OZONE TREATMENT OF KRAFT MILL EFFLUENTS

Part I: General Characteristics

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Part I: General Characteristics

A number of different methods have been proposed and tried to treat the liquid effluents from pulp and paper mills. Conventional waste treatment practices consist of primarily settling of solids followed by secondary biological degradation of the organic constituents. These waste materials contain substantial concentrations of lignin derivatives and other organic materials generated in the pulping, washing and bleaching operations of the plant. Although the primary and secondary treatment processes effectively remove a high percentage of the BOD of the waste, the dark-brown color and pungent odor still remain as does a significant amount of COD.

Several methods for additional tertiary treatment of the kraft waste effluent have been proposed including chemical coagulation, (*3*) (*5*) (*13*) (*17*), ion exchange, reverse osmosis (*9*), carbon absorption (*10*) (*14*), and others (*2*) for the removal of the color bodies. Emphasis has been primarily on lime precipitation which is being tried on a large scale in several plant operations.

This paper reports on a series of studies involved with evaluating the potential of ozone for treating liquid effluents from a kraft pulp mill (*6*) (*8*) (*16*). Of particular concern was the effect that ozone treatment would have on the color, odor, COD, and biodegradability of the various liquid waste effluents. The use of ozone for treating pulp mill waste stems from the fact that ozone is a powerful oxidant second only to fluorine. It has been used to decolorize and deodorize materials. It also has the ability to sever unsaturated ring compounds such as phenols and break them into simpler compounds easier to biodegrade (*4*). Thus, it was felt that ozone might provide an attractive alternate for color, odor and COD removal.

In formulating the study, it was felt that an advantage ozone treatment would have over some of the other color and odor treatment systems would be a simplified process flow system. Unlike lime precipitation, carbon absorption and ion exchange, no chemical regeneration steps are necessary. Excess ozone can be easily converted to oxygen either thermally or catalytically and thus no secondary environmental hazards would be a problem. The process would merely consist of an ozone generator, a gas-liquid contacting system and a gas recycle loop if oxygen rather than air was used to generate the ozone.

EXPERIMENTAL EQUIPMENT

A portable ozonation test apparatus was designed and constructed so that on-site data could be easily obtained (*6*). The test unit consisted of an ozone generator; a venturi gas-liquid contactor; a reaction vessel; measuring and control equipment for temperature, pH, flow and level; and other associated equipment so that the unit was basically self contained. Figure 1 is a schematic diagram and Figure 2 is an actual photograph of the test unit.

The material to be treated is pumped by the feed pump through a rotameter to the reaction vessel. The feed pump was a variable speed peristatic pump capable of 1.5 gpm flow. Two reaction vessels were available having volumes of 0.5 ft^3 and 2.0 ft^3. By varying the level within these reactors as well as the feed rate, a wide range of residence times were possible in the system (15 sec to 1.5 hr). The level was maintained

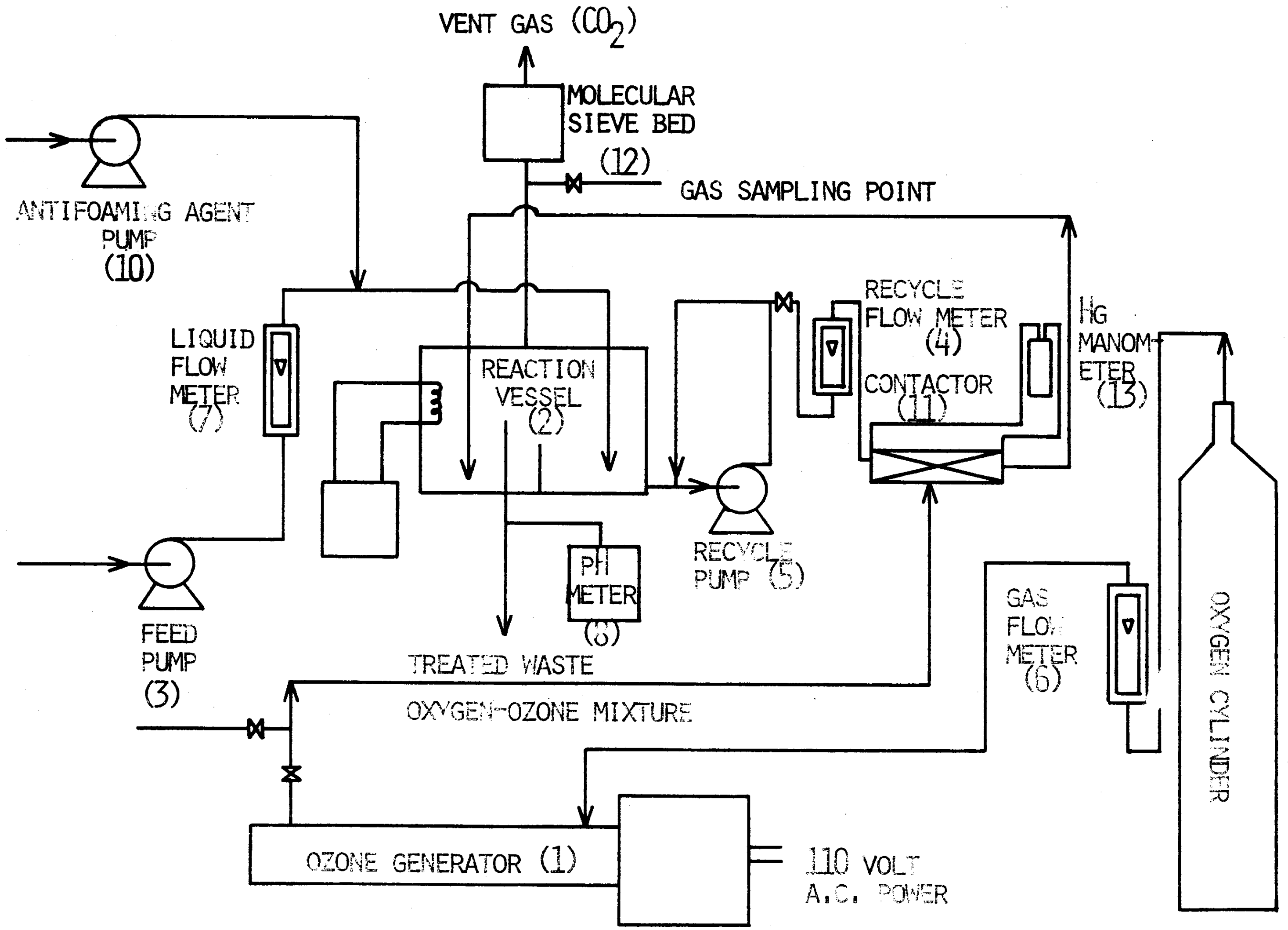

FIG. 1. SCHEMATIC FLOW DIAGRAM OF PORTABLE TEST UNIT

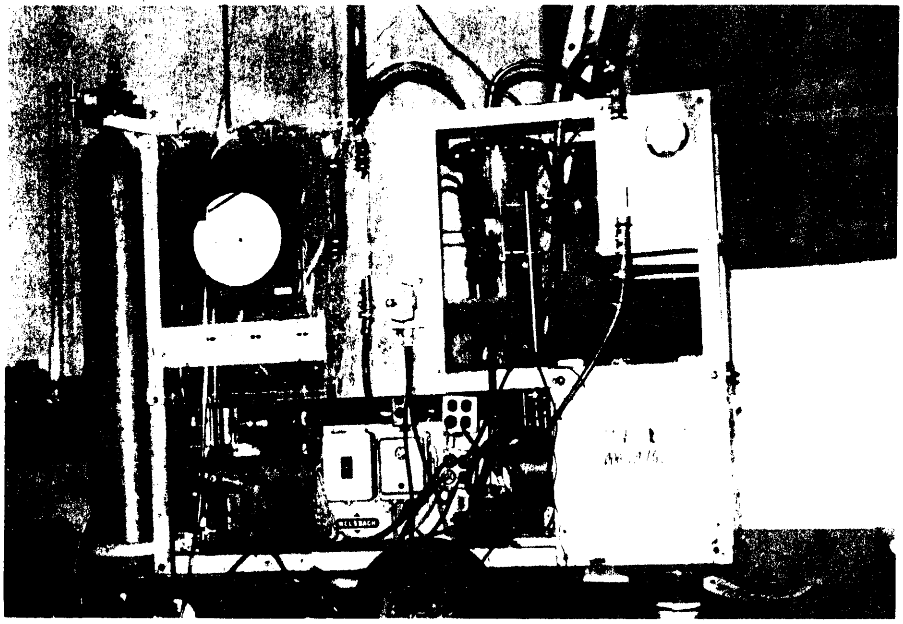

FIG. 1. PORTABLE OZONATION UNIT

by an adjustable overflow weir. The ozone was contacted with the material using venturi-type injector in a recirculation loop. The pump in the recirculation loop was a variable speed, 5 gpm peristalic pump. This configuration allowed a variable ozone dosage to be applied to the liquid material independent of the residence time in the reactor. For example, if the recirculation rate was low, the ozone dosage applied to the material would be lower than if the recirculation rate was higher while the residence time could be held constant by maintaining a constant feed rate to the reactor and a constant reactor volume.

The ozone was produced in a Welsbach C-1-D ozonator capable of generating 0.64 lb/day of ozone using an oxygen feed. No gas recycle was incorporated in the test unit and excess ozone emitted from the reactor was destroyed in a molecular sieve bed.

A small amount of silicone anti-foam agent could be added to the system through a metering pump when necessary to control foaming. A heating element was incorporated in the reactor and hooked up to a control unit for temperature recording and control. The pH was measured on the treated material from the reactor.

Actually two different gas-liquid contacting devices were used. The majority of the data were taken using a standard venturi with a 1/2-inch inlet, a 1/6-inch throat, a 6° contraction section and a 22.6° expansion section (7). A Kenics Corporation 1/2-inch static mixer with eight elements was also used to see if the contacting method had a significant effect on the results.

EXPERIMENTAL RESULTS

Batch Experiments

Initially a series of batch operating tests were run in order to gain insight as to the expected reaction residence time and applied ozone dosage that would be required for satisfactory color and odor removal. These tests were conducted in a two-liter glass diffusion column. The test material was obtained from the Potlatch Corporation's kraft mill in Lewiston, Idaho.

Figure 3 illustrates a typical color removal curve showing the reduction in APHA color units (465 mμ, 7.6 pH, 0.8 micron filtered sample) (*11*) as a function of applied ozone dose. The material treated was effluent from the primary clarifier. Similar results were obtained from other parts of the plant as given in Table I.

Table I

COLOR REDUCTION OF VARIOUS PULP MILL WASTES BY BATCH OZONATION

MATERIAL	OZONE DOSAGE mg/l	COLOR UNITS		
		Initial	Final	% Reduction
Clarifier Inlet	500	3150	800	75
Clarifier Outlet	525	2600	300	88
Bleach Plant	400	1900	600	68
After Secondary Treatment	550	3700	880	76

The COD reduction as a function of applied ozone dose for the clarifier effluent is given in Figure 4. The color removal and COD reduction results obtained are consistent with those reported by Buley (*1*) in his batch ozonation work.

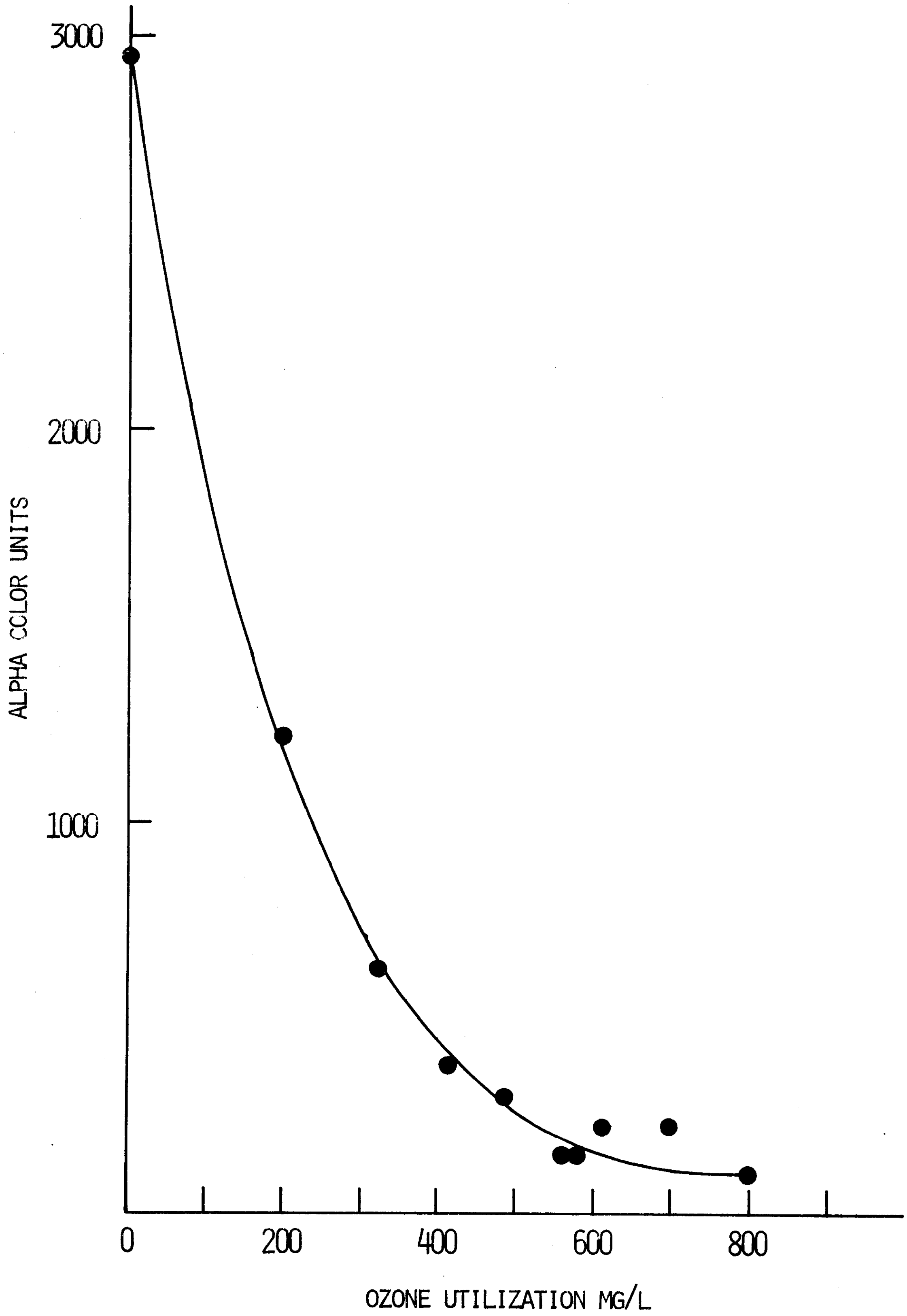

FIG. 3. COLOR AS A FUNCTION OF DEGREE OF OZONATION FOR KRAFT MILL EFFLUENT

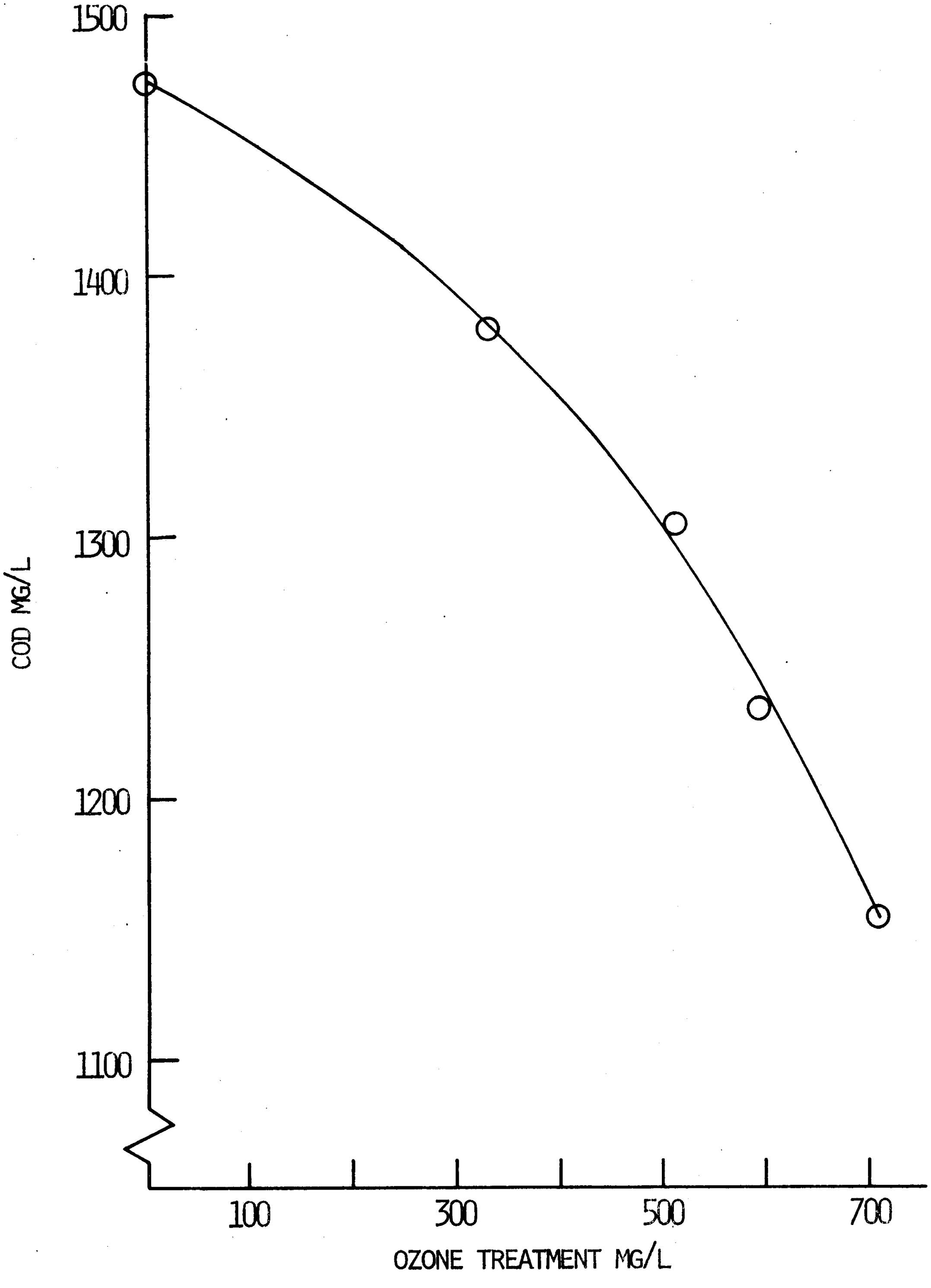

FIG. 4. COD OF KRAFT MILL WASTE AS A FUNCTION OF OZONATION

Pilot Unit Parameters

The results of the batch studies were used to design the portable ozonation pilot unit. The pilot unit was used for a series of tests runs with residence time, temperature, ozone dosage, and recirculation rate as the major independent variables. The residence time was varied between 1.8 and 60 minutes with the bulk of the data taken between 10-20 minutes. The temperature of the reaction was generally kept between 70° and 100°F which is the temperature range over which the material leaves the mill during the year. The applied ozone dosage (in milligrams of ozone per liter of feed to the system) was varied from 60 to 1000; however the actual amount of ozone utilized by the reaction system varied between 20 to 340 mgO_3/l of feed.

The recirculation rate was important in this system since the gas-liquid contact occurred in the recirculation loop. A contact parameter was used in the study to express the effect of the recirculation rate. The contact parameter, CP, is the recirculation rate divided by the feed rate to the reactor, and represents the average number of times a volume of feed is contacted with the ozone gas in the venturi. It is independent of the reactor residence time and is important since the major mass transfer takes place in the high shear area of the venturi throat (7). It was found that little if any ozone residual existed in liquid effluent from the system indicating that all the ozone transferred to the system reacts with the waste or decomposes. Therefore the more chances a waste molecule has in coming into contact with an ozone molecule, the greater will be the degree of reaction. The contact parameter was varied between 1 to 21.

As with the batch tests, the materials used were obtained from the Potlatch Corporation's kraft mill at Lewiston, Idaho. The bulk of the data was obtained from the clarifier effluent and the total plant effluent (a mixture of clarifier effluent and bleach plant effluent) although some bleach plant waste was also tested. The pilot unit was taken to the pulp mill for the tests. A wide variation in characteristics of the test material existed over the duration of the study with the input color units varying between 1830 and 4990, and the input pH between 3.1 and 9.3. Although these widely varying conditions caused data scatter no attempt was made to get consistent input material since actual plant operating conditions were felt to be more significant.

Pilot Unit Results

Generally it was found that complete odor removal and good color reduction could be achieved at an ozone utilization concentration of 200 mgO_3/l feed and a residence time of 10 minutes. With these conditions, a 75-80% color reduction occurred with a 15% reduction in COD and no characteristic odor was perceptible.

The color removal effectiveness was directly related to the amount of ozone utilized in the system as shown in Figure 5. The ozone utilization was, in turn, directly correlatable to the contact parameter as illustrated in Figure 6. The actual applied ozone dosage was not a dominate factor provided sufficient ozone was supplied to the system to satisfy the ozone utilization rate. In the tests, it was found that an applied dosage of 300-400 mgO_3/l feed was sufficient to provide a utilization of about 200-250 mgO_3/l feed by the reacting system. From

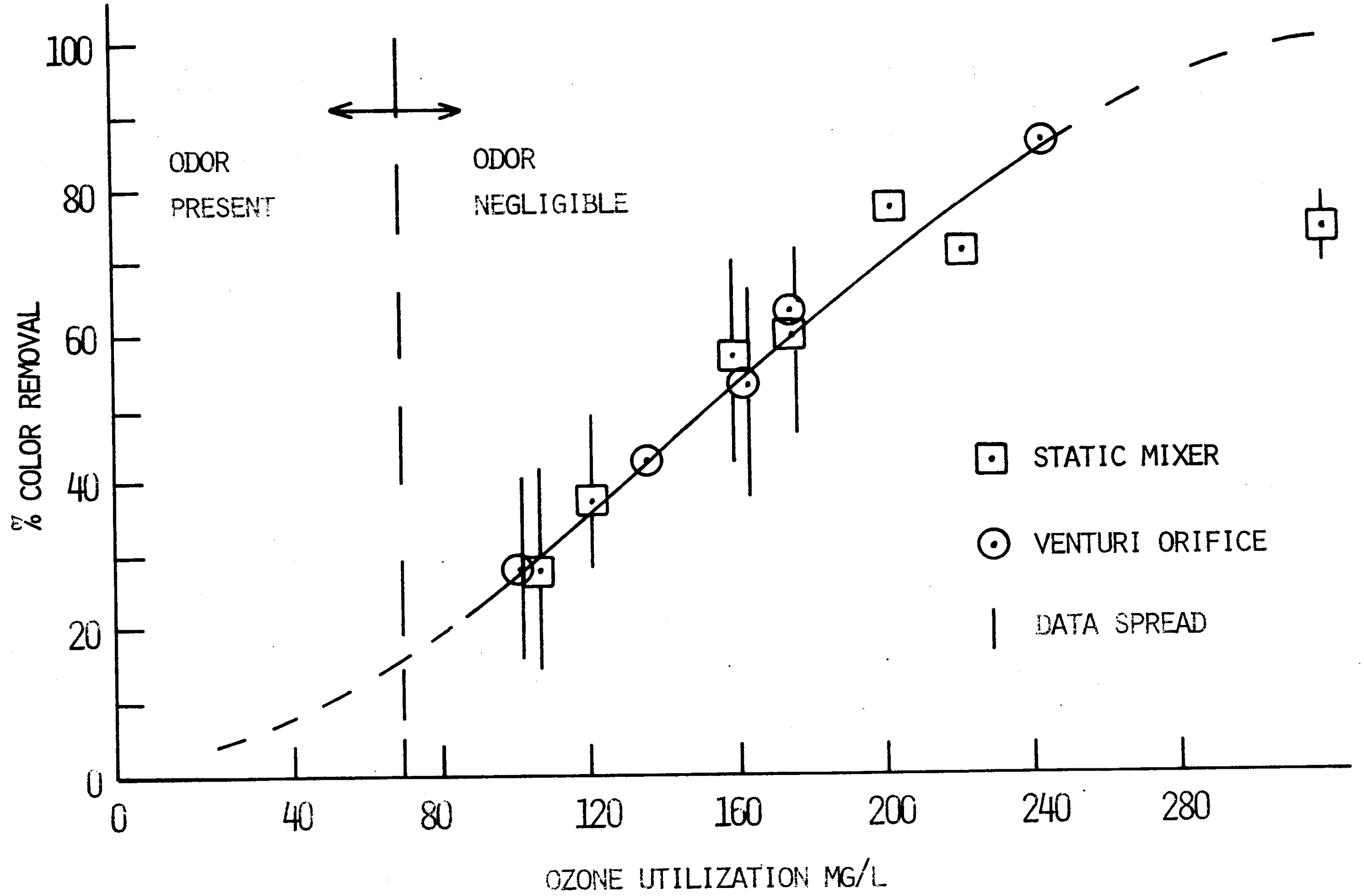

FIG. 5. COLOR REMOVAL EFFICIENCY vs OZONE UTILIZATION

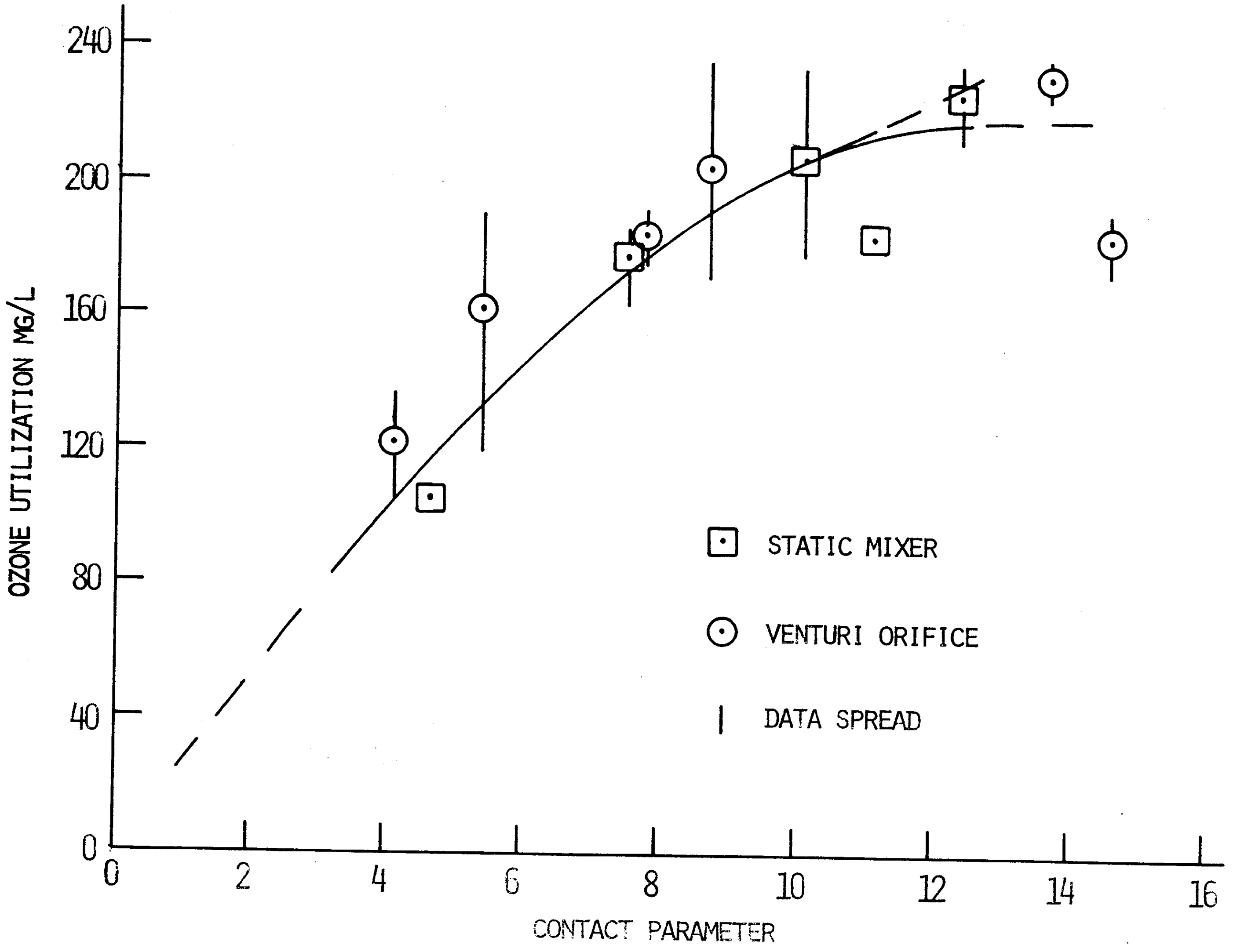

FIG. 6. OZONE UTILIZATION vs CONTACT PARAMETER

Figure 5, the utilization rate would cause a 75-80% color reduction which would typically take a material of 3000 color units to 800 color units. Qualitatively this represents a change from a dark chocolate brown to a light straw yellow. Figure 6 establishes a contact parameter of about 10 to obtain the 200 mg/l utilization rate.

The effect of residence time on the color reduction follows the general pattern given in Figure 3. The color decreases very rapidly at residence times less than 10 minutes and then decreases much more slowly thereafter as given in Table II.

Table II

EFFECT OF RESIDENCE TIME ON COLOR REDUCTION

RESIDENCE TIME min	COLOR UNITS		
	Initial	Final	% Reduction
10	2050	740	64
18	2050	710	65
30	2050	340	83
45	2050	260	87
60	2050	260	87

(applied dose = 340 mg/l)

The results obtained and used to generate Figures 5 and 6 and Table II did not differ significantly between types of effluent treated. The clarifier output, bleach plant and total plant effluents all exhibited the same basic behavior and all data were used in Figures 5 and 6. It was observed, however, that the color reduction was normally better at higher pH values.

Other Effects

Most of the test runs were performed at a temperature of 100°F.

This was done since it was the normal temperature of the clarifier effluent during the summer months. There was some evidence that 85°F is a better operating temperature but it would not be economical to design a plant that would require either energy addition or removal from the system unless absolutely necessary.

One additional positive feature observed was that the dissolved oxygen content of the ozone treated waste became supersaturated at up to 30 ppm which could be beneficial in any subsequent bioxidation process.

ECONOMIC CONSIDERATIONS

Plant Design and Scale-up

A preliminary process design for the ozone treatment of kraft pulp mill waste water was made using the optimum operating conditions obtained in the pilot unit. A modular scale-up approach was used. This method attempts to put the plant on a scale large enough to obtain the cost-size economic advantage, yet avoids specialty and unique pieces of equipment.

The design specifications are given in Table III. The 7.2 mgd feed rate was chosen from municipal plant data on installed costs of ozonation equipment(*15*).

Table III

MODULAR PLANT SPECIFICATIONS

Operating Contitions	Expected Results
Size - 7.2 mgd	Removal of all noxious odors
Residence Time - 12 min max	Color removal - 80%
Ozone Utilization-1.65 lbs/1000 gal	COD reduction - 10-15%
Contact Factor - 10	

Two different plant configurations were used in analyzing the treatment costs. The basic difference between the systems was in the method of gas-liquid contact. System 1 uses a venturi-type contactor outside the reaction vessel while System 2 uses a contactor which is an integral part of the reactor. Both systems used pure oxygen feed to the ozonator with recycle. The process flow diagrams are given in Figures 7 and 8.

Monte Carlo Method

A Monte Carlo uncertainty analysis program was used to predict the probable variation in treatment costs based on the uncertainty existing in all of the variables used in the plant cost estimations. The method, developed at the University of Idaho, requires "best", "optimistic" and "pessimistic" values for each process variable used in the plant cost estimation. The program then computes an accumulative probability function for the treatment cost. This function can be used to estimate both the treatment costs expected from the system and the probability of obtaining such a value in view of the uncertainty that exists in each of the estimations that goes into the final cost calculation. It also allows one to determine the probability of other possible treatment costs. This will be illustrated in the following paragraphs.

Both System 1 and System 2 were analyzed using the Monte Carlo uncertainty program. The treatment cost estimations are given in Tables IV and V. The results are given in Table VI. Figures 9 and 10 give the accumulative probability versus treatment cost for both systems. As can be seen from Figure 10, there is essentially a zero probability that the treatment costs will be less than 35¢/1000 gal and a 100% probability

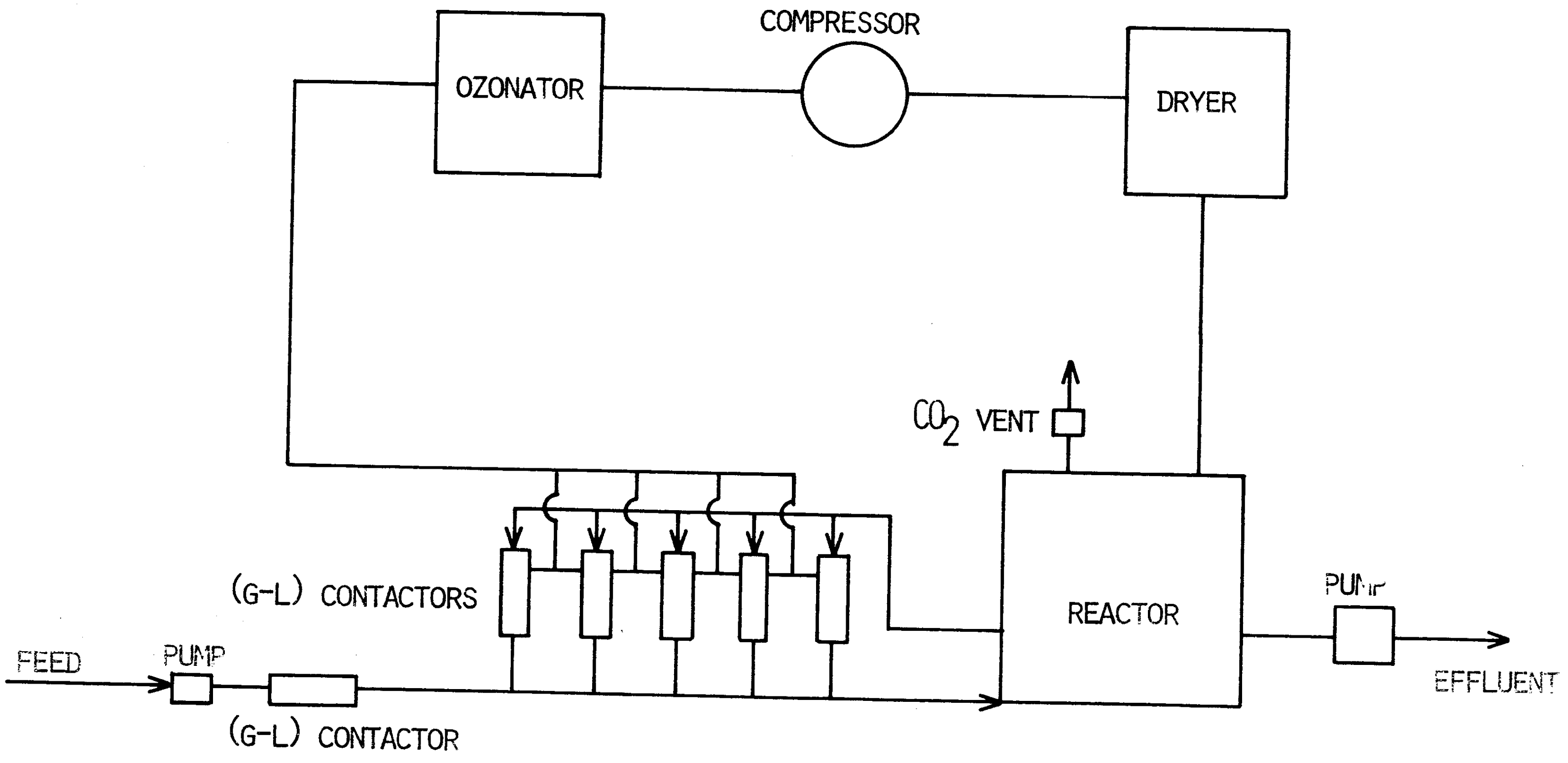

FIG. 7. PROCESS DIAGRAM, SYSTEM 1

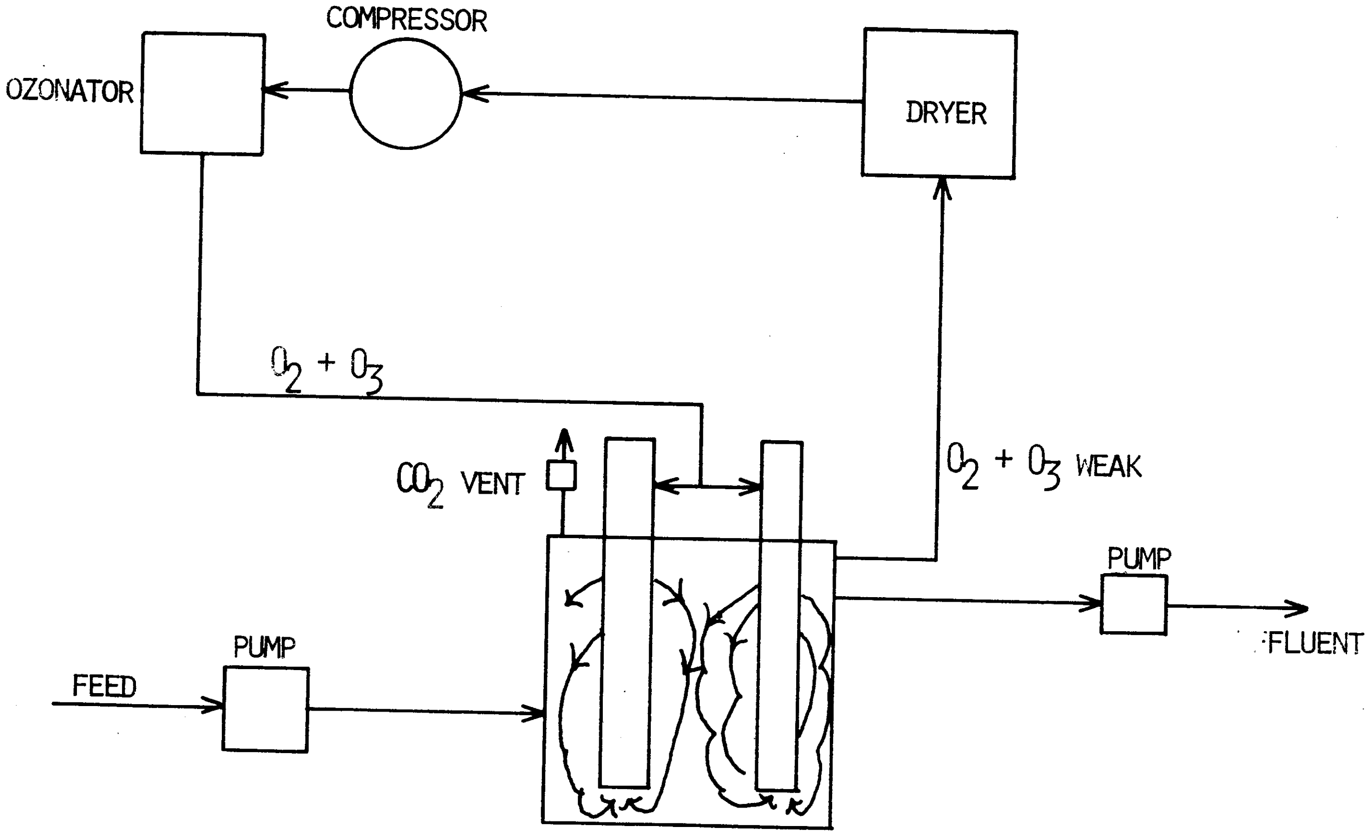

FIG. 8. PROCESS DIAGRAM, SYSTEM 2

Table IV

SYSTEM 1: VALUES FOR COST ESTIMATE

VAR NO	VARIABLE DESCRIPTION	PESS EST	BEST EST	OPT EST
Operating Cost Data:				
1	O_3 lbs/1000 gal	1.90	1.65	1.40
2	Pumping Load (HP)	410.00	400.00	390.00
3	Dryer Load (KW)	25.00	20.00	15.00
4	Contacting Load (HP)	1025.00	1000.00	975.00
5	Compressor Load (HP)	25.00	20.00	15.00
Major Capital Costs:				
6	Pumps & Acc	125000.00	100000.00	75000.00
7	Compressor	14000.00	10000.00	6000.00
8	Dryer	8000.00	7000.00	6000.00
9	Reactor	200000.00	175000.00	125000.00
10	(G-L) Control Device	90000.00	60000.00	30000.00
11	Ozonator ($/lb-$O_3$/day)	85.00	80.00	75.00
Utility Costs:				
12	O_3 $/lb	0.14	0.12	0.10
13	Power $/kw-hr	0.03	0.02	0.01
Estimating Factors:				
14	Ozone Utilization	1.50	1.35	1.20

Table V

SYSTEM 2: VALUES FOR COST ESTIMATE

VAR NO	VARIABLE DESCRIPTION	PESS EST	BEST EST	OPT EST
Operating Cost Data:				
1	O_3 lbs/1000 gal	1.90	1.65	1.40
2	Pumping Load (hp)	410.00	400.00	390.00
3	Dryer Load (kw)	25.00	20.00	15.00
4	Contacting Load (hp)	130.00	90.00	50.00
5	Compressor Load (hp)	25.00	20.00	15.00
Major Capital Costs:				
6	Pumps & Acc	37500.00	30000.00	22500.00
7	Compressor	14000.00	10000.00	6000.00
8	Dryer	8000.00	7000.00	6000.00
9	Reactor	200000.00	175000.00	125000.00
10	(G-L) Control Device	12000.00	9000.00	6000.00
11	Ozonator ($/lb-$O_3$/day)	85.00	80.00	75.00
Utility Costs:				
12	O_3 $/lb	0.14	0.12	0.10
13	Power $/kw-hr	0.03	0.02	0. 1
Estimating Factors:				
14	Ozone Utilization	1.50	1.35	1.20

Table VI

TREATMENT AND CAPITAL COSTS

TYPE COST	SYSTEM 1	SYSTEM 2
Treatment Cost range (¢/1000 gal)	36. -53.	30. -48.
Best Estimate of Treatment Cost (¢/1000 gal)	45.0	39.0
Probability of Obtaining Best Estimate (%)	51.0	50.0
Total Plant Cost (million dollars)	4.3	3.9
Amortized Capital Cost over 20 Years (million/yr)	0.2	0.2
Major Capital Cost (million dollars)	1.6	1.5
Total Operating Cost (thousand dollars/day)	2.7	2.3
Cost Treatment Less Capital Cost (¢/1000 gal)	37.0	37.0

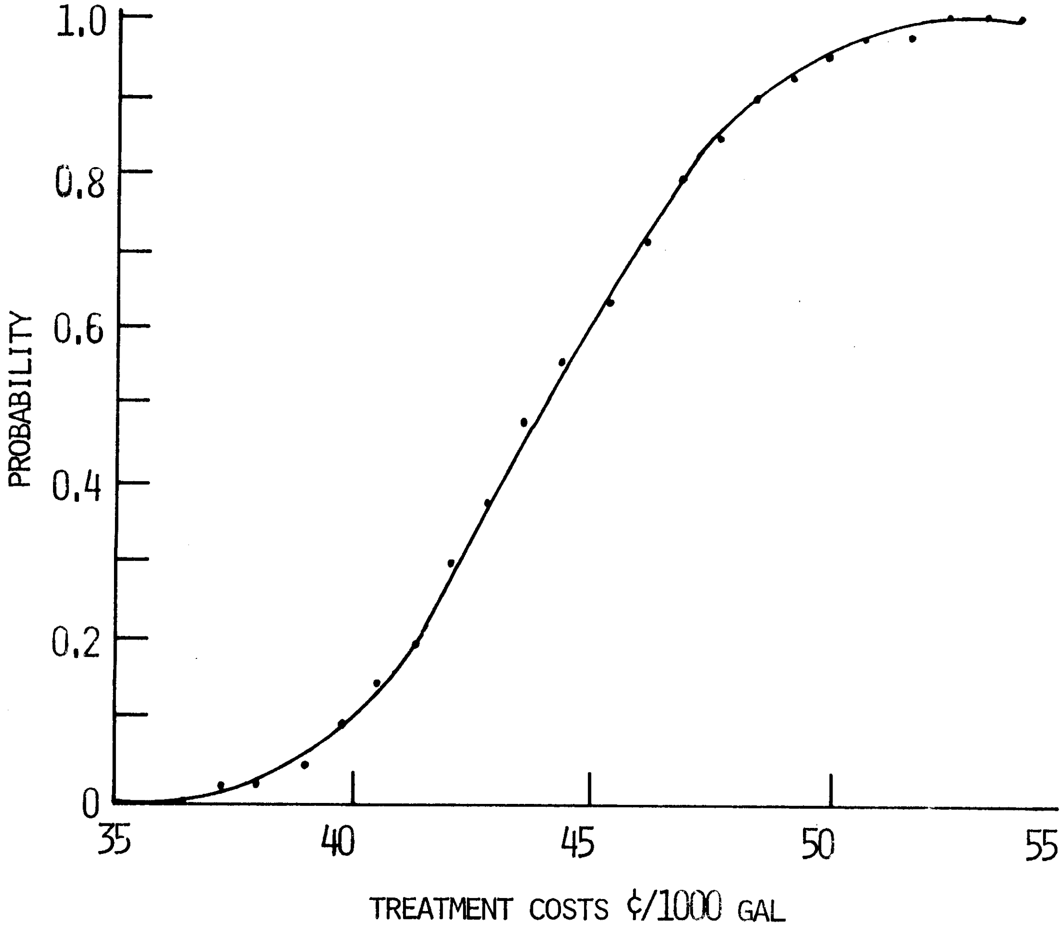

FIG. 9. SYSTEM 1: PROBABILITY OF TREATMENT COST

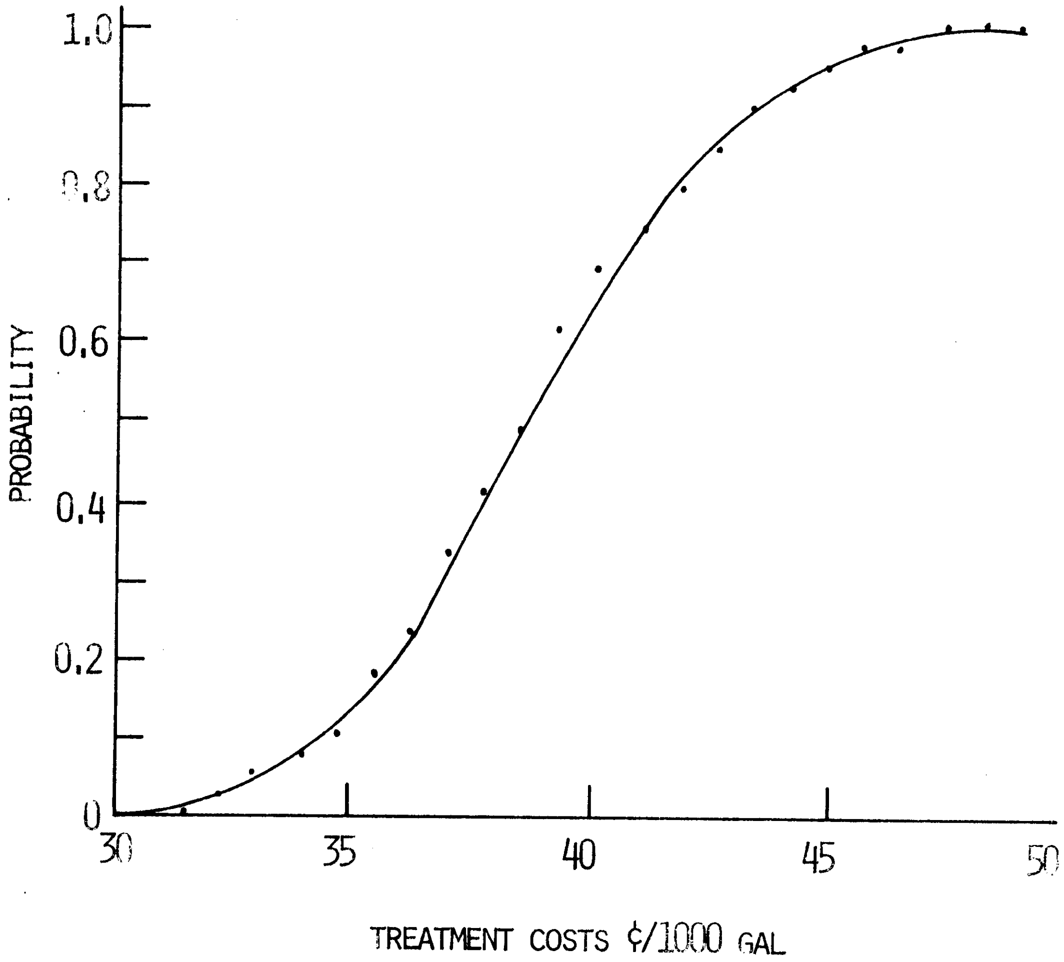

FIG. 10. SYSTEM 2: PROBABILITY OF TREATMENT COST

that the costs will be less than 53¢/1000 gal.

A sensitivity analysis study was also performed to determine upon which variable the treatment cost was most dependent. Thus several variables were arbitrarily changed ±25% from those originally used in the program. Table VII illustrates the effect on treatment costs of these variables. As can be seen, the treatment costs are most effected by ozone utilization both in amount and cost. The capital equipment costs are much less important.

GENERAL DISCUSSION

The results of this study indicate that ozone will completely deodorize and effectively reduce the color of kraft pulp mill liquid effluent. One of the primary advantages of an ozone system is the simple process configuration for such a treatment method. The estimated total treatment costs, in the neighborhood of 40¢/1000 gal, are considerably less than the $1.17/1000 gal reported for a reverse osmosis system (*9*), but substantially higher than published costs of the lime precipitation process. Davis (*3*), for example, indicates that the total cost of the massive lime treatment at the Riceboro, Ga. plant to be about $3.00 per ton of pulp. These costs would translate to about 15¢/1000 gal if 20,000 gal/ton pulp is the water consumption or 6¢/1000 gal if the water used is 50,000 gal/ton pulp (*12*). Gould (*5*) reports that the lime process at Woodland, Maine operates for a cost of about $1.37/ton pulp. These costs seem low when compared to municipal sewage treatment figures. The annual operation and maintenance cost for a 4 million gal/day activated sludge plant is 9¢/1000 gal with a total cost of 30¢/1000 gal (*15*).

Table VII

SENSITIVITY OF PROCESS COST TO A ±25% SHIFT IN VARIABLE COST

VARIABLE NO.	VARIABLE DESCRIPTION	SYSTEM 1 COST CHANGE (¢/1000 gal)		SYSTEM 2 COST CHANGE (¢/1000 gal)	
		+25%	-25%	+25%	-25%
1	Ozone Required	+8.8	-8.7	+8.7	-8.7
4	Contact Load	+1.4	-1.6	+0.1	-0.1
6	Pumps	+0.2	-0.2	nil	nil
9	Reactor Cost	+0.2	-0.2	+0.2	-0.2
10	Contactor Cost	+0.1	-0.1	nil	nil
11	Ozonator Costs	+1.5	-1.4	+1.4	-1.4
12	Ozone Cost	+7.4	-7.4	+7.3	-7.3
17	Excess Ozone Required	+9.1	-9.1	+9.1	-9.1

Base Values (¢/1000 gal): System 1 - 44.6
System 2 - 39.1

It is possible that the ozone treatment costs could be substantially reduced. From the sensitivity analysis, the ozone costs dominate the economics. The estimations were based on about a 60% utilization of the ozone charged to the system. By staging the system as suggested by Buley (*1*), it is expected that a much higher ozone utilization efficiency can be achieved. Thus the sensitivity analysis indicates that utilizing 25% more of the ozone generated would reduce the treatment costs by about 9¢/1000 gallon.

It may well be that ozone treatment is better suited for selected streams of high color and odor where recycle of the water back to the mill is desirable. The simplicity of the system is such that several smaller treatment processes are entirely feasible rather than accumulating all the waste stream for treatment.

A subsequent article reports on the biodegradability of the ozoned mill effluent.

ACKNOWLEDGMENTS

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