THE DEGRADATION OF KRAFT MILL WASTE IN A MARINE ENVIRONMENT

by

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INTRODUCTION

The Kraft Process

Liquid industrial wastes are having an increasing effect upon our environment. One of the major producers of liquid wastes is the wood pulp industry. In recent years pulp production facilities have been expanded to meet the increased demand for wood pulp, and the emphasis has been placed on the Kraft Process as the method of pulp production.

The Kraft, or sulphate, process is a chemical method of separating cellulose fiber from the other materials in wood. Renyolds (6, p. 456-460) states that the process was first proposed in 1879, in Europe, but that acceptance was slow because of the cost of the chemicals. However, with the development of modern chemical recovery processes the production of pulp by the Kraft process began to increase. In the first ten years following World War II, the production of wood pulp rose from 19 million tons to 29.5 million tons annually, sixty per cent of this increase being Kraft process production.

Pulp production by the Kraft process is adaptable to nearly any type of wood. The liquor used in separation of

the cellulose fiber from the other materials is alkaline, therefore resins, fats and waxes do not impede the pulping action. The pulping process can be divided into four basic steps: chipping, cooking, washing and liquor recovery. The cellulose fiber is separated from the other materials in the wood by the black liquor, a sodium hydroxide-sodium sulfide solution, during the cooking step. Washing separates the fiber from the black liquor, spent chemicals, wood chips and organic material.

All of the above steps contribute to the mill waste. Characteristics of the waste vary from mill to mill, but typical values given by the California State Water Pollution Control Board (4, p. 51-60) are as follows. Twenty to thirty thousand gallons of waste are released for each ton of pulp produced. The waste usually has a biochemical oxygen demand of approximately 250 mg/ml, and a total solids load of 1700 to 2500 mg/l. Usually about 65 per cent of the total solids are volatile. Alkalinity of the waste ranges from 100 mg/l to 300 mg/l, and pH ranges from 7.5 to 9.0.

Although the BOD of Kraft waste is relatively low in comparison with wastes from many industrial processes, the quantity of the waste released makes the organic load on a stream very high. Because of this, many of the Kraft mills in coastal regions are releasing their wastes into bays,

estuaries, or directly into the ocean. The number of pulp mills using this technique for waste disposal will increase as new mills are put into operation along the coasts.

Much work has been done on the effect of Kraft waste on rivers and streams, but very little work has been done on Kraft waste in the marine environment.

The Marine Environment

The marine environment contains relatively high concentrations of various salts. According to Carlucci and Pramer (5, p. 388-392), sea water contains most of the known elements as inorganic ions and dissolved gasses. The metal ions occurring in greatest concentration are sodium, calcium and magnesium. Non-metallic ions occurring in greatest concentration are chlorides, sulfates and carbonates. Because of the high chloride ion concentration, salinity is measured as a function of the chloride ion concentration.

Salinity measurements taken off the Oregon coast by the Scripps Institution of Oceanography (8, vol. 1, p. 65-160) in May 1939 show the salinity to vary with depth in the vicinity of land. The variation becomes less evident with increasing distance from shore. The sampling station nearest shore was approximately 25 miles from the beach. Surface salinity at this station was 29,440 mg/l. At a

depth of 100 meters the salinity was 33,720 mg/l. At a distance from shore of approximately 130 miles the surface salinity was 32,000 mg/l, and the salinity at a depth of 100 meters was 33,580 mg/l. Samples taken between 25 and 130 miles from shore indicate that the salinity at a depth of 100 meters is relatively constant and that the surface salinity increases with the distance from shore.

Temperature is an environmental factor which varies with season, weather, location, time of day and depth. Temperature measurements taken by the Scripps Institution of Oceanography (8, vol. 1, p. 65-160) showed the surface temperature to vary between 12.5 and 14.5 degrees centigrade over a three-day period in May 1939. During this period the temperature at 100 meters' depth varied between 7.9 and 8.6 degrees centigrade.

The dissolved oxygen concentration remained approximately constant with respect to distance from land. The concentration of dissolved oxygen at the surface varied between 8.8 mg/l and 9.3 mg/l in the Scripps Institution Studies. Values of dissolved oxygen concentration at a depth of 100 meters were approximately one-half the surface concentration.

Carlucci and Pramer (5, p. 388-392) state that although the important inorganic nutrients are present in sea water, some, such as iron, nitrogen and phosphorus, occur only in

low concentrations. The concentration of organic nutrients in sea water varies with location. In studies by Waksman and Carey (9, p. 545-563) relatively high concentrations of dissolved organic material were found in samples taken in the vicinity of land or bottom deposits containing large amounts of organic matter. Relatively low concentrations of organic matter were found in samples taken some distance from land or bottom deposits.

The salinity, temperature, dissolved oxygen concentration and nutrient concentration are properties of the marine environment which have an effect upon the amount and type of the microbiological population of the sea. However, there are other factors, many of which are not yet understood, which have an effect on life in the marine environment.

Studies by Waksman and Carey (9, p. 545-563) showed that sea water could support bacterial populations of greater than 50,000 cells per milliliter under laboratory conditions. However, these and later studies by Waksman and Hotchkiss (10, p. 384-400) showed that the bacterial population in fresh sea water varied between 500 and 1000 cells per milliliter in the vicinity of land and were as low as one to two cells per milliliter at a distance from land. In addition, when fresh sea water was added to the laboratory cultures a definite destructive effect was noted.

Suggested explanations for the low bacterial population in fresh sea water are as follows:

1. destruction of bacteria by toxic substances in sea water
2. bacteriophages present in sea water
3. adsorption of bacteria in sea water by suspended matter which settles to the bottom
4. the destructive effect of sunlight on the bacteria
5. the presence in sea water of inactive bacteria which develop only under favorable conditions
6. inadequate methods of counting marine bacteria
7. the low concentration of important nutrients in sea water
8. the destruction of the bacterial population by the animal populations of sea water.

Waksman and Hotchkiss state that all of the above explanations are justified to some extent, but that the last seems to be the major reason for the small bacterial population in sea water.

Scope

The scope of this thesis is the study of the degradation of Kraft mill waste in the marine environment. Factors considered in this study were the salinity of the environment of the microbiological cultures maintained in the

laboratory and the period of acclimation of the cultures to the waste. The cultures were kept at room temperature throughout the study.

The study includes a review of the literature, acclimation of the cultures to selected salinity levels, measurement of degradation of the waste at selected periods of acclimation, analysis of the results, and the conclusions made from the analysis.

Degradation was measured by the biochemical oxygen demand of the waste. The rate of oxygen uptake as measured by the velocity constant K' in the monomolecular equation for biochemical oxygen demand given by Babbit and Baumann (3, p. 345-352) was related to the culture's acclimation period to the waste and the salinity level of the culture. The fraction of the chemically oxidizable material satisfied by the first stage biochemical oxygen demand was related to the acclimation period and the salinity level.

STUDY PROCEDURE

The study procedure is divided into five phases. These are: 1. the preparation and maintenance of the environment of the microbiological cultures; 2. the sampling, care and testing of the waste; 3. the selection, acclimation and maintenance of the cultures; 4. the measurement of degradation; 5. the analysis of data. Unless otherwise stated, all tests were run according to procedures given by the American Public Health Association (2).

Preparation and Maintenance of the Environment

The range of approximate salinity levels selected was 0, 10,000, 20,000, 30,000 and 40,000 mg/l. The purpose of the wide range of salinity levels was to simulate the range of salinity levels found in an estuary, as well as the salinity level of the open sea. In maintaining the salinity levels in the laboratory an artificial sea water was used. The solution was a slight modification of Allen's (1, p. 417-439) artificial sea water in that his precautions to avoid contamination of the media were not necessary in this study.

Similarity between the artificial sea water and the natural sea water was verified by the comparison of the biochemical oxygen demand of Kraft waste in seeded artificial

sea water, seeded standard dilution water and fresh sea water. The dilutions of the waste were varied between 0.5%, 1% and 2% by volume. Dissolved oxygen determinations were made by the azide modification of the Winkler method.

The seed used in the standard dilution water was raw sewage and activated sludge. The raw sewage was obtained from the influent of the Corvallis, Oregon, sewage treatment plant, and the activated sludge was taken from the Hillsboro, Oregon, sewage treatment plant. The seed used in the artificial sea water was taken from a laboratory culture built up from two liters of natural sea water taken from the jetty at Newport, Oregon. The culture was kept at room temperature in the laboratory. Feed consisted of a solution of 20 g/l glucose and 10 g/l Bacto-peptone in distilled water. The quantity of feed was varied in steps from 50 millliliters per day at the beginning to 5 milliliters per day when a heavy growth had been obtained.

Acclimation of the microbiological population to the waste was varied to investigate the changes occurring in the degradation periods of acclimation. The acclimation periods selected were 1, 2, 4, 7, 14, 21 and 28 days.

Sampling, Care and Testing of Wastes

The source of the waste used was the Georgia Pacific Kraft mill located in Toledo, Oregon. Samples were taken

at a sampling station maintained by the mill. The waste was not treated in any way prior to sampling. The samples were taken in 2.5-gallon polyethylene cans. All of the samples were transferred to 500-ml flasks and refrigerated at 4° C. within two hours after sampling.

The amount of degradable material was measured by the chemical oxygen demand of the waste. The biochemical oxygen demand of the waste was measured by the Warburg manometric method. The samples were taken approximately 24 hours prior to the Warburg tests. Chemical oxygen demand was run within two hours of the time the sample was taken.

Selection and Acclimation of the Cultures

The cultures used in the Warburg studies were developed from samples of activated sludge obtained from the Hillsboro, Oregon, sewage treatment plant. A two-liter stock culture was acclimated to each selected salinity level. The stock cultures were maintained on a fill and draw cycle in which once a day the cells were settled. Each day 1400 ml of supernatant was withdrawn and replaced with 1400 ml of water of the proper salinity. The process of acclimation of the cultures to the salinity levels was accomplished by increasing the volume of artificial sea water added at the rate of 200 ml per day until the selected

salinity level was reached. The cells were kept in suspension by the diffusion of air through the cultures.

Cultures acclimated to the Kraft waste were developed from the stock cultures. Five hundred milliliters were withdrawn from each stock culture and placed on the same fill and draw cycle. Acclimation to the waste was accomplished by using Kraft waste as part of the daily feed given the cultures.

The stock feed given to both stock and acclimated cultures was a solution of 20 g/l glucose and 10 g/l Bacto-peptone. The stock cultures were given 10 ml twice a day, and the waste-acclimated cultures were given 2 ml twice a day. The waste-acclimated cultures were also given 70 ml of Kraft waste once a day.

Estimated biochemical oxygen demand of the stock feed was 21.5 mg/ml. The desired amount of Kraft waste fed to the cultures was one-fourth of the BOD added each day. Earlier determinations of the strength of the waste had indicated a strength of approximately 400 mg/l, and this figure was used in determining the amount of waste fed to the acclimated cultures.

Measurement of Degradation

The degradation of the waste was measured by the Warburg manometric method as the uptake of oxygen by the

bacterial cells.

Equipment used for the Warburg studies was manufactured by the Precision Scientific Company. The 15 ml flasks had a single sidearm and ground glass fittings; manometers were 300 mm in length. The water bath held twenty manometer-flask units and was set at a shake rate of approximately 80 shakes per minute. The temperature of the water bath was held at 20° C.

Calibration of the flasks and manometers was accomplished by the hydrazine-ferracyanide method. This method is based on the release of a known volume of nitrogen gas in the reaction of the ammonium ion with the ferracyanide ion. The procedure for this method of calibration is given by Umbreit et al. (11, p. 49-50).

The Warburg test procedure used in this study involved three basic steps. The first step was the standardization of the acclimated cultures to a suspended solids level of 2000 mg/l. The cultures were adjusted to a volume of 500 ml and blended in a Waring blender to break up large clusters of cells. Suspended solids determinations were made in triplicate on each culture. The cultures were then adjusted to 2000 mg/l suspended solids by the addition of water or the withdrawal of supernatant.

In the second step of the procedure the flasks were prepared. Two tenths of a milliliter of 4N NaOH was placed

in the center well of each flask as a CO_2 absorbent. One milliliter of waste was placed in the sidearm and three milliliters of the culture was placed in the main compartment of the flask. Duplicate flasks were prepared for each salinity level. Two flasks prepared from the stock culture of 0 salinity were run each week as a control.

The third step was the measurement of the oxygen uptake by the cells during the degradation of the waste. The base rate of respiration of the cells was measured for a minimum period of four hours. The waste was then tipped into the main compartment, and the oxygen uptake measured at appropriate intervals.

Analysis of Data

Measurements of the oxygen uptake were computed as micro-gram of oxygen uptake per milliliter of waste. Smooth curves were drawn through the plotted values of oxygen uptake. The reaction was considered complete when the curve became parallel to the line representing the base rate of respiration or when the oxygen uptake became constant. In cases where the base rate of respiration was not established the rate of oxygen uptake at the end of the test was considered to be the base rate. The total oxygen uptake and the base rate for a typical flask are shown in figure 1. The net oxygen uptake was computed by subtracting the

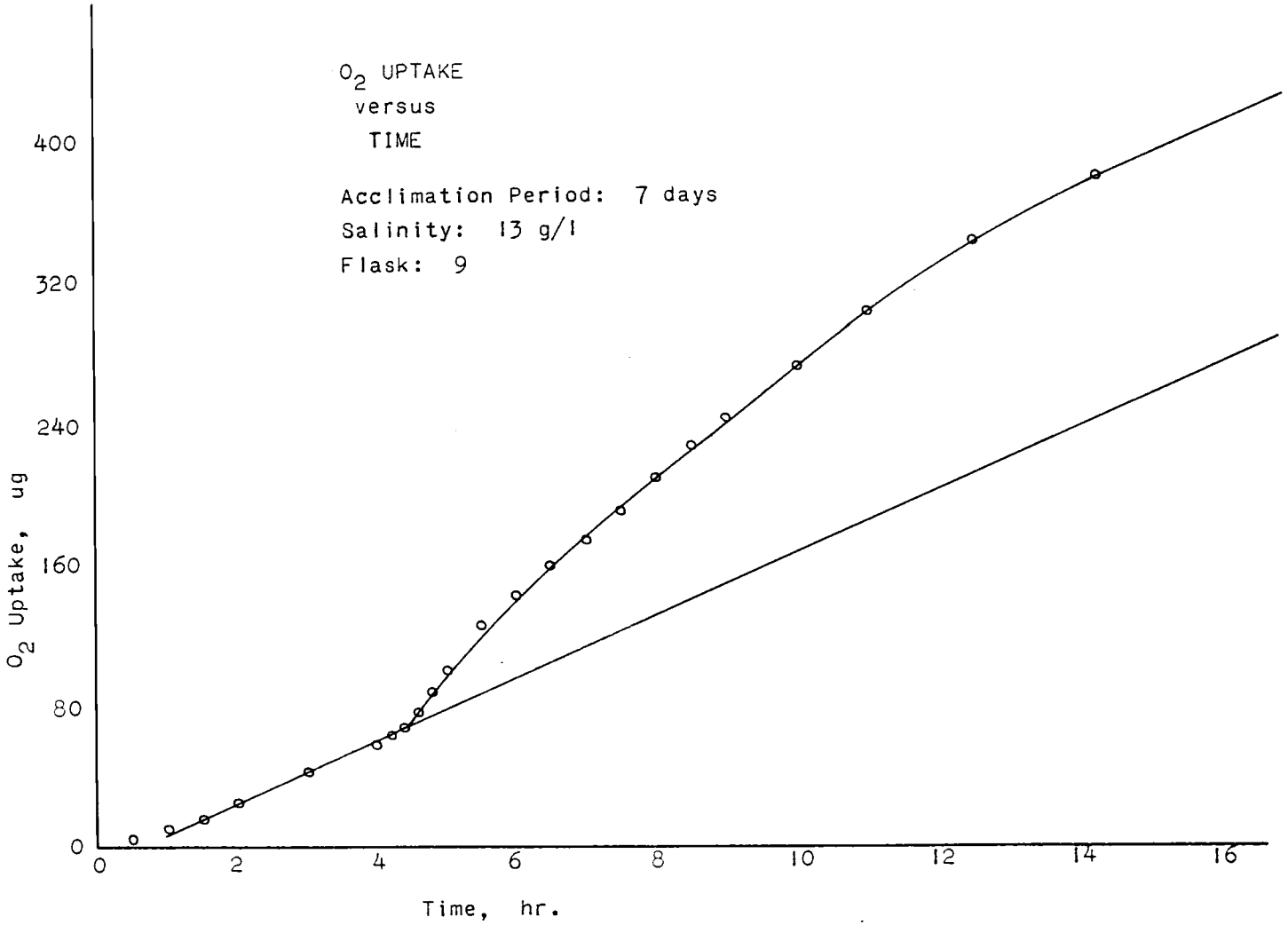
O_2 UPTAKE
versus
TIME
Acclimation Period: 7 days
Salinity: 13 g/l
Flask: 9
400
320
240
160
80
0
O_2 Uptake, ug
0
2
4
6
8
10
12
14
16
Time, hr.

Figure 1.

base rate of respiration from the total oxygen uptake. Figure 2 shows the net oxygen uptake curve for the same flask. The ultimate first stage oxygen demand, L_0, is the net oxygen uptake at the completion of the reaction.

The velocity constant, K', of the monomolecular equation for biochemical oxygen demand may be computed through the use of a plot of the logarithm of the oxidizable fraction remaining, L/L_0, at time, t, versus time. The relationship is developed in the following manner.

$$\frac{dL}{dt} = -KL \qquad (1)$$

$$\frac{dL}{L} = -Kdt \qquad (2)$$

The above equation was integrated, using the limits of L_0 to L, and 0 to t. L is the amount of oxidizable material remaining at time t, and L_0 is the amount of oxidizable material present at t = 0. Integration of the above expression between the limits stated gives the following relationship.

$$\text{Ln}_e \frac{L}{L_0} = -Kt \qquad (3)$$

$$\text{Log}_{10} \frac{L}{L_0} = -K't \qquad (4)$$

From equation 4 it can be seen that the velocity constant, K', is the slope of the Log_{10} L/L_0 versus time curve. The equation was based on the assumption of a first order

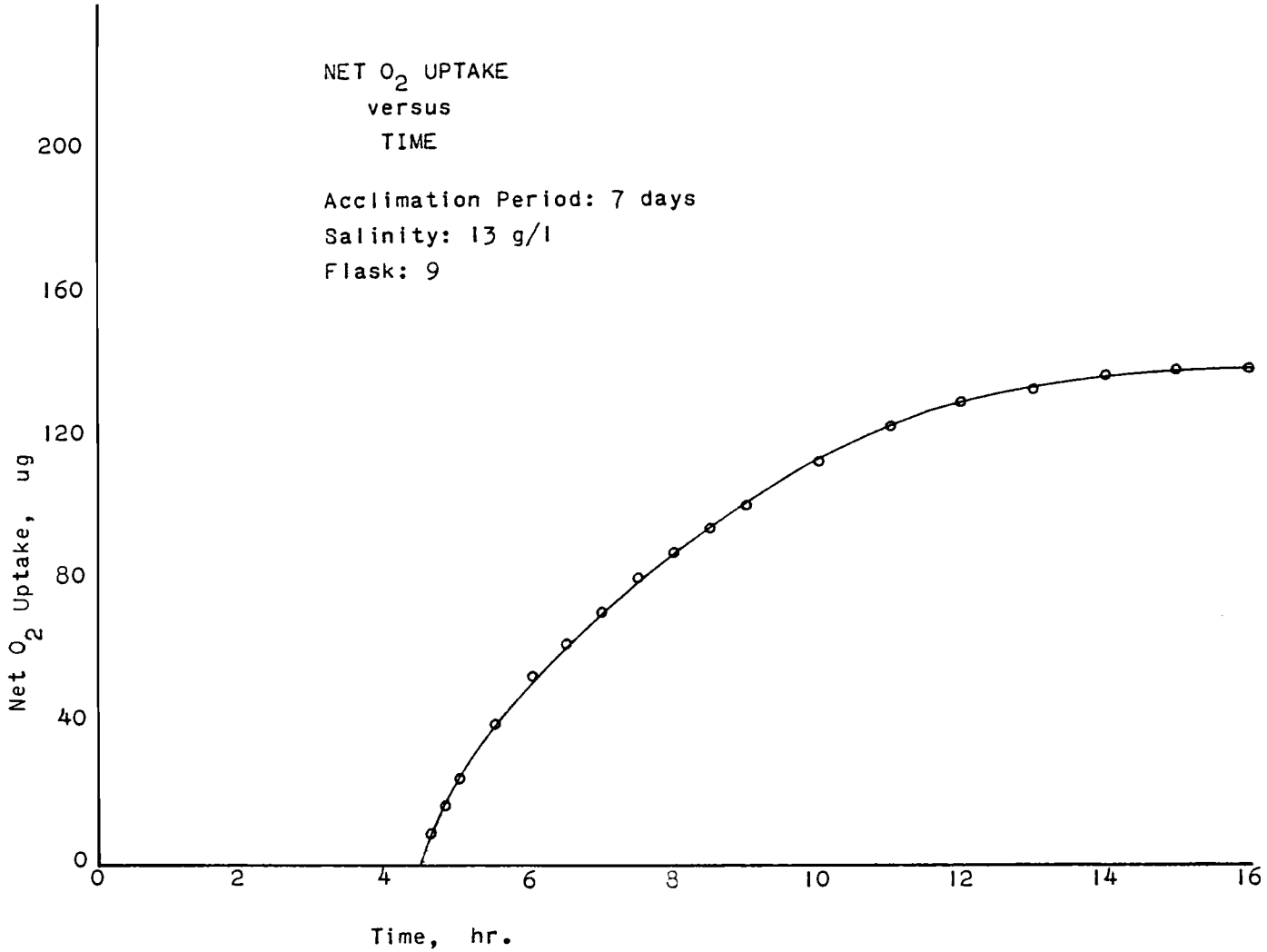
NET O_2 UPTAKE
versus
TIME
Acclimation Period: 7 days
Salinity: 13 g/l
Flask: 9
Net O_2 Uptake, ug
0
40
80
120
160
200
0
2
4
6
8
10
12
14
16
Time, hr.

Figure 2.

reaction, making the curve a straight line. Babbitt and Baumann (3, p. 345-352) state that the assumption has been shown to be approximately correct. Figure 3 shows a typical plot of $Log_{10}\ L/L_0$ versus time, and a sample calculation of K'.

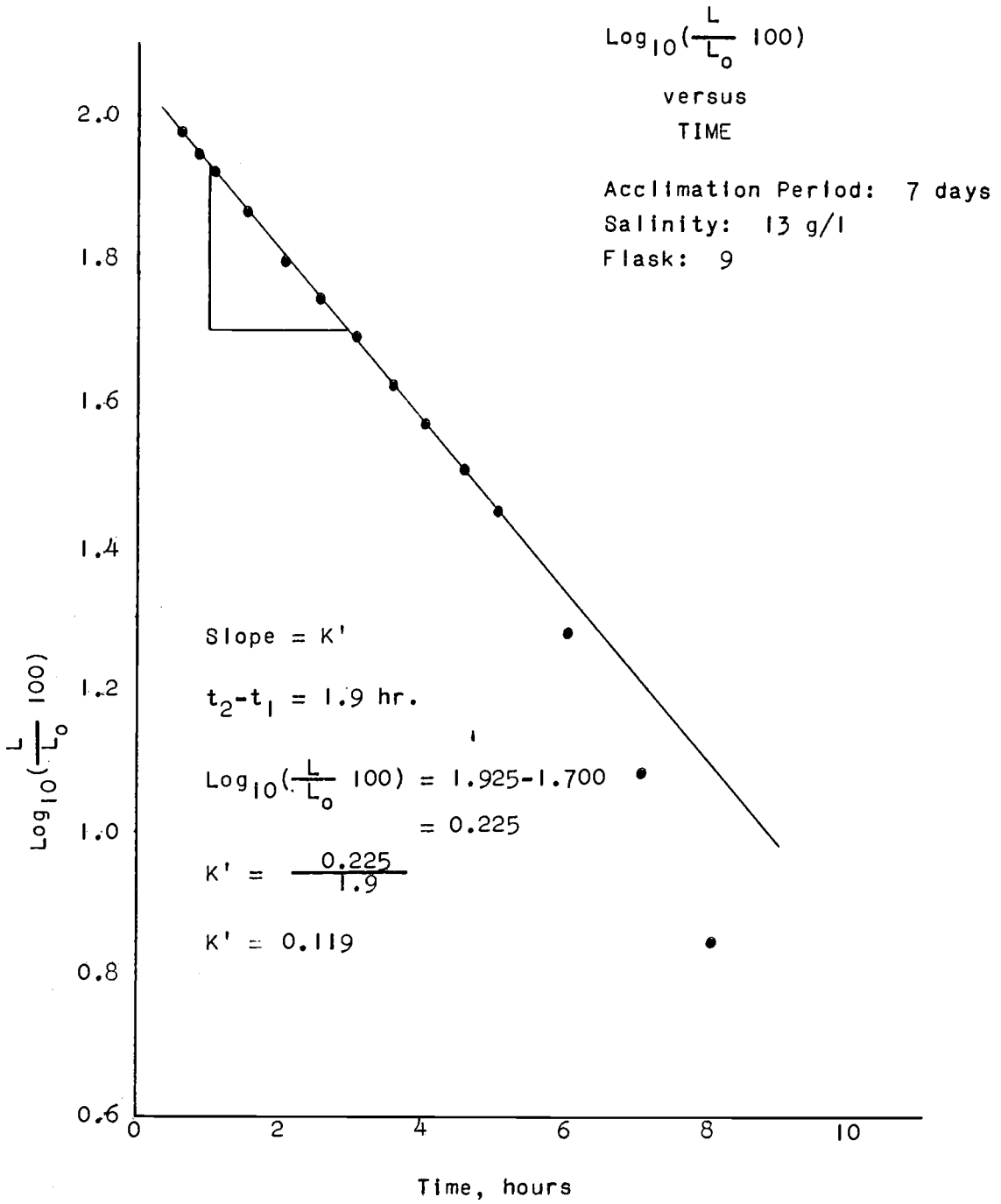
$\text{Log}_{10}(\frac{L}{L_o}\ 100)$
versus
TIME
Acclimation Period: 7 days
Salinity: 13 g/l
Flask: 9
Slope = K'
t_2-t_1 = 1.9 hr.
$\text{Log}_{10}(\frac{L}{L_o}\ 100)$ = 1.925-1.700
= 0.225
$K' = \frac{0.225}{1.9}$
K' = 0.119
$\text{Log}_{10}(\frac{L}{L_o}\ 100)$
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0
2
4
6
8
10
Time, hours

Figure 3.

DISCUSSION OF RESULTS

The results of this study are tabulated in the Appendix. The discussion of the results includes the following items:

1. The similarity between artificial and natural sea water environments
2. The salinity level of the cultures
3. The waste
4. The velocity constant
5. The fraction of the chemical oxygen demand biologically satisfied.

Similarity between Artificial and Natural Sea Water Environments

The results of the biochemical oxygen demand tests run on Kraft waste in artificial sea water, natural sea water and plain dilution water show that degradation of the waste will take place in all three mediums. Available time did not allow the comparison of the microbiological populations of the three mediums, therefore quantitative relationships between the magnitude of the oxygen demand of the waste and the rate of oxidation of the waste in the three mediums could not be developed. Allen's (1, p. 417-439) work showed that the marine bacteria normally found in sea water react favorably to the artificial sea water environment.

Salinity Level of the Cultures

The salinity of the acclimated cultures was determined over an eight-day period at the end of the experiments. Average values of the salinity compared to the estimated salinity of each culture were as follows:

Estimated Salinity	Average Measured Salinity
mg/l	mg/l
0	124
10,000	13,000
20,000	21,300
30,000	29,100
40,000	28,900

The low magnitude of the salinity in the estimated 40,000 mg/l culture was due to dilution by the Kraft waste. A more concentrated artificial sea water solution was made up to compensate for this dilution effect, but an error in preparation made this solution too dilute. Because of the difference between the estimated and measured salinity of this culture, data taken for it were rejected.

Salinity is a function of the chloride concentration. Strickland and Parsons (11, p. 19-21) give the following equation for the relationship:

$$\text{Salinity, mg/l} = 1.805 \text{ cl, mg/l} + 30 \qquad (5)$$

In the above salinity determinations the chloride concentration was measured by the Mohr method (2, p. 78-79) and converted to mg/l of salinity, using equation 5.

For convenience the following nomenclature will be used for the respective cultures in tabulations, curves and discussion from this point on:

O-U	Unacclimated culture of 124 mg/l salinity
O	Acclimated culture of 124 mg/l salinity
13	Acclimated culture of 13,000 mg/l salinity
21	Acclimated culture of 21,300 mg/l salinity
29	Acclimated culture of 29,100 mg/l salinity

The Waste

The chemical oxygen demand of the Kraft waste used in the studies varied from sample to sample. The magnitude of the chemical oxygen demand for each acclimation period is shown below in tabular form.

Acclimation Period days	Date of Sampling	COD mg/l
1	2-3-62	-
2	2-10-62	1165
4	3-17-62	3540[1]
7	2-17-62	1240
14	2-24-62	1065
21	3-3-62	1150
28	3-10-62	860

[1] The sample taken on March 17, 1962, contained a large amount of suspended matter.

Although the chemical oxygen demand, with the exception of the four-day acclimation period, is of the same magnitude for all of the waste samples, the net oxygen uptake, L_0, generally increased with increasing acclimation period. Figure 4 shows the net oxygen uptake, L_0, plotted against acclimation period. The curves were plotted using the mean values of L_0 except where isolated values did not fit an established pattern. It can be seen that the curves are relatively flat at 7 and 14 days' acclimation and again at 21 and 28 days' acclimation. In evaluating this factor, the relative strengths of the wastes used must be considered. The strength of the waste is a function of several factors such as the oxidizable material present, the toxicity of the waste to the culture, and the complexity of the waste. In this study the strength of the waste was evaluated by the chemical oxygen demand only. The net oxygen uptake and its relation to the strength of the waste is discussed later in this thesis.

The unacclimated culture O-U has values of L_0 of the same magnitude as the acclimated cultures up to an acclimation period of 14 days. At 21 days the L_0 value is approximately two-thirds of the L_0 value of the acclimated culture O. At an acclimation period of 28 days this ratio of the net oxygen uptake of the unacclimated culture to the acclimated culture is approximately 1/4.

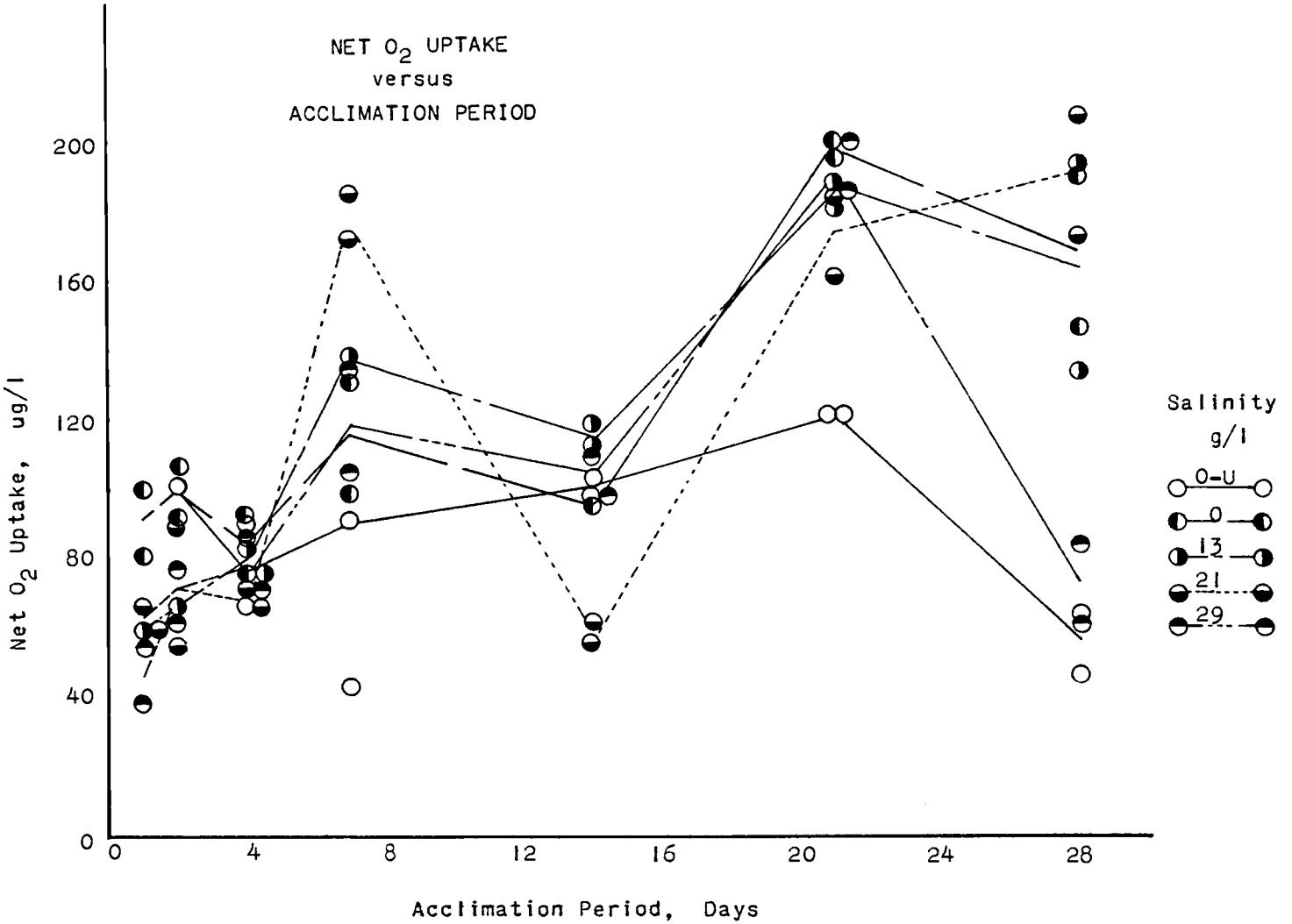
NET O_2 UPTAKE
versus
ACCLIMATION PERIOD
Net O_2 Uptake, ug/l
0
40
80
120
160
200
0
4
8
12
16
20
24
28
Acclimation Period, Days
Salinity
g/l
0-U
0
13
21
29

Figure 4.

Relationship of the Velocity Constant K' to the Period of Acclimation and the Salinity Level

The variation of the velocity constant K' with respect to the period of acclimation is shown in figure 5. The mean K' values were used in drawing the curves except where isolated values did not fit an established pattern.

The range of K' values for acclimation periods of 1 to 7 days is great. At two days of acclimation the magnitude of the velocity constants for all cultures is much greater than for any other period of acclimation. The values at 4 and 7 days of acclimation to the waste are scattered. At acclimation periods of 14 and 21 days the velocity constants vary between 0.17 and 0.23. After 28 days' acclimation to the waste the values of K' vary between 0.08 and 0.15. The velocity constants of the unacclimated culture, O-U, are lower than those of the acclimated culture, O, for all but the 7-day acclimation period. However, the velocity constants of the two cultures are of the same magnitude for acclimation periods of 7 days or more.

Figure 6 is a composite of the bar graphs made each week of the variation of K' with the salinity level of the cultures. It should be noted that the abscissa is not a linear scale of salinity. The magnitude of the velocity

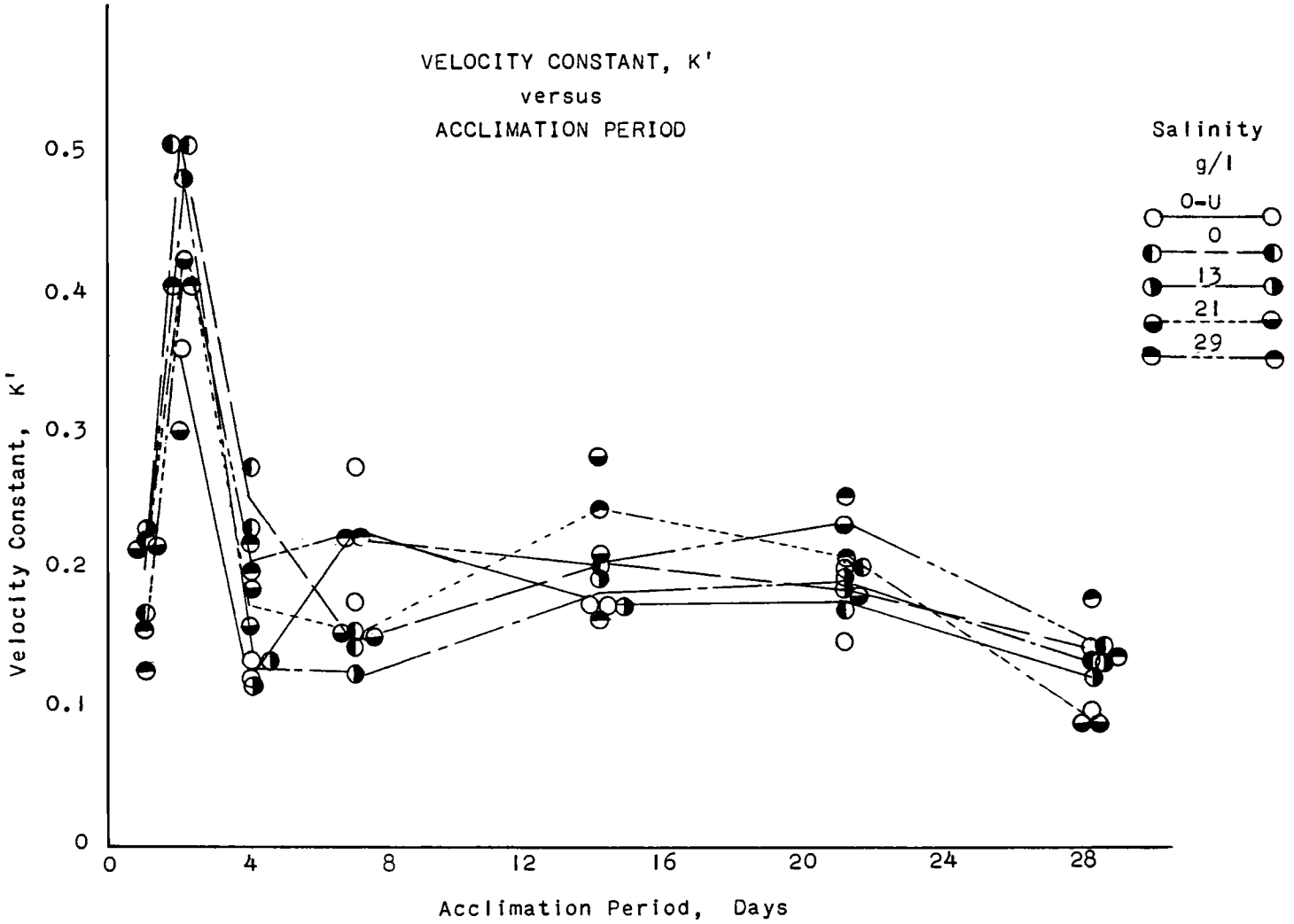
VELOCITY CONSTANT, K'
versus
ACCLIMATION PERIOD
Salinity
g/l
0-U
0
13
21
29
Velocity Constant, K'
0
0.1
0.2
0.3
0.4
0.5
0
4
8
12
16
20
24
28
Acclimation Period, Days

Figure 5.

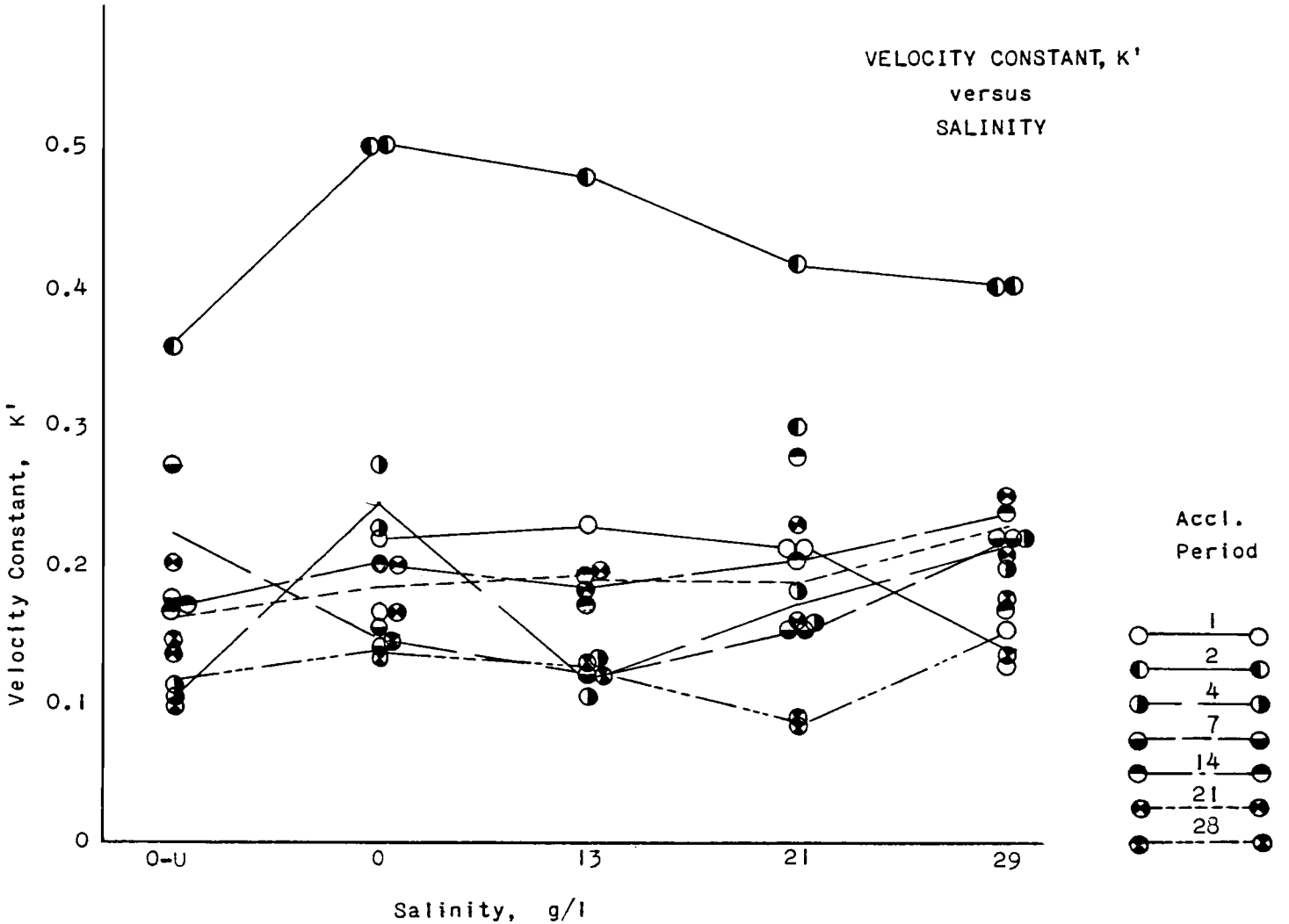
VELOCITY CONSTANT, K'
versus
SALINITY
Velocity Constant, K'
0.5
0.4
0.3
0.2
0.1
0
0-U
0
13
21
29
Salinity, g/l
Accl.
Period
1
2
4
7
14
21
28

Figure 6.

constant is relatively constant for salinity levels of 0 and 13 g/l. At acclimation periods of one and two days the magnitude of K' is less than the magnitude of K' for lower salinity levels. At longer periods of acclimation to the waste the velocity constants are relatively constant at all salinity levels.

The Fraction of the Chemical Oxygen Demand Satisfied

The fraction of the chemically oxidizable material biologically oxidized has been plotted against the period of acclimation to the waste and the salinity level of the cultures. The curves were plotted, using the mean values of L_O/COD except where isolated points did not fit an established pattern.

The relationship of the fraction of the chemical oxygen demand satisfied to the period of acclimation is shown in figure 7. The fraction generally increases with acclimation time. At an acclimation period of 28 days the fraction of the chemical oxygen demand satisfied by culture 29 is less than one-half the fraction satisfied by the other acclimated cultures. Culture 21 is erratic at acclimation periods of 7 and 14 days, but has values of L_O/COD of the same magnitude as the other cultures at 1, 21 and 28 days of acclimation to the waste. The data for the four-day acclimation period were rejected because of the high

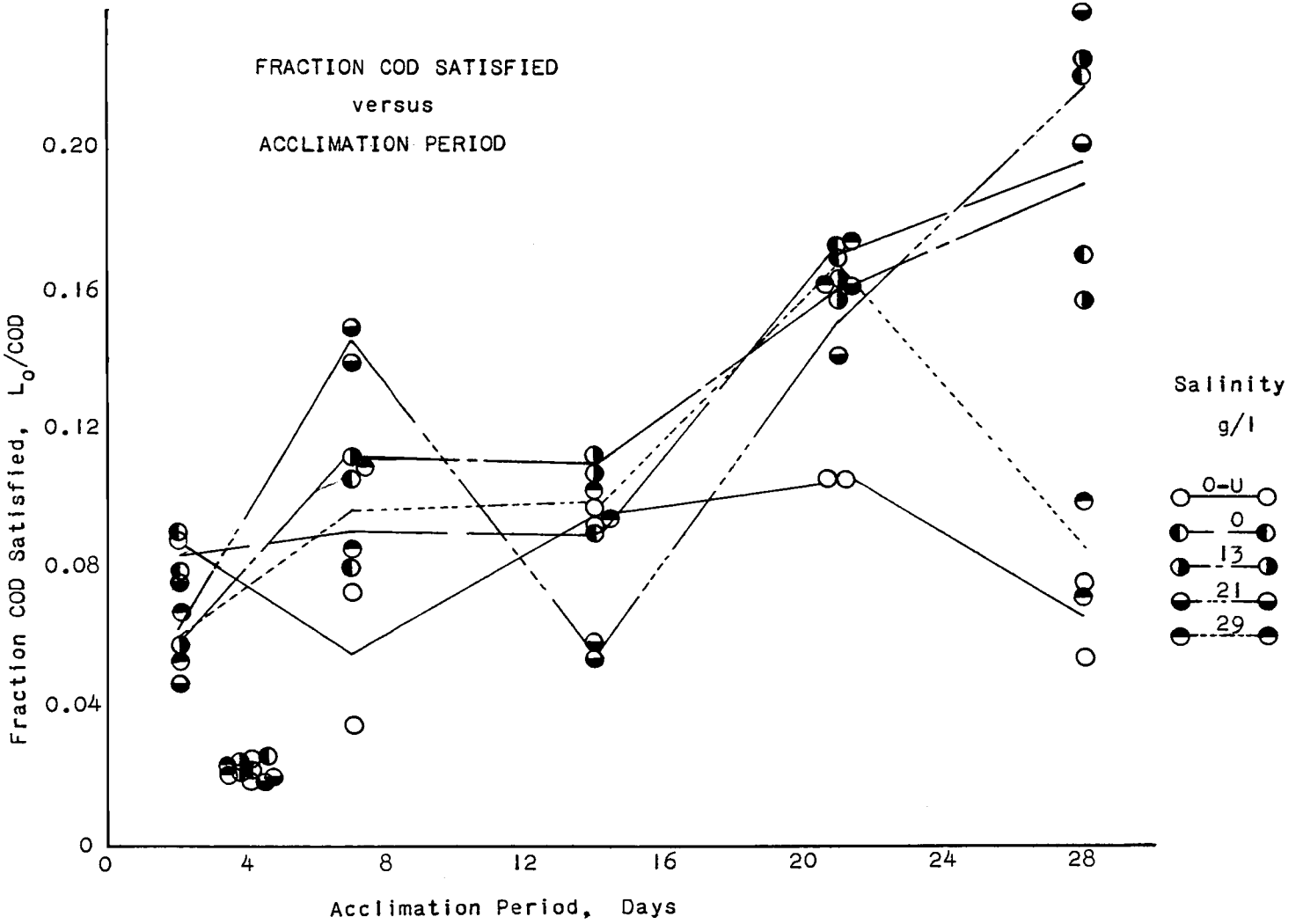
FRACTION COD SATISFIED
versus
ACCLIMATION PERIOD
Fraction COD Satisfied, L_o/COD
0.20
0.16
0.12
0.08
0.04
0
0
4
8
12
16
20
24
28
Acclimation Period, Days
Salinity
g/l
0-U
0
13
21
29

Figure 7.

amount of suspended matter in the sample and the relatively high chemical oxygen demand of the sample.

For periods of acclimation of 1 to 14 days the fraction of the chemical oxygen demand satisfied by the unacclimated culture, O-U, was of the same magnitude as that of the acclimated culture O. At 21 days of acclimation the fraction satisfied by the unacclimated culture was two-thirds of the fraction satisfied by the acclimated culture O, and at 28 days this figure dropped to one-third.

In figure 8 the fraction of the chemical oxygen demand biologically satisfied is plotted against the salinity level of the cultures. It should be noticed that the curve is a composite of bar graphs made up for each acclimation period. The salinity levels are not on a linear scale. The fraction satisfied by cultures O, 13 and 21 increases with the period of acclimation to the waste. With the exception of the 28-day period of acclimation the fraction satisfied by the acclimated cultures is relatively constant for all salinity levels.

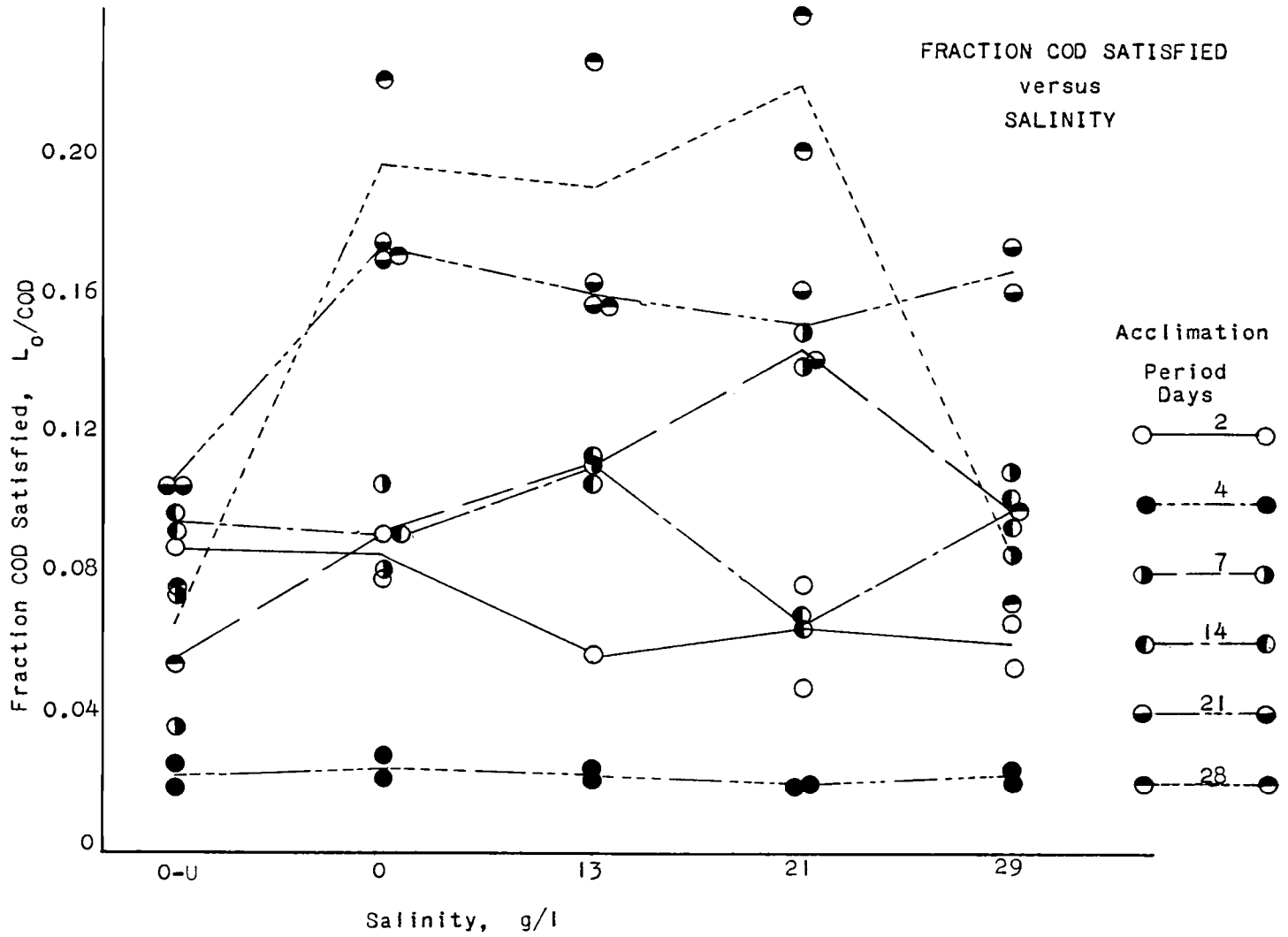
FRACTION COD SATISFIED
versus
SALINITY
Fraction COD Satisfied, L_o/COD
0.20
0.16
0.12
0.08
0.04
0
0-U
0
13
21
29
Salinity, g/l
Acclimation
Period
Days
2
4
7
14
21
28

Figure 8.

CONCLUSIONS

1. The ability of the cultures to degrade the Kraft waste increased with increasing periods of acclimation to the waste.

2. The fraction of the chemical oxygen demand biologically satisfied increased with increasing periods of acclimation to the waste.

3. The fraction of the chemical oxygen biologically satisfied was not affected by the salinity level of the cultures.

4. The magnitude of the velocity constant, K', shows no relationship to the salinity level of the culture.

5. The relationship of the velocity constant, K', to the period of acclimation of the cultures to the waste cannot be determined from the data presented in this thesis.

RECOMMENDATIONS FOR FURTHER STUDY

The author recommends the following areas for further study:

1. The effect of acclimation periods of less than one week on the velocity constant, K'.

2. Investigation of the possible build-up of substances which are inhibitive or toxic to the growth of the microbiological organisms during acclimation to the Kraft waste.

3. The effect of acclimation periods of greater than 28 days on the velocity constant, K'.

4. The effect of acclimation periods of greater than 28 days on the fraction of the chemical oxygen demand biologically satisfied.

5. The effect of temperatures closely approximating natural conditions on the degradation of Kraft waste in the marine environment.

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APPENDIX

Table 1

BOD of Kraft Waste in Artificial Sea Water, Natural Sea Water and Plain Dilution Water

Date of Sampling: 1-11-62

Day	Plain Dilution Water		Fresh Sea Water		Artificial Sea Water	
	Dilution		Dilution		Dilution	
	1%	2%	1%	2%	1%	2%
1	10	35	30	--	60	65
	60	40	30	--	60	150
3	370	--	110	260	--	--
	300	--	--	240	--	--
5	480	--	220	--	--	--
	480	--	320	--	--	--
8	630	--	--	--	--	--
	630	--	--	--	--	--

Date of Sampling: 1-18-62

Day	Plain Dilution Water		Fresh Sea Water		Artificial Sea Water	
	Dilution		Dilution		Dilution	
	0.5%	1%	0.5%	1%	0.5%	1%
1	0	10	0	0	0	0
	40	30	40	0	0	40
3	360	320	0	30	20	50
	360	320	20	20	120	220
5	460	340	40	50	100	200
	480	330	40	50	100	160
8	580	480	100	40	180	290
	640	460	0	50	300	200

Table 1 (Continued)

Date of Sampling: 1-25-62

Day	Plain Dilution Water		Fresh Sea Water		Artificial Sea Water	
	Dilution		Dilution		Dilution	
	0.5%	1%	0.5%	1%	0.5%	1%
1	120	50	80	60	260	80
	100	50	60	60	80	110
3	420	380	380	600	420	170
	440	360	360	620	260	250
5	580	500	460	820	300	280
	580	500	460	780	300	290
8	800	640	420	720	540	360
	840	640	440	760	460	330

Table 2

Chlorides Concentration of Acclimated Cultures, mg/l

Date	Culture				
	0	13	21	29	Estimated 40
3-13-62	--	9000	12,000	15,300	--
3-16-62	49	7150	11,300	--	15,400
3-18-62	49	5930	11,000	16,300	16,000
3-19-62	49	6800	12,100	16,100	15,500
3-20-62	49	6780	12,450	16,550	16,450
3-21-62	148	8440	11,900	16,600	16,550

Table 3

Net Oxygen Uptake

Acclimation Period: 1 day

Time hrs.	Salinity g/l									
	0-U		0		13		21		29	
	Flask									
	-	-	2	4	16	-	14	15	11	13
4.0										
4.2					7			3		
4.4			5	5	14		3	11	3	4
4.6			13	13	19		12	17	5	7
4.8			20	23	23		18	21	8	9
5.0			30	30	27		25	25	10	12
5.5			40	41	35		32	31	14	19
6.0			47	51	39		39	37	18	24
6.5			54	60	43		45	42	21	28
7.0			60	65	47		50	47	24	31
7.5			66	72	50		53	51	26	34
8.0			71	78	53		56	53	28	37
9.0			75	88	56		58	55	30	39
10.0			78	95	58		60	56	32	42
11.0			79	100	59		63	57	35	46
12.0			80	100	59		66	58	36	50
13.0			80				66	60	37	52
14.0								60	38	54
15.0									38	55
16.0										55

Table 3 (Continued)

Net Oxygen Uptake

Acclimation Period: 2 days

Time hrs.	Salinity g/l									
	O-U		O		13		21		29	
	Flask									
	-	17	4	5	6	-	11	12	13	14
4.0										
4.2										
4.4				4	4			3		
4.6		5		23	20		4	12	3	5
4.8		15	19	38	28		12	19	12	12
5.0		24	34	49	36		26	25	18	20
5.5		44	57	73	48		33	36	33	36
6.0		61	73	88	56		41	45	44	50
6.5		76	82	98	60		47	56	52	60
7.0		84	88	104	63		52	60	57	67
7.5		89	92	106	65		53	74	60	70
8.0		95	92	106	66		55	88	62	74
8.5		98	92		66		55	89	62	77
9.0		101						89		77
10.0		101								
11.0										
12.0										
13.0										
14.0										
15.0										

Table 3 (Continued)

Net Oxygen Uptake

Acclimation Period: 4 days

Time hrs.	Salinity g/l									
	0-U		0		13		21		29	
	Flask									
	2	4	5	6	9	11	12	13	14	15
4.5										
4.7		4	8	6	6		2	6		
4.9	5	12	16	14	11	8	7	8	8	6
5.1	8	16	22	22	15	12	12	13	14	13
5.3	12	20	28	30	18	22	17	17	20	18
5.5	16	24	33	36	21	32	20	20	25	24
6.0	22	32	44	48	28	38	30	28	36	33
6.5	27	40	53	56	33	44	37	35	44	41
7.0	32	47	59	64	38	50	42	41	51	48
7.5	36	52	63	71	42	56	46	47	57	53
8.0	41	56	68	76	47	59	50	51	62	57
8.5	44	59	70	80	50	62	54	54	67	61
9.0	46	62	72	83	52	64	56	58	70	64
9.5	48	65	73	85	54	66	58	61	73	67
10.0	50	68	74	87	57	70	59	65	76	69
11.0	54	73	75	89	62	73	60	68	80	70
12.0	57	79	76	91	65	76	62	70	83	71
13.0	60	83	76	92	68	80	64	71	84	72
14.0	63	88		92	72	83	66	71	84	72
15.0	66	90			76	83	66			
16.0	66	90			76					

Table 3 (Continued)

Net Oxygen Uptake

Acclimation Period: 7 days

Time hrs.	Salinity g/l									
	0-U		0		13		21		29	
	Flask									
	2	4	5	6	9	11	12	13	14	15
4.0										
4.2										
4.4				3			6	10	2	8
4.6				12	8		16	19	13	15
4.8		7	7	20	16		24	27	22	24
5.0		11	13	28	24		32	35	30	32
5.5	14	23	27	44	39		52	51	46	48
6.0	22	34	39	56	52		68	64	59	62
6.5	28	42	50	68	61		83	78	69	75
7.0	34	52	60	73	70		97	89	76	88
7.5	38	59	68	86	80		108	100	83	97
8.0	40	64	74	93	87		121	110	88	108
8.5	43	70	79	100	94		132	120	92	114
9.0	44	74	84	107	100		142	129	96	124
10.0	44	82	90	116	112		160	147	101	131
11.0		88	95	124	122		172	158	105	135
12.0		91	97	128	129		182	164	105	135
13.0		91	99	131	132		185	168		
14.0			99	131	136		185	172		
15.0					138			172		
16.0					138					

Table 3 (Continued)

Net Oxygen Uptake

Acclimation Period: 14 days

Time hrs.	Salinity g/l									
	0-U		0		13		21		29	
	Flask									
	2	4	5	6	9	11	12	13	14	15
5.5										
5.7		4			7	4				
5.9	8	10		8	14	14	10	8	8	10
6.1	12	16		14	21	23	16	12	16	22
6.3	20	22		21	26	29	22	16	24	30
6.5	24	28		26	32	34	28	19	32	38
7.0	36	39		40	45	48	36	26	44	52
7.5	44	50		51	56	60	42	32	55	63
8.0	52	58		60	66	71	48	38	64	71
8.5	61	66		68	76	81	53	42	72	78
9.0	68	73		74	84	88	56	45	78	84
9.5	74	80		80	92	95	58	48	84	89
10.0	80	85		86	98	100	60	50	90	92
10.5	84	90		90	102	104	61	52	94	94
11.5	92	97		94	111	110	62	56	101	98
12.5	96	102		96	106	113	62	56	105	99
13.5	98	103		96	119	113			109	99
14.5	98	103			119				109	
15.5										
16.5										

Table 3 (Continued)

Net Oxygen Uptake

Acclimation Period: 21 days

Time hrs.	Salinity g/l									
	0-U		0		13		21		29	
	Flask									
	2	4	5	6	9	11	12	13	14	15
4.0										
4.5	12	18	18	19	18	13	14	8	20	20
5.0	26	38	46	53	41	42	26	44	30	34
5.5	40	54	72	78	64	66	68	66	78	78
6.0	50	64	91	100	84	84	87	86	98	98
6.5	59	76	106	118	99	104	101	104	118	116
7.0	69	85	122	134	114	121	112	116	132	134
7.5	76	95	136	148	128	136	124	127	146	150
8.0	84	101	152	158	140	150	133	140	159	160
8.5	90	106	161	169	152	160	140	152	172	172
9.0	96	113	170	179	160	170	148	161	180	178
10.0	108	118	188	189	170	180	156	172	192	186
11.0	113	121	198	195	178	188	161	185	199	186
12.0	117	121	206	195	180	188	161	185	200	
13.0	121		206		180				200	
14.0	121									
15.0										

Table 3 (Continued)

Net Oxygen Uptake

Acclimation Period: 28 days

Time hrs.	Salinity g/l									
	0-U		0		13		21		29	
	Flask									
	2	4	5	6	9	11	12	13	14	15
4.0										
4.2	2		3	4	8	8	4	8		
4.4	4	4	19	16	18	17	12	14		
4.6	6	6	30	24	24	27	23	20	9	4
4.8	8	8	40	32	30	35	30	26	12	8
5.0	10	11	48	40	37	43	36	32	16	12
5.5	16	17	66	54	50	60	52	46	24	24
6.0	20	21	83	68	60	76	66	57	31	32
6.5	24	24	97	80	70	90	79	68	36	40
7.0	28	28	109	90	80	102	90	79	41	46
7.5	31	30	120	100	88	114	100	88	44	57
8.0	34	33	130	110	95	125	110	97	48	56
8.5	37	35	140	117	101	136	120	104	51	60
9.0	40	37	148	122	106	144	130	112	54	64
10.0	46	41	164	137	116	160	147	127	57	70
11.0	54	44	176	139	124	174	163	140	59	75
12.0	59	45	185	144	128	182	178	153	61	78
13.0	63	46	190	145	132	188	189	161	61	81
14.0	64	46	190	146	134	192	196	168		83
15.0	64			146	134	194	203	172		84
16.0						194	206	173		84
17.0							208	173		
18.0							208			

Table 4

Velocity Constants and Fraction COD Satisfied

Salinity g/l	1 day Acclimation COD = --			2 days Acclimation COD = 1165 mg/l			4 days Acclimation COD = 3540 mg/l		
	K'	L_O mg/l	L_O/COD	K'	L_O mg/l	L_O/COD	K'	L_O mg/l	L_O/COD
U-O	--	--	--	0.357	101	0.087	0.113	66	0.019
	--	--	--	--	--	--	0.109	90	0.025
0	0.161	100	--	0.500	106	0.091	0.270	76	0.021
	0.217	80	--	0.500	92	0.079	0.227	92	0.026
13	0.227	59	--	0.477	66	0.057	0.106	76	0.021
	--	--	--	--	--	--	0.131	83	0.023
21	0.213	60	--	0.294	89	0.076	0.182	66	0.019
	0.213	66	--	0.417	55	0.047	0.159	71	0.020
29	0.125	55	--	0.400	62	0.053	0.197	84	0.024
	0.152	38	--	0.400	77	0.066	0.217	72	0.020

Table 4 (Continued)

Velocity Constants and Fraction COD Satisfied

Salinity g/l	7 days Acclimation COD = 1240 mg/l			14 days Acclimation COD = 1065 mg/l			21 days Acclimation COD = 1150 mg/l		
	K'	L_o mg/l	L_o/COD	K'	L_o mg/l	L_o/COD	K'	L_o mg/l	L_o/COD
O-U	0.270	91	0.073	0.170	98	0.092	0.145	121	0.105
	0.175	44	0.035	0.173	103	0.097	0.200	121	0.105
0	0.154	131	0.105	0.200	96	0.090	0.164	200	0.174
	0.141	99	0.080	--	--	--	0.200	195	0.169
13	0.119	138	0.111	0.170	119	0.112	0.186	180	0.156
	--	--	--	0.192	113	0.106	0.196	188	0.163
21	0.154	172	0.139	0.277	62	0.058	0.232	161	0.140
	0.154	185	0.149	0.203	56	0.053	0.176	185	0.161
29	0.218	135	0.109	0.167	109	0.102	0.208	200	0.174
	0.218	105	0.085	0.243	99	0.093	0.250	186	0.161

Table 4 (Continued)

Velocity Constants and Fraction COD Satisfied

Salinity g/l	28 day Acclimation COD = 860 mg/l		
	K'	L_O mg/l	L_O/COD
O-U	0.097	64	0.075
	0.141	46	0.054
O	0.137	190	0.221
	0.143	146	0.170
13	0.133	134	0.156
	0.124	194	0.226
21	0.081	208	0.242
	0.089	173	0.201
29	0.135	61	0.710
	0.175	84	0.098