Environmental Engineering and Science Graduate Program Civil Engineering Department Manhattan College Bronx, New York

EXPERIMENTS ON THE BENTHAL OXYGEN DEMANDS AND LEACHING RATES

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RAW, DIGESTED AND WET OXIDIZED SLUDGES

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ABSTRACT

Raw and digested sludge from the New York Metropolitan area is presently barged out to sea for ultimate disposal. This report presents the results of laboratory studies to determine the effects of various types of sludge treatment - digestion, wet oxidation and heat treatment - on the benthal oxygen demands and leaching rates of sludge deposits.

Two types of laboratory studies were conducted: (1) Warburg studies to determine the oxygen demand of the sludges when in an aerobic condition and (2) continuous flow reactor studies with the sludge layered on the bottom of reactors to simulate actual sludge deposits.

The results of the studies indicated that treatment of the sludge prior to disposal at sea would significantly reduce the benthal oxygen demands and leaching rates of the bottom deposits. An oxygen diffusion analysis indicated that anaerobic decomposition in the raw, digested, heat-treated and low wet oxidized sludge layers markedly increased the benthal oxygen demands. In contrast the bottom layers of the intermediate and high wet oxidized sludges were relatively dormant with negligible anaerobic decomposition occurring.

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I. INTRODUCTION

Raw and digested sludge from the New York Metropolitan area is presently barged out to sea for ultimate disposal. A recent study (16) in the New York Bight has indicated that the present practice of barging this sludge to a confined dumping area twelve miles off the coastline causes a marked reduction in the dissolved oxygen content of the overlying waters. In the latter part of the summer months the dissolved oxygen content of the water overlying the sludge deposits three feet from the bottom was shown to be less than 1 mg/l while the surface water was about 6 mg/l. A marked change occurred in the benthal ecology of the sludge area and coliform counts indicated the possibility of pathogenic contamination of the shellfish in the

The probability that these sludge deposits, which have been built up over the past 40 years, are deleterious to the ocean environment may require a change in the present sludge disposal policy. Wet oxidation of the sludge prior to disposal will eliminate pathogenic organisms. Depending on the degree of sludge oxidation and sludge stability, the benthal oxygen demand of the sludge may be reduced thus minimizing the effects on the dissolved oxygen resources of the Bight.

This report presents the results of experiments to determine the benthal oxygen demands and leaching rates of raw, digested, wet oxidized and heat treated sludges.

II. LITERATURE REVIEW ON SLUDGE BENTHAL OXYGEN DEMAND

Baity(1) in 1938 utilizing continuous flow 20 liter reactors with primary sludge (8.5% solids, 83% volatile) layered on the bottom, conducted one of the earliest benthal oxygen demand studies. His study was conducted 22°C and lasted for 36 days. Oxygen demand rates were shown to increase with increasing sludge depth as illustrated by the following data:

Sludge Depth (cm)	Benthal Oxygen Demand <u>(g/m² day)</u>
0.1 0.5 1 1.5 2	0.55 1.84 2.89 3.45 3.77
4	5.17

-1-

For the 0.5 cm depth sludge he also determined that the supernatant oxygen concentration did not effect the oxygen uptake rate between 2 to 5 mg/l and that the uptake rate in fresh water was 1.8 times higher than in synthetic sea water (10,000 mg/l chloride). This may have been due to inhibition of nitrification since 50 day BOD's in fresh water exhibited marked nitrification while none occurred in salt water.

In 1941, Fair, Moore and Thomas(5) conducted long term continuous flow reactor studies using Imhoff tank sludge mixed with sand and lime to simulate river muds. They conducted their studies for 450 days in continuous flow reactors with detention times from 4 to 16 hours. In agreement with Baity, their results indicated that the oxygen uptake rate was independent of oxygen concentration from 3.6 to 8 mg/l. After 45 days, the benthal deposits contained about 45% of their original nitrogen content. About 20 to 30% of the nitrogen could not be accounted for and was thought to be lost by denitrification. From their data they also determined the time required for various degrees of sludge stabilization to be:

50%	Stabilization	0.3	yr.	(110 days)
90%	Stabilization	1.5	yr.	(550 days)
99%	Stabilization	5.4	yr.	(2000 days)

They indicated that the data of McGowan et al (1913) on polluted English river muds required about four times longer than the above data for the same degree of stabilization. The English muds continued to exert a significant oxygen demand after 750 days incubation.

Using Fair's data, Camp(2) has estimated the following stabilization times for both summer and winter temperatures:

	2 Stabilization		
<u>Time (days)</u>	Summer k ₄ =0.0032	Winter <u>k₄=0.0016</u>	
100	52	31	
200	77	52	
500	97	84	
1000	99	97	

Note that the time required for 99% stabilization in the summer is about half that estimated by Fair et al for the same data. The equation developed by Camp for the above analysis is:

 $L_{d} = L_{do} 10^{-k_{4}t}$

where L_d = areal BOD of bottom deposit, g/m^2

 L_{do} = initial areal BOD of bottom deposit, g/m²

and t = time from start of decomposition.

Fair et al also reported that the collection of the off gases from the benthal deposits were about 70% methane, indicating active anaerobic decomposition. A recent (1955) study by Grindley(6) on the Thames Estuary indicated that the off gases from benthal deposits had the following compositions (percent by volume):

CH4	72.3%
C0 ₂	16.4%
N ₂	7.8%
H ₂	1.9%
H ₂ S	0.9%
02	0.4%
C 0	0.3%

Thus anaerobic decomposition of benthal deposits can markedly reduce the quantity of oxygen required to stabilize these deposits because of the reduction of the volatile matter and subsequent loss as methane gas. "As to the quantity of oxygen required", Fair et al indicated that, "the upper, aerobic limit appears almost to approach a value of weight for weight of volatile solids (kg of oxygen per kg of volatile matter), for example, while the lower, anaerobic, limit lies at about 10% of this value".

It was also concluded by Fair et al that the rate of oxygen demand is controlled not by oxygen diffusion into the sludge but by diffusion of organic matter into overlying waters. Based on the differences in the estimated magnitude of the two driving forces of oxygen into the sludge and organic matter out of the sludge, Camp concurred with the above conclusion.

Oldaker, Burgum and Pahren(13) also believed that the rate of diffusion of oxidizable substances into the supernatant waters controlled the oxygen uptake rate of the sediment. They conducted studies lasting 100 days on river bottom sediments (recent and aged) at sludge depths of 15 to 20 cm. (No supernatant mixing was employed leaving the possibility of dissolved oxygen stratification in the liquid phase). Camp's benthal equation was used to correlate their results which indicated that nitrification was significant in exerting an oxygen demand. The oxygen demand initially decreased for about the first 40 days then increased due to nitrification. They also concluded that depths above 15 cm had no effect on the benthal oxygen demands which varied from about 0.4 to 1.4 g/m^2 -day. Recent studies on the effect of various parameters on benthal uptake rates have been conducted by Hanes et al(4)(7)(8). In their studies a batch reactor chamber was used with sludge layered on the bottom and a D.O. probe continuously measuring the oxygen concentration in the stirred supernatant. They determined that the benthal oxygen uptake rate of a de-inking sludge increased with increasing concentration tions of seawater as indicated by the following data:

%	Benthal Oxygen Uptake	Rate (g/m ² -day)
Fresh	Without	With
Seawater	<u>Nutrients</u>	Nutrients
_		
0	0 . 9 4	2.33
50	1.18	2.69
100	1.16	3.12

Their results were contrary to those of Baity(1) who used synthetic and aged seawater in continuous flow reactors. Hanes et al stated that both of these conditions cause the toxic properties to differ from those of fresh seawater. Only a portion of the difference in uptake rate ($0.22 \text{ g/m}^2/\text{day}$) was caused by the seawater itself in their studies. Their studies(7) also indicated that the uptake rate of the supernatant waters was a significant (over 50% at times) portion of the total uptake rate. This shows the large effect of leaching in their benthal system.

The study of Davison and Hanes(4) showed this leaching effect to be a function of sludge depth as shown by the following data:

	Benthal	Oxygen		
	Uptake	Rate	Supernata	nt
Sludge	<u> (g/m²</u>	/day)	Leaching,	BOD5
Depth	Initial	Final	(mg/1)	
<u>(cm)</u>	<u>lst 3 days</u>	<u>last 4 days</u>	<u>Initial</u>	Final
1.6	3.2	2.1	3.4	1.5
1.4	4.8	1.7	7.6	1.7
2.8	6.3	1.7	14.6	2.1

In the initial phases of the study, the higher uptake rates at the greater sludge depths were attributed to compaction of the deeper sludges during the early phase. Subsequently leaching out of interstitial water caused a high supernatant BOD and uptake rate.

McDonnell and Hall's(10) studies on mud samples from a highly eutrophic stream showed that the uptake rate increased both with oxygen concentration and sludge depth. They indicated that the effect of oxygen concentration was due to the respiration of a macro-invertebrate population present in their sludge samples. A mathematical analysis indicated that microbial respiration contributed 48 to 45% and invertebrate respiration 52 and 55% of the benthal oxygen demand in the 2 and 25 cm samples, respectively. They agreed with the data of Edwards and Rolly who reported that the proportion of oxygen consumption due to

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invertebrates which were added to their mud cores was 40%. They indicated that the samples of Baity(1), Fair(5) and Hanes(8) demonstrated an independence of uptake rate on oxygen concentration since they contained no invertebrates. The effect of temperature (5-25°C) on benthal uptake rate was determined by the following equation:

$$\frac{\sigma(2)}{\sigma(1)} = \phi(t_2 - t_1)$$

Results of various investigations(10) showed ϕ to vary from 1.067 to 1.080.

McKeown et al(11) have shown that turbulence increases the oxygen demand of cellulosic benthal deposits. Stagnant flow conditions produced oyxgen demands of 0.2 and 0.8 g/m²-day from shallow and deep deposits. Mixing or eddying which approaches scouring conditions increased the demand to 2.7 g/m²-day while slight scouring caused demands of 4.4 g/m²-day. A comparison of in situ measurements of cellulosic benthal deposits with laboratory measurements by Stein and Dennison(11) showed the laboratory benthal oxygen demand to be 50% higher than in the field. A study by Crook and Bella(3) on the Oregon coast indicated that the presence of mud shrimp burrows may significantly increase oxygen uptake rates of tidal flat deposits. Their results also indicated that, under normal flow conditions, the principal oxygen uptake due to tidal flat deposits occurs in the immediate vicinity of the deposits.

Benthal oxygen demand studies were recently conducted by Ogunrombi and Dobbins(12) using continuous flow reactors and a synthetic mud with a composition of 50% primary solids and 50% of a sand-diatomaceous earth mixture. A mathematical model was formulated for data analysis which separated the oxygen demand of the sludge deposits into its two components; 1) the 0_2 uptake rate of the upper aerobic sludge layer caused by oxidation of the organic matter in this layer and of the anaerobic end products diffusing into this layer from the anaerobic lower layer of sludge, and 2) the leaching rate of BOD, La, into supernatant waters which subsequently exerts an oxygen demand. The equations describing each of these rates are:

1)
$$D_b = \frac{CA-C}{T} - K_1L - \frac{dC}{dt}$$

2)
$$L_a = \frac{dL}{dt} + (\frac{1+K}{T})L$$

where $D_{\rm R}$ = benthal 0₂ demand, mg/l/day

L_a = BOD leaching rate, mg/l/day CA-C = influent - effluent D.O., mg/l T = Detention time, days $K_1 = BOD$ rate constant, day⁻¹

L = Ultimate BOD (lst stage) of effluent, mg/l

dc/dt = rate of change of supernatant D.O., mg/1/day

dL/dt = rate of change of supernatant BOD, mg/1/day

These results indicated that L_a was on the average 28% of D_B and both L_a and D_B decreased with time. This was attributed to the development of a physical barrier at the water sludge interface during the course of decomposition as well as to the gradual destruction of the organic matter in the deposit and also the possible deposition of ferric iron. The existence of such a barrier, which would obstruct mass transfer was supported by the observation of a grey-colored surface zone which developed as decomposition proceeded.

A BOD material balance indicated that the total 0_2 demand was never exerted fully because of the production of anaerobic end products which were not oxidized, especially notable with the deeper sludges. (This hypothesis seems reasonable however this data indicates for both reactors 1 and 2 that the degradative rate is zero order for the last 20-30 days of the study and not first order as assumed. This makes their estimate of the ultimate 0_2 demand and their conclusion on the anaerobic decomposition contribution questionable).

A recent study by Fillos(6) using a mixture of raw primary sludge and fine sand showed that the aerobic layer of sludge deposits was not more than a few millimeters thick from the vertical distribution of electrode potential. The anaerobic layer below the aerobic was not uniform in activity (maximum at 1 to 2 inches depth) suggesting a decrease in bacteria with increasing depth. Benthal demands were independent of dissolved oxygen concentration above 2 mg/l and independent of sludge depth above 4 inches. Their data also showed that release of organic material and nutrients by benthal decomposition could be minimized by controlling the dissolved oxygen at about 2 mg/l. An increased release of nutrients, phosphate and ammonia occurred at low oxygen levels. In the case of phosphate this was the result of the following: 1) the bacterial response at low oxygen levels and 2) the destruction of the adsorptive capacity of the mud surface when conditions become reductive.

III. EXPERIMENTAL DESIGN AND PROCEDURE

The experimental design used in this investigation consisted of the following three phases:

1) Sludge preparation and characterization

- 2) A short term (7 day) Warburg study
- 3) A long term (45 day) continuous flow reactor study

The Warburg study was conducted to determine the oxygen uptake rate of the sludges when in an aerobic environment and also the effects of seawater and seed on the oxygen demands of the sludges. The reactor study was conducted to determine the stabilization rates, leaching rates, and benthal oxygen demands of the sludges under simulated field conditions where a portion of the sludge layer was aerobic and a portion anaerobic.

A. Sludge Preparation and Characterization

Table 1 describes the sludge samples used in the study. The raw (primary and activated) and digested sludges were obtained from the sewage treatment plant at Stevens Point, Wisconsin. To obtain the wet oxidized and heat treated sludges, a mixture of the Stevens Point raw primary and activated sludge was treated in the sludge oxidation and heat treatment pilot plant at Zimpro Inc., Rothschild, Wisconsin, by pilot plant personnel. After each pilot plant run, a portion of the slurries was drawn off into a 55 gallon drum and allowed to settle for one to two hours.

The supernatants were siphoned off until they turned cloudy indicating solids pickup. The remaining slurry was analyzed (Table 2) and two gallons of each sample were placed in polyethylene jugs which were packed in dry ice and shipped to Manhattan College. The physical characteristics of the sludge slurries received at Manhattan College are given on the bottom of Table 2.

Before conducting any additional studies on the sludge, the samples were concentrated to more closely simulate compaction of the sludge on the ocean floor and to prevent excessive sludge washout from the continuous flow reactors. As indicated in Table 2, the compaction characteristics of the wet oxidized and heat treated sludges were good. Thus these samples were concentrated by settling overnight. Because of the poor compaction characteristics of the raw and digested sludges these samples were concentrated by centrifuging at 6,000 rpm for 1.5 minutes.

All of the sludges, except for a small portion used as unseeded samples in the Warburg study, were then seeded to insure biological activity in the relatively sterile wet oxidized and heat treated samples. As a seed, one liter of seawater from New York Harbor at the Battery was combined with one liter of synthetic seawater overlying a layer of thickened Ward's Island sludge. The seeding procedure consisted of adding 100 ml of seed to 475 ml of concentrated sludge. This sample was then mixed for 30 minutes with a Bird mixer at 80 rpm to obtain sufficient contact between sludge and seed. Following this the sample was centrifuged to remove 100 ml of centrate thus bringing the final volume back to 475 ml. These seeded sludges were then used for the initial sludge analyses (Table 3), for the Warburg studies. All procedures used for characterizing the sludge and for reactor sludge and effluent analyses were taken from Standard Methods(14) with the exception of the COD for which a rapid COD procedure was used(9). For total and orthophosphate using the Stannous Chloride method, phosphate standards made in synthetic seawater had to be used for calibration purposes.

DESCRIPTION OF SLUDGE SAMPLES

Sample	Description	% Volume Remaining After Sludge Treat.	COD Reduction
А	Raw Primary and Activated Sludge - Stevens Point, Wisconsin	-	-
В	Sample "A" - Low Oxidation Wet Air Oxidized	35.4	6.2
С	Sample "A" - Intermediate Oxidation Wet Air Oxidized	9.8	37.5
D	Sample "A" - High Oxidation Wet Air Oxidized	8.1	70.0
E	Sample "A" - Digested	44*	59.7*
F	Sample "A" - Heat Treated (Wet Combustion without Air)	30.6	0

* Calculated (assuming a constant ash weight in the raw and digested samples - equivalent to approximately 60% volatile solids destruction during digestion) as shown in the Appendix.

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Chemical Analysis	Raw Sludge	Low Oxidized Slurry	Inter- mediate Oxidized Slurry	High Oxidized Slurry	Digested Sludge	Heat Treated <u>Slurry</u>
COD	35.8	59.0	92.6	23.0	30.6	66.2
Total Solids	23.1	45.1	70.4	30.9	26.7	48.8
Volatile Solids	19.0	36.6	51.4	8.2	17.4	38.8
Total Phosphorus	0.30	0.53	1.56	1.62	0.53	0.65
Total Nitrogen	0.61	1.42	1.41	0.84	1.62	1.36
Ammonia Nitrogen	0.33	0.33	0.51	0.79	0.60	0.28
Total Soluble Hardness as CaCO ₃	0.12					
pH (Units)	6.5	5.2	4.7	5.4	6.7	5.3
<u>Physical</u> <u>Characteristics</u> *						
Color	grey brown	grey brown	dark brown	"tea" color	black	grey brown
Odor	septic	slight burnt sludge odor	burnt odor	burnt odor	well digested sludge	septic
Homogeneity	lumpy hairy	lumpy	homo- geneous	homo- geneous	homo- geneoùs	lumpy
Compaction Characteristics	poor	good	good	excellent	poor	good

ANALYSIS OF SLUDGE SLURRIES PRIOR TO COMPACTION CONCENTRATION (g/l)

* Analyzed at Manhattan College

ANALYSIS OF COMPACTED SLUDGES USED FOR STUDY

	Concentration (g/l) in Sample					
<u>Parameter</u>	A	В	<u> </u>	D	<u> </u>	F
Wet Density (g/ml)	1.01	1.02	1.03	1.15	1.03	1.02
COD	180	130	230	200	120	96
Total Solids	99	79	152	320	101	88
Volatile Solids	80	58	108	84	64	65
Total Phosphorus	0.98	1.45	7.2	24.0	3.7	1.05
Total Nitrogen	1.74	1.63	1.08	1.57	3.13	1.26
Ammonia Nitrogen	0.29	0.21	0.44	0.60	0.64	0.20
B0D ₅ *	25	23	50	48	11	26

* Estimated from final core BOD₅ and quantity lost through leaching.

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WARBURG STUDY EXPERIMENTAL DESIGN

Flask Number	Sludge Sample	Type Media	Weight(g) Wet Sludge	Total Sludge & Media Weight (g)
1	None-Control	Synthetic Sea Water	0	20.0
2	None-Control	Synthetic Sea Water	0	20.0
3 .	A-Seeded	Synthetic Sea Water	4.9	20.1
4	B-Seeded	Synthetic Sea Water	4.8	20.0
5	C-Seeded	Synthetic Sea Water	5.2	20.5
6	D-Seeded	Synthetic Sea Water	5.4	20.6
7	E-Seeded	Synthetic Sea Water	4.7	19.9
8	F-Seeded	Synthetic Sea Water	4.9	20.2
9	A-Unseeded	Synthetic Sea Water	5.4	20.7
10	A-Unseeded	Synthetic Sea Water	5.4	20.4
11	B-Unseeded	Synthetic Sea Water	5.4	20.6
12	C-Unseeded	Synthetic Sea Water	4.6	19.8
13	D-Unseeded	Synthetic Sea Water	5.2	20.5
14	E-Unseeded	Synthetic Sea Water	4.6	19.9
15	F-Unseeded	Synthetic Sea Water	5.1	20.4
10	A-Unseeded	lap Water	5.0	19.7
17	A-Unseeded	Tap Water	5.5	19.9
18	E-Unseeded	Tap Water	4.6	21.6

Total Sludge + Media Volume ~ 20 ml Temperature = 15°C Shaker Speed = 60 strokes/min Flask Constant = 0.8

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B. Warburg Study Procedure

The Warburg study experimental design is given in Table 4. A temperature of 15° C was used in the study since this is approximately the maximum temperature in the bottom waters overlying the sewage sludge deposits in the New York Bight(16). The maximum stroke speed was used to attempt to keep the samples well mixed and completely aerobic. The center wlll of each flask contained 0.6 to 1.0 ml (depending on flask type) of 10% KOH solution to absorb CO₂.

For the first 5 days of the study manometer readings were taken at six hour intervals to establish the cumulative amount of oxygen utilized. For the sixth and seventh days, manometer readings were taken during the day over a 4 hour period to obtain additional rate data.

Table 5 gives the composition of the synthetic seawater used in the studies(15). This composition was taken from a Technicon procedure used to simulate seawater in the analysis for phosphate. Although there was some indication in the literature(8) that the type of seawater used affected the benthal uptake rates of the sludge, it was impossible to obtain daily fresh seawater samples. A constant chemical composition seawater was also desired to reduce the necessary analyses. Note the absence of nitrogen and phosphorus in the synthetic seawater. This was desirable so the maximum leaching rates of these nutrients from the sludge samples would be obtained.

TABLE 5

SYNTHETIC SEAWATER COMPOSITION

<u>Chemical</u>	<u>Concentration (g/l)</u>
NaCl	31
MgS0 ₄ • 7H ₂ 0	10
NaHCO ₃	0.2
pH (Units)	7.0

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C. Continuous Flow Reactor Study Procedure

The reactor study was continuous flow with respect to the supernatant (1 to 0.8 day detention time) and batch with respect to the sludge layer. Figure 1 shows a schematic diagram and photograph of the reactors. Basically, the reactor was a plexiglass cylinder (1/8" wall thickness) mounted on a square base with dimensions as indicated in Figure 1. Approximately 1 inch of sludge, equivalent to about 100 g wet weight, was layered on the bottom of each reactor. A 16 mesh plastic screen with four glass rods for supports was placed on the sludge to maintain sludge stability during the oxygen uptake rates when high supernatant turbulence was encountered. An air diffuser stone was hung into each reactor approximately 1 inch below the water surface. Air was continuously supplied to the reactors except during oxygen uptake determinations to keep the reactor dissolved oxygen concentration near saturation and to maintain the supernatant in a well mixed condition.

A photograph of the continuous flow reactor setup is shown in Figure 2. Initially 18 reactors (three for each sludge sample) were placed in a water bath maintained at about 15°C. For each sludge sample the three reactors were designated as reactor, Core #1 and Core #2. The major portion of the study was conducted on the reactor from which the effluent was collected and analyzed and on which the oxygen uptake rates were run. To obtain an estimate of the sludge stabilization rates, the sludge from the Core #1 samples was analyzed after 21 days and the sludge from the reactor analyzed after 45 days. After 45 days, the sludge from the Core #2 samples was mixed with the supernatant and the oxygen uptake rates of the completely mixed samples were measured over the next three days. Along with the results of the Warburg Study this gave another estimate of the sludge oxygen uptake rate when the sludge is exposed to a fully aerobic environment.

A Technicon Auto Analyzer two speed proportioning pump was used to maintain a constant flow of synthetic seawater feed to the reactors. Because of the limited pumping capability only 12 influent tubes were used, one to each reactor and one to each Core #2 reactor. The two core reactors for each sludge sample were set up in series with the effluent from Core #2 being the influent to Core #1. No plastic screen was placed over the Core sludge since these core reactors were not subjected to the high degree of turbulence caused by the oxygen uptake rates.

The supernatant detention time of the reactors was maintained at approximately 1 day (flow = 450 ml/day) for the first 28 days of the study. At this time a spur gear on the proportioning pump became stripped and was replaced along with the influent tubing. A decreased flow of approximately 360 ml/day occurred resulting in an increased detention time of about 0.8 days for the last 17 days of the study.

The oxygen uptake rates were conducted on the reactors using a Model 54 Yellow Springs, temperature compensated, self stirred, BOD bottle probe. The stirring apparatus kept the reactor supernatant in a well mixed condition during the uptake rates thus minimizing any oxygen gradient in the liquid phase. The procedure used in running the oxygen uptake rates was as follows:



a. Schematic Diagram of Continuous Flow Reactor



b. Photographs of Reactors (1) empty and (2) with sludge and D.O. Probe

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- (1) Remove the air diffuser and stop flow to the reactor under study.
- (2) Fill the reactor to overflowing with effluent.
- (3) Place a cover on the reactor. The cover, containing a circular groove with weather stripping in it, fit tightly on the reactor top sealing it from the atmosphere after DO probe insertion.
- (4) Place the DO probe through a hole in the cover. Maintain a water seal around the DO probe.
- (5) Start the stirrer. Allow five minutes for temperature and dissolved oxygen equilibration then begin the uptake rate.

An oxygen uptake rate determination normally lasted from 20 to 30 minutes. Initially a recorder malfunction this technique had to be abandoned. DO probe readings were then taken visually every five minutes to obtain the uptake rates. Towards the end of the study since the uptake rate appeared to be linear during this time period only two readings were taken, one at zero and the other at 20 or 30 minutes.

The temperature of the reactors was controlled at 15° C by keeping the reactors in a water bath with a copper cooling coil and thermostatically controlled heater. Because the tap water temperature was above 15° C, the Warburg cooling unit was used to drop the cooling water temperature to 9° C. This allowed the thermostatically controlled heating unit to maintain the reactor temperature at 15° C + 0.5° C. During the first seven days of the study when the Warburg cooling unit could not be used for this purpose, because of the concurrent Warburg Study, the reactor temperature was controlled at 15° C + 2° C. To minimize temperature gradients in the water bath an adequate degree of mixing was maintained by bubbling air into the bottom of the bath.

Effluent from the reactors was collected for analysis in 1 liter bottles. During the initial phase of the study, when the Warburg study was being run concurrently, a three day composite sample was collected for analysis. However, because of the degradation of organic matter in this time, this was later reduced to a one day composite sample. The analysis performed on the effluent consisted of phosphate, nitrogen and BOD₅. Effluen COD's could not be determined because of the high salt interference. Effluen nitrate determinations were made on the 14th and 33rd days of the study.

To take into account the BOD degradation during sample collection and to get an estimate of the actual effluent BOD_5 , the following equation, developed from semicontinuous flow tank reactor kinetics was used:

 $L_{m} = \frac{Le}{K_{1}t} (1 - e^{-K_{1}t})$

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where

 L_m = measured BOD₅ from 1 day or 3 day composite samples

Le = actual effluent BOD_5 , mg/1

K₁ = first order reaction rate constant obtained from the method of moments on 1-5 day BOD data, day⁻¹

t = collection time, days

Using a K_1 of 0.77/day (Appendix), then

Le = $1.43 L_m$ for t = 1 day

and

Le = $2.57 L_m$ for t = 3 days

These above corrections were applied to the effluent BOD data.

IV. EXPERIMENTAL RESULTS

A. Warburg Study

Figure 3 presents the Warburg cumulative oxygen demands for the six seeded sludges in the sea water media. With the exception of the digested sludge (E), the sludges exerted a lag or acclimation period varying from two to four days. The intermediate and highly oxidized sludges (C and D) had substantially no oxygen uptake rate during the seven day study. Taking the slopes of Figure 3 and plotting the oxygen uptake rates on a volatile solids basis (Figure 4) indicate that the digested sludge had a relatively constant uptake rate in comparison to the raw (A), low oxidized (B), and heat treated (F) sludges. The uptake rates of these latter sludges peaked shortly after their lag periods then fell off (rapidly for B and F) to a rate approaching that of the digested sludge of about 0.5 mg $0_2/gVS$ -hr.

A comparison of the oxygen demands in sea water and tap water (Figure 5) indicated that the cumulative oxygen demands for the raw and digested sludges in tap water were slightly higher than in sea water. For the raw sludge this is caused by the longer acclimation period required in the sea water. After acclimation, the rates of oxygen utilization for the raw sludge for both types of media were the same. In contrast, for the digested sludge no lag period existed and the rate of oxygen utilization in tap water (0.92 mg $0_2/gVS-hr$) was about 30% higher than that in sea water (0.70 mg $0_2/gVS-hr$) for the first five days.

FIGURE 3 CUMULATIVE WARBURG UPTAKE RATES FOR THE SEEDED SLUDGES IN SYNTHETIC SEAWATER



Time - hr.

FIGURE 4 AVERAGE DAILY WARBURG OXYGEN UPTAKE RATES FOR THE SEEDED SLUDGES IN SYNTHETIC SEAWATER



Time (day)



The effect of seed on the raw and digested sludges was negligible because of the high concentration of organisms initially present in both sludges. In the low oxidized and heat treated sludges, where the quantity of microorganisms was negligible before seeding, the seed did decrease the lag period of these sludges (Figure 6).

The lack of microbial activity in the intermediate and high wet oxidized sludges indicates that the sludges were either inadequately seeded or toxic to the microbial population. At the end of the reactor study a heavy metals analysis was made on the various sludges. This analysis indicated that the heavy metals concentration in the sludges increased with increasing degree of oxidation. To determine if these sludges were toxic to the microorganisms an additional Warburg study was conducted with the concentrated sludges. These results (Appendix) indicated that the sludges were not toxic to the microorganisms. Thus the negligivle uptake rates obtained in the first Warburg study for the intermediate and high oxidized sludges were due to inadequate seed.

B. Reactor Study

1. Nitrogen and Phosphate Leaching and Stabilization Rates

The temporal variations of nitrogen and phosphate in the effluents from the continuous flow reactors are shown in Figure 7. The data used for the plots were from the reactors exhibiting the highest and lowest average effluent concentrations. Thus, the effluent concentrations for the other reactors generally fall within the ranges indicated.

For both nitrogen and phosphate, all reactors exhibited initially (for the first few days) high effluent concentrations. This is caused by the initial scouring and flushing of readily soluble materials from the surface of the sludges and replacement of the original sludge interstitial water with synthetic sea water. During the last 30 days of the study, relatively constant or slowly decreasing effluent concentrations were observed. An increase in nitrogen effluent concentrations occurred after the 25th day of the study due to some disturbance of the reactor sludge surfaces when long term and supernatant oxygen uptake rates were attempted on the reactors.

In viewing the above temporal variations in the context of sludge dumping from barges, the initial high effluent concentrations should more closely approximate initial sludge dispersion and nutrient release into overlying waters as the sludge is settling to the bottom rather than actual benthal leaching rates. The effluent concentrations from the reactors in the latter phase of the study should closely approximate actual benthal leaching rates.

Figures 8 and 9 compare the nutrient leaching rates from the various sludges on an aeral basis. The leaching rates shown in these and subsequent figures are the average values for the last 30 + days. These are considered to be representative of the steady state benthal leaching rates of the sludges. In viewing the phosphate data on an areal basis, the digested and intermediate pressure oxidized sludges had the

FIGURE 6 EFFECT OF SEED ON THE WARBURG OXYGEN UPTAKE RATES OF THE LOW PRESSURE WET OXIDATED AND HEAT TREATED SLUDGE



Time (hr.)

FIGURE 7 TEMPORAL VARIATION OF NITROGEN AND PHOSPHATE REACTOR EFFLUENT CONCENTRATIONS



Time from Startup - Days



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FIGURE 9 NITROGEN LEACHING RATES FROM SLUDGES (14 TO 42 DAY AVERAGE VALUES)



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highest leaching rates. From observations of the core samples, the digeste sludge layer was anaerobic with gas being produced and entrapped in the sludge layer. These anaerobic conditions may have been responsible for the relatively high phosphate leaching rate of this sludge. Reactor "A" containing the raw sludge also exhibited septic conditions in the sludge layer. In this reactor the initial phosphate leaching rate was high when the sludge contained a significant phosphate concentration. Even though septic conditions still prevailed in the raw sludge layer at the end of the study, the leaching rates were relatively low since most of the phosphate had already leached from the sludge.

With the exception of the raw sludge, the average areal nitrogen leaching rates are relatively uniform and have about the same magnitude, 0.3 to 0.6 g/m^2 -day, as the phosphate leaching rates.

Table 6 gives the nitrogen and phosphorus data obtained from sludge analyses at 0, 21 and 45 days. The 21 day sludge analyses were run on the core sample reactors. The 45 day sludge analyses were run on the reactors used throughout the study for effluent and oxygen uptake analyses. Although the reactors were run in parallel the core sample reactors were not subjected to oxygen uptake analyses with supernatant stirring. Thus the sludge in the core sample reactors generally received less turbulence than the sludge in the reactors used for the uptake analyses.

The major portion, 75 to 80%, of the phosphate was removed from both the raw and low pressure oxidized sludges while an insignificant portion of the phosphate was removed from the higher oxidized sludges. The low phosphate removal from the heat treated sludge is presumably the result of inaccurate data. The major portion of the ammonia nitrogen, 75 to 98%, was removed from all sludges during the 45 day study while generally 25 to 50% of the total nitrogen was removed during that time.

Table 7 presents a comparison of the nitrogen and phosphate losses measured from the reactor effluent data and from the sludge data. The nitrogen lost from the sludge was about 50% the amount measured in the effluent. Since no nitrogen was present in the influent to the reactors, the difference may be caused by incomplete reduction of nitrogen to ammonia during the sludge analyses.

The effluent nitrogen concentrations after 10 days consisted mainly of organic nitrogen. Prior to this some ammonia nitrogen was present in the effluent. Because of analytical difficulties during this initial period a quantitative estimate of ammonia nitrogen could not be obtained.

To determine of any nitrification was occurring in the reactors, effluent nitrate nitrogen determinations were made after 14 and 33 days. On both dates the nitrate concentrations were zero. Thus, nitrification did not take place in the reactors.

SLUDGE NITROGEN AND PHOSPHATE ANALYSES

	Wei	ght in	Reactor	, mg, fo	r Sludge	es
	A	<u> </u>	<u>C</u>	<u>D</u>	E	<u> </u>
Phosphate initial 21 day 45 day	97 37 25	149 96 30	714 670 (697)	2130 2000 (1730)	370 220 224	104 82 (184)
Total Removal, %	74	80	6	6	40	21
Ammonia Nitrogen initial 21 day 45 day	29 28 6	21 10 3	44 5 1	54 5 2	64 21 5	20 10 5
Total Removal, %	80	86	9 8	96	92	75
Total Nitrogen (TKN) initial 21 day 45 day	171 80 (157)	173 140 132	107 97 67	142 78 76	(313) 348 315	126 82 81
Total Removal, %	53	24	37	46	-	36

NOTE: Numbers in parentheses, because of their inconsistancy, were not used in computations.

NITROGEN AND PHOSPHORUS LOSSES OVER 45 DAYS -COMPARISON OF EFFLUENT DATA WITH SLUDGE DATA

Sludge	Nitrogen Lo Measure	sses (mg) d in	Phosphate Losses (mg) Measured in		
<u>Sample</u>	Effluent	Sludge	Effluent	Sludge	
Α	120	91	88	71	
B	87	41	101	119	
С	102	40	131	44*	
D	101	66	64	130*	
E ···	131	33	144	146	
F	99	45	66	22	

* Data inaccurate because of large phosphate concentration in sludge.

2. BOD₅, COD and Volatile Solids Leaching and Stabilization Rates

Plots of the temporal variation of effluent BOD_5 concentration, Figure 10, have the same general shape as the phosphate and nitrogen temporal curves, initially high concentrations due to flushing followed by relatively uniform low concentrations due to benthal leaching. The initial BOD_5 leaching rate of the digested sludge was relatively low compared to the other sludges. Since the digested sludge was compact and gelatinous in nature after centrifugation, the initial scouring and flushing action of the synthetic seawater only slightly affected the initial BOD leaching rate. The initial effluent from the digested sludge reactor was relatively clear while the remaining effluents were cloudy (reactors A and F) and yellow colored (reactors C and D).

The average areal BOD_5 leaching rates (including both the effluent BOD and the BOD degradation in the supernatant as shown in the Appendix) had approximately the same range (0.3 to 0.6 g/m²-day) as the nitrogen and phosphate leaching rates.

Table 8 indicates that an average of about 14% of the BOD_5 , 11% of the volatile solids, and 23% of the COD was stabilized over the 45 day period. Assuming the volatile solids stabilization rate was linear, it would take over a year to obtain 90% stabilization of the solids, the same order of magnitude as the data of Fair, et al(5).

3. Benthal Oxygen Demand

The temporal variation of the sludge benthal oxygen demands (Figures 12 to 14) exhibited similar characteristics as the leaching rates, high initial oxygen demands due to flushing followed by relatively stable lower benthal oxygen demands. A comparison of the total oxygen demands with the supernatant oxygen demands (that caused by oxidation of the BOD leached into the supernatant) indicate that only during the initial flushing period was the supernatant demand a significant portion of the total demand. During the remainder of the study, the supernatant oxygen demand was normally less than 10% of the total demand. The supernatant oxygen demand was measured by two methods: 1) Withdrawing the reactor supernatant for a short term (one to two hours) oxygen uptake determination, and 2) by multiplying the effluent ultimate COD by the first order BOD reaction rate ($K_1 = 0.77/day$). Both methods agreed well except for the higher uptake rates obtained by supernatant with-drawal on the 26th day of the study. These higher rates, prevalent in all reactors except C and D, were caused by pickup of some sludge suspended solids during withdrawal at this time.

The above data indicates that after the initial flushing stage, oxygen diffusion into the sludge layer with subsequent utilization in the aerobic sludge zone or at the sludge surface is the major cause of the benthal oxygen demands and not leaching of BOD and subsequent reaction in the effluent. FIGURE 10 TEMPORAL VARIATION OF BOD₅ REACTOR EFFLUENT CONCENTRATIONS



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FIGURE 11 BOD₅ LEACHING RATES FROM SLUDGES (15 to 42 DAY AVERAGE VALUES)



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TABLE 8

SLUDGE BOD5, COD AND VOLATILE SOLIDS ANALYSES

BOD ²						
initial 21 day 45 day	2500 2170 1970	2300 2180 1860	5000 4530 4280	4800 4130 4210	1100 1050 1000	2600 2330 (2600)
Total Removal, %	21	19	14	12	10	10
COD						
initial 21 day 45 day	17700 (9800) 12400	12900 8400 8900	22900 16800 16800	17800 14200 14600	12100 8000 9100	9600 9700 8700
Total Removal, %	30	31	27	18	25	9
Volatile Solids						
inîtîal 21 day 45 day	7900 7100 7100	5800 5700 5300	11000 10200 9000	7600 7800 7100	6400 5900 5600	6500 5800 5200
Total Removal, %	10	9	11	7	13	20

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Time - days





It is interesting to note that the oxygen demand of the digested sludge (Figure 14) reaches a minimum after 17 days and subsequently increases to about double this value towards the end of the study. The raw sludge (Figure 12) shows a similar variation though not as marked. Both sludges were septic as evidenced by the observation of gas bubbles trapped in the bottom of the sludge in the 21 day core samples. Increased leaching of these anaerobic decomposition end products into the aerobic zone may have been responsible for increased uptake rates during the latter portion of the study. This condition may have been aggravated by disturbance of the sludge surface layer at this time.

Figure 15 indicates that the average benthal oxygen demands of the wet oxidized sludges are lower than those for the raw, digested and heat treated sludges.

During the study, data on the effect of temperature on the sludge benthal oxygen demands was obtained (Figure 16). Though there was some scatter in the data, the uptake rates did increase with increasing temperature. The temperatue coefficient, ϕ , for the line drawn by eye is 1.064, slightly lower than that obtained by the other investigations.

Long term oxygen uptake rates (about one hour) in which the dissolved oxygen concentration in the reactors was decreased from saturation to close to zero were run on the reactor toward the end of the study. Since some suspended solids were stirred up at this time due to the turbulence from the dissolved oxygen probe mixer, the data was not always reproducible for these runs. However, the data normally indicated that the oxygen uptake rates decreased with decreasing dissolved oxygen concentrations.

At the termination of the continuous flow reactor study (after 45 days) each of the sludges in the remaining core sample reactors was completely mixed and oxygen uptake rates run on the contents over the next few days (Table 9).

TABLE 9

OXYGEN UPTAKE RATES OF COMPLETELY MIXED SLUDGES AFTER 45 DAYS AS SLUDGE DEPOSITS IN REACTORS

Beginning of Mixing Oxygen Uptake Rate, mg/l-h (hr) <u>A B C D</u>	r, for Sludge <u>EF</u>
-48 3.8 1.5 0.7 0.6	3.7 1.9
0 40 16 2.4 0.9	52 16
3 10 3.6	
24 7.2 4.2	4.0 -
48 1.8 1.6	- 6.0
72 2.6 1.8	

Time from



FIGURE 16 TEMPERATURE EFFECT ON REACTOR UPTAKE RATES



Temperature, ^oC

The raw and digested sludges had initial (0 hr) high uptake rates which decreased with time. This is indicative of the oxidation of reduced substances in the sludge caused by the prior anaerobic decomposition that occurred when the sludge was layered in the reactors. The initial uptake rates of the low oxidized and heat treated sludges also indicate that prior anaerobic decomposition had occurred. The uptake rates of the intermediate and high oxidized sludges were relatively low indicating no rapid oxidation of reduced substances and no prior septic condition.

A quantitative estimate of the effect of anaerobic conditions on the oxygen uptake rates of the sludges can be obtained by comparing: 1) the actual uptake rates of the sludge layer assuming anaerobic decomposition occurs in the lower layer with 2) the uptake rates if the bottom sludge layer was dormant with no anaerobic decomposition occurring. A schematic diagram of the two systems is given below.



(1) O₂ Uptake Rate with Anaerobic Decomposition in Lower Layer

(2) O₂ Uptake Rate with Dormant Lower Layer

From an oxygen mass balance on the systems the depth of the aerobic layer can be determined from the following steady state oxygen diffusion equation:

1.
$$d^2 = \frac{2DC}{A}s_{-}$$

where:

d = Depth of aerobic layer, cm

D = Oxygen diffusivity assumed equal to that in water

 $= 0.072 \text{ cm}^2/\text{hr}$ at 15°C

- A = Oxygen uptake rate per unit aerobic sludge volume, mg/cm³-hr
- $C_s = 0$ xygen saturation concentration = 0.008 mg/cm³ at 15°C

For condition 2, the values of the oxygen uptake rate can be estimated from the Warburg uptake rates in Figure 4 as 0.5 mg/gVS-hr for sludges A, B, E, and F after 7 days. This value is assumed to represent the steady state value. Multiplying this by the volatile solids concentrations in the reactors, the average value of oxygen uptake rate for all reactors is: $A = 0.033 \text{ mg/cm}^3$ -hr. From Equation 1, the depth of the aerobic zone, d₂, is equal to 0.187 cm, approximately 7.3% of the total sludge depth. For a sludge surface area of 38.3 cm², the total uptake rate is: $A_{t2} = 0.24 \text{ mg/hr}$.

The actual uptake rates of the sludges (condition 1) can be estimated from the final areal uptake rates, the -48 hr uptake rates in Table 9 converted to an areal basis, by the following equation:

2. $\alpha = Ad$

where:

= Areal sludge uptake rate, mg/cm²-hr

Combining equations 1 and 2 gives:

3. $d = 2DC_s/a$

Using equation 3, the actual aerobic zone depths and oxygen uptake rates are presented in Table 10 for each sludge.

TABLE 10

EFFECT OF ANAEROBIC DECOMPOSITION ON BENTHAL OXYGEN DEMAND

<u>Sludge</u>	<u>(cm)</u>	<u>% of Total</u>	(mg/cm ³ -hr)	Total Uptake Rate, A _{tl} , (mg/hr)	Ratio of Actual to Dormant Sub-layer <u>Uptake Rate A_t1/A_t</u>
А	0.032	1.3	1.13	1.40	5.8
В	0.080	3.2	0.18	0.55	2.3
С	0.170	6.8	0.039	0.25	1.0
D	0.200	7.9	0.029	0.22	1.0
E	0.033	1.3	1.06	1.34	5.6
F	0.064	2.5	0.28	0.69	2.9

The raw and digested sludges, which exhibited the highest benthal oxygen demand rates, had the thinnest aerobic sludge layer, only 1.3% of the total depth. Diffusion of the end products of anaerobic decomposition from the anerobic sublayer into the aerobic layer causes a sludge benthal oxygen demand 560 to 580% greater than the demand that would be exerted if the lower layer was dormant. Thus anaerobic decomposition has a major effect on the benthal oxygen demands of these sludges. If the total sludge layer, 1 inch, of the raw and digested sludges was maintained aerobic the total oxygen uptake rate would be hgiher than the present rates of sludges A and E (1.34 to 1.40 mg/hr). However, this would require an oxygen concentration at the sludge surface of 1480 mg/l, much higher than the 8 mg/l available.

The effect of anaerobic decomposition on the benthal oxygen demands of the low wet oxidized and heat treated sludges is about half that of the raw and digested sludges. In the more highly oxidized sludges, no effect of anaerobic decomposition is seen. These results agree well with the visual observations of the sludge core samples and with the uptake rates of the completely mixed core samples in Table 9. Thus, condition 2 accurately describes the data from the more highly oxidized sludges; i.e., the lower 92 to 93% of the sludge is dormant while the upper 6 to 7% is being stabilized aerobically. In the 45 days of the study, a microbial population capable of active anaerobic decomposition has not established itself in the intermediate and high wet oxidized lower sludge layers.

V. APPLICATION OF DATA

To determine the relative effects of the various sludges on a disposal system, the benthal oxygen demands and leaching rates per unit weight of sludge must be combined with the relative amounts of sludge to be disposed of from the various treatment processes as indicated by equation 4.

4. R =
$$(W/W_{i})(\alpha_{vs}/\alpha_{vsi})$$

where:

- R = Relative benthal oxygen demand or leaching rate of the sludges
 - The weight (or rate) of oxygen utilized or nutrient leached by the treated sludge per unit weight (or rate) utilized or leached by the raw sludge

FIGURE 17 FLOW DIAGRAM OF SLUDGE DISPOSAL PROCESS



During sludge treatment a portion of sludge volatile solids is destroyed. The sludge is then concentrated and separated from the supernatant. Since the supernatant from the wet oxidation process contains a substantial portion of the original organic matter or COD, it will be assumed that this supernatant will be biologically oxidized in a separate treatment unit as shown in Figure 17. The quantity of waste sludge produced in supernatant treatment is then recycled back to the sludge treatment unit and combined with the initial quantity of raw sludge. Table 11 shows the relative quantities of sludge to be disposed of from each of the treatment processes (calculated as shown in the Appendix).

TABLE 11

RELATIVE QUANTITIES OF SLUDGE REQUIRING ULTIMATE DISPOSAL FROM THE VARIOUS TREATMENT PROCESSES

	Relative Weight
Sludge	Solids, W/W _i
А	1.00
В	0.86
С	0.31
D	0.013
E	0.40
F	0.77

The areal benthal oxygen demands and leaching rates obtained in this study were multiplied by the initial weight of volatile solids per unit surface area of the sludges in the reactors to convert the rates to a unit volatile solids basis (Table 12). The relative benthal oxygen demands and nutrient leaching rates shown in Table 13 and Figures 18 and 19 were then calculated from equation 4.

Figure 18 indicates that sludge treatment prior to ocean disposal significantly decreases the sludge benthal oxygen demand. The intermediate and high pressure wet oxidized sludges showed the most significant reduction, greater than 90%, while the low pressure wet oxidized, digested and heat treated sludges exhibited 40 to 60% reductions in benthal oxygen demand.

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TABLE 12

	0x	ygen <u> </u>	B	<u>0D5</u> ØVS	_Nitrog ∕	en (TKN) VS	Phosphat 	e (as PO ₂ /VS
Sludge	<u>m</u> 2 <u>g</u>	mg g VS-day	<u>m²-day</u>	mg g VS-day	<u>m</u> 2 <u>g</u>	mg g VS-day	m2-day	mg g VS-day
А	8.3	4.0	0.66	0.32	0.60	0.29	0.31	0.15
В	3.8	2.5	0.41	0.27	0.36	0.24	0.35	0.23
C	2.7	0.94	0.45	0.16	0.37	0.13	0.62	0.21
D	1.7	0.86	0.26	0.13	0.35	0.18	0.26	0.13
Ε	6.8	4.1	0.39	0.23	0.41	0.25	0.61	0.36
F	5.5	3.2	0.51	0.30	0.38	0.22	0.21	0.12

AVERAGE* SLUDGE BENTHAL OXYGEN DEMANDS AND LEACHING RATES ON AN AREAL AND ON A UNIT INITIAL VOLATILE SOLIDS BASIS

* Average of relatively steady state valves from approximately 11th to 42nd day of reactor study.

TABLE 13

AVERAGE RELATIVE BENTHAL OXYGEN DEMANDS AND NUTRIENT LEACHING RATES FOR THE VARIOUS SLUDGE DEPOSITS

_		Relative	Relative Leaching Rate**				
<u>S</u>	ludge	Oxygen Demand*	BOD ₅	Nitrogen	Phosphate		
A	Raw	1.00	1.00	1.00	1.00		
В	LPO	0.54	0.72	0.71	1.30		
С	IPO	· 0.07	0.16	0.14	0.43		
D	HPO	0.003	0.005	0.008	0.01		
Ε	DIG	0.41	0.29	0.35	0.96		
F	ΗT	0.62	0.72	0.58	0.62		

* mg/day of oxygen used by the treated sludge per mg/day used by the raw sludge (from Figure 4).
 ** mg/day of nutrient leached from the treated sludge per mg/day leached by the raw sludge (from Equation 4).

FIGURE 18 AVERAGE RELATIVE BENTHAL OXYGEN DEMANDS FOR EACH SLUDGE





FIGURE 19 AVERAGE RELATIVE NUTRIENT LEACHING RATES FOR EACH SLUDGE

The nitrogen and BOD_5 leaching rates of the treated sludges (Figure 19) showed reductions similar to those exhibited by the benthal oxygen demands. However, the relative phosphate leaching rate of the low pressure wet oxidized sludge was greater than that of the raw sludge while the digested sludge had a rate about equal to the raw sludge. This is due to the low final phosphate concentration in the raw sludge with a concomitant low leaching rate.

Figure 20 shows the average relative benthal oxygen demands of the sludges as a function of the COD reduction effected during sludge treatment. With heat treatment and low pressure oxidation, where little or no COD reduction occurs, a 40 to 50% decrease in average benthal demand is obtained. When significant COD reductions (greater than 35%) are obtained by wet oxidation, over a 90% reduction in benthal oxygen demand occurs. However with the significant COD reduction (approximately 60%) obtained by anaerobic digestion only a 60% reduction in benthal oxygen demand can be consistently realized. Thus, for the same degree of COD reduction during sludge treatment, the wet oxidation process is more efficient in reducing the sludge benthal oxygen demand than sludge digestion.

VI. CONCLUSIONS

 The benthal oxygen demands and nutrient leaching rates of raw primary + activated sludge can be significantly reduced by treatment of the sludge before disposal at sea.

2. A benthal oxygen demand reduction of about 50% can be obtained by either heat treatment, low pressure wet oxidation, or digestion.

3. A benthal oxygen demand reduction greater than 90% can be obtained by intermediate and high pressure wet oxidation of the sludge.

4. After the initial flushing of the reactors, the major portion of the sludge benthal oxygen demand was due to diffusion of oxygen into the sludges where it was utilized in the aerobic surface sludge layers. Only a small portion of the demand was due to oxidation of leached substances in the supernatant.

5. The depths of the aerobic sludge layers were relatively thin varying from 0.032 cm (1.3% of the total depth of one inch) for the raw and digested sludges to 0.2 cm (7.9% of the total depth) for the highly oxidized sludge.

6. From an oxygen diffusion analysis, it was estimated that anaerobic decomposition in the lower sludge layers significantly increased the benthal oxygen demands of the raw, digested, heat treated and low wet oxidized sludges.

7. Negligible anaerobic decomposition occurred in the lower sludge layers of the intermediate and high wet oxidized sludges.

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FIGURE 20 EFFECT OF THE DEGREE OF COD REDUCTION OBTAINED IN SLUDGE TREATMENT ON THE RELATIVE SLUDGE BENTHAL OXYGEN DEMANDS



8. For the same degree of volatile solids reduction during sludge treatment, the wet oxidation process is much more efficient than sludge digestion in reducing the sludge benthal oxygen demand.

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Estimated Amounts and Costs of Wastes Barged to Sea in 1968(a) 1.

Reference 17

	<u>Pacific Coa</u>	<u>st Disposal</u>	Atlantic Coast	Disposal Cost
Wastes	Ions		10115	
Dredging Spoils	7,320,000	\$3,175,000	15,808,000(c)	\$8,608,00
Industrial Wastes (chemicals, acids, caustics, cleaners, sludges, waste liquors, oily wastes,				
etc.)				•
Bulk	981,000	991,000	3,011,000	5,406,001
Containerized	300	16,000	2,200	17,001
Garbage and Trash(b)	26,000	392,000	-	-
Miscellaneous (airplane parts, spoiled food,				
confiscated material, etc.)	200	3,000	_ *	-
Sewage Sludge	-		4,477,000(d)	4,433,000
Construction and Demolition Debris			574,000	430,000
TOTALS	8,327,500	4,577,000	23,872,200	18,894,000

(a) Does not include outdated munitions.
(b) At San Diego 4,700 tons vessel garbage at \$280,000 per year were discontinued in November 1968.

 (c) Includes 200,000 tons of fly ash.
 (d) Tonnage on wet basis. Assuming average 4.5 percent dry solids, this amount to approximately 200,000 tons dry solids per year being barged to sea.

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Gulf Coast	Disposal
Tons	Cost
15,300,000	\$3,800,000

690,000	1,592,000
6,000	171,000



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2. Determination of the COD and Volume Reduction During Digestion

For a one-liter volume of raw sludge using data from Table 2:

Weight of ash = 23.1 - 19.0 = 4.1 g

Ash concentration in digested sludge =

26.7 - 17.4 = 9.3 g/1

Volume of digested sludge = $\frac{4.1 \text{ g}}{9.3 \text{ g/l}}$ = 0.44 l

Volatile solids destruction in digestion, %Wg

 $\frac{\%Wg}{100} = \frac{TVS Destroyed}{TVS Initial} - \frac{TVS Final}{TVS Initial}$

 $\%Wg = 100 (1 - \frac{17.4(0.44)}{19.0}) = 59.7\%$

3. Effluent K₁ Data

BOD (mg/1) in Sludge						
Date	A	B	<u> </u>	D	E	F
8/22/70	0	0	0	0	0	0
8/23/70	0.9	0.9	0.9	0.7	1.0	1.3
8/24/70	1.3	1.4	1.3	0.9	1.5	1.7
8/25/70	1.6	1.6	1.4	0.9	1.6	1.8
8/26/70	1.6	1,6	1.5	1.1	1.7	2.0
8/27/70	1.6	1.6	1.5	1.2	1.8	2.1
K ₁ *(1/day)	0.75	0.81	0.81	0.69	0.76	0.81

 $*K_1$ obtained by Method of Moments; Avg $K_1 = 0.77/day$

Total Phosphate (mg/l as PO ₄)						
<u>Days</u>	A	<u> </u>	<u> </u>	dge	<u> </u>	F
1-3 3-6 6-8 8-11 11-13 14-15 15-18 18-19 19-20 25-26 27-28 29-31 31-32 34-35 35-36 37-39 41-42	25.0 13.8 6.3 8.0 7.3 5.8 3.5 3.9 - 3.0 2.5 2.0 3.8 1.4 1.5 1.1 1.1	18.8 21.3 12.3 9.0 10.4 7.8 5.1 4.6 2.9 2.8 2.1 1.9 2.6 1.8 1.5 1.5 1.1	18.8 13.8 15.5 12.0 11.3 8.1 7.9 5.8 5.1 5.8 5.1 5.8 5.4 4.8 6.8 4.1 3.5 4.4 5.3	13.1 6.8 4.9 9.4 3.8 3.6 3.4 2.6 3.5 2.0 2.0 2.0 2.0 2.0 2.8 1.8 2.1 1.4 2.0	22.5 22.5 12.2 10.0 9.8 8.6 7.0 3.6 5.9 5.8 5.4 7.0 4.5 5.3 4.4 4.6	21.3 11.6 4.9 3.8 3.8 3.8 3.8 5.7 1.7 1.6 1.1 1.1 1.5 1.0 0.9 1.1 0.8
		Tota	l Nitrogen	(mg/las	N)	
Days	A	<u> </u>	<u>C</u>	D	<u> </u>	F
3-6 6-8 8-11 14-15 18-19 27-28 32-33 34-35 39-40 41-42	18.3 7.5 7.3 9.8 6.2 5.7 5.2 3.1 4.2	15 6.3 5.6 4.2 4.2 4.1 3.5 3.2 2.9 1.8	20 8.4 6.9 3.1 3.6 5.3 2.8 4.1 2.5	22.6 5.4 5.6 2.0 1.4 5.0 3.8 6.2 2.2 2.4	30 9.7 6.3 4.5 3.4 7.1 2.9 5.6 2.2 1.9	17.3 8.4 4.2 3.6 - 6.3 3.1 2.2 1.7

4. Reactor Effluent Analyses, Oxygen Uptake Rates And Description of Sludge Core Samples

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BOD<u>5*, mg/1</u> Sludge A В E С D F Days 69.5 1-3 206 185 257 247 14.1 13.9 20.0 48.9 18.8 4.1 17.5 3-6 11.1 23.2 6.2 9.8 13.4 6-8 12.1 2.6 2.3 3.0 4.7 14-15 6.0 3.2 8.6 1.3 0.3 1.6 3.2 19-20 1.3 22-24 4.9 4.1 3.9 3.3 3.9 6.9 2.9 2.3 25-26 2.9 3.4 2.6 2.9 27-28 2.0 -------2.1 4.4 29-31 2.3 2.8 1.8 2.8 2.4 1.0 31-32 1.7 2.0 1.4 1.6 1.9 3.3 0.6 1.0 1.1 32-33 2.0 2.0 3.1 . 0.7 1.7 1.4 34-35 1.4 35-36 1.4 1.1 1.1 2.4 1.1 40-41 1.1 0.7 1.7 0.2 0.6 0.7 41-42 0.8 1.0 0.4 0.4 0.4 0.3

APPENDIX 4 CONTINUED

* Corrected for degradation during sample collection time as indicated in the procedure section.

		Total	Organic (arbon - TO	C*, mg/1	
		Note the second s	<u> </u>	uage		
Days	<u> </u>	<u> </u>	<u> </u>	D	<u> </u>	F
1-3	33	57	91	67	11	68
3-6	12	36	48	21	10	24
6-8	18	15	18	9	9	24
8-11	21	13	18	6	3	
11-13	16	10	8	3	1	11
14-15	11	8	6	1	1	10

*TOC was discontinued because the high salt concentration in the effluent coated and created hot spots in the organic carbon combustion chamber. Values not corrected for degradation during sample collection.

APPENDIX 4 CONTINUED

Reactor Oxygen Uptake Rates, mg/l/hr

Total S	ludge +_Su	pernatant	Rate/(Te	mperature)
		Sludge		

			Jiuu	<u> </u>		
Day	<u> </u>	B	<u> </u>	D and D	E	F
6	7.6(15)	4.6(15)	4.8(17.5)	2.9(17)	3.0(15)	7.5(15.3)
7 .	5.5(15.3)	3.0(16.2)	2.8(16.8)	1.8(17)	1.8(15.5)	6.0(16.2)
8	4.1(14.8)	2.3(14)	1.3(14)		-	~
רר	4.2(15.3) 5.4(17.3)	2.4(16.3)	1.9(15.5)	1.0(15.1)	2.9(15)	3.7(15.2)
12	4.2(14.5)	1.7(14.5)	1.7(14.5)	1.0(14.5)	2.2(15)	2.9(15.2)
13	4.6(16.5)	2.4(16.8)	1.5(16.9)	1.2(16.6)	2.5(16.5)	3.6(16)
14	2.9(15)	-	-	-		
18	3.4(14)	1.9(14)	1.0(13.6)	0.6(14.4)	1.8(14.4)	3.1(14.4)
19	3.8(15)	-	-	-	-	-
20		1.9(14.9)	1.2(14.9)	0.7(14.6)	2.4(14.6)	2.2(14.9)
22*	3.6(15)	1.3(15)	1.2(15)	0.8(15)	-	-
23	3.6(15.3)		1.2(15)	-	2.4(15)	-
25	3.0(19.4)	1.8(19.4)	1.5(19.4)	1.2(19)	2.4(18.6)	2.4(18.5)
	2.7(15)	1.5(14.9)	1.2(14.9)	0.7(14.9)	2.1(15)	1.6(15)
28	3.2(15)	1.8(15)	1.3(14.9)	0.8(14.9)	2.7(14.9)	2.7(14.9)
29**	-	-	_	e 4	-	- '
32	4.2(15)	2.1(15)	1.3(14.9)	0.6(14.9)	4.6(14.9)	2.7(14.9)
34	4.2(14.8)	1.4(14.5)	0.9(14.5)	0.5(14.5)	4.7(14.5)	1.8(14.5)
35	4.4(15)	0.8(15)	0.8(14.9)	0.6(14.8)	3.8(16.1)	2.2(16.1)
36	-		-		- *	2.2(15.5)
39	5.4(14.5)	1.5(14.5)	1.2(14.2)	0.6(14.2)	3.8(14.1)	1.4(14.2)
40	-	.	1 -	4	3.7(14)	-
41			-	1	-	1.9(14.1)
42	— (1.5(15.6)	-		- .	
43	3.8(15)	ian, '	0.7(14.8)	0.6(14.8)	-	1 22

* Scraped reactor sides ** Feed pump stopped overnight

Reactor Effluent and Supernatant Oxygen Uptake Rates (mg/1/hr)

	Sludge						
Days	<u> </u>	<u> </u>	<u> </u>	D	E	F	
			Effluent				
1-3	2.70	2.20	1.16	1.83	2.14	1.11	
3-6	0.13	0.12	0.73	0.17	0.05	0.14	
6-8	0.12	0.17	0.23	0.15	0.13	0.15	
8-11	0.21	0.08	0.09	0.05	0.04	0.09	
11-12	0.19	-		-		_	
			Supernatant				
12	0.35			-	-	2 4 Mark	
15	0.30	0.10	0.07	0.07	0.14	0:14	
26	0.50	0.30	0.10	0.20	0.20	0.20	

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APPENDIX 4 CONTINUED

Description of 21 Day Sludge Core Samples

<u>Sludge</u>	Color	Odor	Gas	Approximate Depth in.
А	Grey	Septic	Bubbles on Bottom	1.1
В	Grey-Brown	Slight Vegetable	None	1.1
С	Dark Brown	Burnt Sludge	None	0.9
D	"Tea"	Slight Burnt Sludge	None	1.0
Е	Black	Septic	Bubbles on Bottom	1.0
F	Grey-Brown	Mud Flats	None	1.1

NOTE: A thin layer of loose, fluffy sludge existed on top of the compact sludges.

5. Determination of BOD Leaching Rates

To determine the actual BOD leaching rates from the sludges, the BOD sink - degradation in the supernatant - had to be estimated and combined with the measured effluent BOD's to obtain the total BOD leaching rate. Modeling of the reactor BOD kinetics (Ogunrombi and Dobbins(12)) was used to determine the total leaching rates as indicated below:



BOD LEACHING SCHEMATIC

The equation describing the leaching rate is given as:

$$L_{h} = V(dL/dt) + L(Q + K_{1}V)$$

where:

 $L_{\rm b}$ = Benthal BOD₅ leaching rate, mg/day

V = Reactor volume, liters

Q = Reactor flow rate, 1/day

 $K_1 = BOD$ first order reaction rate constant, day⁻¹ (base e)

and VdL/dt = rate of change of mass of BOD_{π} in supernathat, mg/day.

The above equation was solved numerically, $dL/dt = L/t = L_2 - L_1/t_2 - t_1$, using a time interval of 3 days. For a flow rate of 0.36 l/day for days 0 to 27 and 0.45 l/day for days 28 to 42 (the last day of BOD data collection), a supernatant volume of 0.36 liters, and a

 $K_1 = 0.77/day$, the above equation was used in the following forms to calculate the average leaching rates over the three day intervals:

$$L_{\rm b} = 0.44L_2 + 0.20L_1$$
 $0 \le t \le 27$ days

and

 $L_b = 0.48L_2 + 0.24L_1$ 28 $\leq t \leq 42$ days

These rates were then used to determine the average, maximum, and minimum rates in Figure 11.

6. Determination of the Relative Quantities of Sludge Requiring Ultimate Disposal From the Various Treatment Processes

The quantity of organic matter in the supernatant from the sludge treatment units and in the concentrated sludge can be determined from the data in Tables 1 through 3. A schematic diagram of the solids or COD distribution in the sludge and supernatant phases in the initial slurries and in the compacted sludges is shown in Figure A-1.



Figure A-1. Schematic Diagram of Solids or COD Distribution in Initial Slurry and Compacted Sludge

A mass balance between the raw sludge and the initial sludge slurries obtained from Zimpro Inc. yields the following equation for the supernatnat organic matter concentrations, expressed either as COD or TVS:

A-1.
$$C_s = \frac{C_o(100 - \%Wg)}{100g} - \frac{(\%V_1)C_1}{-\%V_1}$$

where:

 C_{c} = Supernatant concentration, g/1

 $C_0 = Concentration in raw sludge, g/l$

 $C_1 = Concentration in sludge slurry, g/1$

%Wg = Percent of COD oxidized in sludge treatment (the percent of TVS oxidized is assumed equal to the percent COD oxidized)

%V₁ = Percent volume of slurry remaining after sludge treatment = volume slurry x 100/volume raw sludge = 100 V₁/V₀ A mass balance between the raw sludge and compacted sludge yields the following equations for the distribution of the organic matter expressed as either COD or TVS between the supernatant and compacted sludge:

A-2.
$$\%W_2 = \frac{100(1-C_s/C_0) - \%W_g}{1-C_s/C_2}g_{-}$$

and

A-3.
$$%W_{s2} = 100 - %W_{g} - %W_{2}$$

where:

- $%W_2$ = Percent of original organic matter in compacted sludge = 100 W_2/W_0
- %Ws2 = Percent of original organic matter in supernatant = 100 Ws2/Wo

 C_2 = Concentration in compacted sludge, g/l

Table A-1 and Figure A-2 (the distribution of TVS and COD in the various sludges and supernatants) were calculated from the data of Tables 1 through 3 using the above equations.

TABLE A-1

Total Volatile Solids and COD Distribution in Supernatant and Compacted Sludges

	TVS	5	TVS		
Sludge	Compacted C ₂ (g/l)**	Sludge %W2	Superna C _c (g/1)	tant %W_2	
	······		يبينه ويتكرنه ورسه	S Z	
A*	80	100.0	0.0	0.0	
В	58	63.0	7.4	30.8	
C	108	24.3	7.6	38.2	
D	84	1.1	5.5	28.9	
E *	64	40.0	0.0	0.0	
F	65	55.0	10.2	45.0	
	COL) [.]	COD		
	Compacted	, Sludae	Supernat:	ant.	
Sludae	$C_{2}(a/1) **$	%Wo	$C \left(\frac{\alpha}{1} \right)$	%W _	
			Signi	<u>s2_</u>	
A*	180	100.0	0.0	0.0	
В	130	46.0	19.6	47.8	
C	230	23.0	14.7	39.5	
D	200	3.4	9.6	26.6	
E *	120	40.0	0.0	0.0	
F	96	49.0	22.4	51.0	
* Assumes	the concer	tration	in Supernata	ant is neg	ligible
** From Ta	ble 3		•	Ŭ	-

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To determine the quantity of excess or waste activated sludge generated by separate biological treatment of the wet oxidized supernatants it is assumed that (a) the weight of excess sludge TVS is equal to 0.6 times the weight of the supernatant BOD_5 , and (b) the supernatant BOD_5 concentration is equal to 0.5 times the supernatant COD concentration. Applying the above assumptions yields the following:

A-4.
$$W_w = 0.3xyW_o$$

where:

- W_w = Weight of waste activated sludge
- W_o = Weight of influent total volatile solids to sludge treatment unit
 - x = Fraction of original COD in supernatant = (%W_{s2}/100)_{COD}
 - y = Ratio of COD to TVS concentrations in influent to sludge treatment unit (raw sludge concentrations in Table 2) = 35.8/19.0 = 1.88

The weight of sludge TVS existing after treatment, W, is then:

A-5. $W = z W_0$

where:

z = Fraction of original TVS remaining in compacted sludge after treatment = $(\%W_2/100)_{TVS}$

Knowing that

A-6.
$$W_0 = W_1 + W_1 = 0.564XW_0 + W_1$$

or by rearranging

A-7. $W_i = (1 - 0.564x)W_o$

this can be divided into Equation A-5 to yield

A-8.
$$W/W_1 = z/1 - 0.564x$$

which was used to determine the values given in Table 11.

7. Warburg Toxicity Study

A metals analysis by Zimpro Inc. on the initial sludge slurries and on the supernatant and cake after filtering indicated that the major portion of the metals did concentrate in the sludges. From this data the concentrations of metals in the compacted sludges used in the reactor study were calculated and shown to increase with increasing degree of oxidation as indicated in Table A-2.

Because of the higher metal concentrations in the intermediate and highly oxidized sludges, an additional Warburg study was conducted after completion of the reactor study to investigate the possibility of toxic effects on the microorganisms in the sludge layers. Two experimental runs were conducted as shown in Table A-3. In the first run settled sewage was used as seed for the various sludges while in the second run, one gram of digested sludge was mixed with the intermediate oxidized sludge to insure the presence of an active microbial population in the sludge.

Figure A-3, the results of the first Warburg run on the concentrated sludges (19 g sludge, 1 ml seed) indicated that only sludge C, the intermediate oxidized sludge, exhibited no oxygen uptake rate. Sludge F exhibited a lag or acclimation period similar to the results of the original Warburg study, while the remaining sludges had initially high uptake rates followed by much lower rates after the first few days. Figure A-4 showed that sludge C

TABLE A-2

	Total Solids Concen- tration		Met	als Concer	itration,	mg/l	
<u>Sludge</u>	<u>(g/1)</u>	Lead	Zinc	Chromium	Copper	Nickel	Titanium
А	99	23	92	23	49	4	12
В	79	18	78	16	35	5	7
С	153	74	274	50	118	10	23
D	320	350	1500	403	493	38	130
Е	101	49	174	34	94	3	30
F	88	22	104	20	41	3	13

Concentration of Metals in Compacted Sludges

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<u>Sludge</u>	Manganese	<u>Cadmium</u>	Arsenic	Iron	Aluminum	Magnesium	<u>Calcium</u>		
A	23	<1	0.2	1500	232	221	2800		
B	14	<1	<0.1	884	155	90	1220		
C	43	2	0.2	3730	551	224	4000		
D	202	10	2.2	20000	3000	2240	20000		
E	38	1	0.7	1930	472	295	2900		
F	16	<1	<0.1	926	184	133	1630		

J .

TABLE A-3

Warburg Toxicity Study Experimental Design Temperature = 15°C, Shaker Speed = 60 strokes/min

Flask No.	Sludge Sample	Wet Sludge Weight (g)	Settled Sewage Volume (ml)	Total Volatile Solids Concentration in Flask (g/1)			
		1	<u>RUN #1</u>	n Angelen en e			
] - 4	Tap Water Blank	0	0	0			
5 6	A B	19 19	1	65 73			
7 8 9	C D	19 19	1	109 89			
10 11	F	19 19 5	1 15	48 72 27			
12-13 14	C C	3	17 19	16 5.5			
15 16-17 18	D D D	5 3 1	15 17 19	22 13 4.5			
	RUN #2						
1-2	Tap Water Blank	0	0	0			
3 4 5	C&E C&E	7+1 10+1	12	41 57			
5-6 7	C&E C&E	15+1 17+1	4	84 95			

did exhibit an oxygen uptake rate after greater dilutions with the seed. Figure A-5, the results of the second Warburg run showed that sludge C in a concentrated state did exhibit an oxygen uptake rate when seeded with digested sludge after an acclimation period of 3 to 6 days.

The results of this study therefore indicated that all the sludges at concentrations near those used in the reactor study did exhibit an oxygen uptake rate when properly seeded. Using as a toxicity criteria the absence of any oxygen uptake rate, it is concluded that the sludges are not toxic to the microorganisms in the sludge layers. FIGURE A-2 DISTRIBUTION OF COD BETWEEN SLUDGE AND SUPERNATANT FOR THE HEAT TREATED AND WET OXIDIZED SLURRIES AND COMPACTED SLUDGES



% COD Reduction





Oxygen Uptake Rate mg/I÷hr.

Time (days)

FIGURE A-4 WARBURG TOXICITY STUDY DATA FOR DILUTED INTERMEDIATE AND HIGH OXIDIZED SLUDGES



Time (days)

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Time (days)

-72-