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EXPERIMENTAL INVESTIGATION OF THE WET OXIDATION DESTRUCTION OF SHIP-BOARD WASTE STREAMS

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Naval Ship Research and Development Center Annapolis, Maryland

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means for the ultimate destruction of organic wastes. This process was investigated by conducting experiments in a 1-gallon pressure vessel with a variety of wastes under different conditions. Waste types used in the experiments were sanitary, food, oil, municipal sludge, glucose, and cellulose. Results showed that the wet oxidation process obeys first-order kinetics consisting of two separate and distinct reactions. The first, a fast reaction, exhibits reaction rate constants ranging from 0.06 to 0.18 minute⁻¹, while the second, a slower reaction, has reaction rate constants ranging from 0.003 to 0.008 minute⁻¹. Catalysts have their main influence on the fast reaction, increasing its rate by a factor of three. Applying wet oxidation to destroy waterborne organic wastes consists in taking advantage of the fast reaction. Reduction in organic waste content, expressed as chemical oxygen demand, ranged from 60% to 85%, depending on the waste material, after 15 minutes of reaction time. The use of catalysts can increase this figure to 95%. Additional removal of organic matter can be achieved by further processing the wet oxidation effluent through a reverse osmosis membrane. The wide range of materials capable of being destroyed by wet air oxidation, the innocuous, sterile nature of the effluent, and its potential to be recycled for certain applications with little or no posttreatment make this process a candidate for the ultimate destruction of shipboard wastes.

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INTRODUCTION

Most waste water streams issuing from Navy ships are very dilute. This applies to sanitary (human), shower, lavatory, laundry, galley, and bilge water. Even when reduced volume flow equipment is employed, the resulting sanitary waste stream is 95% to 99% water. Nevertheless, the organic content of these waste streams pollutes the environment.

Continued unencumbered naval operations in United States and foreign harbors, navigable waters, contiguous zones and territorial waters are faced with increasingly stringent local, regional, national, and international water pollution abatement requirements. Consequently, at least some of the Navy's ships must have the capability for shipboard destruction of their wastes by 1980.

One way this can be achieved is by "burning" the waste in water. This is called wet oxidation, which is a process whereby organic wastes dissolved or suspended in water are converted to water, carbon dioxide, small amounts of low molecular weight organic acids, and a very small amount of fine inorganic ash. This process is conducted with an excess of oxygen at temperatures ranging from 475° to 600° F* in a pressure vessel which maintains the water as a liquid. Air overpressure can range from 50 to 300 lb/in⁶.** The resulting operating pressures range from approximately 600 to 1850 lb/in⁶.

Advantages of this process are:

 Aqueous waste streams, such as those identified above, are converted directly into sterile, innocuous effluents.
No known pathogenic microorganisms survive under these conditions.

• Energy requirements are substantially less than for incineration, since only a small amount of the water being treated converts to steam.

• Oxidation of the organic waste releases heat, so that the process can be thermally self-sustaining.

^{*}Abbreviations used in this text are from the GPO Style Manual, 1973, unless otherwise noted.

^{**}All pressures mentioned in this report will be expressed in pounds per square inch gage, unless specifically noted otherwise.

• The process is relatively rapid and is particularly suitable where space is at a premium.

• Essentially no contaminants are released to the atmosphere.

• The effluent water after minimal posttreatment, such as filtration to remove inorganic ash, is adequate for selected reuse, such as sanitary flush or laundry. Flash distillation of the hot effluent water has potential for higher quality reuse application.

Disadvantages of the process are:

• It is conducted at elevated pressures.

• Materials of construction for the pressure vessel and auxiliary equipment must be carefully selected to be corrosion resistant.

 Heavy-duty air compressors are required to supply air against the operating steam pressure.

Results of experiments in wet oxidation presented in this report are intended to enhance understanding of the process, identify its limitations, and provide technology leading to shipboard application of the process.

BACKGROUND

The commercial application of wet oxidation for the destruction of sewage sludge and other organic wastes has been reviewed and investigated.¹ Current effort in wet oxidation for shipboard application involves two recently completed U.S. Coast Guard contracts for a prototype pilot plant processing dilute sewage consisting of sanitary, laundry, shower, lavatory, and galley wastes from a crew of 10 to 20 men.^{2,3} In addition, the U.S. Navy has recently awarded a contract for the construction of its first land-based wet oxidation plant capable of destroying spent propellants as well as industrial and domestic wastes. A research contract,⁵ issued by the U.S. Navy, to conduct small-scale wet oxidation plant processing

¹Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

experiments with several shipboard wastes, has been completed. The application of wet oxidation for the destruction of wastes generated in a space station is being investigated as part of a NASA contract.⁶ The National Materials Advisory Board of the National Academy of Sciences has recently completed an investigation of materials of construction for wet oxidation pressure vessels intended for shipboard application.⁷ As a result of significant advancement in wet oxidation technology for shipboard application, the Navy has recently procured two closed-loop (no discharge) shipboard systems for treatment of sanitary wastes.⁵ A laboratory evaluation of one of these systems will be conducted here.

APPARATUS AND EXPERIMENTAL PROCEDURES

Experiments were conducted in a 1-gallon pressure vessel (Serial N71-1740, Autoclave Engineers, Inc., Erie, Pennsylvania), equipped with an electric heating jacket and magnetic drive stirring assembly, fitted with a hollow stirring shaft and two impellers for air dispersion and mixing. A schematic diagram of the apparatus is shown in figure 1. The autoclave was constructed of Hastelloy B. A liner and all internally wetted parts of the autoclave were constructed of either Hastelloy B or C. A second liner and set of internally wetted parts for the autoclave were made of commercially pure titanium, to be used during experiments in which an especially high acid concentration was expected.

Six different waste feeds were employed for the wet oxidation experiments: concentrated sanitary waste from a reduced flush sanitary waste collection system, tomato juice as simulated food waste, oil-in-water emulsions, sludge from the underflow of a primary clarifier of a municipal wastewater treatment plant, glucose solutions, and paper (cellulose) slurries. The feeds required various means of preparation ranging from manual shaking, macerating with a blender to ultrasonic mixing before being suitable for injection into the autoclave. Appenaix A provides additional detail on the waste feed materials used. The main variables examined in these experiments in addition to feed type included temperature, oxygen content, reaction rate, pH, and effect of salt water.

In most cases, experiments were conducted in the same manner. The autoclave was charged with the predetermined amount of water, air, or oxygen, and the heater was turned on. Stirring rate was maintained at 1000 r/min.



Figure 1 Wet Oxidation Apparatus

The feed was placed in the injection cylinders, usually including a 100-ml distilled water flush in the last cylinder. When the autoclave reached the desired operating temperature and pressure, the feed was rapidly injected by using highpressure air. This established a sharply defined experiment starting point. Samples were removed from the vessel at designated time intervals, beginning at 30 seconds and continuing to 90 minutes from the time of feed injection. The samples were then analyzed for chemical oxygen demand (COD) according to the procedure in <u>Standard Methods</u>.⁹ A more detailed operating procedure for the experiment is described in appendix B.

RESULTS

CHEMICAL OXYGEN DEMAND

The most direct procedure for presenting the effectiveness of the wet oxidation process is in terms of the percent reduc-This is illustrated in tion in COD as a function of time. figure 2, which shows the time-dependent degree of destruction of various wastes. Each data point is the arithmetic mean obtained from a number of runs conducted with each feed type at 500° F. The number of runs is shown in the figure. Detailed results of each individual experiment, including calculated arithmetic means and standard deviations, are presented in Table 1 presents the summarized results of many appendix C. runs with the feed types arranged in order of decreasing difficulty of destruction. Cellulose is the easiest to destroy, while the most difficult material is the reduced flush sanitary waste, probably due to its high urine content. Examination of the variances from which the standard deviations are derived for the reduction in COD shows, in general, that variance decreases significantly with time. This is illustrated in table 2. The large variance early in a wet oxidation experiment is caused partly by the large relative error in removing a sample from the autoclave at the precise time period indicated, but may also be influenced by the complexity of the oxidation reactions occurring. As the oxidation progresses, the concentration of large molecules being oxidized decreases, and the concentration of low molecular weight carboxylic acids, primarily acetic acid, increases.² Since the samples taken after the first 10 minutes of the wet oxidation process consist of the low molecular weight compounds, whose oxidation process is simpler, the repeatability of the COD determination improves as shown by the decrease in variance.



Figure 2 Wet Oxidation of Various Feeds at 500° F (Combined Runs)

TABLE 1 WET OXIDATION OF VARIOUS FEEDS AT 500° F (COMBINED RUNS)

	Re	eduction in	Number	Range of		
Waste	15 M in	Standard Deviation	60 Min	Standard Deviation	of Runs	mg/l
Concen- trated sanitary	56	8	70	5	8	1,310-1,980
Tomato	68	3	74	2	5	9,090-10,880
juice Oil-in- water	73	9	78	7	18	2,810-4,310 7,670-12,850
emulsion Primary sludge	76	7	83	5	15	1,720-3,890
Glucose	77	4	81	3	15	9,030-14,540
Cellulose	85	9	90	7	10	400-1,440

TABLE 2 - VARIANCE IN REDUCTION OF CHEMICAL OXYGEN DEMAND FOR PRIMARY SLUDGE AT 500° F (see Table 1-C, Appendix C, 15 Runs)

					_			(0 F	00 5
Elapsed time, min	0.5	1.5	3.5	5•5	10.5	15.5	30.5		90.5
Mean % reduction in COD	43.8	53.6	62.2	68.4	73.2	76.4	80.1	82.9	84.5
Standard deviation	14.5	12.7	11.3	10.4	7.5	6.6	5•5	5.2	5.1
Variance	210	161	128	108	56	44	30	27	26

REACTION KINETICS

The chemistry of wet oxidation has been shown to obey first-order kinetics with respect to the organic matter present.¹ Thus:

$$-\frac{dC}{dt} = k_1 C, \qquad (1)$$

where C is the concentration of organic wastes usually expressed as the COD in milligrams per liter, and k_1 is the specific reaction rate constant. Equation (1) states that the rate of decrease (destruction) of the wastes is proportional to the concentration of the wastes. (First-order kinetics for this process is valid only when an excess of oxygen is maintained throughout the reaction.)

Rearranging equation (1) and integrating yields:

$$\ln \frac{c_o}{c} = k_1 t, \qquad (2)$$

where C_0 is the concentration of organic wastes at the start of the reaction. Equation (2) can be expressed graphically by plotting the logarithm of C_0/C against time t. The slope of the resulting straight line can be used to calculate the specific reaction rate constant k_1 .

The course of the wet oxidation reaction can be illustrated by plotting the percent COD reduction in figure 2 as a function of time. A perhaps more effective way of presenting the data is to utilize equation (2). Figures 3 through 10 present the data in this fashion, along with the percent COD reduction for comparison. A smooth curved line can be drawn through all the data points in these figures. However, linear fits with good correlation coefficients can be obtained. Instead of a single straight line, as might be expected from equation (2), two or three straight lines can be fitted to the data, the lines having progressively smaller slopes and therefore smaller values of the specific reaction rate constant. In order to provide for uniform analysis and comparison of the data, the first four data points, ranging from 0.5 to 10.5 minutes after initiation of the reaction were fitted to one straight line, while the subsequent data points were fitted to a second line. Observation of the data points in figures 3 through 10 shows that three linear plots could also have been constructed. The specific reaction rate constant, k_1 , is determined from the slope of the first line, while k_2 is determined from the slope

of the second line. It is clear the k_2 is always smaller than k_1 for this reaction. Results presented in figures 3 through 10 show that regardless of feed type at least two major reactions occur. These can be adequately modelled as two consecutive first order reactions with separate rate constants. The first of these is rapid, involving the hydrolysis and oxidation of large molecules, such as proteins, carbohydrates, and cellulose. This results in the formation of water, carbon dioxide, and low molecular weight organic residues consisting primarily of acetic acid and its homologs.² The wet oxidation of these organic residues occurs at a much lower rate and is the second of these reactions. The concept of two consecutive reactions is supported by pH data presented later in the report, acidity being a measure of the reaction progress.



Figure 3 Wet Oxidation of Concentrated Sanitary Waste (500° F, 8 Runs)

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Figure 4 Wet Oxidation of Tomato Juice (500° F, 5 Runs)



Figure 5 Wet Oxidation of Oil-in-Water Emulsions (500° F, 0.1%, 5 Runs)



Figure 6 Wet Oxidation of Oil-in-Water Emulsions (500° F, 0.5%, 13 Runs)





Figure 8 Wet Oxidation of Primary Sludge (600° F, ll Runs)



Figure 9 Wet Oxidation of Glucose (500° F, 14 Runs)



Reaction rate constants calculated from the slopes of the linear plots in figures 3 through 10 are presented in table 3. The distinction between the fast and slow reactions is further illustrated by the ratio of k_1/k_2 , where k_1 and k_2 are the specific reaction rate constants for the fast and slow reactions, respectively. The waste types in table 3 are arranged in the same order as they are in table 1. This order was determined from the percent reduction in COD obtained after 15 minutes of wet oxidation. It is seen from table 3 that this order is approximated by the values of k_1 . Results of all reaction rate constants D.

Waste	k ₁ , min ⁻¹ (fast)	k ₂ , min ⁻¹ (slow)	k ₁ /k ₂	No. of Runs	
Concentrated sanitary	0.06	0.008	7.5	8	
Tomato juice	0.07	0.004	17.5	5	
Oil, 0.1% in water	0.11	0.004	27.5	5	
Oil, 0.5% in water	0.14	0.003	47.0	13	
Primary sludge ⁽¹⁾	0.12	0.007	17.0	15	
Glucose	0.13	0.004	32.0	14	
Cellulose	0.18	0.007	26.0	10	

TABLE 3 AVERAGE SPECIFIC REACTION RATE CONSTANTS FOR VARIOUS WASTES WET OXIDIZED AT 500° F

⁽¹⁾ Primary sludge wet oxidized at 600° F resulted in an average k_1 of 0.11 min⁻¹ and k_2 of 0.011 min⁻¹ based on 11 experiments.

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INFLUENCE OF OXYGEN

Wet oxidation must be conducted with an excess of oxygen to maximize reaction rate and prevent the formation of carbon. Table 4 shows the ratios of oxygen available at various pressures to oxygen demand, as affected by COD level. In most experiments a substantial excess of oxygen was present. Both dissolved and gaseous oxygen participate in the wet oxidation process. At high temperatures and pressures, oxygen is very soluble in water, as seen from table 5. The amount of excess oxygen remaining throughout each of two typical experiments conducted with primary sludge at 500° F is shown in tables 6 and 7.

TABLE 4 RATIOS OF OXYGEN AVAILABLE AT VARIOUS PRESSURES TO CHEMICAL OXYGEN DEMAND

					2	
		Prec	harge Pr	essure, 1	b/in	
COD.mg/1	100.00	200 00	300 00	400 02	500 O2	500 Air
002,	100 02			-	_	
		70 (77 0	06 5	17.5
1,000	19.3	38.0	57.9	70 6	190.0	8.8
2,000	9.6	19.3	29.0	20.0	40.2	5.0
3,000	6.4	12.9	19.3	25.7	52.2	5.0
4,000	4.8	9.6	14.5	19.3	24.1	4.4
5,000	3.9	7.7	11.6	15.4	19.3	3.5
6,000	3.2	6.4	9.6	12.9	16.1	2.9
7,000	2.8	5.5	8.3	11.0	13.8	2.5
7,000	2.0	<u>л</u> 8	7.2	9.6	12.1	2.2
8,000	2.4	4.0	6 4	8.6	10.7	1.9
9,000	2.1	4.)	Б. 8	77	9.6	1.8
10,000	1.9	2.9	5.0	7.0	8.8	1.6
11,000	1.8	3.5	5.2	1.0	0.0	1 /1
12,000	1.6	3.2	4.8	0.4	0.0	1.7
13,000	1.5	3.0	4.4	5.9	7.4	1.7
14.000	1.4	2.8	4.1	5.5	6.9	1.2
15,000	1.3	2.6	3.9	5.1	6.4	1.2
	1					

TABLE 5 SOLUBILITY OF OXYGEN IN WATER^{10,11}

Temper- ature °F	Precharge Pressure 1b/in [#]	Partial Pressure O ₂ at Operating Temperature 1b/in ²	Solub ml O₂∕g H₂O	ility mg O ₂ /l H ₂ O
500	100	180	0.8	1150
500	300	540	2.4	3450
500	500	900	3.5	5000
600	100	200	1.4	2000
600	300	600	4.2	6000

TABLE 6 OXYGEN REMAINING, PRIMARY SLUDGE 500° F (EXPERIMENT 11202)

Time min	Reduction %	COD Removed mg/1	COD Remaining mg/l	O₂ Remaining mg/l	Ratio of O2:COD Remaining	Fraction of O₂ Remaining
0.0 0.5 1.5 3.5 5.5 10.5 15.5 30.5 60.5 90.5	0.0 64.7 74.4 84.1 87.4 84.1 87.4 90.6 93.8 97.1	0 2000 2300 2600 2700 2600 2700 2800 2900 3000	3090 1090 760 510 370 460 360 280 190 130	57,900 55,900 55,600 55,200 55,200 55,200 55,200 55,100 55,000 54,900	18.7 51.3 73.2 108.4 149.2 120.2 153.3 196.8 289.5 422.3	1.00 0.96 0.96 0.95 0.95 0.95 0.95 0.95 0.95

Time min	Reduction %	COD Removed mg/1	COD Remaining mg/l	O₂ Remaining mg∕]	Ratio of O2:COD Remaining	Fraction of O ₂ Remaining
0.0 0.5 1.5 3.5 5.5 10.5 15.5 30.5 60.5 90.5	0.0 48.8 59.1 66.8 69.4 74.6 77.1 79.7 82.3 84.8	0 1900 2300 2600 2700 2900 3000 3100 3200 3300	3890 1980 1630 1280 1160 960 850 760 690 620	17,500 15,600 15,200 14,900 14,800 14,600 14,500 14,500 14,400 14,300 14,200	4.5 7.9 9.3 11.6 12.8 15.2 17.0 18.9 20.7 22.9	1.00 0.89 0.87 0.85 0.84 0.83 0.83 0.82 0.82 0.81

TABLE 7 OXYGEN REMAINING, PRIMARY SLUDGE 500° F (EXPERIMENT 11102)

As a result of this oxygen excess, a consistent influence of oxygen partial pressure on waste destruction was not demonstrated. This is illustrated in figures 11 through 1^{l_1} , comparing air versus oxygen for different waste types. The air results are based on a 500 lb/in² charge at ambient temperature, while the oxygen results consist of combinations of pressures ranging from 100 to 500 lb/in².

















INFLUENCE OF TEMPERATURE

Figure 15 illustrates the effect of varying the wet oxidation reaction temperature from 500° to 600° F when processing primary sludge.





An increased reduction in COD of approximately 7% is achieved by increasing the reaction temperature 100° F. This incremental improvement at the higher temperature is not sufficient to accept the substantially higher operating pressure which results. Table 8 shows that the saturated steam pressure more than doubles, increasing from 680 lb/in² at 500° F to 1545 lb/in² at 600° F.

Prossure	Autocla	Autoclave Temperature, ° F				
riessuie	450	5 0 0	550	600		
Precharge, lb/in~g						
100	170	180	190	200		
200	340	360	380	100		
300	515	540	570	595		
400	685	720	760	795		
500	855	900	950	995		
750	1280	1350	1 425	1490		
Saturated steam,					Î	
lb/in [°] a	425	680	1020	1545		
					_	
Note: The precharg temperature at the inter row and colu steam pressu operating pr	e pressur is found section o mn. Addi re to thi essure of	e at o by tak f the ng the s yiel the a	perati ing th approp satur ds the utocla	ng e value riate ated total ve.		

TABLE 8 OPERATING PRESSURES FOR THE AUTOCLAVE

INFLUENCE OF pH

Addition of sulfuric acid, reducing the initial pH to 2, was investigated with the concentrated sanitary waste. Results are shown in figure 16, which illustrates that acid addition gives no advantage in oxidizing this waste.

Measurement of pH was carried out on a number of samples taken from the autoclave. Results are presented graphically in figures 17 through 20, showing pH versus wet oxidation reaction time for different feed types. The initial pH is that for the waste mixture as it would exist under ambient, nonoxidizing conditions. All figures show a rapid increase in acidity from an essentially neutral initial condition. This increase in acidity is attributed to the formation of low molecular weight carboxylic acids and carbon dioxide. Some rise in pH after the initial drop (30-second sample) is observed in all cases, but it is very small for cellulose and oil, and core pronounced in the case of primary sludge. Recovery of pH in the case of the primary sludge experiments is attributed primarily to the slow hydrolysis of organic nitrogen to ammonia.



Figure 16 Wet Oxidation of Concentrated Sanitary Waste at 500° F (Combined Runs) Acid Versus No Acid Addition



Figure 17 Acidity Changes During Wet Oxidation Reactions (Primary Sludge, 20 Runs, 500° and 600° F Data Combined)



Figure 18 Acidity Changes During Wet Oxidation Reactions (Oil-in-Water Emulsions, 500° F, 3 Runs)



Figure 20 Acidity Changes During Wet Oxidation Reactions (Glucose, 500° F, 3 Runs)

INFLUENCE OF SALT CONCENTRATION

To illustrate the influence of salt concentration, experiments were conducted with glucose in distilled water and in synthetic sea water (3.5% salt content) prepared in accordance with ASTM method D-1141-52. Figure 21 shows no effect attributable to salt content.



Figure 21 Wet Oxidation of Glucose at 500° F (Combined Runs) Effect of Synthetic Sea Water

INFLUENCE OF CATALYSTS

All foregoing experiments were conducted without the deliberate addition of materials that could serve to catalyze the reaction. An autocatalytic effect might occur during the rapid portion of the reaction as a result of the sharp drop in pH. The influence of catalysis was examined as part of a sponsored effort under contract.⁵ Some results of this effort are presented in this report.

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Experiments conducted were very similar in apparatus and procedure to those reported thus far. A 1-gallon autoclave (Autoclave Engineers, Inc.) was used, operating temperature was 475° F, but larger volumes of waste feed could be injected resulting in higher initial values for C₀. Sulfuric acid was added, reducing the pH to 1.5-2.0; a proprietary catalyst was used; and the pressure vessel was lined with ceramic tile or carbon. Waste feeds used were a primary underflow sludge from a domestic sewage treatment plant and a concentrated sanitary waste consisting of fecal matter, urine, and paper.

Results are presented in table 9 along with data from an earlier section of this report for comparison. Graphical presentation of the data is given in figures 22 and 23. Figure 22 illustrates that ceramic tile and carbon lining have an equal and significant effect in enhancing the rate of wet oxidation. Figure 23 shows a noticeable influence of the catalyst on the rate of wet oxidation.

Reduction in COD after (%)		Initial COD	k ₁ , min ⁻¹	k_2 , min ⁻¹	Number of Runs	Special Conditions			
15 Min 60 Min Concentrated Sanitary Waste									
80	90	37,000	0.08	0.002	1	Unlined, catalyst,			
92	96	37,000	0.20	0.011	1	acid Carbon lined, catalyst,			
92	95	41,000	0.29	0.011	1	acid Tile lined, catalyst,			
56	70	1,310-1,980	0.06	0.008	8	acid None			
Primary Sludge Waste									
73	87	15,400	0.03	0.009	1	Carbon lined, no catalyst,			
81	91	10,700	0.05	0.006	1	acid Carbon lined, catalyst,			
76	83	1,720-3,890	0.12	0.007	15	acid None			

TABLE 9 - CATALYTIC EFFECTS DURING WET OXIDATION



Figure 22 - Catalytic Effects During Wet Oxidation of Concentrated Sanitary Waste (475° F, Catalyst Present, Acid Added)





REVERSE OSMOSIS AS A POSTTREATMENT PROCESS FOR WET OXIDATION

To evaluate the effectiveness of reverse osmosis (RO) as a posttreatment step to wet air oxidation, product effluent collected from the autoclave after 90 minutes at 500° F was passed through an RO cell equipped with a cellulose acetate membrane operated at 400 lb/in². A schematic of the RO system is shown in figure 24. Results shown in table 10 illustrate that RO can serve as an effective posttreatment step for wet oxidation effluents.



Figure 24 Wastewater System Used to Evaluate Performance of Reverse Osmosis Membranes

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		TAI	BLE 1	10	
REVERSE	OSMOSIS	OF	WET	OXIDATION	EFFLUENT

Waste Feed Producing Effluent	RO Flux Rate gal/ft ² /d	COD, mg Wet Oxida- tion Effluent	RO Effluent	COD Reduction (%)
Oil-in-water Primary sludge Concentrated sanitary	8.4 9.1 7.0	1120 355 385	540 155 70	51 56 82

DISCUSSION

For ultimate disposal of shipboard aqueous organic wastes, wet oxidation is unique in that:

• It produces a sterile liquid usable as a process fluid with no or minimal posttreatment.

• It operates at temperatures substantially below those required for incineration.

It can be thermally self-sustaining after start-up.

• It operates at pressures similar to those used for steam turbine propulsion systems.

It produces essentially no air pollutants.

• It is particularly suitable where space is at a premium.

The effectiveness of wet oxidation is often measured in terms of the percent reduction in COD and how this reduction is affected by temperature, time, catalysis, and oxygen utilization. While this is useful, it can be misleading. Aqueous wastes, such as sanitary, laundry, and galley, are pollutants not only because they lower the oxygen content of waters containing marine life, but also because they are in various stages of decay and carry disease-causing organisms. Exposure to wet oxidation conditions for 10 minutes destroys all organisms, converts a large percentage of the organic waste to carbon dioxide and water, and converts the rest to inoffensive, soluble, easily biodegradable, low molecular weight organic compounds.²

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Between 300° and 500° F, temperature plays a significant role on the effectiveness of wet oxidation. This has been illustrated for various sanitary sludges. Thus, an eightfold increase in reduction of COD was found from 300° to 500° F.¹² Above 500° F, or even at 475° F, a leveling-off effect is This is confirmed by results shown in figure 15; observed.12 namely, the additional waste destruction obtained at 600° versus 500° F is small. This reduced effect of temperature on sludge destruction is caused by the rapid conversion of the wastes at these higher temperatures to low molecular weight organic acids which oxidize at rates 30 to 40 times slower, as illustrated in table 3. Consequently, it is not practical to operate wet oxidation above 500° F, because the additional waste destruction does not warrant the penalty of the substantial increase in steam pressure. Such an increase in steam pressure would not only require a heavier pressure vessel but a larger air compressor.

Examination of the reaction rates for a variety of wastes has convincingly demonstrated the presence of at least two major reaction stages. The first stage, or fast reaction, is 30 to 40 times faster than the second major stage of the reaction. This has important implications with regard to design of wet oxidation pressure vessels. The drop in pH during the initial portion of the reaction is an independent measure of the rapid events occurring in the wet oxidation process.

Catalysts appear to enhance the wet oxidation process. The main advantage of catalysts is to permit operation of the process at lower temperatures without loss of effectiveness. Reducing operating temperature and therefore pressure implies a smaller, lighter reaction pressure vessel and air compressor. Use of catalysts, however, carries a potential penalty. If the catalyst is dissolved or suspended in the aqueous medium, it is lost upon discharge; further, the catalyst itself may be a pollutant when discharged. If the catalyst is stationary, effective contact between it and the aqueous medium must be maintained. Decline in catalyst potency requiring frequent replacement or regeneration may be expensive and time consuming.

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FUTURE EFFORT

Future effort in wet oxidation will be primarily concerned with the evaluation of a 30-man closed-loop process for treatment of shipboard sanitary waste. This process utilizes a fourcompartment agitated autoclave operating at 600 lb/in² pressure and 450° F for the destruction of human wastes. Raw waste is passed through the autoclave in a slightly ammoniacal catalyzed aqueous solution (pH 8 to 9) which, after wet oxidation and filtration, is reused as a flushant. Excess water accumulated is exhausted as a vapor and injected into the engine exhaust. The system envelope is approximately $4 \times 6 \times 3$ feet. Evaluation of chip system will consist of an extensive laboratory investigation followed by shipboard installation and further performance investigation. Delivery of the unit is expected in September 1974.

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APPENDIX A

WASTE FEED MATERIALS

CELLULOSE

Cellulose feed was prepared by placing weighed sheets of toilet paper in a blender with distilled water. The mixture was macerated for approximately 2 to 3 minutes until the sheets were disintegrated into small fibrous pieces suitable for injection. In spite of this preparation, the cellulose fibers often matted and clogged the injection lines, resulting in failure or partial failure of all the feed to inject.

Cellulose was selected to test in the wet air oxidation unit, since it represents a variety of waste products generated on board ship.

GLUCOSE

Stock solutions of glucose were prepared whenever needed by dissolving a known amount of glucose in 1 liter of distilled water. The glucose feed provided an ideal system with which to investigate various parameters of the wet air oxidation process, since it formed a true solution eliminating injection problems and had identical characteristics from one batch of feed to the next.

PRIMARY SLUDGE

Domestic sewage sludge was obtained from the Maryland City Sewage Treatment Plant. Samples of sludge were taken from the primary clarifiers' underflow and were refrigerated until needed. The sludge was macerated in a blender prior to placing it in the injection cylinders.

OIL

Oil-in-water emulsions were used for feeds to simulate bilge water. The emulsions were prepared by mixing 0.1% or 0.5% oil in water with an ultrasonic mixer to form stable emulsions. The oil used was one designed to emulsify easily.

TOMATO JUICE

Tomato juice was selected as a feed to simulate a food waste, since it has a high COD value, consists of organic molecules typical of food wastes, and was already in a stable suspension facilitating injection.

REDUCED FLUSH SANITARY WASTE

The reduced flush sanitary waste came from the vacuum collection tank of the Jered Vacu-Burn sewage treatment system (STS) This is an STS designed for shipboard use and operates with a significantly reduced volume of flushing water. The sludge consists entirely of human waste (feces and urine) and toilet paper in concentrated form.

APPENDIX B

DETAILED OPERATING PROCEDURE

An appropriate amount of distilled water is added to the pressure vessel via the blowpipe, and a known overpressure of either oxygen or air is then added from the precharge gas cylinders. The temperature controller is then set for the desired temperature and turned on.

As the pressure vessel attains operating temperature, the feed material is prepared and placed in the injection cylinders, normally with 100 ml of distilled water in the final cylinder as a line flush during injection. When operating temperature is reached, the magnetic stirrer is turned on and the feed injected utilizing high-pressure air.

At 30 seconds after injection, the first sample is taken via the sample tube and ice-water-cooled condenser. Eight more samples are taken at 1.5, 3.5, 5.5, 10.5, 15.5, 30.5, 60.5, and 90.5 minutes after injection.

Upon completion of an experiment, the remaining liquid in the pressure vessel is removed through the blowpipe. The injection cylinders, feed lines, and pressure vessel are all flushed with distilled water prior to beginning the next experiment.

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APPENDIX C

RATE OF REDUCTION IN CHEMICAL OXYGEN DEMAND FOR VARIOUS WET OXIDATION RUNS

C-i.

TABLE 1-C - PRIMARY SLUDGE, 500° F, AIR OR OXYGEN

			Initial							
Bun No			Sa	mple	Time,	min				COD
Run NO.	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/l
11272A 11272B 11222 11202 11172B 11172A 11152b 11132B 11132A 11102 11092 11062 11022 10312 10162 Mean Standard	41.4 37.8 34.8 64.6 52.6 54.3 48.2 60.0 60.3 49.0 49.6 37.2 15.0 19.9 43.8	53.1 50.3 46.7 75.4 63.1 63.2 59.6 61.9 66.1 58.1 56.2 41.0 28.5 32.6 53.6	58.4 59.8 58.7 83.6 70.7 70.5 68.4 68.4 67.1 61.9 51.0 58.3 39.6 44.9 62.2	66.7 68.5 64.5 88.0 77.5 75.6 74.5 72.1 75.2 70.3 69.8 57.7 63.4 48.7 53.0 68.4	68.9 71.0 73.6 85.1 80.7 78.8 79.0 79.0 79.6 75.4 73.9 64.4 57.9 62.8 73.2 7.5	74.1 72.1 77.8 88.5 83.1 80.9 81.1 79.3 81.3 78.1 77.0 67.8 63.0 69.6 76.4 6.6	78.1 77.2 82.4 91.0 85.4 83.7 83.4 82.5 84.6 80.5 79.2 71.7 76.8 69.8 75.7 80.1	82.6 79.7 85.3 93.9 87.8 86.1 85.0 86.6 82.2 79.6 75.7 79.7 72.8 80.4 82.9	84.4 81.0 87.0 95.9 89.1 87.5 87.2 86.4 87.7 84.0 80.7 77.0 80.7 76.0 83.3 84.5 5.1	1720 2030 3230 3090 3550 3550 3600 3780 3640 3890 3560 1860 1960 1880 1940

TABLE 2-C - PRIMARY SLUDGE, 500° F, OXYGEN

Bup No			Initial COD							
Run NO.	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/l
11132B 11132A 10162 11222 11202 11172B 11172A Mean	60.0 60.3 19.9 34.8 64.6 52.6 54.3 49.5	61.9 66.1 32.6 46.7 75.4 63.1 63.2 58.4	68.4 72.4 44.9 58.7 83.6 70.7 70.5 67.0	72.1 75.2 53.0 64.5 88.0 77.5 75.6 72.3	77.0 79.6 62.8 73.6 85.1 80.7 78.8 76.8	79.3 81.3 69.6 77.8 88.5 83.1 80.9 80.1	82.5 84.6 75.7 82.4 91.0 85.4 83.7 83.6	85.0 86.6 80.4 85.3 93.9 87.8 86.1 86.4	86.4 87.7 83.3 87.0 95.9 89.1 87.5 88.1	3780 3640 1940 3230 3090 3550 3350
Standard deviation	16.2	14.2	12.2	11.0	7.1	5.7	4.5	4.0	3.9	

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C-1

	Reduction in COD, %										
Run No.			Sa	mple	Time,	, min				COD	
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/l	
11272B	37.8	50.3	59.8	68.5	71.0	72.1	77.2	79.7	81.0	2030	
11272 A	41.4	53.1	58.4	66.7	68.9	74.1	78.1	82.6	84.4	1720	
11152в	48.2	59.6	68.4	74.5	79.0	81.1	83.4	85.7	87.2	3600	
11092	49.6	56.2	61.9	69.8	73.9	77.0	79.2	79.6	80.7	3560	
11102	49.0	58.1	67.1	70.3	75.4	78.1	80.5	82.2	84.0	3890	
11062	32.2	41.0	51.0	57.7	64.4	67.8	71.7	75.7	77.0	1860	
10312	15.0	28.5	39.6	48.7	57.9	63.0	69.8	72.8	76.0	1880	
				_							
Mean	39.0	49.5	58.0	65.2	70.0	73.3	77.1	79.7	81.4		
Standard											
deviation	12.4	11.2	10.0	8.9	7.1	6.3	4.8	4.4	4.0		

TABLE 3-C PRIMARY SLUDGE, 500° F, AIR

TABLE 4-C PRIMARY SLUDGE, 600° F, AIR OR OXYGEN

	_	Reduction in COD, %											
Run No.			Sa	ample	Time	<u>, min</u>				COD			
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/l			
11162	72.2	77.8	81.4	83.0	85.2	86.5	89.4	94.3	93.8	3940			
11152A	71.8	77.4	81.1	83.3	86.0	87.0	90.3	92.4	93.2	3610			
11142	71.5	74.7	77.2	78.5	82.4	83.5	86.0	88.3	86.9	3480			
10182	41.7	57.4	66.2	70.8	76.4	79.9	86.0	92.9	96.0	2040			
09222	53.5	64.2	72.1	75.0	79.1	82.0	85.9	89.4	90.8	2560			
08252	69.4	74.2	77.8	81.5	84.7	85.8	88.4	88.9	92.3	17180			
08152	56.8	60.2	72.8	74.5	79.8	81.4	86.2	90.1	92.4	2240			
08112	53.8	57.2	67.2	70.2	76.3	-	83.5	88.6	89.8	1110			
08102	46.7	63.2	70.8	76.1	78.7	81.9	85.0	89.3	90.8	6890			
08082	43.5	58.2	67.8	72.9	77.8	80.8	85.1	89.3	94.7	2080			
08072	39.8	54.4	64.1	69.3	74.9	77.6	82.4	87.5	88.5	2440			
Mean	56.4	65.4	72.6	75.9	80.1	82.6	86.2	90.2	91.8				
Standard	10.8	8 0	6.0	51	30	3.0	2.4	2.3	2.7				
ueviation	12.0	0.9	0.0		<u></u>		C • T	2					

C-2

TABLE 5-C OIL-IN-WATER EMULSION, 500° F, AIR OR OXYGEN

		Reduction in COD, %									
Run No.			Sa	mple	Time,	min	<u></u>			COD	
Run No.	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/1	
01293B	63.1	71.1	76.6	79.5	82.3	83.7	84.5	85.8	87.1	4,310	
0129 3 A	66.1	72.4	78.9	80.0	80.6	84.0	84.8	86.3	87.3	3,530	
01263B	60.2	65.7	72.1	75.5	78.7	80.1	81.6	83.3	84.4	4.160	
01263A	42.4	50.6	58.8	63.3	67.3	69.8	72.3	75.5	75.5	2,810	
01243	44.5	53.2	55.9	65.2	69.0	70.0	73.5	76.5	77.5	2,950	
01233	43.1	62.3	71.0	74.6	75.6	77.1	78.7	80.3	81.8	10,870	
01223B	47.0	61.1	72.1	74.2	76.5	78.0	79.6	81.1	82.8	11,780	
01223A	50.1	60.8	70.4	70.4	75.2	76.3	78.1	78.2	78.1	10,690	
01193в	32.9	57.3	64.7	69.1	70.2	69.6	74.4	75.7	111.5	9,050	
01193A	26.8	45.8	68.4	75.2	79.7	81.1	81.1	84.0	84.5	10,970	
01183	40.6	57.3	76.5	81.1	84.9	86.0	86.7	87.5	88.2	12,850	
01163	5.4	31.9	64.1	72.5	76.4	78.2	80.3	-	83.4	7,070	
01103A	38.1	42.3	48.4	56.7	66.0	67.0	73.2	-	1/4.2	9,700	
01093B	16.4	16.4	42.8	51.6	59.3	60.4	65.9	67.0	67.0	8,920	
01093A	23.5	30.5	37.4	-	60.0	60.0	63.5	68.7	68.7	11,280	
01083	18.9	25.3	33.8	44.5	59.4	59.4	61.6	65.8	66.9	9,300	
01043в	37.9	46.0	58.9	64.1	68.1	70.7	72.1	76.2	77•7	8,580	
01043A	19.9	27.0	38.8	48.2	54.1	57.6	62.3	68.2	71.7	8,650	
		1							-0 6		
Mean	37.6	48.7	60.5	67.4	71.3	72.7	75.2	77.5	78.6		
		1							1		
Standard		1			ļ						
deviation	16.8	16.7	14.6	11.3	9.0	9.1	7.9	7.1	6.9		

Harden of a

TABLE 6-C	-	OIL-IN-WATER	EMULSION,	500°	F,	AIR

			Rec	luctio	on in	COD,	%			Initial
Run No.			Sa	mple	Time	<u>, min</u>				
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/1
01193A 01183 01163 01043A Mean	26.8 40.6 5.4 19.9 23.2	45.8 57.3 31.9 27.0 40.5	68.4 76.5 64.1 38.8 62.0	75.2 81.1 72.5 48.2 69.3	79.7 84.9 76.4 54.1 73.8	81.1 86.0 78.2 57.6 75.7	86.7 80.3 62.3 76.4	84.0 87.5 68.2 79.9	84.5 88.2 83.4 71.7 82.0	10,970 12,850 7,670 8,630
Standard deviation	14.6	13.7	16.3	14.5	13.6	12.5	12.6	10.3	7.1	

TABLE 7-C - OIL-IN-WATER EMULSION, 500° F, OXYGEN

	Reduction in COD, %											
Run No.			Sa	ample	Time	, min		_		COD		
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/1		
01083 01193B 01223A 01243 01263A 01293B 01293A 01263B 01233 01223B 01093B 01093A 01093A 01043B 01103 Mean	18.9 32.9 50.1 44.5 42.4 63.1 66.1 47.0 16.4 23.5 37.9 38.1 41.7	25.3 57.3 60.8 53.2 50.6 71.1 72.4 65.7 62.3 61.1 16.4 30.5 46.0 42.3 51.1	33.8 64.7 70.4 55.9 58.8 76.6 78.9 72.1 71.0 72.1 42.8 37.4 58.9 48.4 60.1	44.5 69.1 70.4 65.2 63.3 79.5 80.0 75.5 74.6 74.2 51.6 - 64.1 56.7 66.8	59.4 70.2 75.2 69.0 67.3 82.3 80.6 78.7 75.6 76.5 59.3 60.0 68.1 66.0 70.6	59.4 69.6 76.3 70.0 69.8 83.7 84.0 80.1 77.1 78.0 60.4 60.0 70.7 67.0 71.9	61.6 74.4 78.1 73.5 72.3 84.5 84.8 81.6 78.7 79.6 65.9 63.5 72.1 73.2 74.6	65.8 75.7 78.2 76.5 75.5 85.8 86.3 83.3 81.1 67.0 68.7 76.2 - 77.0	66.9 77.3 78.1 77.5 75.5 87.1 87.3 84.4 81.8 82.8 67.0 68.7 77.7 74.2 77.6	9,300 9,050 10,690 2,950 2,810 4,310 3,530 4,160 10,870 11,780 8,920 11,280 8,380 9,700		
Standard deviation	15.4	17.2	14.7	10.8	7.8	8.3	7.3	6.6	6.8			

TABLE 8-C - GLUCOSE, 500° F, AIR OR OXYGEN

			Initial							
Run NO.			Sa	mple	Time	<u>min</u>		<u> </u>		COD
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/1
02203 02213 02223 03053B 03053A 03023 03213 03223 03073B 03153 02233 02263 03073A 03123 03163 Mean Standard	28.3 37.5 9.2 42.0 61.3 51.6 54.0 58.3 52.6 20.2 21.8 25.4 36.3 57.0 40.1	58.4 64.5 54.8 51.4 66.4 57.4 67.0 58.5 57.9 58.0 63.5 70.1 60.3	63.6 68.4 66.1 58.0 68.6 61.8 70.4 71.8 66.0 66.8 67.0 66.8 75.5 67.2 4.3	68.7 76.3 70.5 61.0 72.4 64.8 73.5 71.9 67.9 68.7 71.0 70.6 70.0 71.6 79.5	74.7 80.3 74.2 67.7 75.3 71.1 78.4 77.2 72.5 73.9 75.5 73.9 75.9 75.9 75.9 75.9 75.9 75.9 75.9 75	76.2 81.9 76.7 69.3 76.9 69.5 78.2 74.6 77.5 77.4 75.9 76.6 77.8 84.3 76.8	78.0 83.6 79.8 71.5 79.4 75.8 81.0 80.5 77.4 81.8 79.1 77.9 78.6 81.4 85.5 79.4 85.5	79.4 84.6 82.0 74.3 81.9 77.8 82.1 82.2 79.5 84.3 81.1 79.5 84.3 81.1 79.5 83.6 86.7 81.2	80.6 85.4 83.0 - 82.8 78.7 83.3 84.1 80.8 85.8 85.8 82.1 79.5 79.8 85.0 86.7 82.7	10,660 10,660 10,540 10,580 10,520 9,030 14,490 10,610 11,540 10,660 10,270 10,470 10,860 14,540
Ineviation	1 10.0	1 2.5					- Andrew Street	dimension of the local distance of the local		

TABLE 9-C - GLUCOSE, 500° F, AIR

		Reduction in COD, %											
Run NO.			Sa	mple	Time	min				COD			
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/1			
02203 02213 02223	28.3 37.5 9.2	58.4 64.5 54.8	63.6 68.4 66.1	68.7 76.3 70.5	74.7 80.3 74.2	76.2 81.9 76.7	78.0 83.6 79.8	79.4 84.6 82.0	80.6 85.4 83.0	10,660 10,660 10,540			
Mean	25.0	59 . 2	66.0	71.8	76.4	78.3	80.5	82.0	83.0				
Standard deviation	14.4	4.9	2.4	4.0	3.4	3.2	2.8	2.6	2.4				

TABLE 10-C - GLUCOSE, 500° F, OXYGEN

	Reduction in COD, %									
Run No.			Sa	ample	Time.	, min				COD
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/l
03053B 03053A 03023 03213 03223 03073B 03153 02233 02263 03073A 03123 03163	42.0 61.3 51.6 54.0 58.3 46.3 52.6 20.2 21.8 25.4 36.3 57.0	51.4 56.4 57.4 63.6 67.0 58.5 55.5 57.8 57.9 58.0 63.5 70.1	58.0 68.6 61.8 70.4 71.8 - 66.0 66.8 67.0 68.8 75.5	61.0 72.4 64.8 73.5 71.9 67.9 68.7 71.0 70.6 70.0 71.6 79.3	67.7 75.3 71.1 78.4 77.2 72.5 73.9 75.5 73.9 74.8 75.9 83.1	68.3 76.9 69.5 79.5 78.2 74.6 77.5 77.4 75.9 76.6 77.8 84.3	71.5 79.4 75.8 81.0 80.5 77.4 81.8 79.1 77.9 78.6 81.4 85.5	74.3 81.9 77.8 82.1 82.2 79.5 84.3 81.1 79.5 79.8 83.6 86.7	- 82.8 78.7 83.3 84.1 80.8 85.8 82.1 79.5 79.8 85.0 86.7	10,440 10,580 10,520 9,030 14,490 10,610 11,540 10,660 10,270 10,470 10,860 14,540
Mean	43.9	60.6	67.5	70.2	74.9	76.4	79.2	81.1	82.6	
Standard deviation	14.7	5.5	4.6	4.5	3.8	4.0	3.4	3.2	2.6	

TABLE 11-C GLUCOSE, 500° F, DISTILLED WATER, AIR, OR OXYGEN

		Reduction in COD, %								Initial
Run No.		Sample Time, min								
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/l
					0- 0	<u></u>	0	06	06 -	
03163	57.0	70.1	75.5	79.3	83.1	84.3	85.5	86.7	86.7	14,540
03123	36.3	63.5	68.8	71.6	75.9	77.8	81.4	83.6	85.0	10,860
03073A	25.4	58.0	67.7	70.0	74.8	76.6	78.6	79.8	79.8	10,470
02263	21.8	57.9	67.0	70.6	73.9	75.9	77.9	79.5	79.5	10,270
02233	20.2	57.8	66.8	71.0	75.5	77.4	79.1	81.1	82.1	10,660
02223	9.2	54.8	66.1	70.5	74.2	76.7	79.8	82.0	83.0	10,540
02213	37.5	64.5	68.4	76.3	80.3	81.9	83.6	84.6	85.4	10,660
02203	28.3	58.4	63.6	68.7	74.7	76.2	78.0	79.4	80.6	10,660
Mean	29.5	60.6	68.0	72.3	76.6	78.4	80.5	82.1	82.8	
Standard deviation	14.4	5.0	3.4	3.6	3.3	3.1	2.8	2.7	2.7	

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TABLE 12-C GLUCOSE, 500° F, 3 1/2% SYNTHETIC SEA WATER, OXYGEN

	Reduction in COD, %								Initial	
Run No.			Sa	mple	Time,	min				COD
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/l
03053B 03053A 03023 03213 03223 Mean	42.0 61.3 51.6 54.0 58.3 53.4	51.4 66.4 57.4 63.6 67.0 61.2	58.0 68.6 61.8 70.4 71.8 66.1	61.0 72.4 64.8 73.5 71.9 68.7	67.7 75.3 71.1 78.4 77.2 73.9	69.3 76.9 69.5 79.5 78.2 74.7	71.5 79.4 75.8 81.0 80.5 77.6	74.3 81.9 7 7.8 82.1 82.2 79.7	- 82.8 78.7 83.3 84.1 82.2	10,440 10,580 10,520 9,030 14,490
Standard deviation	7.4	6.6	5.9	5.5	4.4	4.9	4.0	3.5	2.4	

TABLE 13-C CELLULOSE, 500° F, AIR OR OXYGEN

			Red	luctio	on in	COD,	%			Initial
Run No.			Sa	mple	Time,	min		(0 -		
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/1
12182B 12142B 12142A 12112A 12062 12052 12042B 12042B 12042A 12192A 12202A Mean	38.5 10.4 5.1 57.7 13.5 25.5 27.6 9.7 14.8 22.5	46.3 50.3 36.9 11.4 66.2 29.1 37.4 36.0 18.1 40.5 37.2	51.8 60.0 65.3 29.0 81.6 61.5 68.7 51.0 44.9 65.4 57.9	58.8 68.9 72.2 48.4 90.0 85.8 88.1 72.0 61.1 72.9 71.8	68.0 75.8 80.9 66.7 94.6 93.3 94.5 93.7 72.0 76.5 81.6	72.0 79.5 82.7 71.4 95.4 93.6 95.0 94.5 82.2 81.8 84.8	75.0 83.3 87.6 77.8 96.2 94.1 95.5 95.1 82.6 86.2 87.3	76.5 85.6 89.6 81.8 96.9 95.5 96.3 96.0 - 87.6 89.5	81.3 87.9 89.6 83.3 97.3 93.0 96.5 96.2 85.0 88.9 89.9	400 420 450 510 700 780 1,440 430 450
Standard deviation	16.9	15.6	14.5	13.5	11.4	9.3	7.7	7.3	5.7	

		Reduction in COD, %								
Run No.		Sample Time, min								COD
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/l
12182B 12142B 12142A 12142A 12112A 12062 Mean	38.5 10.4 5.1 57.7 27.9	46.3 50.3 36.9 11.4 66.2 42.2	51.8 60.0 65.3 29.0 81.6 57.5	58.8 68.9 72.2 48.4 90.0 67.7	68.0 75.8 80.9 66.7 94.6 77.2	72.0 79.5 82.7 71.4 95.4 80.2	75.0 83.3 87.6 77.8 96.2 84.0	76.5 85.6 89.6 81.8 96.9 86.1	81.3 87.9 89.6 83.3 97.3 87.9	400 420 450 490 510
Standard deviation	24.7	20.2	19.3	15.6	11.3	9.8	8.4	7.7	6.2	

TABLE 14-C CELLULOSE, 500° F, AIR

TABLE 15-C CELLULOSE, 500° F, OXYGEN

		Reduction in COD, %								
Run No.	0.5	1 5	3 5	E E	10 5	15 5	30.5	60.51	90.5	mg/1
·	0.5	1.9	2.2	9.9	10.9		2007			
12052 12042B 12042A 12192A 12202A	13.5 25.5 27.6 9.7 14.8	29.1 37.4 36.0 18.1 40.5	61.5 68.7 51.0 44.9 65.4	85.8 88.8 72.0 61.1 72.9	93.3 94.5 93.7 72.0 76.5	93.6 95.0 94.5 82.2 81.8	94.1 95.5 95.1 82.6 86.2	95.5 96.3 96.0 - 87.6	93.0 96.5 96.2 85.0 88.9	700 780 1,440 430 450
Mean	18.2	32.2	58.3	75•9	86.0	89.4	90.7	93.8	91.9	
Standard deviation	7.8	8.9	10.0	11.0	10.8	6.7	5.9	4.1	4.9	

	TA	BLE	16	-C
REDUC	ED	FLUS	H	SANITARY
500°	F,	AIR	OR	OXYGEN

1			Rec	luctio	on in	COD,	%			Initial
Run No.			Sa	imple	Time,	, min				COD
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/1
04023 03303 03293 04043A 04043B 04063 04093A 04093B Mean Standard	6.9 25.7 28.3 5.0 16.6 8.7 10.5 14.1 14.5	13.6 31.2 36.2 15.9 24.0 16.5 18.0 22.0 22.2	18.2 37.8 47.2 26.2 28.2 24.6 27.4 29.9 29.9	25.4 42.6 54.2 35.3 35.6 30.2 34.1 39.2 37.1	39.0 54.2 63.7 - 48.0 42.4 44.6 49.3 48.7	51.1 62.5 67.7 59.6 47.3 49.9 53.4 55.9	63.2 70.1 73.1 56.7 66.5 57.3 60.0 61.1 63.5	69.1 74.2 78.3 69.5 71.8 64.0 66.4 65.8 69.9	72.0 76.3 80.3 73.8 75.4 68.5 70.5 69.6 73.3	1,810 1,840 1,980 1,680 1,950 1,310 1,700 1,700
deviation	8.6	8.0	8.9	8.7	8.2	7.5	5.9	4.7	3.9	<u></u>

TABLE 17-C REDUCED FLUSH SANITARY 500° F, ACID AND OXYGEN

1	<u>. </u>		Red	luctic	n in	COD,	%			Initial
Bun NO		Sample Time, min								COD
Kun Ko.	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/1
05093 05103 05143B 05143A 05163B 05183 Mean	12.8 8.4 15.2 23.5 17.8 20.9 16.4	20.6 18.5 23.0 31.9 19.5 38.6 25.4	27.7 31.0 34.3 38.2 25.3 46.4 33.8	41.2 39.2 40.5 43.2 30.5 51.0 40.9	47.7 51.9 50.6 50.0 41.6 58.7 50.1	56.1 55.5 56.0 55.6 58.8 62.2 57.4	61.7 64.1 61.7 60.7 63.9 66.5 63.1	66.5 67.2 65.2 64.8 69.2 69.3 69.3	70.0 70.1 69.0 67.5 71.9 70.4 69.8	1,330 1,470 1,390 1,490 4,800 5,020
Standard deviation	5.5	8.1	7.7	6.6	5.6	2.7	2.1	1.9	1.5	

TABLE 18-C TOMATO JUICE 500° F, AIR OR OXYGEN

			Red	luctic	on in	COD,	10			Initial
Run No.			Sa	mple	Time	, min				COD
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	mg/l
04123 04133 04163 04173 04193	36.8 - 35.3 35.2 42.4	42.2 55.0 45.8 46.0 51.1	52.1 60.9 52.7 53.6 60.1	54.0 63.7 56.8 57.5 64.8	59.2 66.9 62.6 64.4 69.8	63.1 69.6 65.9 67.6 71.9	67.9 72.8 69.6 70.8 74.1	71.6 75.0 72.4 73.5 75.7	74.7 76.4 73.8 74.8 75.7	9,090 10,020 9,200 10,880 10,660
Mean	37.4	48.0	55.8	59•3	64.5	67.6	71.0	73.6	75•4	
Standard deviation	3.4	5.0	4.3	4.7	4.0	3.4	2.5	1.7	1.4	

APPENDIX D

REACTION RATE CONSTANTS FOR VARIOUS WET OXIDATION RUNS

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400 b r m⁻¹₂₁₀

Sample No	kı -	k_2
Sample No:	min ⁻¹	min -
04023	0.041	0.009
03303	0.051	0.007
03293	0.089	0.007
040434	0.074	0.008
	0.048	0.008
04063	0.052	0.009
0/10032	0.070	0.008
040975	0.067	0.006
040978		
$M_{000} = 0.06$	Mean =	0.008
Mean = 0.00	- 0.02 Standar	d deviation = 0.001
	Bange =	0.006-0.009
Range = 0.04 - 0.09	Runge -	

TABLE 1-D REDUCED FLUSH SANITARY 500° F, AIR OR OXYGEN

TABLE 2-D TOMATO JUICE 500° F, AIR OR OXYGEN

Sample No.	k ₁ min ⁻¹	k ₂ min ⁻¹
04123	0.066	0.006
04133	0.054	0.004
04163	0.076	0.004
04173	0.080	0.004
04193	0.096	0.003
Mean = 0.07	Mean =	0.004
Standard deviation =	0.02 Standa	rd deviation = 0.016
Range = 0.05-0.10	Range	= 0.003-0.006

Sample No.	k ₁ min ⁻¹	k2 min ⁻¹
0129 3 B	0.112	0.004
0129 3 A	0.155	0.004
01263B	0.096	0.004
0126 3A	0.088	0.003
01243	0.084	0.004
Mean = 0.11 Standard deviation = 0 Range = 0.08-0.16	Mean = 0 .03 Standard Range =	0.004 d deviation = 0.0004 0.003-0.004

TABLE 3-D 0.1% OIL-IN-WATER EMULSION 500° F, AIR OR OXYGEN

Sample No.	k ₁ min ⁻¹	k ₂ min ⁻¹		
01233	0.150	0.003		
0122 3 B	0.158	0.003		
0122 3A	0.104	0.001		
01193B	0.139	0.004		
01193A	0.217	0.003		
01183	0.233	0.003		
01163	0.252	0.004		
01103A	0.060	0.003		
01093B	0.121	0.003		
01093A	0.065	0.003		
01083	0.074	0.003		
01043B	0.111	0.004		
0104 3 A	0.087	0.006		
Mean = 0.14 Standard deviation Range = $0.06-0.25$	Mean = 0 = 0.06 Standard Range =	0.003 d deviation = 0.001 0.001-0.006		
Range = 0.06 - 0.25	Range =	0.001-0.000		

TABLE 4-D 0.5% OIL-IN-WATER EMULSION 500° F, AIR OR OXYGEN

Sample No.	$\frac{k_1}{\min^{-1}}$	k ₂ min ⁻¹
11162 11152A 11142 10182 09222 08252 08152 08152 08112 08102 08082	0.093 0.128 0.054 0.130 0.119 0.096 0.115 0.092 0.149 0.140	0.012 0.006 0.008 0.022 0.009 0.008 0.012 0.011 0.011 0.010 0.017 0.010
08072 Mean = 0.11 Standard deviation = Range = 0.05-0.15	0.128 Mean = (= 0.03 Standard Range =	0.010 0.011 1 deviation = 0.005 0.006-0.022

TABLE 5-D PRIMARY SLUDGE, 600° F, AIR OR OXYGEN

TABLE 6-D PRIMARY SLUDGE, 500° F, AIR OR OXYGEN

Sample No.	k ₁ min ⁻¹	k2 min ⁻¹
	0.104	0.008
112 (24	0.130	0.005
112728	0.120	0.008
11222	0.120	0.015
11202	0.209	0.007
11172B	0.142	0.006
11172 A	0.121	0.006
11152в	0.136	0.000
11132B	0.075	0.000
11132A	0.093	0.008
11102	0.106	0.005
11092	0.097	0.003
11062	0.093	0.005
11022	0.106	0.005
10312	0.097	0.006
10162	0.104	0.009
Mean = 0.12 Standard deviation Range = 0.08-0.2	Mean = 0 on = 0.03 Standard 1 Range =	.007 deviation = 0.003 0.003-0.015

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Sample No.	k ₁ min ⁻¹	k ₂ min ⁻¹
	0.1/17	0.003
02203	0.147	0.003
02213	0.107	0.007
02223	0.201	0.001
03053B	0.076	0.004
03053A	0.062	0.004
03023	0.061	0.004
13213	0.105	0.003
03223	0.073	0.004
03153	0.089	0.007
00033	0.179	0.004
02233	0 174	0.004
02203	0.164	0.004
03073A	0.130	0.006
03123	0.139	0.003
03163	0.154	0.00)
Mean = 0.13 Standard deviatio Range = 0.06-0.20	Mean = 0 on = 0.05 Standard 0 Range =	.004 deviation = 0.001 0.003-0.007

TABLE 7-D GLUCOSE, 500° F, AIR OR OXYGEN

TABLE 8-D CELLULOSE, 500° F, AIR OR OXYGEN

Sample No.	k ₁ min ⁻¹	k ₂ min ⁻¹
12182в	-	0.006
12142 B 12142 A	0.079	0.008
12112 A 12062	0.108 0.210	0.008
12052 12042в	0.268	0.005
12192 A 12202 A	0.122 0.229	0.005
12042 A	0.248	0.006
Mean = 0.18 Standard deviation Range = $0.06-0.27$	Mean = 0 = 0.08 Standard Range =	0.007 1 deviation = 0.001 0.005-0.008

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