (COD), color and odor of waste water. COD is a measure of oxygen required to oxidize pollutants in the water and a high COD is undesirable. Microorganisms use pollutants as food and also require dissolved oxygen. Low dissolved oxygen levels in the water will kill fish and other types of aquatic life.

The ozone method of treatment is not in wide use in the U.S. since the cost of ozone production has been prohibitive, although it is used for water supply purification in Europe. However, research into ozone production under current investigation indicates that a significant reduction in such cost is feasible. In addition, proposed government regulations may require tertiary treatment. Tertiary treatment is expensive so ozone treatment might be competitive with other oxidation (biological) processes.

One advantage of ozone use is that any unused ozone decomposes into oxygen, which can then be used for other purposes or vented to the atmosphere. Other methods have undesirable end-products, such as activated sludge and carbon, which must be disposed of when no longer useful. Also, ozone is an excellent bactericide with none of the undesirable effects of chlorine.

The first objective of this research was to build a portable test unit that generated ozone and could be used to treat any type of waste water. Polluted water from a Kraft pulp mill was selected as a

suitable test case, having a high COD, a chocolate-brown color, and a noxious odor. This water provided an excellent test for the treatment potential of ozone. Since the biochemical oxygen demand (BOD) in such water is only about one-tenth of the COD, ozone treatment was an obvious choice over a process involving biodegradation.

The second objective of this research was to determine the optimum operating conditions for ozone treatment of pulp wastes based on reduction of COD, color and odor. Evolutionary Operation (EVOP), first developed by G.E.P. Box, was chosen as the systematic method for such determination.

II. REVIEW OF THE LITERATURE

A. Ozone Uses

Ozone, being a strong oxidizer, has been in use for many years, particularly in Europe, as a disinfectant for water supplies. Buydens (7) and Ivers (12), among others, report improved taste and color with this treatment of river water used for municipalities. Their laboratory tests indicate 100% removal of harmful bacteria and viruses. Ozone appears to be preferable to chlorination for this purpose since ozone decomposes into oxygen which has no undesirable after-effects as would be present with chlorination. In fact Buydens and Fransolet (8) used ozone to oxidize chlorine, chlorine dioxide, and chlorite ions left in water after chlorination. These, they believe, could influence the health of the water users.

Much research has been done in other areas involving the oxidation potential of ozone. Deitz and Moller (10) report the use of ozone to treat hot alkaline industrial waste water. The purified water is completely free of harmful bacteria and viruses and is used by Gerber Products Co. to clean glass bottles intended for food for human consumption.

Other experimental studies indicate that ozonization is an excellent method for bleaching wood pulp. Ancelle and Plancon (1) report its advantages over the use of chlorine dioxide in pulp bleaching.

One of the fast-rising areas of ozonization research is that of waste water treatment. Historical work includes that of Baylis (5), whose work in 1935 indicated significant reduction of color, odor and bacteria through ozonation. The work of Huibers, et al. (11) is an illustration of a more recent study on ozone treatment of secondary

effluents from treatment plants. Effective reduction of COD, color and odor is reported from their studies.

Other investigators (4) report effective oxidation of phenols from water with ozonation. Since a large part of pulp mill waste water contains phenol groups, ozonation is thus thought to be an excellent tertiary treatment for such water.

The high cost of ozone production can be diminished by improved generation methods as well as using cheaper sources of high purity oxygen in such production. Work by Steinberg and Beller (16) indicates ozone synthesis by high energy radiation costs half that required by the conventional method of electric discharge. The Linde Division of Union Carbide describes a relatively inexpensive method (using molecular sieve beds) for generating high purity (95%) oxygen.

B. Current Methods for the Treatment of Pulp Mill Effluent

The oldest method of treatment of pulp mill effluent has been primary treatment using a clarifier to rid the waste water of suspended solids. Probably the most common method of secondary treatment is the activated sludge process using aerobic bacteria (14), with mechanical aerators providing the oxygen. Its purpose is to lower the BOD. Variations on this process include that done by Barton and Byrd (2), who report good BOD removal by concentrating the liquor in evaporators, sending the condensed vapor through the activated sludge process, and burning the solid matter for energy. This method of treatment is expensive due to the energy requirement of the evaporators and the capital cost of the necessary equipment. Ozone treatment, in contrast, would not require these costs.

Tertiary treatments thus far studied consist of two main methods for color removal which are activated carbon adsorption and lime precipitation. Tempe, et al. (17) conclude that activated carbon provides a satisfactory treatment for this purpose. Davis (9) reports excellent results with a second method for color removal, lime treatment. Lime reacts with the color-producing bodies and the resulting material settles out. Both methods have limitations, however. When the activated carbon and lime beds are saturated with the color producing bodies, they must be regenerated or discarded. Careful control must be used in regeneration to avoid air pollution. Discarding the saturated beds might cause additional pollution problems. Although little research is reported concerning the odor problem, Huibers, et al. (11) report ozonization is effective for odor reduction as well as in COD-BOD reduction and color removal.

C. Gas-Liquid Contact Systems

Gas-liquid contact systems can be divided into two general categories: (1) low shear rate, and (2) high shear rate. Absorption columns are characterized by a low shear rate while venturi scrubbers provide high shear rates.

The reaction between ozone and pollutants is limited by the necessity of dissolving the ozone in the waste water. A contact device providing a high shear rate (high turbulence) would promote better mass transfer than a low shear rate device. High shear rates promote higher mass transfer coefficients and therefore faster reaction rates. Work by Jackson and Collins (13) on the use of venturi aerating devices indicate increased oxygen transfer to the liquid over conventional

methods--e.g., spargers and diffusers. Huibers, et al. (11) report approximately twice the COD reduction with a high rather than low shear rate device. (Thus a venturi gas-liquid method was chosen for the portable ozone unit described in this thesis. Sizing of the venturi was based on the work by Jackson and Collins).

III. DESIGN OF PORTABLE TEST UNIT

A. Preliminary Work

Preliminary tests on a batch process were conducted to yield information for the construction of the continuous system used on the portable test unit, i.e., flow rates, residence times and temperatures. A schematic diagram of the batch process is shown in Figure 1. The reaction vessel was a two-liter glass diffusion column with a sample valve near the bottom. Ozone was produced by a Welsbach C-1-D model ozone generator provided by the Welsbach Corporation. All tests run in these studies used pure oxygen as feed to the ozone generator. A wet test meter made by the Precision Scientific Co. and an electric timer from the Lab-Line Instruments Co. were used to determine the ozone-oxygen flow rate out of the ozone generator. A potassium iodide solution was used to destroy any unabsorbed ozone in the gas before it passed to the test meter.

B. Tests

The test for COD level employed in these studies was taken from Standard Methods for the Examination of Water and Waste Water (15). The test procedure and a sample calculation are outlined in the Appendix A. Color tests were done with a Bausch and Lomb spectrophotometer in the form of light transmittance at a wave length of 420 Å. No apparatus was available for determination of odor, so personal judgments on the severity of odor were made. Ozone concentrations were determined by the method outlined in Basic Manual of Applications and Laboratory Ozonization Techniques (3), published by the Welsbach Corporation. The procedure and a sample calculation are outlined in the Appendix B.

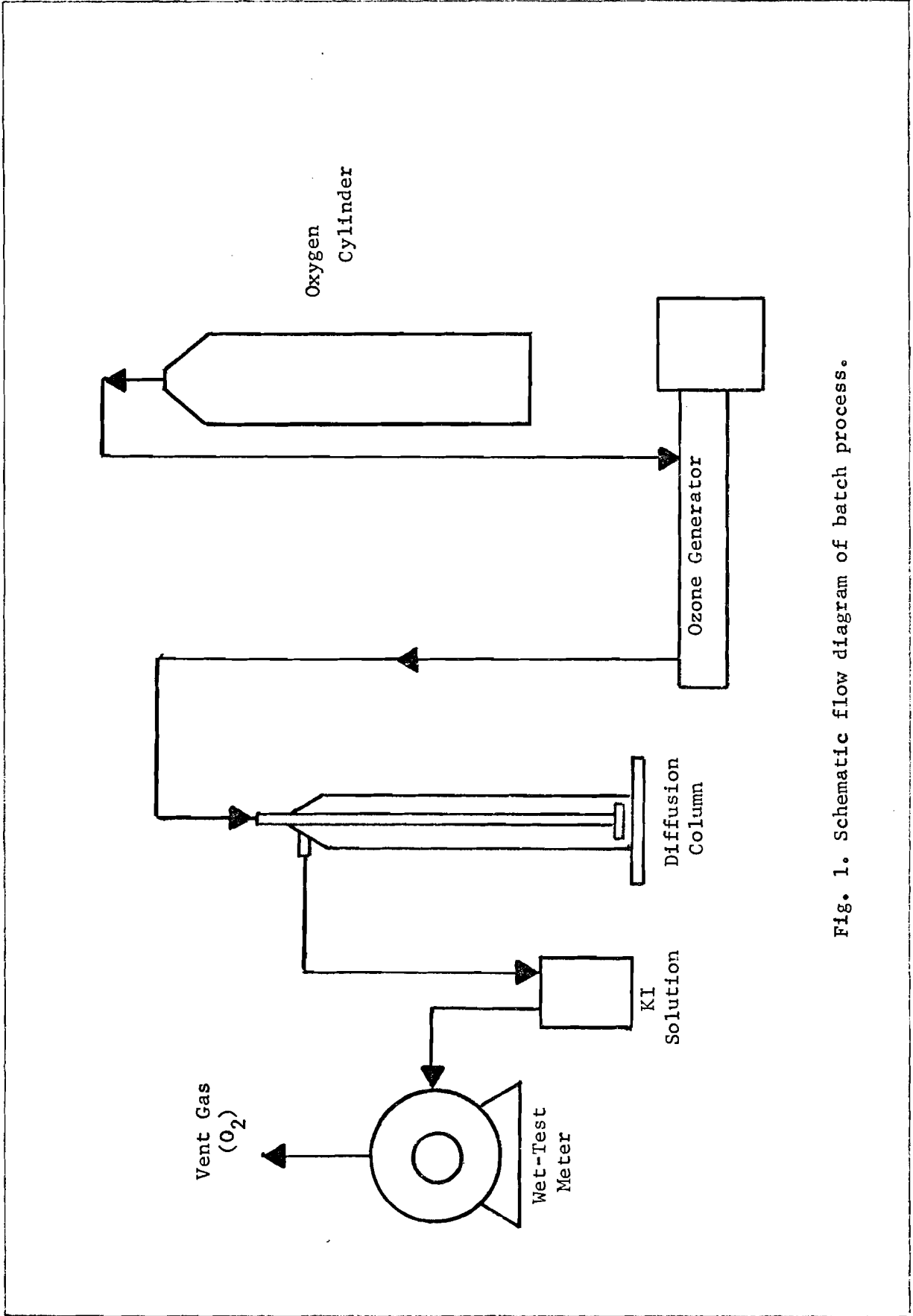


Fig. 1. Schematic flow diagram of batch process.

The batch process tests were run on the following types of pulp mill waste: (1) clarifier inlet, (2) bleach plant outlet, and (3) secondary treatment outlet. The effects of treatment time and variation of the gas flow rate on the waste water were recorded. As shown in Figure 2, ozone produced is a non-linear function of gas flow rate.

Originally, 500 ml samples were treated in a glass bottle for five minutes with varying gas flow rates. COD, odor and color tests were run on these samples before and after treatment. Results are shown in Table 1. No conclusions were drawn other than that ozonization was reducing these variables and that a better testing apparatus was needed to improve results. Although the gas-liquid contact method (a diffusion bulb) used in these tests was the same as finally adopted in the apparatus shown in Figure 1, the geometry of the original reaction vessel prevented contact of all waste water with the oxygen-ozone mixture. At this point it was decided to have a slender glass column (also shown in Figure 1) made so that all the liquid would be in contact with the gas mixture. A valve was attached to the cylinder so that samples could be withdrawn, COD and light transmittance could be determined with contact time, and a residence time for the continuous process could be established.

Initial tests with the new diffusion column were run for five minutes. Some of the results are shown in Figure 3, 4 and 5. Figures 3 and 4 show that for a given type of pulp mill waste, the effect of ozone concentration on light transmittance and COD was not very significant. The effect of ozone concentration on light transmittance for different types of pulp mill waste is illustrated in Figures 4 and 5. Such similarity in results provided the rationale for treating only one type of pulp mill waste with the portable test unit. The reaction

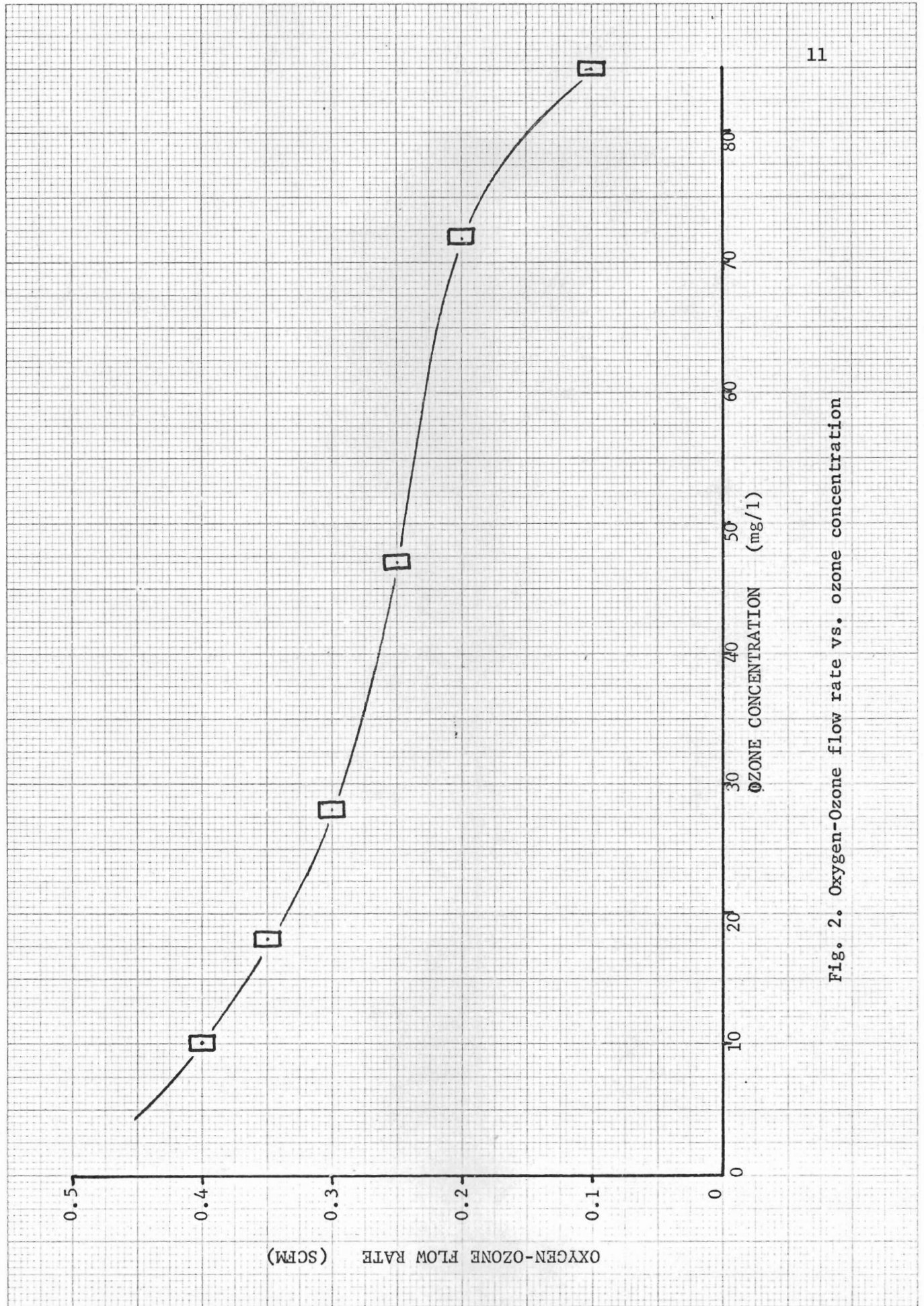


Fig. 2. Oxygen-Ozone flow rate vs. ozone concentration

Table 1. Chemical oxygen demand and light transmittance after a five minute treatment period.

SAMPLE	GAS FLOW RATE (SCFM)	O ₃ CONC (mg/l)	COD BEFORE TREATMENT (mg/l)	COD AFTER TREATMENT (mg/l)	LIGHT TRANSMITTANCE BEFORE TREATMENT (%)	LIGHT TRANSMITTANCE AFTER TREATMENT (%)
Clarifier Inlet	.338	21	1150	416.0	6	37
Bleach Plant	.317	23	1050	403.2	19	49
Clarifier Outlet	.322	23	1040	640.0	9	73
After Secondary Treatment	.306	26	950	391.0	4	35
Clarifier Inlet	.338	21	1070	453.0	6	37
Clarifier Inlet	.354	18	970	507.0	6	23
Clarifier Inlet	.350	18	1120	421.0	6	22
Clarifier Inlet	.339	16	950	476.0	7	23
Bleach Plant	.364	15	980	450.0	15	62

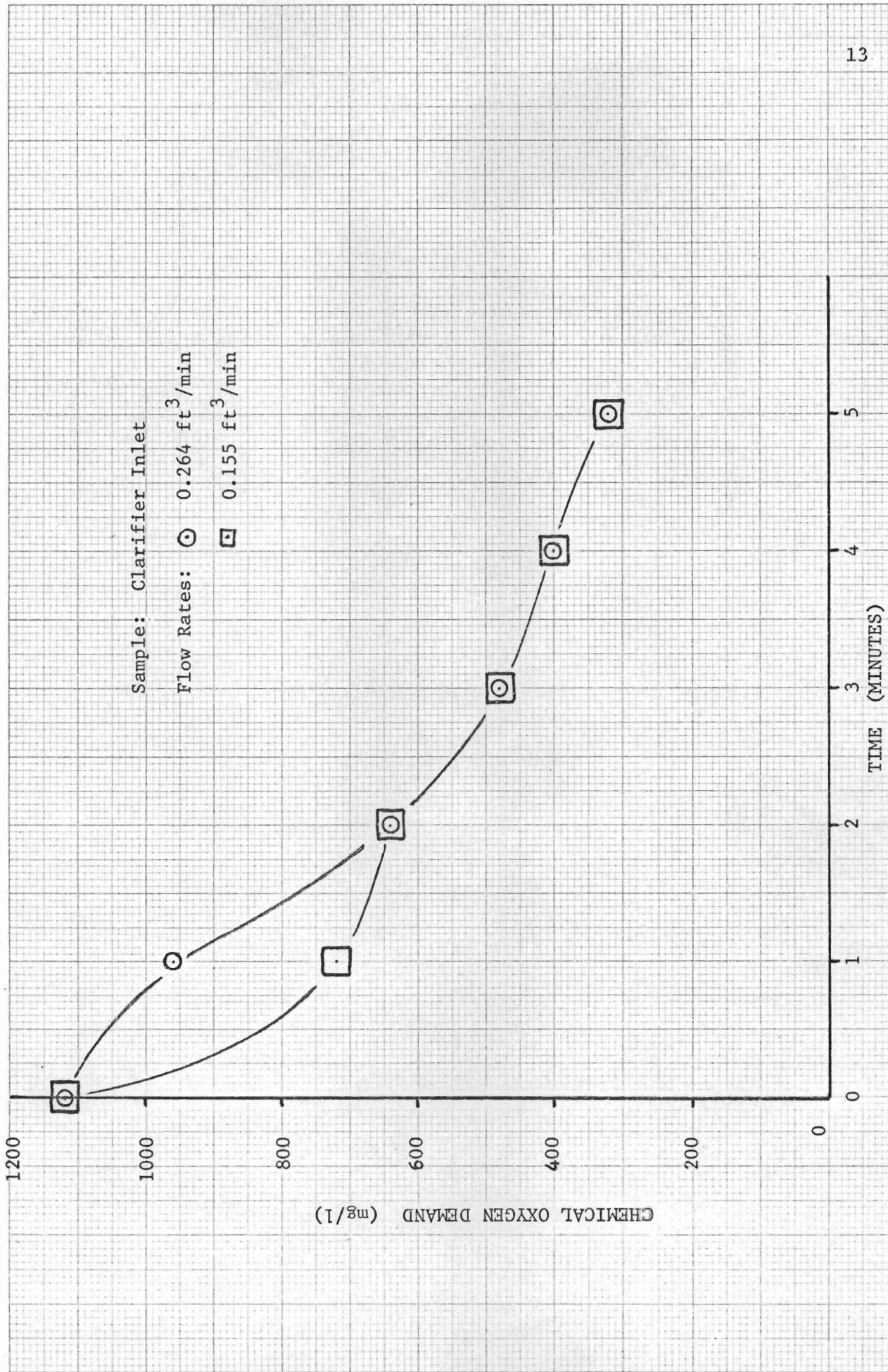


Fig. 3. Chemical oxygen demand vs. time

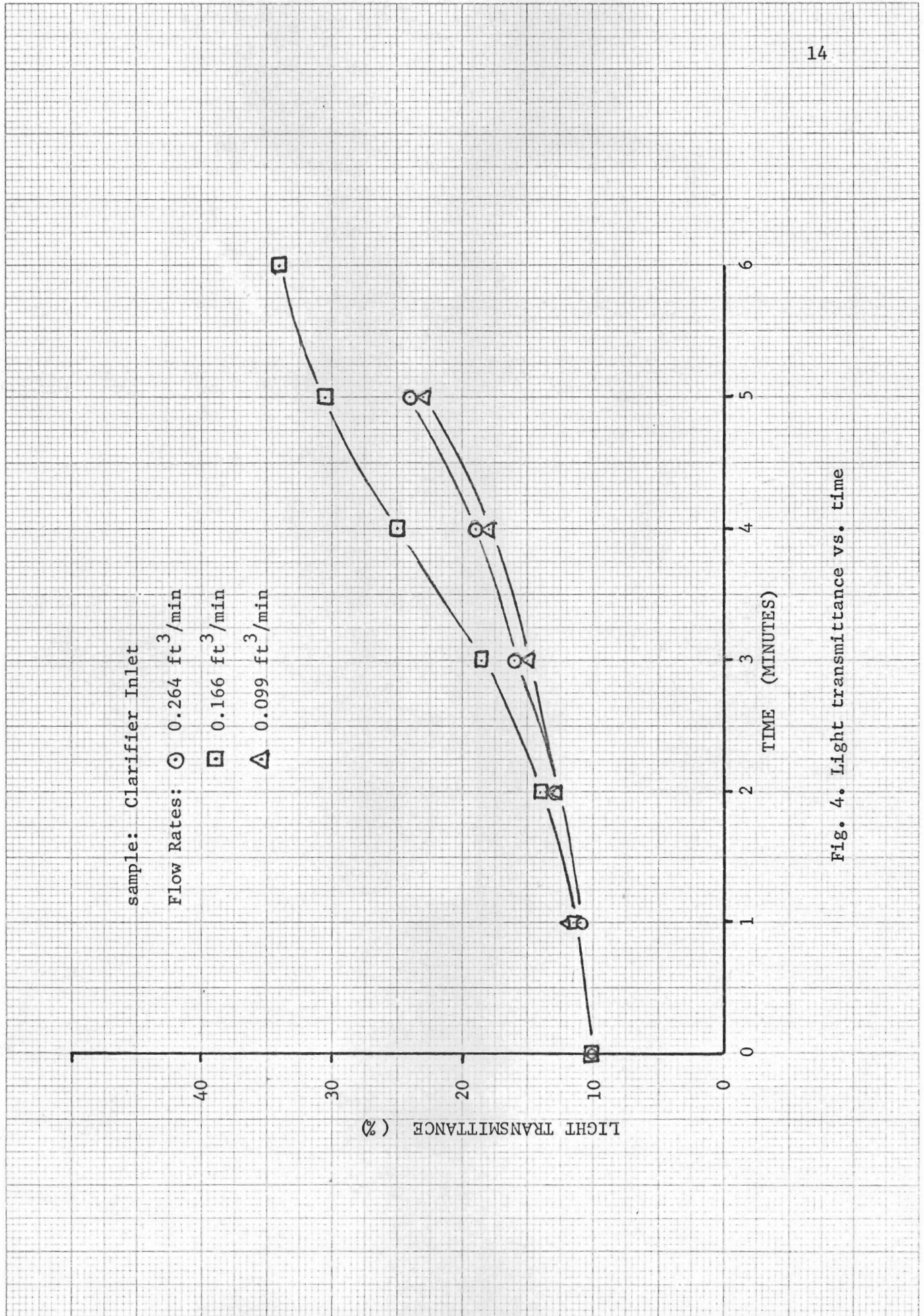


Fig. 4. Light transmittance vs. time

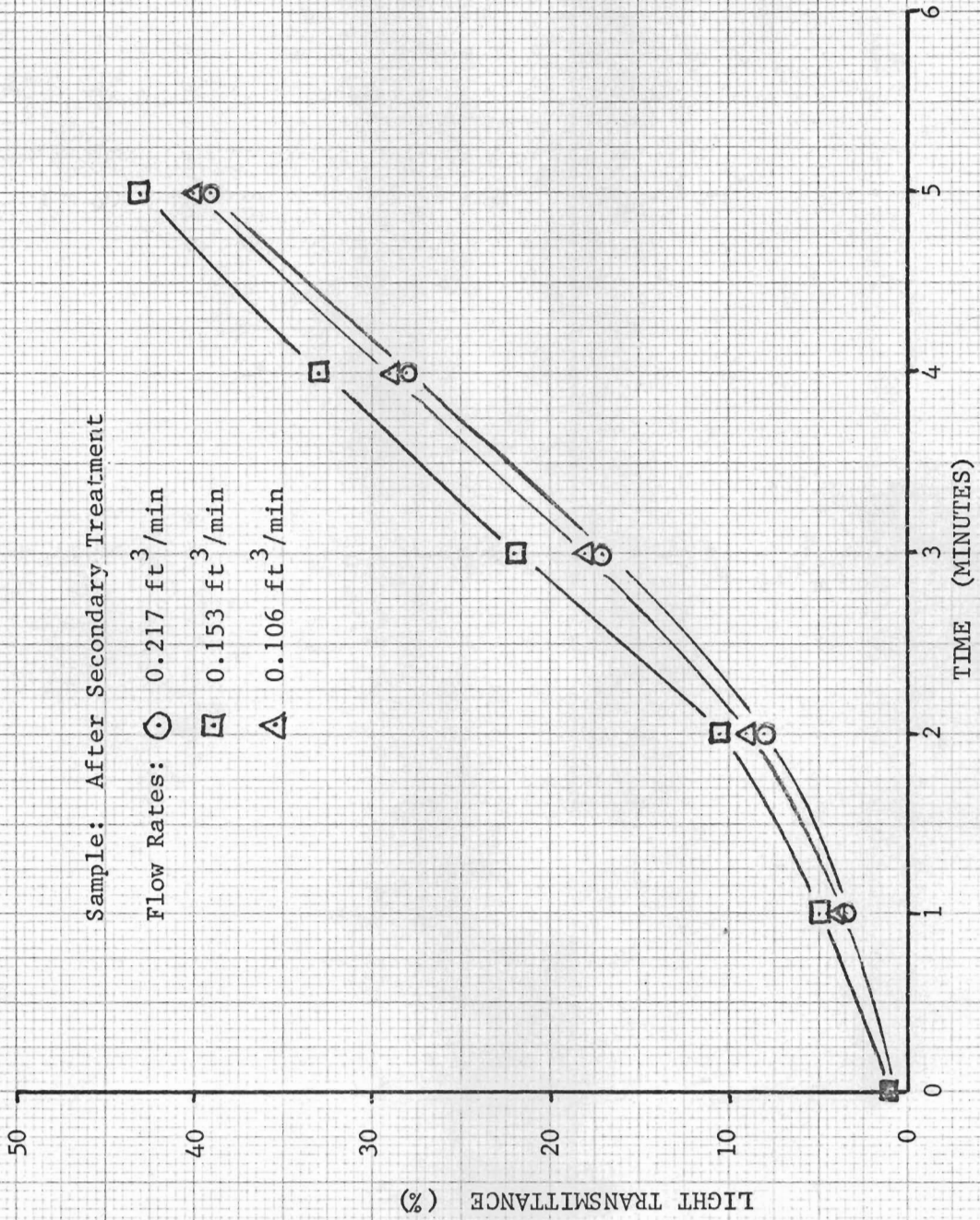


Fig. 5. Light transmittance vs. time

between ozone and the contaminants was still proceeding after five minutes so the tests were extended to ten minutes. Typical results of these tests are illustrated in Figures 6 and 7. Figures 6 and 7 show effects of ten-minute ozone treatment on different types of pulp mill waste. Again, similar results of COD and color reduction led to treatment of one type of pulp mill waste with the portable test unit. Such "S"-shaped curves of COD reduction and light transmittance are to be expected since the amount of ozone available limits the reaction rate. Initially the change is gradual since the concentration of contaminants is high in comparison to the concentration of ozone. As the concentrations become more equal, the reaction rate increases. As most contaminants are oxidized after approximately six minutes, the reaction rate decreases and the curve levels off. A ten-minute limit to the test was chosen because the slope of the curve near this point indicated a slow reaction rate. As a check, one test was run for thirty minutes, resulting in a light transmittance of 98% and a COD of 50 mg/l. It was considered economically infeasible to run the tests over ten minutes since the major portion of the pollutants were already oxidized (average light transmittance at ten minutes, 55%; average COD at ten minutes, 210 mg/l).

A nominal residence time for the continuous system was set at six minutes as this was the point where the reaction between ozone and the pollutants slowed considerably. This is illustrated in Figures 6 and 7. Samples of ozone in the gas stream taken before and after contact with the waste water indicated that only about 13% of the available ozone was being used.

The following calculations were made to give an estimate of the

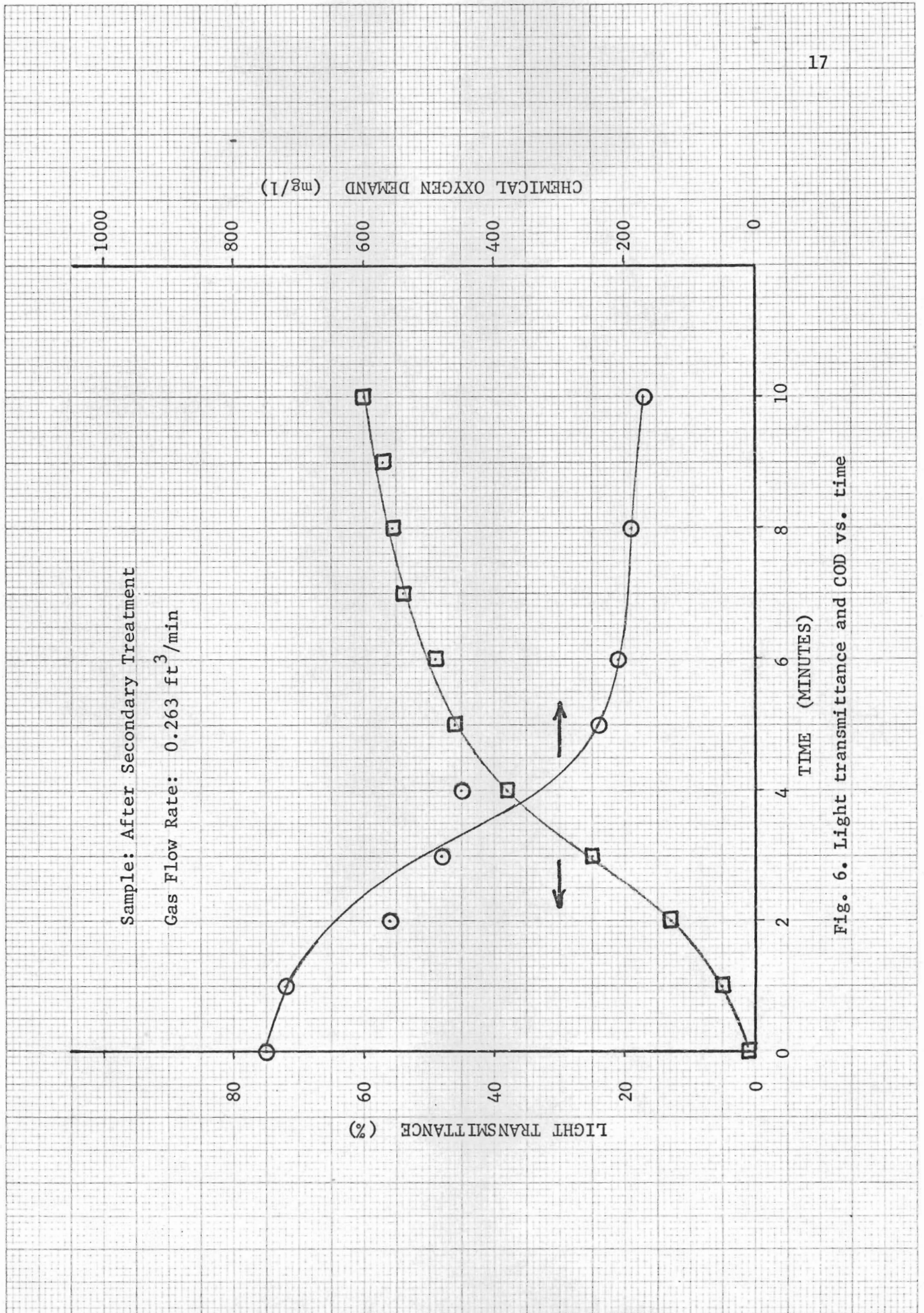


Fig. 6. Light transmittance and COD vs. time

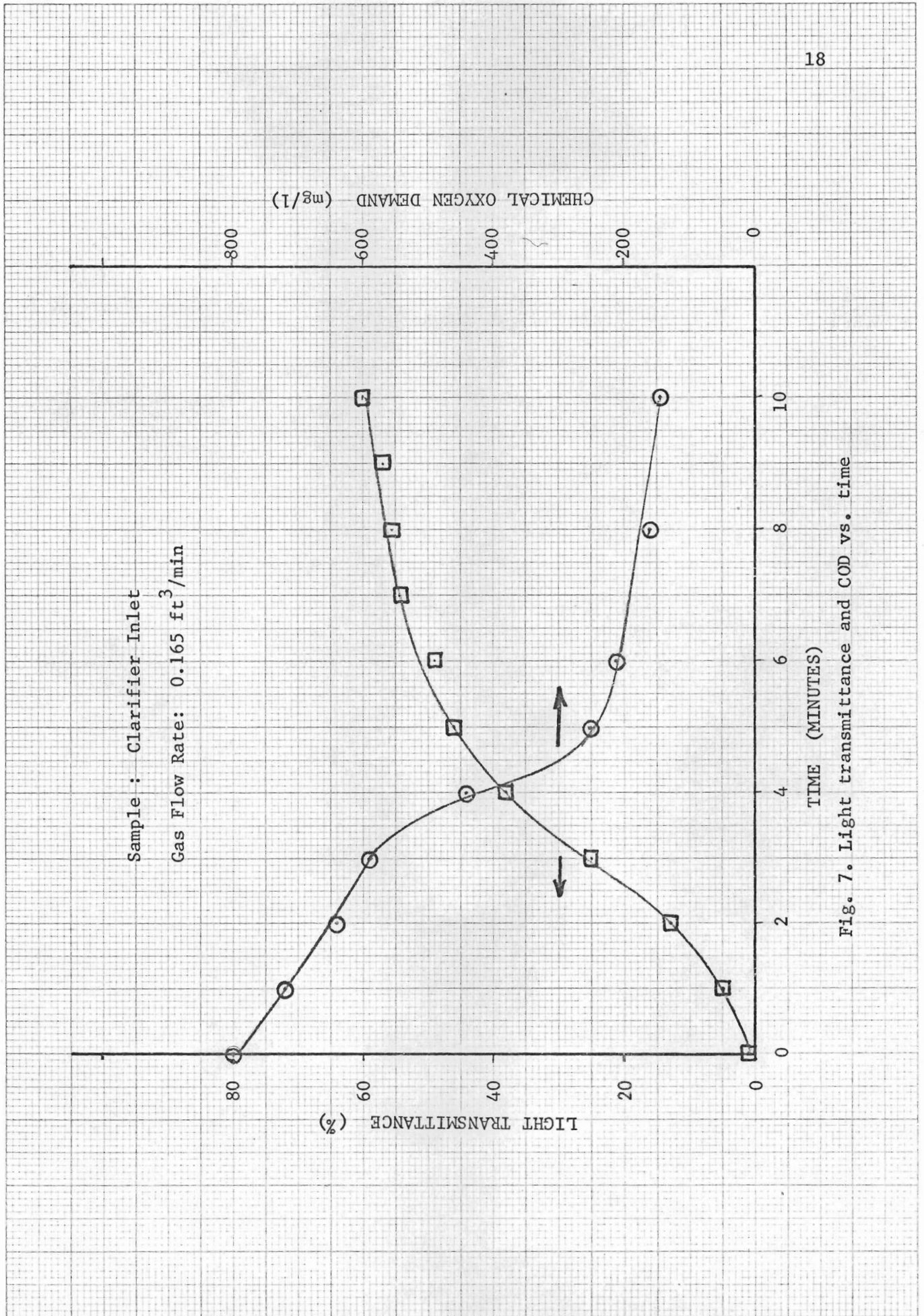


Fig. 7. Light transmittance and COD vs. time

flow rate and the tank volume to be used in the continuous process:

$$\frac{\text{Sample Volume}}{\text{Ozone Utilization Rate}} = \text{Approximate Tank Volume}$$

$$\frac{1 \text{ liter}}{.13} = 7.7 \text{ liters (maximum)}$$

$$\text{Liquid Feed Rate} = \frac{\text{Tank Volume}}{\text{Residence Time}}$$

$$\frac{7.7 \text{ liter}}{6 \text{ min.}} = 1.28 \text{ liter/min.}$$

Final sizing of the tank and the feed pump was such that sample volumes and liquid feed rates could be varied above and below the values calculated above.

D. Portable Test Unit

The portable test unit was constructed around the ozone generator, the frame consisting of 2-inch angle iron and 1/8-inch aluminum sheet. An overall view is shown by the photographs in Figure 8. A schematic flow diagram is shown in Figure 9.

A list of the equipment used is as follows:

- (1) Welsbach Model C-1-D Ozone Generator
- (2) Welsbach Ozone Meter
- (3) 1.5 gpm peristaltic pump (variable speed)
- (4) 5 gpm peristaltic pump
- (5) Foxboro Recorder
- (6) 2.16 scfm gas flow meter
- (7) 1.44 gpm liquid flow meter
- (8) Beckman pH Meter
- (9) Thermocap Relay

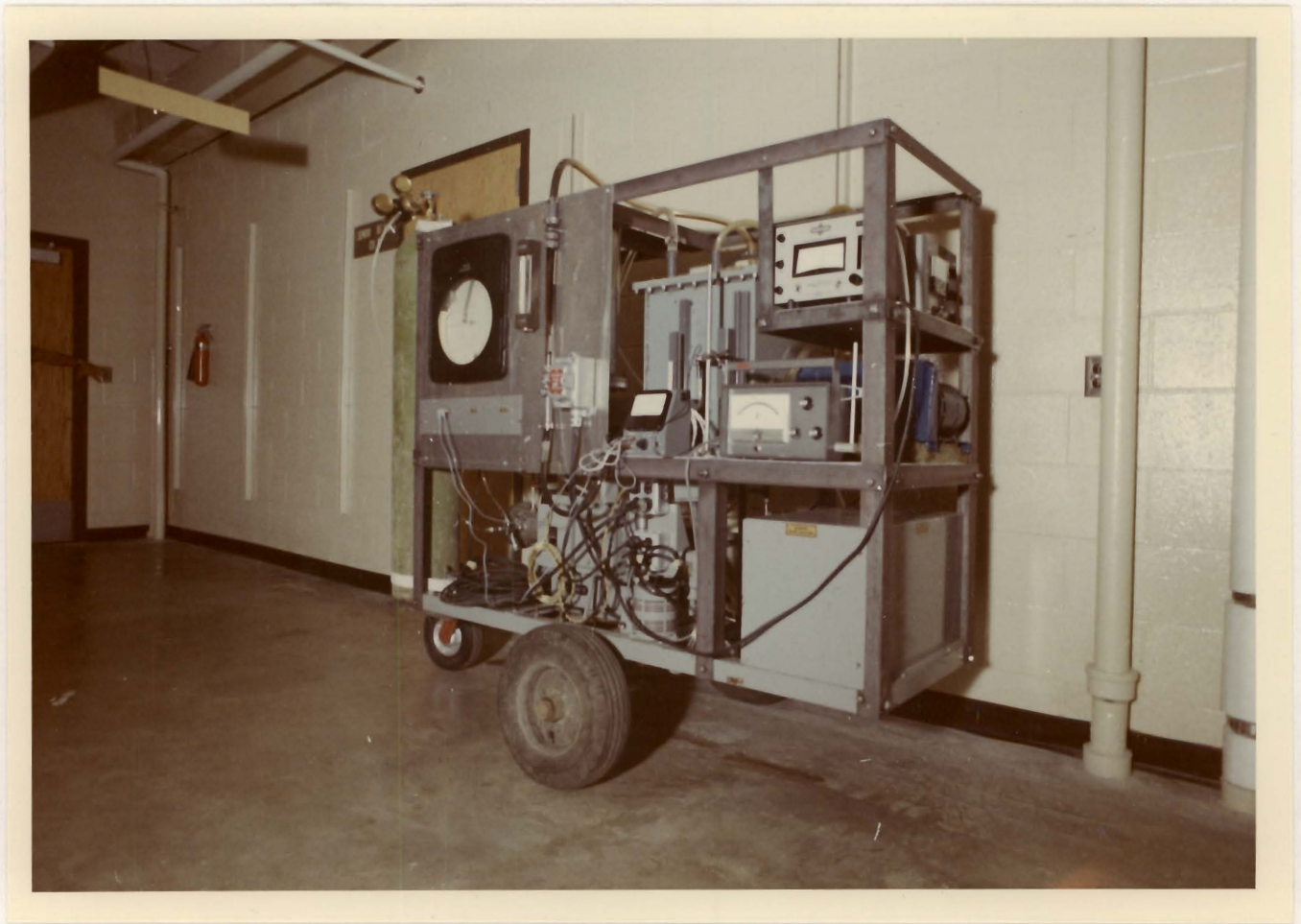


Fig. 8. Portable ozone test unit photographs

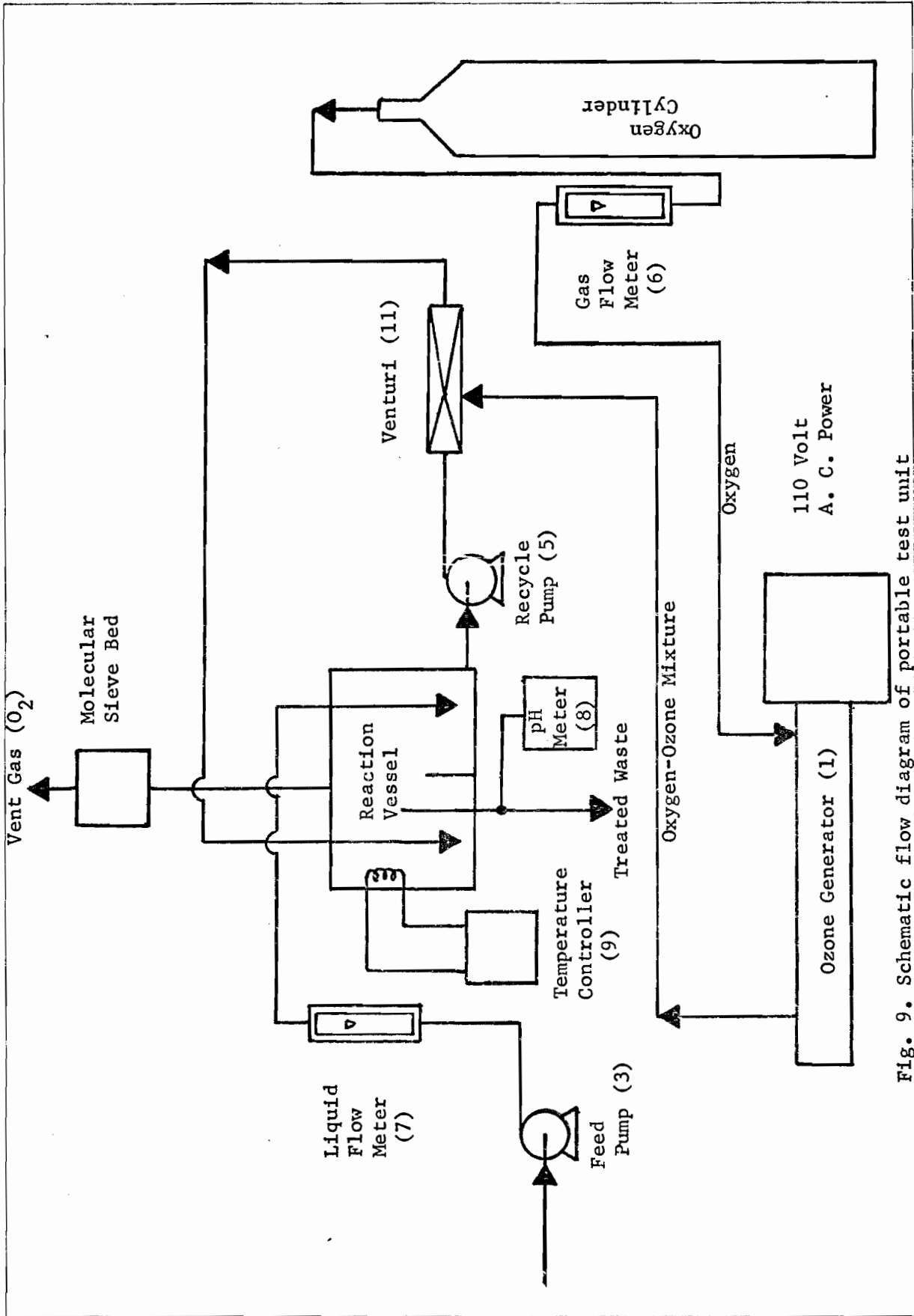


Fig. 9. Schematic flow diagram of portable test unit

(10) Cole-Parmer Tele-Thermometer (YSI Model)

(11) Venturi gas-liquid contactor

The Welsbach ozonemeter was intended to monitor the ozone concentration of the gas prior to its contact with the liquid. However, its poor reliability required the use of the titration method described in the Appendix B. The titration method was also used to determine ozone concentration in the treated waste and vent gas.

The feed pump was a 1.5 gpm peristaltic pump, chosen because it covers the range above and below that suggested by the results of the batch process. A peristaltic pump operates by squeezing a fluid through a tube. This squeezing action is accomplished by rollers. The flow rate of this pump could be varied depending upon the size of tube used. Also it produces a nearly constant flow rate regardless of the head against which it is pumping. The 5 gpm peristaltic pump was chosen for the recycle loop. The venturi placed in this loop downstream of the pump was the point of gas-liquid contact.

A venturi was chosen as the method of gas-liquid contact since good mass transfer occurs in the throat and in the expansion section downstream. In addition, the high shear rate with the venturi was preferred over the low rate of other methods, e.g., a contact column. Ozone was introduced through taps in the throat of the venturi. The suction in the throat of the venturi prevented any waste from backing up into the gas line. The venturi was turned out on the lathe from PVC stock. A cross-section of the venturi, with dimensions, is shown in Figure 10.

The Foxboro Recorder was used to keep a continuous record of temperature in the reaction vessel and the pH of the treated waste water.

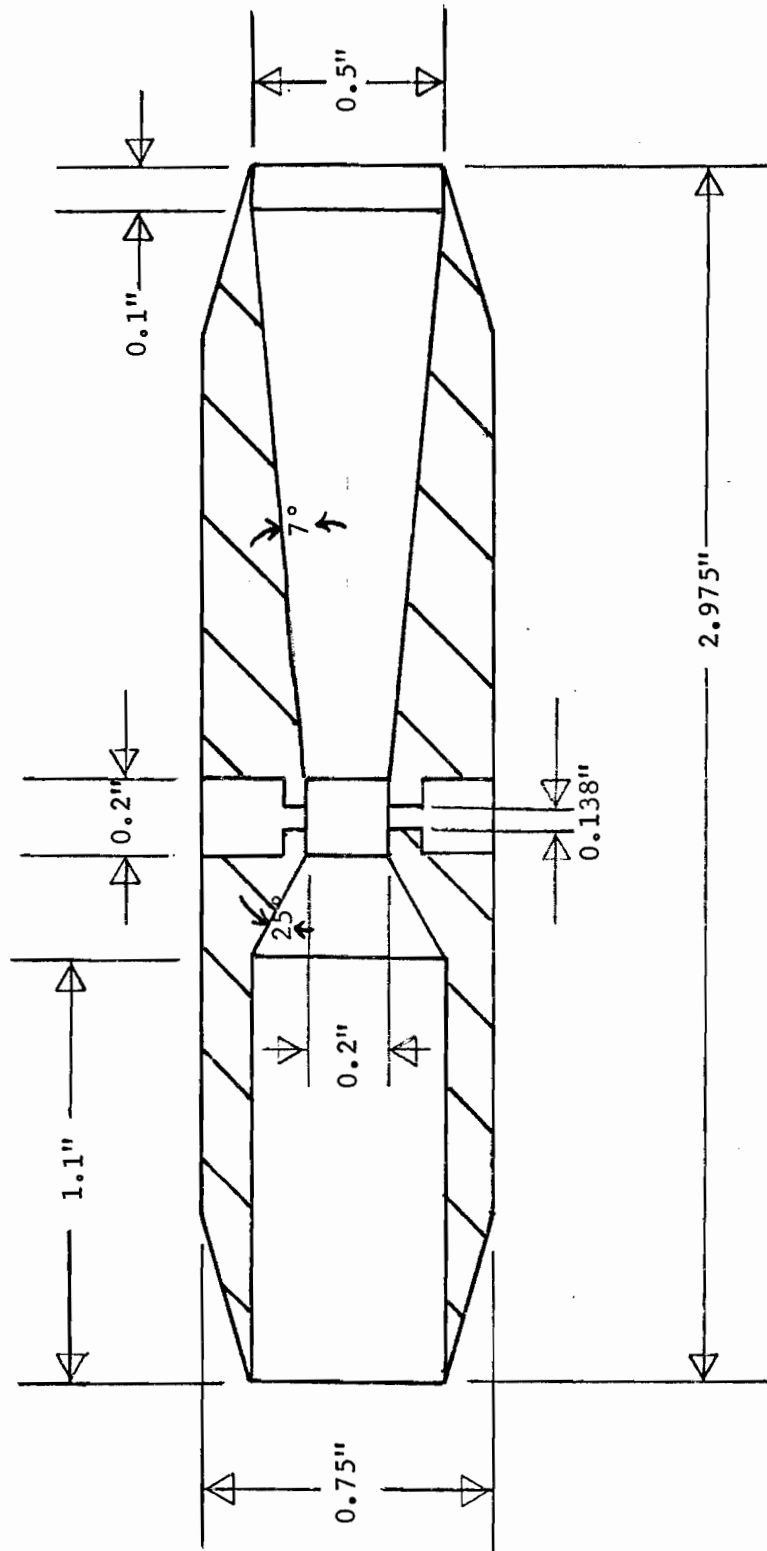


Fig. 10. Cross section of venturi used for gas-liquid contact

There were two temperature probes in the tank that sent signals to a switching relay which in turn sent signals to the Tele-Thermometer.

The pH of the liquid waste water varied from 7.3 to 7.5 and ozonization reduced this, at the most, by 0.2, indicating little significance in pH reduction. Also, the pH printout on the recorder was so erratic (varying as much as 100% from one minute to the next at identical operating conditions) that no conclusions could be drawn.

The Thermocap relay was wired to a heating coil in the reaction vessel so the tank temperature could be controlled and its effects on COD, color and odor noted.

Figure 11 is a more detailed diagram of the reaction vessel than that shown in Figure 9. The vessel was constructed of 1/4-inch PVC sheet and has overall dimensions of 15 x 15 x 18 inches. The untreated pulp mill waste was introduced close to the inlet of the recycle loop. The purpose was to insure that most of the fresh feed was treated. The liquid-gas mixture in the recycle loop was fed back to the reaction vessel on the side of a baffle opposite the feed inlet. Again, this was to insure that the untreated waste was treated. The overall effect of this design was to approximate a continuous stirred-tank reactor.

The liquid level in the tank was maintained by a standpipe. A baffle was placed inside the pipe to prevent the formation of a vortex which, in early runs, sucked some ozone through the standpipe. It should be noted that the standpipe is part of a trap designed to prevent the escape of ozone. At the top of the outside portion of the trap is a box from which samples of treated waste water were taken. Also, insertion of the pH probe into the box allowed continuous pH

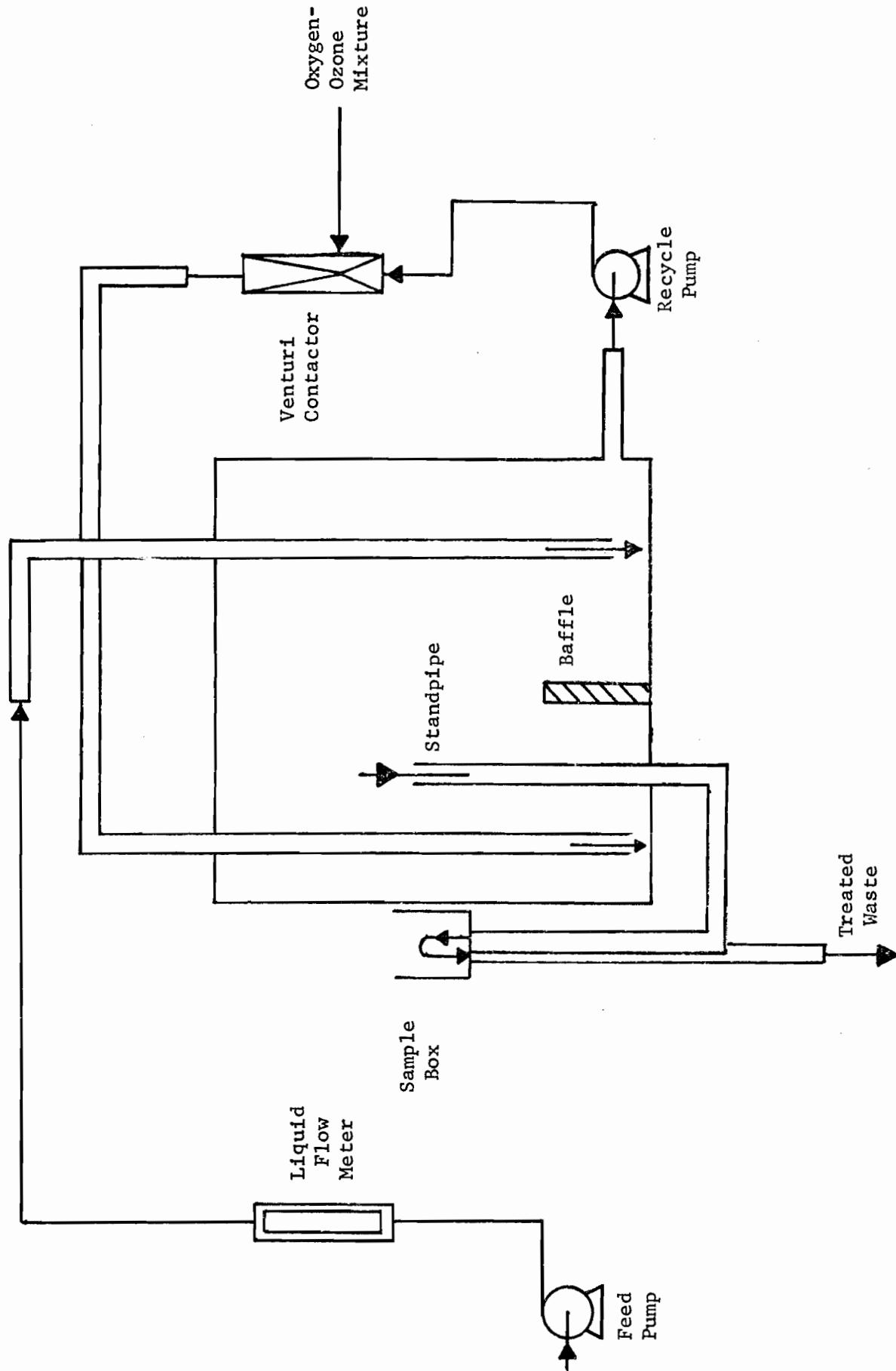


Fig. 11. Schematic flow diagram of reaction vessel

readings. At the top of the reaction vessel is a vent through which all unused ozone passed through a molecular sieve bed. Here the excess ozone was converted to oxygen. All connections between pieces of equipment were with Tygon tubing, chosen for its flexibility and resistance to ozone.

A brief summarization of the operation of the test unit follows. The waste water flows from the feed pump through the liquid flow meter to the reaction vessel. Next it is pumped into the recycle loop and through the venturi where it is put into contact with the ozone-oxygen mixture. This gas-liquid mixture returns to the tank where it circulates until it goes out the standpipe. Any unused ozone should react with the liquid already in the tank. Any remaining ozone goes out the vent.

IV. PERFORMANCE OF THE PORTABLE TEST UNIT USING KRAFT PULP MILL WASTE

A. Limitations

There are several limitations inherent in this unit. First, the gas flow rate should be kept below approximately 0.5 scfm. Above this rate the amount of waste water going through the venturi is reduced to the point where a considerable amount of the waste water is untreated, flowing out the standpipe before it can be treated. Although exact amounts of untreated waste were not established at or above 0.5 scfm, experience showed that test results at such flow rates were poor.

Second, ozone concentrations at high gas flow rates are too low, theoretically, for satisfactory reaction rates. Third, the amount of ozone produced by this ozone generator at a reasonable gas flow rate (0.1-0.4 scfm) will only treat a fixed quantity of pollutants. An attempt to treat more than this amount results in less than satisfactory performance of the test unit.

Last, foaming proved to be a severe problem. A foam trap was placed just upstream of the molecular sieve which alleviated part of the problem. However, some means to prevent foam from going out the standpipe should be devised. This problem was avoided in these runs by adding a silicone anti-foam agent to the sample before treatment. The anti-foam agent did not add to the COD of the sample.

B. EVOP Process

This procedure was adopted from "Evolutionary Operation: A Method For Increasing Industrial Productivity" (6). In the process of optimizing the operation of the test unit, residence time, gas flow rate, and

reaction vessel temperature were chosen as independent variables. It should be noted at this point that all residence times were calculated based on a tank volume of 1.62 gallons. Equal residence times for different tank volumes do not produce the same results because of the ozone production rate limitation. Therefore, tank volume should always be included when speaking of residence time.

In the EVOP Process, four starting points are needed if three independent variables are chosen. (In this thesis runs were made at every point.) To determine the starting points, the approximate range limits of the variables must be known. Within this range, an incremental change in values is chosen, this being designated as the step size. For instance, if the temperature range is 75°-95°F, a convenient step size might be two degrees with a "low" of 85°F and a "high" of 87°F.

Table 2 is a general table for choosing the coordinates of the starting points under the EVOP Process.

TABLE 2

<u>Point</u>	<u>Temperature</u>	<u>Residence Time</u>	<u>Gas Flow Rate</u>
1	Low	Low	Low
2	Low	Low	High
3	Low	High	High
4	High	High	High

Tests are run at each of the four points and the resulting effect on COD, light transmittance (color), and odor are noted. The COD, color, and odor are converted to a 0.0-1.0 scale; the worst results are defined as 0.0 and the best as 1.0. A COD value of 1200 mg/l, a light transmittance

of 0% and the sample odor were designated as 0.0. A COD of 200 mg/l, a light transmittance of 60%, and no odor were designated as 1.0. Personal judgment based on experience was used to determine values for the desirability factors of 1.0. Anything between 0.0 and 1.0 is found by linear interpolation. These numbers are called desirability factors, d_{ij} , where "i" refers to the point and "j" refers to the responses, COD, color and odor in this case. In these tests responses are labeled as follows:

$$\begin{aligned}d_{i1} & - \text{COD} \\d_{i2} & - \text{light transmittance} \\d_{i3} & - \text{odor}\end{aligned}$$

An overall desirability factor, D_i , is calculated thusly,

$$D_i = \sqrt[3]{d_{i1}d_{i2}d_{i3}}$$

Table 2 is extended by the addition of the desirability factors (see Table 3).

TABLE 3

Point	Temperature	Residence Time	Gas Flow Rate	d_{i1}	d_{i2}	d_{i3}	D_i
1	Low	Low	Low	d_{11}	d_{12}	d_{13}	D_1
2	Low	Low	High	d_{21}	d_{22}	d_{23}	D_2
3	Low	High	High	d_{31}	d_{32}	d_{33}	D_3
4	High	High	High	d_{41}	d_{42}	d_{43}	D_4

Obviously, the point with the lowest D_i is the worst point. Point 5 is calculated by the following method (temperature being chosen here as an example):

new $T = 2 \times (\text{ave. temp. of best } D_i \text{'s}) - (\text{temp. of worst } D_i)$

A sample calculation is shown in the Appendix C.

This process continues until an optimum (the greatest value of D_i) is found. At the optimum the step size is reduced and the above process repeated until a new optimum is reached. Further reduction of step size continues until an optimum, accurate within experimental limits, is reached.

This method has been shown to be effective and rapid in reaching optimum operating conditions and is superior to the time-consuming method in which one parameter is varied and the rest held constant.

C. Preliminary Data for EVOP

It should be noted at this point that the only waste water treated with the portable test unit was the clarifier inlet waste, this being due to the time-consuming process of bringing samples from their source in sufficient quantity to use the EVOP Process. Since the characteristics of the clarifier inlet waste changed over a period of a few days, fresh samples had to be brought in often. The COD, light transmittance, and odor of these fresh samples did not vary significantly.

After completion of the test unit, several runs were made to determine the operating range of the three independent variables used in EVOP. The results of these runs are shown in Table 4. If the tank volume is doubled, the residence time must be doubled to get the same reduction of COD, color and odor. Runs 13-16 of Table 4 show fairly good results for a residence time of 5.7 minutes at 0.82 gallons. Runs 5-8 have poor results since the residence time did not go up in direct proportion with the tank volume (for good results the residence

Table 4. Preliminary test data required for EVOP process

POINT	LIQUID FEED RATE (GPM)	TANK VOLUME (GAL)	GAS FLOW RATE (SCFM)	TANK TEMPER- ATURE (°F)	HOLDING TIME (MIN)	COD (mg/l)	LIGHT TRANS- MITTANCE (%)	ODOR
1	1.44	8.6	0.4	75	8.1	960	9	present
2	1.44	8.6	0.4	95	8.1	1020	9	present
3	1.44	8.6	0.1	75	8.1	880	9.5	present
4	1.44	8.6	0.1	95	8.1	920	9	present
5	.144	8.2	0.4	75	31.2	880	11	present
6	.144	8.2	0.4	95	31.2	910	11	present
7	.144	8.2	0.1	75	31.2	790	14	present
8	.144	8.2	0.1	95	31.2	840	13.5	present
9	1.44	1.22	0.4	75	.85	1180	2	present
10	1.44	1.22	0.4	95	.85	1180	2	present
11	1.44	1.22	0.1	75	.85	970	3	present
12	1.44	1.22	0.1	95	.85	1020	3.5	present
13	.144	.82	0.4	75	5.7	400	19	none
14	.144	.82	0.4	95	5.7	430	19.5	none
15	.144	.82	0.1	75	5.7	320	26	none
16	.144	.82	0.1	95	5.7	360	27	none

time should have been approximately 57 minutes rather than 31.2 minutes for the volume of 8.2 gallons).

Also, higher temperatures seem to hinder the effectiveness of the unit. A probable explanation might be that the higher temperatures tend to decompose the ozone before it has a chance to react with the pollutants and/or prevent the ozone from dissolving into the waste water.

The good results of runs 13-16 influenced the choice of starting points for EVOP. The starting points used and EVOP's progression to the optimum are presented in Table 5.

Table 5. EVOP process used to determine the optimum operating conditions of the portable test unit.

POINT	TANK TEMP- ERATURE (°F)	RESIDENCE TIME (MINUTES)	GAS FLOW RATE (SCFM)	d ₁ (COD)	d ₂ (COLOR)	d ₃ (ODOR)	D
17	80	9	0.2	.66	.58	1.0	.726
18	80	9	0.25	.68	.58	1.0	.736
19	80	11	0.25	.76	.64	1.0	.786
20	85	11	0.25	.78	.66	1.0	.801
21	83.3	11.7	0.30	.88	.72	1.0	.860
22	85.6	13.5	0.28	.80	.68	1.0	.817
23	85.6	10.1	0.28	.72	.67	1.0	.784
24	80	11.5	0.30	.87	.72	1.0	.855
25	80	11.5	0.32	.86	.69	1.0	.840
26	80	12	0.32	.90	.73	1.0	.870
27	85	12	0.32	.96	.75	1.0	.896
28	83.3	12.2	0.33	.92	.73	1.0	.875
29	85	11.9	0.31	.95	.73	1.0	.886
30	85	11.9	0.33	.95	.75	1.0	.894
31	85	12.1	0.33	.96	.75	1.0	.896
32	85	12.1	0.33	.94	.73	1.0	.882

V. RESULTS AND CONCLUSIONS

The results of the EVOP Process are indicated on Table 5.

A check on the optimum point was made using higher starting points, with results being identical within the limits of experimental error.

Starting with the first four points of Table 5, point 17 was the worst, and point 21 was calculated as illustrated on page . D_i for point 21 was now the best. Using points 18 through 21, the process was repeated resulting in point 22. In this case there was no improvement in D_i , so point 19 replaced point 18 as the worst. Using the same points in this new order, point 23 resulted. D_i for point 23 was worse than the D_i 's of points 19, 20, 21 and 22. Therefore, the step size around point 21 was reduced and points 24,25,26 and 27 were selected in this step size and another run was made through EVOP, with point 27 producing the best D_i (0.896). Further reduction of step size produced no improvement in D_i .

Based on the results of the above process, the optimum operating conditions are a reactor vessel temperature of 85°F, a residence time of 12 minutes (for a 1.62 gallon tank volume), and a gas flow rate of 0.32 scfm. It should be pointed out that the COD test is not very accurate when small differences in COD are required, as is the case with those around the optimum. Based on this, the operating conditions could be varied by 10-15% with only a small change in results of COD reduction.

Table 6 gives the ozone concentration and mass flow rates at each trial point. Ozone utilization rates were determined for points 17, 21 and 27 for comparison with the batch process and for general information. There is a significant improvement in ozone utilization rates

Table 6. Ozone data acquired through EVOP process.

POINT	GAS FLOW RATE (SCFM)	GAS FLOW RATE (l/min)	OZONE CONC. (mg/l)	MASS FLOW RATE OF OZONE (mg/min)	VENT GAS FLOW RATE (l/min)	VENT GAS OZONE CONC. (mg/l)	VENT GAS MASS FLOW RATE OF OZONE (mg/min)	OZONE UTILIZATION (%)
17	0.20	5.66	71.8	406.7	5.66	25.8	146.2	64
18	0.25	7.08	47.0	332.8				
19	0.25	7.08	47.0	332.8				
20	0.25	7.08	47.0	332.8				
21	0.30	8.50	28.0	237.9	8.50	8.7	73.75	69
22	0.28	7.93	32.0	253.7				
23	0.28	7.93	32.0	253.7				
24	0.30	8.50	28.0	237.9				
25	0.32	9.06	22.0	199.4				
26	0.32	9.06	22.0	199.4				
27	0.32	9.06	22.0	199.4	9.06	4.9	45.0	77
28	0.32	9.06	22.0	199.4				
29	0.31	8.78	29.0	255.0				
30	0.33	9.35	21.0	196.3				
31	0.33	9.35	21.0	196.3				
32	0.33	9.35	21.0	196.3				

over the batch process. In all the runs made in the EVOP Process, no residual ozone was found in the treated waste water.

In conclusion, the portable test unit operated as expected. Optimum operating conditions have been determined and significant results established under these conditions. COD in treated waste water was reduced by 80%, light transmittance was increased from 2% to 49% and odor was reduced until it was imperceptible. (See picture of treated and untreated waste water, Figure 12). Although designed for tertiary treatment, these runs have been made with untreated waste water. Better results and lower costs could naturally be expected if the unit is used as designed.

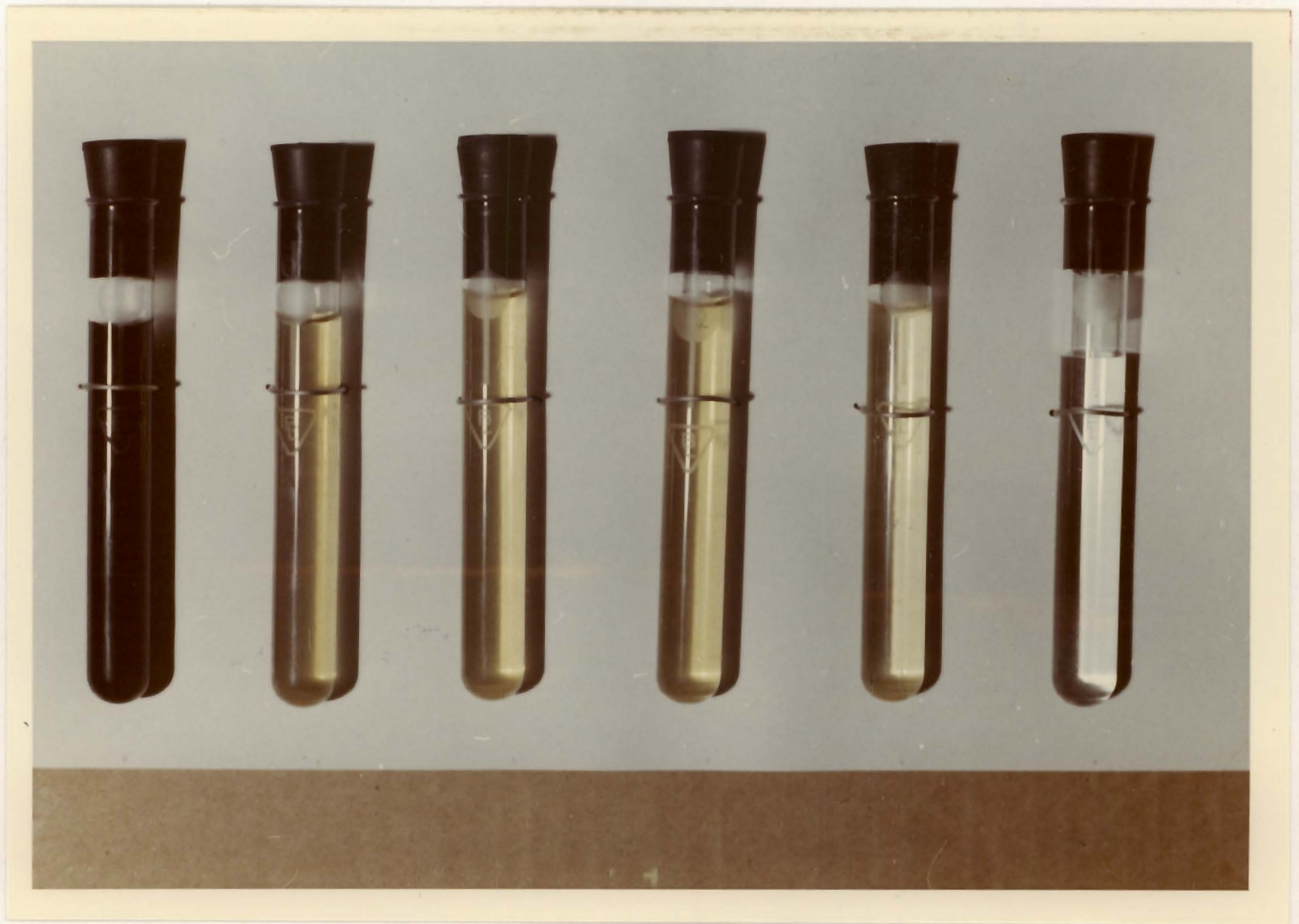


Fig. 12 Waste Water Photographed Before and After Ozonization.

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APPENDICES

APPENDIX A

The Chemical Oxygen Demand Test

The Chemical Oxygen Demand test indicates the quantity of oxidizable organic compounds present in a water.

The procedure for the test is as follows:

- (1) Place 20 ml of sample and 20 ml of distilled water (called the blank) in two 250 ml flasks.
- (2) If chloride ions are present in the sample, add 0.4 mg of mercuric sulfate to each.
- (3) Add to each flask 10 ml of 0.25 N potassium dichromate.
- (4) Next add 30 ml of concentrated sulfuric acid containing silver sulfate to each flask.
- (5) Add mixing beads and reflux for two hours.
- (6) Cool the samples to room temperature, dilute to approximately 140 ml, and add 2-3 drops of ferroin indicator to each flask.
- (7) Titrate the excess dichromate with 0.10 N ferrous ammonium sulfate.

The end point is sharp from blue-green to reddish-brown.

The following equation is used to determine the COD:

$$\text{COD} = \frac{(a-b)c \times 8000}{\text{ml of sample}} \text{ mg/l}$$

where a = ml of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ used for blank

b = ml of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ used for sample

c = normality of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$

As an example, let a = 25 ml

b = 24 ml

c = 0.10 N

then,

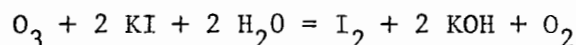
$$\text{COD} = \frac{(25-24)(0.1)(8000)}{20}$$

$$\text{COD} = 40 \text{ mg/l}$$

APPENDIX B.

Determination of Ozone Concentrations By the Iodometric Method

In brief, ozone is absorbed in potassium iodide solution. The liberated iodine is titrated with standard sodium thiosulfate. The reaction is usually written:



No correction is needed for the ozone removed since the reaction produces no change in volume.

1. Liquid Samples

- (a) Place 50 ml of potassium iodide in a 250 ml flask.
- (b) Add 100 ml of ozone-containing sample.
- (c) To this solution add 10 ml of 1 M sulfuric acid.
- (d) Using starch as an indicator, titrate the sample with 0.10 N sodium thiosulfate.

The end point is sharp from deep purple to clear.

2. Gas Samples

- (a) Place about 400 ml of KI in an absorption column.
- (b) Start the passage of ozonized air through the column.
- (c) Stop the flow when about 3 liters has passed through and note the flow rate.
- (d) To this solution add 10 ml of 1 M sulfuric acid.
- (e) Using starch as an indicator, titrate the sample with 0.10 N sodium thiosulfate.

The end point is sharp from deep purple to clear.

The concentration of ozone is then:

$$c = \frac{(\text{Normality of thiosulfate}) (\text{volume of thiosulfate})}{\text{sample volume in liters}} \quad (24)$$

in mg/l.

APPENDIX C.

EVOP Calculation Procedure

As an example, start with the four points used in the thesis.

<u>Point</u>	<u>Temperature, T</u>	<u>Residence Time, t</u>	<u>Gas Flow Rate, GFR</u>
1	80°F	9 min.	0.2 scfm
2	80°F	9 min.	0.25 scfm
3	80°F	11 min.	0.25 scfm
4	85°F	11 min.	0.25 scfm

Assuming point 1 gives the worst results, the following calculations are performed to find each variable for the next point:

$$\text{new value} = 2 \times (\text{average of best values}) - (\text{worst value})$$

$$T = 2 \times \frac{(80 + 80 + 85)}{3} - (80)$$

$$t = 2 \times \frac{(11 + 11 + 9)}{3} - (9)$$

$$\text{GFR} = 2 \times \frac{(.25 + .25 + .25)}{3} - (.2)$$

Therefore, the coordinates of point 5 are as follows:

$$T = 83.33^\circ\text{F}$$

$$t = 11.67 \text{ min.}$$

$$\text{GFR} = 0.3 \text{ scfm}$$

APPENDIX D.

Operation of the Portable Test Unit

- (1) Turn on the main power switch and allow instruments to warm up for at least 10 minutes.
- (2) Make sure the cooling water to the ozone generator is turned on.
- (3) Adjust the standpipe to whatever tank volume is desired.
- (4) Start feed pump and adjust to desired flow rate.
- (5) Bleed oxygen through the lines for about 5 minutes before turning the ozone generator on. There must be at least 4 psi in the generator for it to operate.
- (6) Next start the recycle pump.
- (7) Turn on the ozone generator, and adjust the gas flow rate again, if necessary.
- (8) Place the pH probe in the sample box on the exterior portion of the standpipe.

- PRECAUTIONS:
- (a) Make sure the hose from the sample box is in a floor drain.
 - (b) Any cleaning of the ozone generator should be done only after consulting the operation manual.
 - (c) Check the Tygon tube in the recycle pump for wear every 4 hours of operation and replace when necessary.
 - (d) A temperature calibration curve for the recorder will be provided with this thesis.