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November 1975

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PILOT-PLANT DEMONSTRATION OF WET OXIDATION FOR TREATMENT OF SHIPBOARD WASTEWATERS

G. W. Bridges and W. M. Fassell

November 1975

FINAL REPORT

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16. Abstract

Two processes were demonstrated: (1) acidic wet oxidation of wastewater and direct discharge of the effluent; and (2) ammoniacal wet oxidation and recycling of toilet flushings.

Fifty-gallon batches of wastewater were treated in a full-scale (20-man) prototype system. Wet oxidation was effected in a continuous-flow (30ℓ/hr) horizontal autoclave in which wastewater and air were reacted cocurrently in a series of stirred chambers. The total pressure of the reactor was 600 psi, and the temperature ranged from 400 to 480 °F. Percentage reduction in COD ranged from about 65 to 95 in tests conducted on body sewage and simulated wastewaters from the galley and bilge. Laundry water proved indestructible; sodium lauryl sulfate, the most prevalent modern detergent, was unaffected.

An engineering design is presented for a 20-man shipboard waste treatment system in which body sewage and solid galley waste are conducted through the reactor in an ammoniacal liquor which is recycled as flushant to recirculating toilets. Residual inorganic solids are removed by filtration. Steam is vented continuously to maintain a constant volume. Heat to sustain the process is drawn from the exhaust gases from the ship's engines. The system can be operated for 60 days after which the flushant must be changed and the accumulative solids removed from the filter.

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BARBER-COLMAN CO.
Resource Recovery Systems Division
1882 McGaw Avenue
Irvine, California 92714

FINAL REPORT

Contract No. DOT-CG-31323-A

by

D.W. Bridges and W.M. Fassell

Prepared for

U.S. COAST GUARD

DEPARTMENT OF TRANSPORTATION
400 Seventh St., S.W.
Washington D.C. 20590

FRONTISPIECE. VIEW OF THE PILOT PLANT

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Chemical analysis was performed by Fred J. Gierke, Deborah Halberg and Calvin E. Foster.

Edward Gold, Mark A. West, George Pagonis, Theodore Crane and Lucas Gordon assisted in mechanical design. Howard Gilsdorf and Barney Morelock constructed the WETOX reactors.

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LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS

General

BOD	biochemical oxygen demand, the quantity of oxygen consumed in oxidizing organic matter in a specified time at a specified temperature by biological means, a standard method of chemical analysis.
COD	chemical oxygen demand, the quantity of chemical oxidant (potassium dichromate, reported as oxygen) consumed in oxidizing organic matter in boiling 50 vol-pct sulfuric acid in the presence of a silver catalyst.
C.P.	commercially pure (titanium metal)
PURETEC®	registered trademark of RRS used to designate certain of its wastewater treatment systems
RRS	Resource Recovery Systems, Ltd., formerly a division of the Barber-Colman Co.
TOC	total organic carbon, a method of chemical analysis in which organic matter is burned to carbon dioxide gas
WETOX®	registered trademark of RRS used to designate its process (and reactor) for wet oxidation

The following types of WETOX® reactors are mentioned in the text:

210	a two-compartment, 10-inch dia. reactor built for the U.S. Coast Guard; the so-called Lab Model
410-L	a four-compartment, 10-inch dia. reactor specially constructed for performing laboratory research
410-M and 412-M	four-compartment reactors (12 inches in diameter) specially constructed for shipboard (marine) usage

Specific To Section 2

Q	quantity of heat; see page 2-14 for definitions of specific components

Specific To Section 3

C	catalyst, a main effect in factorial experiments; also concentration of COD or dissolved oxygen in certain equations

SYMBOLS, ABBREVIATIONS AND ACRONYMS (CONTINUED)

C_i	concentration of oxygen at the film interface; see page 3-76
C_ℓ	saturation concentration (of dissolved oxygen) in the liquid; see page 3-69
C_r	concentration of oxygen at reaction zone; see page 3-76
CS	effect of interaction between catalyst and salinity in factorial experiments
DO	dissolved oxygen; see page 3-69
H^{-1}	reciprocal of the Henry's Law constant
K_L	overall coefficient of mass transfer; see page 3-75
P_{H_2O}	pressure exerted by saturated steam
$P_{O_2}^V$	partial pressure of oxygen gas in the vapor phase of the reactor, see page 3-69
R	residence time, a main effect in factorial experiments
R^2	fraction of the variance accounted for by multiple regression analysis
S	salinity, a main effect in factorial experiments
SC	effect of interaction between salinity and catalyst in factorial experiments
S.E.	standard error, which is synonymous with standard deviation according to Davies *et al.*, *The Design and Analysis of Industrial Experiments*, Hafner Publishing Co., New York, 1954, p. 591, and equals the square root of the variance
SR	effect of interaction between salinity and residence time in factorial experiments
SS	sum of squares, the accumulative total of the squares of the deviations of the effect values from their means
SW	seawater
T	temperature, a main effect in factorial experiments
TR	effect of interaction between temperature and residence time

SYMBOLS, ABBREVIATIONS AND ACRONYMS (CONTINUED)

TW	tapwater
W	wetted wall, a main effect in factorial experiments
WR	effect of interaction between the wetted wall and the residence time in factorial experiments
WS	effect of interaction between the wetted wall and salinity in factorial experiments
WSR	effect of interaction between wetted wall, salinity and residence time in factorial experiment
a	specific area of interphase contact; see page 3-75
b	regression coefficient; the slope of the least-squares line in linear regression analysis; multiple regression coefficients are denoted by subscripts in multiple regression analysis beginning on page 3-30
c*	coded effect of catalyst in multiple regression analysis; see page 3-33
dc/dt	derivative of concentration (oxygen or COD) with respect to time; see page 3-75
k	pseudo-first-order reaction rate constant; see page 3-40; specific compartments denoted by subscripts 1, 2, 3 and 4
k_i	initial reaction rate constant
k_ℓ	late-stage reaction rate constant
r	the correlation coefficient as defined on bottom of page 3-34; also the rate of reaction (reduction in COD) as defined on page 3-40
r^2	the coefficient of determination, the fraction of variance accounted for by linear regression analysis
r_{max}	maximum rate of wet oxidation; see page 3-76
r_{ox}	rate of (wet) oxidation; see page 3-76
s*	coded effect of salinity in multiple regression analysis; see page 3-33
s*c*	effect of interaction between salinity and catalyst in multiple regression analysis; see pages 3-39 and 3-47
t*	coded effect of residence time in multiple regression analysis; see page 3-33

SYMBOLS, ABBREVIATIONS, AND ACRONYMS (CONTINUED)

x	independent variables in regression analysis; individual variables denoted by subscripts in multiple regression analysis; mean denoted by bar, i.e., $\bar{x}$
y	response parameter in regression analysis; mean denoted by bar, i.e., $\bar{y}$
π	total pressure of gases and vapors confined in the reactor
ρ	density
τ	mean residence time (of liquid) per compartment

Specific to Section 4

k	rate constant for ammoniacal wet oxidation
k_i	initial rate constant for fast (beginning) ammoniacal wet oxidation
k_ℓ	late-stage rate constant for sluggish (end) ammoniacal wet oxidation

Specific to Section 6

A	area of insulation shell (on reactor)
P_m	total pressure of gases and vapors confined in reactor
P_w	pressure exerted by saturated steam; see page 6-31
Q	quantity of heat; see page 6-32
R_A	gas-law-related constant for air; see page 6-31
R_W	gas-law-related constant for water; see page 6-31
ΔT	temperature difference between insulation shell and ambient
U	overall coefficient of heat transfer; see page 6-33
a	subscript denoting air
f	subscript denoting feed (influent)
h	specific enthalpy of the chemical phase indicated by a subscript; see page 6-32
ℓ	subscript denoting liquid phase

SYMBOLS, ABBREVIATIONS AND ACRONYMS (CONTINUED)

m	subscript denoting mixture (of gases and vapors), the vapor phase
$\dot{m}$	mass flow rate of substance specified by subscript; see page 6-31
v	subscript denoting vapor phase
w	subscript denoting water (or steam)
ω	saturation humidity, the maximum mass of water vapor absorbed by a unit mass of dry air at a specified temperature; see page 6-31

Specific to Appendix A

C	concentration of organic matter expressed as COD; $C = Q/V$
F	Laplace transform; see page A-6
Q	quantity of organic matter in a compartment expressed as COD
V	capacity (volume) of compartment for liquid
i	subscript denoting parameter(s) associated with initial (fast) reduction in COD
k	reaction rate constant for the COD-reduction process
ℓ	subscript denoting parameter(s) associated with late-stage (slow) reduction in COD
n	subscript designating the position of a compartment with respect to the inlet end ($n = 0$ denotes the feed)
t	time after start-up; i.e., elapsed time after commencement of pumping influent to preheated reactor
v	flow rate of influent (and of effluent)
τ	residence time of liquid in a compartment; $\tau = V/v$
∞	subscript denoting parameter(s) associated with steady state

Specific to Appendix B

A	the cross-sectional area of the compartment or tank in which the air is dispersed
C	the concentration of organic matter expressed as COD

SYMBOLS, ABBREVIATIONS AND ACRONYMS (CONTINUED)

F	the feed rate, that is, the mass of wastewater fed to the reactor in a unit interval of time
$\dot{M}_\ell$	the mass flow rate of the liquid-phase slurry
P	the agitator shaft power during dispersion
V	the geometric volume of the walled-off portion of the reactor's interior occupied by the agitating mass of liquid and entrained air
V*	the active volume (the actual volume of reacting liquid) in the indicated compartment
f	the fraction of organic solids in the feed
f*	the fraction of the agitated mass which is entrained air
n and n-1	subscripts denoting adjacent compartments
r_n	the rate of reaction
u	the flow rate of air
v_t	the so-called bubble terminal velocity
β	the ratio, mass air added: mass solids added
ω	the humidity factor, that is, the mass of water (lost as steam) in each unit mass of dry air added to the reactor
ρ	the density of the liquid in the reactor
σ	the interfacial tension
τ	the mean residence time

Specific to Appendix C

avg.	average, subscript designating that mean value of a parameter
b	slope of trend (least-squares) line, regression coefficient in linear regression analysis
k	reaction rate constant for wet oxidation in liquid phase of compartment designated by subscript
k_i	reaction rate constant for initial (fast) stage of wet oxidation

SYMBOLS, ABBREVIATIONS, AND ACRONYMS (CONTINUED)

k_ℓ	reaction rate constant for late-stage wet oxidation
$-r$	rate of wet oxidation
r^2	coefficient of determination,the fraction of the variance accounted for by linear regression analysis

Specific to Appendix D

M	molecular weight of the substance indicated by a subscript
MBAS	methylene-blue-active substances, a method of chemical analysis for the determination of detergent
P	partial pressure of substance denoted by subscript
SLS	sodium lauryl sulfate, active substance in many detergents
W	weight (actually mass)
im	immiscible (water-insoluble) substances, a subscript
s	steam, a subscript

Specific to Appendix E

k	reaction rate constant for wet oxidation
r^2	coefficient of determination, fraction of the variance accounted fo by linear regression analysis

Specific to Appendix F

C	concentration (COD) of organic species in liquid phase of stream or compartment denoted by subscript
C°_ℓ	initial concentration (COD) of the organic species which degrade by the late-stage wet-oxidation process(es)
k	reaction rate constant for wet-oxidation process(es) denoted by subscript
ℓ	subscript denoting late-stage wet oxidation
n	subscript denoting a particular compartment (n = o designates the influent)

SYMBOLS, ABBREVIATIONS AND ACRONYMS (CONTINUED)

τ	mean residence time in a particular compartment

Specific to Appendix G

C	concentration of the reactant in the indicated compartment
ΔC_i	the change in concentration caused by the destruction effected by the initial (fast) reaction
C_ℓ°	initial concentration (COD) of the organic species which degrade by the late-stage wet-oxidation process(es)
[COD]	concentration of organic matter expressed as COD
$(\frac{dC}{dt})_n$	derivative of concentration with respect to time for compartment n
V	the capacity for liquid of the first compartment
f	the fraction of the COD in the influent to compartment n remaining in the effluent from compartment n
f_n	the fraction of the COD contained in the feed (or influent to the first compartment) which remains in the effluent from the nth compartment
f_d	the fraction of the initial COD which has been destroyed by treatment in n compartments
k_n	the pseudo first-order reaction rate constant for the chemical reaction taking place in compartment n
m_n	the capacity of compartment n for liquid
$\dot{m}$	the mass flow rate of reactant through the reactor
n	number of the compartment from inlet end (n = o designates the influent
r	rate of wet oxidation
r_1	the rate of reaction (per volume of liquid) for the late-stage oxidation taking place in the first compartment
v	the volumetric flow rate of the liquid as measured at room temperature
α	angle to horizontal whose tangent is the reciprocal of the mean residence time; see page G-8, equation G-12

SYMBOLS, ABBREVIATIONS AND ACRONYMS (CONTINUED)

ρ	the density of the liquid at room temperature
ρ_T	the density of the liquid at the operating temperature of the reactor

Specific to Appendix H

DO	dissolved oxygen
H^{-1}	reciprocal of the Henry's Law constant partial pressure
X	mol fraction
m	molal concentration

Specific to Appendix J

C	concentration of organic matter (expressed as COD) in compartment designated by subscript
k	reaction rate constant
n	subscript denoting compartment number
r	rate of reduction in COD
τ	mean residence time

SECTION 1

INTRODUCTION

This document--the final report of Dept. of Transportation, U.S. Coast Guard, contract no. DOT-CG-31323-A--summarizes pilot-plant and engineering design studies which were conducted to evaluate the feasibility of wet oxidation for shipboard wastewater treatment. The contract was performed by the Barber-Colman Co. at its Resource Recovery Systems Division facilities in Irvine, California

1.1 STATEMENT OF PROBLEM

Current regulations governing environmental pollution control prohibits the discharge of sanitary sewage within the territorial waters of the United States. While no restrictions exist as to the discharge of shower water, galley waste and laundry water, it is believed that future regulations may limit their discharge. Oily waste, such as bilge water, also cannot be discharged if the oil leaves a visible sheen or contains more than 12 ppm water-insoluble oil.

1.1.1 PROBLEMS CONFRONTING OWNERS OF EXISTING SHIPS

All water craft, existing and future, must comply with the new regulations. Since each person aboard ship typically generates daily wastewater amounting to about twice his weight, on-board treatment is mandatory for most vessels; otherwise, their mobility and/or payload would be drastically reduced.

According to government statistics, there are presently over 100,000 commercial carriers and fishing vessels and 8 million recreational water craft affected by the new law.

Compliance is particularly difficult in the case of existing craft. Retrofitting an existing vessel has always been a problem. For centuries, naval architects have toiled to create ships in which space and weight were minimized to maximize speed and maneuverability. Likewise, conservation of living space and deadweight are equally important in the design of freighters and passenger vessels. Aboard any existing vessel, there simply is no large amount of excess space in which to install a wastewater treatment system.

The problem is further complicated by the fact that the use of a sanitary waste collection system is rare in present day ships. This approach up to now has been deliberately avoided to conserve space, maximize hull integrity and reduce construction and maintenance costs. The installation of piping for a central sanitary waste collection aboard an existing vessel is difficult because of limited working space, bulkheads to penetrate and interference from existing plumbing, air conditioning and electrical raceways.

Then, too, some consideration must be given to the health and comfort of the crew: Life aboard ship has always been somewhat confining and ventilation is limited. The odor of wastewater has always presented problems in its treatment. In well-planned communities, the sewage plant is located away from the residential area. Aboard ship, this is not possible. The crew quarters on many vessels are dispersed throughout the interior. A system is required that accomplishes treatment without excessive noise and odor. Further, the system must not slosh over into the bilge during rough weather or require shutting down during such periods.

1.1.2 PROBLEMS PERTAINING TO CANDIDATE TREATMENT SYSTEMS

Under the "No Discharge" rules, the number of possible ways in which shipboard sewage can be handled are limited. The possible methods that have been considered include:

- Holding Tanks
- Evaporation/Incineration
- Closed Circuit Wet Oxidation

Holding tanks require substantial space but require little attention from the crew while underway. Modest aeration is required and the tanks must be vented to prevent the objectionable odors of anaerobic bacterial growth and the explosion hazards of evolved methane. Only capacity limits the time between pump-outs, and dockside facilities must be available for discharge.

The evaporation/incineration systems are somewhat more complex in operation and some versions require the use of substantial quantities of energy to evaporate the water or reduce the water content of the sludge. Problems have been encountered with odors but use of gas treatment systems, such as catalytic after-burners, has reportedly solved this problem. Evaporation of fecal material and urine, especially in the presence of sea water, causes build-up of scale and/or char on the heated surface, requiring frequent cleaning if system efficiency is to be maintained.

Wet oxidation seems uniquely applicable for the on-board processing of marine sanitary waste. The process is simple, adaptable to closed-loop (no discharge) or open-loop operation. If ultimately required, galley waste can be added to the system with minor modifications. Shipboard wastewater is the sort of pollutant that wet oxidation is ideally suited to treat. The daily waste generated aboard ship constitutes a sizeable quantity of water contaminated with small but significant amounts of suspended, dispersed (colloidal) and dissolved organic matter--in some cases ten times the maximum permissible limit for lawful disposal. Wet oxidation is a convenient method for treating organic-containing liquors without first performing costly evaporation or dewatering as would be required before incineration.

1.1.3 PROBLEMS SPECIFIC TO WET OXIDATION

Aboard ship space and weight are premium. Wastewater treatment systems must be compact, light in weight and effective. Wet-oxidation systems, heretofore, have had few of these attributes. Moreover, the most effective processes have been those conducted at the highest temperatures and, therefore, in the heaviest reactors.

If wet oxidation is to be applied aboard ship to treat conventional sanitary sewage and other wastewaters, a highly effective, low-temperature, low-pressure process must be used. Several years ago, the Barber-Colman Co. undertook the development of just such a system.

1.2 PROGRAM OBJECTIVE

The purpose of this program was to demonstrate the feasibility of applying low-temperature, low-pressure wet oxidation for shipboard wastewater treatment. As a guide to development, the U.S. Coast Guard established the design specifications listed in Table 1-1.

1.3 OUTLINE OF THE PROGRAM

The contract, which was awarded to the Barber-Colman Co. in September 1972, was based on a proposal submitted in March 1972.

TABLE 1-1

SUMMARY OF SYSTEM REQUIRMENTS FOR A 20-MAN SHIPBOARD WASTEWATER TREATMENT SYSTEM

Requirement or Imposed Condition	Specifications
Complement:	20 Men.
Daily Hydraulic Load:	35 gallons/person/day with average peak loads, 200 pct. of daily average.
Weight of System:	Maximum, 1000 pounds loaded; i.e., including weight of in-process wastewater.
System Envelope:	Maximum, 4 feet long by 3 feet wide by 4 feet high.
Size of Components:	Must pass through 26" x 66" door and 24" x 24" hatch.
System Environment:	From 40° to 140°F. Permanent trim from the normal horizontal plane in the longitudinal direction up to 3°. Permanent list to either side of the vertical up to 15°. Pitching 10° up or down from the normal horizontal plane. Dynamics rolling of 40° in any direction from the normal horizontal plane with a period of roll of 10 seconds.
Power Requirement:	Maximum, 4 kw for operation in a 120/208 V, AC, 3-phase electrical circuit or any of the following alternates: 440 V, AC, 3-phase; 120/240 V, AC, single phase; or 120 V, DC.
Maintenance:	Minimal. All valves, fittings, pumps and motors shall be standard items. Materials--best for corrosion-resistance.
Operation:	Automatic; minimum attention from crew.
Hydraulic Head:	Must eject against maximum head of 50 feet.
Type of Waste:	All shipboard wastewaters, including sanitary, galley scullery, shower, laundry and lavatory wastes, and discharges from deck drains below water level.
Suspended Solids:	Influent: Average, 500 mg/ℓ; range from 4900 to 200 mg/ℓ; Effluent: Maximum, 50 mg/ℓ.
Biochemical Oxygen Demand, BOD:	Influent: Average, 500 mg/ℓ; range from 1800 to 150 mg/ℓ; Effluent: Maximum, 50 mg/ℓ.
Total Coliform:	Effluent: Maximum, 240 MPN/100 mℓ.
Temperature:	Influent: From 28 to 95°F.
pH:	Influent: From 6 to 9.
Salinity:	Influent: From 0 to 35,000 ppm.

1.3.1 ORGANIZATION

For contractual purposes, the various efforts requested by the Coast Guard were identified formally as tasks. These are listed below:

Task I - Theoretical Analysis of the Wet-Oxidation Subsystem;

Task II - Design, Procurement, Fabrication and Assembly of Physical Hardware;

Task III - Preparation and Submission of a Detailed Test Plan and Operating Procedures for a Proposed Laboratory Testing Program;

Task IV - Performance of the Laboratory Testing Program;

Task V - Analyses of Test Data; and

Task VI - Preparation of a Preliminary Design of a 20-man Prototype System.

1.3.2 PLANNED TECHNICAL APPROACH AND ACTUAL COURSE OF EVENTS

Originally Task II--the construction of a two-compartment reactor called the Lab Model--was to have been followed by Task IV--performance of the laboratory testing program. In other words, Task IV was to have been performed in the Lab Model. Actually Task IV was conducted concurrently with Task II. In March 1972, Barber-Colman Co. submitted its proposal to the Coast Guard and simultaneously began construction of the proposed 4-compartment shipboard reactor. There was a delay in funding the contract; and by the time funds were made available, the 4-compartment reactor was completed. With the concurrence of the Coast Guard, Task IV was initiated immediately; the 4-compartment reactor was used until the 2-compartment Lab Model was constructed.

The originally proposed technical approach contemplated direct-discharge treatment. However, soon after the submission of the proposal, the Federal Government adopted a no-discharge policy. Laboratory testing was initiated as originally conceived; however, simultaneously Barber-Colman Co. undertook independently the development of a closed-loop (no-discharge) system. Midway in the Program, when the closed-loop process had been demonstrated to be feasible, laboratory testing of the original concept was halted; and an evaluation of the closed-loop method was initiated.

SECTION 2

CHEMISTRY OF WET OXIDATION OF SHIPBOARD WASTE

Although wet oxidation is an industrially important chemical process, it is not discussed extensively in most widely read technical books. Consequently, many readers may be unfamiliar with the basic principles and state of the art. In this section of the report, a brief review of the known facts is presented. Other chemical aspects of the general problem--treatment of shipboard wastewaters--also are included.

Wet oxidation is a form of combustion in which matter is burned under liquid. The combustible matter which is generally organic is dissolved or suspended in the liquid which is usually water. The process takes place at practical rates only at temperatures above the normal boiling point of water. The slurry or solution of combustible material is confined with steam, air and the combustion products in a pressure vessel called an autoclave. Combustible substances, being fuels, liberate considerable heat when subjected to wet oxidation, and the process can be autogenetic. Wet oxidation is particularly advantageous for the destruction of watery wastes such as slimes and sludges that are costly to incinerate and are often pathogenic. The process is also well suited for the disposal of toxic and hazardous materials, because they are burned under water; and, consequently, there is much less danger of air pollution or explosion.

2.1 HISTORICAL DEVELOPMENT

The treatment of organic matter with confined steam is an ancient art. The autoclave was invented by Denis Papin, who in 1681 used a bronze "pressure cooker" equipped with a safety valve to extract marrow from bones. The first commercial use of autoclaves was probably by Bayer in 1888 for the extraction of alumina from bauxite. The first intentional introduction of air into an autoclave to effect wet oxidation may have been by R. W. Strehlenert in 1912. Testrup applied for U.S. Patent 1,116,953 in 1912 claiming the invention of a process in which sewage sludge was heated in an autoclave to de-slime it; William K. Porteous was granted U.S. Patent 2,131,711 in 1939 to conduct basically the same process aboard ships. Franz Fischer probably was the first to react sewage sludge and oxygen in an autoclave. The important milestones in the evolution of wet oxidation are depicted in Figure 2-1.

In the past, total destruction of organic wastes by wet oxidation has been achieved only at very high temperatures (above 550 °F) and very high pressures (2000 psi). Large-scale utilization of the process has been limited. Users have experienced exorbitant maintenance costs; capital equipment costs have been high. In extractive metallurgy, efficient wet oxidation has been practiced for over twenty years at low temperatures (400 °F) and low pressures (600 psi). The Barber-Colman Company has applied established metallurgical practice to organic waste disposal in its WETOX* process, which is carried out in highly efficient, mechanically stirred horizontal autoclaves. Equipment of the same basic design has been in continuous service for nearly 25 years in extractive metallurgical operations.

2.2 BASIC NATURE OF WET OXIDATION

Extensive research has established that wet oxidation generally takes place in the following manner: In an excess of oxygen, combustion proceeds at a rate which is directly proportional to the concentration of the combustible substances. Macromolecules, however, react faster than compounds having low molecular weights. Consequently, in the wet oxidation of most organic wastes combustion proceeds more rapidly initially as the macromolecules comprising much of nature oxidize to carbon dioxide; but in the process, smaller-molecular-weight fragments also form and remain in the liquid. As combustion progresses, the low molecular weight substances rapidly accumulate in the partially oxidized wastewater. The rate of wet oxidation abruptly slackens as the smaller molecules resist destruction and burn very slowly. Typical behavior is illustrated in Figure 2-2.**

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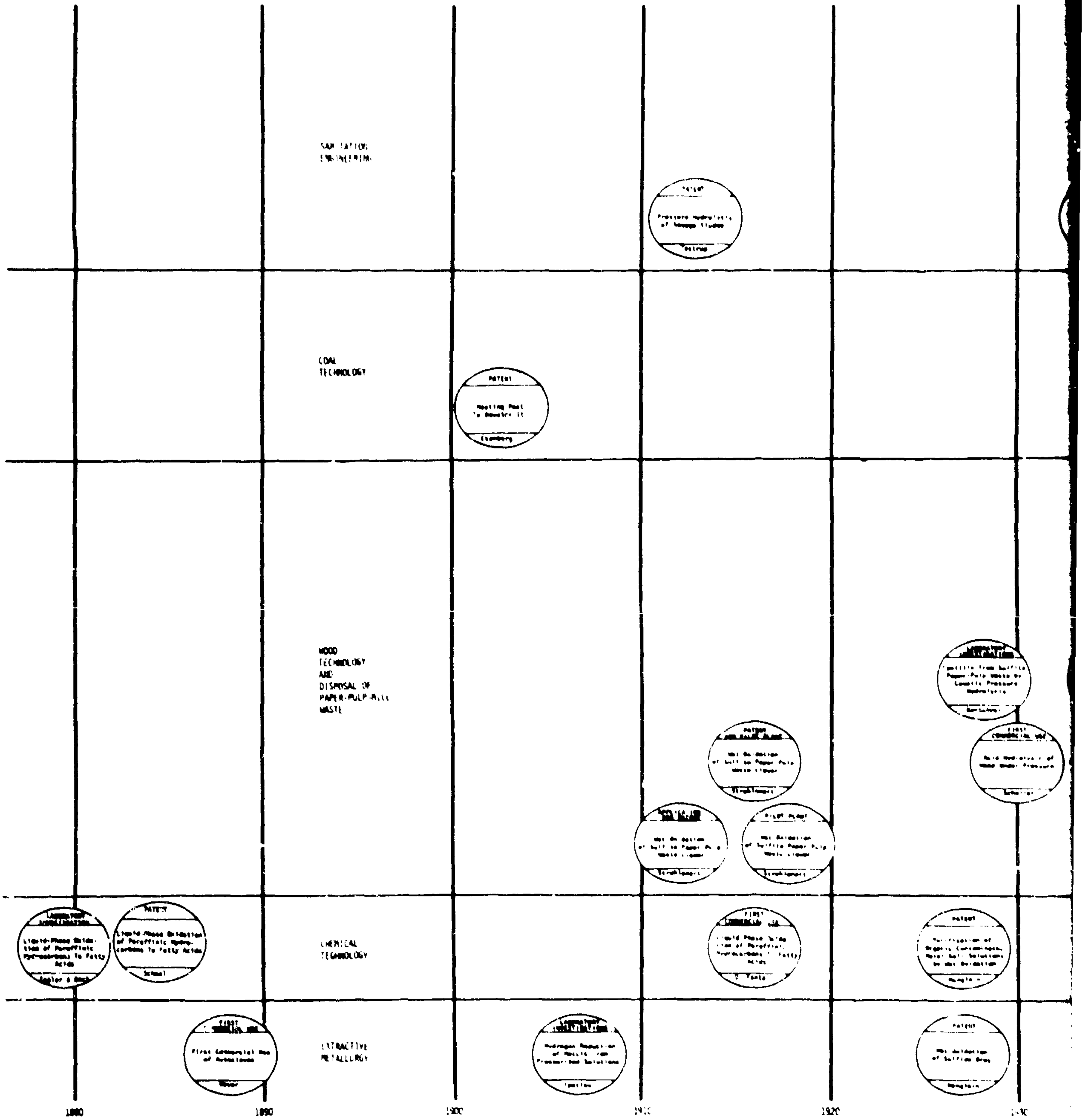
* WETOX and PURETEC are registered trade marks of the Barber-Colman Co.

** In this figure and throughout the ensuing discussion, in accordance with accepted practice, chemical oxygen demand (COD) is used as an index of the total concentration of organic matter. The COD of all influent and effluents was determined by chemical analysis as specified in Standard Methods for the Examination of Water and Wastewaters, Thirteenth Edition.

SANITATION ENGINEERING
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COAL TECHNOLOGY
PATENT
Heating Peat to Dewater It
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LABORATORY INVESTIGATION
Vanillin from Sulfite Paper-Pulp Waste by Caustic Pressure Hydrolysis
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Acid Hydrolysis of Wood Under Pressure
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Wet Oxidation of Sulfite Paper Pulp Waste Liquor
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LABORATORY INVESTIGATION
Liquid-Phase Oxidation of Paraffinic Hydrocarbons To Fatty Acids
PATENT
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Liquid Phase Oxidation of Paraffinic Hydrocarbons To Fatty Acids
PATENT
Purification of Organic Contaminated Metal Salt Solutions by Wet Oxidation
FIRST COMMERCIAL USE
First Commercial Use of Autoclaves
LABORATORY INVESTIGATION
Hydrogen Reduction of Metals from Pressurized Solutions
EXTRACTIVE METALLURGY
PATENT
Wet Oxidation of Sulfide Ores
1880
1890
1900
1910
1920
1930

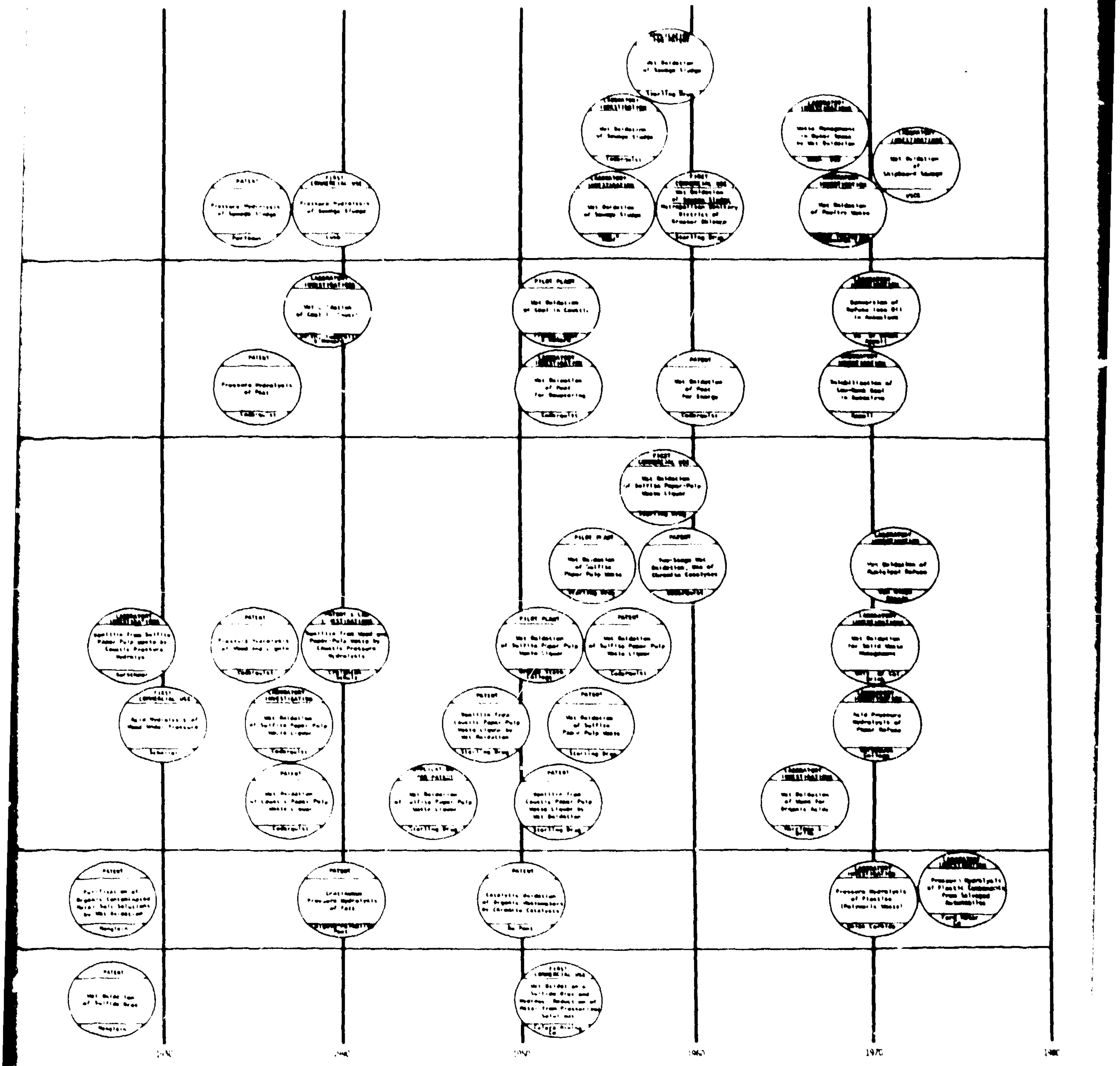


FIGURE 2-1. CHRONOLOGY OF WET OXIDATION AND RELATED TECHNOLOGY

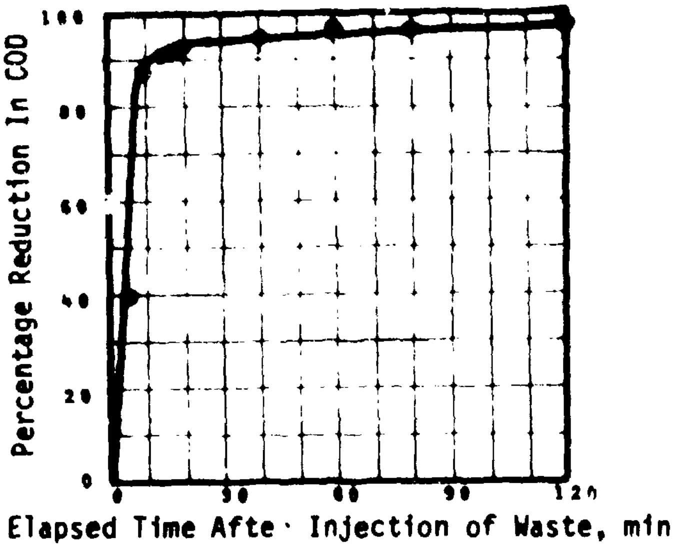
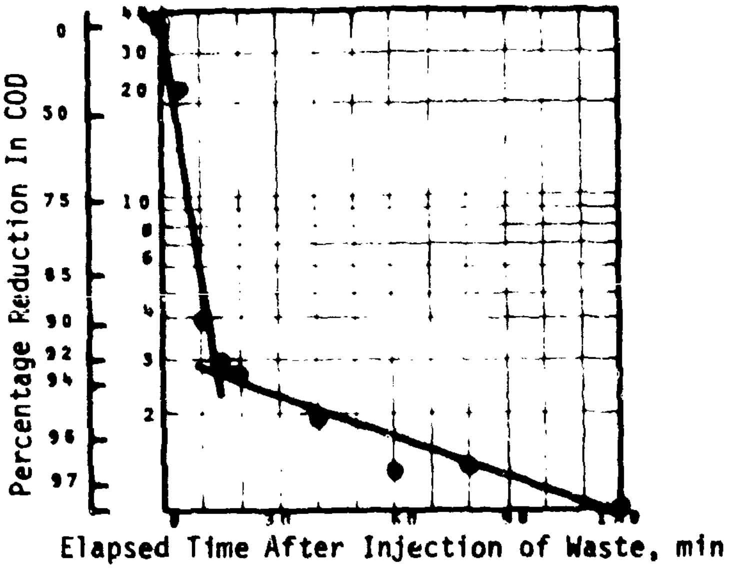


FIGURE 2-2. (Left, top of page). TYPICAL PLOT, PERCENTAGE REDUCTION IN COD, BATCH TEST ON MIXED FECES AND URINE. (Data of Batch Test No. 303).

FIGURE 2-3. (Right, center of page). DATA OF FIGURE 2-2 REPLOTTED IN SEMI-LOGARITHMIC MANNER.



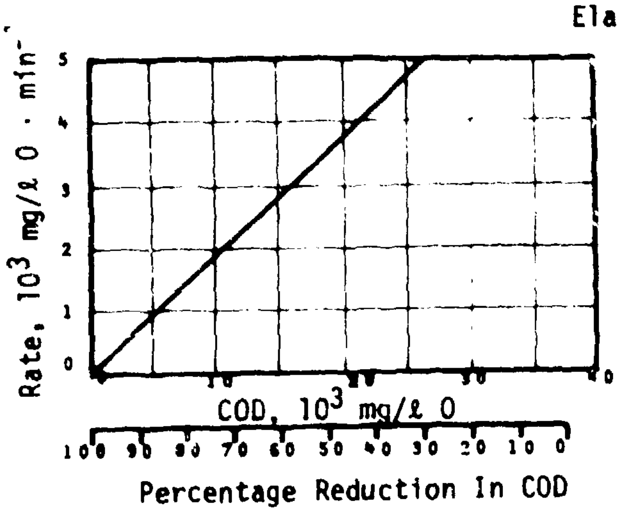


FIGURE 2-4. (Left, Bottom of page). PLOT OF RATE VS. COD, SAME DATA AS FIGURES 2-2 AND 2-3.

The over-all reaction is actually a series of interconnected steps, each of which limits the rate of wet oxidation during a portion of the over-all destruction process. The characteristics of these rate-limiting steps are revealed by replotting the data of Figure 2-2, as is done in Figure 2-3. Plotted in this semi-logarithmic manner, the trend in the (logarithm of) COD is seen to fall along two different straight lines. Occasionally, there are three, but generally the correlation is highly significant when all of the datum points are fitted to two lines. In the language of chemical kinetics, the conformance of rate data to graphical correlation like that exhibited in Figure 2-3 is indicative of a chemical process governed by successive pseudo-first-order rate-limiting steps. The point at which the slope of the trend line abruptly changes marks a transition in the rate-limiting process.

In Figure 2-4, the data of Figures 2-2 and 2-3 have been replotted; the rate (r) is shown as a function of COD and percentage reduction. Figure 2-4 exemplifies the typical behavior observed in hundreds of tests. The rate of wet oxidation (r) decreases linearly with decrease in COD, but at a critical percentage reduction there is an abrupt change in the magnitude of the rate. Beyond the transition, the rate of destruction is much less and decreases much slower with change in COD. Generally, the transition in the rate-limiting step occurs after two-thirds to three-fourths of the organic matter has been destroyed. The transition can, however, be delayed by the use of catalyst until as much as 90 percent of the waste has been destroyed. The rate-limiting processes can also be accelerated by catalysts.

2.3 PROCESS VARIABLES

The rate and extent of wet oxidation depends on a number of factors. The following series of batch tests delineate the principal variables affecting the wet oxidation of shipboard sewage. In these tests, feces were macerated with spent toilet paper and urine to yield a concentrated body sewage.

The standard operating procedure was to preheat 700 to 1000 mℓ water (or a mixture of tapwater and sea water) in a one-gallon, stainless-steel autoclave which was stirred by an impeller rotating at a fixed speed. When the autoclave and its contents had been heated to the desired temperature, a measured volume of the macerated waste was injected into the reactor from a pressurized bomb. Generally, nitrogen was used to inject the waste followed immediately by a known quantity of air. On introduction of the sewage, the temperature of the reactor cooled some 80 to 100 degrees Fahrenheit, but recovered to the desired level within 4 to 7 minutes. Small samples of the liquid-phase slurry were removed periodically during the reaction and assayed for chemical oxygen demand (COD). The temperature of the liquid phase was monitored continuously and controlled within 5°F over essentially all of the sampling interval.

The series of tests established that the rate and extent of wet oxidation was affected by the following process variables:

(1) Temperature. The data presented graphically as Figure 2-5 demonstrates that wet oxidation like most chemical reactions increases with increasing temperature.

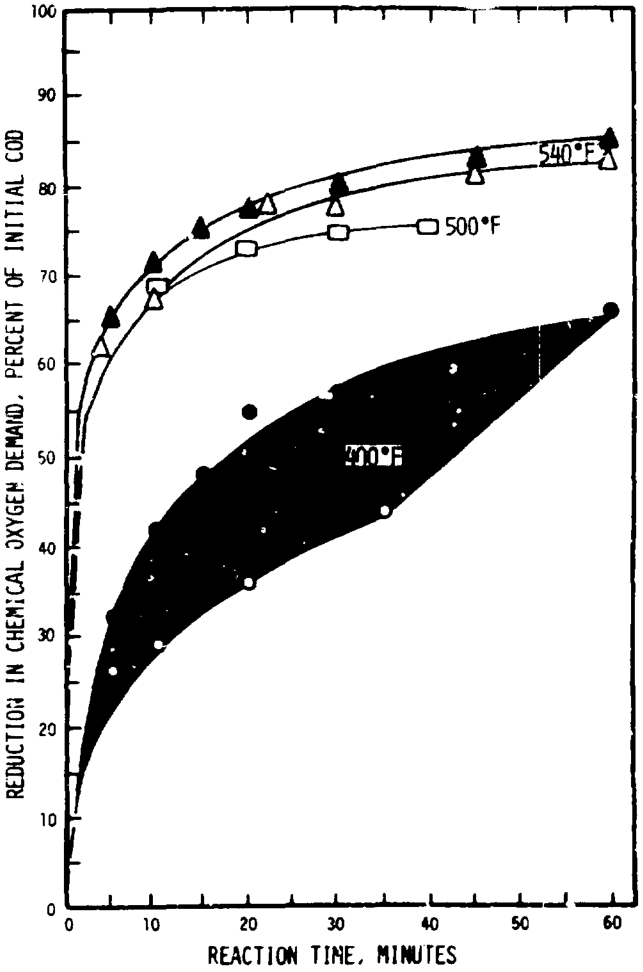


FIGURE 2-5. EFFECT OF TEMPERATURE ON WET OXIDATION OF FECES AND URINE IN TAP WATER (CONDUCTED IN STAINLESS STEEL AUTOCLAVE)

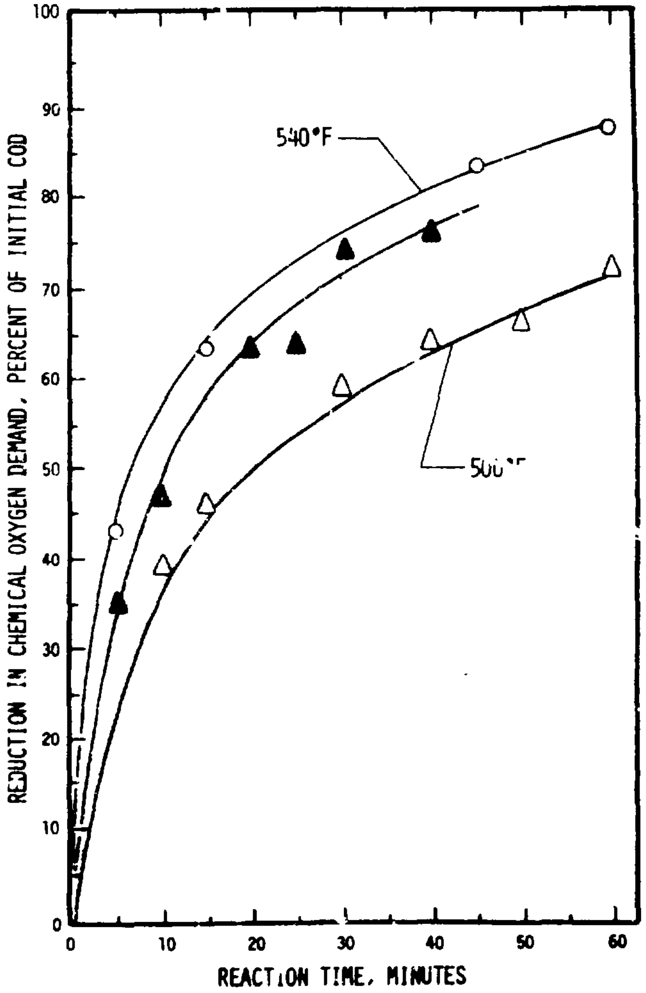


FIGURE 2-6. EFFECT OF TEMPERATURE ON WET OXIDATION OF FECES AND URINE IN 40% SEAWATER (CONDUCTED IN STAINLESS STEEL AUTOCLAVE)

(2) Salinity. Comparison of Figures 2-5 and 2-6 indicates that wet oxidation occurred less rapidly initially in sea water than in tap water, although the difference in efficacy tends to be less pronounced for long durations. Figure 2-7 shows the effect of seawater on the wet oxidation of simulated sewage at 540°F.

(3) Defficiency of Oxygen. As illustrated in Figure 2-8, wet oxidation of simulated sewage does not take place in an oxygen-deficient environment. However, above a threshold level (O_2/COD>0.8), the rate and extent of wet oxidation can not be increased by the use of excess oxygen.

(4) Nature of the Wetted Wall. The rate and extent of wet oxidation can be increased by lining the interior of the stainless-steel autoclave with a porous carbon substance such as felt; see Figure 2-9. However, as can be seen from Figure 2-10, salinity has a strong negative effect even in a carbon-lined reactor.

(5) Acidity. Most natural wastewaters are neutral or alkaline. As a result of wet oxidation organic acids form that cause the effluent to become acidic. In the course of these investigations, it soon became apparent that acid catalyzes wet oxidation. In Figures 2-9 and 2-10 (as well as in Figures 2-5 and 2-6), the shaded bands indicate experiments in which all other conditions were the same but the pH of the influent--the lower pH, the more rapid and the greater the reduction in COD.

In addition to the factors listed above, which were identified before the program began, catalysts proved a significant process variable. Early in the program, catalysts suitable for acidic wet oxidation began to evolve from concurrent related research and were incorporated into the Coast-Guard sponsored investigation. Barber-Colman Co. catalyst 10,480 was evaluated extensively; the results are described in Section 3. Figures 2-2, 2-3, and 2-4, which were presented earlier in this section of the report, were derived from experiments with Barber-Colman Co. catalyst 10,480.

Later in the program, catalysts suitable for use in non-acidic circuits began to evolve from independently-funded research. These led to termination of the investigation of the acid circuit and initiation of the efforts described in Section 4.

The initially approved program plan, the results of which are presented in Section 3, evolved from the foregoing batch experiments. Emphasis was placed on development of a process in which efficient wet oxidation could be accomplished in dilute acid at relatively low temperatures.

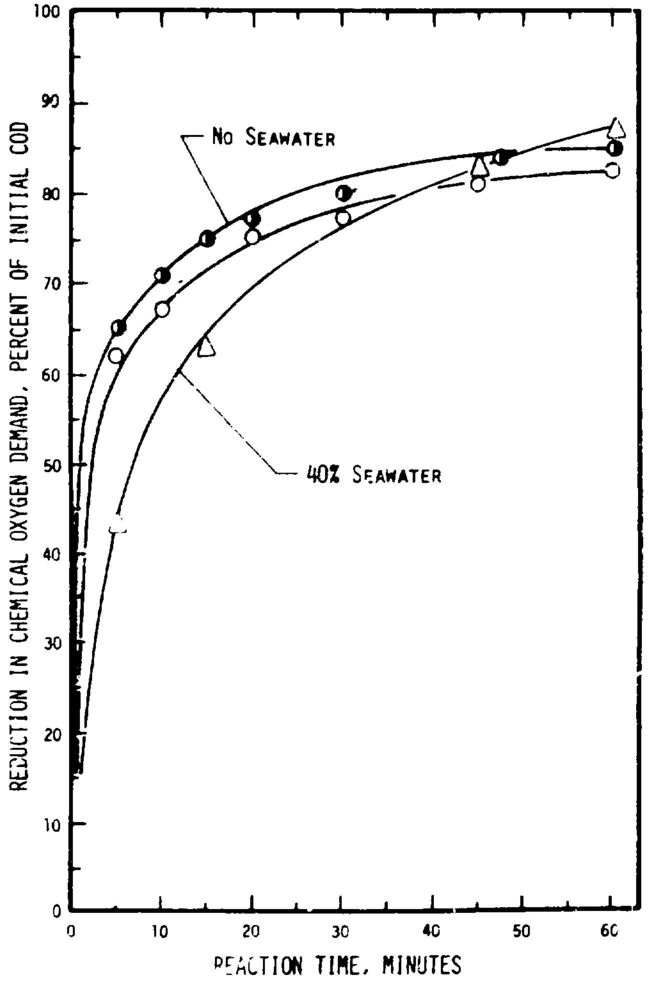


FIGURE 2-7. EFFECT OF SEAWATER OF WET OXIDATION OF SIMULATED SEWAGE. EXPERIMENTS CONDUCTED AT 540°F IN STAINLESS STEEL AUTOCLAVE.

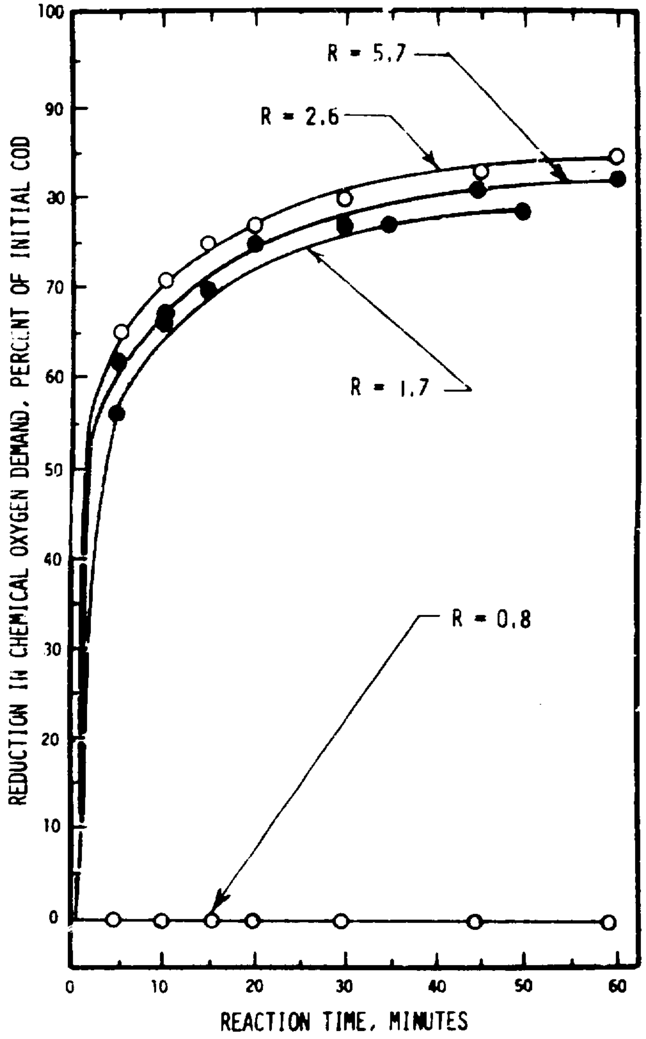


FIGURE 2-8. EFFECT OF RATIO, R, OF OXYGEN SUPPLIED TO OXYGEN DEMANDED ON WET OXIDATION OF FECES AND URINE IN TAPWATER AT 540°F IN STAINLESS STEEL AUTOCLAVE.

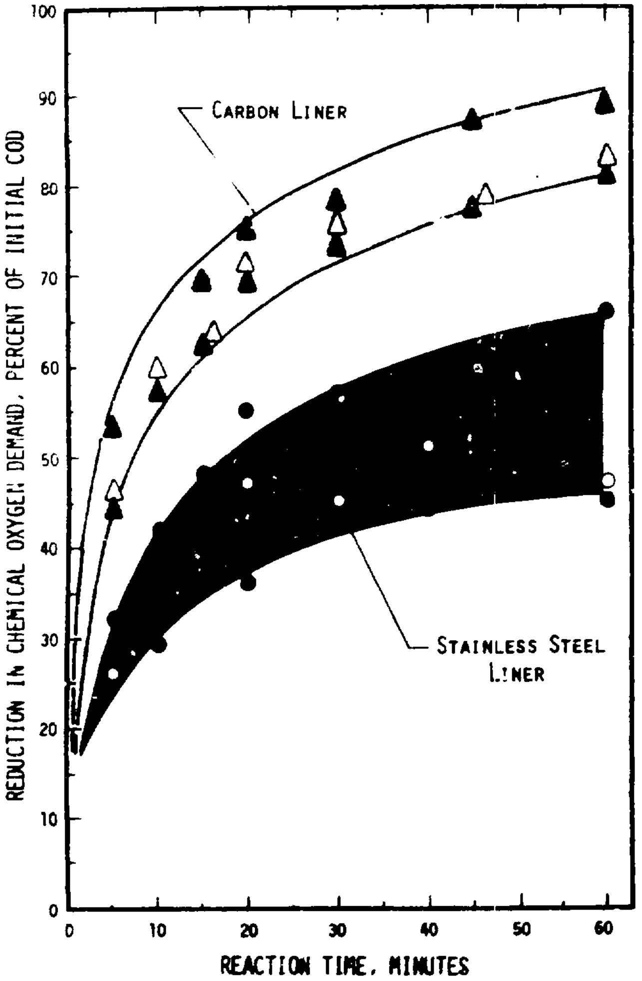


FIGURE 2-9. EFFECT OF LINER MATERIAL ON WET OXIDATION OF SIMULATED SHIPBOARD SEWAGE. EXPERIMENTS CONDUCTED AT 400°F.

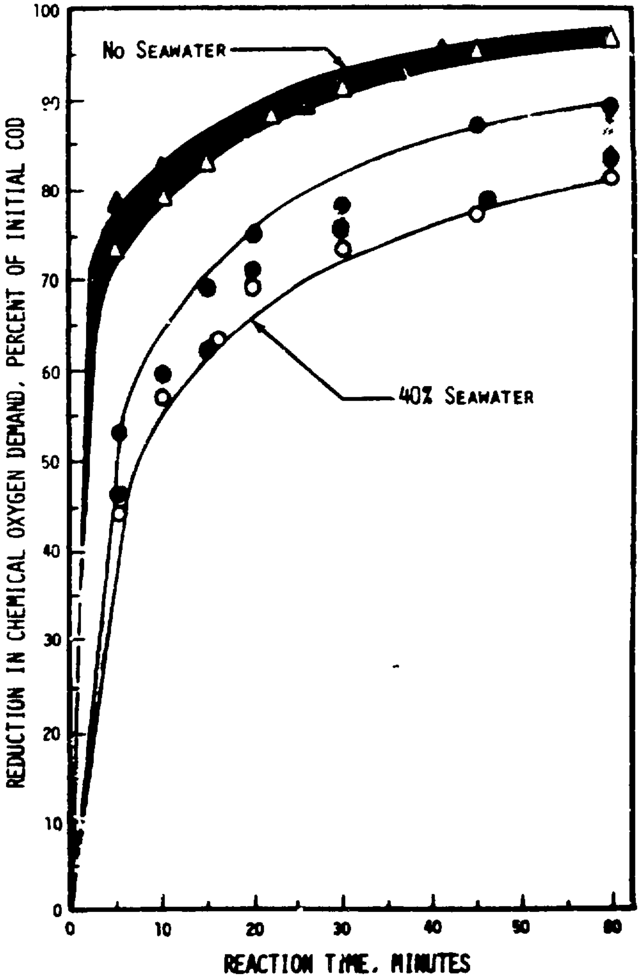


FIGURE 2-10. EFFECT OF SEAWATER ON WET OXIDATION ON SIMULATED SEWAGE. EXPERIMENTS CONDUCTED AT 400°F.

Process variables had been identified that made the goal realistic. For instance, the use of carbon as a lining resulted in more complete wet oxidation of sewage at 400°F than at 540°F in its absence. The properties of water are such that the operation of an autoclave at 540°F requires the confinement of gases--oxygen, nitrogen, and carbon dioxide--and steam at twice the pressure that operation at 400°F entails. Consequently, the ability to perform efficient wet oxidation at comparatively low temperatures is of considerable importance. A carbon-lined reactor made of conventional boiler fittings would be suitable for use at 400°F because the total pressure would be less than 600 psi. On the other hand, an autoclave would have to withstand internal pressures in excess of 1200 psi at 540°F; this would entail specially constructed, heavy walls. Not only would operation at 540°F require heavier, more costly equipment, a substantial volume of air or oxygen must be compressed to pressures in excess of 1200 psi and continually fed to the autoclave. High-pressure compressors and pumps of the type needed would be costly, heavy and require considerable electrical energy to operate--these are important considerations for shipboard usage. Moreover, operation at 540°F results in excessive continual removal of steam in the exiting vapors that must be replaced to maintain that operating temperature. Heat exchanger requirements are considerably greater at 540°F than at 400°F.

2.4 MASS-BALANCE CONSIDERATIONS

Extensive surveys have been conducted in recent years to establish the nature and quantity of shipboard wastewaters. The findings, which are reviewed in following subsections, were used in planning meaningful evaluation tests and in sizing the recommended shipboard wet-oxidation systems.

2.4.1 WASTE GENERATION

Aboard small ships man lives rather Spartan-like, and his daily waste is predictable with reasonable certainty. According to statistics cited in a recent report*, the distribution of the components comprising shipboard wastewaters is as follows:

	Daily Per Capita Mass, Grams	
	BOD	Suspended Solids
Galley Waste	19	12
Laundry Waste	3	4
Body Waste	68	90
	90	106

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*National Academy of Sciences, MRIS Report, A Synthesis of Current Information on Treatment and Disposal of Vessel Sanitary Wastes, July, 1971 (Prepared by Maritime Information Committee, 2101 Constitution Ave., Washington, D.C. 20418).

The above statistics are reported in terms of biochemical oxygen demand (BOD) which is an index of the biodegradable matter contained in the waste. The BOD is primarily important in assessing the environmental impact of discharging a wastewater or treatment effluent. The chemical oxygen demand (COD) of the wastewater, on the other hand, is a more useful index for wet oxidation. Both COD and BOD are reported as mg/ℓ O. The COD of most raw wastes (natural substances) is greater than the BOD.

a. Human Excretion.

Because about 75 percent of the BOD and 85 percent of the suspended solids originate from the toilets and urinals, the body sewage is the essential component of the combined wastewater. Body waste is defined in the same quoted source* as a mixture of urine, feces, and paper which may vary as follows:

	Daily Per Capita Mass, Grams		
	Minimum	Maximum	Average
Urine	1198	1530	1416
Feces	75	180	170
Paper	18	100	34
	1291	1810	1620

See Section 6.2 for the chemical analyses of feces and urine.

b. Galley Waste.

According to another recent survey[†], the daily garbage generated aboard naval vessels is about 1.1 lb per man. In addition, 1.9 pounds of trash--paper, wood, glass, metals and plastics--are discarded daily by each man aboard.

c. Laundry Waste.

According to Gauthey and Ventriglio, about 0.04 pounds of detergent is discharged daily in the wastewater contributed by one person aboard ship.

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*National Academy of Sciences, MRIS Report

[†] Cdr. J. R. Gauthey and F. J. Ventriglio, "The Naval Ship Systems Command Research and Development Program On Pollution Abatement," ASME Publication 73-ENAs-41, presented before the Intersociety Conference on Environmental Systems, San Diego, July 16-19, 1973.

2.4.2 WATER USAGE

Aboard ships the amount of water consumed daily varies widely. While at sea, fresh water is premium; in port, municipal water supplies often are tapped. The urinals and water closets aboard contemporary ships are flushed by whatever water is beneath the vessel--brackish or salt water is pumped aboard for use as flushant. According to Gauthey and Ventriglio*, the following volumes of wastewater are generated aboard ship daily:

Sewage	6 to 26 gal/man/day
Combined wastewaters from wash basins, showers, laundries, dishwashers and galley drains	30 gal/man/day

The Coast Guard has established that 700 gallons (or 35 gallons per man) of combined wastewaters are generated daily aboard small patrol boats with a nominal complement of 20 men and that the average BOD of these wastewaters is 500 mg/ℓ O.† These values were established as design specifications for this program.

The normal operation of a vessel generates large quantities of oil-contaminated wastewaters. A destroyer in port accumulates in its bilge 3500 gallons daily of water containing about 0.1% oil (of which 90% is free); whereas the accumulation of oily water in the bilge of an aircraft carrier at sea is estimated to be 210,000 gallons daily. Ballasting fuel tanks generates about one-tenth of the total bilge wastewaters.

2.4.3 OXYGEN REQUIREMENTS

As a rule of thumb, a gram of dry organic matter requires one gram of oxygen for complete combustion; that is to say, one gram of oxygen is consumed in converting all of the carbon to CO_2 and all of the hydrogen to H_2O. The rule holds for nearly all natural biological substances and most of the organic compounds found in domestic wastewater.††

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* Work cited on page 2-12.

† T.S. Scarano and R.W. Ard, Jr. "Coast Guard Research and Development in Shipboard Wastewater Treatment", ASME Publication 73-ENAs-37 presented before the Intersociety Conference on Environmental Systems, San Diego, July 16-19, 1973.

††F.J. Zimmermann, "New Waste Disposal Process", <u>Chemical Engineering</u>, August 25, 1958, pp. 117-120.

In this program, oxygen supply also was computed based on influent COD. As stated in Section 2.3, the rate and extent of wet oxidation is not affected by the amount of oxygen made available above a threshold level (O_2/COD>0.8).

In terms of air flow, at 70°F,

$$1\ \text{scfm air} \equiv 7900\ \text{mg/min O.}$$

2.5 FUNDAMENTALS PERTAINING TO THERMAL BALANCE

The sketch provided in Figure 2-11 shows the flow of matter and heat energy through the particular type of reactor used in this program. The practical application of wet oxidation depends on efficient heat exchange between the incoming wastewater (feed) and the hot exiting vapor, steam, gases and liquid effluents. Otherwise, the energy required to maintain the reactor at the (elevated) operating temperature is prohibitive.

Heat is removed from the reactor in the vapor-phase effluent (Q_1), in the liquid-phase effluent (Q_2) and through the body of the reactor (Q_3). The energy required to sustain the reaction (Q_8) is

$$Q_8 = (Q_1 + Q_2 + Q_3) - (Q_4 + Q_5 + Q_6 + Q_7), \qquad (2\text{-}1)$$

where Q_4 is the sensible heat of the feed (incoming wastewater);
Q_5 is the sensible heat of the incoming compressed air;
Q_6 is the heat generated in stirring the reacting wastewaters; and
Q_7 is the heat liberated in the combustion of the organic wastes.

Each of these energy components is discussed in following subsections.

2.5.1 ENERGY FLOW FROM THE REACTOR

Heat is leaked from the reactor through its body and intentionally withdrawn as sensible heat in the effluents. All of these energy flows are potential sources of heat loss.

a. Q_1, Heat Contained in Exiting Vapor-Phase Effluent.

Exiting gases from the reactor are saturated with steam and, consequently, contain considerable heat. The quantity of energy withdrawn as steam depends on the temperature of the reactor and the flow of gases which in turn is directly proportional to the influent strength, i.e., the COD of the feed. Figure 2-12 shows a series of isotherms covering the ranges of temperature, air flow and COD of interest.

In multiple-compartment reactors, most of the heat is liberated in the compartment (s) nearest to the feed inlet; and the rear of the reactor tends to be colder than the front (feed). Generally, the flow of air (and other

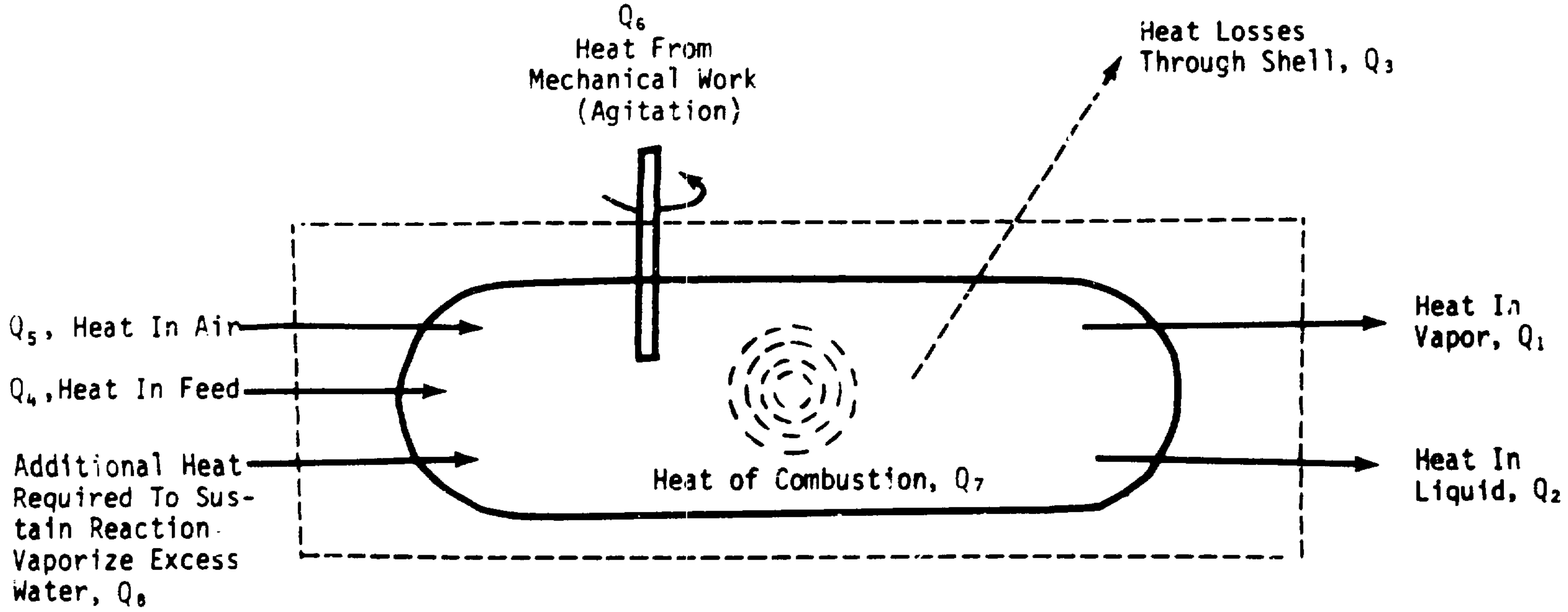

FIGURE 2-11. FLOW OF MASS AND ENERGY THROUGH CONTINUOUS-FLOW WETOX REACTOR.

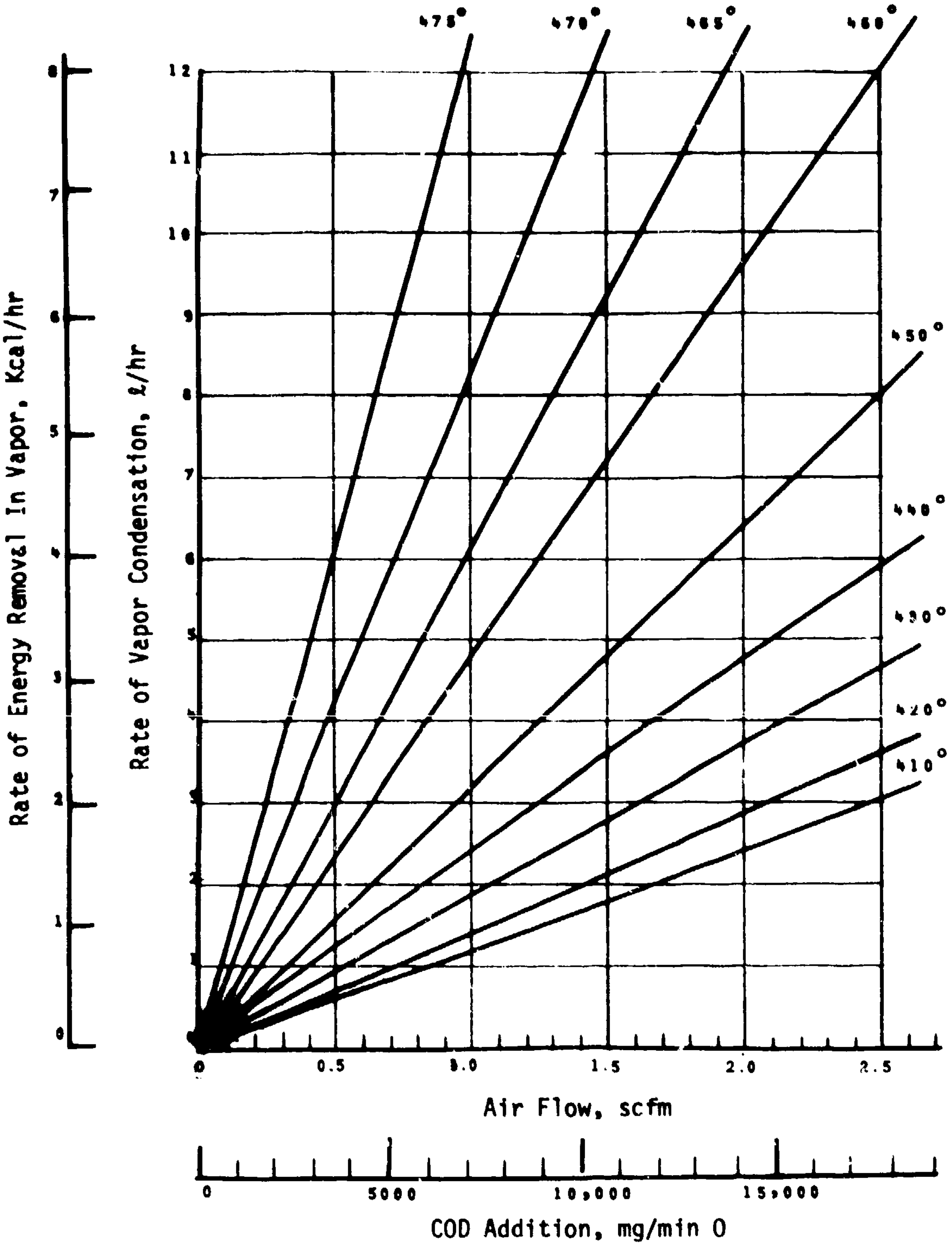

FIGURE 2-12. SERIES OF ISOTHERMS SHOWING RATE OF CONDENSATION AND ENERGY REMOVAL CORRESPONDING TO GIVEN FLOW OF SATURATED STEAM

gases) is cocurrent; and, thus, the spent gas (and steam) is withdrawn from the coldest end. As can be seen from Figure 2-12, the steam content of the vapor phase can vary widely in the temperature range used in low-pressure wet oxidation.

The nature of water is such that in low-pressure, wet-oxidation processes like the WETOX the specific enthalpy does not vary significantly with the operating temperature: the temperature range of interest coincides with that at the top of the steam dome in the familar Mollier Diagram (enthalpy-entropy plot). The energy of saturated steam is greatest at 450°F and changes very little between 400 and 500°F--at both higher and lower temperatures, the enthalpy of saturated steam is less.

b. Q_2, Heat Contained In Exiting Liquid-Phase Effluent.

The liquid-phase effluent from the reactor is comprised of the spent solids, dissolved salts and the bulk of the water that entered in the feed. Due to the removal of steam from the reactor in the exiting gases, the volume of liquid effluent is often significantly less than the volume of feed. In the treatment of present-day shipboard wastewaters, the volume of liquid effluent is essentially the same as the influent volume; because the flow of air is very small. Steam condensation from the treatment of municipal sewage sludge, on the other hand, can range from 20 to 50 percent of the influent volume.

c. Q_3, Heat Conduction From the Reactor; Convection Losses to Ambient

There is, of course, a steady flow of energy out of the reaction chambers through the walls of the reactor. In most cases, the outer shell of the reactor is insulated and routinely about 100°F. There is a steady-state loss of heat to the atmosphere by convection. See Section 6.4.2 for the results of specific computations.

2.5.2 ENERGY ADDED IN FEED

Sensible heat is added to the reactor in the incoming masses of wastewaters and, to a lesser extent, of the compressed air.

a. Q_4, Sensible Heat of the Feed.

Significant portions of the sensible heat contained in the effluents from the reactor are transfered to the incoming wastewater (feed). Generally tube-and-shell heat exchangers are used in wet-oxidation systems.

In the design of a heat exchanger for treatment of present-day, shipboard wastewaters, there are two major considerations. First, the design should be such that as much energy as possible is recovered from the effluents. Secondly, the liquid should be cooled to 212°F or less to prevent it from flashing to steam upon depressurization. (The liquid also must be cooled somewhat before filtration.)

One possible design that accomplishes these objectives is a series exchanger in which the feed is contacted first with the liquid-phase effluent and the effluent is cooled to the lowest practical temperature. The feed then passes through a second section in which it is contacted with the vapor-phase effluent and the feed is heated to the maximum practical temperature.

In the treatment of concentrated wastewaters, the amount of steam exiting from the reactor may exceed the "cooling power" of the feed. In other words, all of the steam can not be condensed. If the system requires further condensation to maintain a water balance, a third section can be added to the exchanger and additional cooling water pumped aboard.

If the influent strength is not too great, the venting of some steam may be desirable. For example, in the closed-loop treatment scheme discussed in Sections 4 and 6, steam losses are advantageous because they compensate for water build-up from the decomposition of urine and feces. Partial balance also can be achieved in some cases by operating the reactor so that the rear (exit) end is held purposely as cold as possible (See the discussion in Section 2.5.1a.).

In a practical shipboard system, heat-exchanger efficiency probably can not exceed 70-85 percent, because the treatment system is weight-limited. (As the temperature of the heated feed approaches the temperature of the cooled effluent, the temperature difference across the walls of the exchanger approaches zero; and the area requirement for additional exchange of heat approaches infinity.)

b. Q_5, Sensible Heat of Input (Compressed) Air.

Depending on the source, the sensible heat of the input air can range from nil to a moderate amount. Certain types of compressors deliver air as hot as 350°F. However, unless the wastewater is especially strong, the amount of air supplied is so much less than the mass of influent water that the contribution of the compressed air is negligible by comparison. For example, in Section 6.2, a detailed balance is presented for a system in which the influent strength is about twice that of present-day shipboard sewage. The mass of air supplied to the reactor is one-fortieth that of the water.

2.5.3 ENERGY GENERATED IN THE REACTOR

Wet oxidation can be carried out autogeneously. In the treatment of paper-pulp waste, the heat liberated in large reactors is sufficient to sustain the process. Potentially, wet oxidation could be used to generate useful electrical energy. In the treatment of municipal sewage sludges, surplus energy has been used to power the electrical motors of the air compressor.

a. Q_6, Heat Generated in Agitation.

In the processes evaluated in this program, wet oxidation was accelerated by continuously stirring the reacting wastewaters. A portion of the mechanical work expended in this agitation of the reactants is converted to heat. A mechanical stirrer powered by a one-horsepower motor releases 2545 BTU per hour to the liquid.

b. Q_7, Heat From Combustion.

Considerable energy is released in the combustion of most organic substances. The so-called fuel value of settled sewage solids is typically 10,000 BTU per pound of volatile solids*. Raw primary sewage sludge has a volatile-solids content of about 70 percent**. Solids from shipboard sewage probably are equivalent in most respects to raw primary sewage sludge.

In wet oxidation, however, complete combustion is seldom obtained; 85-90 percent reduction in COD is typical. Consequently, in this program, the heat of combustion was taken as 6000 BTU per dry pound of organic solids.

2.6 METHODS OF CHEMICAL ANALYSIS

In the program, chemical analysis was accomplished by the standard methods listed in Table 2-1 unless otherwise stated in the text.

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* W.J. Weber, Jr., Physicochemical Processes for Water Quality Control, published by Wiley-Interscience, N.Y., N.Y., in 1972.

**D.P. Chynoweth and R.A. Man, "Volatile Acid Formation in Sludge Digestion", chapter in Anaerobic Biological Treatment Processes, Advances in Chemistry Series 105, published by the American Chemical Society, Washington, D.C., 1971, page 42.

TABLE 2-1

STANDARD METHODS USED IN CHEMICAL ANALYSIS

General Description (Type, Purpose, etc.)	Source of Method
Chemical Oxygen Demand, (COD); Dichromate Reflux	APHA-AWWA, Standard Methods for the Examination of Water and Wastewater, 13th Edition, 1971, Part 220, pp 495-499.
Chemical Oxygen Demand (COD); Dichromate Reflux in Presence of Excessive Chloride	EPA Manual 16020-07/71, Methods for Chemical Analysis of Water and Wastes, 1971, STORET No. 00340, pp 24-28
Biochemical Oxygen Demand (BOD)	APHA-AWWA, Standard Methods for the Examination of Water and Wastewater, 13th Edition, 1971, Part 219, pp 489-495.
Dissolved Oxygen (Modified Winkler with Full-Bottle Technique)	EPA Manual 16020-07/71, Methods for Chemical Analysis of Water and Wastes, 1971, STORET No. 00300, pp 53-59.
Nitrogen-Ammonia (Distillation-Titration Procedure)	EPA Manual 16020-07/71, Methods for Chemical Analysis of Water and Wastes, 1971, STORET No. 00610, pp 134-140.
Chloride (Mercuric Nitrate Method)	APHA-AWWA Standard Methods for the Examination of Water and Wastewater, 13th Edition, 1971, Part 112B, pp 97-99.
Solids (Suspended)	EPA Manual 16020-07/71, Methods for Chemical Analysis of Water and Wastes, 1971, STORET No. 00530, pp 278-279.
Coliform (Total, Membrane Filter Procedure)	APHA-AWWA, Standard Methods for the Examination of Water and Wastewater, 13th Edition, 1971, Part 408A, pp679-683.

SECTION 3

EXPERIMENTAL EVALUATION OF AN ACID CIRCUIT FOR WET OXIDATION (AND OVERBOARD DISCHARGE) OF SHIPBOARD WASTEWATERS

The initially proposed program evolved about an experimental evaluation of the wet oxidation of acidified shipboard sewage and other wastes. Direct (overboard) discharge was contemplated. Several series of continuous-flow tests were conducted. Analysis of the test results indicated that acidic wet oxidation in some respects was not as promising as an alternative which had evolved during the testing period from concurrent related research. Consequently, the evaluation of the acid circuit was terminated in May 1973--seven months after initiation of technical effort--and an investigation of the alternative (ammoniacal, closed-loop wet oxidation) was commenced.

3.1 DESCRIPTION OF TEST EQUIPMENT AND PROCEDURE

The tests described in this section--the evaluation of continuous-flow, acidic wet oxidation--were conducted in the Barber-Colman Co., Resource Recovery Systems Division, pilot plant at Irvine, California.

3.1.1 PILOT-PLANT FLOW CHART

A schematic flow chart of the pilot plant is shown in Figure 3-1. The assemblage of equipment includes the essential devices to

(1) macerate biowaste and blend it with water into simulated wastewater,

(2) feed (pressurized) reactants (air and wastewater) to the reactor,

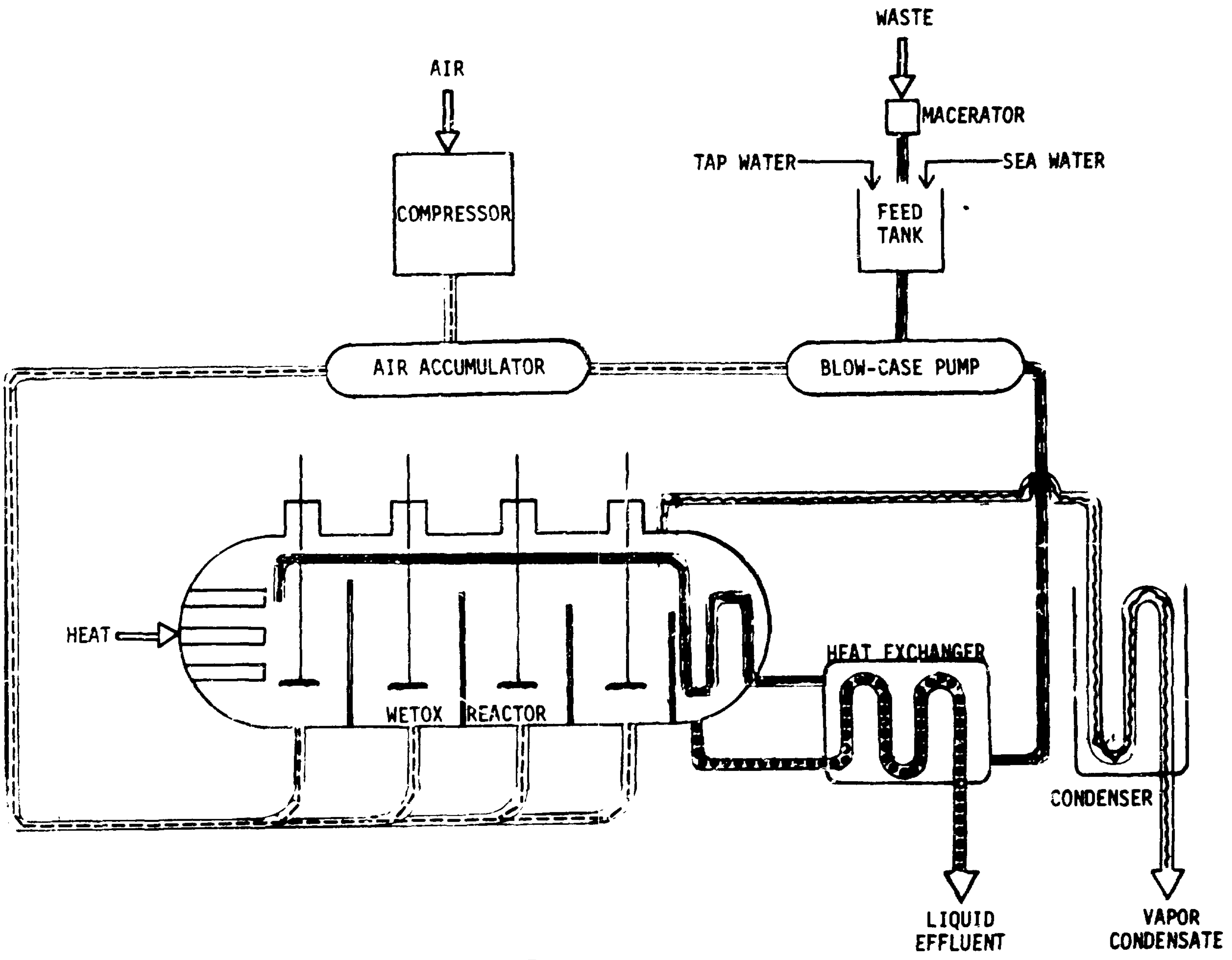

FIGURE 3-1. FLOWCHART, WETOX PILOT PLANT.

(3) perform wet oxidation in a continuous-flow reactor at elevated temperature and pressure,

(4) sample the reactor during the test (while it is at elevated temperature and pressure),

(5) control and monitor the important operating conditions such as temperature and pressure,

(6) discharge and store (depressurized) liquid-phase autoclave effluent, and

(7) condense and store steam and volatile matter vented with the spent gases from the reactor.

a. Preparation of Influent

Accumulated feces and urine were macerated and simultanteously blended with tap water or a mixture of tap water and sea water in a commercial-size garbage disposer. Tap water was supplied by the Irvine Ranch Water District (IRWD) which derives most of its water from the Colorado River. The IRWD tap water is classed as extremely hard and contains an appreciable quantity of dissolved salts. Sea water was obtained from the Newport Bay, on the California coast of the Pacific Ocean.

b. Storage of Influent

Influent for each test was blended the morning of the test and stored in a 50-gallon head tank. The bottom of the head tank is connected to a centrifugal pump whose discharge is divided between a return to the top of the head tank and the inlet to the blow-case pumps. Most of the discharge is returned to the head tank which also contains a constantly operating mechanical stirrer--circulating and stirring the influent continually in this manner assures that a constant COD is being fed to the reactor throughout the test.

Generally the addition of sulfuric acid was made to the head tank at the beginning of the test. Reagent-grade acid was used and was diluted with water before adding it to the tank.

c. Feed System

Influent is added to the reactor by a blow-case pumping system which discharges influent one liter at a time into the first compartment of the reactor. The "pump" is a stainless-steel, one-liter, vertically mounted, cylindrical bomb containing level-sensing, conductivity probes at the top and at the bottom. The inlet and outlet to the bomb are through pressurized air-activated valves. These valves are regulated by an electronic activating-and-timing circuit which governs the feed system and establishes the pumping cycle. Typically the pumping cycle is about two minutes in duration and consists of four steps:

(1) Waste In. A signal from the timer opens the inlet valve, and influent flows into the bomb until the upper conductivity probe signals the valve to close. (The bomb now contains one liter of waste.)

(2) Air In. After a lapse of a few seconds, a signal from the timer activates another valve; air flows into the bomb compressing the influent under 700-800 psi.

(3) Waste Out. After a few seconds, the outlet valve is opened and the waste is injected into the reactor. The lower conductivity probe signals the electronic circuit to close the outlet valve following the discharge of the influent. (Generally the waste traverses through a heat exchanger before entering the first compartment of the reactor.)

(4) Air Out. Following the discharge of the influent, the signal which shuts off the outlet valve also vents the compressed air from the bomb and, thus, prepares it for the next cycle.

d. Air System

Compressed air is derived for the blow-case pumps and the reactor from a common compressor. Air from the compressor is stored in a 2-ft long, 6-in. dia. cylinder or accumulator and dispensed from it as needed. The pressure of the accumulator is maintained between 700-850 psi; whenever, the pressure falls below that level, a mercury switch activates the air compressor.

Air is supplied to the reactor from an air manifold through a flowmeter. Individual valves in the manifold determine the flow to individual compartments. Air enters each compartment of the reactor through separate inlets located directly beneath the impeller.

e. The Wet-Oxidation Reactor

Wet oxidation is accomplished in a multiple compartment reactor, i.e., a tubular shaped autoclave whose long axis of symmetry parallels the horizon and whose interior is partitioned into a number of compartments. Detailed drawings and discussion of the construction of one such reactor are presented in Section 5. In following paragraphs, the chemical aspects of the reactor are outlined.

Basically the Barber-Colman Co. WETOX reactor is a pressurized version of the continuous stirred tank reactor--the CSTR widely used in chemical engineering. The interior is divided into approximately equally sized compartments, each containing a vertically mounted agitator and separate air inlet. The reactants pass continuously through the isolated compartments of the multiple chambered reactor. The flow of reactants is much slower than the speed of mixing in the constantly stirred chambers or tanks, and incoming fluid immediately blends with the much larger mass of constantly stirred liquid already present in the vessel. As fresh wastewater is added to the first compartment, the level of the agitating liquid rises above the overflow opening in the barrier between the first and second compartments--a portion of the liquid spills over into the second compartment and in so doing causes a portion of the liquid in the second compartment to spill into the third and so on throughout the reactor. In this manner, the wastewaters cascade from compartment to compartment during treatment undergoing intimate mixing continuously. At steady state, the concentrations of the reactants in individual compartments are invariant. The rate of reaction and extent (percentage reduction) depend on the mass flow through the reactor and the operating conditions.

Most of the tests described in this section were performed in a 4-compartment, 10-in. OD reactor, 40 in. long. The reactants are mixed sequentially in a series of four mixing chambers. The interior of the reactor is subdivided into 5 chambers, four of which are approximately equal in size and contain agitators. The fifth chamber located at the rear of the reactor is smaller than the others; it contains no agitator and serves as a settling basin. Automatically controlled, separate vents for the vapor and liquid phases are located in the settling basin. The chambers or compartments are formed by four approximately, equally spaced vertically positioned plates of 1/4-in. thick titanium metal. Each plate (partition) is fastened securely to the periphery of the reactor shell to form a water-tight dam. Each partition has a small notch or weir at the liquid level, approximately 7.5 inches above the floor of the reactor. The weir in each partition is 0.25 in. lower than that in the preceding wall, causing liquid to cascade from compartment to compartment as fresh influent enters the first compartment.

f. Condensation of Exiting Vapors.

Compressed air is fed continually to each compartment in proportion to the input COD. The incoming air is introduced through small openings in the floor of each compartment beneath the liquid. Rising bubbles of gas are mixed thoroughly with the agitating liquid and become saturated with steam (and volatile organic species). As air and wastewater are added to the reactor, its total pressure increases until it exceeds the desired maximum and a pressure-regulated valve is actuated. Each time the valve opens, steam (water-saturated gas and vapors) passes from the reactor through the vapor vent generally located in the rear. All exiting gas (vapors and steam) are passed through a 100-ft coil of copper tubing submerged in water maintained at 70-75°F. The volume of vapor condensate is measured for each test and the COD of a representative sample is determined. The amount of vapor condensate collected during a test is directly proportional to the air flow and temperature of the exiting vapor.

g. Discharge and Storage of Liquid Effluent

The liquid-phase discharge from the reactor is a slurry of insoluble (mainly inorganic) solids suspended in a liquor containing residual water-soluble organic matter as well as dissolved inorganic salts and acid. This liquid-phase slurry is depressurized by a separate liquid let-down system and collected in a storage tank.

The liquid let-down system is activated by a conductivity probe located in the settling basin at the rear of the reactor adjacent to the fourth mixing compartment. Whenever, the level of liquid in the settling basin rises above the probe, a ball-cock valve opens for a timed interval and liquid is forced out of the reactor. The liquid discharge from the autoclave generally passes through a tube-and-shell heat exchanger countercurrent to the flow of influent. Liquid enters the effluent storage tank at about 160°F.

3.1.2 TEST PROCEDURE

Each individual test was performed during the course of a working day--an 8-to 9-hour period encompassing influent preparation, equipment start-up, preheating the reactor, treating the influent, sampling and shut-down. Typically 35 to 40 gallons of influent were pumped to the reactor during the course of each test.

The influent was prepared for test by macerating accumulated feces, toilet paper and urine in a commercial garbage disposer, adding acid, and storing the acidified influent in a 50-gal feed tank.

Preheating the reactor to temperature requires about one hour and is accomplished by electrical heaters. Six electrically heated rods protrude into the first compartment of the reactor. Each is about 1 in. OD and 10 in. long.

The nature of wet oxidation is such that in the reactors used in these investigations a period of from one to two hours was required to achieve 95 percent of steady state. That is to say, influent must be pumped to a preheated reactor (maintained at constant operating conditions) for one to two hours before the concentrations of the reactants become sufficiently invariant to warrant sampling. A mathematical derivation of the time to reach steady state is presented in Appendix A; the resulting formulas* were used to guide the continuous-flow tests.

After reaching a steady state, the contents of each compartment and of the feed tank were sampled hourly. Generally 3 to 5 hourly samples were taken from each sampling station. All samples were assayed for chemical oxygen demand (COD) and acidity. Some samples were analyzed for other constituents as well; these are discussed in later sections.

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*Appendix B describes the method used to determine residence time which is essential to estimating not only the time to reach steady state but also the rate of reaction.

Samples of the liquid phase can be removed from any of the mixing compartments as desired during the test by manually operated sampling tubes. By opening a small-bore valve, liquid is forced under pressure from the center of the reactor well below the liquid level. The sample passes through 1/8-in. OD titanium tubing into a water-cooled condenser. The superheated liquid is chilled to about 180°F and collected in a standard glass-stoppered BOD bottle.

The temperature of each reaction chamber is recorded continuously on a multiple-point strip chart. At steady state, the temperature of individual compartments does not vary more than five Fahrenheit degrees. In some of the tests described in this section, there was, however, a pronounced temperature gradient through the reactor. That is to say, the heated first compartment was hotter than the other unheated compartments. The maximum gradient from the front to rear compartment was 30 to 50°F.

The reactor is fed by the previously described blow-case pump subsystem which injects one liter of influent into the first compartment during the 20-second injection period of an approximately 2-minute pumping cycle. The introduction of the cold feed causes the temperature of the first compartment to drop about 5°F momentarily, but the input from the electrical heaters is sufficient to reheat the liquid to the desired temperature before the next injection of influent. Thus the tracing of the temperature of the first compartment, as continuously recorded on the strip chart, has a characteristic sinesoidal shape. This chart can be utilized in determining the rate of influent addition to the reactor as well as recording the total volume of influent added to the reactor during a test. A typical tracing of the first-compartment temperature is shown in Figure 3-2.

The air flow is monitored by reading and adjusting the flowmeter as needed. The flow of air does not vary more than 2-3 percent during a test.

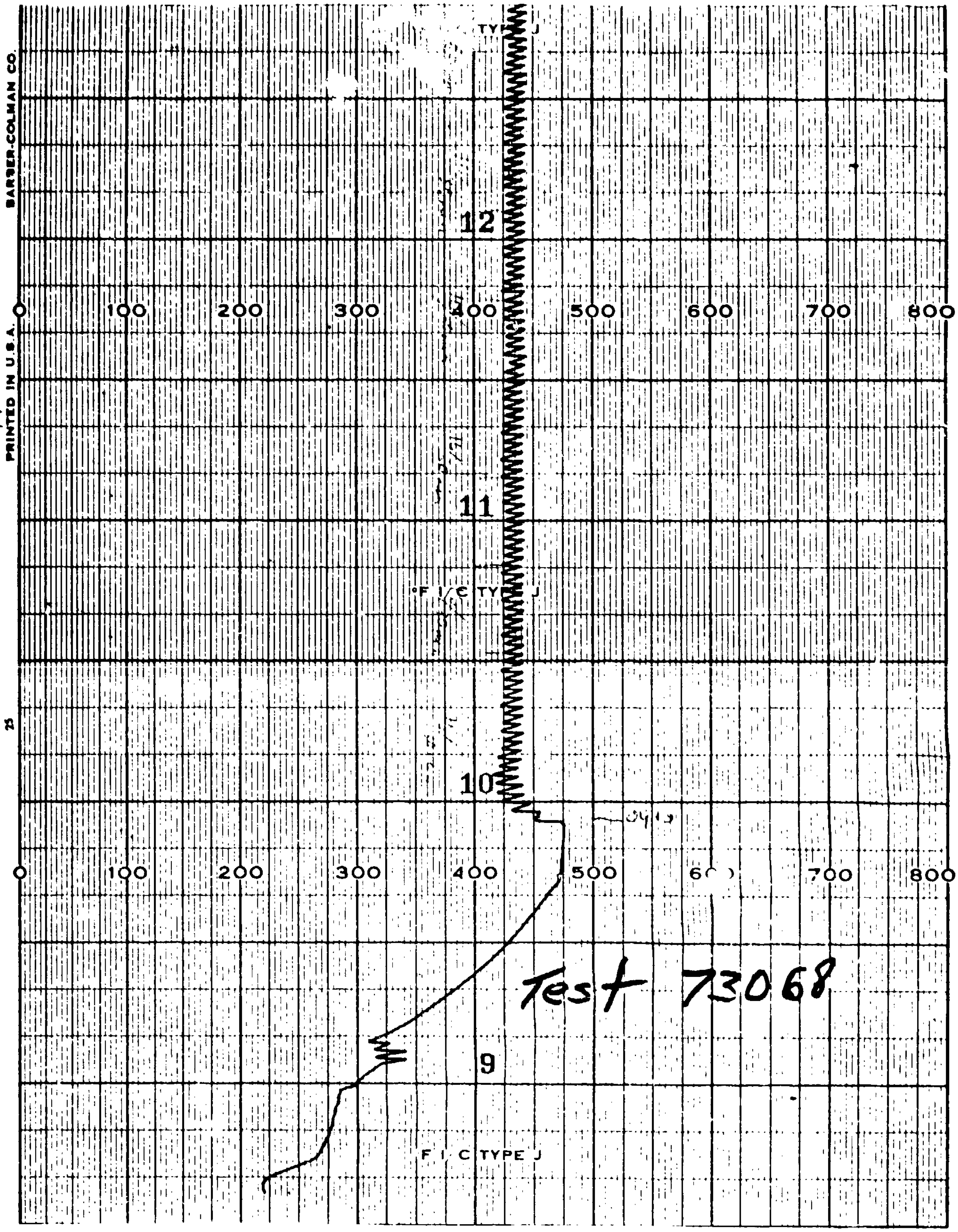

FIGURE 3-2. TEMPERATURE OF COMPARTMENT ONE.

3.2 COMPILATION OF TEST RESULTS

Twenty-two tests (on simulated shipboard sewage) were conducted in the evaluation of the acid, direct-discharge circuit. Brief summaries of these tests are presented in following subsections. A complete report is presented in Appendix C--a chronology which includes the purpose of individual tests, description of the test procedure, tables summarizing the pertinent operating conditions and chemical analysis of hourly samples, any unexpected perturbations and relevant observations, and any changes in equipment and flow of reactants in the process. A tabular compilation of the test results and pertinent operating conditions also is included in Appendix C (Section C.5).

An additional three tests were conducted during the same time period in which simulated bilge water, shipboard laundry wastewater and galley waste were subjected to continuous-flow wet oxidation. These tests, which were funded by the U.S. Navy, are described in Appendix D.

An important series of batch experiments is described in Appendix E. The series was conducted in the presence of Barber-Colman Co. catalyst 10,480 and exemplifies the apparent role of the wetted wall in wet oxidation. Other batch tests pertaining to the acid circuit are described in Appendix C (Section C.2) and in Section 2.2 of the main report.

The evaluation of the continuous-flow tests on simulated sewage is facilitated by subdividing the tests into two groups--a test series conducted in a carbon-lined reactor and a test series conducted in an unlined reactor. (This division of the tests into two groups is a requisite step in the statistical analysis presented in Section 3.3 for reasons which are discussed in that section.)

3.2.1 TESTS CONDUCTED IN A CARBON-LINED REACTOR

In this series of tests, wet oxidation was effected in a carbon-lined, 4-compartment reactor which was operated at fixed temperature: that is to say, in each test the temperature of individual compartments was the same. As only the first compartment is externally heated, there is a temperature gradient from the front to the rear. (The temperature gradient is especially pronounced when, as was the case in this series, the reactor is operated in conjunction with an internal heat exchanger.) The speed of agitation in the mixing chambers was also held constant in this series; all agitators rotated at 800 rpm.

Each compartment of the reactor contained platelets of 1/4-in. thick porous carbon attached to the walls of the reactor and the barriers between compartments. Initially 15 to 20 Sq. in. of each mixing chamber was covered with carbon. Later on, the amount of carbon was increased tenfold. The analysis of the test data indicates that the variation in the amount of carbon did not affect process efficacy significantly.

In individual tests, the levels of three variables--salinity of the influent, the presence (or absence) of Barber-Colman Co. catalysts, and acidity--were varied intentionally. The operating conditions and mean percentage reduction in COD are listed in Table 3-1 for each test of the series. The influent COD and the supply/demand ratio of oxygen (O_2/COD) varied somewhat but did not significantly affect the results.

The mean residence time was held constant in this series of tests and was about 15 minutes per compartment. Based on the means of hourly samples from the second, third and fourth compartments, the percentage reduction in COD was calculated for 30,45 and 60 minutes of treatment. The resulting values are listed in Table 3-1 and are used as response parameters in the statistical analysis presented in Section 3.3.

Percentage reduction in COD ranged from about 65 to nearly 90 percent after 60 minutes treatment in the 4-compartment reactor. The least reduction was accomplished when treating influent containing seawater; the most reduction was accomplished in the treatment of non-saline influent wet-oxidized in the presence of Barber-Colman Co. catalyst 10,480.

3.2.2 TESTS CONDUCTED IN UNLINED (TITANIUM) REACTORS

Eleven tests were conducted in continuous-flow reactors, the interiors of which were unlined. That is to say, in these tests unlike those previously described in Section 3.2.1, no porous carbon or other ceramic substance was affixed to the wetted wall of the reactor. For reasons which are discussed later (in Section 3.3.3), it is advantageous to perform a separate evaluation of these tests.

Data from the tests in unlined reactors are summarized in Table 3-2. In the series, four principal variables were varied intentionally:

- o Temperature of the reactor
- o Residence time (per compartment)
- o Salinity of the influent
- o Barber-Colman Co. catalyst 10,480

The levels of the other principal variables--acidity, oxygen supply, and stirring speed--were fixed within a range known to produce a constant effect on the percentage reduction in COD.

The level of salinity and the utilization of Barber-Colman Co. catalyst 10,480 greatly affected the percentage reduction in COD. For example, at the end of 60-minutes over-all residence in the reactor, in the presence of the catalyst, 89.1 pct of the COD contained in a tap-water influent was reduced; whereas, in the absence of the catalyst, about 75 pct of the COD was reduced in influent comprised of 1 part sea water and 2 parts tap water.

TABLE 3-1

OPERATING CONDITIONS AND RESULTS FOR TESTS CONDUCTED IN A CARBON-LINED REACTOR

Test No.	Mean Temperature, °F All Compart's*	Salinity**	Acidity g/ℓ H_2SO_4	Acidity Effl. pH	Catalyst 10,480	Influent COD, mg/ℓ O	O_2/COD	Percentage Reduction In COD After 30 min	Percentage Reduction In COD After 45 min	Percentage Reduction In COD After 60 min
72346	445	1/3 SW	6	1.5	No	1880	8	62.4	64.3	65.6
72347	445	1/6 SW	6	1.5	No	1500	10	67.8	60.8	73.5
72349	445	TW	6	1.5	No	1600	9	59.9	72.4	74.8
72350	445	TW	6	1.5	No	1800	8	72.7	75.7	78.5
72353	445	TW	6	1.4	No	1600	9	75.2	78.5	81.1
73029	453	1/3 SW	1	2.8	Yes	1800	5	68.0	71.6	74.1
73051	443	TW	3	2.0	Yes	2300	3	83.4	86.9	89.2
73054	448	TW	0	4.8	Yes	1900	3	71.6	74.4	79.2

---

* Mean temperature of first compartment was 475°F in all tests

**TW denotes that the influent was tapwater containing macerated feces and urine

SW denotes that the influent contained sea water; the fraction of SW in the influent is indicated for each test

TABLE 3-2

OPERATING CONDITIONS AND RESULTS FOR TESTS CONDUCTED IN UNLINED REACTORS†

Test No.	Temp, °F Max.	Temp, °F Mean	Residence Time, min Compart	Salinity*	Catalyst	O_2/COD	Agitator Speed rpm	PERCENTAGE REDUCTION IN COD Over-all Residence Time, Minutes 20	30	40	45	60	80	90	120
72332	475	454	15	TW	No	7	800		68.4		71.3	75.9			
72335	475	454	15	TW	No	12	800		63.8		69.2	71.6			
73064	475	454	15	TW	Yes	4	1200		76.1		79.1	82.4			
73068	440	420	15	TW	Yes	9	1200		73.0		76.8	80.2			
73072	445	422	15	1/3 SW	Yes	3	1200		69.1		70.6	71.8			
73075	425	402	18	TW	Yes	4	1200		59.4**		64.0**	66.4**			
73079	480	457	30	TW	Yes	2	1200		86.7			89.1		91.6	94.1
73082	475	448	20	TW	Yes	1	1200	78.0		82.0		83.5	85.5		
73086	475	450	20	1/3 SW	No	1	1200	69.6		70.4		73.3	75.1		
73089	475	451	20	1/3 SW	No	1	1200	72.0		75.6		78.7	80.8		
73124	450	450	20	TW	No	1	1200	56.0		58.8		72.2	74.2		76.3

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† 6-8 g/ℓ H_2SO_4 added to influent in each test; effluent pH ranged from 1.5 - 1.7

* TW Denotes that the influent was tapwater containing macerated feces and urine
SW denotes that the influent contained sea water; the fraction of SW in the influent is indicated for each test

**36, 54 and 72 minutes, respectively

3.3 STATISTICAL ANALYSIS OF TEST RESULTS

Because wet oxidation is strongly affected by a number of process variables, the evaluation of performance is difficult. The intentional variation of the principal variables, one at a time, is generally thwarted by unintentional fluctuations in other extraneous variables. Moreover, varying one factor at a time is not a safe practice. There are often strong interactions between variables that escape detection unless a test series is conducted in which all combinations of the different factors are investigated at all levels. Data from test series in which several factors are varied simultaneously are evaluated generally by statistical analysis; for example, factorial experimentation and multiple regression analysis.

3.3.1 VARIANCE IN REPLICATES

Customarily the first step in performing a statistical analysis is to establish the reproducibility of a test. In evaluating the acid circuit, at least one set of nearly identical experiments were included intentionally in each major test series for this purpose. For example, in Table 3-1, there are three nearly identical tests: Nos. 72349, 72350 and 72353. Likewise, in Table 3-2, there are two sets of replicates: Test Nos. 72332 and 72335; and Test Nos. 73086 and 73089.

The variance in the response to treatment for each replication is summarized in Tables 3-3, 3-4 and 3-5. (The pertinent operating conditions are also listed in the tables so that the reader can ascertain quickly the degree to which replication was achieved.) The coefficients of variation range from 2.1 to 5.2 percent; the mean coefficient is 4.0 percent, which is well within the precision of chemical analysis, which has been established in the following manner:

> The American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation jointly prepared a set of synthetic unknown samples containing potassium acid phthalate and sodium chloride. Aliquots of the unknown samples were assayed for COD by 74 laboratories. The coefficient of variation was 6.5 percent for the chemical analysis of samples that contained no sodium chloride and 10.8 percent for the determination of COD in samples containing 1000 mg/ℓ Cℓ.

TABLE 3-3

VARIANCE IN REPLICATES, CARBON-LINED REACTOR, TAP WATER INFLUENT

	Test No.		
	72349	72350	72353
Operating Conditions:			
Mean Temp, Compart. 1, °F	475	475	475
Mean Temp, Over-All, °F	445	445	445
Speed of Agitation, rpm	800	800	800
Air Flow, scfm	1	1	1
Mean Residence Time, min/compart	15	15	15
Supply-Demand Ratio, O_2/COD	9	8	9
Influent Characteristics:			
COD, mg/ℓ O	1600	1800	1600
Salinity Level	TW	TW	TW
Acid Addition, g/ℓ H_2SO_4	6	6	6
Effluent pH	1.5	1.5	1.4
Catalysts:			
Barber-Colman Co. 10,480	None	None	None
Porous Carbon, cm^{-1}	0.2	0.2	0.2

Response To Treatment

Mean Percentage Reduction In COD	
Data of Compart 2 (30 min total residence)	72.6
Data of Compart 3 (45 min total residence)	75.5
Data of Compart 4 (60 min total residence)	78.1
Standard Deviation	
Data of Compart 2	2.6
Data of Compart 3	3.0
Data of Compart 4	3.2
Coefficient of Variation, Pct. of Mean	
Data of Compart 2	3.6
Data of Compart 3	4.0
Data of Compart 4	4.1

TABLE 3-4

VARIANCE IN REPLICATES, UNLINED REACTOR, TAP WATER INFLUENT

	Test No.	
	72332	72335
Operating Conditions		
Mean Temperature, Compart. 1, °F	475	475
Mean Temperature, Over-All, °F	454	454
Speed of Agitators, rpm	800	800
Air Flow, scfm	0.9	0.9
Mean Residence Time, min/compart.	15	15
Supply-Demand ratio, O_2/COD	7	12
Influent Characteristics:		
COD, mg/ℓ O	1800	1100
Salinity Level	TW	TW
Acid Addition, g/ℓ H_2SO_4	6	6
Effluent pH	1.5	1.5
Catalysts	None	None

Response To Treatment

Mean Percentage Reduction In COD	
Data of Compart. 2 (30 min total residence)	66.1
Data of Compart. 3 (45 min total residence)	70.2
Data of Compart. 4 (60 min total residence)	73.8
Standard Deviation	
Data of Compartment 2	3.2
Data of Compartment 3	1.5
Data of Compartment 4	3.0
Coefficient of Variation, Pct. of Mean	
Data of Compartment 2	4.9
Data of Compartment 3	2.1
Data of Compartment 4	4.1

TABLE 3-5

VARIANCE IN REPLICATES, UNLINED REACTOR, SEA WATER INFLUENT

	Test No.	
	73086	73089
Operating Conditions:		
Mean Temperature, Compart. 1, °F	460	460
Mean Temperature, Over-All, °F	450	451
Speed of Agitators, rpm	1200	1200
Air Flow, scfm	0.2	0.2
Mean Residence Time, min/compart.	15	15
Supply-Demand Ratio, O_2/COD	1.3	1.4
Influent Characteristics:		
COD, mg/ℓ O	2700	2600
Salinity Level	1/3 SW	1/3 SW
Acid Addition, g/ℓ H_2SO_4	6	6
Effluent pH	1.6	
Catalysts	None	None

Response To Treatment

Mean Percentage Reduction In COD	
Data of Compart. 1 (20 min total residence)	70.8
Data of Compart. 2 (40 min total residence)	73.0
Data of Compart. 3 (60 min total residence)	76.0
Data of Compart. 4 (80 min total residence)	78.0
Standard Deviation	
Data of Compartment 1	1.7
Data of Compartment 2	3.7
Data of Compartment 3	3.8
Data of Compartment 4	4.0
Coefficient of Variation, Pct of Mean	
Data of Compartment 1	2.4
Data of Compartment 2	5.0
Data of Compartment 3	5.0
Data of Compartment 4	5.2

3.3.2 LINEAR REGRESSION ANALYSIS (ESTABLISHING EFFECT OF TIME IN THE REACTOR ON PERCENTAGE REDUCTION IN COD)

Having determined the variance in identical tests, the next logical step in the statistical analysis of the test results is to establish the effect of time. Because time is the most prevalent variable in the compiled results, subsequent analysis is strengthened by applying time-dependent data in an intelligent manner.

Linear regression analysis was applied to the data from individual tests (and to means from replicated tests). A firm linear relationship was found to exist between the mean percentage reduction in COD (after treatment in two or more compartments) and the residence time in the reactor. There is a scientific basis for the observed relationship.

The nature of wet oxidation is such that most of the reduction in COD is accomplished in the first compartment of a multiple chambered reactor. A mathematical derivation is presented in Appendix F, which shows that the increased percentage reduction in COD gained from prolonging treatment in an n-compartment reactor can be estimated from the following expression:

$$\Delta(\%\ \text{red.}) = 100(C_\ell^\circ/C_0)k_\ell\tau\cdot n$$

In equation 3-1, C_ℓ° is the initial COD of the organic species degraded by the late-stage, wet-oxidation process whose reaction rate constant is k_ℓ; C_0 is the influent COD; and τ is the residence time per compartment for a reactor with n compartments, each of nearly equal capacity. Since in an individual test, all of these parameters are fixed, plots of pct. reduction vs. n are linear. For example, in Figure 3-3, the appropriate data from two sets of replicated tests are presented. The straight lines joining the datum points are the "least-squares" fits.

The significance of the fits can be established by the magnitude of the parameter r^2, the coefficient of determination, which is the fraction of variance accounted for by the regression analysis. In other words, $r^2 = 1$ is a perfect fit. The magnitude of the effect--the percentage increase in reduction--is defined by the so-called regression coefficient (b) which geometrically is the slope of the least-squares line. These two parameters--b and r^2--are tabulated below:

Test Nos.	b	r^2
73086 and 73089	2.445	0.994
72332 and 72335	3.825	0.998

A more complete discussion of the factor--time in the reactor--is presented in Section 3.5.5.

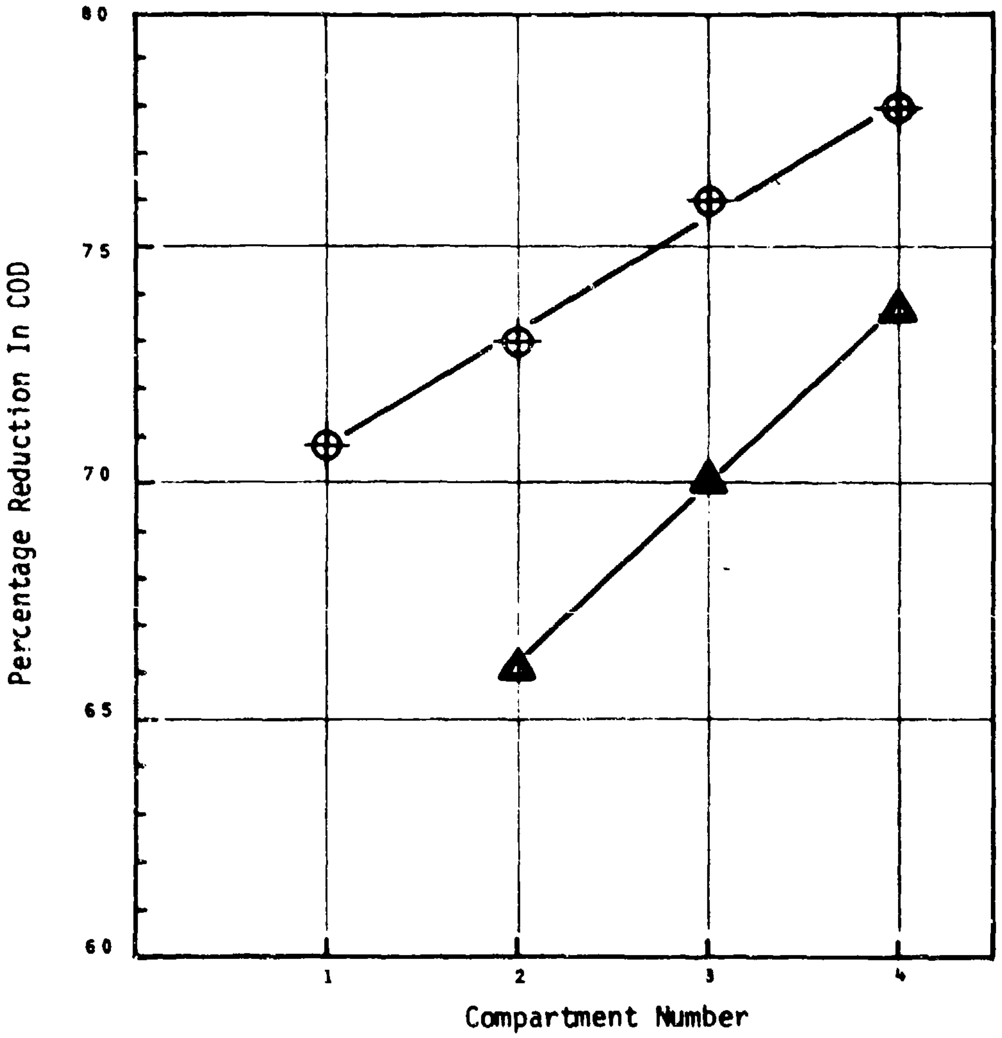

FIGURE 3-3. RELATIONSHIP BETWEEN PERCENTAGE REDUCTION IN COD AND COMPARTMENT NUMBER FOR REPLICATED TESTS

⊕ Mean of Test Nos. 73086 and 73089

▲ Mean of Test Nos. 72332 and 72335

3.3.3 FACTORIAL EXPERIMENT IDENTIFYING PRINCIPAL INTERACTION EFFECTS

Data from 8 of the 22 continuous-flow tests, which were conducted on simulated shipboard sewage, can be assembled into a three-factor (or 2^3) factorial experiment, the analysis of which reveals strong interaction between two of the process variables: the nature of the wetted wall and the salinity of the wastewater. Knowledge of this interaction greatly facilitates the statistical analysis of the tests conducted to evaluate the acid circuit.

a. Design of the Experiment

A factorial experiment is actually a series of tests, each of which is performed in a prescribed manner. The over-all purpose of the experiment is to study the effect on some observable quantity (the so-called response to treatment) caused by varying two or more factors, such as temperature, pressure, etc. Two or more levels (definite values) of each factor are chosen and all* combinations of these levels are tested. The test matrix--the particular combinations of the factor levels (and the order in time in which they are tested)--is referred to as the Design of the experiment.**

The Design of our experiment is shown in Figure 3-4. The low and high levels of the three factors, which were varied deliberately, are summarized below:

Factor	Low Level	High Level
Wetted wall of reactor	Bare titanium	Porous Carbon lining
Salinity of influent	Tap water (TW)	1/3 sea water (SW)
Over-all residence time	40-45 min	60 min

The levels of the remaining factor were held constant or within a range in which their effect on the response was known to be constant; the mean settings for these extraneous variables are listed in Table 3-6:

> In all 8 tests, the mean temperature of the reactor was the same, 450 ± 5°F. The stirring speed was either 800 or 1200 rpm; in this range the effect of agitation is constant. There was an excess of oxygen: the supply-to-demand ratio (O_2:COD) ranged from 1.3:1 to 12:1; at these levels, the rate and extent of wet oxidation is insensitive to the exact value of the ratio. In all tests, 6 g/ℓ H_2SO_4 was added to the influent; the effluent pH ranged from 1.4 to 1.6. Barber-Colman Co. catalysts were not used in these particular tests.

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* All of the combinations are tested in a Complete Factorial Design. Only certain combinations are treated in Fractional Factorial Experiments.

**See the Design and Analysis of Industrial Experiments, edited by O.L. Davies Hafner Publishing Co., 1954, for a discussion which is both authoritative and readable.

OVER-ALL RESIDENCE TIME (R)	WETTED WALL OF REACTOR (W)			
	BARE TITANIUM (W-)		POROUS CARBON (W+)	
	NON-SALINE INFLUENT TW (S-)	SALINE INFLUENT 1/3 SW, 2/3 TW (S+)	NON-SALINE INFLUENT TW (S-)	SALINE INFLUENT 1/3 SW, 2/3 TW (S+)
40-45 min (R-)	Mean, Tests 72332 and 72335 70.2%	Mean, Tests 73086 and 73089 73.0%	Mean, Tests 72349, 72350 and 72353 75.5%	Mean, Test 72346 64.3%
60 min (R+)	Mean, Tests 72332 and 72335 73.8%	Mean, Tests 73086 and 73089 76.0%	Mean, Tests 72349, 72350 and 72353 78.1%	Mean, Test 72346 65.6%

FIGURE 3-4. DESIGN OF THE (2^3) FACTORIAL EXPERIMENT.

TABLE 3-6

COMPILATION OF EXTRANEOUS VARIABLES AND LEVELS IN THE FACTORIAL EXPERIMENT

Test No.	Temp, °F		Acidity		Air Flow scfm	O_2 / COD	Influent COD, mg/ℓ O	Agitators rpm	Catalyst 10,480
	Max.	Mean	Add'n g/ℓ H_2SO_4	Effluent pH					
72332	480	454	6	1.5	0.9	7	1800	800	None
72335	480	454	6	1.5	0.9	12	1100	800	None
72346	480	445	6	1.5	1.0	8	1800	800	None
72349	480	445	6	1.5	1.0	9	1600	800	None
72350	480	445	6	1.5	1.0	8	1800	800	None
72353	480	445	6	1.4	1.0	9	1600	800	None
73086	475	450	6	1.6	0.2	1.3	2700	1200	None
73089	475	451	6		0.2	1.4	2600	1200	None

For success, the levels of the factors (in a factorial experiment) should be chosen so that the difference in response (the so-called effect) caused by treatment at one level compared to the other is linear, that is, directly proportional to the change in magnitude of the factor. In practice, generally, this is accomplished by selecting levels which are not too far removed from their mean.

b. Calculation of Effects By Yates' Method*

The differences between the means of the observed responses (for levels of one factor, averaged over all levels of the other factors) is called the Main Effect of that factor. Sometimes the effect of one factor is different at different levels of one or more of the other factors. In such cases, there is said to be an Interaction between the two factors.

In practice, the Main Effects and Two-Factor Interaction Effects are calculated by numerical methods such as those due to F. Yates. Table 3-7 summarizes the calculated effects (and interaction effects) of wetted wall (W), salinity (S) and residence (R) on the percentage reduction in COD for the factorial experiment.

The dimensional units of the calculated effects are percent reduction in COD. In other words, according to the results of the factorial experiment, changing the level of salinity--from that associated with the low level (tap water) to that of the high level (1/3 sea water)--will diminish the reduction in COD 4.675 percentage points, all other factors being the same and at the mean of the levels.

c. Application of t-Test for Significance

The significance of the calculated effects can be established by the so-called t-test which statistically compares the magnitude of the effect with its standard error (S.E.): the magnitude of the effect must exceed 1.96 S.E. to be significant at the 95-pct level and 2.58 S.E. for 99-pct significance. That is the effect must exceed 1.96 S.E. to be reproducible 19 out of 20 times and 2.58 S.E. to be reproducible 99 out of 100 times. Since the three sets of replicated tests, which were evaluated in Section 3.3.1, comprise 7 of the 8 tests in the factorial experiment, the standard error (S.E.) associated with these replicates can be used for the factorial experiment. In other words, a reasonable value for the standard error is 3.07, the mean of the standard deviations listed in Tables 3-3, 3-4 and 3-5 for the replicated tests. For significance the value of an effect must exceed the following:

95-pct 1.96 S.E. = 6.02

99-pct 2.58 S.E. = 7.92

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*See the Design and Analysis of Industrial Experiments, edited by O.L. Davies Hafner Publishing Co., 1954; pp 263-5, 283-5; for a discussion of Yates' Method.

TABLE 3-7

CALCULATION OF EFFECTS BY YATES' METHOD*

Treatment Combination	Response	Col. 1	Col. 2	Col. 3	
(1)	70.2	145.7	283.0	576.5	
w	75.5	137.3	293.5	-9.5 - 4W	W = -2.375
s	73.0	151.9	-3.4	-18.7 = 4S	S = -4.675
ws	64.3	141.6	-6.1	-28.7 = 4WS	WS = -7.175
r	73.8	5.3	-8.4	10.5 = 4R	R = 2.625
wr	78.1	-8.7	-10.3	-2.7 = 4WR	WR = -0.675
sr	76.0	4.3	-14.0	-1.9 = 4SR	SR = -0.475
wsr	65.6	-10.4	-14.7	-0.7 = 4WSR	WSR = -0.175

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[*] See the Design and Analysis of Industrial Experiments, edited by O.L. Davies Hafner Publishing Co., 1954; pp 263-5, 283-5; for a discussion of Yates' Method.

According to the foregoing criteria, only the two-factor interaction effect (WS) significantly affects the treatment. In other words, in 19 out of 20 tests, there would be discernible interaction (an effect above the level attributable to random error).

d. Analysis of Variance (Application of F-Test for Significance)

Alternatively, significance can be established by performing a so-called analysis of variance. In this test of significance, an arithmetic subdivision or partition of the sum of squares* is made, and each partition is weighted according to the associated degrees of freedom. The resulting mean squares are then examined by the F-test. Table 3-8 presents a summary of the analysis of variance for the factorial experiment.

In the F-test, the ratio of the variance (mean square) due to an effect is compared with the variance (mean square) attributed to random error. In other words, one determines whether the effect is real or merely owing to one's inability to determine precisely the response to treatment.

An estimate of the error variance can be obtained by squaring the standard error (the mean standard deviation) from the replicated tests in the experiments:

$$(S.E.)^2 = 9.425.$$

Based on one degree of freedom, a mean square of $3.84 \times 9.425 = 36.2$ would be required for significance at the 5% level, according to Davies**. To be significant at the 1% level, a mean square should exceed $6.63 \times 9.425 = 62.5$. Thus, according to the F-test, the interaction effect (WS) is highly significant (>99%) and the main effect (S) is significant (>95%).

---

* The sum of squares (SS) is the accumulative total of the squares of the deviations of the effect values from their mean. In practice, however, SS is calculated by squaring the appropriate effect total and dividing by 2^3. The effect totals are listed in column 3 of Table 3-7.

**Design and Analysis of Industrial Experiments, edited by O.L. Davies, Hafner Publishing Co., 1954, p. 266. The values, 3.84 and 6.63, are the F-values for a variance based on one degree of freedom with a variance based on an infinite sampling.

TABLE 3-8

ANALYSIS OF VARIANCE

Source of Variation	Sum of Squares $(\mathrm{Col.3})^2 \div 8$	Degrees of Freedom	Mean Square
Main effects:			
Lining reactor with carbon (W)	11.2813	1	11.2813
Using Tapwater (S)	43.7113	1	43.7113*
Increasing Compartment (R)	13.7813	1	13.7813
Interaction:			
WS	102.9613	1	102.9613**
WR	0.9113	1	0.9113
SR	0.4513	1	0.4513
WSR	0.0613	1	0.0613
Total	173.1591	7	

---

* Significant, greater than 95%

**Highly significant, greater than 99%

3.3.4 FACTORIAL EXPERIMENTS IDENTIFYING SALINITY AS A SIGNIFICANT FACTOR

The foregoing 2^3 design (Figure 3-4) can be partitioned into two 2^2 designs and a third 2^2 design can be assembled from other tests. These 2^2 factorial experiments identify salinity as a major factor affecting the percentage reduction in COD.

a. Significance of Salinity in Unlined Reactors

Salinity possibly does not greatly affect wet oxidation in unlined reactors unless Barber-Colman Co. catalyst 10,480 is present. The evidence is presented in following subsections.

(1) Uncatalyzed Treatment. The left-hand side of the 2^3 design (shown in Figure 3-4) constitutes a 2^2 factorial experiment from which one can establish the relative effects of salinity and residence on the percentage reduction in COD (as the result of 450°F, uncatalyzed treatment in the unlined titanium reactor). The two-factor design appears below:

Over-All Residence Time (R)	SALINITY OF INFLUENT	
	Non-Saline Influent TW (S-)	Saline Influent 1/3 SW, 2/3 TW (S+)
40 - 45 min (R-)	Mean Tests 72332 + 72335 70.2%	Mean Tests 73086 + 73089 73.0%
60 min (R+)	Mean Tests 72332 + 72335 73.8%	Mean Tests 72086 + 73089 76.0%

Application of the Yates' method yields the following values for the main effects and the interaction effect:

Treatment Combination	Response, Pct. Red.	Col. 1	Col. 2	
(1)	70.2	143.2	293.0	
s	73.0	149.8	5.0 = 2S	S = 2.5
r	73.8	2.8	6.6 = 2R	R = 3.3
sr	76.0	2.2	-0.6 = 2SR	SR = -0.3

None of the calculated effects are significant: In Section 3.3.3c, it was established that the magnitude of an effect must exceed 6.0 to be significant at the 95-pct level and 7.9 to be highly significant (>99%).

One concludes that the salinity of the influent does not affect significantly the efficacy of wet oxidation in an unlined, 450°F reactor (in the absence of Barber-Colman Co. catalyst 10,480).

Although the treatment of saline influent (in the uncatalyzed tests in the unlined reactor) in the foregoing factorial experiment consistently resulted in a greater percentage reduction in COD than resulted from the treatment of non-saline influent, the differences in efficacy are not statistically significant. In other words, they are within experimental error.

(2) Catalyzed Treatment. Two tests--Nos. 73068 and 73072--can be assembled into a 2^2 factorial experiment in which salinity proves to be a significant negative factor; the design is shown below:

Over-All Residence Time (R)	SALINITY OF INFLUENT (S)	
	Non Saline (TW), 420°F Influent (S-)	Saline (1/3 SW), 420°F Influent (S+)
5 min (R-)	Test No. 73068 76.8%	Test No. 73072 70.6%
60 min (R+)	Test No. 73068 80.2%	Test No. 73072 71.8%

In the above design salinity and residence are again the factors in two tests performed in an unlined reactor. In this experiment, however, the mean temperature was 420°F--25 degress less than in the previous design--and Barber-Colman Co. catalyst 10,480 was present. (As these factors are constant throughout the experiment, the analysis is, of course, valid; but direct comparison with the previous 2^2 design is obscured.)

Application of the Yates' method yields the following values for the effects in the 420°F tests:

Treatment Combination	Response, Pct. Red.	Col. 1	Col. 2	
(1)	76.8	147.4	299.4 = Total	
s	70.6	152.0	-14.6 = 2S	S = -7.3
r	80.2	-6.2	4.6 = 2R	R = 2.3
sr	71.8	-8.4	-2.2 = 2SR	SR = -1.1

The main effect (S) is significant, according to the criteria of Section 3.3.3c: The value exceeds 6.02. None of the other effects are significant.

One concludes that the salinity of the influent significantly affected process efficacy in an unlined reactor at 420°F (in the presence of Barber-Colman Co. catalyst 10,480) but did not affect treatment in an unlined reactor at 450°F (in the absence of the catalyst).

b. Significance of Salinity In Carbon-Lined Reactor

The right-hand side of the 2^3 factorial experiment (displayed in Figure 3-4) can be recast as a 2^2 design from which one can establish the relative effects of salinity and residence on the response to treatment in the carbon-lined reactor. The two-factor (2^2) design is as follows:

Over-All Residence Time (R)	SALINITY OF INFLUENT (S)	
	Non Saline Influent TW (S-)	Saline Influent 1/3 SW, 2/3 TW (S+)
45 min (R-)	75.5%	64.3%
60 min (R+)	78.1%	65.6%

By the Yates' method or its equivalent, one can calculate the following effects:

Treatment Combination	Response, Pct. Red.	Col. 1	Col. 2	
(1)	75.5	139.8	283.5	
s	64.3	143.7	-23.7 = 2S	S = -11.85
r	78.1	-11.2	3.9 = 2R	R = 1.95
sr	65.6	-12.5	-1.3 = 2SR	SR = -0.65

In this experiment, the main effect (S) is highly significant: The criterion (established in Section 3.3.3c from the known standard error in replicated tests) specifies that an effect greater than 7.9 is significant above the 99-pct level. Therefore in the carbon-lined reactor, one can conclude that salinity has a pronounced negative effect on efficacy--the predicted percentage reduction in COD is nearly 12 points less in the treatment of mixed seawater (1/3 SW) and tapwater than in the treatment of tapwater influent. Barber-Colman Co. catalyst 10,480 was not used in these tests.

3.3.5 MULTIPLE (LINEAR) REGRESSION ANALYSIS OF TESTS IN CARBON-LINED REACTOR

Additional information concerning the relative importance of the individual process variables can be extracted from the test data by multiple regression analysis. Examination of the series performed in the 4-compartment, carbon-lined reactor is particularly rewarding. By restricting analysis to data generated in the carbon-lined reactor (or alternatively performing the same sort of analysis on data from the unlined reactor), one avoids the strong interaction effect between salinity and the nature of the wetted wall. Since none of the other two-factor interactions proved significant in the factorial experiment, multiple (linear) regression analysis is probably adequate. (In other words, there may not be a need for cross-product terms in the polynomial expressions one derives in multiple regression analysis.)

In the series of tests conducted in the carbon-lined reactor, the operating temperature and speed of agitation were fixed. The supply-demand ratio of oxygen varied somewhat; but, in all tests, supply was well in excess of demand and, therefore, the variation probably did not affect the rate or extent of wet oxidation (cf. Section 2.3, Figure 2-8). Salinity, acidity and catalyst (Barber-Colman Co. 10,480) were varied purposely; together with residence time, these factors mainly determined the response to treatment. The purpose of the ensuing regression analysis is to ascertain the relative importance of each factor.

In multiple (linear) regression analysis, the response (y) is assumed to be equal to a constant ($\bar{y}$) plus a series of linear terms, one for each of the n variables (x_1, x_2, . . . x_n) that significantly affect the response. Each term containing a variable, in turn, consists of a constant--the so-called regression coefficient b_i--multiplied by the corresponding variable x_i; that is to say,

$$y = \bar{y} + \Sigma b_i x_i \tag{3-2}$$

Equation 3-2 is called the response function.

Multiple regression analysis is not infallible. Unless the input data conform closely to certain restrictions, the effects of individual variables on the response parameter are obscure. When the number of variables approaches the number of tests, almost any set of data can be fitted. Most authorities agree that the most effective regression analysis employs only a few truly significant factors. The primary purpose is to establish the identity of these important factors.

The regression analysis of the test series conducted in the carbon-lined reactor indicates that essentially all of the variance is accounted for by three factors: time, salinity and catalyst. The resulting residual variance is about the same as that established for the replicated tests examined in Section 3.3.1. In other words, we have fitted the data as well as we are entitled to, in view of the experimental error inherent in the input data. The results of the analysis are displayed graphically in Figure 3-5: A family of response surfaces is shown, each surface applicable for a specific over-all residence time.

Figure 3-5 was constructed by applying the method of least squares to the data* from Table 3-1. A 4x4 matrix of normal equations was derived. The inverse matrix was obtained, and the regression coefficients were determined. The results can be expressed either graphically or as a polynomial:

$$y = \bar{y} + b_1x_1 + b_2x_2 + b_3x_3 \qquad (3\text{-}3)$$

The constant $\bar{y}$ (in Equation 3-3) is, of course, the value of the response parameter (y) when all of the x-variables equal zero. In multiple regression analysis, however, the investigated range of variables often does not include zero. In such cases, the variables are "coded". That is to say, they are redefined in such a manner that a linear function of each variable has the value of zero when that variable has a value near the mean of the investigated range. When these coded variables are substituted for the corresponding x_i, $\bar{y}$ becomes the response to treatment under a set of mean conditions; that is, the response to treatment when each variable is fixed at or near the centerpoint of the range encompassed by the levels of the variable. Graphically, this centerpoint is the midpoint of the response surface--for example, the center of the triangular planes depicted in Figure 3-5.

In Equation 3-3, if percentage reduction in COD is used as the response paramete (y), then for the particular test matrix contained in Table 3-1 an appropriate mean response $\bar{y}$ may be defined as follows:

$\bar{y}$ is the percentage reduction in COD from wet oxidation of acidified shipboard sewage in an excess of oxygen in a carbon-lined reactor under the following conditions: Max. temp., 475°F; mean temp, 450°F; stirring speed, 800 rpm; and mean residence time, 45 min. A catalyst one half as potent as Barber-Colman Co. catalyst 10,480 is assumed to be present; and the salinity level is comparabl to that resulting from influent comprised of 1 part sea water and 5 parts IRWD tap water.

The 95-pct confidence range for $\bar{y}$ was found to be 71.3 - 74.7. In other words, based on the regression analysis of the series of 8 tests conducted in a carbon-lined reactor, wet oxidation under the specified mean conditions should result (19 out of 20 times) in a reduction in COD ranging from 71 to 75 percent.

Other predicted responses are summarized on the following page:

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*Specifically, the input data in the analysis consisted of the 24 means

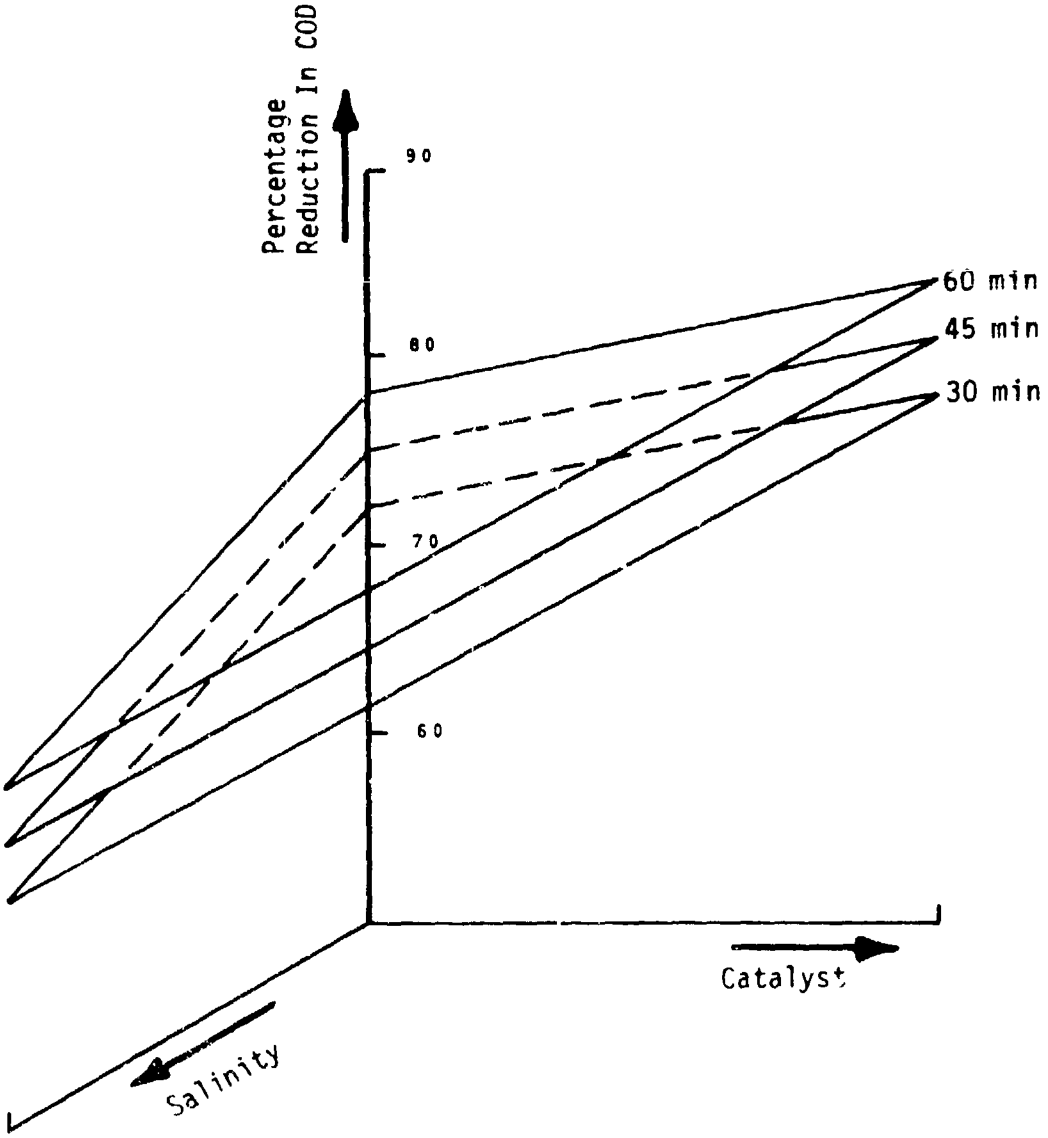

FIGURE 3-5. RESPONSE SURFACES, WET OXIDATION AT 475°F IN A CARBON-LINED REACTOR.

Residence Time, min	Salinity Level	Catalyst (10,480)	Percentage Reduc. In COD
30	tap water	none	72
45			75
60			78
30	1/3 sea water	none	62
45			65
60			68
30	tap water	present	78
45			81
60			84

That is to say, the above values are solutions to the least-squares polynomial,

$$\text{Pct. Red. in COD} = 73.0 + 2.8t^* - 5.2s^* + 2.9c^*, \qquad (3\text{-}4)$$

which resulted from the regression analysis. (In other words, Equation 3-4 is the algebraic solution corresponding to the graphical solution shown in Figure 3-5.) In equation 3-4

$$t^* = [\text{Over-all residence time (min)} - 45] \div 15$$

$$s^* = [\text{Fraction sea water} - 1/6] \div 1/6$$

$$c^* = +1, \text{ when catalyst is present}$$

$$= -1, \text{ when catalyst is absent}$$

The analysis of variance indicates that all of the independent variables--time, salinity and catalyst--significantly affect the response.* Listed in the order of significance, salinity is the most important, then, catalyst and, lastly, residence time. The 95-pct confidence ranges for the regression coefficients (and the mean response) for equation 3-4 are listed on the following page:

---

*The three variables are all significant according to an F-test based on an error variance formed from the residual sum of squares (lack of fit) divided by the 20 degrees of freedom remaining from the regression analysis. Acceptance

Variable	95-pct Confidence Range
Mean Response ($\bar{y}$)	71.3 to 74.7
Residence time (b_1)	0.9 to 4.7
Salinity (b_2)	-3.4 to -7.0
Catalyst (b_3)	1.3 to 4.5

The relative importance of the independent variables to a multiple regression analysis often is determined by stepwise removal of the variables from the polynomial expression and re-evaluation of the resulting function. The square of the multiple-correlation coefficient (R^2)* is the generally accepted index for judging the closeness of fit. For the case at hand, stepwise removal of the factors reveals the following relative importance:

Variables In Polynomial	R^2
Time, salinity and catalyst	0.998
Time and salinity	0.997
Salinity	0.526
Salinity and catalyst:	
30-min data	0.998
60-min data	0.998

The incorporation of other variables such as pH into the regression analysis is unrewarding. The addition of pH as a fourth independent variable does not significantly affect the analysis; and the substitution of pH for one of the other variables, say catalyst, leads to an inferior solution ($R^2 = 0.997$). In the particular set of data under analysis (Table 3-1), the effect of acidity probably can not be distinguished from the effect of catalyst; this is a property of the specific test matrix and is detectable by calculating the appropriate correlation coefficients**. In fact, as Barber-Colman Co. catalyst 10,480 functions only in fairly acidic water, the two variables--catalyst and pH--possibly should not be treated as separate independent variables.

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* R^2 equals the fraction of the sum of squares or variance accounted for by the regression analysis. In other words, $R^2 = 1$ is a perfect fit.

**In our case (the analysis of the data from Table 3-1),

$$r_{12} = 0.022;\ r_{13} = 0.013;\ r_{14} = 0.059$$
$$r_{23} = 0.038;\ r_{24} = -0.071$$
$$r_{34} = 0.753$$

where r is the correlation coefficient and the subscripts 1,2,3 and 4 denote time, salinity, catalyst and pH, respectively.

3.3.6 FACTORIAL EXPERIMENTS AND MULTIPLE REGRESSION ANALYSIS IDENTIFYING FACTORS AFFECTING TESTS CONDUCTED IN THE UNLINED REACTOR

Eleven continuous-flow tests were conducted in the 4-compartment, unlined reactor. The operating conditions and the resulting percentage reductions in COD are compiled in Table 3-2, which was presented in Section 3.2.2. In this series, there were deliberate variations in four factors: mean residence time per compartment, mean temperature, salinity and catalyst. Table 3-9 summarizes for each test the levels of these factors (and the resulting percentage reduction in COD achieved at the end of 60 minutes (over-all) residence time.

a. Effect of Temperature

In Table 3-9 the tests are grouped according to the levels of the principal two factors, salinity and catalyst. Temperature does not seem to have significantly affected the reduction in COD achieved in most of these tests. Test No. 73075, however, is not grouped with the other tests, because in this test, which was conducted at a very low temperature (for wet oxidation), temperature was obviously a significant variable. The following factorial experiments demonstrate the point.

(1) Treatment at 400°F compared to treatment at 420°F. Data from Test Nos. 73068 and 73075 can be used to construct the 2^2 design shown below:

OVER-ALL RESIDENCE TIME (R)	MEAN TEMPERATURE (T)	
	402°F (T-)	420°F (T+)
Compart 2 36 min vs 30 min (R-)	59.4%	73.0%
Compart 3 vs 4 54 min vs 60 min (R+)	64.0%	80.2%

The following values of the principal effects can be calculated by the Yates' method:

Treatment Combination	Response, Pct Red.	Col. 1	Col. 2	
(1)	59.4	132.4	276.6	
t	73.0	144.2	29.8 = 2T	T = 14.9
r	64.0	13.6	11.8 = 2R	R = 5.9
tr	80.2	16.2	2.6 = 2TR	TR = 1.3

TABLE 3-9

SERIES OF CONTINUOUS-FLOW TESTS IN UNLINED REACTOR GROUPED ACCORDING TO TEMPERATURE, SALINITY AND CATALYST

Test No.	Mean Residence Time, min/ Compart.	Mean Temp, °F	Salinity	Catalyst 10,480	Pct Red. in COD @ 60 min	Group Mean and Variation $\bar{x}$	$100s/\bar{x}$
73079	30	457	TW	Yes	89.1	83.8	4.5
73064	15	454	TW	Yes	82.4		
73082	20	448	TW	Yes	83.5		
73068	15	420	TW	Yes	80.2		
73072	15	422	1/3 SW	Yes	71.8		
72332	15	454	TW	No	75.9	73.2	3.2
72335	15	454	TW	No	71.6		
73124	20	450	TW	No	72.2		
73089	20	451	1/3 SW	No	78.7	76.0	5.0
73086	20	450	1/3 SW	No	73.3		
73075	18	402	TW	Yes	64.0		

Based on the criteria established in Section 3.3.3c , the main effect T is highly significant because it exceeds 7.9. Therefore, one concludes that wet oxidation at 400°F in an unlined reactor is significantly inferior to treatment at 420°F, primarily because of the effect of temperature. According to the analysis, one can increase the reduction in COD by 15 percent by operating at 420°F instead of 400°F.

Note that the main effect (R) is nearly significant (at the 95-pct level)--a value of 6 is significant, the calculated value is 5.9. This is one of the few factorial experiments assembled in this report in which residence time is an important factor.

These tests were conducted in the presence of Barber-Colman Co. catalyst 10,480.

(2) Treatment at 420°F compared to treatment at 455°F. Data from Test Nos. 73064 and 70368 can be assembled into the following 2^2 design:

Over-all Residence Time (R)	MEAN TEMPERATURE (T)	
	420°F (T-)	454°F (T+)
45 min (R-)	Test No. 73068 76.8%	Test No. 73064 79.1%
60 min (R+)	Test No. 73068 80.2%	Test No. 73064 82.4%

Application of the Yates' method yields the following values for the effects of temperature and residence:

Treatment Combination	Response Pct Red.	Col. 1	Col. 2	
(1)	76.8	155.9	318.5	
t	79.1	162.6	4.5 = 2T	T = 2.25
r	80.2	2.3	6.7 = 2R	R = 3.35
tr	82.4	2.2	-0.1 = 2TR	TR = -0.005

At these levels, 420 and 455°F, there is no significant effect caused by temperature. In other words, wet oxidation at 420°F is just as effective as treatment at 455°F. At least this appears to be so, based on two tests (conducted in an unlined reactor in the presence of Barber-Colman Co. catalyst 10,480).

b. Interaction of Salinity and Catalyst

Assuming that wet oxidation at 420°F is indeed comparable to treatment at 450-455°F, the group means from Table 3-9 can be used to construct the following 2^2 factorial experiment:

Salinity (S)	Catalyst 10,480 (C)	
	Absent (C-)	Present (C+)
Non Saline Influent TW (S-)	Mean, Test Nos. 72332, 72335 + 73124 73.2%	Mean, Test Nos. 73064, 73068, 73079 + 73082 83.8%
Saline Influent 1/3 SW, 2/3 TW (S+)	Mean, Test Nos. 73086 + 73089 76.0%	Mean, Test No. 73072 71.8%

Calculation of the effects by the Yates' method is summarized below:

Treatment Combination	Response, Pct. Red.	Col. 1	Col. 2	
(1)	73.2	157.0	304.8	
c	83.8	147.8	6.4 = 2C	C = 3.2
s	76.0	10.6	9.2 = 2S	S - -4.6
cs	71.8	-4.2	-14.8 = 2CS	CS = -7.4

The two-factor interaction effect (CS) is greater than 6, which is the value established in 3.3.3c for 95-pct confidence; therefore, one concludes that there is a significant interaction between salinity and catalyst. The following multiple regression analysis seems to confirm the importance of the interaction.

Multiple regression analysis was applied to data from 10 of the 11 tests--the test at 400°F (No. 73075) was omitted; because only in this test was temperature a significant factor, and by omitting the test one less factor need be considered. Data from the first and second compartments in Test No. 73124 also were not included; because in this test these compartments comprised a PLAG (partitioned liquid and gas) reactor, whereas all of the other data was from a PLOG (partitioned liquid, open gas) reactor. Otherwise all of the data* collected during the program from unlined reactors was grouped for multiple regression analysis.

Of the various expression formulated from multiple regression analysis of the selected data, the most significant was the following:

$$\text{Pct Red.} = 75.1 + 2.5t^* - 4.3\, s^*c^* \qquad (3\text{-}5)$$

where t^* = [Over-All Time in Reactor - 50] ÷ 20;
s^* = +1, when the influent is 1/3 sea water, and
= -1, when the influent is tap water;
c^* = +1, when Barber-Colman Co. catalyst 10,480 is present
= -1, when Barber-Colman Co. catalyst 10,480 is absent.

The R^2 associated with Equation 3-5 is 0.996. Compared to the error variance formed from the residual sum of squares (and the residual 30 degrees of freedom), both the residence time and the cross product (the level of salinity times the level of catalyst) are significant variables.

An alternative polynomial,

$$\begin{matrix}\text{Pct Red.}\\ \text{@ 60 min}\end{matrix} = 77.2 - 1.6s^* + 3.2c^*, \qquad (3\text{-}6)$$

can be derived by multiple (linear) regression; but none of the factors other than the mean is significant.

One concludes that there is a strong interaction between salinity and catalyst which possibly overshadows all other effects. The interaction is revealed in Equation 3-5--the result of multiple regression analysis--and in the 2^2 factorial experiment on page 3-38. In the analysis of both series of tests--those in carbon-lined reactors and those in unlined reactors--salinity interacted with another factor. The possible physicochemical significance of these two-factor interactions is discussed in Section 3.3.8.

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*Specifically, the input data consisted of 33 means derived from 103 hourly samples taken during 10 tests. Thus, the mean replication factor was 3.1. In other words, each datum point is based on chemical analysis of about 3 independent samples.

3.3.7 ANALYSIS BASED ON RATE CONSTANTS

In the preceeding sections, the statistical analysis of the continuous-flow tests was conducted by using percentage reduction in COD as the response parameter. Alternatively, as we have done in this section, one can use pseudo first-order rate constants as the response parameter.

The rate of reduction in COD can be calculated for any compartment of a CSTR from a simple mass balance. A pseudo rate constant can be calculated, if one assumes (accepts) that wet oxidation occurs by a series of first-order chemical reactions. The following appropriate formula is derived in Appendix G.

$$k_n = r_n/C_n = (C_{n-1} - C_n)/C_n\tau_n \qquad (3\text{-}7)$$

where k is the pseudo rate constant;

r is the rate of reduction in COD;
C is the COD of the liquid slurry;
τ is the mean residence time per compartment; and
n is a subscript denoting a specific compartment.

Physicochemically, k_n may be regarded as the weighted mean of all of the rate constants for the various chemical reactions which take place in compartment n and contribute to the reduction in COD.

a. Variance in Rate Constants

Values of r_n and k_n were calculated for each set of hourly samples taken in each continuous-flow test; they are included in Appendix C. Mean values of k_n and the associated coefficients of variation also were calculated and are listed in Tables C-46 and C-47, Appendix C. The coefficients of variation for k_n are an order of magnitude greater than those for the corresponding percentage reduction in COD; principally, because the rate constants are, in essence, equal to the difference between two comparatively large numbers (C_{n-1} and C_n) which are not determinable any more precisely than the magnitude of their difference.

The over-all mean of the coefficients (of variation) ranged from 14 to 46 percent and was the least in the case of k_1 and the greatest for k_2. One would expect that the determination of k_1 would be the most precise because its magnitude is the greatest--5 to 10 times that of the other k-values. Likewise, one would anticipate the greatest uncertainty in calculating k_2, because the transition in rate behavior from the initial fast to the late-stage slow rate of wet oxidation--generally coincides with treatment in the second compartment. (See Section 3.4 for an expanded discussion of this point.)

In Tables 3-10 and 3-11, the mean rate constants are listed with the pertinent operating conditions for the two major series of tests, that is, for those conducted in the carbon-lined reactor and for those conducted in the unlined reactor. The discernible trends in the magnitude of the rate constants are summarized in following subsections:

(1) Variation of k_n, Carbon-Lined Reactors. In Table 3-10, mean values of k_n are arranged according to the level of salinity and the presence or absence of catalyst. Significant trends in the magnitude of k_n are readily apparent:

(a) The value of k_1 is greatest for the test in which non-saline wastewater was wet-oxidized in the presence of Barber-Colman Co. catalyst 10,480.

(b) In the tests in which no catalyst was present, the value of k_1 was the least when the level of salinity was the greatest and vice versa.

(c) In tests in which the catalyst was present but little or no acid was added to the influent, the value of k_1 was essentially the same for wet oxidation of saline wastewater as for non-saline wastewater.*

(d) Trends in k_1 were paralleled by trends in k_2, k_3 and k_4.

(2) Variation of k_n, Unlined Reactors. The mean values of k_n in Table 3-11 are grouped according to temperature, salinity and catalyst. The following observations concerning the trends in k_n seem appropriate:

(a) Temperature does not affect the magnitude of the rate constant nearly as much as the presence or absence of the catalyst and the level of salinity.

(b) In the presence of Barber-Colman Co. catalyst 10,480, k_1 is greater for the wet oxidation of non-saline wastewater than for otherwise identical treatment of saline wastewater.

(c) Contrarily, in the absence of the catalyst, k_1 is less in the wet oxidation of non-saline wastewater than in otherwise identical treatment of saline wastewater.

(d) In tests performed with Barber-Colman Co. catalyst 10,480 on non-saline wastewater, the value of k_1 was the greatest when the mean residence time per compartment was the greatest and varied accordingly.

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*Perhaps a better way of expressing this observation is to say: The catalyst did not "work" in two tests, because there was not enough acid present.

TABLE 3-10

MEAN RATE CONSTANTS FOR CONTINUOUS-FLOW TESTS CONDUCTED IN CARBON-LINED REACTOR*

Test No.	Salinity	Catalyst 10,480	Acidity g/ℓ H_2SO_4	Acidity Efflu. pH	Mean Rate Constant, min^{-1} k_1	k_2	k_3	k_4
73051	TW	Yes	3	2.0	0.244	0.016	0.022	0.016
73054	TW	Yes	0	4.8	0.131	0.014	0.008	0.022
73029	1/3SW	Yes	1	2.8	0.136	0.012	0.011	0.011
72349	TW	No	6	1.5	0.126	0.011	0.006	0.007
72350	TW	No	6	1.5	0.161	0.005	0.009	0.009
72353	TW	No	6	1.4	0.198	0.010	0.013	0.012
72347	1/6SW	No	6	1.5	0.118	0.009	0.007	0.008
72346	1/3SW	No	6	1.5	0.104	0.004	0.004	0.002

---

*The following conditions were common in all tests: Mean temperature, 450°F; influent COD, 1500-2300 mg/ℓ O; O_2/COD = 3-10; stirring speed, 800 rpm; mean residence time, 15 minutes per compartment

TABLE 3-11

MEAN RATE CONSTANTS FOR CONTINUOUS-FLOW TESTS CONDUCTED IN UNLINED REACTOR*

Test No.	Mean Residence Time, min/Compart.	Mean Temp, °F	Salinity	Catalyst 10,480	Mean Rate Constant, min^{-1}			
					k_1	k_2	k_3	k_4
73079	30	457	TW	Yes	0.216	0.007	0.010	0.017
73064	15	454	TW	Yes	0.116	0.032	0.011	0.015
73082	20	448	TW	Yes	0.173	0.012	0.005	0.008
73068	15	420	TW	Yes	0.150	0.009	0.010	0.013
73072	15	422	1/3SW	Yes	0.095	0.024	0.005	0.006
72332	15	454	TW	No	0.076	0.028	0.007	0.013
72335	15	454	TW	No	0.089	0.016	0.012	0.006
73089	20	451	1/3SW	No	0.124	0.007	0.007	0.006
73086	20	450	1/3SW	No	0.111	0.002	0.017	0.004
73075	18	402	TW	Yes	0.075	0.004	0.007	0.005

---

*The following conditions were common in all tests: Acidity level, 6-8 g/ℓ H_2SO_4; stirring speed, 800-1200 rpm; O_2/COD = 1-12 b **Factorial Experiments**

Two 2^2 factorial designs can be assembled from the data of Tables 3-10 and 3-11. Analysis of the designs, which is presented in following subsections, again indicate significant two-factor interaction in the test data.

(1) Interaction Between Salinity and the Wetted Wall. The following 2^2 design is assembled from the same tests used in the 2^3 design examined in Section 3.3.3a; in the present case, however, the response parameter is the mean value of k_1, the first-compartment rate constant.

SALINITY OF INFLUENT (S)	WETTED WALL (W)	
	Bare Titanium (W-)	Porous Carbon (W+)
Non-Saline Influent (S-)	Mean, Tests 72332 + 72335 0.082	Mean, Tests 72349, 72350 0.162
Saline Influent (S+)	Mean, Tests 73086 + 73089 0.118	Mean, Test 72346 0.104

Application of the Yates' method gives the following values for the effects:

Treatment Combination	Response k_1, min^{-1}	Col. 1	Col. 2	
(1)	0.082	0.244	0.466	
w	0.162	0.222	0.066 = 2W	W = 0.033
s	0.118	0.080	-0.022 = 2S	S = -0.011
ws	0.104	-0.014	-0.094 - 2WS	WS = [illegible]7

The two-factor interaction effect WS has the greatest numerical (absolute) value.

If we use the same rationale we used in Section 3.3.3c (for determining the significance of an effect), then the standard error (S.E.) associated with a mean effect is equivalent to the mean standard deviation for the [illegible]s of replicates comprising the experiment; and 1.96 S.E. is the minimum va of a significant effect. An effect greater than the value, 2.58 S.E., is highly significant. In the case at hand, the mean standard deviation is

0.0128; and $1.96\bar{s} = 0.025$; $2.58\bar{s} = 0.033$. According to this criterion for establishing significance, both the main effect W and the two-factor effect WS have highly significant effects on the response parameter (k_1). In other words, in 99 out of 100 tests, in the presence of a porous-carbon wall the magnitude of k_1 would be greater than in tests in which the carbon liner was absent other things being equal. Moreover, one is 99 percent certain that the rate constant would be less when saline wastewater is treated than when non-saline wastewater is treated. Note that Barber-Colman Co. catalyst 10,480 is absent in the tests comprising the design.

(2) Interaction Between Salinity and Catalyst. The following 2^2 design was assembled from tests conducted in the unlined reactor in the presence of sufficient acid to yield pH 1.5 effluent; the mean residence time per compartment was from 15 to 20 minutes in all tests.

CATALYST (C)	SALINITY OF INFLUENT (S)	
	Non-Saline Influent (S-)	Saline Influent (S+)
ABSENT (C-)	Mean of Tests 72332 + 72335 0.082	Mean of Tests 73086 + 73089 0.118
PRESENT (C+)	Mean of Tests 73064, 73068, + 73082 0.146	Mean of Test 73072 0.095

By Yates' method or its equivalent, the following effects can be calculated.

Treatment Combination	Response k_1, min^{-1}	Col. 1	Col. 2	
(1)	0.082	0.200	0.441	
s	0.118	0.241	-0.015 = 2S	S = -0.008
c	0.146	0.036	0.041 = 2C	C = 0.020
sc	0.095	-0.051	-0.087 = 2SC	SC = -0.044

Using the same criterion for significance (that we used in Section 3.3.3c and 3.3.7b (1)), the mean standard deviation for the various sets of replicates is 0.0105; 1.96$\bar{s}$ = 0.021; and 2.58$\bar{s}$ = 0.027. Consequently, the main effect (C) is nearly significant (at the 95-pct level) and the interaction effect (SC) is highly significant (>99 pct). In other words, in an unlined reactor and in the presence of acid (pH 1.5 effluent), the use of Barber-Colman Co. catalyst significantly increased the magnitude of k_1, the first-compartment rate constant. In addition, the presence of sea water had a highly significant adverse effect on the magnitude of k_1.

3.3.8 PHYSICOCHEMICAL INTERPRETATION OF THE TWO-FACTOR INTERACTION

In the statistical analysis of each principal test series, significant two-factor interaction was revealed. In one series, the effect of salinity depended on whether the wetted wall was lined with porous carbon or just bare titanium; and, in the other series, the effect of salinity depended on whether or not Barber-Colman Co. catalyst 10,480 was present. Sea water in the presence of porous carbon without Barber-Colman Co. catalyst 10,480--and alternatively in the presence of the catalyst but without porous carbon--caused a diminution in efficacy: Wet oxidation of sewage in a mixture of one part sea water and two parts tap water resulted in 7 to 15 percent less reduction in COD than wet oxidation of tap water under otherwise identical conditions.

These interaction effects may be partly mathematical, but there is an equally strong possibility that the origin is physicochemical. The importance of the "nature of the reaction vessel's surface" on the liquid-phase oxidation of organic compounds has been noted by Emanuel[†] who also emphasizes the importance of catalysis[††]. Experiments described in Appendix E demonstrate that the rate and extent of wet oxidation can be increased significantly by conducting batch tests in a titanium container lined with porous carbon, ceramic tile or brick. The use of Barber-Colman Co. catalyst 10,480 further enhances the reduction in COD. Chromatographic analysis indicates that the principal species remaining after the initial stage of wet oxidation is acetate. In the presence of a ceramic substance such as porous carbon, tile or brick, Barber-Colman Co. catalyst 10,480 accelerates the combustion of acetate.

[†] N.M. Emanuel, "Present State and Main Trends of Research on Liquid-Phase Oxidation of Organic Compounds", chapter in Oxidation of Organic Compounds Vol. I, (No. 75 in Advances in Chemistry Series) published by American Chemical Society, Washington, D.C., 1968, pp. 1-5.

[††] N.M. Emanuel, E.T. Denisov, Z.K. Maizus, Liquid-Phase Oxidation of Hydrocarbons, translated from Russian by B.J. Hazzard, published by Plenum Press, New York, 1967, 350 pp.

The role of salinity may be that of an inhibiter or poison. Something in sea water probably adsorbs on the wetted wall and, as a consequence, lessens (poisons) its active area; or alternatively reacts with Barber-Colman Co. catalyst 10,480 and inhibits it. A catalytic process of this nature can be expressed by chemical equations of the following general type:

$$s^* + \text{catalyst} = s^*c^*; \text{ and} \qquad (3\text{-}8a)$$

$$s^* + \text{wall} = s^*..w \qquad (3\text{-}8b)$$

In Equation 3-8a, some active substance in sea water represented by the symbol s^* reacts with the catalyst to form s^*c^*, a non-catalytic species whose formation reduces the amount of catalyst. Equation 3-8b expresses analogous behavior between s^* and the wall; $s^*..w$ denotes units of s^* adsorbed on the surface of the wall. The adsorbed species block active sites on the surface which otherwise would be used in wet oxidation.

We used the symbol s^*c^* for the inhibited portion of the catalyst in Equation 3-8a to emphasize its possible identity with the cross-product term (s^*c^*) we used in the multiple regression analysis presented in Section 3.3.6. Likewise $s^*..w$ was used in Equation 3-8b to indicate its relationship to the interaction effect WS of Section 3.3.3c.

3.4 COMPARISON OF CONTINUOUS-FLOW AND BATCH TESTS

In this program, batch tests played their customary role: The precursor to continuous-flow tests--small controlled laboratory experiments performed prior to full-scale, pilot-plant tests. For example, several series of batch tests were conducted to establish the optimum conditions for the continuous-flow tests which were described and statistically analyzed in the previous sections. These batch tests are described in Appendices C and E. In this section of the report, results from these small batch tests are compared with the pilot-plant results. In a sense, the comparison measures the success in scaling the process to the proportions needed for shipboard applications.

Full-scale, continuous-flow performance--specifically, the percentage reduction in COD achievable in a CSTR--can be predicted from small batch tests by graphical and algebraic methods. Both are commonly used in chemical engineering. Appropriate methods are reviewed in Appendix G.

3.4.1 TREATMENT IN ABSENCE OF BARBER-COLMAN CO. CATALYSTS

Early in the program (before the development of Barber-Colman Co. catalyst 10,480), a series of batch tests was performed on aliquots of the same waste used in Continuous-flow Test Nos. 72332 and 72335. In these batch tests, which are described in Section C.2 of Appendix C, the influent was a mixture of macerated feces, urine, toilet paper, toiletries and table scraps--a simulated, combined shipboard wastewater--suspended in pH 1.5 tap water. (The exact make-up of the wastewater is listed in Table C-2, page C-4, Appendix C.)

a. Performance In Unlined Reactors

Two of the batch tests were performed in an unlined titanium container under essentially the same conditions. The results were remarkedly consistent, as one can judge from the following tabulation of reaction-rate parameters:

	Batch Test No. 238	Batch Test No. 239	Mean $\bar{x}$*
Initial rate constant, k_i, min^{-1}	0.057	0.059	0.058
Late-stage rate constant, k_ℓ, min^{-1}	0.01	0.006	0.008
Transition, pct red. in COD	57	67	62

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*The coefficients of variation ($100s/\bar{x}$), in percent of the mean $\bar{x}$, are 2.4, 35.4 and 11.4, respectively, where s is the standard deviation.

In Figure 3-6, the network of solid lines is a Jones plot* constructed from the data of Batch Test No. 238. The construction assumes a mean residence time of 15 minutes per compartment. The plot indicates that the rapid initial phase of wet oxidation--the degradation of the raw waste--is accomplished wholly in the first compartment of the CSTR when operated under these conditions. The slower, sluggish burning of the remaining small-molecular-weight species is the dominant reaction taking place in the other (subsequent) compartments.

The predicted percentage reduction in COD can be calculated more accurately from the formula given in Appendix G than from the plot. The formula is reproduced below:

$$\text{Pct. Red.} = 100[1 - \Pi(1 + k_n\tau_n)^{-1}] \qquad (3\text{-}9)$$

Expressed in words, the percentage reduction can be calculated by forming a product of the appropriate reciprocal terms $(1 + k_n\tau_n)^{-1}$, subtracting the product from 1, and multiplying the result by 100. A reciprocal term is included in the product for each compartment. In Equation 3-9, n denotes the compartment; τ is the mean residence time for the compartment; and k is the dominant reaction-rate constant for the compartment.

Using the rate parameters derived from Batch Test No. 238, values were calculated from Equation 3-9 for the percentage reduction in COD after treatment in a series of from one to four compartments. In each compartment, the mean residence time was assumed to be 15 minutes, which was the time allotted for treatment in Continuous-flow Test Nos. 72332 and 72335. (The other pertinent conditions were also essentially the same in the continuous-flow tests as in the batch test.) The calculated (predicted) values and the corresponding ones from the actual continuous-flow tests are tabulated below:

Compartment No.	Over-all Mean Residence Time, Min.	Percentage Reduction In COD Predicted Value	 Test No. 72332	 Test No. 72335
1	15	46.1	54.8	55.1
2	30	53.1	68.4	63.8
3	45	59.2	71.3	69.2
4	60	64.6	75.9	71.6

The observed values are consistently greater than the predicted. In other words, full-scale performance exceeded expectations.

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*See Appendix G for discussion of Jones plots.

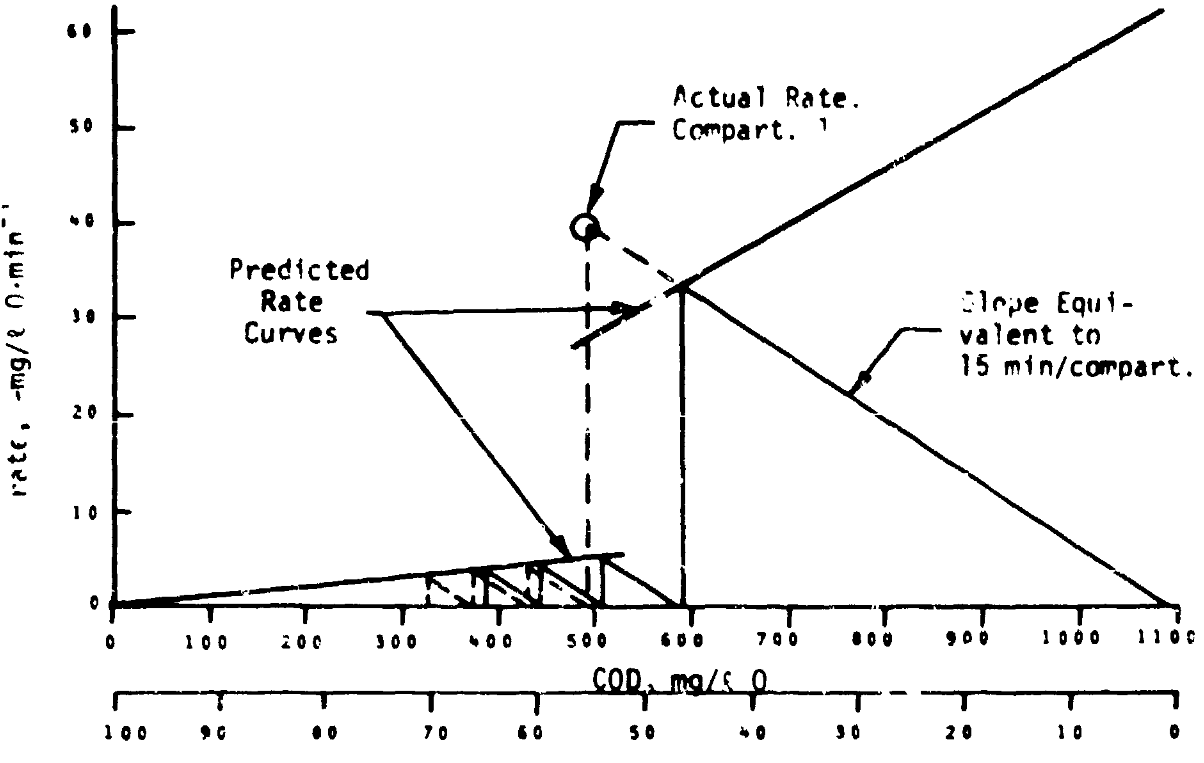

FIGURE 3-6. COMPARISON OF PREDICTED AND ACTUAL PERFORMANCE IN UNLINED REACTORS WITHOUT BARBER-COLMAN CO. CATALYSTS. The solid lines are a Jones plot based on small batch tests, whereas the dashed lines are based on actual performance in full-scale, continuous-flow tests.

As can be seen from Figure 3-6, superior wet oxidation was achieved in the continuous-flow tests, because the reaction rate in the first compartment was much greater than that predicted from small batch experiments. Therefore, the percentage reduction gained in the first compartment was correspondingly greater than the predicted value--expressed in terms appropriate for someone making a Jones plot, the triangular construction has been enlarged: The hypoteneuse has been extended, and therefore, is longer and so are the sides. The percentage reduction achieved in each subsequent compartment is progressively greater than the predicted value although the rates in these compartments are about what was predicted because the enlargement of the first triangular construction "pushed" all of the subsequent triangles further along the (inverted) abscissa.

The mean k_1 for the two uncatalyzed continuous-flow tests (performed in an unlined reactor) are listed below and compared with k_i, the initial rate constant, from the batch tests:

	Batch Test No		Continuous-Flow Test No.	
	238	239	72332	72335
Mean Value of k_i or k_1, min^{-1}	0.057	0.059	0.076	0.089
Group Mean	$\bar{x} = 0.058$		$\bar{x} = 0.0825$	
Variation	2.4%		11.1%	

The mean value of k_1 is 42 percent greater than the mean k_i. The late-stage rate of wet oxidation, on the other hand, was essentially the same in the continuous-flow tests as in the batch tests. The mean of k_3 and k_4 values--the rate constants calculated from Equation 3-7 for the third and fourth compartments--was 0.01 min^{-1}. The mean k_i for the two batch tests was 0.008 min^{-1}.

b. Performance In Carbon-Lined Reactors

In one batch test, a sleeve of porous carbon--a 3/8-in. thick, 4 in. ID cylindrical tube about 10 in. long--was inserted upright inside the titanium cylinder to simulate a carbon-lined reactor. The experiment (Batch Test No. 240) is described in Section C.2, Appendix C. As in the previous two tests, no Barber-Colman Co. catalyst was used; and the waste was slurried in pH 1.5 tap water. The following reaction-rate parameters were calculated for Batch Test No. 240 by linear regression analysis:

k_1, min^{-1}	0.038
k_2, min^{-1}	0.006
Transition, pct red. in COD	90

In Figure 3-7, the solid lines form a Jones plot based on the small-scale experiment, Batch Test No. 240. The plot is drawn for the case in which the mean residence time in each compartment is 15 minutes. According to the prediction, in contrast with the previous case, in a carbon-lined, 4-compartment reactor wet oxidation should proceed in a monotonous manner. In other words, the rate constant should be the same in all compartments. The rate of reduction should decrease steadily with decreasing COD. There should be no abrupt changes in the rate in adjacent compartments. In practice, this was not the case.

Three continuous-flow tests (Nos. 72349, 72350 and 72353) were conducted under essentially the same conditions as Batch Test No. 240. In all three tests, the magnitude of k_1--the mean rate constant for the reactions taking place in the first compartment--was much greater than the mean rate constants for the other compartments. The k-values are listed below:

	Mean Rate Constant, min^{-1}			
	k_1	k_2	k_3	k_4
Test No. 72349	0.126	0.011	0.006	0.007
72350	0.161	0.005	0.009	0.009
72353	0.198	0.010	0.013	0.012
Group mean	0.162	0.009	0.009	0.009
Coef. Variation	22.3%	37.1%	37.6%	27.0%

From the mean rate parameters for the group of three continuous-flow tests, mean actual rates can be computed and compared with the predicted values. A graphical comparison is presented in Figure 3-7. As one can see, the nature of the actual continuous-flow wet oxidation is markedly different than the predicted behavior.

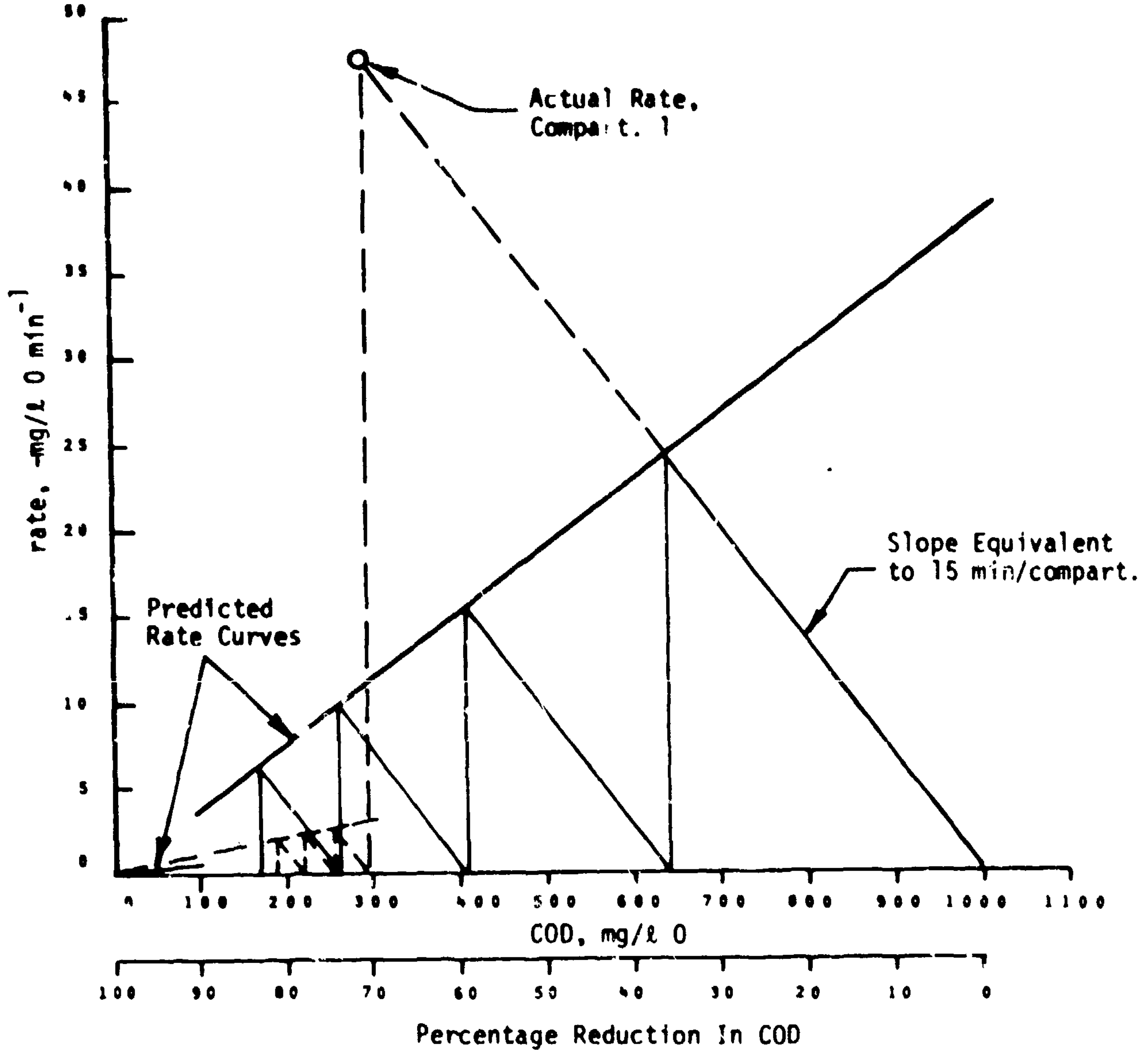

FIGURE 3-7. COMPARISON OF PREDICTED AND ACTUAL PERFORMANCE IN CARBON-LINED REACTORS WITHOUT BARBER-COLMAN CO. CATALYSTS. The solid lines are a Jones plot based on a small batch tests, whereas the dashed lines are based on actual full-scale, continuous-flow tests.

Predicted values of percentage reduction in COD can be calculated from the batch-test data by Equation 3-9 and compared with the actual values. Such a comparison is presented below:

		Percentage Reduction In COD			
			Continuous-Flow Test		
Compartment No.	Over-All Mean Residence Time, min	Predicted Value	72349	72350	72353
1	15	36.3	65.3	70.8	72.1
2	30	59.4	69.9	72.7	75.2
3	45	74.2	72.4	75.7	78.5
4	60	83.5	74.0	78.5	81.1

A much greater amount of destruction occurred in the first compartment of the continuous reactor than was predicted--r_1 was four times the predicted value--but the rate of reaction in subsequent compartments was only one-fourth the predicted value. Circumstances were such that the over-all percentage reduction achieved in the 4-compartment reactor was nearly as great as predicted. The increase in k_1 compensated for the earlier transition to a rate constant comparable to k_ℓ.

3.4.2 TREATMENT IN PRESENCE OF BARBER-COLMAN CO. CATALYST 10,480

A series of batch tests was conducted in which a mixture of macerated feces, urine and toilet paper was subjected to acidic wet oxidation in the presence of Barber-Colman Co. catalyst 10,480. These experiments are described in detail in Appendix E. A summary of reaction-rate parameters derived from these batch tests is presented in Table 3-12. In following discussion, Jones plots are constructed from representative data from these small batch experiments; and the predicted performance is compared with that actually achieved in full-scale, continuous-flow tests.

a. Performance In Unlined Reactors

Three batch tests were conducted in an unlined titanium reactor in the presence of Barber-Colman Co. catalyst 10,480. In two of the three batch tests, there was very little late-stage wet oxidation--in the third, the rate of late-stage oxidation was the same as observed in the full-scale, continuous-flow tests.

A series of three continuous-flow tests was conducted under essentially same conditions as the batch tests. In each continuous-flow test, the mean residence time per compartment was different than the others in

TABLE 3-12

REACTION-RATE PARAMETERS DERIVED FROM BATCH TESTS IN WHICH BARBER-COLMAN CO. CATALYST 10,480 WAS PRESENT

Wetted Wall	Batch Test No.	Rate Constant min^{-1}		Transition*, % Red. in COD
		k_i	k_ℓ	
Unlined titanium	301	0.066	0.002	85
	302	0.091	0.002	87
	305	0.099	0.008	86
Carbon Lined	303	0.182	0.011	92
Tile Lined	307	0.247	0.011	92
	308	0.134	0.006	91
Brick Lined	304	0.211	0.008	86

---

*Percentage reduction in COD corresponding to a transition in rate behavior.

the series. As can be seen from Figure 3-8 the percentage reduction achieved in the first compartment is progressively greater for increasing residence time. From the following tabulation, one sees that the value of k_1--the first compartment rate constant--was greatest for the longest residence time and considerably greater than the K-values for the other compartments:

Continuous-Flow Test No.	Mean Residence, min per compartment	Mean Rate Constant, min^{-1}			
		k_1	k_2	k_3	k_4
73064	15	0.116	0.032	0.011	0.015
73082	20	0.173	0.012	0.005	0.008
73079	30	0.216	0.007	0.010	0.017

Unlike the performance in several of the batch tests, in all three of the continuous-flow tests late-stage wet oxidation was slow but persistent--as rapid as it ever is.

The actual percentage reduction in COD is compared to the value predicted from Batch Test No. 305 in the following subparagraphs:

(1) Mean Residence Time, 15 min./compartment.

The predicted percentage reduction (calculated from Equation 3-9) is compared below with the actual means:

Compartment No.	Over-All Residence Time, min	Percentage Reduction in COD	
		Predicted	Actual
1	15	60.0	65.6
2	30	84.0	76.1
3	45	85.7	79.1
4	60	87.2	82.4

Actual performance is inferior to the prediction.

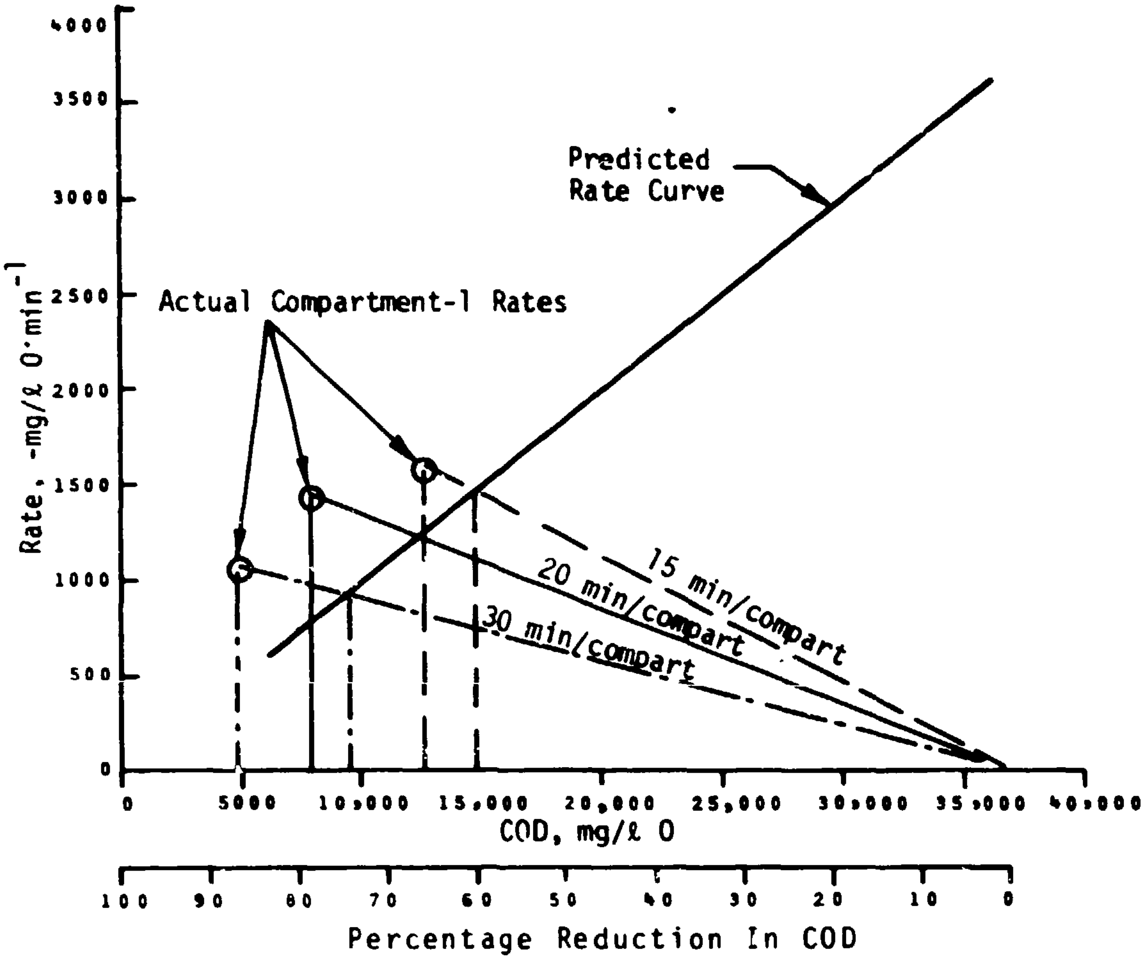

FIGURE 3-8. COMPARISON OF PREDICTED AND ACTUAL, FIRST-COMPARTMENT PERFORMANCE IN UNLINED REACTOR WITH BARBER-COLMAN CO. CATALYST 10,480.
The predicted rate curve is based on small batch tests. The actual rates are based on mean values from continuous-flow tests.

(2) Mean Residence Time, 20 min./compartment.

The predicted and actual percentage reductions are compared below:

Compartment No.	Over-All Residence Time, min	Percentage Reduction in COD	
		Predicted	Actual
1	20	66.7	78.0
2	40	71.3	82.0
3	60	75.2	83.5
4	80	78.6	85.5

Actual performance surpasses expectations.

(3) Mean Residence Time, 30 min./compartment.

The predicted and actual percentage reductions are compared below:

Compartment No.	Over-All Residence Time, min	Percentage Reduction in COD	
		Predicted	Actual
1	30	75.0	86.7
2	60	79.8	89.1
3	90	83.7	91.6
4	120	86.9	94.1

Actual performance in the full-scale, continuous-flow reactor is far superior to that predicted from the small-scale batch experiments. Indeed the over-all percentage reduction predicted for treatment in the cascade of 4 compartments was achieved in practice in one compartment.

b. Performance In Carbon-Lined Reactors.

Batch Test No. 303 was performed in a titanium container into which a porous-carbon tube had been inserted to simulate a carbon-lined reactor. Barber-Colman Co. catalyst 10,480 also was used to accelerate wet oxidation. These and the other conditions were essentially those maintained in Continuous-Flow Test No. 73051.

The solid lines in Figure 3-9 form a Jones plot based on the results of Batch Test No. 303 for the mean residence time maintained in Continuous-Flow Test No. 73051, i.e., 15 minutes/compartment. The predicted percentage reduction is compared below with the reduction actually achieved in the continuous-flow reactor:

	Percentage Reduction In COD			
	Compartment No.			
	1	2	3	4
Predicted From Batch Test No. 303	73.2	92.8	93.8	94.7
Mean, Continuous-Flow Test No. 73051	78.1	82.0	86.3	88.4

Actual full-scale performance is less than predicted. As in some of the previously discussed cases, the actual rate in the first compartment was greater than predicted from the batch test; but the percentage reduction accomplished in the initial phase of oxidation was less. Only the first-compartment rate constant was an order of magnitude greater than the others ($k_1 > 10k_2 = 10k_3 = 10k_4$); theory predicted that $k_1 = k_2 > 10k_3 = 10k_4$. The mean rate constants for the continuous-flow test are tabulated below:

	Continuous-Flow Test No. 73051			
	Compartment No.			
	1	2	3	4
Mean k, min^{-1}	0.244	0.016	0.022	0.016
Coefficient of Variation, Pct of Mean	12.5	45.5	35.7	26.1

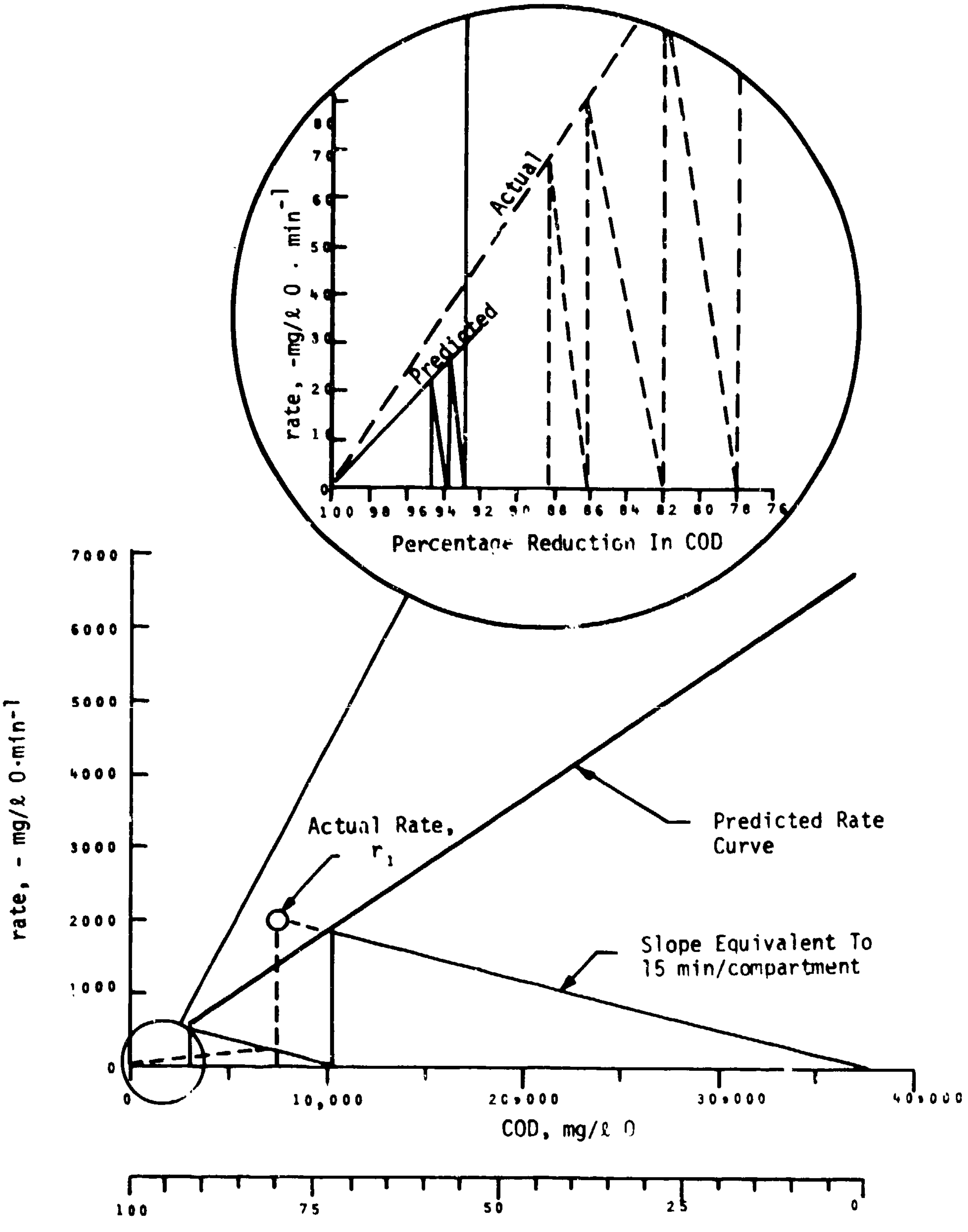

FIGURE 3-9. COMPARISON OF PREDICTED AND ACTUAL PERFORMANCE IN CARBON-LINED REACTORS WITH BARBER-COLMAN COMPANY CATALYST 10,480.

3.5 PARAMETRIC ANALYSIS

As an integral part of the evaluation of the acid circuit, continuous-flow and/or batch tests were conducted to establish the effect of the following parameters on wet oxidation:

1. Influent strength
2. Type of wastewater
3. Influent pH
4. Salinity
5. Time in the Reactor
6. Reactor Pressure
7. Reactor Temperature
8. Dissolved Oxygen Concentration in the Reactor
9. Source of Oxygen
10. Degree of Agitation
11. Types and Concentrations of Catalysts

These parameters were specified for investigation by the Coast Guard in its RFP and in the resulting contract. Technical efforts to evaluate each parameters were identified in the Test Plan submitted by Barber-Colman Co. as PERT Events 4001 through 4011, inclusive.

In following subsections, the foregoing analysis of test data is summarized according to each parameter.

3.5.1 INFLUENT STRENGTH

Review of shipboard waste generation and water usage were presented in Sections 2.4.1 and 2.4.2. The combination establishes the strength of the influent, which in this program generally was measured in terms of COD, that is, the chemical oxygen demand of the dissolved and/or suspended organic matter.

a. General Discussion

The strength of a wastewater is, of course, a very important parameter affecting the design and scale of any treatment system. Extensive batch experiments and confirming continuous-flow tests have established the basic chemical kinetics of wet oxidation. Reduction in COD occurs as the result of a series of chemical reactions, each of which is pseudo-first order with respect to the COD of the liquid slurry. Consequently, the rate of wet oxidation is directly proportional to the influent strength. That is to say, on a mass basis, the rate of reduction, e.g., in mg/ℓ O· min^{-1}, is directly proportional to the COD. On the other hand, the percentage reduction in COD is the same for a fixed time of reaction regardless of the influent strength, all other things being equal. In other words, the extent of wet oxidation on a percentage basis is independent of influent strength.

Since the analysis presented in Sections 3.3 and 3.4 deals mainly with the chemical aspects of the process, influent strength is not an important factor: Percentage reduction is the principal response parameter in most of the analysis and it is independent of influent strength (COD). In Section 6, on the other hand, the preliminary design of a 20-man treatment system is presented and, here, influent strength is the primary factor.

In designing shipboard wastewater-treatment systems, there are restrictions placed on the total weight and volume that, in turn, limit the size of the reactor. Influent strength, under these circumstances, determines the allowable residence time and in the end, to a large extent, the feasibility of the application. Specific examples are presented in the next section.

b. Specific Effect On The Acid Circuit.

According to the design specifications which were established for this program (cf. Section 2.4.2), a 20-man, direct-discharge system would have to treat 700 gallons (2650ℓ) combined wastewaters daily. Since the 4-compartment prototype reactor used in the program holds about 30 liters of liquid (at 450°F), the mean allowable residence time would be about 4 minutes per compartment, if the prototype reactor were used to treat the combined wastewaters. If only the body sewage were treated, the volume of influent would be about 350 gallons (1325ℓ); and the mean allowable residence time would be about 8 minutes per compartment, a total of 32 minutes.

3.5.2 TYPE OF WASTEWATER

Five classes of shipboard wastewaters were investigated. Those from a biological origin responded to treatment in the acid circuit; whereas, some man-made organic chemicals defied wet oxidation.

a. Body Sewage.

Several series of continuous-flow tests were conducted on mixtures of feces and urine comparable in strength to current shipboard body sewage. That is to say, the influent had a COD comparable to that of toilet and urinal flushings from systems using contemporary water closets. The percentage reduction in COD ranged from about 58 to nearly 87 (after 30 minutes residence under widely different conditions.) Treatment for 60 minutes resulted in percentage reduction in COD ranging from about 65 to nearly 90. The salinity-- in some cases-- was the strongest negative factor, and the strongest positive effect was the presence of Barber-Colman Co. catalyst 10,480.

These tests on body sewage are described in detail in Appendix C. An analysis of the test results is presented in Sections 3.3 and 3.4 of the main report.

b. Combined Shipboard Wastewaters.

Several continuous-flow tests were conducted on a mixture of macerated body sewage, toilet paper, table scraps and toiletries, equivalent to the daily per-capita waste aboard a small ship (without laundry facilities). The percentage reduction in COD was about 68 after 30 minutes of treatment and about 75 at the end of 60 minutes. (The evaluation was not extensive; and the maximum possible destruction probably was not achieved.)

Details of the tests on combined shipboard wastewaters are presented in Section C.2, Appendix C. Test results are analyzed in Section 3.3 and 3.4 of the main report.

c. Laundry Wastewater.

A continuous-flow test was conducted on a simulated shipboard laundry water. Less than 10 to 30 percent of the input COD and total organic carbon (TOC) was reduced by wet oxidation at 450°F. Chemical analysis for methylene-blue-substances (MBAS) indicates that sodium lauryl sulfate (SLS), the principal active constituent of most modern detergents is virtually unoxidized.

The test on laundry wastewater is described in detail in Section D.1, Appendix D.

d. Bilge Water.

A continuous-flow test was conducted on an approximately 0.1 percent mixture of automotive diesel fuel in water, simulating bilge water. Nearly four-fifths of the input COD reported in the vapor condensate. In practice, the vapors from wet oxidation aboard ship could be burned by mixing them with the main-engine exhaust. Therefore, the effluent COD--which was 10 to 15 percent of the input COD--is probably a more practical index of process efficacy than the over-all percentage reduction in COD. Viewed in this light, treatment of bilge water significantly reduced the level of organic matter entrained or dissolved in the wastewater--treated water contained about one tenth as much organic as untreated water.

The test on bilge water is described in detail in Section D.2, Appendix D.

e. Galley Waste

The contents of three 6-lb, 12-oz. cans of beef stew was macerated in 40 gallons of tapwater and used as influent in a continuous-flow test in which no acid or catalyst was added. In this treatment of simulated galley waste, about 60 percent of the input COD was destroyed in 40 minutes of wet oxidation; 10 percent of the input COD, however, was volatilized and could be burned in the exhaust gases. Therefore, the level of destruction might be considered to be about 67-70 percent.

The details of the test on galley waste are presented in Section D.3, Appendix D.

3.5.3 INFLUENT PH

The acidity of the liquid-phase slurry affects the rate and extent of wet oxidation. During low-temperature wet oxidation, low-molecular-weight organic compounds accumulate in the liquid phase during the initial destruction of the waste; these small fragments of the original waste are extremely difficult to oxidize. In the presence of a strong mineral acid like sulfuric, less of these refractory small-molecular-weight substances form in the initial wet oxidation.

Graphs showing the effect of acidity on the wet oxidation of simulated shipboard sewage were presented in Section 2.3. Acidity similarly influences wet oxidation of most other wastes; for example, in Figure 3-10, data is presented from continuous-flow tests conducted on raw primary municipal sewage sludge; and, in Figure 3-11, the results from the wet oxidation of unacidified wastewater from a commercial-aircraft recirculating toilet are compared with results from acidic wet oxidation of the same wastewater, which was decidedly ammoniacal (very urinous) and contained 2 to 3 pct toilet paper.

Evaluation of the requirements for shipboard treatment of combined wastewaters led Barber-Colman Co. to propose an acid-catalyzed wet-oxidation process, the evaluation of which is the topic of this portion of the report. The acid-circuit process also utilizes catalytic agents which, in the presence of acid, further accelerate the destruction of most naturally formed organic substances. (The effect of acidity on Barber-Colman Co. catalyst 10,480 is evident by examination of the test results presented in Table 3-10, Section 3.3.7.)

3.5.4 SALINITY

In the statistical analysis of continuous-flow tests conducted on simulated shipboard sewage (cf. Section 3.3), salinity was found to be the dominant factor. The wet oxidation of wastewaters containing sea water generally was more difficult than treatment of non-saline wastewaters. In the absence of the catalyst and porous carbon, however, there is some evidence that salinity is not a deterrent. In fact the response to treatment was greater in the presence of sea water than in the absence of sea water, but the sampling of data is too small for confidence.

3.5.5 TIME IN THE REACTOR

In nearly all of the continuous-flow tests performed in this program, the mean residence time was 15 to 20 minutes per compartment; and most of the percentage reduction in COD was accomplished in the first one or two compartments. Prolonging treatment in additional compartments resulted in an increase in the over-all reduction ranging from 2 to 6 percent (per compartment). A break-down by test and test series is provided in Tables 3-13 and 3-14. Formulas derived in Appendix F and discussed in Section 3.3.2 indicate that the additional percentage reduction is a linear function of the number of compartments; that is,

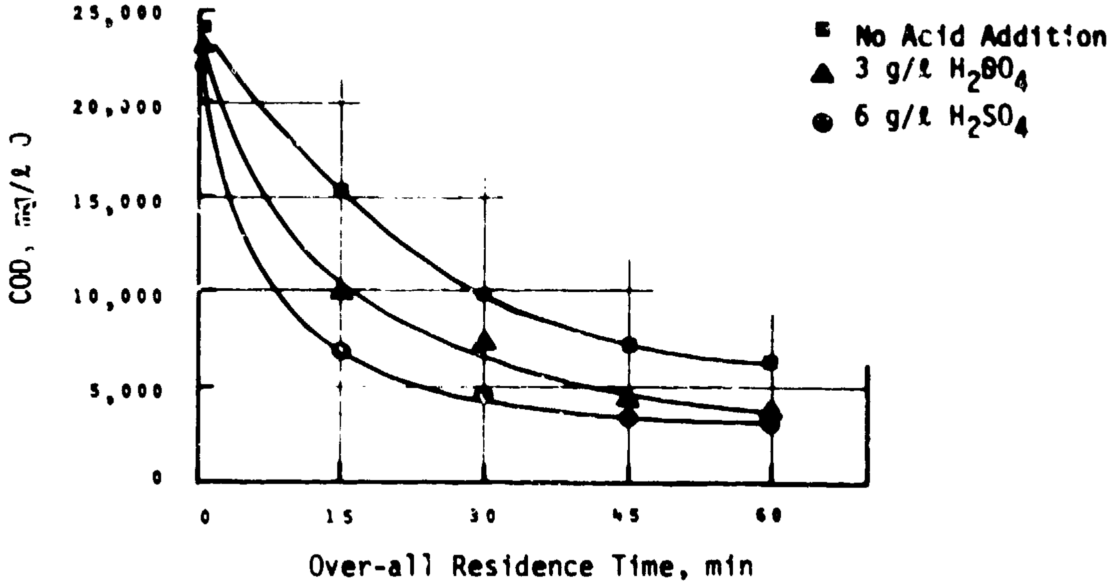

FIGURE 3-10. EFFECT OF ACIDITY ON CONTINUOUS-FLOW WET OXIDATION OF RAW PRIMARY SEWAGE SLUDGE.

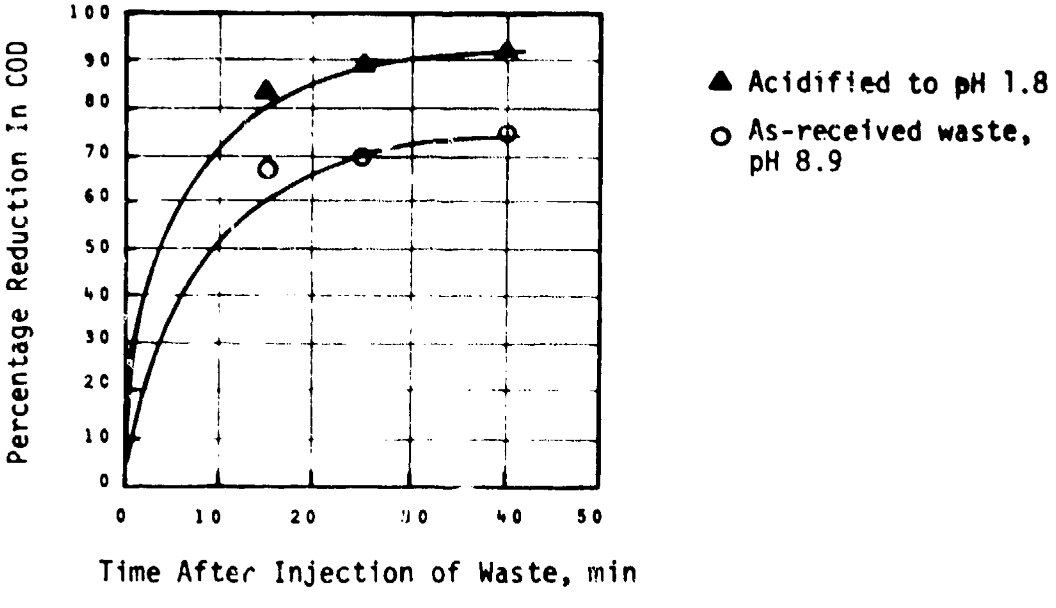

FIGURE 3-11. EFFECT OF ACIDITY ON BATCH-TEST WET OXIDATION OF AIRCRAFT-TOILET WASTE.

TABLE 3-13

ADDITIONAL PERCENTAGE REDUCTION IN COD ACHIEVABLE BY PROLONGING WET OXIDATION IN CARBON-LINED REACTORS*

Test No.	Salinity	Catalyst 10,480	Acidity		Pct. Red. After 30 min in two Compart.	(b) Additional Pct Red. per additional Compartment	Rate of Increase from Additional Treatment, Pct
			g/ℓ H_2SO_4	Efflu. pH			
73051	TW	Yes	3	2.0	83.4	2.9	3.5
73054	TW	Yes	0	4.8	71.6	3.8	5.3
73029	1/3SW	Yes	1	2.8	68.0	3.0	4.4
72349	TW	No	6	1.5	69.9	2.4	3.4
72350	TW	No	6	1.5	72.7	2.9	4.0
72353	TW	No	6	1.4	75.2	3.0	4.0
72347	1/6SW	No	6	1.5	67.8	2.8	4.1
72346	1/3SW	No	6	1.5	62.4	1.6	2.6

---

*The following conditions were common in all tests: Mean temperature, 450°F; Influent COD, 1500-2300 mg/ℓ 0; O_2/COD = 3-10; stirring speed, 800 rpm; mean residence time, 15 minutes per compartment

TABLE 3-14

ADDITIONAL PERCENTAGE REDUCTION IN COD ACHIEVABLE BY PROLONGING WET OXIDATION IN UNLINED REACTOR*

Test No.	Mean Residence Time, min/Compart.	Mean Temp, °F	Salinity	Catalyst 10,480	Pct Red. in COD from Base Treatment		(b) Additional Pct Red. per add'n compart.	Rate of increase from additional treatment, Pct
					20 min in one Compart.	30 min in two Compart.		
73079	30	457	TW	Yes		86.7**	2.5	2.9
73082	20	448	TW	Yes	78.0		2.4	3.1
73064	15	454	TW	Yes		76.1	3.2	4.2
73068	15	420	TW	Yes		73.0	3.6	4.9
73072	15	422	1/3SW	Yes		69.1	1.4	2.0
72332	15	4[illegible]2	TW	No		68.4	3.8	5.8
72335	15	454	TW	No		63.5		
73089	20	451	1/3SW	No	72.0		2.4	3.4
73086	20	450	1/3SW	No	69.6			
73075	18	402	TW	Yes		59.4†	3.5	5.9

---

* The following conditions were common in all tests: Acidity level, 6-8 g/ℓ H_2SO_4; stirring speed, 800-1200 rpm; O_2/COD = 1-12

**30 min in one compartment

† 36 min in two compartments

$$\begin{matrix}\text{Total Pct} \\ \text{Red. in COD}\end{matrix} = [b \cdot n] + \begin{matrix}\text{Pct. Red. From} \\ \text{Base Treatment}\end{matrix} \qquad (3\text{-}10)$$

where b is a constant; and
n is the number of additional compartments.

In Equation 3-10, all compartments are assumed to equal in capacity; and the base treatment is defined as either a mean over-all residence time of

30 minutes in two compartments, or
20 minutes in one compartment.

The value of b is listed for each test in the next to the last (on the right) columns of Tables 3-13 and 3-14.

3.5.6 REACTOR PRESSURE

The total pressure of the reactor <u>per se</u> is not an important variable, but rather a means of operating at elevated temperatures and/or increasing the concentration of dissolved oxygen. The primary purpose of this program was to establish the feasibility of relatively low temperature, low pressure wet oxidation as a means of treating shipboard wastewaters. The standard Barber-Colman Co. reactor operates at 600 psi, maximum pressure; and is constructed in accordance with standard ASME codes pertaining to other common pressure-vessels such as boilers. Exhaustive trade-off studies indicate that a low-pressure system is mandatory for shipboard applications--no other concept has a practical weight. In keeping with the objective of demonstrating a low-pressure process the reactor pressure was held at 600 psi throughout this program.

In batch tests, the total pressure of the reactor has been varied and found to cause little change in the extent or rate of wet oxidation. Moreover, conducting batch experiments in the presence of intentionally added excess nitrogen or carbon dioxide gas had no discernible effect.

3.5.7 REACTOR TEMPERATURE

The mean temperature of the reactor ranged from 400 to 455°F in various continuous-flow tests; and the temperature of the first compartment frequently was 475-480°F. Statistical analysis of the test data is presented in Section 3.3; the analysis indicates that process efficacy is relatively insensitive to the temperature of the reactor over most of the investigated range: Specifically, the percentage reduction in COD from treatment at a mean temperature of 455°F is no greater than the percentage reduction from otherwise identical treatment at 420°F. Treatment at 400°F, on the other hand, is inferior--the reduction at 400°F is, in some cases, 15 percentage points less than otherwise comparable treatment at 420°F.

Since steam confined above 490°F exerts a pressure in excess of 600 psi and the reactor is not built to withstand more than 600 psi, the processes under investigation are intended for use at or below 490°F. Moreover, in view of the markedly lower level of reduction at 400°F compared to that at 420°F, treatment below 420°F does not appear practical. Thus, the temperature range of the processes is very narrow: In practice, about 60 Fahrenheit degrees, 420 to 480°F.

3.5.8 DISSOLVED-OXYGEN CONCENTRATION IN REACTOR

The solubility limit of oxygen in water can be determined from the following equation which is derived in Appendix H:

$$C_\ell = \frac{32 \times 10^6}{18} \rho H^{-1} P_{O_2} \qquad (3\text{-}11)$$

where C_ℓ is the saturation concentration in the liquid expressed in mg/ℓ O;
ρ is the density of water;
H^{-1} is the reciprocal of the Henry's Law constant; and
P_{O_2} is the partial pressure of oxygen expressed in atmospheres.

Expressed in terms appropriate to estimating the concentration of dissolved oxygen (DO) from the process variables monitored in the program, C_ℓ depends on the magnitude of three parameters: temperature, overpressure and the value of O_2/COD. Overpressure is defined as the total pressure of the reactor minus the steam pressure and is equal to the combined partial pressures of the vapors and gases confined in the reactor.

In the WETOX reactor, compressed air is fed into each mixing chamber through orifices located in the bottom of the chambers beneath the liquid phase. Unabsorbed and unreacted oxygen rises to the surface of the liquid and accumulates with other gases and steam in the so-called vapor-phase region of the reactor. The partial pressure of oxygen in the vapor phase, which is denoted by the symbol $P^V_{O_2}$, can be estimated from the following semi-empirical formula:

$$P^V_{O_2} = (\pi - P_{H_2O}) \{0.2[O_2/COD) - 0.8]/(O_2/COD)\} \qquad (3\text{-}12)$$

where π is the total pressure in the reactor (600 psi in this program); and
P_{H_2O} is the steam pressure.

The quantity $(\pi - P_{H_2O})$ is the so-called overpressure.

Since the liquid is agitated constantly and the oxygen above it continually "folded" into it, the concentration of DO in the bulk liquid can be found by substituting Equation 3-12 into Equation 3-11. The DO of greatest concern is that of the first compartment, because most of the reaction takes place there. Resulting values of the compartment-1 C_ℓ are listed in Table 3-15 for the tests comprising the two major series in the evaluation of the acid circuit.

One sees immediately in scanning Table 3-15 that the concentration of dissolved oxygen was essentially constant in most of the tests. In 13 of 18 tests, the value of C_ℓ ranges from 31 to 39 mg/ℓ O. The range for all tests is 20 to 140 mg/ℓ O.

Note that at 475°F the overpressure is one-tenth of the total pressure. There is little room for anything in the reactor but steam. The air flow in the 475°F tests (performed in this program) was excessive. The O_2/COD value ranged from 3 to 12; consequently, the partial pressure of oxygen was about 10 psi. Had the 475°F tests been run at O_2/COD near unity, the partial pressure of oxygen would have been about 3 psi--the same as the partial pressure of ambient (14.7 psi) air.

The three test--Nos. 73082, 73086 and 73089--are representative of recommended practice. These three tests were performed with values of O_2/COD ranging from 1.1 to 1.4; the partial pressure of oxygen ranged from 6 to 11 psi; and C_ℓ varied from 20 to 38 mg/ℓ O. The mean temperature of the first compartment ranged from 460 to 465°F. The performance in these tests was as good as in tests in which excessive air was supplied. As a matter of fact, the rate of reduction in COD achieved in the first compartment was greater in Test No. 73082 than in any other test in the program.

3.5.9 SOURCE OF OXYGEN

In this program, compressed air was the source of oxygen in all continuous-flow tests. Supplemental batch tests were conducted with both compressed air and pure oxygen. There was no discernible difference in the rate or extent of wet oxidation attributable to the source of oxygen.

The use of compressed pure oxygen (or of oxygen-enriched air) does not appear to be practical aboard small ships and, therefore, was not investigated in the pilot-plant studies. Moreover, there would be little advantage gained by their use. Extensive research indicates that the rate and extent of wet oxidation can not be increased by the use of excessive oxygen; therefore, there is little point in oxygen enrichment. In addition, as wet oxidation does not occur satisfactorily below 420°F, a pressure vessel is required primarily to confine steam. Heavy walled reactors would be needed even if pure oxygen were used in place of air.

TABLE 3-15

CONCENTRATION OF DISSOLVED OXYGEN IN BULK LIQUID OF FIRST COMPARTMENT

Test Serie	Test No.	C_ℓ mg/ℓ O	Temp °F	$(\pi - P_{H_2O})$ psi	$\frac{O_2}{COD}$	$P^V_{O_2}$ psi
Carbon	72346	38	475	60	8	11
	72347	39	475	60	10	11
	72349	39	475	60	9	11
	72350	38	475	60	8	11
	72353	39	475	60	9	11
	73029	36	475	60	5	10
	73051	31	475	60	3	9
	73054	31	475	60	3	9
Unlined	72332	38	475	60	7	11
	72335	40	475	60	12	11
	73064	34	475	60	4	10
	70368	131	435	238	9	44
	73072	105	435	238	3	35
	73075	140	412	317	4	51
	73079	45	465	110	2	13
	73082	20	465	110	1.1	6
	73086	34	460	133	1.3	10
	73089	38	460	133	1.4	11

3.5.10 DEGREE OF AGITATION

The high efficacy of the wet-oxidation processes demonstrated in this program is due to the intense agitation which is characteristic of the WETOX reactor. The rate and extent of wet oxidation are considerably greater in a stirred vessel than in an unstirred one. For example, consider the following data of Wheaton et al.*

Test Condition**	Stirred	Not Stirred
pH	7.5	7.7
Total Solids g/100 ml	1.81	1.91
Ash g/100 ml	1.60	1.63
Effluent COD mg/liter	2150	4784

The foregoing test results are from conventional laboratory, batch experiments performed in a one-liter autoclave normally stirred at 1500 rpm and were performed at relatively high temperature.

a. Effect On WETOX Process

Effective wet oxidation at low temperatures can only be accomplished by efficient mixing and aeration of reactants; consequently, the WETOX process is always conducted in agitated reactors. The Jones' plots presented in Figure 3-12 summarize actual experiments conducted on (unacidified) sewage sludge and dramatically demonstrate the effect of agitation. In an unstirred reactor, the rate of destruction is so slow that less than 58 percent reduction in COD is accomplished in 60 minutes; whereas in the same 60 minutes in a four-compartment continuously stirred reactor, about 78 percent reduction in COD is achieved. The comparison is made for reactors operating with a mean residence time of 15 minutes per compartment. In the presence of acid and/or catalyst, the extent of destruction can be greater than in this case in which unacidified sludge was treated.

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* R.R. Wheaton, J. R. C. Brown, R. V. Ramirez, and N. G. Roth, "Investigation of the Feasibility of Wet Oxidation for Spacecraft Waste Treatment", NASA Contractor Report No. 66450, Aug. 30, 1967, Contract NAS 1-6295 conducted by Whirlpool Corporation, St. Joseph, Mich., for NASA.

**Mixed body waste (10 percent feces in urine) at 550°F and 500 psi initial oxygen pressure.

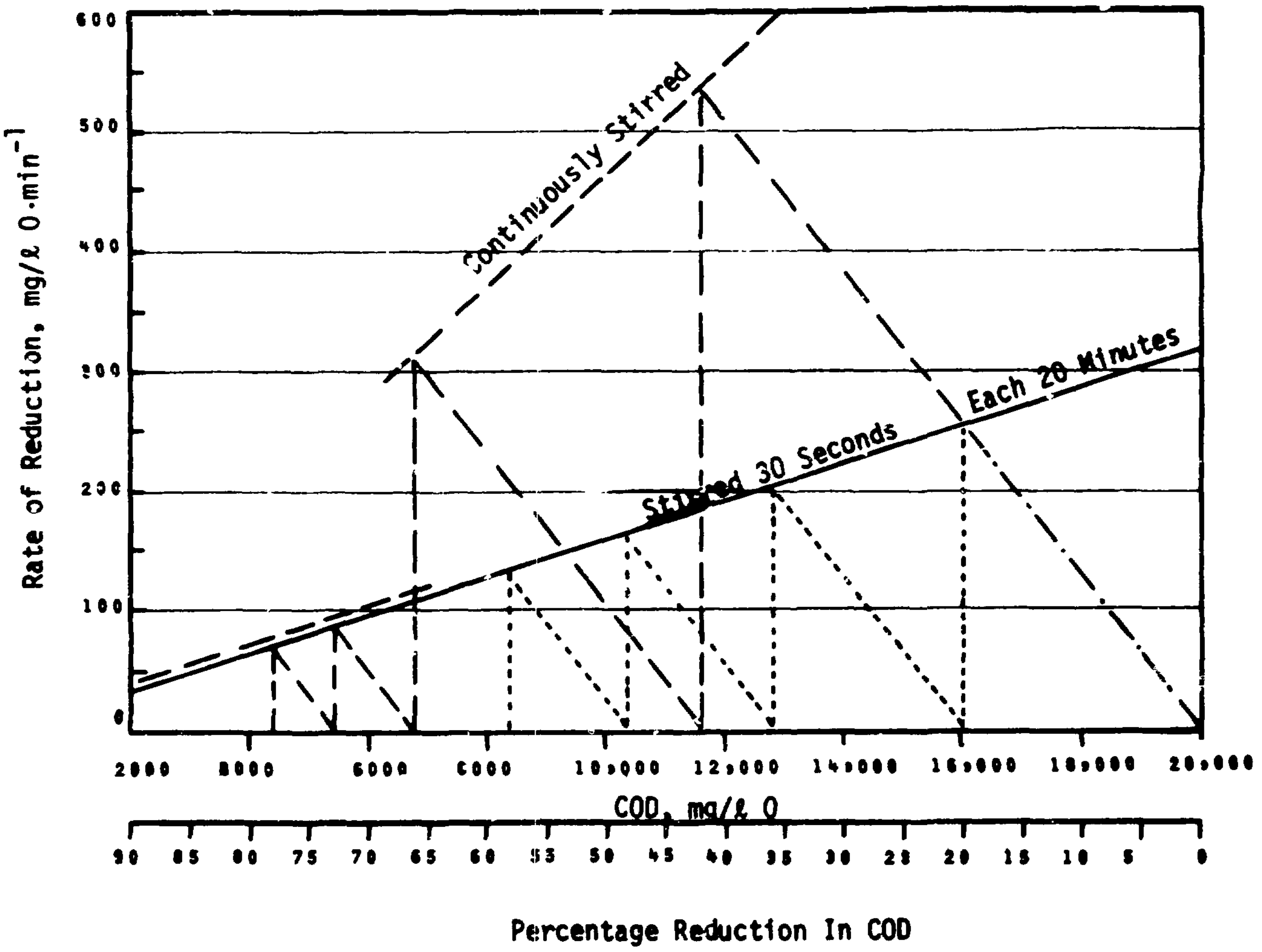

FIGURE 3-12. EFFECT OF STIRRING ON WET OXIDATION OF UNACIDIFIED SEWAGE SLUDGE

During the performance of the "non-stirred" experiment, the liquid phase was stirred for 30 seconds each 20 minutes to assure homogeneity just prior to sampling. Otherwise, the liquid was undisturbed (at least by mechanical stirring). There are, of course, other causes of movement in the wet oxidizing waste; e.g., the evolution of carbon dioxide and steam as well as the liberation of heat in the combustion process tend to stir the slurry. Present commercial treatment of sewage sludge depends on these non-mechanical methods to achieve agitation. The "non-stirred" example of Figure 3-12 is representative of the low level of destruction achieved in contemporary sewage practice.

Note in Figure 3-12 that in the case of non-stirred wet oxidation there is no "break" in the rate curve: The rate of wet oxidation decreases monotonously with increase in percentage reduction in COD. The fast, initial rate-limiting step apparently is comparable to the slow, late-stage rate in the non-stirred mode. There is no discernible transition in the rate-limiting processes.

During the program, the importance of agitation was inadvertently demonstrated in Test 73086, which is described in Appendix C, page C-54. In this test, the agitator in the second compartment did not operate during most of the test. The rate constant for the unstirred compartment was 3 to 6 times less than the corresponding value in the other (stirred) compartments, i.e., in compartments 3 and 4.

b. Estimation of Efficiency.

The degree of agitation can be estimated in the following manner:

In the WETOX reactor, compressed (650-750 psi) air flows continuously into each mixing chamber through an orifice located in the bottom of the compartment beneath about seven inches of constantly stirred liquid. The air stream is broken up by the action of the stirrer into countless small bubbles, each filled with essentially pure air at a greater pressure than that of the system. As these bubbles rise through the liquid, they expand; and during the expansion, oxygen dissolves into the liquid.

The universally accepted mechanism of gas absorption is the so-called two-film theory first described by Whitman*. According to this theory, mass is transferred in the bulk of the phases by convection currents; and concentration differences are negligible except in the immediate vicinity of the interface between the phases. Here, convection ceases; and on either side of the interface a thin film of essentially stagnant fluid exists through which the transfer of matter is by molecular diffusion. The rate of transfer by diffusion is proportional to the concentration gradient (of each diffusing species) and to the interfacial surface area over which diffusion occurs.

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*W.G. Whitman, "The Two-Film Theory of Absorption", Chem. and Met. Engr. 29, (1923) p 147.

The rate of absorption can be greatly increased by agitation of the liquid phase. Mixing the phases is effective because:

(1) It disperses the air (oxygen) into the liquid as small bubbles, thus increasing the effective interfacial area for mass transfer.

(2) It circulates the liquid in swift eddy currents, delaying the escape of air bubbles from the liquid and thus increasing the contact time for mass transfer.

(3) It causes turbulent shear, thus reducing the thickness of the stagnant liquid film and, hence, resistance to mass transfer.

Most of the absorption takes place during bubble formation. As much as eighty percent of the total absorption occurs during interfacial formation, that is to say, during the creation and expansion of the bubbles*. Interphase mass transfer occurs across the interfacial films formed at the boundaries of individual pockets of gas.

In cases involving chemical reaction, generally the liquid-film resistance is much greater than that of the gas film; and transfer is slowest through the liquid film**. It becomes the rate-limiting path.

Specifically, the rate of absorption is dependent on three factors: (1) the liquid-film resistance, (2) the concentration gradient of oxygen, and (3) the interfacial area. An appropriate mathematical expression for dc/dt, the rate of absorption, is

$$dc/dt = K_L a(C_i - C_r) \simeq K_L a C_i \qquad (3\text{-}13)$$

where K_L is the over-all coefficient of mass transfer;

---

* W. W. Eckenfelder, Jr., "Process Design of Aeration Systems for Biological Waste Treatment", <u>Chemical Engineering Progress</u>, July 1956, pp 286-292.

**J. M. Coulsen and J. F. Richardson, Chap. 19, "Absorption of Gases", <u>Chemical Engineering</u>, Vol. 2, Pergamon Press, New York (1955).

a is the specific area of interphase contact;

C_i is the oxygen concentration at the film interface and;

C_r is the oxygen concentration of the bulk waste liquor in the immediate vicinity of the reaction zone.

According to the theory, the interfaces of the bubbles are saturated with oxygen. In other words, C_i is the appropriate saturation concentration--the solubility limit set by the partial pressure of oxygen in the bubble. When a chemical reaction such as oxidation takes place immediately following absorption, C_r is assumed to be zero. One assumes that oxygen is consumed as rapidly as it can be absorbed. Generally the terms K_L and a are combined; the resulting term K_La is called the over-all transfer coefficient by some and the aeration efficiency by others*.

The magnitude of K_La is greatly affected by agitation and is used as a measure of mixing effectiveness. There are various methods of estimating K_La; the method used by Cooper et al.** is most appropriate for our needs. In their study of sulfite oxidation, they assumed that the rate of absorption was at least as great as r_{ox}, the rate of oxidation:

$$dc/dt \geq r_{ox} \tag{3-14}$$

Since oxidation can never proceed faster than absorption, one can estimate K_La by determining r_{max}, the maximum rate of wet oxidation, and substituting the value in Equation 3-13. That is to say,

$$r_{max} \approx K_LaC_i \tag{3-15}$$

The value of C_i can be calculated from Equation 3-11. The expanding bubbles are filled with pure air at 700 psi; therefore, the partial pressure of the confined oxygen is 140 psi. Substitution of this value for P_{O_2} in Equation 3-11 gives an expression for C_i (in terms of temperature-dependent parameters).

Since the temperature is monitored in every test (and the rate of oxidation also is measured), we appear to possess the necessary information to establish the value of K_La. Unfortunately, however, it isn't that simple; primarily because wet oxidation is not a process limited by absorption, as the following discussion exemplifies.

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* R. Steel, Biochemical Engineering, published by Heywood & Co. Ltd. (1958); see pages 164-165.

**C. M. Cooper, G. A. Fernstrom and S. A. Miller, "Performance of Agitated Gas-Liquid Contactors", Industrial and Engineering Chemistry, Vol. 36, (1944), pp 504-609.

c. Effect of Absorption on WETOX Process.

During the period in which this program was conducted, other programs were also in progress at the Barber-Colman Co., RRS Division, pilot plant. Some of these other programs shared the same 4-compartment WETOX reactor in which most of the Coast Guard program was performed. Twice weekly continuous-flow tests were conducted on simulated shipboard wastewaters; and, during the remainder of the week, the reactor was utilized to treat raw primary sewage sludge and other wastes.

The essential parameters affecting absorption--speed of agitation, size and shape of the reaction chamber, the quantity and nature of the air flow, etc. --were the same for tests in which similar wastewaters of widely varying COD were evaluated. Representative test data are presented in Table 3-16. Values of r_1/C_1 and k_1 are listed in the table for pairs of tests in which all other things were equal except the influent COD.

Look at the values of r_1/C_1 and compare them with the values of k_1 for the various pairs of tests in Table 3-16. The parameter r_1/C_1 is the rate of oxidation in the first compartment divided by the saturation concentration of DO in the liquid film of the air bubbles. According to the absorption theory presented in the last section, a constant value of r_1/C_1 would be indicative of an absorption-limited process. The values in Table 3-16, however, increase with increasing influent COD, whereas k_1, the rate constant for the first compartment, is independent of influent COD.

The data indicate that the rate of wet oxidation, as previously stated in Section 3.5.1, is directly dependent on the COD of the influent. The process is governed by a first-order chemical reaction. There is no evidence that the rate of wet oxidation slackens (in the treatment of strong waste) due to limitations in absorption. In other words, demand never exceeds supply--provided air is supplied in proportion to COD so that $O_2/COD>0.8$.

The data of Table 3-16 were compiled from observations and chemical analysis of samples from the first compartment. Since most of the reaction takes place in the first compartment, the rate (r_1) is greater than in any other compartment; and, if oxidation is to exceed absorption anywhere in the reactor, one would expect it to be in the first compartment. The data of Table 3-16 indicate that absorption was always greater than oxidation in the tests on shipboard sewage; and the conclusion is probably true in the case of raw primary sewage sludge as well.

Cooper *et al*. found that the rate of absorption and, hence, the rate of sulfite oxidation varied widely according to the geometry of the reaction vessel, the type of impeller, the depth of liquid, the power input and rotational speed of the agitators. They report values of K_La ranging from 4.4 to 1110 $mg/\ell\ O \cdot min^{-1}\ atm^{-1}$; converted to the same units, the values

TABLE 3-16

COMPARISON OF PERFORMANCE, FIRST COMPARTMENT*

Test No.†	Reactor Lining	Mean Temp, °F	Stirring Speed rpm	Influent COD mg/ℓ 0	r_1 mg/ℓ 0 min^{-1}	r_1/C_i mg/ℓ 0 min^{-1} mg^{-1}	Type of Waste**	k_1 min^{-1}	Pct. Red. in COD @ 60 min
73010	Carbon	475	800	5,875	333	0.67	L	0.31	96
73024	Carbon	475	800	16,500	728	1.46	OSS	0.14	80
73029	Carbon	475	800	1,765	82	0.16	SSS	0.14	74
73051	Carbon	475	800	2,265	120	0.24	FSS	0.24	89
73053	Carbon	475	800	35,460	1790	3.59	NSS	0.24	88
73071	None	430	1200	17,140	638	1.54	OSS	0.10	80
73072	None	435	1200	2,540	91	0.22	SSS	0.10	72
73080	None	460	1200	23,600	820	1.75	NSS	0.16	88
73082	None	465	1200	3,365	128	0.27	FSS	0.17	84

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†Each test is assigned a five-digit number. The first two numbers denote the year and the last three the day of the year on which the test was run.

*All tests performed in a 4-compartment, continuous-flow reactor in the presence of Barber-Colman Co. catalyst 10,480 and with acid addition to the influent. The mean residence time was 15 minutes per compartment except in Test Nos. 73080 and 73082 in which it was 20 minutes per compartment.

**L denotes lemon-processing-plant wastewater
OSS denotes old sewage sludge, 13-14 days old
NSS denotes new sewage sludge, 1-2 days old
SSS denotes saline shipboard sewage, 1/3 sea water
FSS denotes fresh (water) shipboard sewage, tap-water influent

of r_1/C_1 in Table 3-16 range from 9 to 194. Assuming that the WETOX agitator is as efficient as the best used by Cooper, absorption can take place five times as fast as the fastest rate of wet oxidation listed in Table 3-16. In other words, if the influent strength were about 180,000 mg/ℓ O, the process might become absorption-limited.

d. Comparison With Conventional Aerobic Treatment.

The nature of the liquid phase has a pronounced effect on K_La. According to Eckenfelder*, in conventional aerobic treatment of wastewaters, the mass transfer rate in certain waste liquors may be only 10 to 20 percent of that attainable in pure water. As little as 50 ppm of certain anionic detergents reduces the transfer rate to 50 percent that of pure water. As much as 60 percent reduction in transfer rate can be caused by the presence of anti-foam agents. The transfer coefficient for fresh sewage may be about 26 to 46 percent of K_La for water; the transfer coefficient for septic sewage may be as low as 16 to 19 percent of that for pure water. Eckenfelder* states that oxygen transfer studies show a variation in K_La for pulp and paper mill waste from 60 to 120 percent of water.

The following values of K_La are cited by Eckenfelder as representative of conventional processes.

Aeration System	Waste	Temp °C	K_La mg/ℓ O $min^{-1}mg^{-1}$
Colaflex	sewage	17	0.035
Impingement	paper	36	0.082
Drilled pipe	paper	33	0.043
Jet	dairy	25	0.057
Saran tubes	sewage	23	0.083

The mean value of r_1/C_1 for 18 tests on simulated shipboard sewage is 0.18 min^{-1}, which is two to three times the values cited by Eckenfelder as representative of conventional wastewater treatment. The corresponding value for tests on sewage sludge in the same reactor is about 20 to 100 times as great. One concludes that the degree of agitation in the WETOX reactor is much more efficient than in any conventional aerobic process.

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*Same reference cited on page 3-75.

3.6 CONCLUSIONS (EVALUATION OF ACID CIRCUIT)

A sufficiently thorough investigation has been performed to establish the efficacy of the acid circuit: Most shipboard wastes are destroyed by acidic wet oxidation at relatively low temperatures and pressures. The effluent has none of the putrid and pathogenic characteristics associated with raw sewage. The effluent is sterile and, therefore, contains no coliform, other bacteria or virus. Only a small quantity of inorganic solids remains after treatment. Detergents, however, are not affected. The effluent also contains water-soluble organic compounds which are biodegradable; and the level of concentration exceeds the EPA guidelines for effluent quality. In short, the original concept--direct discharge of treated wastewaters--may not be viable.

Specific conclusions based on the pilot-plant results described in this section of the report are summarized below:

(1) <u>Applicability</u>.

All of the various shipboard wastewaters are amendable to wet oxidation in the acid circuit except those generated in the laundry. Consequently, there is little purpose in treating combined shipboard wastewaters, as originally defined. Body sewage, toilet paper, toiletries and table scraps are recommended as satisfactory influents.

(2) <u>Maximum Efficacy</u>.

If the wastewater from the laundry is excluded from treatment, the maximum allowable residence--the total time in the 4-compartment prototype reactor--is about 30 minutes. (See Section 3.5.1 for further discussion of this point.)

A perusal of Tables 3-13 and 3-14, which are presented in Section 3.5.5, indicates that the reduction in COD from a 30-min treatment can range from 60 to 85 percent, depending on the operating conditions and the nature of the influent. For example, in treating saline wastewater the maximum efficacy is about 75 percent reduction in COD (for a 30-min over-all residence in the absence of any catalyst*).

---

*Neither porous-carbon liners nor Barber-Colman Co. catalyst 10,480 is recommended for the treatment of saline wastewaters in the acid circuit.

Treatment of non-saline wastewaters, on the other hand, would result in 85 percent reduction at the end of 30 minutes (in the presence of Barber-Colman Co. catalyst 10,480). Another possible alternative would be to use some sort of advanced toilet system to reduce water usage in disposing of body sewage--a number of suitable systems exist--one is discussed in Section 6. If the strength of a non-saline influent were doubled by use of an advanced toilet, then the allowable residence time would be 60 minutes and the following reduction in COD would be obtained:

Treatment of saline influent	80
Treatment of non-saline influent	90

(3) Effluent Quality

The data cited above in paragraph (2) indicates that wet oxidation in the acid circuit of saline body sewage from the commonly used, present-day toilets would result in 75 percent reduction in COD. (The allowable residence time is 30 minutes.) Assuming that the average influent COD* is 2400 mg/ℓ O, the effluent would contain residual organic matter with a COD of 600 mg/ℓ O.

Chromatographic analysis indicates that the principal organic species remaining after acidic wet oxidation is acetate (and other small-molecular-weight compounds like formaldehyde, propionate and butyrate). Since the COD is essentially the same as BOD for acetate† and closely related substance, the BOD of the effluent also would be 600 mg/ℓ O.

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*Computations presented in Section 6.1 indicate that the daily body waste of 20 men comprises 2375 grams organic matter (on a dry basis). As stated in Section 2.4.2, each gram of organic waste requires one gram of oxygen for complete combustion. In other words, the total oxygen demand is 2,375,000 mg O). According to data cited in Section 2.4.1, body sewage accounts for 75 percent of the total BOD. Assuming that body sewage also represents 75 percent of the COD, the total oxygen demand of the combined body waste and galley waste is 3,166,667 mg O. The total volume of the combined sanitary and galley wastewaters was estimated in Section 3.5.1 to be 350 gallons or 325 liters. The COD of the autoclave influent is, therefore, 2400 mg/ℓ O.

†See page 14-20, Table 2, Industrial Pollution Control Handbook, edited by H.F. Lund, published by McGraw-Hill Book Co., N.Y., N.Y., 1971.

The goals established for this program specify an effluent BOD of 50 mg/ℓ O or less, in accordance with EPA proposed standards. Clearly the acid-circuit effluent is too contaminated for direct discharge. According to the estimate formulated above in paragraph (3), the BOD of the effluent is 12 times the allowable level. Suppose that an advanced toilet system was used in conjunction with a non-saline flushant and Barber-Colman Co. catalyst 10,480. Let us further assume as in paragraph (2) above that the influent from the advanced system has twice the COD as the conventional system: 4800 mg/ℓ O instead of 2400 mg/ℓ O. According to the computations and supporting data cited in paragraph (2) above, treatment can be extended to 60 minutes; and 90 percent reduction in COD can be achieved. The effluent would have an oxygen demand (COD or BOD) of 480 mg/ℓ O.

Paradoxically, we have doubled the residence time and, thus increased the reduction in COD from 75 to 90 percent, but the effluent quality has only improved 20 percent. The BOD is nearly ten times the allowable.

SECTION 4

EVALUATION OF AN AMMONIACAL CLOSED LOOP

Two processes were investigated in the program. An acid circuit for direct-discharge treatment was described in Section 3. In this section, an ammoniacal closed loop is discussed. Each system was evaluated in an entirely different manner than the other. In the case of the direct-discharge system, maximization of the percentage reduction in COD was the first concern. Series of tests were conducted to establish the effect of process parameters on the efficacy of the system. Statistical analysis was used to determine the optimum process conditions. In the development and evaluation of the closed loop, the primary concern was the effect of the accumulating salts (in the recirculating hydraulic load) on wet oxidation. The investigation emphasized repetitive use of the same waters in small-scale, simulated closed loops.

4.1 EVOLUTION OF THE CONCEPT.

Soon after the program began, impending Governmental regulations were announced that prohibited the discharge of treated as well as untreated wastewaters. The original technical approach was clearly no longer viable. No discharge would be allowed. The immediate answer was a closed loop in which autoclave effluent was reused as flushant. Feasibility studies began on an acid-circuit, closed loop but quickly established that sodium chloride rapidly accumulated in the in-process waters and, in an acid circuit, proved to be very corrosive. (Sodium chloride is a constituent of urine; the amount passed passed by a typical human is computed from published statistics in Section 6.2.) Moreover, prospective customers were concerned that the use of an acidic flushant would corrode plumbing aboard existing vessels and cause increased expenditures (for special corrosion-resistant plumbing) in future shipbuilding.

At this point, Barber-Colman Co. catalyst 24,130 evolved from an in-house project concerning the recovery of silver from photographic film. Unlike the catalysts used in the acid circuit, Barber-Colman Co. catalyst 24,130 did not require the presence of acid and, in fact, was most potent in ammoniacal solutions.

Laboratory tests were initiated on body waste; the results of batch experiments were most promising. The wet oxidation of body sewage was practical in an ammoniacal solution; and the reaction was accelerated by Barber-Colman Co. catalyst 24,130. There was, however, some uncertainty as to whether the liquid phase in a continuous-flow reactor would remain ammoniacal--all of the ammonia might be swept from the reactor in the exiting gases. A test was conducted in the same 4-compartment WETOX reactor used in the evaluation of the acid circuit and described in Section 3.1.1. The continuous-flow test was highly successful; the fears were groundless. The effluent was decidedly ammoniacal, and extensive reduction in COD occurred. Moreover, Barber-Colman Co. catalyst 24,130 proved stable and effective in accelerating wet oxidation.

During the spring of 1973, the concept of ammoniacal closed loop was demonstrated under U.S. Navy Contract No. N00174-73-C-0140. The results of the demonstration are presented in Appendices I and J. Several semi-batch tests were performed; and two continuous-flow tests conducted. In one of the continuous-flow tests, over 13 pounds of organic matter--in the form of 6-months to 1-year old body waste from campsite latrines--were treated during a 5-day period in a closed loop. At the conclusion of the tests, only 11 percent of the COD added to the system remained. In the other continuous-flow tests, over 19 pounds of organic matter (as raw primary sewage sludge) was added to a closed loop during a 4-day campaign. At the conclusion of the test, 14.5 percent of the added COD remained in the system.

The two continuous-flow tests described in the last paragraph were conducted consecutively. The liquid used in the second was derived entirely from the first. At the conclusion of the second test, about 33 pounds of waste had been added to a circulating volume of about 50 gallons. Computations presented in Section 6 indicate that the tests provide a good simulation of a 20-man shipboard closed loop after six days of service.

The results of the foregoing tests were presented formally to the Coast Guard in June 1973; and a no-cost redirection was requested on 20 July 1973. A revised test plan also was submitted. The Coast Guard concurred with the request. A contract modification was received on 1 September 1973. The results of the revised program are presented in Section 4.2 and in Section 6.

4.2 FURTHER INVESTIGATION OF THE AMMONIACAL CLOSED LOOP

In the redirected program, laboratory tests were conducted to establish the effect of the longevity on process efficacy. The primary concern was whether wet oxidation would continue to occur as extensively after 30 or 60 days as demonstrations had shown that it did in flushant after 5 or 6 days of simulated service.

4.2.1 SIMULATED CLOSED-LOOP TEST.

The plan of attack was straightforward: to inject repetitively macerated feces and urine into the same one liter of ammoniacal solution containing Barber-Colman Co. catalyst 24,130.

In order to truly simulate the proposed flow sheet in the one-gallon Autoclave Engineer's autoclave, the sampling system was modified so that the vapor phase could be removed after each charge of fecal material and urine. This would represent the vapor-phase condensate that would normally be vented to the engine exhaust system in the continuous closed-loop PURETEC System, described in Section 6.1.

The procedure used in the performance of the recycle batch tests is as follows:

> One liter of water, ammonium hydroxide and catalyst was placed in the one-gallon autoclave as the initial charge of fresh water. Approximately 300 mℓ of macerated feces and urine was then injected and allowed to react for 60 minutes at 450 - 470°F. Sufficient oxygen was charged to the autoclave to react with the COD of the charge.
>
> At the end of the reaction time, the gas burner was turned off and 300 mℓ of vapor-phase condensate was removed from the autoclave via a vapor phase vent and an ice-water cooled condenser.
>
> Within 15 minutes, a second charge of 300 mℓ of macerated human waste was added to the autoclave together with the required oxygen and the process was repeated.

Over 25 cycles were performed in this manner with the initial water charge in the autoclave.

The chemical oxygen demand of the vapor-phase condensate remained relatively constant throughout the test and ranged between 11,000 and 14,000 mg/ℓ COD.

By compiling a composite of the total oxygen demand in the vapor phase condensate sampled, adding to it the oxygen demand of the liquid phase and subtracting this from the COD added, it is possible to estimate the COD destroyed. The material balance obtained in this manner is on the following page.

Total COD in Influent	954,366 mg 0
Total COD Vented Via Vapor	-80,000 mg 0
Total COD in Liquid Phase After 25 Cycles	-17,455
Net COD Destroyed In 25 Cycles	856,911
Over-all Percentage Reduction in COD	89.8%

Less than 2 percent of the input COD remained in the liquid-phase effluent. The TOC (total organic carbon) content of the liquid effluent was 8500 ppm C. About 65 grams of solids remained at the end of the 25 cycles; 5.4 percent of the dried solids was volatile at 550°C indicating that the solids were essentially inorganic. Figure 4-1 is a photograph of the liquid effluent and solids remaining from the simulated closed loop. The liquid is clear with a faint musty smell; it is slightly ammoniated but decidedly not urinous.

During the 25-cycle test, fecal material and urine equivalent to about 954 grams of (dry) organic solids were added to one liter of ammoniacal solution. Computations presented in Section 6.2.1 indicate that the amount of organic waste added to the one liter of synthetic flushant was equivalent to that added to the 20-man shipboard closed loop in 65 days of service. The chloride concentration, on the other hand, was 23,000 mg/ℓ Cℓ equivalent to that aboard ship after 23 days, indicating that the amount of urine added to the system was less in proportion to the feces than it should have been.

The pH of the vapor-phase condensate remained fairly constant throughout the 25-cycle test and ranged from 9.3 to 9.8. The pH of the liquid after 25 cycles was 8.3. The ammonium-ion concentration diminished rather quickly to a level about 80 percent of the initial NH_4OH charge and remained constant thereafter.

The concentration of catalyst in the liquid phase was less than charged after 25 cycles. Possibly small quantities of catalyst occluded in the insoluble inorganic ash or coated on the titanium liner of the autoclave. In any event, the loss was minor and no adverse effect was observed. No catalyst was detected in the vapor-phase condensate.

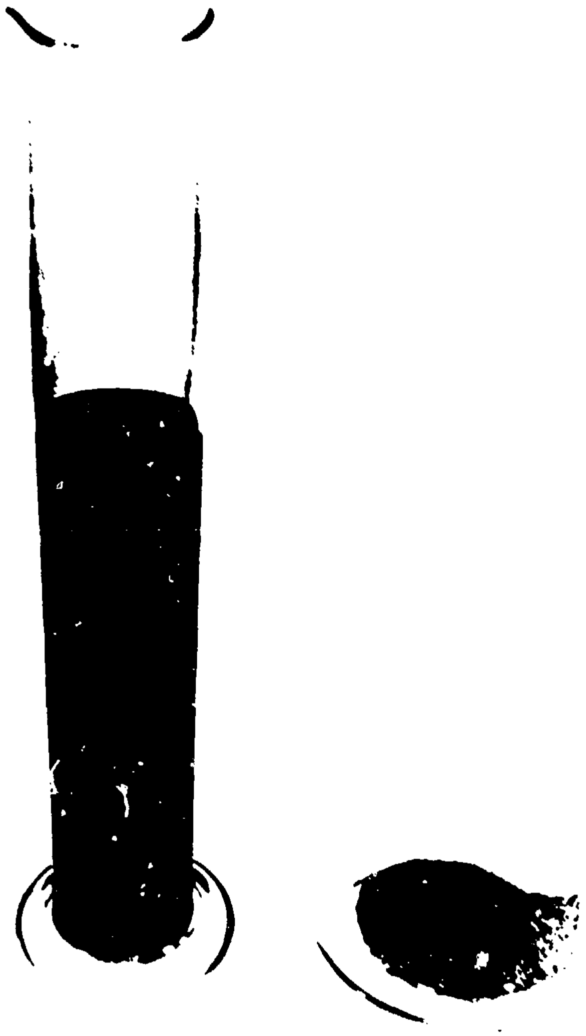

FIGURE 4-1. CLOSED-LOOP SOLUTION AND SOLIDS. EQUIVALENT TO SHIPBOARD FLUSHANT AFTER ABOUT 60 DAYS.

4.2.2 EFFECT OF CHLORIDES ON AMMONIACAL WET OXIDATION

A series of batch tests was conducted to establish the effect of sodium chloride on ammoniacal wet oxidation. Wheaton et al.* had reported that wet oxidation of mixed feces and urine in the presence of 400 g/ℓ NaCℓ was 10 percent less effective than wet oxidation under the same conditions in the absence of sodium chloride. The evaluation of the acid circuit had demonstrated that salinity adversely affected Barber-Colman Co. catalyst 10,480. Over 50 percent of the accumulating dissolved salts in the closed loop are the chlorides of sodium and potassium.

The procedures for these batch tests were identical to those described in Section 2.3 of the main report and in Appendices E and J. Because chloride seriously impairs the accuracy of chemical analysis for COD, the efficacy of the process was monitored by chemical analysis for total organic carbon (TOC). The standard method recommended by the EPA Water Quality Office** was used for determination of TOC, which was accomplished with a Dow-Beckman Carbonaceous Analyzer Model No. 915 (dual channel).

As can be seen from Figure 4-2, there is little differences in the behavior of waste which can be attributed to the level of sodium chloride. All of the data lie within a scatter band whose extremities contain as many points from tests containing 90 g/ℓ NaCℓ as from tests with no NaCℓ. Aboard ship the closed-loop waters will contain about 90 g/ℓ NaCℓ after 55 days service.

In Table 4-1, the rate constants are listed for the tests comprising the series. Calculated means for k_i are listed below for various groups of data.

Group	Mean k_i, min^{-1}	Coefficient of Variation, pct
All six tests	0.056	32
Four tests with NaCℓ	0.066	12
Two tests without NaCℓ	0.035	4

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* R.B. Wheaton, J.R. Calloway Brown, R.V. Ramirez, and N.G. Roth, "Investigation of the Feasibility of Wet Oxidation for Spacecraft Waste Treatment", NASA Contractor Report No. 66450, Prepared under Contract NAS 1-6295 by Whirlpool Corp., St. Joseph, Mich., August 30, 1967.

**Methods For Chemical Analysis of Water and Wastes 1971, EPA Manual 16020-07/71, pages 221-229 (STORET Nos. 00680 and 00681), available from Superintendent of Documents, U.S. Government Printing Office.

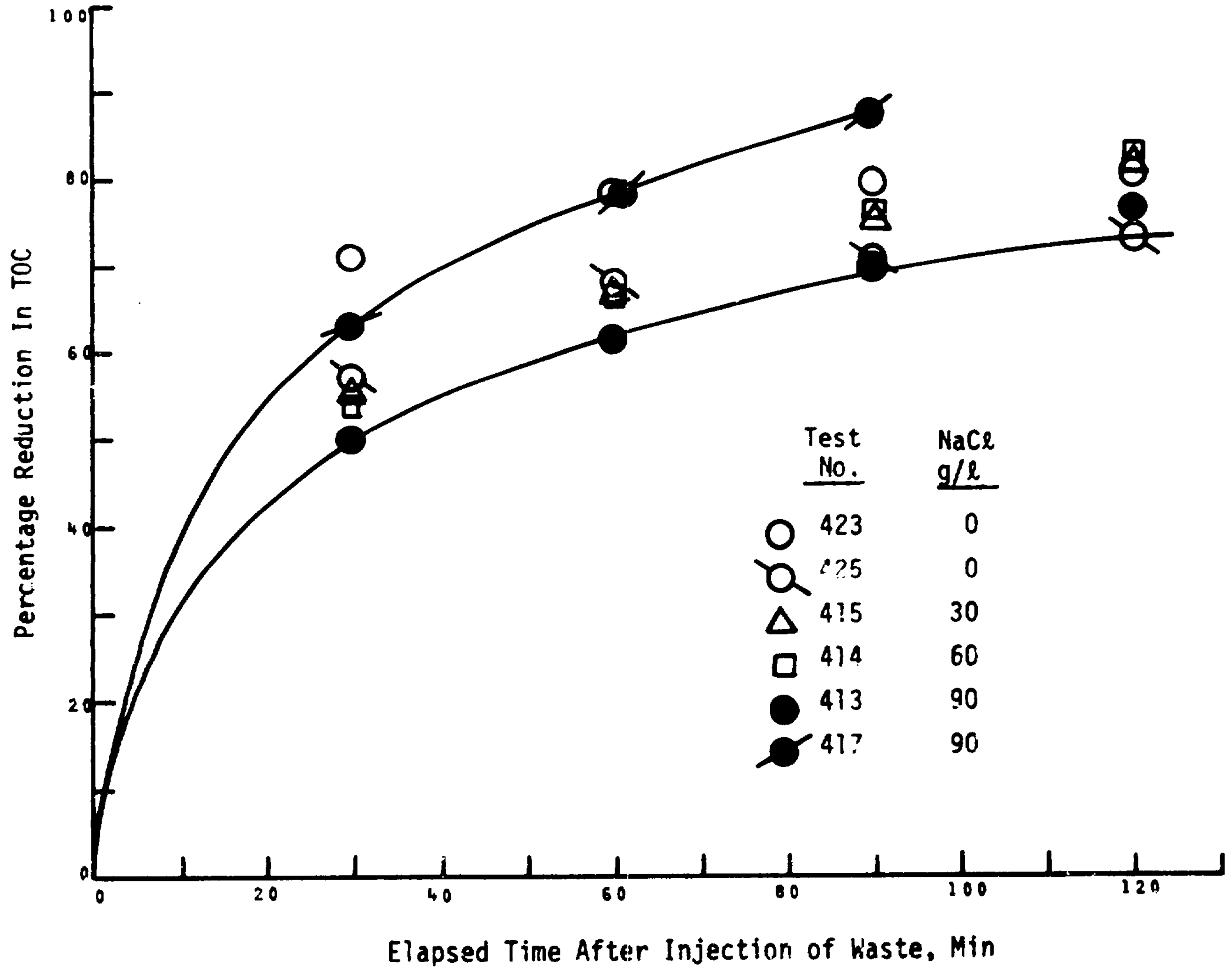


FIGURE 4-2. EFFECT OF SODIUM CHLORIDE ON WET OXIDATION OF AMMONIACAL FECES-AND-URINE MIXTURES.

TABLE 4-1

RATE PARAMETERS AND PERCENTAGE REDUCTION AMMONIACAL WET OXIDATION WITH BARBER-COLMAN CO. CATALYST [illegible],130

Batch Test No.	423	425	415	414	413	417
NaCℓ, g/ℓ	0	0	30	60	90	90
Mean Temp, °F	460	455	455	475	470	460
Rate Constants						
k_i, min^{-1}	0.041	0.029	0.072	0.067	0.054	0.070
k_ℓ, min^{-1}	0.002	0.003	.010	.009	.008	.015
Transition pct red. TOC	78	66	56	59	56	54
Pct Red. in TOC						
@ 30 min	71	66	56	54	50	63
60 min	79	75	67	66	62	78
90 min	80	78	75	76	70	87
120 min	81	80	81	82	76	-

Although k_i is less for the tests without $NaC\ell$, the transition to the late-stage rate of reduction occurs later (at a greater percentage reduction) than in tests with $NaC\ell$. Consequently, over-all reduction is comparable in all cases. The late-stage rate constant is extremely small in the tests without $NaC\ell$.

Samples taken during the batch tests in which there was no $NaC\ell$ present were assayed for COD as well as TOC. The reduction in COD paralleled that in TOC. Figure 4-3 is a semi-logarithmic plot for one of these tests (Batch Test No. 423). The least-squares fits of the data from COD analysis gave the following values for the rate parameters:

Test No.	k_i, min^{-1}	k_ℓ, min^{-1}	Transition Pct. Red.
423	0.046	0.005	79
425	0.037	0.004	72

The results of these batch tests agree reasonably well with the continuous-flow tests (and supporting batch tests) reported in Appendix J for the wet oxidation of Forestry Service vault waste and primary sewage sludge. At least, the agreement is good for the comparison of reduction in TOC. However, in the batch tests on vault waste and sewage sludge, in the reduction of COD, the initial rate constant (k_i) was significantly greater than the corresponding value for TOC. This type of behavior also has been observed sometimes in the wet oxidation of macerated feces and urine. For example, examine Figure 4-4: The value of k_i for COD is 4 times that for TOC. The response to treatment as measured by TOC is exactly the same in this batch test as in the previously described ones (Batch Test Nos. 423 and 425), but the response of COD is markedly different.

Most natural matter is comprised of three basic substances: proteins, carbohydrates, and lipids. Of the three a unit mass of lipid consumes much more dichromate. (Cellulose also undergoes extremely rapid initial reduction in COD.) Apparently the influent in Batch Test No. 337 was comprised of a greater percentage of fats and/or paper than those used in Batch Test Nos. 423 and 425. Of the two indices, TOC has the firmer base, because in TOC analysis the amount of organic carbon actually burned to carbon dioxide is detected. In chemical analysis for COD, the amount of dichromate consumed is arbitrarily converted (mathematically) to the equivalent oxygen. One assumes complete combustion in COD but may not achieve it.

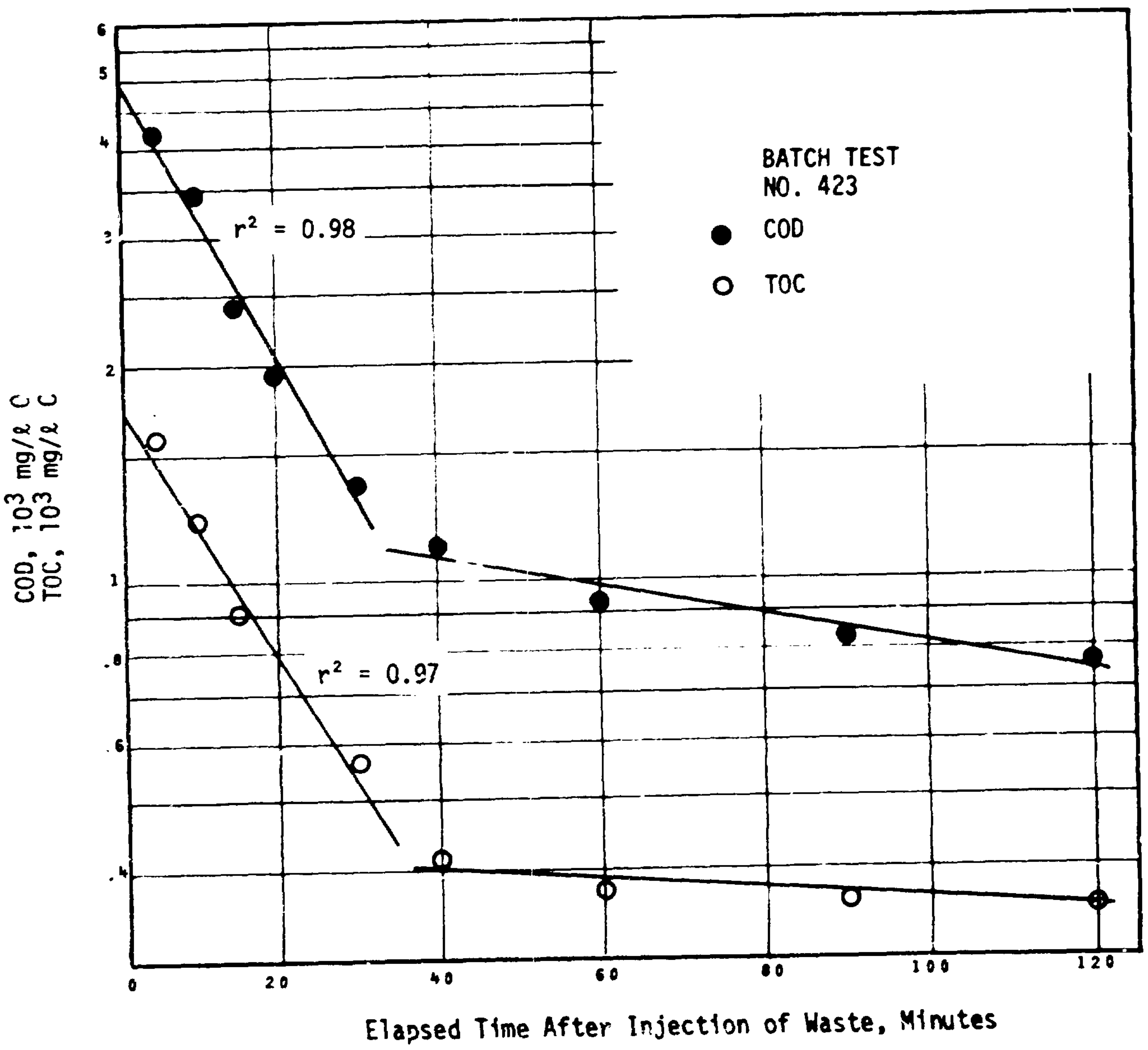


FIGURE 4-3. COMPARISON OF REDUCTIONS IN TOC AND COD.

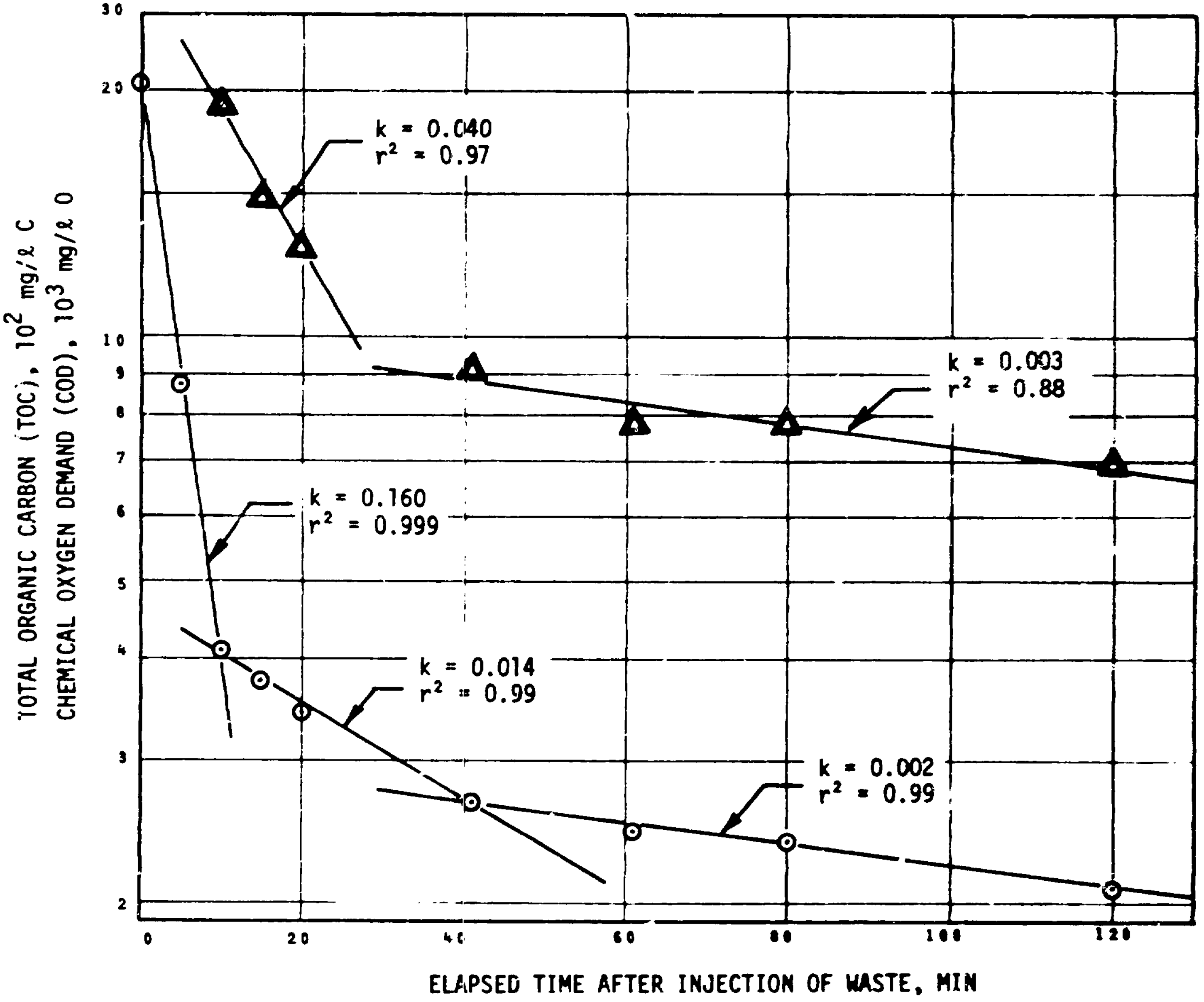


FIGURE 4-4. SEMI-LOGARITHMIC PLOT SHOWING DECREASE IN COD (⊕) AND IN TOC (▲) WITH INCREASING REACTION TIME, BATCH TEST NO. 337

4.3 CONCLUSIONS (EVALUATION OF CLOSED LOOP)

Based on the foregoing tests and those described in Appendices I and J, we concluded that the closed-loop concept was viable and proceeded with Task VI, the preliminary design of a prototype system. The resulting design is presented in Section 6.

Compared to the direct-discharge (acid) circuit, the ammoniacal closed loop has the following advantages:

- o <u>Substantially less disposal problems</u>. No treated waste discharged overboard. Spent flushant is removed from the system every 60 days. The entire volume of the closed loop--about 43 gallons, less than one-tenth of the daily discharge from the open (acid) circuit--is pumped from the vessel at dockside and disposed of ashore (probably by evaporation).
- o <u>More compatible with existing ships</u>. The flushant is ammoniacal and, therefore, compatible with all common plumbing and santitation equipment.
- o <u>Less onboard storage of chemical and supplies</u>. No acid is required. Treatment of the combined body sewage and galley waste in the acid circuit would have consumed 130 pounds of sulfuric acid monthly. About the only onboard storage associated with the closed loop are normal maintenance items such as chart paper, a section of link belt, an assortment of valves, and special tools.

SECTION 5

DESIGN AND CONSTRUCTION OF A LABORATORY MODEL OF THE WET OXIDATION UNIT

As Task II, a two-compartment reactor was designed, constructed and checked-out. In the Contract, this reactor is referred to as the Lab Model, actually the Lab Model is one half of the proposed prototype. At the end of the contract, this reactor will be delivered to the Coast Guard.

5.1 DESIGN

A preliminary engineering design is shown in Figure 5-1 for the proposed Lab Model, which is two full-scale compartments of the four-compartmented proposed shipboard autoclave. The full-scale autoclave is indicated by the extended network of "dashed lines" in the same figure. Utilization of the Lab Model will permit full-scale confirmation of feasibility (by the Coast Guard) without incurring the expense of a full-size reactor and of its operation. As the reader knows, from reading Sections 3 and 4, the evaluation of the processes by Barber-Colman Co. was accomplished in a full-size shipboard reactor.

The autoclave shown in Figure 5-1, unlike any other commercially available, was specifically designed for use as a small, wet-oxidation reactor. Most small autoclaves are designed and used for sterilization; a few are suitable for laboratory research in which the effect of elevated temperature on chemical reactivity can be investigated, provided care is taken to isolate the

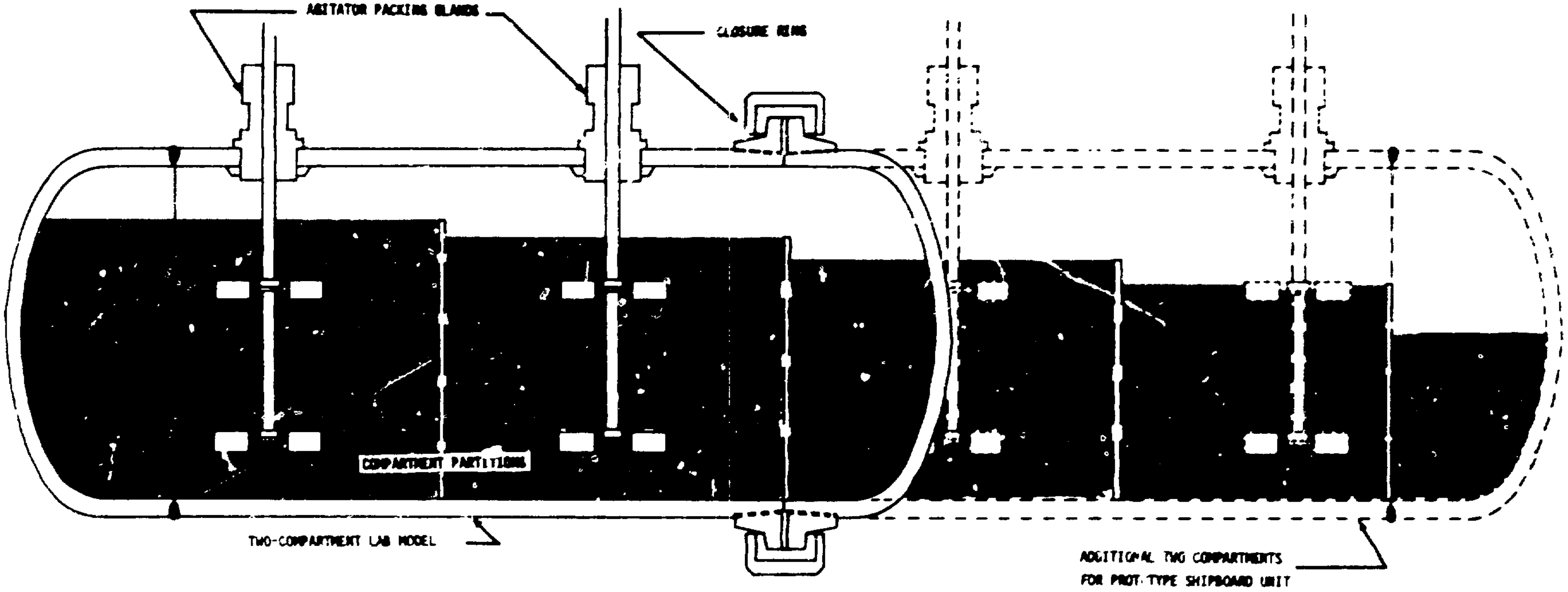


FIGURE 5-1. DRAWING OF THE LAB MODEL (WHICH IS A SECTION OF THE BARBER-COLMAN COMPANY SMALL WETOX REACTOR FOR REMOTE AREAS AND APARTMENTS.

reactive substances. (This is generally accomplished by sealing the reactants in glass vials or confining the liquid portion in a corrosion-resistant inner liner.) In the Barber-Colman autoclave, wet oxidation can be conducted continuously without extensive corrosion of the autoclave. Moreover, it is the only type of reactor in which complete wet oxidation can be affected under practical conditions. The salient features of its design are described in following subsections.

a. Material of Construction

The Barber-Colman autoclave is constructed entirely of titanium metal. This is especially important to the success of the Coast Guard program because:

- Titanium has a long, proven history of successful application in wet-oxidation processes.
- Titanium is the least costly of possible candidate materials.
- The low density and high strength-to-weight ratio of titanium are critical in achieving the weight limitations imposed on shipboard application.

The wall thickness is 0.50 inch, and all welds are subjected to the nondestructive testing (NDT) requirements of the ASME unified pressure-vessel code and all applicable sections of MIL-STD-278 C (SHIPS) (Military Standards--Fabrication, Welding, and Inspection of Machinery, Piping and Pressure Vessels for Ships of the U. S. Navy).

b. Closure Ring

In order to provide accessibility without the very large weight and cost penalties imposed with standard ASME-code flanges, a special type wedge-ring closure, shown in Figure 5-2, is used to couple the two halves of the autocalve. This type of closure has been successfully used for many years on high-pressure vessels operating to 2000 psi. The use of a closure ring enables easy disassembly of the autoclave for maintenance and retrofitting; some means of accessibility to the interior is essential in a small compartmented autoclave. In a design like that of the closure ring, one must use materials with matched coefficients of thermal expansion. In this case, a 12-percent chromium steel (AISI No. 422) has been used for the closure wedge, closure ring and retaining ring. This alloy closely matches the coefficient of thermal expansion exhibited by titanium; hence, thermal stresses are minimized. Because it is neither good practice to weld up the closure wedge of titanium nor economically feasible to upset forge a single unit, a buttress of tapered threads has been specially designed to avoid bonding stresses or the creation of stress-concentrating notches.

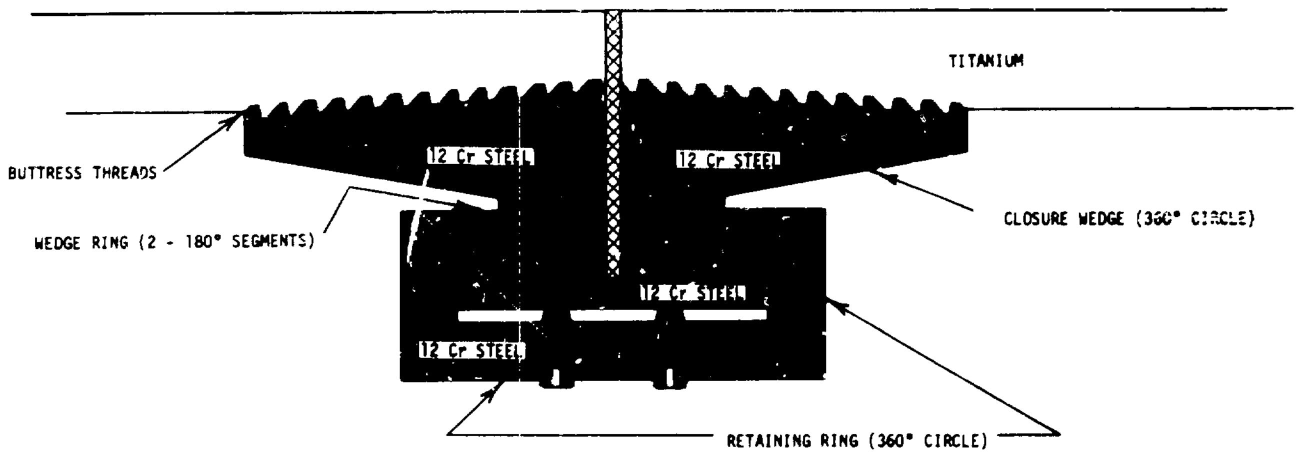


FIGURE 5-2. CLOSURE JOINT DETAIL

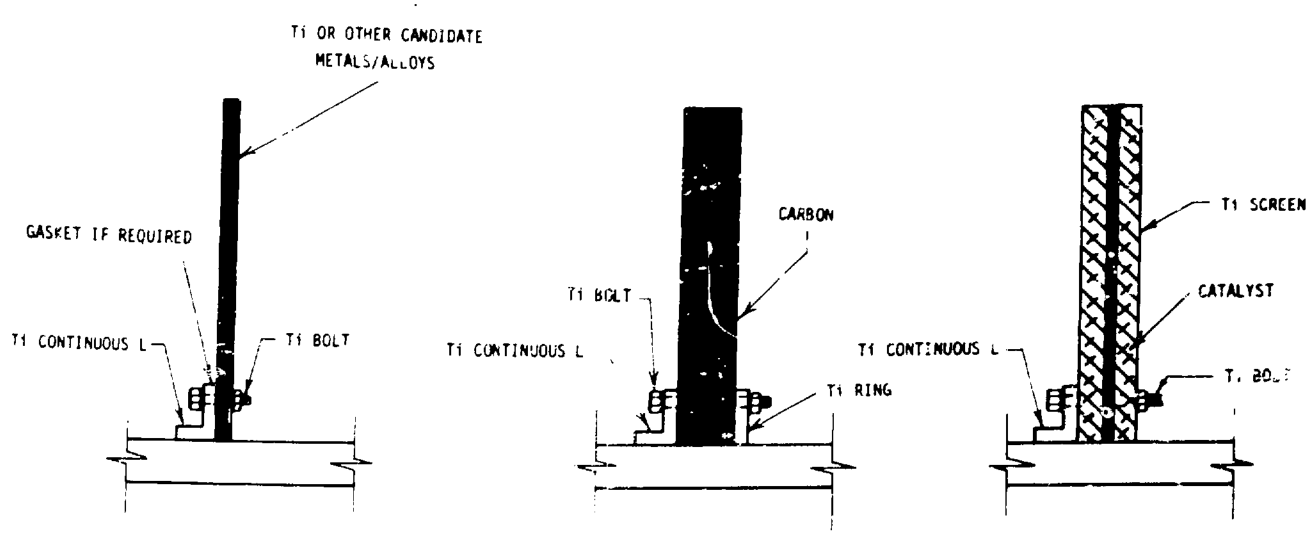


FIGURE 5-3. INTERCHANGEABLE PARTITION WALLS

On the four-compartmented unit used in most of the laboratory evaluation (cf. Sections 3 and 4), the closure ring is placed in the longitudinal center joining compartments 2 and 3; whereas, in the Lab Model, the same closure ring is placed between the end of compartment 2 and the weld cap. This design feature, which is shown in Figure 5-1, enables the Lab Model to be utilized as one half of the proposed shipboard prototype reactor without modification.

c. Partition Walls

As shown in Figure 5-3, the partitions which divide the laboratory and full-scale reactors into compartments, are removable in both units. Three types of partitions were utilized in the laboratory research: (1) an inert wall of titanium or some other metal; (2) a catalytic wall formed by bonding two blocks of porous carbon or some other permeable form to a center divider of titanium; and (3) back-to-back "cages" of titanium-metal screen bonded to a center divider of titanium sheet.

The cage-type partition facilitates the use of particulate catalysts as well as the storage of test coupons to evaluate corrosion resistance of candidate materials of construction. Placing the heterogeneous catalysts in the partitions solves several technical difficulties: The standard form of most heterogeneous catalysts is porous particulate media, which are friable and would be rapidly pulverized by the impellers if added directly to the reactor; moreover, the positioning of a basket containing catalysts in the main reaction zone might degrade the degree of agitation. Likewise, the cages are ideal for storage of test coupons for evaluation of corrosion, because only a small piece of the candidate is needed and the specimen is securely retained (out of the path of the main experiment).

d. Agitators

By dividing the autoclave at its mid-point, it is possible to install the agitators and partition walls using very small openings through the body of the autoclave. This vastly improves its safety factor and makes possible an enormous weight saving over designs employing forged or drawn outlets with standard ASME weld-neck flanges and closures. Further, the length of the agitator shaft is reduced by at least 6 inches in the case of a 10-inch diameter autoclave. This reduces side loads on the agitators, resulting in improved bearing or packing life. Since the roll, pitch and yaw of the vessel will add to the lateral bearing loads, this point is of considerable importance at sea.

e. Monitoring Probes

For thermocouples, pressure sensors, sampling tubes, and inlet and effluent discharge, typical lightweight, all-titanium fittings similar to that shown in Figure 5-4 were used in the Lab Model.

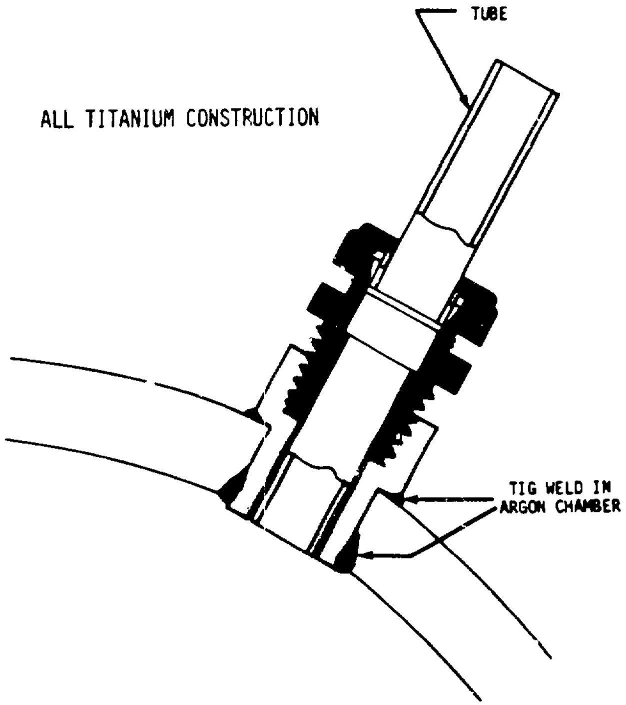


FIGURE 5-4. DETAIL FOR TYPICAL SHELL PENETRATION. (TO BE USED FOR SAMPLING AND MEASURING PROBES)

5.2 ASSEMBLY

The two-compartment reactor was constructed and assembled for use in the laboratory testing program in April 1973. At the end of the contract, the reactor will be delivered to the Coast Guard.

Two views of the assembled reactor are presented as Figures 5-5 and 5-6. Figure 5-5 is a photograph from the side and clearly shows the side ports used in sampling the liquid phase contained in each compartment during a continuous-flow test. Generally, samples are withdrawn hourly from each compartment. The superheated fluid passes through coiled tubing submerged in cold water within the vertical cylinder prominently visible in the lower center of the picture. Figure 5-6 displays the reactor viewed from the outlet end--the discharge tube is clearly visible in the lower center of the photograph.

The Coast Guard reactor is controlled from a separate instrument stand which is shown in Figure 5-7, a photograph from the front. Visible in the figure are the pressure gauge which indicates the total pressure of the reactor. Below the pressure gauge, there are two solid-state Barber-Colman Company temperature indicating controllers, which automatically maintain the temperature of each compartment. Across the center of the stand are six lighted switches, each of which controls individual electrical heaters, which supply additional energy to the reactor.

Figure 5-8 is a photograph of the partially assembled reactor; through the opened end one can see the six heaters and agitator assembly in the first compartment.

A rear view of the nearly assembled reactor is shown in Figure 5-9. A concentric shell of rolled metal sheet surrounds the reactor and forms, a 4-inch wide cavity which during assembly is filled with powdered ceramic material for thermal insulation. The four flanged pipes protruding from the rear of the reactor form part of the service lines for influent and effluent; other similar ducts are used for sampling lines and measurement probes.

5.3 ENGINEERING DESIGN DRAWING

Figure 5-10 is an engineering design drawing of the 2-compartment Lab Model. In the drawing (Figure 5-10), numbers enclosed in ovals refer to other drawings and circled numbers to parts and items listed on the other drawings. A complete set of drawings (full size) was submitted to Headquarters, U.S. Coast Guard, at completion of the Contract.

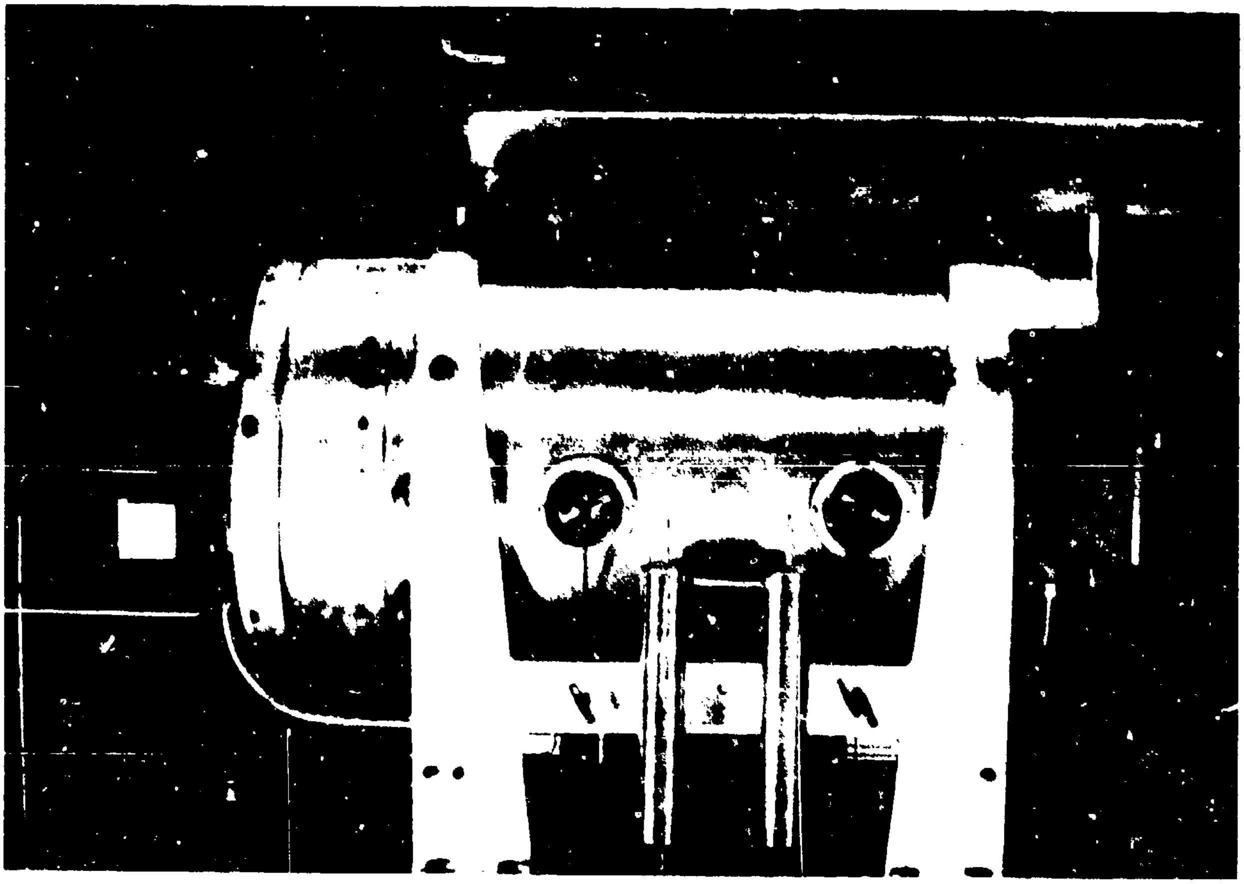


FIGURE 5-5. ASSEMBLED TWO-COMPARTMENT COAST GUARD REACTOR VIEWED FROM THE SIDE FROM WHICH SAMPLES ARE WITHDRAWN BY THE TWO WATER-COOLED VERTICAL CONDENSERS IN THE LOWER CENTER OF THE PHOTOGRAPH.

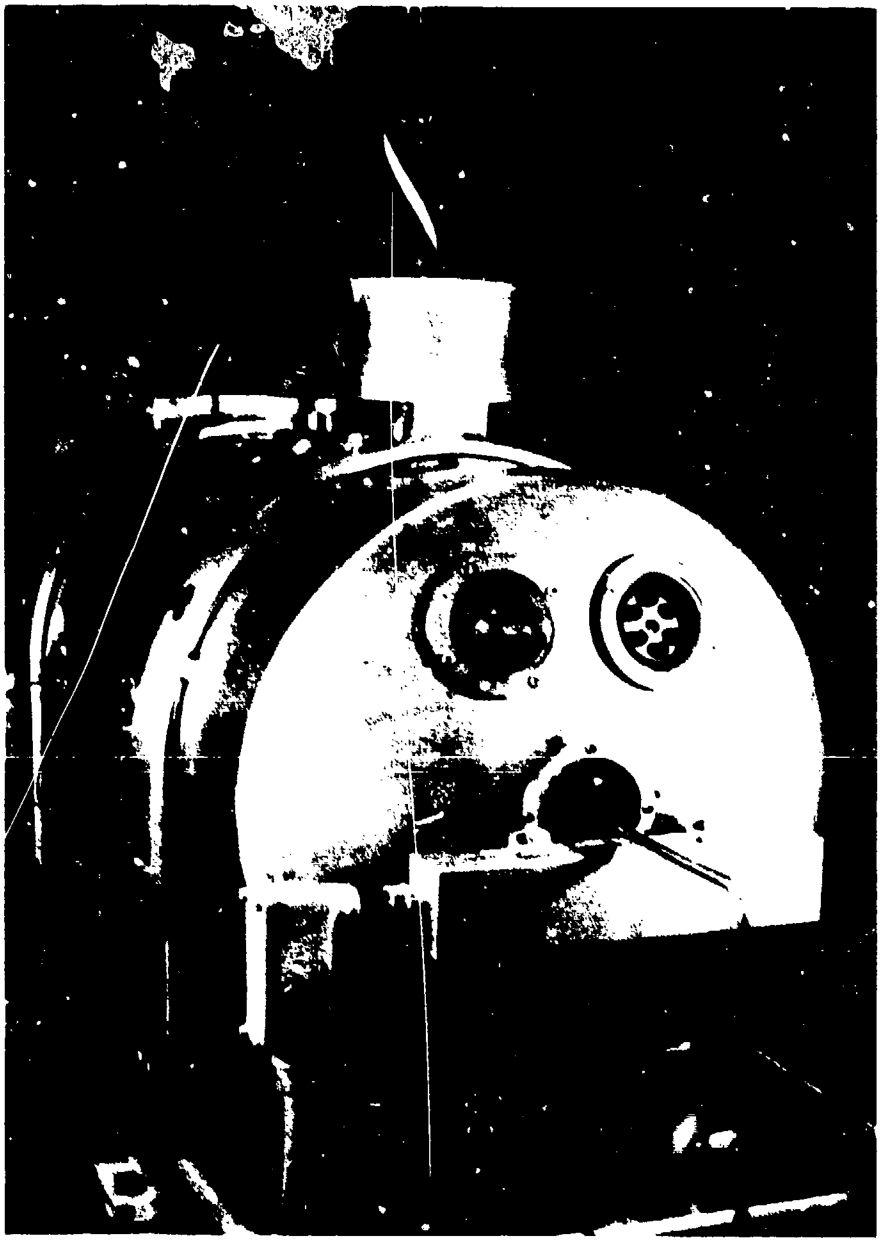


FIGURE 5-6. ASSEMBLED TWO-COMPARTMENT COAST GUARD REACTOR VIEWED FROM THE DISCHARGE END.

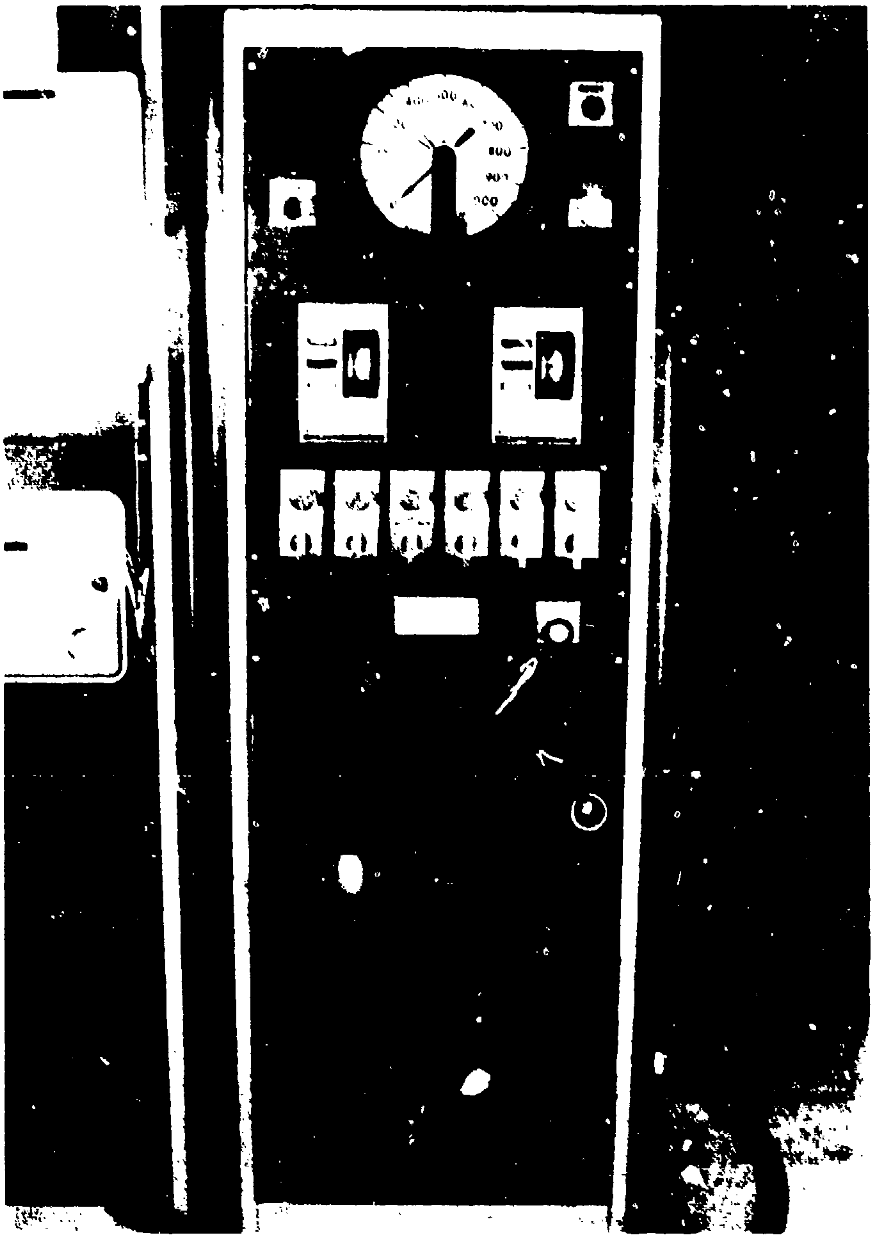


FIGURE 5-7. CONTROL CABINET FOR THE TWO-COMPARTMENT COAST GUARD REACTOR.

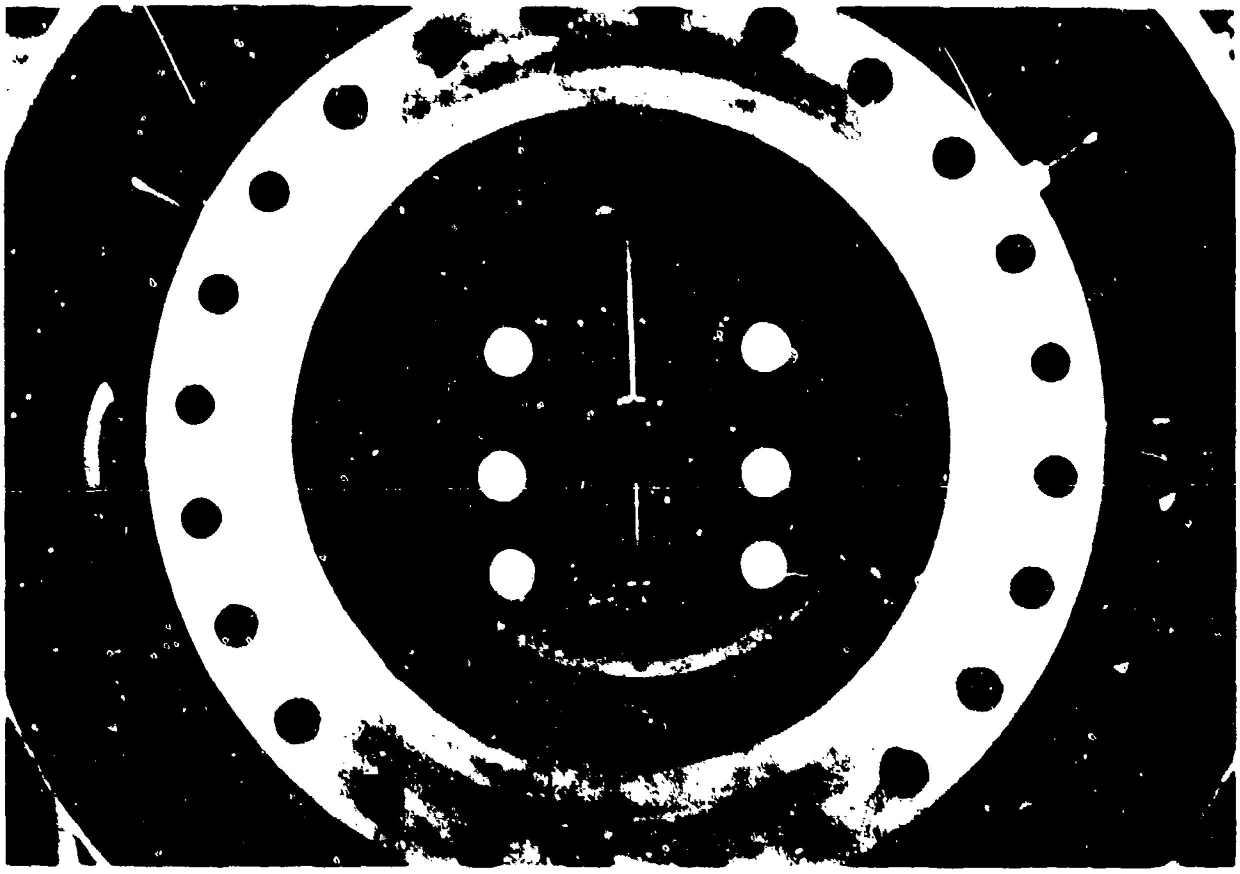


FIGURE 5-8. PARTIALLY ASSEMBLED TWO-COMPARTMENT COAST GUARD REACTOR VIEWED FROM THE OPEN REAR END. SIX HEATERS AND AGITATOR ASSEMBLY ARE VISIBLE IN THE FIRST COMPARTMENT.

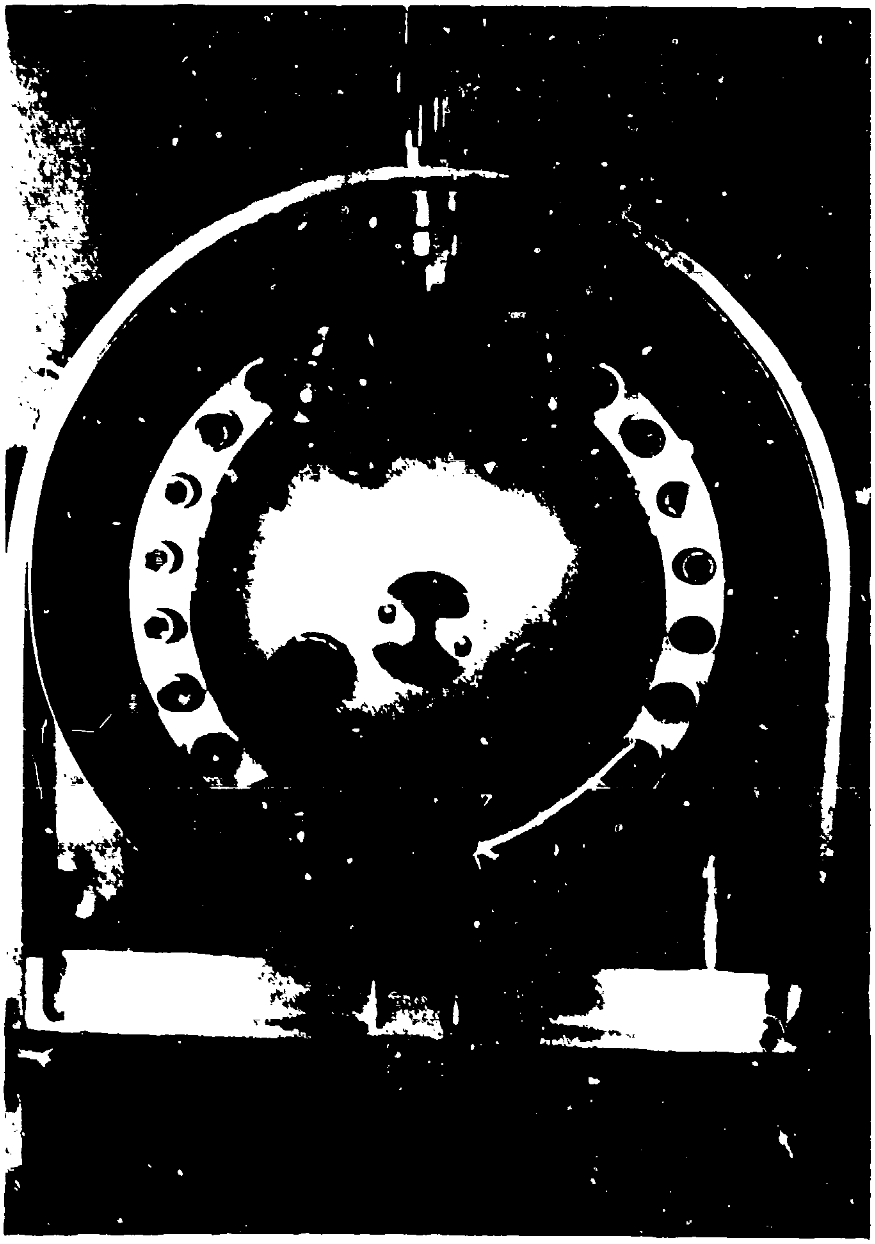
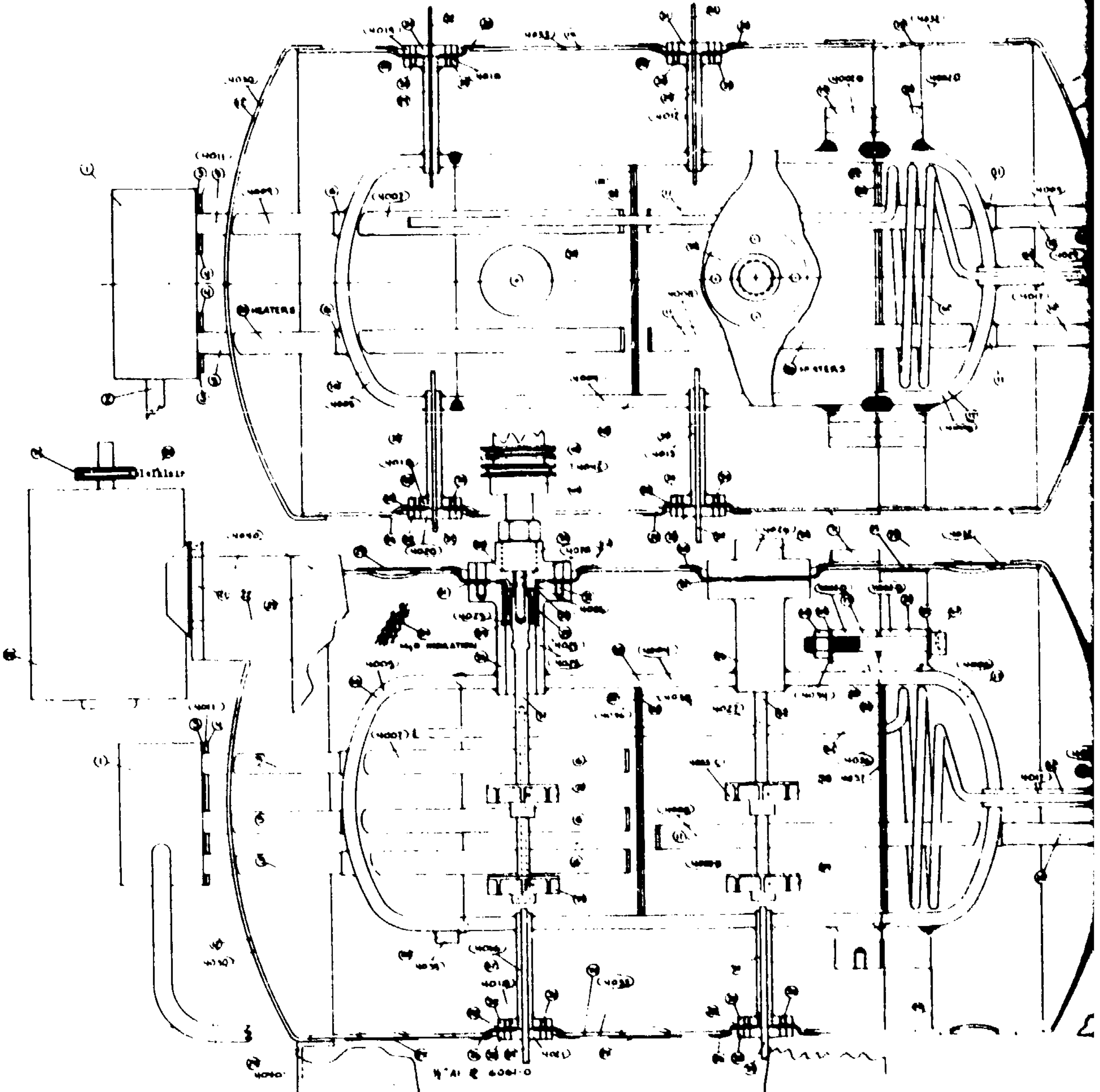


FIGURE 5-9. REAR VIEW OF NEARLY ASSEMBLED TWO-COMPARTMENT COAST GUARD REACTOR. POWDERED CERAMIC THERMAL INSULATION IS ADDED IN THE CONCENTRIC CAVITY VISIBLE IN THE PHOTOGRAPH BETWEEN THE REACTOR AND SURROUNDING SHEET-METAL SHELL.

NOTE: USE NO THREAD COMPOUND ON THIS ASSEMBLY
ALL THREADS TO BE DRY



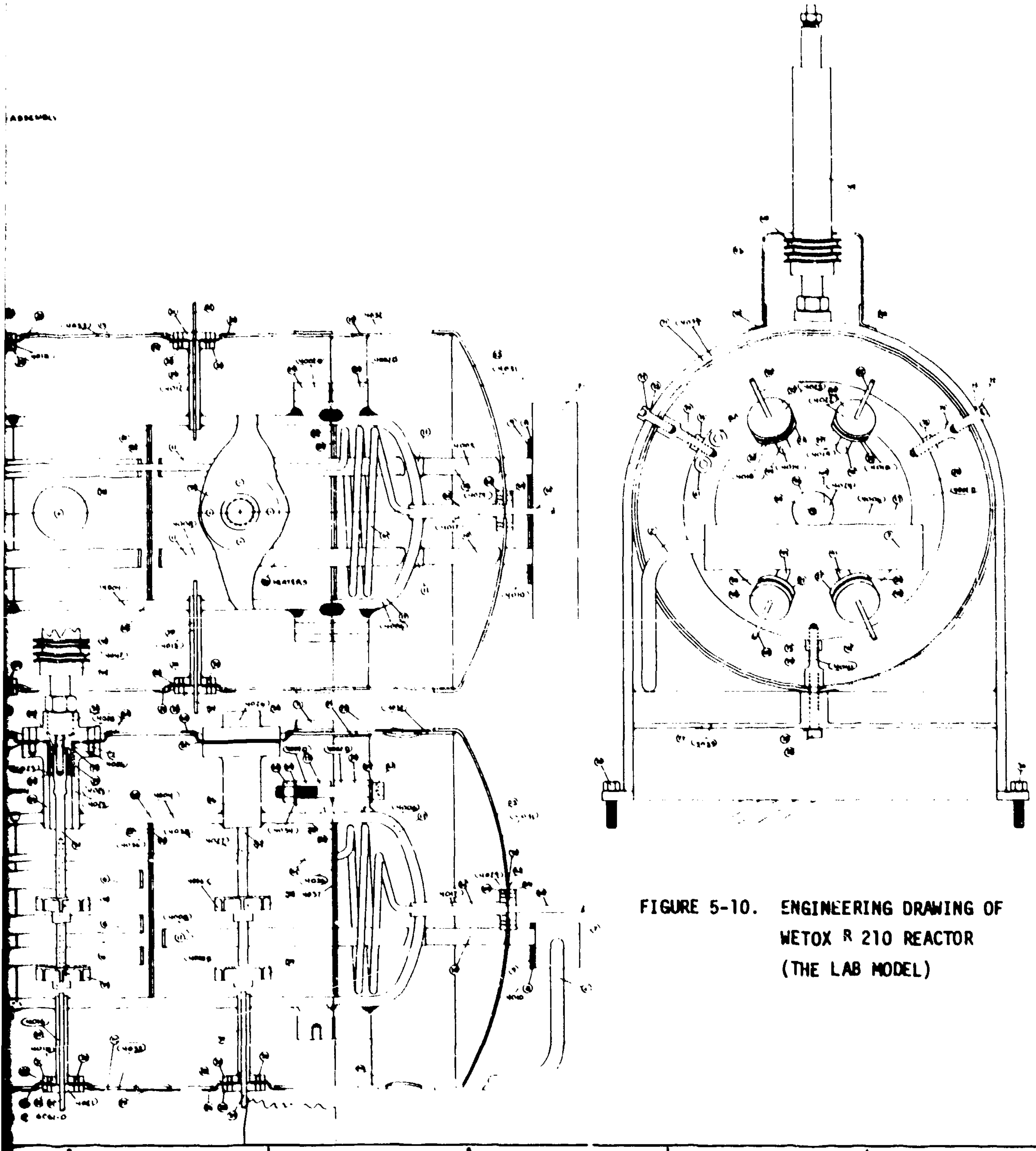


FIGURE 5-10. ENGINEERING DRAWING OF WETOX R 210 REACTOR (THE LAB MODEL)

SECTION 6

PRELIMINARY DESIGN OF 20-MAN PROTOTYPE SYSTEM

The preliminary design presented in this section is that recommended for trial at sea. Basically, the proposed design is the PURETEC Marine Sewage Treatment System, which has culminated from independent investigations by Barber-Colman Co. and has been demonstrated under U.S. Coast Guard Contract No. DOT-CG-31323-A and U.S. Navy Contract No. N00174-73-C-0140. Laboratory and pilot-plant evaluation of the process is reviewed in Section 4.

For marine waste treatment, the PURETEC system appears to offer many advantages over other possible methods of meeting the anticipated "No Discharge" requirement. The advantages that we believe have been demonstrated are:

- Very efficient destruction of human waste.
- System reliability over a broad range of feed rates.
- Complete absence of corrosion from accumulation of inorganic salts.
- Light-weight, compact system with minimum reagent consumption.
- Simple system that requires very little attention for operation.
- Growth capability to handle galley waste, if required by future rule changes.

6.1 GENERAL DESCRIPTION OF THE PROCESS

In its simplest form, the system concept is shown in Figure 6-1--a closed loop in which a sterile, filtered effluent is reused as flushant. As in any closed-loop sewage-treatment system, water must be eliminated to compensate for the urine added. The solids--largely inorganic ash from the fecal material--must be in a form that can be handled easily without odor or biological activity.

In the wet oxidation of feces, urine and toilet paper, the resultant solids are sterile inorganic compounds such as silicates, phosphates and calcium salts. The quantity per man-day is 7 grams, or one pound every 60 days. This small quantity of odorless solids can easily be stored aboard ship and disposed of ashore safely. The solids and liquid effluents are sterile, since no bacteria, mold, spores or virus can withstand the temperature used for wet oxidation. The excess water is eliminated by venting the vapor discharge from the WETOX reactor to the engine exhaust stack.

When the ship's engines are running, waste heat from the exhaust gases is used as fuel for the WETOX reactor. At dockside, electrical heaters sustain the reaction. These and other details of the PURETEC Marine Waste Treatment System are shown in the flow chart, Figure 6-2.

Any type of low-flush-volume toilet/urinal combination can be used. Solid waste must be macerated to less than 1/4-in. particles. A number of macerators are suitable. Those used in recreational vehicles work very well. The sewage load is quite variable aboard ship; peaks occur at watch changes. Surge capacity is included to meet this demand and level out the feed rate to the chemical reactor. The macerated waste is pumped into the reactor via a heat exchanger. This preheats the influent and cools the effluent before filtration.

The PURETEC System uses basically the same WETOX reactor demonstrated in this program. In the marine model, provisions have been made to prevent end-to-end surging because of ship motion. One of the problems that has plagued shipboard waste-treatment systems investigated by the Navy and Coast Guard has been the effect of the ship's motion on processes that involve settling. In our case, violent agitation is desired and no settling is necessary.

The vapor phase--steam, unused oxygen, nitrogen and carbon dioxide--is vented from the WETOX reactor through the propulsion-unit stack. The vapors contain no solids or salts that accumulate in the exhaust system. The trace organic compounds present are rapidly oxidized or destroyed without odor or char build-up. As much as 25 percent of the influent water can be removed by this method.

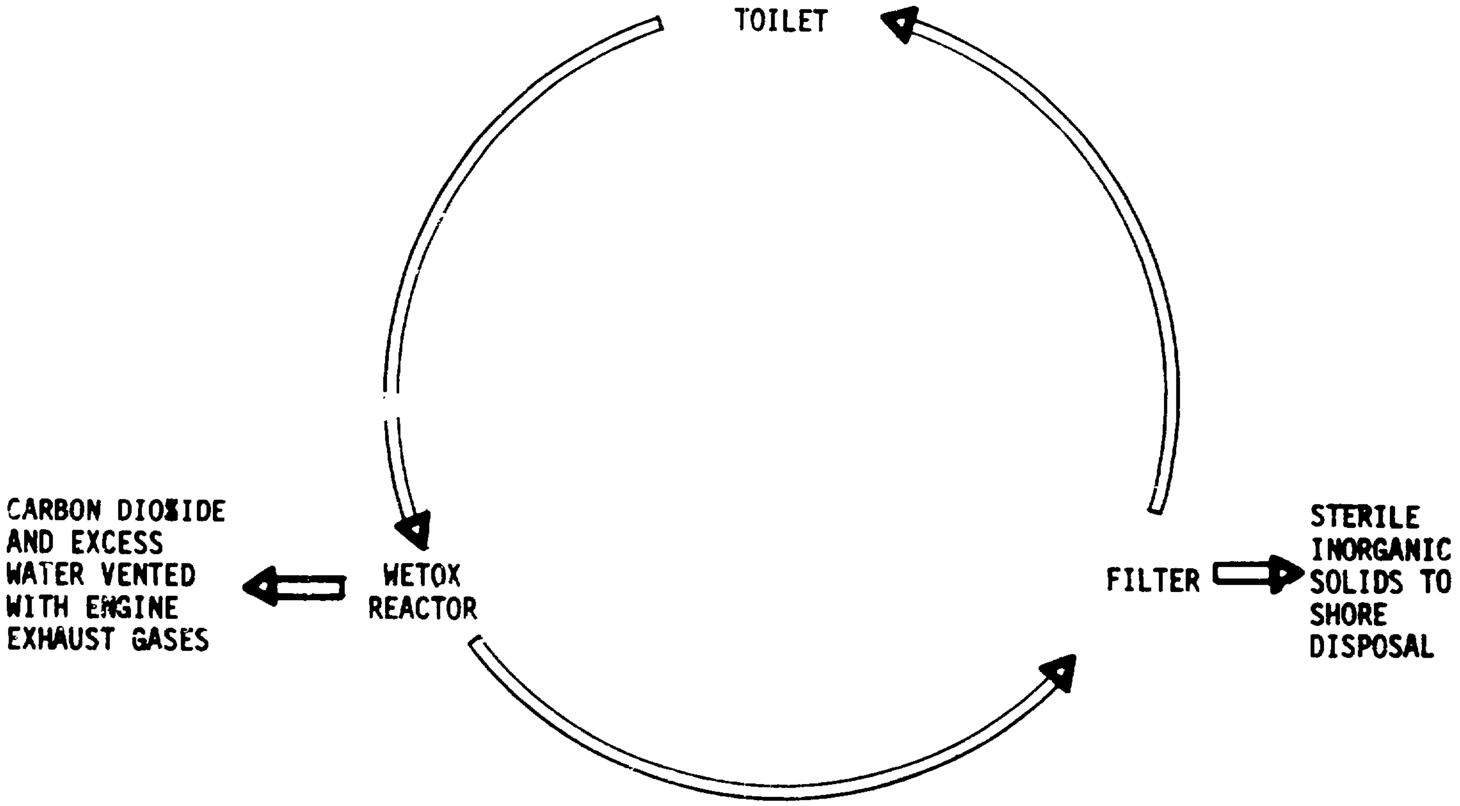


FIGURE 6-1. CONCEPT OF THE CLOSED LOOP.

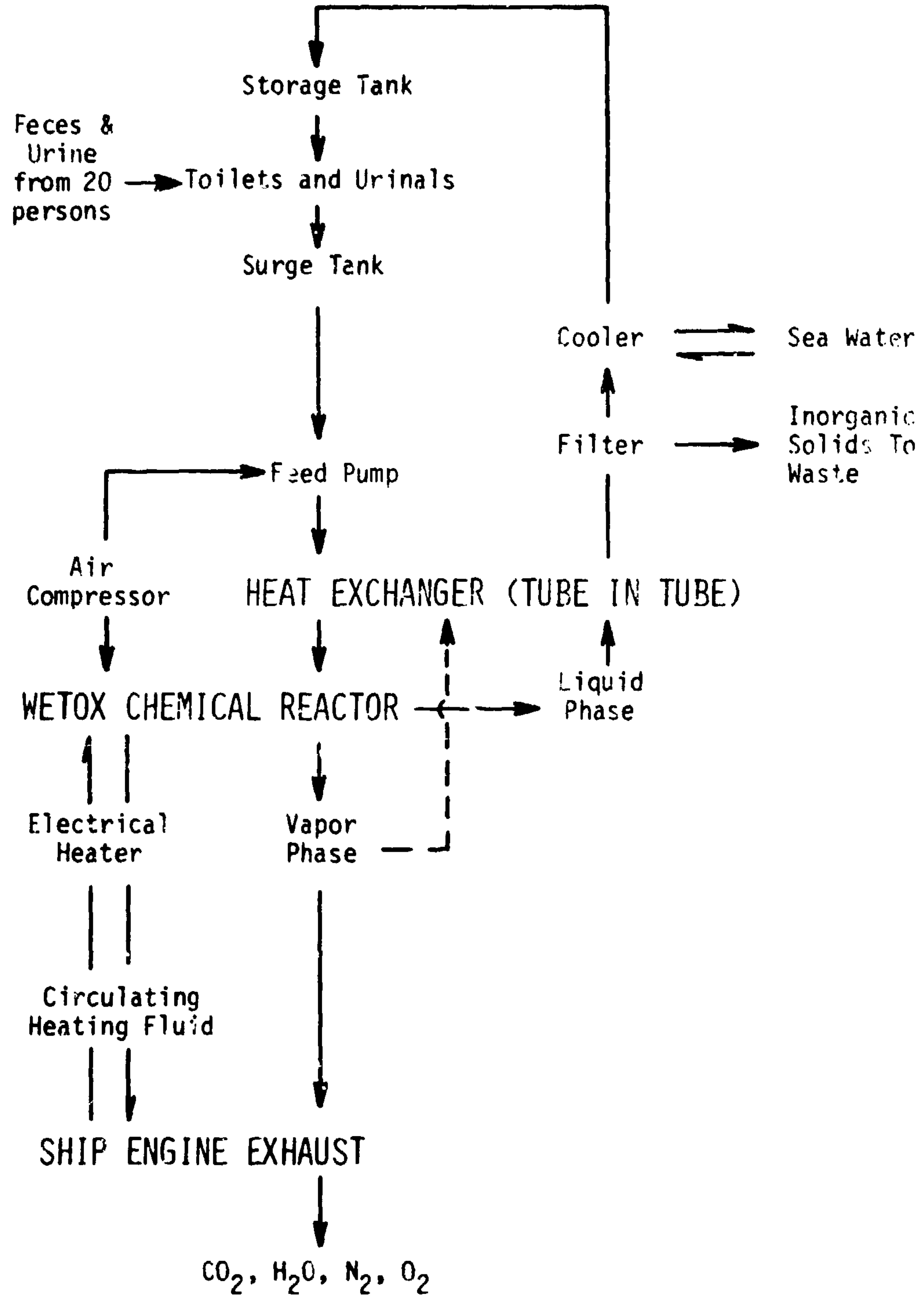


FIGURE 6-2. FLOW CHART, PURETEC MARINE WASTE TREATMENT SYSTEM.

The liquid phase is conducted from the reactor via a heat exchanger and reduced to atmospheric pressure for filtration. The autoclave effluent is filtered using a totally enclosed precoat filter very much like that used in a home swimming pool. This unit has sufficient capacity to retain all inorganic solids for a 30-day period at the rated system capacity. The filtered effluent is recycled for reuse in the heads.

The Barber-Colman PURETEC Sewage Treatment System utilizes a catalyzed ammoniacal solution as the carrier. This solution contains a biocide to preclude any possibility of infection or odor. During operation, no reagents other than air are required. Once every sixty to ninety days, depending on usage, the system is discharged to shore for final disposal and the system is recharged with fresh water and catalyst. This periodic recharging is necessary to remove the dissolved salts which accumulate principally from urine.

6.2 REQUISITE SIZE OF SYSTEM

The requisite size of a system is presented in this section for the treatment of the body waste generated by 20 men. Some galley waste, in the form of strained solids, could be included. The system has capacity for additional organic solids but can not accommodate additional water.

6.2.1 WASTE LOAD

The basic nature of shipboard waste was described in Section 2.4.1. At least three-fourths of the contamination--75 pct of the BOD and 85 pct of the suspended solids--is derived from human excretion. A comprehensive compilation of the daily excretion for a typical man is presented in Table 6-1. These data are in agreement with are in agreement with values reported by NASA and others*.

a. Quantity of Organic Waste and Oxygen Requirements

The body sewage of 20 men will contain the following amounts of organic matter:

Fecal organic material	633.6 g/day		
Urinous organic material	544.5		
Total organic excreta		1188.0	
Estimated toilet tissue		1188.0	
Total organic material to be oxidized			2376.0 g/day

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*T.R. Camp, Water and Its Impurities, Reinhold Publishing Co., N.Y., N.Y., 1963; see page 241.

TABLE 6-1.

COMPOSITION BY WEIGHT IN GRAMS OF DAILY PER CAPITA HUMAN EXCRETA*

	Feces	Urine	Totals
Amino Acids	24.00	2.30	26.30
Ammonia	0.06	0.70	0.76
Calcium	0.55	0.20	0.75
Chlorine	0.04	8.40	8.44
Cholesterol	0.58	--	0.58
Crestimine	--	1.70	1.70
Fats, Neutral	2.00	--	2.00
Fats, Saponified	2.40	--	2.40
Fatty Acids	2.20	--	2.20
Hippuric Acid	--	0.60	0.60
Lactic Acid	--	2.50	2.50
Magnesium	0.19	0.20	0.39
Nitrates	--	0.50	0.50
Phenols	0.11	0.02	0.13
Phosphates	--	2.50	2.50
Phosphorous	0.70	--	0.70
Potassium	0.50	1.50	2.00
Soap	0.39	--	0.39
Sodium	0.12	5.00	5.12
Sulfur	0.16	1.60	1.76
Urea	--	20.00	20.00
Uric Acid	--	0.60	0.60
Water	136.00	1368.00	1504.00
TOTALS:	170.00	1416.32	1586.32

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*Reproduced from MRIS Report, "Treatment and Disposal of Vessel Sanitary Wastes", National Research Council, July 1971, p. 16.

According to the previous estimate, the system must treat daily about 5-1/4 pounds of organic waste.

For the wet oxidation of human waste and cellulose, about one pound of oxygen is required for the combustion of one pound dry organic solids. (This design value was discussed in Section 2.4.3.) As compressed air is 23.14 percent by weight oxygen, the daily requirement computes to be 10,268 g/day of air or 0.2 scfm (standard cubic feet per minute).

b. Water Build-up.

For a 20-man crew, the daily contribution of water to the closed loop is estimated to be

Water added from feces	2720 g/day	
Water added from urine	27360	
Total water added to system		30,080 g/day

In terms of weight, if all of this incoming water is retained in the closed loop, 66.3 pounds would be added to the system each day.

c. Build up of Dissolved Salts.

Each man also contributes inorganic matter daily to the closed loop which accumulates as dissolved salts. For a 20-man system, the following build-up in salts would occur:

	Daily total mass, grams	
	Source	
	Feces	Urine
Chloride ion	0.8	168.0
Magnesium	3.8	4.0
Phosphate	19.3*	153.2
Potassium	10.0	30.0
Sodium	2.4	100.0
Sulfate	9.6	96.0
	45.9	551.2

Over fifty percent of the dissolved salts are the chlorides of potassium and sodium.

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*Excluding insoluble calcium phosphate.

In computing the above estimates, it has been assumed that organic phosphorus is oxidized to phosphate and sulfur to sulfate. Nitrate-and-ammonium nitrogen were not included in the estimate, because the pilot-plant tests indicated that there was little build-up of either ammonium salts or nitrates. Ammonium-nitrogen was found in the condensed vapors from pilot-plant, closed-loop tests.

6.2.2 SIZE OF COMPONENTS AND DRY WEIGHT

Most of the components comprising the system are over weight but are the smallest available. The basic items--the air compressor, the WETOX reactor, and the recirculating toilets--could be used to treat the body waste generated aboard a ship with a much larger complement.

In following subsections, the components comprising each sub-system are briefly described, and the weight listed.

a. Toilets.

In order to increase the strength of the sewage and thereby reduce the hydraulic load in the closed-loop system, a recirculating toilet such as the Monogram Industries, Commerical Marine toilet, JET-O-MATIC Model 160M-PA is recommended. The specifications are listed below:

Number Required	Description	Size	Total Weight Pounds
2	Jet-O-Matic Toilet Model 160 M-PA	18 in. high 19-1/2 in. wide 24-7/8 in. deep	76

According to the manufacturer's literature, the toilet will accommodate approximately 16 man-days of waste prior to removal of the spent flushant and replenishment with fresh flushing solution. Normally the toilet holds an eight-gallon charge (approximately 30 liters), and the sewage strength of the spent flushant at the end of the recommended use cycle would be approximately 35,000 to 40,000 mg/ℓ O (COD).

In the PURETEC system recommended for 20 men, the toilet flushant need not be used nearly as long as the manufacturer says it can be used; because flushant is continually processed. (In fact, flushant must be delivered continuously to the reactor at the rate of 15 liters per hour.) The mean COD of spent flushant in the PURETEC system will be about 7000 mg/ℓ O; consequently, there should be no problems from an esthetic or odor-control viewpoint.

In formulating an estimate of weight and space requirements, we have included two toilets in the proposed system. Alternatively, a system for 20 men could be based on the use of one toilet and one urinal.

b. Feed System.

Flushant is withdrawn continuously from the water closets of the toilets and flows to a nearby macerator/pump. Macerated sewage is pumped to a holding tank constructed of light-weight, corrosion-resistant titanium. The WETOX reactor is fed by the same blow-case pump system used in the pilot plant described in Section 3.1.1c. The specifications for these three items comprising the feed system are listed below:

Number Required	Description	Size	Total Weight Pounds
2	Macerator/Pump	6" x 6" x 10"	30
1	Feed, Holding Tank 16 ga. Titanium	14 in. dia. 25 in. high	13.5
1	High-Pressure Feed Pump	19-1/2 in. high 16 in. Long 12-1/2 in. wide	35.0
			78.5

Because the toilets undoubtedly are separated by some distance, each must be supplied with a separate macerator/pump.

c. Air Compressor.

The air requirements for the 20-man system were computed in Section 6.2.1a--about 0.2 scfm is needed. This is well below the flow from the smallest high-pressure, continuous-duty compressor available. Therefore, the system is designed to be used in conjunction with a compressor which operates intermittently as needed to fill a high-pressure reservoir (or accumulator).

Two types of small, continuous-duty compressors are available, namely, the Bauer model P3-32E3 and th Loebersdorfer Mashine Fabrik Aktiengesellschaft (LMF) V3/3308 L 20. No equivalent American-made compressor is known to us, that is, one of comparable size capable of high-pressure, continuous-duty performance. Both of the above units require 2.7 to 2.8 horsepower at their full-rated capacity. The Bauer unit operates at 1100 rpm and the LMF unit at 750 rpm.

The weight and dimensions for the Bauer compressor are listed on the following page with the other components comprising the sub-system:

Number Required	Description	Size	Total Weight Pounds
1	Compressor	29-1/4 in. high 16-3/4 in. wide 14-1/2 in. deep	150
1	Air Accumulator & Regulator	7-1/4" dia. 23-1/2" long	35
			185

d. WETOX-Reactor, Heat-Exchanger Assembly.

In the PURETEC Marine Waste Treatment System, the reactor and heat exchanger are combined into a single assembled unit. The salient features of the assembly are discussed in Section 6.3. The weight and dimensions of the components are as follows:

Number Required	Description	Size	Total Weight, Pounds
1	Wetox Reactor-Heat Exchanger Assembly	20 in. dia. 55 in. long	275*
1	Vapor-Phase Let-Down Valve	14 in. high 10 in. long 4 in. wide	18
1	Liquid-Phase Let-Down Valve	6 in. dia. 8 in. high	5
			298

e. Filter and Accessories.

As stated previously in Section 6.1, solids discharged from the WETOX reactor are removed from the effluent before its reuse as flushant. The effluent is filtered using the same sort of unit used in home swimming pools. The weights and dimensions of the components are listed on the following page.

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*Including weight of two electrical heaters mounted in base of assembly to heat Therminol 66 heating fluid; See Section 6.3.7.

Number Required	Description	Size	Total Weight, Pounds
1	Filter	16 in. dia. 24 in. high	30
1	Filter Feed Pump		20
1	Effluent Holding Tank	20 in. dia. 26 in. high*	20
			70

f. Heating System.

The PURETEC Marine Waste Treatment System includes provisions to supply heat, if needed, to the WETOX reactor. Generally, additional heat is required unless a particularly strong sewage is being treated. (See Section 2.5.3b for further discussion.) The additional energy required to sustain the proposed 20-man shipboard treatment system is about 0.40 kilowatts and is computed in Section 6.4.

In the proposed design, the additional energy can be supplied from waste heat given off by the ship's main engines by the PURETEC heating system. Basically, the heating system is a heat-transfer loop. A section of the engine-exhaust pipe is surrounded by a coiled length of tubing containing a heat-transfer fluid such as Monsanto Therminol 66. The fluid is heated by the hot exhaust gases and pumped as needed through the tubing to the WETOX reactor. The same tubing surrounding the exhaust pipe is also joined to a heating jacket which surrounds concentrically the outer surface of the front end of the reactor. Thus, heat from the engine exhaust is transferred to the WETOX reactor, and the process is sustained without the expenditure of electrical or other purchased energy.

There are also mechanical advantages gained by the use of the heat-transfer system in lieu of the electrical heaters used in the pilot-plant reactor described in Section 3.1.1; these mechanical aspects are discussed in Section 6.3.

The basic components of the heating system are listed on the following page.

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*Overall dimensions: The holding tank contains both influent and effluent. The influent is contained within an inner cylinder 14 in. dia.; whereas the effluent is contained in an outer ring whose outside diameter is 20 inches and whose height is 26 inches. See Figures 6-3 and 6-11.

Number Required	Description	Size	Total Weight Pounds
1	Heater, Therminol	4 in. dia. 38 in. long	30
1	Heater Pump	7 in. high 6 in. wide 16 in. long	25
1	Accumulator for Heated Fluid	4 in. dia. 12 in. long	12
	Heat-Transfer Fluid	1 gallon	6
			73

Three electric heaters are provided in the system to maintain the temperature of the heating fluid when the ship is at dockside.

g. Structural Support.

The PURETEC Marine Waste Treatment System is assembled on a structure of 6061-T6 aluminum angle-shaped channel. The structural support members have been treated to protect them from corrosion. The over-all dimensions and weight are tabulated below:

Description	Size	Total Weight Pounds
Structure Support	5-ft., 8-in. long 4-ft. wide	75

h. Control Console and Instruments.

The various controls and instruments are mounted in a conveniently located console. The total weight and over-all dimensions of the assembled console are listed below:

Description	Size	Total Weight Pounds
Control Console Including Gauges & Instruments	30 in. X 48 in. X 10 in.	50

6.2.3 VOLUME AND WEIGHT OF IN-PROCESS WATER

One of the main advantages of the PURETEC Marine Waste Treatment System is the small amount of in-process water. Less wastewater is generated by using toilets with a recirculating flushant. Surge capacity is gained by temporary build-up in the strength of the recirculating flushant. Over-all savings are made by continuous treatment of the flushant. Water build-up is prevented by continuous venting of steam from the reactor. The estimated total volume and weight of water in the closed loop are listed below:

Location	Weight* Pounds	Capacity for Water Volume Gallons
JET-O-MATIC Toilets	120	14.4
Feed Holding Tank	125	15
Effluent Holding Tank	125	15
Filter	71	8.5
Heat Exchanger	29	3.5
Misc. Piping & Pumps	29	3.5
	499	59.9

In metric units, the volume of water in the closed loop is 226.75 liters.

6.2.4 TOTAL WEIGHT AND SPACE REQUIREMENT

In Table 6-2, the weights are listed for the various sub-systems comprising the PURETEC® Marine Waste Treatment System. The weight of in-process water is included in the table; and the percentage of the total weight is indicated for each item. The hydraulic load (in-process water) represents over one-third of the total weight of the system; and the WETOX® reactor and its integral heat exchanger also comprise about one-fourth of the total weight. The air compressor is the next (third) heaviest item in the system; as we have stated previously, it has more capacity than required but is the smallest available.

The space required for the PURETEC® Marine Waste Treatment System--shown isometrically in Figure 6-3 is 5'-8" long by 4'-0" wide by 3'-0" high. The control console, which may be located remotely from the sewage treatment equipment, will occupy a deck space, 2'-6" wide by 10" deep. The control console will require access in front only. Its overall height will be approximately 4'.

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*Water only, excluding weight of component.

TABLE 6-2

WEIGHT OF 20-MAN
PURETEC MARINE WASTE TREATMENT SYSTEM

Item	Weight Pounds	Percentage of Total
Recirculating toilets	76.0	5.4
Feed System	78.5	5.6
Compressed-Air System	185.0	13.2
WETOX-Reactor & Heat-Exchanger, Combined Assembly	298.0	21.2
Filter and Accessories	70.0	5.0
Heating System	73.0	5.2
Structural Support	75.0	5.3
Control Console and Instruments	50.0	3.6
In-Process Water	499.0	35.5
	1404.5	100.0

4

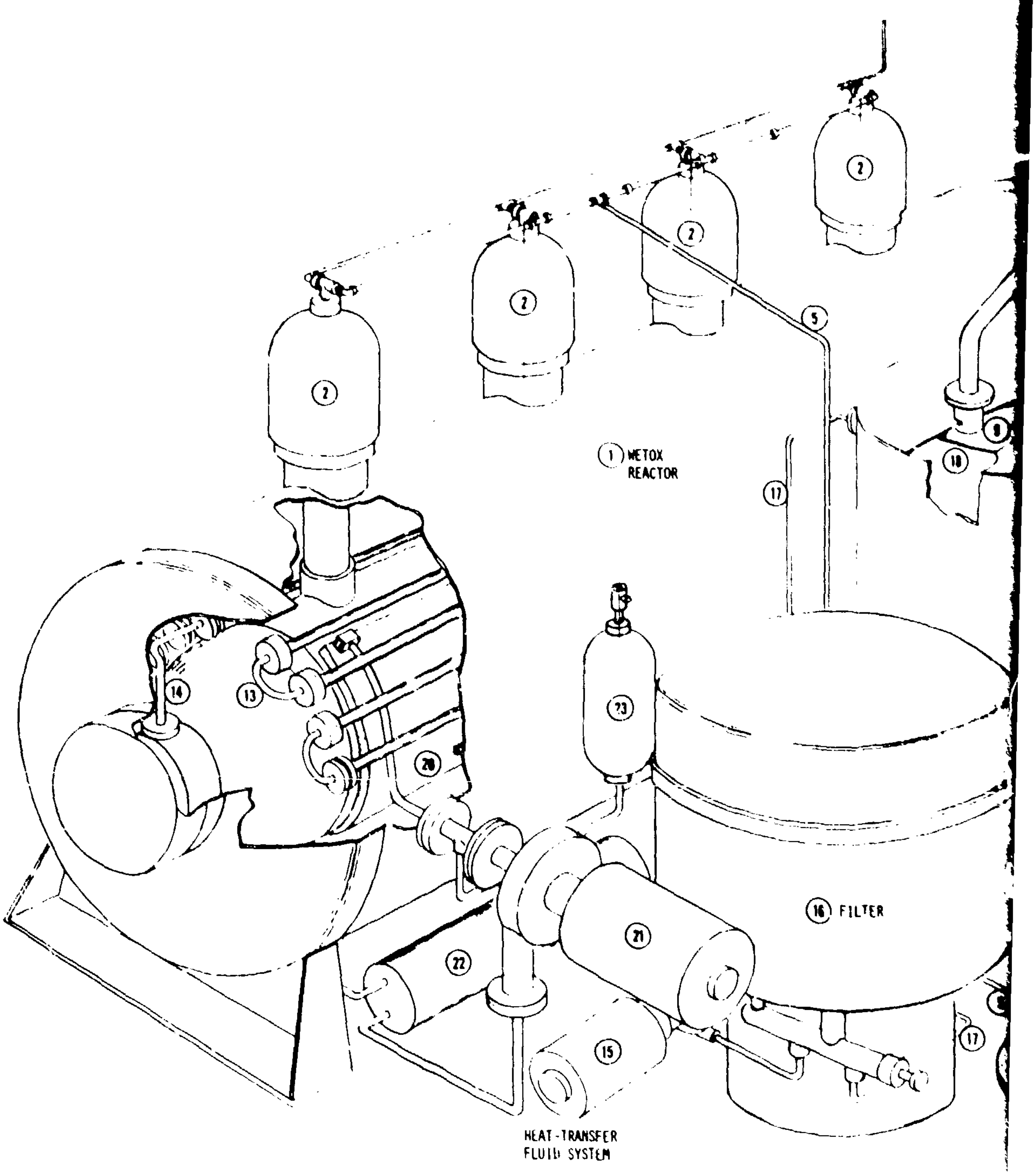
3

D

C

B

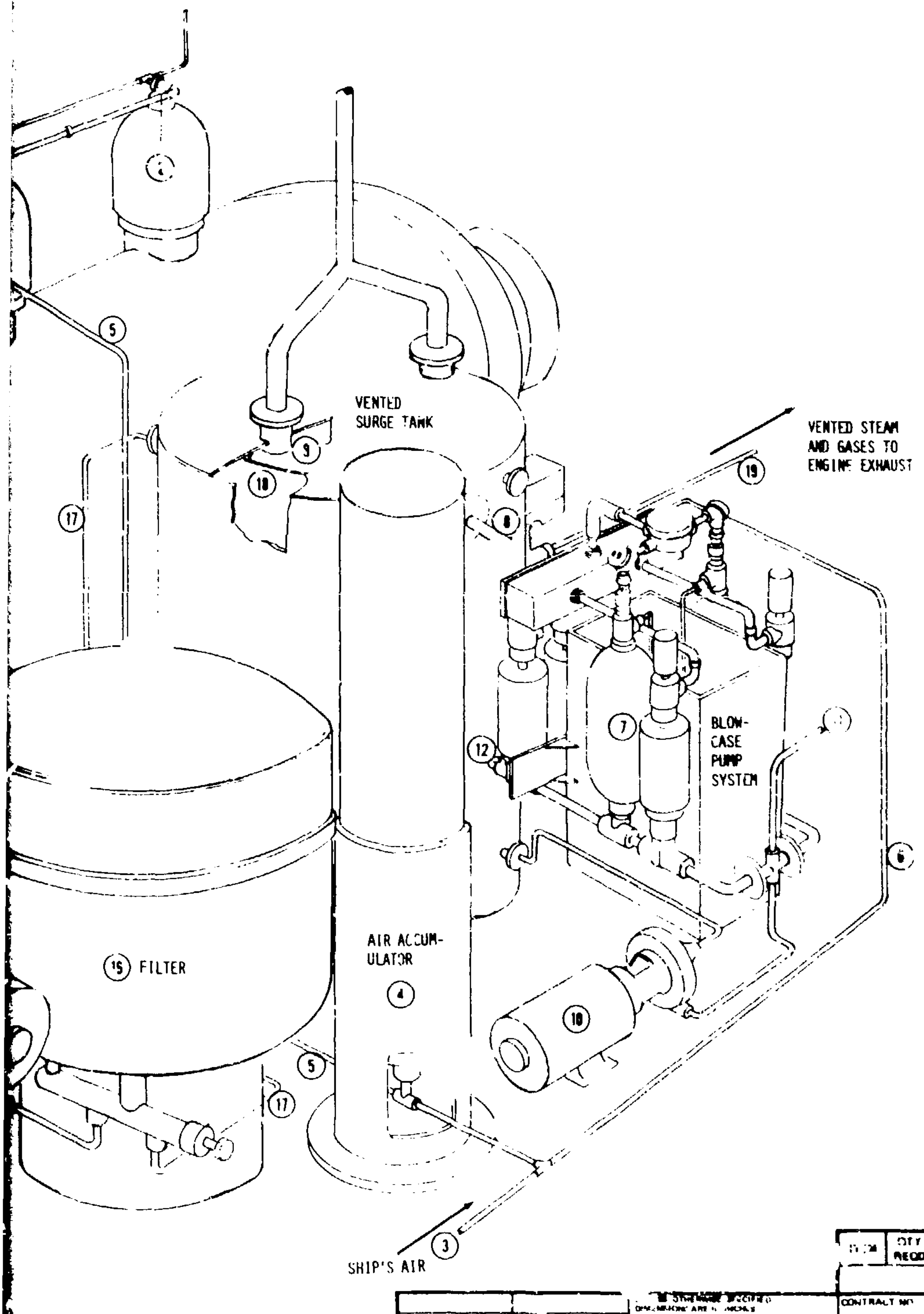
A



NOTES: UNLESS OTHERWISE SPECIFIED

DO NOT SCALE DWG

REVISIONS				
ZONE	LTR	DESCRIPTION	DATE	APPROVED



ITEM	QTY REQD.	CODE IDENTY	PART NO.	NOMENCLATURE OR DESCRIPTION

PARTS LIST

UNLESS OTHERWISE SPECIFIED
DIMENSIONS ARE IN INCHES
TOLERANCES ±1/32
ANGLES ±1°
3 PLACE DECIMALS ±.005
2 PLACE DECIMALS ±.010
MATERIAL

NEXT ASSY	USED ON
APPLICATION	

MAT'L WT
QTY REQD

CONTRACT NO

PREPARED	G. Parsons	DATE 5 13 76
CHECKED		
ENGINEER		

SUBMITTED
APPROVED

BARBER COLMAN COMPANY
RESOURCE RECOVERY SYSTEMS
IRVINE, CALIFORNIA

PURETEC MARINE WASTE
TREATMENT SYSTEM
MODEL 412 M

SIZE	CODE IDENT NO	DRAWING NO
D		

SCALE
SHEET OF 1

FIGURE 6-3 ISOMETRIC VIEW

KEY TO FIGURE 6-3

PURETEC MARINE WASTEWATER TREATMENT SYSTEM

The system as illustrated in Figure 6-3 comprises a Marine WETOX reactor 1--a continuous-flow autoclave whose interior is divided into four compartments, each of which is stirred by separate mechanical agitators 2. Ship's air enters the system through line 3 and is stored in an accumulator 4 from which it is dispensed through line 5 to the reactor and through line 6 to the blow-case pump 7. Raw wastewater enters through line 8 from macerators located near the toilets and is stored in the inner ring of the vented surge tank 9. The raw wastewater is circulated continually by pump 10 to the blow-case pump; the excess is returned to the surge tank via line 11. Raw wastewater is ejected by compressed air from the blow-case pump through line 12 to the heat exchanger 13 and into the reactor through inlet [illegible]. After treatment the liquid-phase effluent is cooled and transported via pump 15 to the filter 16. Filtered liquid is returned through line 17 to the outer ring of the surge tank 18. Vented steam, spent gases and some vapors exit from the reactor through line 19 and are discarded with the ship's engine exhaust gases.

The reactor is heated by a heat-transfer fluid which is circulated through a jacket 20 encircling the bottom portion of the reactor's exterior. The fluid is pumped continually by pump 21 through the electrical heater 22 and coiled tubing housed in the ship's engine exhaust stack. Surplus heat-transfer fluid is held in the reservoir 23.

6.3 MECHANICAL DESIGN

In the preliminary design study conducted in Task VI of this contract, a number of design improvements have been developed as a result of both independent effort by Barber-Colman and work performed in this contract. These improvements have been incorporated in the preliminary design presented in this report.

In the following subsections, each item of equipment will be discussed and the rationale presented for the choice of design approach and resulting equipment selection. In some instances, it is impossible at this time to state with certainty that the selected item will have the desired durability. Uncertainties where they exist will be carefully pointed out for subsequent study on a prototype system.

6.3.1 MATERIALS OF CONSTRUCTION

The choice of a satisfactory material of construction to contain wet-oxidation reactions has been a controversial subject for years. In spite of the outstanding performance of commercially pure titanium for over eight years of continuous service in the Calera Mining Company cobalt* refinery from 1950-1959, there are many that consider the use of other alloys such as stainless steels, nickel base super alloys and other specialty alloys. In a recent report,** the suitability of titanium for wet-oxidation reaction equipment was reaffirmed.

In the treatment of shipboard sewage, substantial quantities of sodium chloride and ammonia as well as organic acids such as acetic are formed. In addition rather surprising quantities of inorganic ash or solids result from the wet oxidation of feces, urine and toilet tissue. The combined abrasive action of the solids plus the tendency of nickel-containing alloys to form a soluble nickel pentamine complex lead to rapid deterioration of nickel-base alloys. Under identical conditions, titanium is untouched for hundreds of hours as clearly demonstrated in our laboratory. Even at NaCl-concentrations of 90 g/ℓ no indication of attack has been observed with C.P. Titanium.

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* W. M. Fassell, Jr., "Hyper-Atmospheric Extractive Metallurgy, Its Past, Present and Future", Pure and Applied Chemistry, Vol. 5, 1962, pp 683-699.

J. S. Mitchell, "Cobalt Pressure Leaching and Reduction at Garfield", Journal of Metals, March 1957, pp 343-35.

**National Materials Advisory Board, "Materials for Wet Oxidation Processing Equipment (Shipboard)", Report No. NMAB-312, December 1973, 79 pp.

Intuitively, one would anticipate that titanium would erode rapidly when used in agitators or heat exchangers, because it is a relatively soft metal. Such is not the case. The titanium agitators used in the Barber-Colman 410-L system for over 15 months show no measurable erosion. This was also observed in the Calera Mining Co. refinery. There titanium agitators operated continuously in a reactor treating a 20% slurry of inorganic gangue minerals for over 8 years. In the presence of oxygen and superheated water, titanium apparently forms a very thin protective outside layer with outstanding chemical inertness and abrasion resistance.

For the above reasons, C.P. titanium has been used for all wetted surfaces above 100°F in the recommended shipboard design. No other material is known that equals its record of service.

6.3.2 MARINE TOILETS

As discussed in Section 6.1, the proposed zero-discharge, recirculating sewage-treatment process requires the use of a limited-volume flush toilet. For small systems the Jet-O-Matic toilet model 160M-PA with slight modifications appears to be the best choice. In a recent program conducted by Monogram Industries for the U.S. Army Corps of Engineers, an improved version of the 160M-PA has been developed.

The improvements involve the incorporation of a bowl seal above the liquid level that is activated by the closing of the lid. This prevents escape of odors and splashing of the flushant under rough sea conditions. The unit is of conventional shape and uses a small quantity of 10 psi air for its activation. Since compressed air is necessary for the wet-oxidation process, no special equipment is required. The pneumatic system avoids the use of electric motors and the problem of reduced voltage D.C. power required to operate some types of marine toilets.

This toilet does not contain an internal macerator/pump for sewage discharge. The unit is, however, equipped with a very simple self-cleaning sieving system to prevent recirculating suspended solids in the flushant.

6.3.3 MACERATOR/PUMP

Each toilet will require a small macerator/pump to reduce the particle size of suspended solids and transfer the used flushant to the influent holding tank of the waste treatment system. Transfer of the used flushant and refilling will be programmed on a time basis. This will insure a constant supply of used flushant to the wet-oxidation system. The time sequence control, which can be adjusted for the anticipated use factor, reduces the required surge capacity and the weight of on-board process water.

The macerator/pump units located at each toilet or head will only operate during flushant transfer. Under normal conditions it is anticipated that the macerator/pump will operate approximately 30 sec every 30 min.

Small low-volume sewage macerators are a recently developed product designed for recreational vehicles. In general, they appear to lack sufficient durability for marine or industrial use. A number of plastic types were examined and one was evaluated during the program for the maceration of feces and toilet tissue. The unit, a self-priming macerator/pump (JABSCO model no. 17460-0003), worked well; and no problems were encountered in its use.

Based on discussions with E.F. McKiernan, Marine Sanitation Systems, Monogram Industries, Inc., excellent service has been experienced with the all-metal Oberdorfor Model 214M USF. This macerator/pump employs a bronze housing with stainless-steel cutter blades. In addition, the impeller design includes a vortex breaker that appears to serve much the same function as a choke breaker on large industrial pumps. In essence, it breaks up large particles prior to their entry into the macerator proper.

Considerable question exists as to the ability of small macerators to ingest items such as cigarette butts, bottle caps, book matches, chewing tobacco and other extraneous waste.

In addition, the ammonia level present may have a corrosive effect on the bronze components of the macerator/pump. Stainless steel may be required.

6.3.4 FEED AND EFFLUENT HOLDING TANKS

The used flushant from the macerators will be conducted from the heads to the sewage treatment system. Limited tests suggest that common steel piping may be satisfactory. Plastics such as PVC and stainless steel are not effected by the flushant.

A number of configurations were examined for the feed and effluent holding tanks. Because of weight and space limitations, the approach selected was a double-concentric, cylindrical tank totally sealed and vented overboard. The inner tank receives the influent (used flushant) while the outer tank holds the autoclave effluent. This concentric tank design provides a reasonable head for the feed pumps and will act as a secondary heat exchanger to equilibrate the feed and effluent temperature.

All connections will be flanged to avoid any tendency to leak under the ships motion. This tank will be fabricated from titanium to preclude possible corrosion and minimize weight.

6.3 5 HIGH-PRESSURE FEED PUMP

The used flushant must be pumped into the reactor or autoclave at approximately 650 psi (autoclave pressure plus flow loss in the heat exchanger).

At the small flow rates required for shipboard wet-oxidation processes, no standard commercial item is known to exist that will pump macerated sewage at the required pressure.

Positive displacement-piston or diaphragm pumps using small ball-check valves are not satisfactory because particulate material invariably lodges on the seat and causes leakage. This results in erosion or "wire drawing" of the check-valve seat and high back-leak rates.

We recommend the use of a blow-case pump based on developments over twenty years ago, in which this type of pump was found to be ideal for the injection of abrasive ore concentrates into a wet-oxidation autoclave. A small version of this design has been developed and successfully used over the past 15 months to pump a variety of organic waste materials.

The system consists of two small pressure vessels that are alternately filled with the influent feed at atmospheric pressure, valved off and pressurized to a static pressure slightly above the autoclave pressure. After pressurization the interconnecting valve to the small vessel and heat exchanger/autoclave is opened allowing the feed solution to enter the pressurized system. When the small chamber is empty as determined by a level sensor, the valve is closed and the residual gas pressure vented to atmospheric pressure. By proper sequencing, flow velocities through the valves are low and the differential pressures are small.

For slow pumping rates as required in this system a single one-liter-capacity pressure vessel will be adequate. Two cylinders are provided in the design, one system will be in reserve in the event of malfunction or stoppage. (Further details concerning the blow-case pump and its electrical control are presented in Section 6.5. The sequence of operation and the detection of the fluid level in the small pressure vessels is controlled by a solid-state logic circuit containing an adjustable timer to control the delay time between cycles. Variations in this delay time from one to 99 seconds are possible.

In order to insure prompt filling of the blow-case pump, the influent is delivered to the inlet valve port under a slight positive pressure. Because of the tendency of the waste material to settle, the best arrangement is to provide a closed-loop circulating system for continuous transport of the feed up to the inlet valve. In the marine waste treatment system the circulating loop would feed back to the influent holding tank.

The circulating pump used must be capable of handling small solid particles and macerated toilet tissue without excessive wear or clogging. Hair often is a problem in sewage since it tends to tangle around pump impellers. For this service, a small progressive cavity pump appears to be the most reasonable choice. Pumps of this type, such as the Moyno, are widely used to handle sewage and sludge in municipal plants. Both Moyno and centrifugal pumps have been used on our systems without problems. It should be noted that some question exist as to the durability of the very small progressive cavity pumps. Optional equipment should be evaluated for a prototype system.

6.3.6 HEAT EXCHANGER

In contrast to other wet-oxidation processes, the Barber-Colman Co. PURETEC System separates the liquid and vapor phases at the point of discharge from the autoclave or reactor. For closed-loop marine waste treatment, this is a unique advantage since the vapor phase which is free of suspended solids and salts can be vented to the exhaust stack of the propulsion or auxiliary engines. This provides a means of elimination of excess water (from urine).

In order to achieve maximum temperature rise in the influent, tube-in-tube type heat exchangers are used. These are fabricated from C.P. Titanium including all flanges. Gaskets are blue asbestos-titanium chevron type.

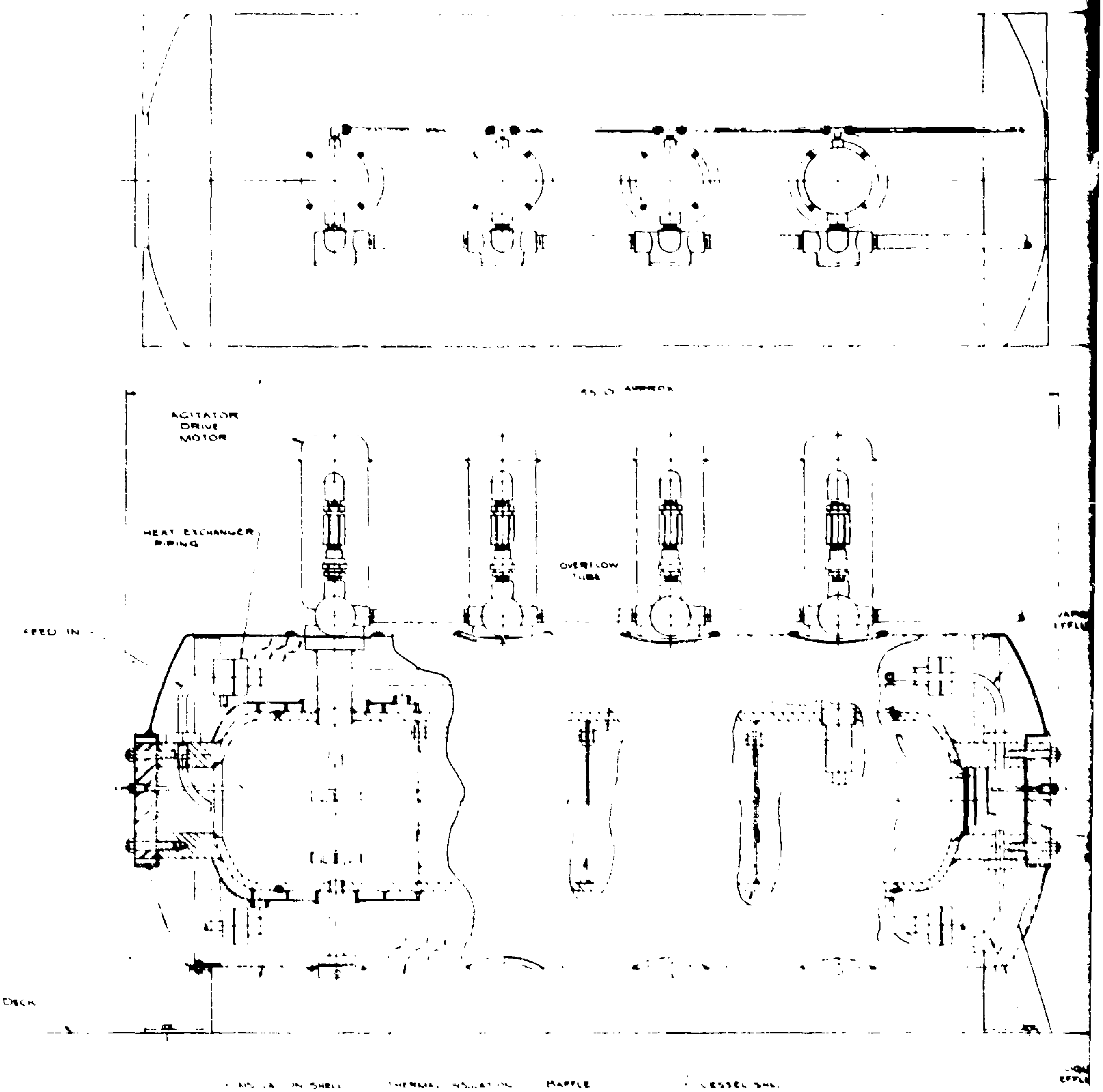
Titanium heat exchangers are unusual in that they do not tend to scale. In over 15 months operation it has not been necessary to clean our titanium exchanger. Recent examination showed it to be clean and free of scale.

As shown in Figure 6-4 the heat exchanger is positioned around the reactor. This design results in substantial weight and space reduction since the reactor serves as the structural support and the exterior shell is common. In addition, the thermal losses are minimized; and exposure of interconnecting piping is avoided. From a safety viewpoint, the confinement of all heated, pressurized piping within the WETOX Reactor enclosure is a distinct advantage.

6.3.7 WETOX REACTOR

As a result of one and a half years operating experience with the Barber-Colman (Model 410-L) Pilot-Plant reactor, a number of design concepts were found awkward; and some of the selected purchased components were lacking in durability. The proposed preliminary design reflects the changes in configuration and equipment that we feel represents a substantial improvement in hardware reliability.

The WETOX Reactor Model 410M shown in Figure 6-4 represents the latest design concepts for shipboard use. In this model, the large (ring) closures ie (10" ID) used on both the 410-L and the 210 U.S. Coast Guard unit described in Section 5 has been eliminated. The large size and weight of the closure rings or flanges



NOTES UNLESS OTHERWISE SPECIFIED
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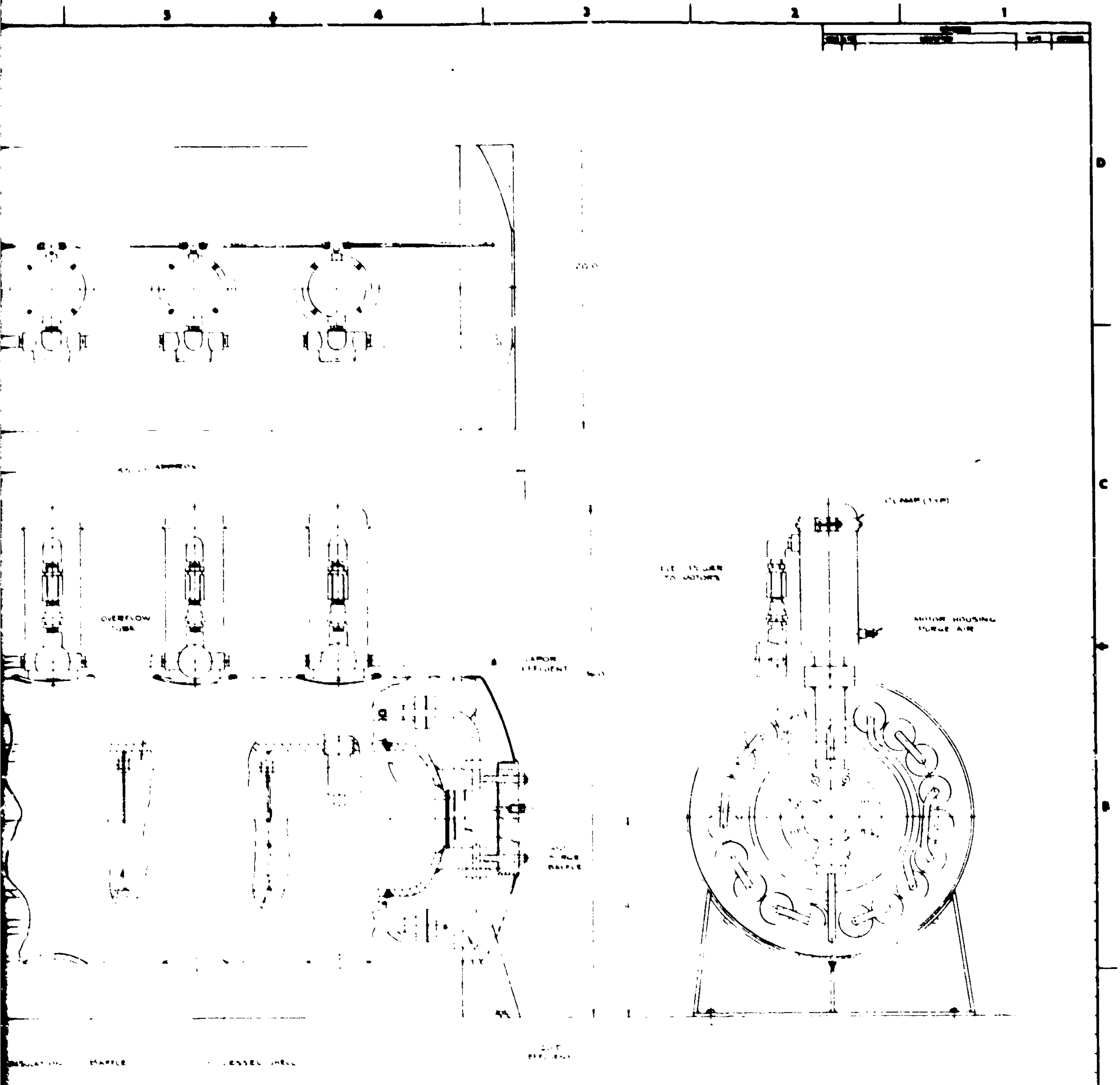

PARTS LIST

BARBER-COLMAN COMPANY

AUTOCLAVE 410M

RRS-1 410-4

required has been replaced by two 3 1/2" diameter hand holes at either end of the reactor. Substantial weight and cost savings are achieved by this change. Access to the interior of the reactor is somewhat limited, but there is little need for interior maintenance other than occasionally removing or replacing an agitator. (Ample room has been provided to affect the removal of an agitator.) In a laboratory reactor, one might remove partitions and install catalyst supports such as were described in Section 5.1; aboard ship such operations are not contemplated.

a. Agitators

In all stirred autoclaves like the WETOX Reactor, agitator drives and seals have been a problem. In large equipment, packed seals have proven to be durable and leak free. In small autoclaves, many styles have been used over the years; but none is ideal.

The initial design used on the 410-L (pilot-plant) reactor was a lantern-ring type packed seal. Leakage rate could not be reduced to an acceptable level. These were replaced with mechanical seals using tungsten carbide-graphite sealing surfaces. These proved to be entirely unsatisfactory.

Finally, all agitator drives were replaced with a modified autoclave Engineers Magnadrive unit (Series 3/4-10, 5000). This drive assembly uses a stator and rotor magnetically coupled through a thin-wall, tubular stationary separator. Heat-resistant ceramic magnets are used. This drive has no moving seal and, in theory, should provide an ideal solution to the problem. In practice, substantial difficulty has been encountered in maintaining the bearings on the inner rotor. These are exposed to the autoclave environment and suffer rapid chemical attack. Some improvement in life has been achieved using tungsten carbide as the journal with Grafoil bearing. This configuration will operate approximately 500 hours before bearing replacement is required.

Based on work performed some years ago*, a direct coupled pressurized motor drive system is currently under evaluation. Earlier work showed that such a system was capable of at least one-year, trouble-free operation.

In the pressurized motor drive, the air required is introduced into the motor compartment and conducted down the agitator drive shaft to the lower impeller. This provides partial cooling of the motor and prevents back diffusion of corrosive vapor into the motor. In addition, a vapor seal is used to insure that the air flow is directed down the shaft into the impeller shear zone.

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*W.H. Dresher, T. M. Kaneko, M. E. Wadsworth & W. M. Fassell, Industrial and Engineering Chemistry, V. 47, p. 1681, Sept. 1955.

Additional water cooling of the motor is incorporated in the pressurized motor housing.

b. Heating System.

As shown in Figure 6-4 the heat necessary for start-up and run conditions with low-energy feed, such as shipboard sewage, is supplied by an external atmospheric-pressure heating jacket surrounding the number one and two reactor compartments. This jacket is heated using Therminol-66-heat-transfer fluid so that only a small temperature differential is required between the source and sink. This avoids the possible charring or carbonization of the feed material in contact with hot surfaces.

Earlier designs used titanium-sheathed immersion heaters operating at high watt densities. Two problems were encountered with electrically heated immerged rods, namely (1) interdiffusion of the heater sheath (INCONEL) into the titanium causing the formation of a brittle TiNi intermetallic compound, (2) partial charring of the organic waste on the hot wall of the immersion tube resulting in the formation of colloidal carbon (a dark yellow to brown carmel-color, liquid-phase effluent), and (3) scale build-up on the wetted surface of heaters increasing the fouling factor (for heat transfer).

The use of Therminol-66-heat transfer fluid makes possible the utilization of waste heat from the propulsion engine while underway. While in port or in the event sufficient energy is not available, an electric heater is incorporated to provide heating as required to maintain the desired reaction temperature.

Because of the low viscosity of non-aqueous heat-transfer fluids and the absence of a pipe-thread compound that will withstand the temperature and thermal cycling, the heat transfer system uses all flanged joints and a seal-less pump.

6.3.3 FILTER

The liquid-phase effluent requires filtration before its reuse in the toilets. In the selection of a filter, two factors were considered. The first was a filter capable of producing a clear filtrate, and the second was the ease in discharging the solids remaining after treatment. An ordinary home swimming-pool filter was found to be suitable. These devices are made to withstand chlorinated waters which are more corrosive than our autoclave effluent. The solids are deposited on a precoated bed of diatomaceous earth. The area of the bed is sufficient to accommodate the solids from 20 men for a period of 30 to 60 days in a totally enclosed chamber. There will be no need to handle the solids at sea. Even though the solids are sterile inorganic compounds, handling them may be psychologically [illegible] to some.

6.4 SYSTEM BALANCE AND ENERGY REQUIREMENTS

Mass and thermal balances were computed for the proposed system and were used in establishing the requisite size of the waste-treatment equipment described in Section 6.2. The results of these mathematical analyses are presented in following subsections. The (electrical) energy requirements are summarized in Section 6.4.3.

6.4.1 MASS BALANCE

Three classes of matter--organic, inorganic and water--are added continually to the closed loop. Water and organic matter are removed continuously. The inorganic substances accumulate unchecked. Mass balances are included in this section for the inorganic and organic substances; a water balance is incorporated in a following thermal balance (Section 6.4.2).

a. Accumulation of Inorganic Salts.

According to the estimate formulated in Section 6.2.1c, about 600 grams of dissolved salts are added daily to the circuit. Expressed in units of concentration, the burden of the closed loop increases daily 3.7 grams per liter. About 50 percent of the accumulating salts are chlorides of sodium and potassium. The chloride-ion level increases 1.0 g/ℓ · day^{-1}.

The projected load of dissolved salts is tabulated below for typical periods:

Number of Days, Flushant Used	g/ℓ Total Salts	g/ℓ $C\ell^-$
15	56	15
30	111	30
45	166	45
60	222	60
75	278	75
90	333	90

In addition, insoluble inorganic solids are deposited continuously on the filter. About 10 pounds of so-called wet ash is removed monthly in filtration.

The solubilities of the principal dissolved salts are listed below for comparison:

Salt	Solubility, g/ℓ @ 20° C*
NaCℓ	360
KCℓ	340
$MgSO_4 \cdot 7H_2O$	355
$NH_4Cℓ$	370

One concludes that the system is saturated with respect to most dissolved salts by the end of about 90 days service. It becomes saturated much earlier, however, with sparsely soluble substances like calcium sulfate and magnesium ammonium phosphate, which are removed continuously from the circulating liquid by filtration.

Routine replacement of all flushant is recommended every 60 days.

b. Dispensation of Organic Matter.

Each day 2376 grams of organic waste enter the system. Assuming that one gram of oxygen is required for each gram of organic matter**, the mean COD of the raw waste in the influent to the WETOX reactor is 6500 mg/ℓ O.

The 20-man PURETEC Marine Waste Treatment System is designed to feed 15 ℓ/hr of spent flushant to the WETOX reactor which holds the equivalent of 30 room-temperature liters at 450°F. In other words, the mean residence time is 30 minutes per compartment.

A hypothetical Jones plot is presented in Figure 6-5 for the 20-man system, based on the batch tests described in Section 4.2.2. Specifically, the Jones plot was constructed from the means of the rate parameters for the four tests performed in the presence of NaCℓ. The abscissa of the plot is in units of COD, although the batch tests were monitored by analysis for TOC. Other tests described in Section 4.2.2 indicate that the rate parameters for COD are essentially the same or exceed those for TOC. An arrow indicates the COD of the raw-waste portion of the influent; there is, of course, a circulating load of relatively inactive acetate and related ions. The

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* Lange's Handbook of Chemistry, 11th Ed., published by McGraw-Hill Book Co., N.Y., N.Y., 1973; Table 10-2.

**See Section 2.4.3.

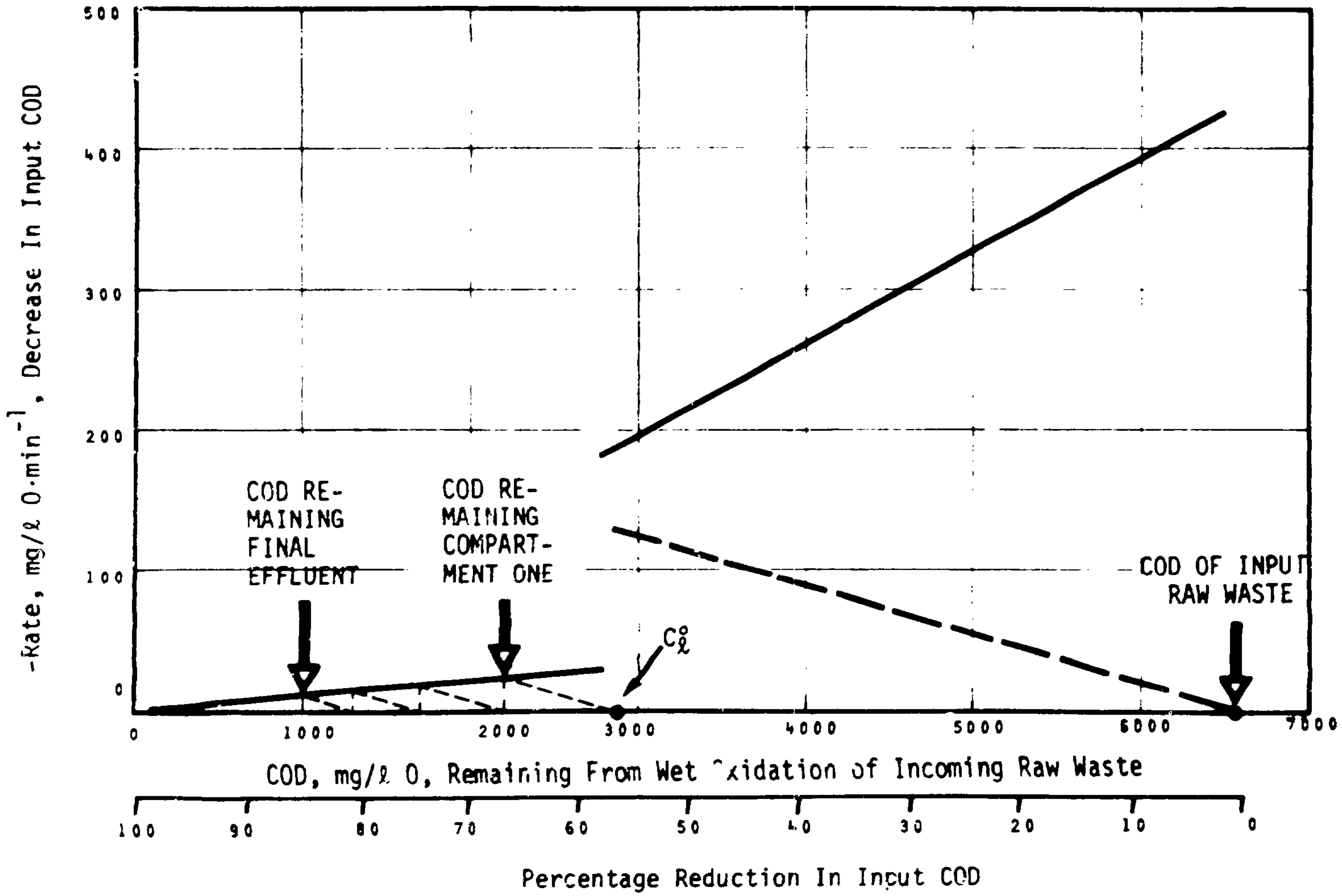

FIGURE 6-5. JONES PLOT FOR 20-MAN CLOSED LOOP

flow of influent and chemical kinetics are such that the late-stage, slow rate of reaction dominates in each compartment. In other words, the raw waste is injected into a preponderance of acetate. This is the special case discussed in Section G.3 of Appendix G, and the graphical solution presented in Figure 6-5 is in accordance with the methods outlined in Section G.3, Appendix G.

According to the plot, about 85 percent reduction in COD (or in TOC) will be accomplished in the 4-compartment reactor. In addition to the reduction accomplished by wet oxidation, there will be a continuous removal of COD in the vented vapor phase. About 8 percent of the water fed to the reactor is expelled in the engine exhaust as steam. The COD of vapor-phase condensate generally is about the same as the COD of the liquid-phase effluent; therefore, about one percent of the influent COD is vented in the exiting vapors. The predicted over-all percentage reduction is about 86, which is in good agreement with the pilot-plant results reported in Appendix I.

Based on the results of the simulated closed-loop test described in Section 4.2.1, the autoclave effluent ("rejuvenated" flushant) after 65 days will contain 8 to 10 g/ℓ carbon (TOC, total organic carbon). One should bear in mind, however, that the destruction of raw waste is 100 percent. By the time the wastewater exits from the first compartment of the reactor, the excreta have been burned to innocuous, sterile compounds. The autoclave effluent is essentially ammonium acetate and inorganic salts in water. The nature of 50- to 60-day old flushant can be judged visually from Figure 4-1. The liquid is a clear solution with a faint musty smell--lightly ammoniated, decidedly not urinous.

6.4.2 COMBINED WATER AND ENERGY BALANCE

Heat must be supplied to sustain the system, and water continuously removed to maintain balance.

a. Imposed Air Flow For Water Balance.

In formulating a thermal balance, consideration was taken to remove from the system as steam an amount of water equivalent to that added in the body waste of 20 men. The amount of water computes to be 30 liters daily or 2.76 lb/hr. Some of the other parameters needed for the following analysis are listed below:

Volume of liquid in reactor	30 ℓ (@ 450°F)
Influent flow rate	15 ℓ/hr
Reactor total pressure	600 psi
Reactor mean temperature	450°F
Pressure of saturated steam	422 psi (@ 450°F)

The spent gases leaving the reactor are saturated with steam; and the so-called humidity ratio[*] (the mass of water per unit mass of dry air) is

$$\omega = (R_a/R_w)\,[P_w/(P_m - P_w)] \qquad (6\text{-}1)$$

$$= 0.622\,[422/(600 - 422)]$$

$$= 1.47 \text{ lb steam per lb air}$$

In Equation 6-1,

R_a is 53.3 ft lbf/lbm - °R;

R_w is 85.7 ft lbf/lbm - °R;

P_w is 422 psi, the steam pressure @ 450°F; and

P_m is 600 psi, the total pressure of the reactor.

The subscripts a, w and m denote air, water and mixture, respectively.

The mean COD of the influent was computed to be 6600 mg/ℓ O (See Section 6.4.1 b.). The corresponding requisite air flow is 0.175 scfm (0.795 lb/hr) (cf. Section 6.2.1a). At this air flow, the loss in steam is

$$\dot{m}_w = \omega \cdot \dot{m}_a \qquad (6\text{-}2)$$

$$= 1.47(0.795) = 1.17 \text{ lb/hr}$$

This rate of loss is less than the rate of addition; and water would accumulate in the system. Either the air flow or the reactor temperature must be changed[**]. If the temperature is maintained at 450°F, which in this case appears to be the best alternative, the air flow must be increased to about 0.4 scfm to achieve a balance:

$$\dot{m}_a = \dot{m}_w/\omega = 2.76/1.47 = 0.4 \text{ scfm} \qquad (6\text{-}3)$$

As the compressor has a rated capacity in excess of 3 scfm air, the increased requirement is of no consequence. The system is designed to enable the compressor to operate intermittently (about 20 to 30 percent of the time).

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[*] J.E. Lay, Thermodynamics, published by Charles E. Merrill Publishing Co., Columbus, Ohio, in 1963, page 444.

[**] See Section 2.5.2a.

Whenever, too much water is being lost, the air flow can be reduced; and when too much is accumulating, the flow can be increased. Since the mean flow of air is nearly double the oxygen requirement of the system, the process will be insensitive to fluctuations in the design flow.

b. Thermal Balance.

General considerations were discussed in Section 2.5, and the various components were identified for a thermal balance. The energy required to sustain the reaction was defined as Q_B.

$$Q_B = (Q_1 + Q_2 + Q_3) - (Q_4 + Q_5 + Q_7), \qquad (6\text{-}4)$$

where Q_1 is the heat removed from the reactor in the vapor-phase effluent;

Q_2 is the heat removed from the reactor in the liquid-phase effluent;

Q_3 is the heat lost through the exterior walls of the reactor;

Q_4 is the sensible heat of the feed (incoming wastewater);

Q_5 is the sensible heat of the incoming compressed air;

Q_6 is the heat generated in stirring the reacting wastewaters; and

Q_7 is the heat liberated in the combustion of the organic wastes.

The specific contribution of each component* is tabulated below for the 20-man PURETEC Marine Waste Treatment System:

(1) Q_1, Heat Removed From Reactor In Vapor-Phase Effluent.

$$\begin{aligned} Q_1 &= \dot{m}_v \cdot h_v \qquad (6\text{-}5) \\ &= 2.76\ (1204.6) = 3325 \text{ BTU/hr} \end{aligned}$$

(2) Q_2, Heat Removed From Reactor In Liquid-Phase Effluent.

$$\begin{aligned} Q_2 &= (\dot{m}_f - \dot{m}_v)h_\ell \qquad (6\text{-}6) \\ &= (33.225 - 2.76)\ (437.2) = 13{,}320 \text{ BTU/hr} \end{aligned}$$

(3) Q_3, Heat Lost Through Reactor Walls.

$$\begin{aligned} Q_3 &= UA\Delta T \\ &= 2(25.75)\ (105 - 70) = 1800 \text{ BTU/hr} \end{aligned}$$

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*In the following computations, the subscripts f, v and ℓ denote feed, vapor-phase effluent, and liquid-phase effluent, respectively; $\dot{m}$ denotes mass flow; and h is the specific enthalpy.

where U is 2 BTU/hr · ft^2 · °F*

A is area of insulation shell

ΔT is temperature difference between insulation shell and ambient

(4) Q4, Sensible Heat of Incoming Wastewater.

Assuming a heat-exchanger efficiency of 75%, T_f = 362°F; and

$$Q_4 = \dot{m}_f h_f \qquad (6\text{-}8)$$
$$= 33.225\ (-13.61) = 13{,}740\ \text{BTU/hr}$$

(5) Q5, Sensible Heat of Incoming Air.

$$Q_5 = 0 \qquad (6\text{-}9)$$

(6) Q6, Heat Generated In Stirring Reactants.

$$Q_6 = 4(0.2\ \text{hp/agitator})\ (2547\ \text{BTU/hp} \cdot \text{hr}) \qquad (6\text{-}10)$$
$$= 2040\ \text{BTU/hr}$$

(7) Q7, Heat Generated From Combustion

$$Q_7 = 0.218\ \text{lb/hr}\ (6000\ \text{BTU/lb}) \qquad (6\text{-}11)$$
$$= 1310\ \text{BTU/hr}$$

(8) Q8, Energy Required To Sustain Reaction.

$$Q_8 = (Q_1 + Q_2 + Q_3) - (Q_4 + Q_5 + Q_6 + Q_7) \qquad (6\text{-}12)$$
$$= 1355\ \text{BTU/hr or,}$$
$$0.4\ \text{kilowatt}$$

The estimated energy to sustain the reaction, Q_8, is probably too low based on the performance of the 4-compartment pilot-plant reactor. Heat is lost around the agitators and into the structural support. These heat losses are not included in the analysis presented above, but are allowed for in the estimate of required energy presented in Section 6.4.3.

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*R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, Chemical Engineers' Handbook, 4th Edition, McGraw-Hill Book Co., N.Y., N.Y., 1963.

6.4.3 ELECTRICAL (ENERGY) REQUIREMENTS

Maximum (dockside) requirements for electrical energy are presented in Table 6-3. At sea with the engines running, the heating fluid (Therminol 66) is designed to circulate through coiled tubing immersed in the exhaust stack. Waste heat from the exhaust gases probably will supply 80 to 90 percent of the energy needed to sustain the reactor at 450°F. Consequently, under way, the average electrical energy consumption will be about 3 kilowatts.

TABLE 6-3

MAXIMUM ELECTRICAL ENERGY REQUIREMENTS
20-MAN PURETEC MARINE WASTE TREATMENT SYSTEM

Item	Energy Consumption, Watts Average	Peak	Pct. of Total
Macerator/pumps	150	500	3
High-pressure feed pump	100	100	2
Agitators, WETOX reactor	750	990	14
Filter/feed pump	100	100	2
Heater--Therminol 66	2500	5000	48
Pump, therminol 66	750	750	14
Air compressor, 30% duty cycle	670	2240	13
Control console 1	200	200	4
	5220	9880	100

6.5 SYSTEM CONTROLS

In the shipboard wet-oxidation system, the parameters that must be monitored and controlled include the following five:

- Pressure
- Temperature
- Influent Feed Rate
- Air Flow
- System Volume

6.5.1 PRESSURE CONTROL

The total pressure of the reactor is maintained at a constant 600 psig by controlling the rate of vapor-phase discharge. That is to say, the combined pressure of water vapor, carbon dioxide, nitrogen and unused oxygen gases is never allowed to exceed 600 psig.

The pressure control system is shown schematically in Figure 6-6.

The Bauer compressor delivers air at 2800 to 3000 psig and is activated by a mercury switch G_1. The pressure gauge G_1 contains high-limit/low-limit contacts which regulate the operation of the compressor so that the pressure in the accumulator is maintained between 750 and 2700 psig. If required by shipboard electrical-load limitations, the compressor motor may be interlocked with the electric heaters (used to heat the Therminol 66) so as to inhibit their operation when the compressor is on. (The compressor will run 20 to 30 percent of the time.) Valve V_1 is a ball-type check valve to prevent back leakage through the compressor when it is not in operation.

The accumulator is a vertically mounted, cylindrical pressure vessel (bomb) and discharges its air from its lowest point so that any oil or moisture not removed by the compressor oil-and-water trap does not accumulate in the cylinder.

High-pressure air from the accumulator is reduced in pressure to 630 to 700 psig by regulator R_1. Compressed air at this point is conducted to the blow-case pump, which is air-operated, and to a manifold from which air is supplied to the reactor for wet oxidation. Flow control to the manifold is determined by the opening in orifice O_2 set for the normal air requirement.

In the event that excess water accumulates in the system, valve V_2 is opened and an additional 20 to 25 percent air enters the reactor, thus increasing the mass flow of steam from the reactor and balancing the system. (See Section 2.5.1a.)

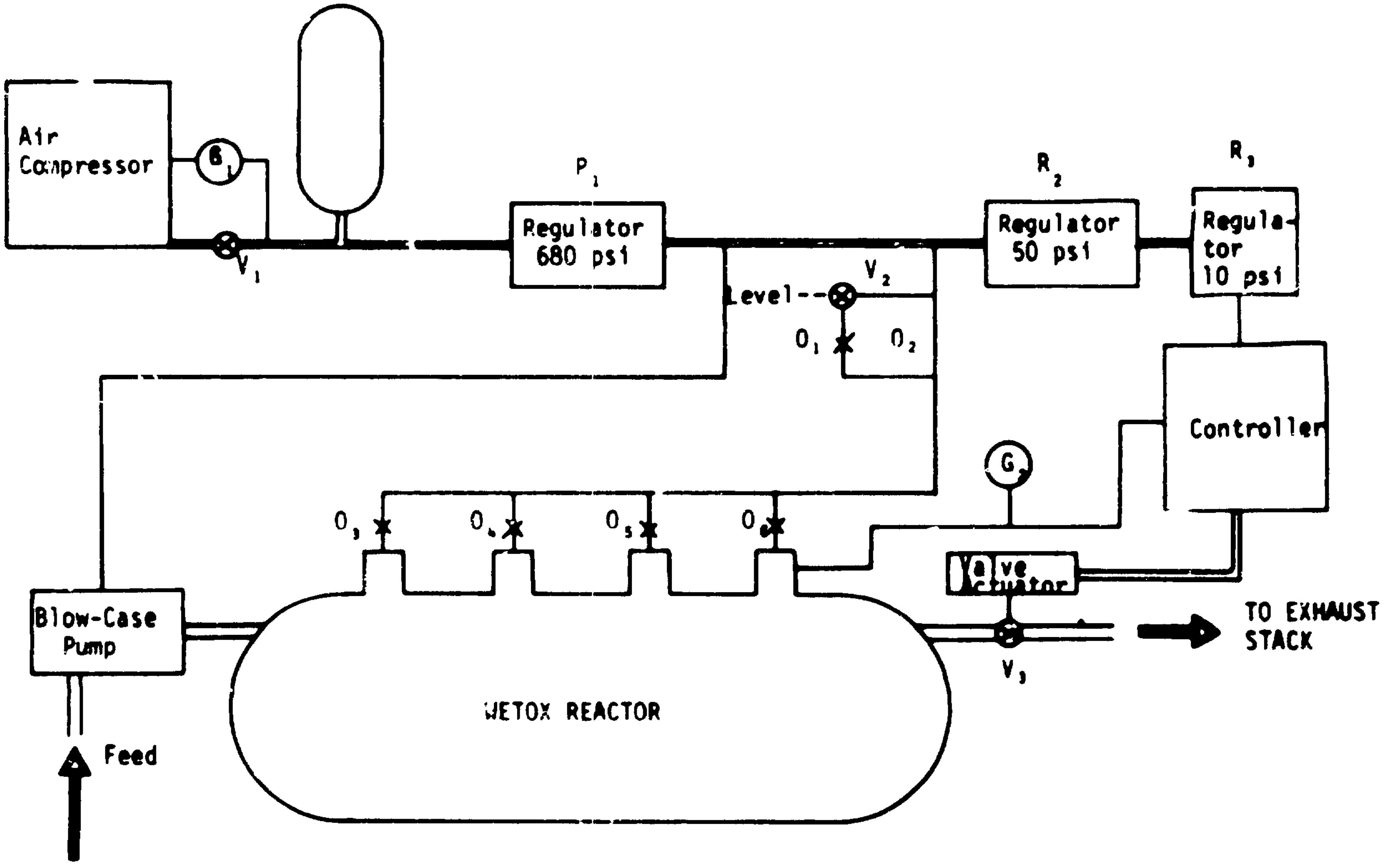

FIGURE 6-6. SCHEMATIC PRESSURE CONTROL SYSTEM.

Air distribution to the reactor is controlled by a series of orifices, O_1 through O_6, whose openings are proportional to the oxygen requirements of the process.

Pressure within the reactor is sensed at the fourth-agitator drive unit and fed back to the pneumatic controller. Gauge G_2 located in this line provides a visual reading of the pressure and, in addition, will activate a high-level alarm (bell) set at 620 to 625 psi.

The pressure controller operates on low-pressure instrument air obtained via regulator R_2; and regulator R_3 positions the valve activator operating valve V_3 which controls the exiting mass flow of vapor phase from the reactor.

The system is arranged so that in the event of loss of power, valve V_3 opens automatically reducing the pressure of the reactor atmospheric.

6.5.2 TEMPERATURE CONTROL

The desired operating temperature of the WETOX reactor is 450 to 465°F. (See Section 3.5.7.)

The temperature control/heating system is shown schematically in Figure 6-7.

In order to begin heating, the pump P_1 must be on to pressurize the heating system and line-pressure sensor. Thermocouple TC 3 sensing the temperature is below the set point (desired temperature) will signal the valve actuator to open valve V_1 thus bypassing the engine exhaust over the heating coils--providing limit control (2) and the recording controller are below their set points. (If either are above the set-point value, the valve actuator is disabled and V_1 is closed or remains closed.)

In the event sufficient heat is not available from the engine exhaust, thermocouple TC 2 will signal the limit control (2) to energize the heaters--providing the temperature is below the set point of the controlling recorder which monitors the reactor temperature TC 1.

The therminol-66 heater is equipped with a demand-type SCR controller to proportion the energy input depending on the difference (ΔT) between the actual and desired temperature.

In the event of pump failure or thermocouple failure, the system automatically is disabled.

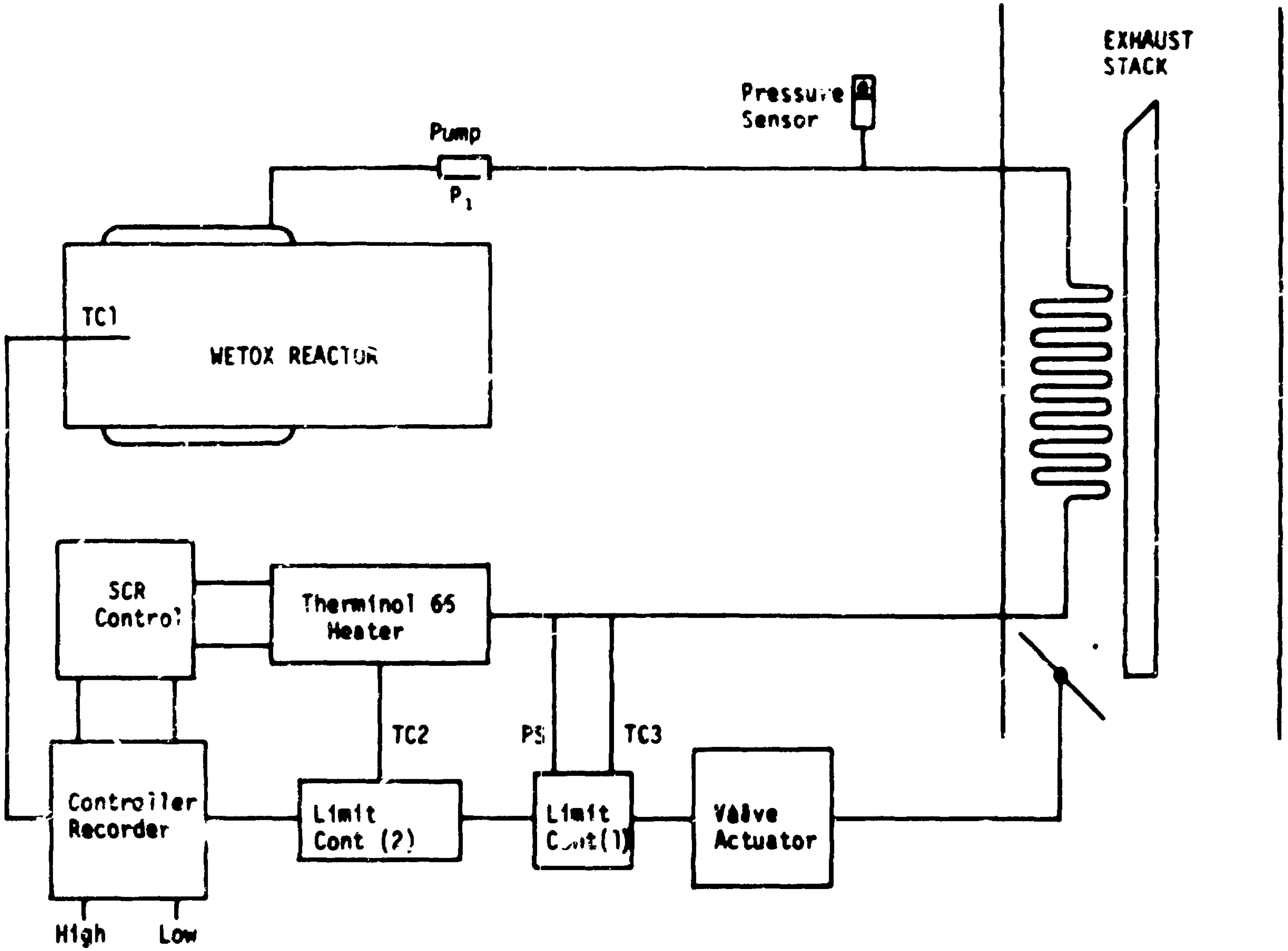

FIGURE 6-7. SCHEMATIC TEMPERATURE CONTROL SYSTEM.

6.5.3 INFLUENT FEED RATE

The flow of influent to the reactor is fixed at the design rate for the normal ship complement. In the event the size of the crew is less, for example, when the ship is in port, the system continues to operate at the design rate. No significant energy savings would be effected by operating at a reduced rate of feed.

As mentioned in Section 6.3.5, the blow-case pump will use only one cylinder with the other held in reserve. The control circuit for the high-pressure pumping system is shown schematically in Figure 6-8. The operation of the blow-case pump was described in Section 3.1.1c; mechanical aspects are discussed in Section 6.3.5.

6.5.4 AIR-FLOW AND SYSTEM VOLUME

As discussed in Section 6.4.2a, in the 20-man shipboard system, air flow is set primarily to achieve water balance. The requisite air flow for water balance computes to be about twice that required for wet oxidation, i.e., the system is designed to operate at a O_2/COD ratio of 2:1. As mentioned earlier, the quantity of air is so small that exact control is unwarranted.

a. Air-Flow Controls.

As shown in Figure 6-6, the air-supply line to the reactor has a bypass orifice (O_1) that can be opened to increase the air-flow rate. The quantity of steam vented from the reactor is directly proportional to the air flow. (See Sections 2.5 and 6.4.2a for further discussion.) Thus by controlling the air flow, the system fluid volume is adjusted to compensate for the increased water (urine) load.

b. Volume Controls.

The volume of the system is controlled by monitoring the combined level of the influent and effluent storage tanks. By means of a pressure-sensitive level sensor, the output signal will be added and compared to a standard. If the combined levels are above the control point, the bypass solenoid is activated; and an orifice is opened for an increased air flow.

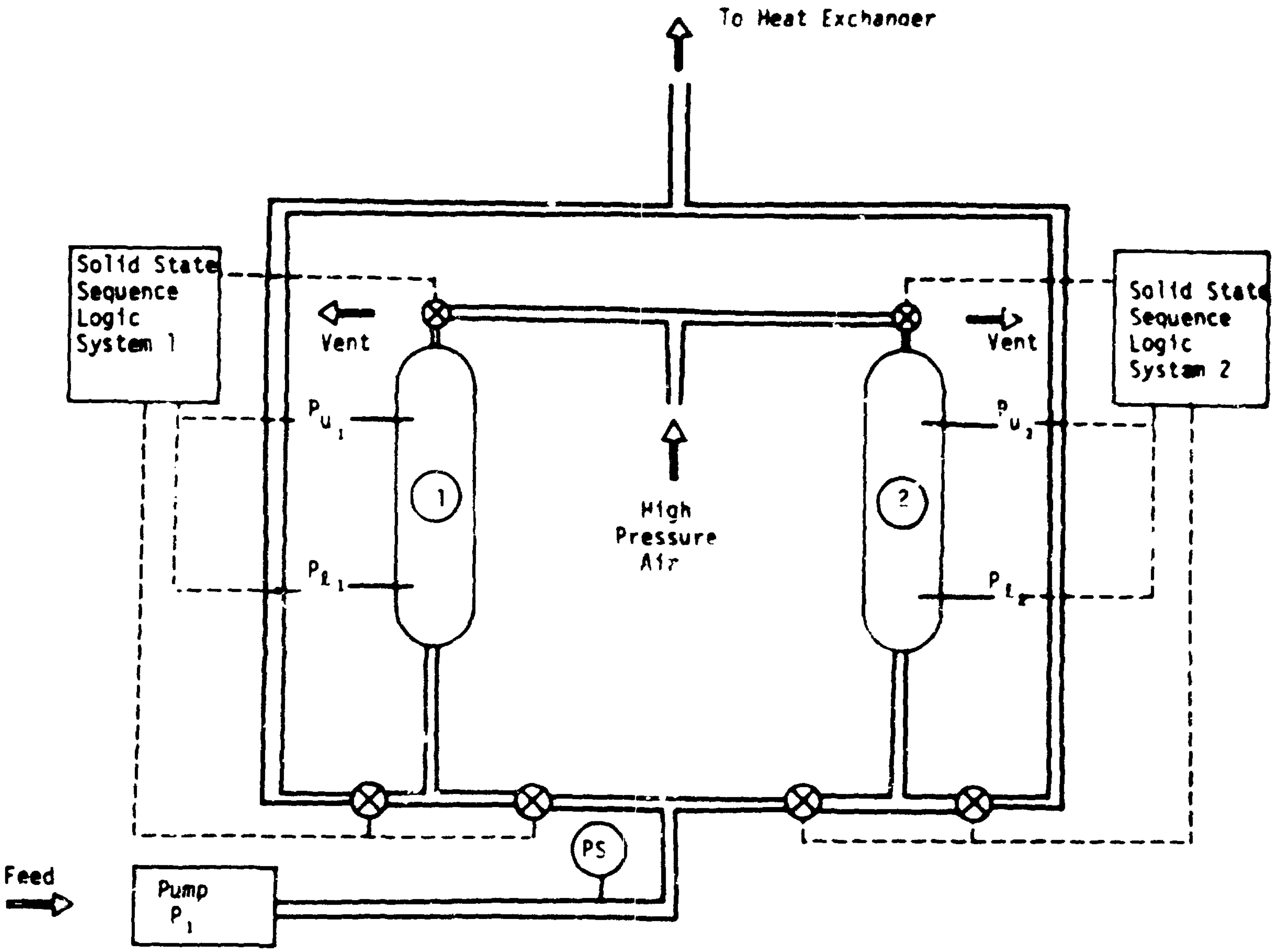

FIGURE 6-8. SCHEMATIC BLOW-CASE PUMP CIRCUIT.

6.6 EQUIPMENT SPECIFICATIONS--PURFTE^ Marine Waste Treatment System--Model 410 M.

6.6.1 RECIRCULATING TOILET

Model	JET-O-MATIC 160M-PA (Model 602) (Modified)
Weight (empty)	38 lbs.
Dimensions	18" high x 19 1/4" wide x 25" deep
Usable Capacity	14 gallons U.S. (Approx. 160 uses)
Holding Tank and Cover	Modified PVC
Toilet Bowl	Polished Stainless Steel
Toilet Seal	Plastic - Open Front
Filter Pump Assembly	Noryl Plastic, Neoprene rubber and Stainless Steel.
Flush Actuator Assembly	Anodized aluminum (push button actuated) valve with brass pressure reducer/regulator.
Disposal Outlets	Botton drain valve (fits 3" Standard toilet floor flange)
Bowl Seal	Neoprene Rubber Bowl Seal Above Water Line-Operation Controlled by Toilet Seat Lid.
Pressurized Air Usage	1/3 cu. ft. at 10 psi/10-second flush
Fire Rating	Underwriters Laboratory
(Plastics)	Yellow Label

6.6.2 MACERATOR/PUMP

Model	Oberdorfer, 214M USF
Flow Rate	12 gallons/min
Motor	1/3 H.P. 3450 RPM 115 V 60 HZ Single Phase TEFC.

Materials	Bronze w/Stainless Steel Cutters/Neoprene Seals
Weight	14 lbs.

6.6.3 FEED HOLDING TANK

Size	14 in. Dia. x 25 in. high
Type	Totally Closed
Volume	16 Gallons
Outlets	1 - 1 1/2 in. Flange-Vent 2 - 3/8 in. Flanged Outlets 1 - 1/2 in. Flanged Outlets
Instrumentation	Level Sensor
Material	Titanium CR Grade 2 ASTM B-265 0.063 in. Thick Neoprene Gaskets
Power Required	None

6.6.4 HIGH PRESSURE FEED PUMP

Model	Barber-Colman Co.
Capacity	1 Liter/Cycle
Flow Rate	60 Liters/hr. Max
Pressure	1800 psi Dot Rating 3A1800
Materials	All Wetted Parts Type 316 Stainless Steel
Control	Solid State Logic Control Circuit
Booster Pump Model	Moyno Model BM 10 SSQ
Motor	1/10 H.P. 1725 RPM 110 V. 60 HZ Single Phase TEFC
Materials	All Wetted Parts Type 316 Stainless Steel

6.6.5 WETOX REACTOR AND HEAT EXCHANGER

Type	Barber Colman Co. WETOX Reactor Model 410-M - 4 Compartment Horizontal Agitated, ASME Code Section VIII, All Titanium, C.P. ASTM B265
Operating Pressure	600 psig
Operating Temperature	475°F Max
Agitator Drive	Totally Enclosed Pressurized Motor, 1/3 H.P. 1150 RPM 208-220 Volts 3 Phase Water Cooled
Agitator	Direct Drive-Titanium Shaft, 3 in. Diameter, Cast Titanium B-C Part No. RRS-7207-4003-3
Heat Exchanger	Tube-in-Tube Type For Vapor and Liquid Phase All Wetted Parts C.P. Titanium Grade 2.
Interconnection	All Joints Flanged w/Flexotalic Gaskets Ti/Blue Asbestos
Heater Jacket	Heating Jacket Surrounding # 1 & 2 Compartment - All C.P. Titanium Grade 2 With Flanged Connections To Therminol 66 Heating System.
Insulation	Fiberfrax
Exterior Shell	Type - 316 Stainless Steel 10 and 12 gal.

6.6.6 VAPOR-PHASE LET-DOWN SYSTEM

Type	Masoneilan, Micropak 29000 Series
Body	Type 316 Stainless Steel with Stellite #6 Plug, 316 Stainless Steel Stem and 17-4 PH Stainless Seat.
Operation	Pneumatic With Series 2700 Controller - Fail Safe,ie,Opens on Loss of Instrument Air

6.6.7 LIQUID PHASE LET-DOWN SYSTEM

Type	Whitey "NB" Series Severe Service Part No. SS-6NBF6 Modified w/-7NC Normally Closed Pneumatic Actuator
Control	Pneumatic Control Using 50-60 psig Instrument Air. Actuation Controlled by Solid State Level Controller From Probe Signal Within Phase Separation Section of Reactor

6.6.8 FILTER

Type	Upright--Nautilus Diatomaceous Earth Model 24-NS
Materials	Body Stainless Steel With Filter Element Support of Polycarbonate--Dacron Filter Cloth
Cleaning	Automatic Back Wash to Drain (Back Washes from Top to Botton to Insure Complete Cleaning)
Capacity	48 Gallons/Minute, Maximum Flow
Media Replacement	Quick-Opening Clamp Assembly
Solids Volume	Sufficient to Hold Solids From 20 Man Crew For 60 Days

6.6.9 FILTER FEED PUMP/REFILL SUPPLY PUMP

Type	Moyno Model BM 10-SSQ
Motor	1/10 H.P. 1725 RPM 110V 60 HZ Single Phase TEFC
Materials	All Wetted Parts, Type 316 Stainless Steel

6.6.10 EFFLUENT HOLDING TANK

Size	19 1/4 in. Dia. x 26 in. High
Type	Totally Closed
Volume	16 Gallons

Outlets	1 - 1 1/2 in. Flange (Vent) 1 - 3/8 in. Flange 1 - 1/2 in. Flange
Instrumentation	Level Sensor

6.6.11 HEATER-THERMINOL 66

Type	Barber-Colman Model RRS 4 Pass Tube Type
Heaters	Chromalox Type C 3/4" Dia. x 24" Long 1250 Watts @ 240 Volts 23 Watts/in^2 #C516
Insulation	Fiberfrax
Construction	All Welded w/Flanged Connection For All Therminol Lines
Control	Iron-Constantan Thermocouple 520-Series Barber-Colman Co. Controller Barber-Colman Co. CA31 Power Controller

6.6.12 PUMP, THERMINOL 66

Type	Centrifugal, Seal-Less
Model	Chempump Model GAT
Pumping Rate	20 Gallons/Min @ 40 Foot Head
Max Fluid Temp.	1000°F
Materials	Steel/316 Stainless Steel
Motor	1 H.P. 220/440 Volts 3 Phase 60 HZ 3450 RPM - Continuous Duty Class H Insulation Totally Enclosed.
Weight	80 Pounds

6.6.13 ACCUMULATOR-THERMINOL 66 EXPANSION TANK

Type	Spring Loaded, Bellow Type Accumulator
Size	4 in. Dia. x 12 in. High Effective Expansion Volume 100 in^3
Controls	High Level and Low Level Alarm System Pressure Relief Valve and Catch Pot
Weight	12 Pounds

6.6.14 HEAT TRANSFER FLUID THERMINOL 66

Type	Therminol 66 As Manufactured by Monsanto Chemical
Use Range	0 to 605°F
Toxicity	Non-Toxic, Non-Irritating With No Special Handling Problems
Flammability	Flash Point 355°F Fire Point 382°F
System Volume	@ 70°F 1 Gallon = 8.5 lbs.

6.6.15 STRUCTUAL SUPPORT

Type	Aluminum Structural Shapes As Required - 6061T6 Alloy Welded
Corrosion Protection	Chemical Conversion Coating w/2 Coats of Epoxy Paint
Dimensions	4 ft., 6 in. Long x 4 ft. Wide
Weight	75 Pounds

6.6.16 COMPRESSOR, HIGH-PRESSURE AIR

Type	3 Stage, High Pressure
Model	Bauer P3-32
Duty	100% Continuous

Outlet Pressure	3200 psig
Actual Free Air Delivered	3.4 SCFM
Speed	1100 RPM
Connecting Rod Bearing	Needle
Wrist Pin Bearing	Needle
Crankshaft Bearings	Ball and Roller
Valves	Disc Type
Coolers	Air Cooled Interstage and After Cooler
Separators	Water and Oil Separator Between 2nd and 3rd Stage And After 3rd Stage
Safety Valves	Between Each Stage
Motor	3 H.P. 220/440V 3 Phase 60 HZ TEFC 1725 RPM 150 Pounds

6.6.17 AIR ACCUMULATOR AND REGULATOR

Type Accumulator	Aluminum Alloy, Scuba Tank As Manufactured by U.S. Divers Professional Model
Working Pressure	3000 psi
Certification	DOT-SP6498-3000
Regulator Type	High Pressure, Ballast and Grove, Mighty Mite With Over Pressure Relief w/Grove Loader.
Max Working Pressure	6000 psi
Material	Type 303 Stainless Steel

6.6.18 CONTROLS AND INSTRUMENTATION

Pneumatic Controller	Masoneilan Controller Model 2700 Proportional
Level Sensor	Pressure Tranducer Type

Master Controller	Recording-Controller Barber-Colman Company Model 533
Therminol 66	Limitrol, Barber-Colman
Limit Controls	Model 531L
Heater Control	Barber-Colman Company CA31 Phase Angle Fired Power Controller
High Pressure	Barber-Colman Company Socio State
Pump Control	Blow Case Pump Logic Control System
Pressure Gauges	Ashcroft Front Mounted Back Connected with High Level Alarm Model 1377 TAX SGEE

6.7 DRAWINGS

Figures 6-9, 6-10, and 6-11 are views of the PURETEC Marine Waste Treatment System from the end, side and top, respectively.

6.8 SCALE-UP OF THE SYSTEM AND SCALING FACTORS

The prototype system requires no scaling. It is sufficient to treat the sanitary waste of about 40 persons using the type of toilet described in Section 6.2.2a (See page 6-8). Normal engineering problems will arise, however, in integrating the system into specific existing vessels. For example, under U.S. Navy Contract Nos. N00406-74-C-0961 and N00167-75-M-8130, RRS constructed two of the PURETEC® Marine Sewage Treatment Systems illustrated in Figure 6-3 on pages 6-15 and 6-16. One of the two systems is undergoing evaluation at the Naval Ship Research and Development Center, Annapolis, Maryland. The second unit will be installed aboard the Planview at the U.S. Naval Shipyard, Bremerton, Washington. Originally the first unit was to have been installed aboard the High Point (PCH-1) after completion of shore tests at Annapolis. To accomodate the system aboard the High Point, however, required subdivision into four groups, each to be located in a different part of the hull: the influent-effluent tank was accommodated in a separate area. The pumps were mounted on a common skid. The reactor and other apparatus were mounted as a unit; and the control console was housed by itself.

Further scale up to 80 persons is possible without changes to the basic reactor heat exchanger or control systems. To serve 80, the influent/effluent tank size would have to be increased as would the number of toilets in the system. The remaining changes would be primarily adjustments in the flow rates and control levels.

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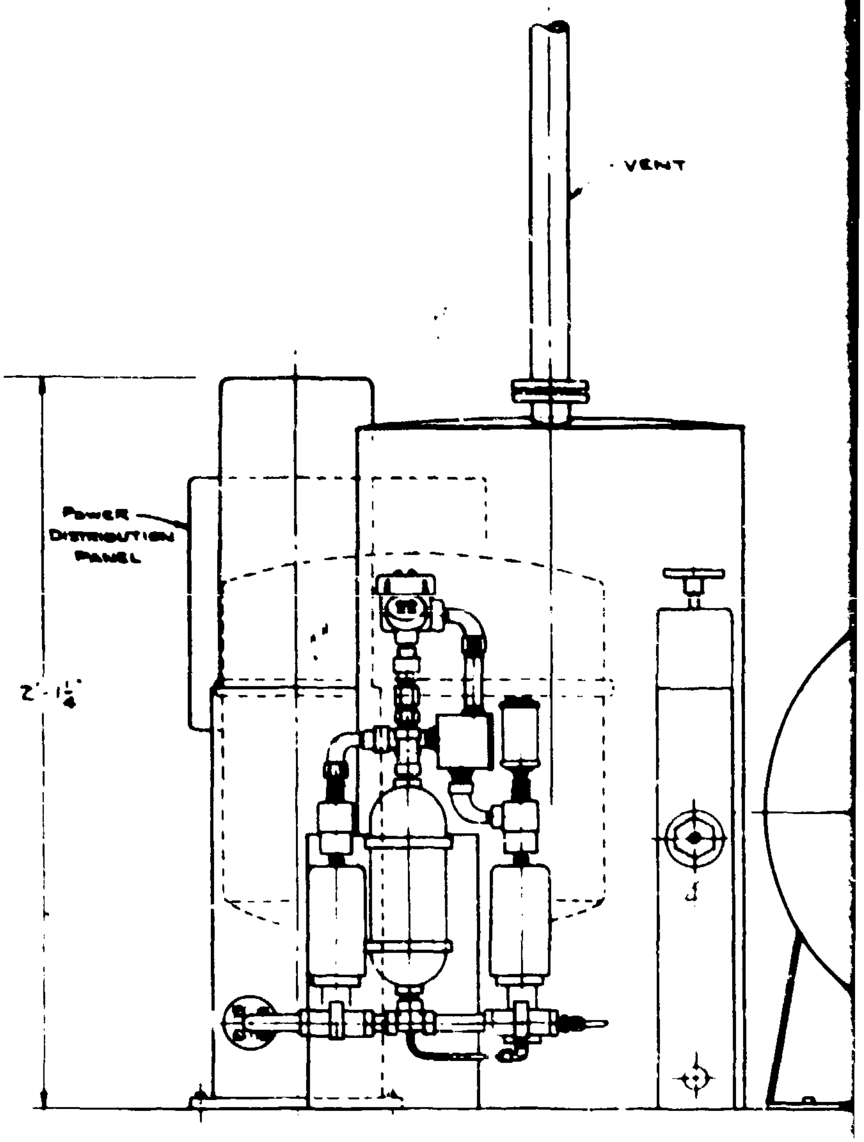
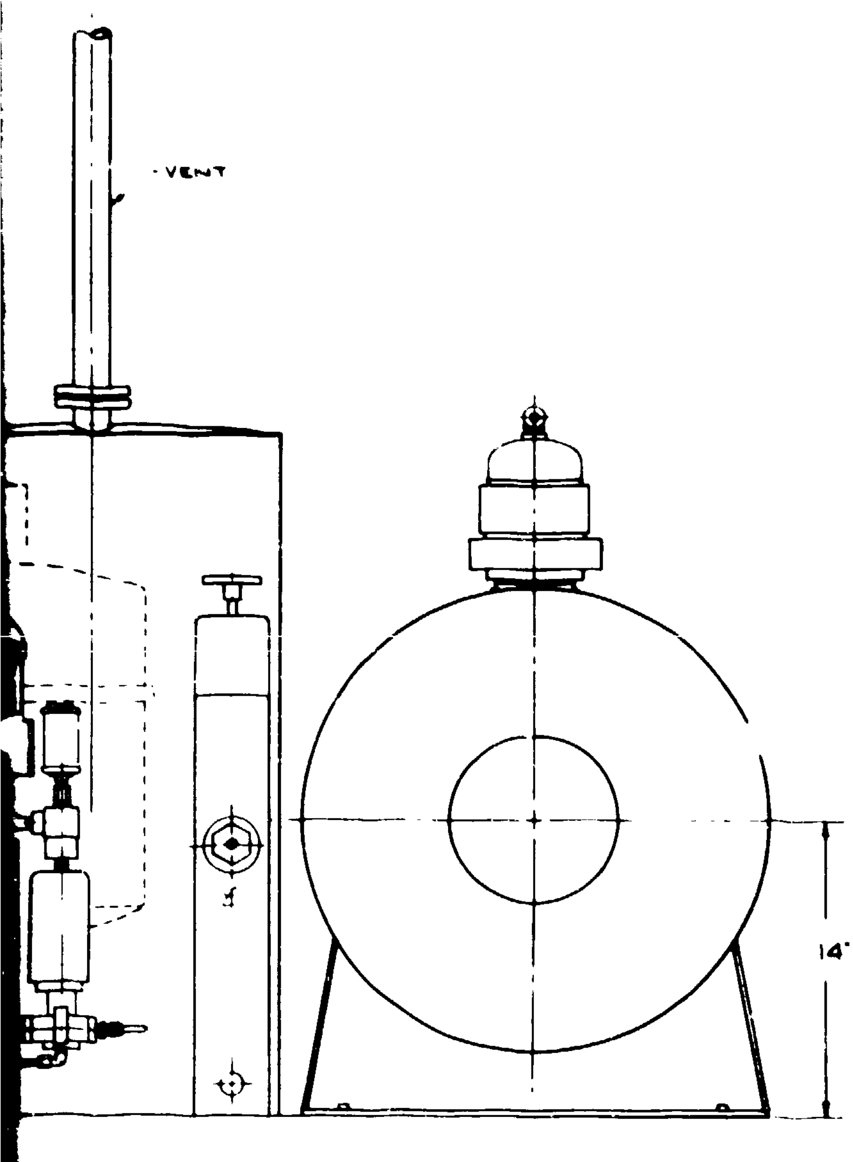


END VIEW

NOTES: UNLESS OTHERWISE SPECIFIED

DO NOT SCALE DWG.



VIEW

	1-412-M
NEXT ASSY	USED ON
APPLICATION	

ITEM	QTY. REQD.	CODE IDENT	PART NO.	NOMENCLATURE OR DESCRIPTION

PARTS LIST

CONTRACT NO.

BARBER-COLMAN COMPANY
RESOURCE RECOVERY SYSTEMS
[illegible], CALIFORNIA

PURETEC MARINE WASTE
TREATMENT SYSTEM
MODEL 412 M

D

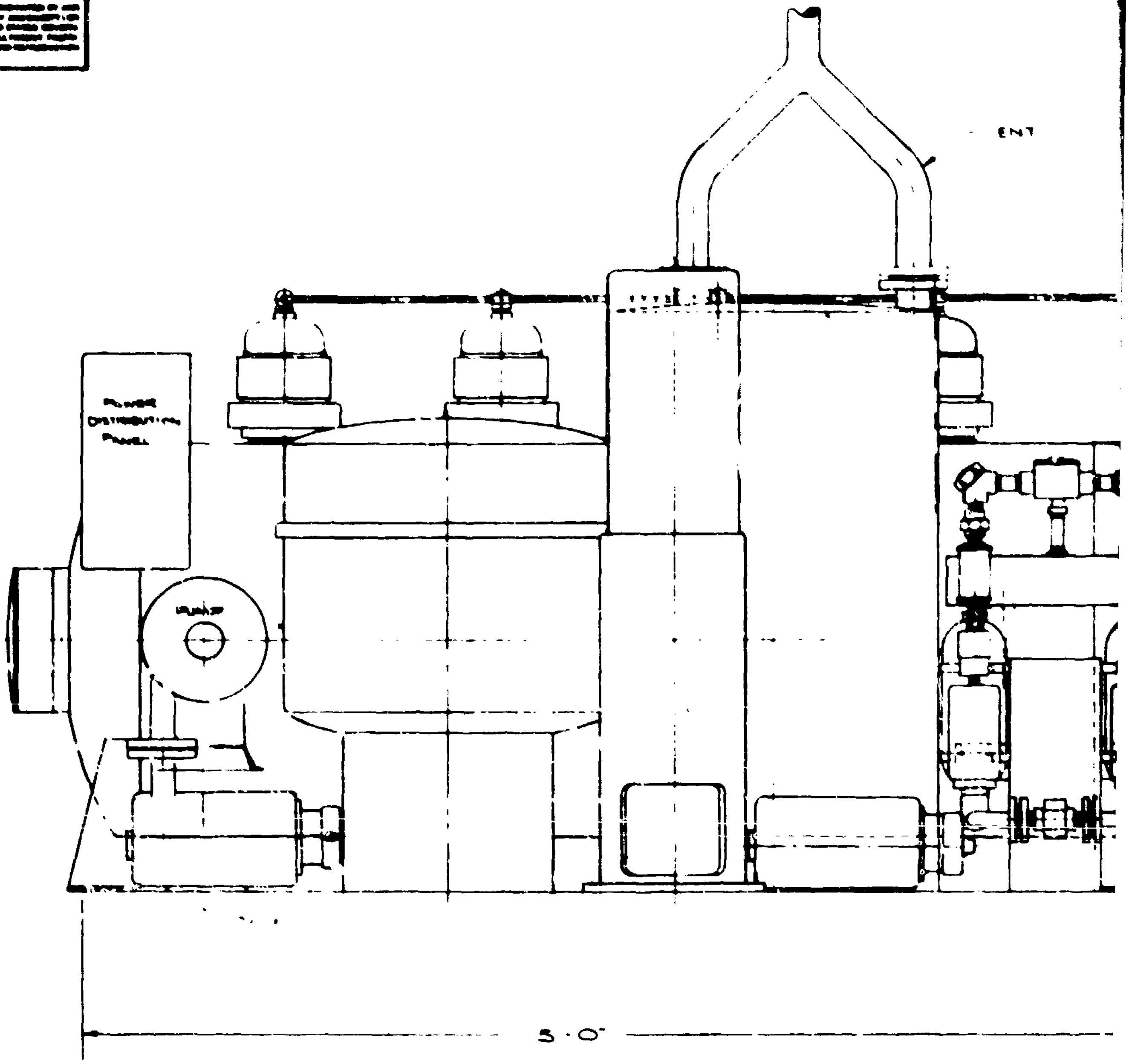
RRS-2-412-3

SCALE 1/4

SHEET 3 OF 3

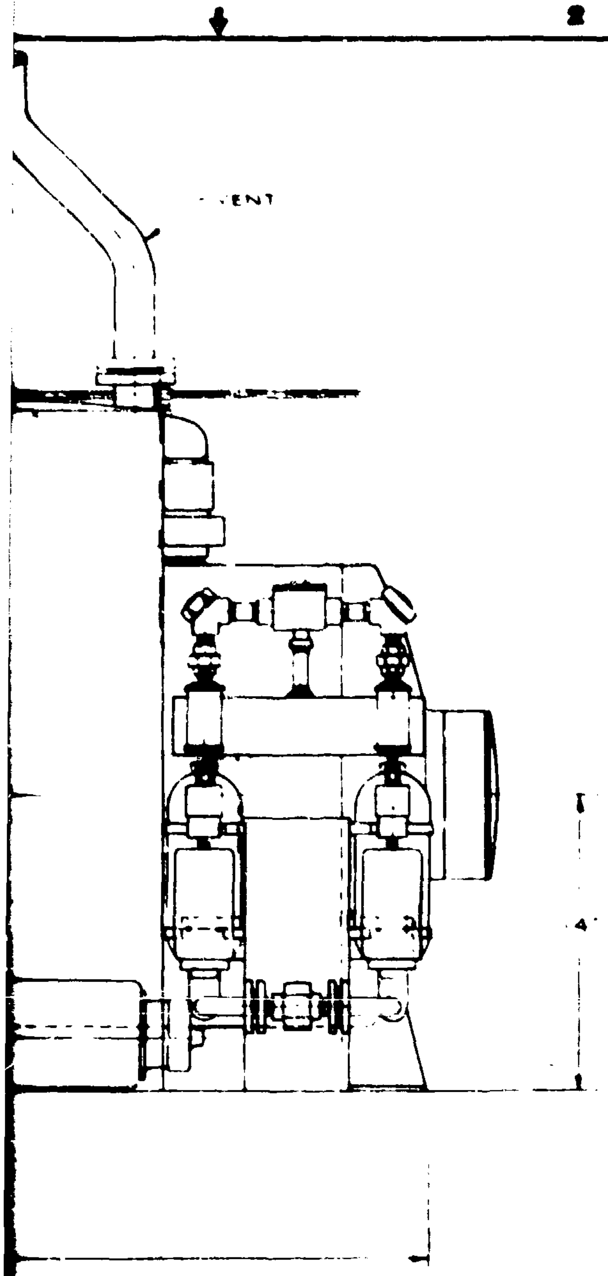
FIGURE 6-9. END VIEW

[illegible]



FRONT VIEW

NOTICE: UNLESS OTHERWISE SPECIFIED
DO NOT SCALE DWG.



	1-412-M
NEXT ASSY	USED ON
APPLICATION	

PARTS LIST

BARBER-COLMAN COMPANY

PURETEC MARINE WASTE
TREATMENT SYSTEM
MODEL 412 M

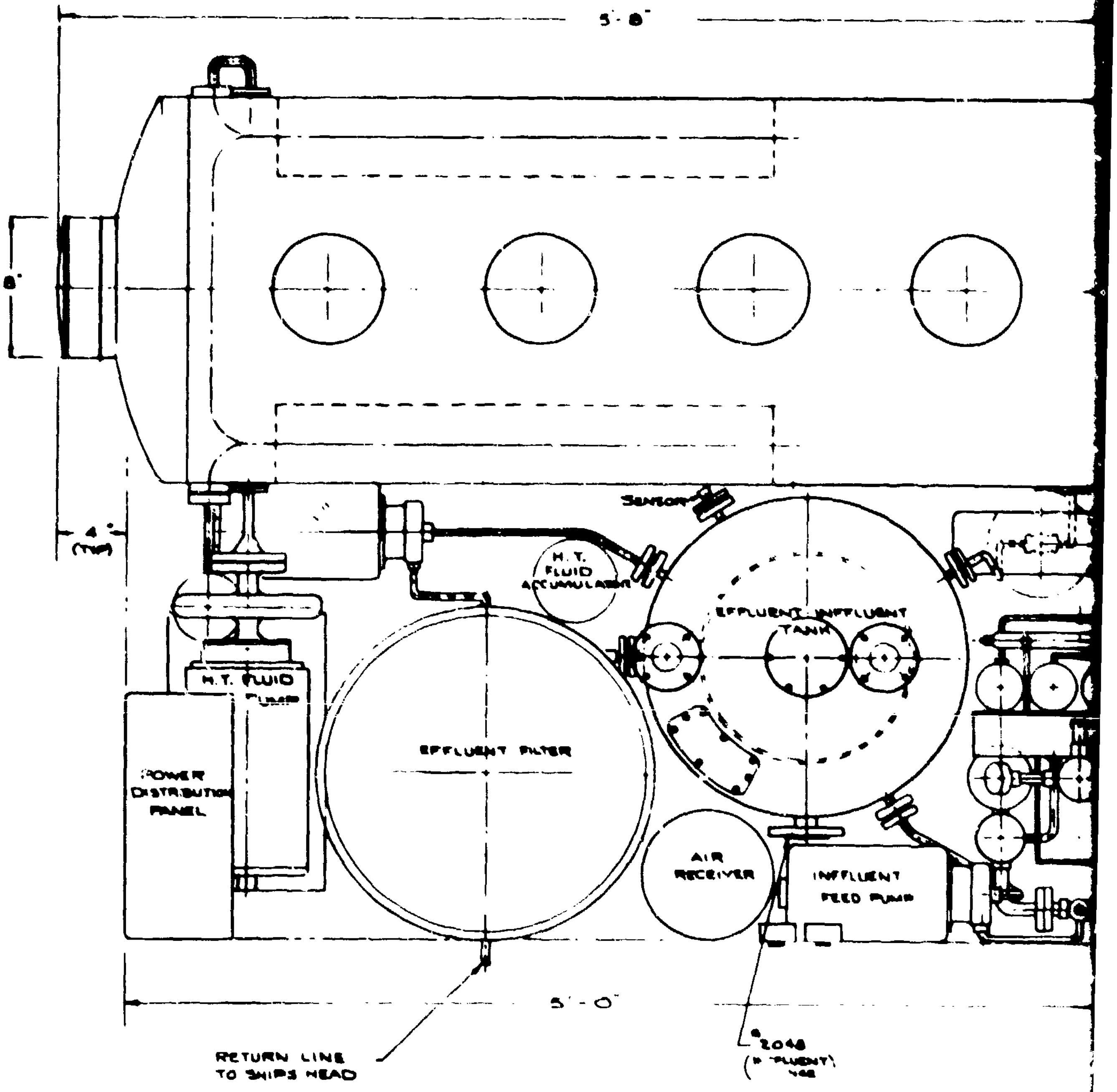
D

RRS-2-412-3

SCALE 1/4

SHEET 2 of 3

FIGURE 6-10. SIDE VIEW


5'-8"
8"
4"
(TYP)
SENSOR
H.T. FLUID ACCUMULATOR
EFFLUENT INFLUENT TANK
H.T. FLUID PUMP
POWER DISTRIBUTION PANEL
EFFLUENT FILTER
AIR RECEIVER
INFLUENT FEED PUMP
5'-0"
RETURN LINE TO SHIPS HEAD
2048
(INFLUENT)

PLAN VIEW

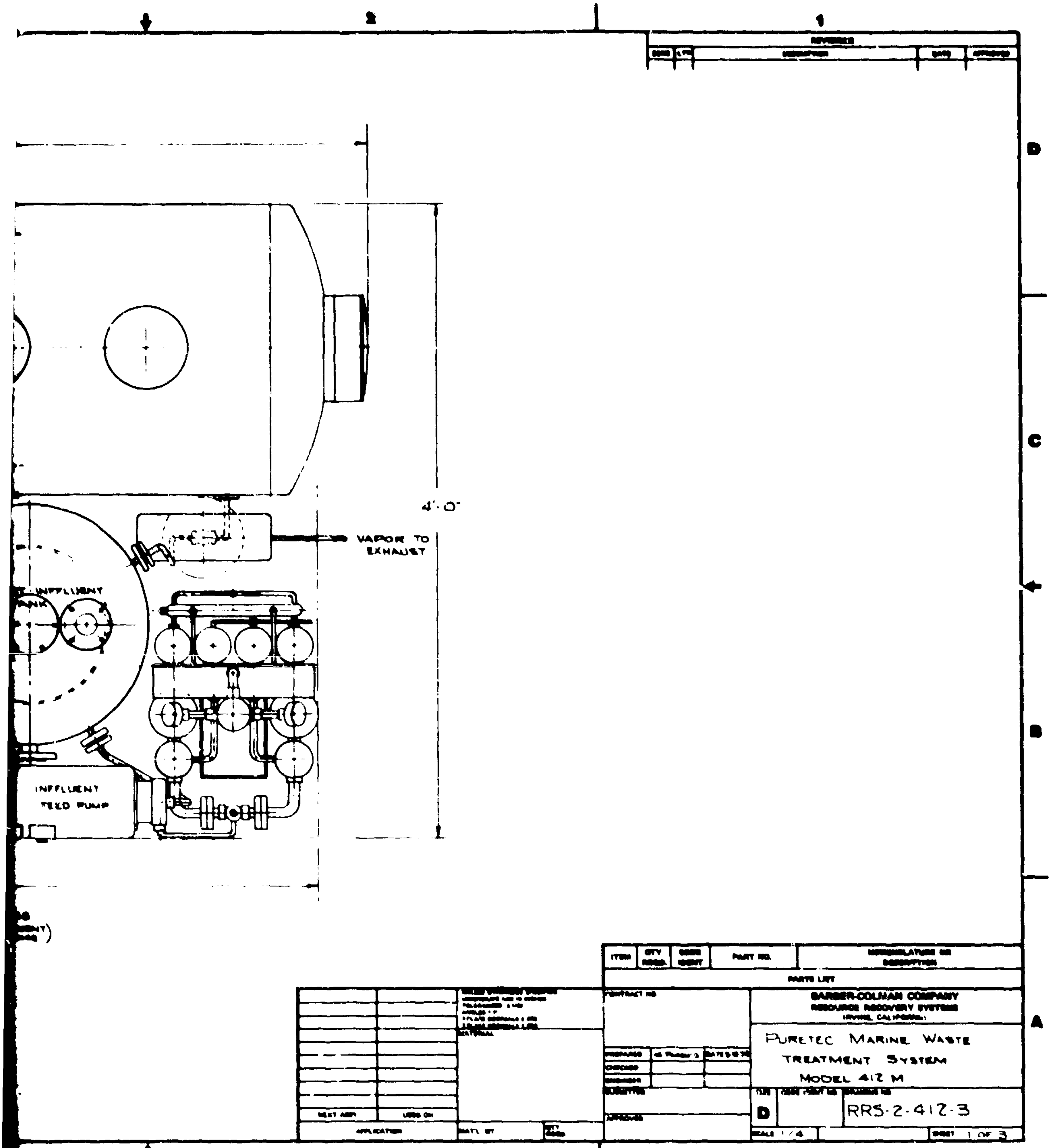


FIGURE 6-11. TOP VIEW

APPENDIX A

ESTIMATION OF THE TIME
TO REACH A STEADY STATE

In the main report, all indices of process efficacy--percentage reduction in COD, rate constants, concentrations--are steady-state values. The formulas derived in this appendix were used as a guide in estimating the time to reach a steady state.

APPENDIX A

ESTIMATION OF THE TIME TO REACH A STEADY STATE

Elementary discussion of chemical reactor theory generally is restricted to the characteristics exhibited at steady state: Behavior is described only for continuous-flow systems in which the chemical reactions have proceeded under fixed conditions of flow, feed, temperature, etc., for a sufficiently long time that the concentrations in the various sections of the reactor have become invariant. In most textbooks, expressions are derived relating steady-state concentration with the rate of chemical reaction and flow for various types of reactors. The discussion of transients effects is limited to the treatment of nonideal flow and dispersion models, in which measurements made in the transient regime are used to estimate the degree of nonideality (inefficiency). The emphasis placed on steady-state behavior is, of course, understandable. In practice, most chemical reactions are conducted continuously under fixed operating conditions, and the transient periods associated with start-up and shut-down are relatively brief and unimportant. In our research program, however, there were special circumstances that warranted an analysis of the transient state; an estimate was needed of the time required to reach a steady state.

Generally, in our program, the reactor was flushed with water at the end of each day's test, and the following morning preheated to the operating temperature before the flow of influent was commenced. Influent was then pumped into the reactor at a fixed rate and the system allowed to come to a steady state after which hourly sampling was initiated to establish process efficacy for the particular set of conditions. The success of such a modus operandi requires some knowledge of the time required to establish a steady state.

The time required to achieve steady state can be calculated for an ideal system; i.e., one in which mixing is ideal and there is no short circuiting or leakage between compartments. In following paragraphs, a derivation is presented for the transient-state operation of a preheated, initially water-filled, continuous stirred tank reactor (CSTR).

The following symbols will be used in the derivation:

Q = quantity of organic matter in a compartment expressed as COD

n = subscript designating the posititon of a compartment with respect to the inlet end (n = 0 denotes the feed)

t = time after start-up; i.e., elapsed time after commencement of pumping influent to preheated reactor

v = flow rate of influent (and of effluent)

V = capacity (volume) of compartment for liquid

C = Q/V concentration of organic matter expressed as COD

τ = V/v = residence time of liquid in a compartment

k = reaction rate constant for the COD-reduction process

i = subscript denoting parameter(s) associated with initial (fast) reduction in COD

ℓ = subscript denoting parameter(s) associated with late-stage (slow) reduction in COD

Since mass balance dictates that the CHANGE IN MASS equals INPUT minus DESTRUCTION minus OUTPUT, the following network of equations define mass balance within a n-compartment CSTR:

$$dQ_1/dt = C_0 v - (Q_1/V_1)k_1V_1 - (Q_1/V_1)v \tag{A-1a}$$

$$dQ_2/dt = (Q_1/V_1)v - (Q_2/V_2)k_2V_2 - (Q_2/V_2)v \tag{A-1b}$$

$$dQ_{n-1}/dt = (Q_{n-2}/V_{n-2})v - (Q_{n-1}/V_{n-1})k_{n-1}V_{n-1} - (Q_{n-1}/V_{n-1})v \tag{A-1c}$$

$$dQ_n/dt = (Q_{n-1}/V_{n-1})v - (Q_n/V_n)k_nV_n - (Q_n/V_n)v \tag{A-1d}$$

Alternatively, by letting $D = d/dt$; $Q_n/V_n = C_n$; and $\tau_n = V_n/v$,

the equations can be rewritten in the so-called operator form:

$$(\tau_1 D + 1 + k_1\tau_1)C_1 = C_0 \tag{A-2a}$$

$$(\tau_2 D + 1 + k_2\tau_2)C_2 = C_1 \tag{A-2b}$$

$$(\tau_3 D + 1 + k_3\tau_3)C_3 = C_2 \tag{A-2c}$$

$$(\tau_n D + 1 + k_n\tau_n)C_n = C_{n-1} \tag{A-2d}$$

The above network of equations is deceptively simple in appearance. Integration is tedious, and the resulting expressions are unwieldy. Much simpler expressions, which are accurate enough for most practical purposes, can be obtained by redefining some of the terms; specifically,

(1) Let the residence time by the same in all compartments; i.e., $\tau = \tau_1 = \tau_2 = \tau_3 = \tau_n$.

(2) Let all of the rate constants except that for the first compartment be equal. Specifically, let

$k_1 = k_i$, the rate constant for the initial reduction in COD; and

$k_2 = k_3 = k_n = k_\ell$, the rate constant for the late-stage reduction in COD.

The first of the above changes in nomenclature is permissible, because WETOX reactors like most CSTR's are divided into compartments of approximately equal volume. The second change is based on the nature of wet oxidation as observed in some 500 batch and continuous-flow tests; the simplification is appropriate in nearly every case.

Incorporating these changes in the differential equations yields the series:

$$[D + (1 + k_i\tau)/\tau]C_1 = C_0/\tau \tag{A-3a}$$

$$[D + (1 + k_\ell\tau)/\tau]C_2 = C_1/\tau \tag{A-3b}$$

$$[D + (1 + k_\ell\tau)/\tau]C_n = C_{n-1}/\tau \tag{A-3c}$$

where $n \geq 2$.

We are now ready to attempt a solution; i.e., estimate the time required to reach a steady state throughout the reactor. For example, suppose that the reactor comprises four compartments. Then, the series of differential equations become

$$(D + a)C_1 = C_1/\tau \tag{A-4a}$$

$$(D = b)C_2 = C_1/\tau \qquad \text{(A-4b)}$$

$$(D + b)C_3 = C_2/\tau \qquad \text{(A-4c)}$$

$$(D + b)C_4 = C_3/\tau \qquad \text{(A-4d)}$$

where $a = (1 + k_1\tau)/\tau$ and $b = (1 + k_\ell\tau)/\tau$.

The corresponding Laplace Transforms* are

$$F = (F_3/\tau)/(s + b) = (F_2/\tau^2)/(s + b)^2 = (F_1/\tau^3)/(s + b)^3 = (C_0/\tau^4)/s(s + a)(s + b)^3 \qquad \text{(A-5a)}$$

$$F_3 = (F_2/\tau)/(s + b) \qquad \text{(A-5b)}$$

$$F_2 = (F_1/\tau)/(s + b) \qquad \text{(A-5c)}$$

$$F_1 = (C_0/\tau)/s(s + a) \qquad \text{(A-5d)}$$

The symmetry in successive transforms is clearly evident; and the general expression defining the Laplace Transform for the nth compartment is

$$F_n = (C_0/\tau^n)/s(s + a)(s + b)^{n-1} \qquad \text{(A-6)}$$

---

*The Laplace Transform has been denoted by the symbol F; that is,

$F = \int_0^\infty f(t)e^{-st}\,dt$, in which

s is a mathematical parameter. By the transformation, the operation of differentiation with respect to 5 becomes multiplication by s. The transformation is facilitated by the boundary conditions:

$t = o;\ C_1 = C_2 = C_3 = C_n = o.$

Inversion of the Laplace Transform F_n yields C_n, the concentration in the nth compartment, which is the last compartment to come to a steady state in a n-compartment reactor*:

$$C_n = \frac{C_o}{(1 + k_i\tau)(1 + k_\ell\tau)^{n-1}} \left\{ 1 + \left[\frac{(1 + k_\ell\tau)}{\tau(k_i - k_\ell)}\right]^{n-1} \exp[-(1 + k_i\tau)t/\tau] - \frac{(1 + k_i\tau)(1 + k_\ell\tau)^{n-2}t^{n-2}}{t^{n-1}(k_i - k_\ell)(n - 2)!} \cdot \exp[-(1 + k_\ell\tau)t/\tau] \right\} \qquad \text{(A-7)}$$

Although it may not be obvious, the first term on the right-hand side of Equation A-7 is $C_{n\infty}$, the steady-state concentration in compartment n. That is to say,

$$C_{n\infty} = C_o/(1 + k_i\tau)(1 + k_\ell\tau)^{n-1} \qquad \text{(A-8)}$$

(Equation A-8 is derived in Appendix G.) As t approaches infinity (in Equation 7), C_n approaches $C_{n\infty}$, the steady-state concentration. For most practical purposes, we may assume to be at steady state when the concentration C_n is some reasonable fraction of the steady-state value--greater than 0.95, for example. In other words, when $C_n/C_{n\infty} \geq 0.95$, we are practically at steady state.

---

*The inversion of a Laplace Transform is facilitated by the use of special tables. A table adequate for our problem is contained in Standard Mathematical Tables, 18th Ed., S.M. Selby (Editor), published by the Chemical Rubber Co., Cleveland, Ohio, 1970. One also needs to be familiar with the algebraic technique of partial fractions. The discussion given by M.G. Salvadori and R.J. Schwarz in their textbook, Differential Equations in Engineering Problems, Prentice-Hall, Inc., Englewood Cliffs, N.J., has been especially prepared for the application of partial fractions to Laplace Transforms.

For instance, suppose that we wish to estimate the time to achieve 95 percent of steady state in a two-compartment autoclave like the Coast Guard reactor for a continuous-flow test in which saline sewage is treated under conditions such that the mean residence time is 20 minutes per compartment. For uncatalyzed wet oxidation of saline sewage, k_l and k_ℓ are typically 0.1 and 0.005 min.$^{-1}$, respectively. Substitution of these values in Equation A-7 yields the expression:

$$C_2/C_{2_\infty} = 0.95 = 1 + 0.58 \exp(-0.15t) - 1.58 \exp(-0.55t) \qquad \text{(A-9)}$$

An exact solution of Equation A-9 by algebraic manipulation is probably not possible. The equation can, however, be solved easily once one becomes aware that the second term on the right-hand side rapidly approaches zero as t increases. Neglecting this second term, the Equation A-9 becomes

$$\exp(-0.055t) = 0.0316 \text{ and} \qquad \text{(A-10a)}$$

$$t_{0.95} \doteq -18.182\ \ell n(0.0317) = 62.8 \text{ min.} \qquad \text{(A-10b)}$$

In other words, about one hour is required to establish 95 percent of steady state in the treatment of saline sewage under the specified conditions. In a four-compartment reactor like that used during the initial phase of the Coast Guard contract, $t_{0.95} = 118.3$ minutes--nearly two hours are required to reach 95 percent of steady state.*

Because the time to reach steady state is the longest when the rate of chemical reaction is the slowest, the preceding examples are worst-case solutions: The wet oxidation of saline sewage is slower than treatment of non-saline wastewater. Let us repeat some of the foregoing computations for the non-saline case. As in the previous examples, assume that the reactor is operating at a flow corresponding to a mean residence time of 20 minutes in each of n equal-size compartments. As typical values of k_l and k_ℓ, let us use 0.24 and 0.02 min.$^{-1}$, respectively.

---

*$C_4/C_{4_\infty} = 0.95 = 1 + 0.19 \exp(-0.15t) - 2.39 \times 10^{-3}\, t^2 \exp(-0.055t)$

The term 0.19 exp(0.15t) rapidly approaches zero and can be neglected; the equation then becomes

$t^2 \exp(-0.055t) = 20.92$

Trial and error will quickly establish that t = 118.3 minutes

An applicable general expression suitable for our purpose is

$$C_n/C_{n\infty} = 1 + (b/\Delta k)^{n-1} \exp(-at) - [ab^{n-2}/ k)(t^{n-2}/(n-2)]\exp(-bt) \qquad \text{(A-11}$$

where

$a = (1 + k_i\tau)/\tau = 0.29$

$b = (1 + k_\ell\tau)/\tau = 0.07$

$k = k_i - k_\ell = 0.22$

Equation A-11 expresses the concentration in the nth compartment as a function of elapsed time and the steady-state concentration.

Figure A-1, graphical solutions of Equation A-11 are shown for n = 2, 4, and According to the graph presented in Figure A-1, the concentration in the rth compartment achieved a value which is 95 percent of the steady-state concentration in about 90 minutes; whereas, in the wet oxidation of saline sewage under otherwise identical conditions, 120 minutes were required to reach 95 percent. Likewise, in the treatment of non-saline sewage, the second compartment reacnes 0.95 of steady state in about 45 minutes; whereas,about 60 minutes were required in the case of saline sewage.

Note in Figure A-1 the difference in the trend of the various $C_n/C_{n\infty}$ curves: The curve depicting the fraction $C_2/C_{2\infty}$ as a function of time rises monotonically and approaches the steady-state value (unity) asymptotically: whereas the fractions $C_4/C_{4\infty}$, which are initially zero, immediately rise--with the first charge of influent to the reactor--to a transient level which, depending upon the eventual extent of reduction in COD, may exceed the steady-state value*. (According to Equation A-11, at t = 0.05 min., $C_4/C_{4\infty} = C_6/C_{6\infty} \approx 1.003$.) Both the curves for $C_4/C_{4\infty}$ and for $C_6/C_{6\infty}$ exhibit minima. In other words, in the fourth and sixth compartments (of a reactor operating under the imposed conditions), the concentration increases at first until a maximum value is achieved, then decreases, and asymptotically approaches the steady-state concentration. By differentiating Equation 11 (and setting the differential equal to zero), one can determine the precise location of the minima: $C_4/C_{4\infty}$ is a minimum when t = 28.6 minutes, whereas $C_6/C_{6\infty}$ is a minimum when t = 57.1 minutes.

---

*The first charge of influent to the reactor causes an immediate "domino effect": a cascading displacement of liquid from compartment to compartment and the discharge of diluted raw wastewater from the rear of the reactor. During the transient phase, liquid in compartments near the discharge end of the reactor may contain more organic matter than at steady state.

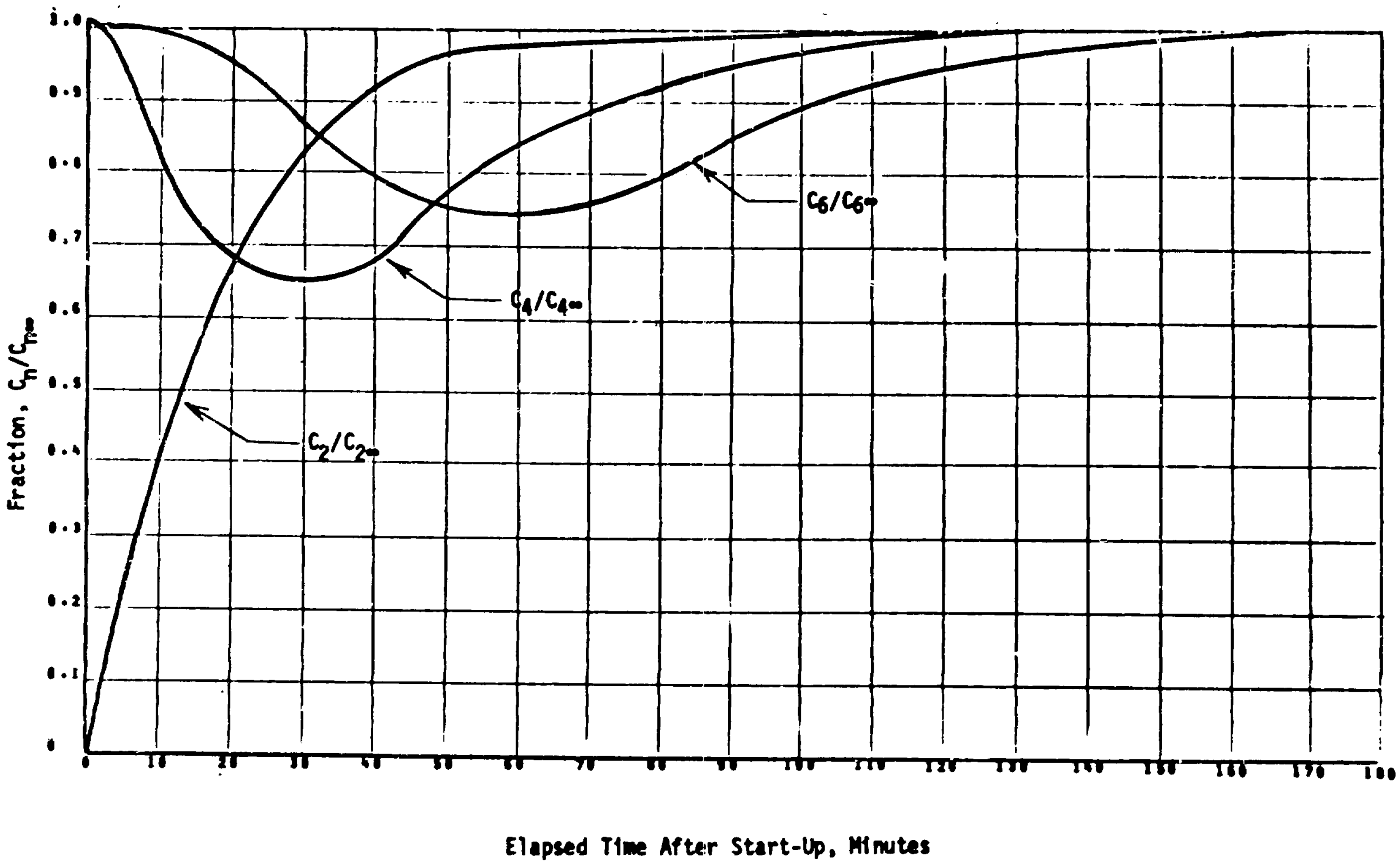


FIGURE A-1. FRACTION OF STEADY-STATE CONCENTRATION ACHIEVED DURING TRANSIENT PERIOD FOLLOWING START-UP FOR COMPARTMENTS 2, 4 AND 6.

APPENDIX B

ESTIMATION OF MEAN RESIDENCE TIME

Generally, mean residence time is computed on the basis of volume flow. In the WETOX process, however, the reacting solutions undergo considerable volume change due to temperature; and residence time is best determined on a mass-flow basis. Suitable formulas are derived in this appendix.

APPENDIX B

ESTIMATION OF MEAN RESIDENCE TIME

In the WETOX reactors, in which this program was performed, wet oxidation takes place in a series of continuously stirred compartments. At steady state, r_n, the rate of reaction, can be calculated for compartment n from the expression:

$$-r_n = (C_{n-1} - C_n)/\tau_n, \qquad \text{(B-1)}$$

where C is the concentration of organic matter expressed as COD; n and n-1 are subscripts denoting adjacent compartments; and τ is the mean residence time; that is, the average time interval during which matter undergoes chemical reaction in the compartment. The negative sign (in front of the left-hand term r_n) in Equation B-1 indicates that the concentration of COD decreases with time.

Expressed mathematically in symbols, the mean residence time, τ_n, is defined by the following formula:

$$\tau_n = \rho V^*/\dot{M}_\ell \qquad \text{(B-2)}$$

where ρ is the density of the liquid in the reactor;

V^* is the active volume (the capacity for liquid) of the indicated compartment; and

$\dot{M}_\ell$ is the mass flow rate of the liquid-phase slurry.

Each of the parameters comprising Equation B-2, in turn, are functions of the operating conditions prevailing in the reactor. In following subsections each parameter is defined; and a typical value or range of values is calculated for the wet oxidation of shipboard sewage.

B.1 MASS FLOW RATE

As described in Section 2.5 of the main report, in the type of reactor used in this program, the wastewater exits from the reactor in two streams: vented vapor and liquid slurry. The degree of partitioning is determined by the prevailing operating conditions, particularly, temperature and air flow. Mathematically, the mass flow rate of liquid, M_ℓ, is defined by the following formula:

$$\dot{M}_\ell = F - fF\beta\omega, \qquad \text{(B-3)}$$

where f is the fraction of organic solids in the feed;

F is the feed rate, that is, the mass of wastewater fed to the reactor in a unit interval of time;

β is the ratio, mass air added: mass solids added; and

ω is the humidity factor, that is, the mass of water (lost as steam) in each unit mass of dry air added to the reactor.

In the wet oxidation of shipboard sewage (in the range of concentration used in this program), the quantity $fF\beta\omega$--the mass of steam vented during processing--is less than 2 to 5 percent of the mass flow rate of feed (F); consequently, in this program, the following approximation generally was used:

$$\dot{M}_\ell \simeq F \qquad \text{(B-4)}$$

B.2 ACTIVE VOLUME

It generally is conceded that in wet oxidation the reaction occurs only in the liquid phase. Accordingly, in Equation B-2, the mean residence time is defined for the liquid; and the active volume of concern also is that of the liquid. In general, in a well-stirred reactor, V*, the volume occupied by liquid, is determined from the following expression:

$$V^* = V(1 - f^*), \qquad \text{(B-5)}$$

where V is the geometric volume of the walled-off portion of the reactor's interior occupied by the agitating mass of liquid and entrained air; and

f* is the fraction of the agitated mass which is entrained air.

In stirred vessels, as the flow of air is increased--and/or the mechanical power expended in stirring is increased--the fraction of entrained air increases; and, consequently, the mass of liquid in the reactor diminishes. According to the 1963 (Fourth) Edition of Perry's Chemical Engineers's Handbook, f*, the fraction of entrained air, can be estimated by the following formula:

$$f^* = (u/Av_t)^{0.5}[(f^*)^{0.5} + 0.0216\ (P/V)^{0.4}\rho^{0.2}(\sigma)^{-0.6}], \qquad \text{(B-6)}$$

where u is the flow rate of air in cm^3/sec;

A is the cross-sectional area of the compartment or tank over which the air is dispersed, in cm^2;

v_t is the so-called bubble terminal velocity, which generally is taken to be 26 cm/sec;

P is the agitator shaft power during dispersion, in ergs/sec;

V is the volume of agitated mass, in cm^3;

ρ is the liquid density in gm/cm^3; and

σ is the interfacial tension, in dynes/cm.

In Equation B-6, f* appears on both sides of the equation. According to Valentin*, this is essential so that

$f = u/Av_t$, when $P/V = 0$.

In other words, in unstirred vessels, the gas hold-up (the fraction of entrained air) increases in direct proportion to the velocity of the air flow. (The quantity u/A, the flow rate of gas divided by the cross-sectional area, generally is referred to as the superficial velocity of the gas.)

Equation B-6 is from the work of Calderbank**, which according to Perry's Chemical Engineers' Handbook is "probably the most fundamental study to date of mechanical gas dispersion by agitators". The investigations were conducted in upright cylindrical tanks ranging from 6 to 20 in. in diameter over a power-input range to 0.2 horsepower and gas-flow velocities to 3.6 ft^3/min per ft^2 of cross-sectional area. As one will presently see from the computations which follow, the range covered by Calderbank in his study encompasses the conditions commonly used in this program. However, it should be noted that in the multiple compartment reactors used in this program, dispersion is effected by mechanically stirring liquid in a cylinder lying, if you will, on its side. To our knowledge, there are no published studies of dispersion in vessels geometrically similar to the horizontal-cylinder arrangement used in this program.

The following values of the parameters comprising Equation B-6 are representative of the range used in this program:

Air flow. The range from 0.2 to 1.0 scfm was investigated. As the value of f* will be the greatest when the air flow is the greatest, we shall concern ourselves with the value,

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*F.H.H. Valentin, Absorption In Gas-Liquid Dispersions, E. & F.N. Spon, Ltd., London, 1967, p. 148.

**See Valentin, op. cit., for a summary of the work of Calderbank and of others.

1.0 scfm. However, because air is compressed before its delivery to the reactor, the actual flow in the reactor is

$(1.0\ ft^3/min)(14.7\ psi/600\ psi) = 0.0245\ ft^3/min.$

In units appropriate for Equation B-6, the maximum actual air flow used in the program was

$(0.0245\ ft^3/min)(1728\ in^3/ft^3)(16.39\ cm^3/in^3)(1\ min/60\ sec)$

$= 11.565\ cm^3/sec.$

Cross-sectional Area. The reactors used in this program are divided internally into compartments approximately as long as the diameter. About eight-tenths of the volume is filled with agitating liquid and entrained air. The properties of a circle are such that the chord of the segment encompassing 80 percent of the area is about eight-tenths as long as the diameter. Consequently, the cross-sectional area over which air is dispersed in each compartment is

$A \approx 0.8D^2.$

Expressed in numbers, the area is

$0.8(9.75\ in.)^2$ or $76.05\ in.^2$

Converted to metric units, the approximate cross-sectional area is

$(76.05\ in.^2)\ (6.45\ cm^2/in.^2)$ or $490.6\ cm^2$

Power Input. Mechanical stirring was accomplished by agitator drive units which, according to the vender literature, deliver 0.1 horsepower at 1000 rpm. Converted to metric units, in this program, the mean power input (from each agitator) was

$(0.1\ hp)(7.456 \times 10^9\ erg/sec.\ hp) = 7.456 \times 10^8\ erg/sec$

Volume (Capacity for Liquid). The geometric volume of the space provided for liquid in individual compartments of the reactors used in this program ranged from 7500 to 10,000 cm^3. (Exact values are cited elsewhere for specific compartments). For the purpose of formulating an estimate of gas hold up, let us use as a representative volume,

$V = 0.8\ (\pi/4)D^3$

$= 582.4\ in.^3$ or $9543\ cm^3$

where D is 9.75 in.

Density (of water at elevated temperatures). For practical purposes, the liquid in the reactor can be assumed to have the same density as water. In the temperature range of WETOX processes, 250-500°F, the density of water decreases linearly with increasing temperature in accordance with the following expression:

$$\rho_T = 1.15649 - 0.00075T \qquad \text{(B-7)}$$

where T is the operating temperature in °F. Equation B-7 was derived by the method of least squares (by linear regression analysis) from data taken from the Handbook of Chemistry and Physics*.

At 475°F, the density of water is 0.800 g/cc according to Equation B-7.

Interfacial Tension. A perusal of the data compiled in Lange's Handbook of Chemistry** indicates that the interfacial tension of the liquid phase probably must be estimated from known lower-temperature values. For the purpose at hand, we assume that the interfacial tension is 50 dynes/cm based on the value listed in the handbook for water at 130°C.

Substituting the various estimates of parameters into Equation B-6 yields the following expression:

$$f^* = (0.03f^*)^{0.5} + 0.0054$$

Trial-and-error methods will result in the solution:

$$f^* = 0.0081.$$

In other words, in the tests conducted in this program, the volume of entrained air was probably less than one percent of the agitated mass. Consequently, for most purposes, the geometric volume was assumed to be the active volume; that is to say,

$$V^* \simeq V$$

B.3 REPRESENTATIVE RESIDENCE TIME

In Figure B-1, a graphical solution is presented for the formula,

$$\tau_n = \rho V_n / F,$$

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* Op. Cit., 38th Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1956, page 1990.

**Op. cit., 11th Edition, page 10-265 and 10-269.

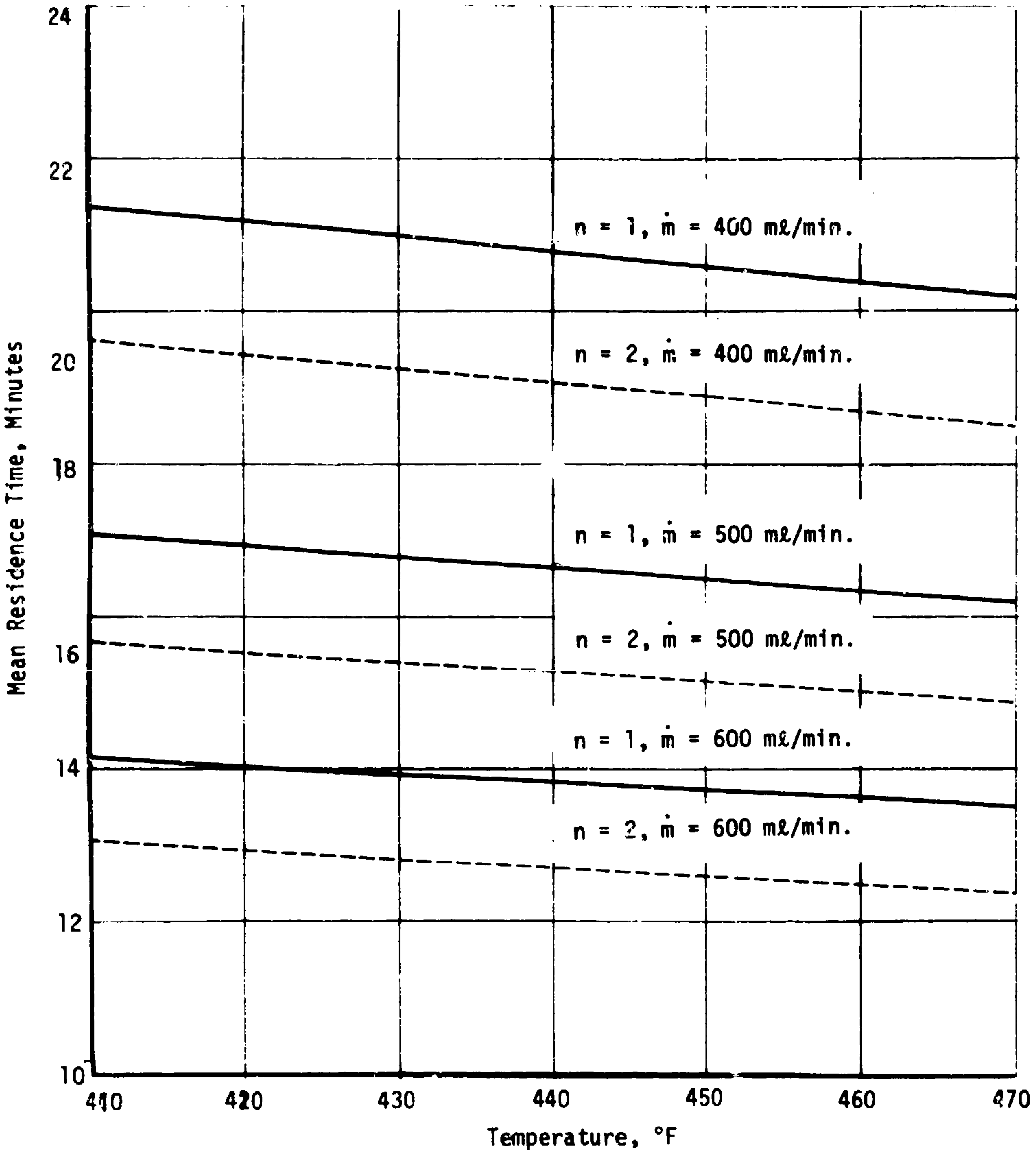

FIGURE B-1. MEAN RESIDENCE TIME FOR COMPARTMENTS 1 AND 2 FOR SEVERAL FLOW RATES AND VARIOUS OPERATING TEMPERATURES.

which is appropriate for the two-compartment reactor built by Barber-Colman Company for the Coast Guard. The capacities are 10,070 and 9230 cm^3 for the first and second compartments, respectively. The usable volume was determined by subtracting the volume of liquid displaced by heaters and impellers from the geometric volume below the weirs in the partition walls.

APPENDIX C

CHRONOLOGICAL PRESENTATION
OF TEST RESULTS

Evaluation of the Acid Circuit

Section 3 of the report presents a summary of continuous-flow tests conducted to evaluate the wet oxidation of acidified shipboard wastewaters. In the main body of the report, the discussion is not presented chrorologically. In this appendix, the tests are presented in the order in which they were performed. Moreover, the original interpretation is preserved, although often it conflicts with the conclusions expressed in Section 3. For instances, there were differences in the makeup to the influent in Test Nos. 72349, 72350 and 72353; and, in the appendix, these variations in makeup were treated as process variables. Re-examination of the data, however, indicated that the effects were secondary; and, in Section 3.3, the three tests are considered replicates. Likewise, in certain tests, the heat exchanger was not used, but this was not considered important in the statistical analysis presented in Section 3.3.

C.1 CONTINUOUS TREATMENT OF COMBINED SHIPBOARD WASTE

Two tests were conducted during the last week of November 1972 in the four-compartment, continuous-flow reactor described in Section 3 of the report. Approximately 27 gallons (102 liters) of simulated combined shipboard wastewaters were treated during a four-hour period on 27 November and 58 gallons (219 liters) during 7-1/2 hours on 30 November.

Pertinent operating conditions which were maintained during the test are summarized in Table C-1.

TABLE C-1

CONTINUOUS-FLOW RUN OF NOVEMBER 27 AND 30, 1972

(Test Nos. 72332 and 72335)

Summary of Operating Conditions:

Reactor Temperature	
First Compartment	470 - 480°F
Second Compartment	460 - 465°F
Third Compartment	440 - 450°F
Fourth Compartment	420 - 440°F
Total Pressure	600 psi, max.
Steam Pressure	550 psi, max.
Air Flow	4.8 scfm
Pumping Rate	0.433 ℓ/min; November 27 0.467 ℓ/min; November 30
Residence Time, Average	15 min./compartment; Nov. 27 14 min./compartment; Nov. 30
Speed of Agitators	800 rpm

Feed was prepared for the tests in 35-40 gallon batches. Typical makeup can be ascertained from Table C-2, a listing of the ingredients blended in the wastewater used on 27 November. In essence, feed was prepared by macerating the daily waste of one person and diluting it to 35 gallons, the established per-capita-day volume of combined shipboard wastewaters.

After two hours of continuous flow, samples were taken from each compartment hourly and assayed for chemical oxygen demand (COD). Results of chemical analysis and the calculated percentage reductions in COD are listed in Table C-3 for the run of 27 November and in Table C-4 for the run of 30 November.

TABLE C-2

CONTINUOUS-FLOW RUN OF
NOVEMBER 27, 1972

(Test No. 72332)

Composition of Influent:

Table Scraps

Shells from two eggs.

Grease from frying two eggs.

Coffee grounds from percolating six cups.

Trimmings from one steak.

Remains from one salad.

Remains from one serving of beef and noodles.

Peels from one orange.

One-third slice of bread.

Toiletries

Shaving cream from one shave.

Toothpaste from one brushing.

Body Waste

Feces from one individual, collected over a 24-hour period.

Urine, one quart.

Municipal Water

Thirty-five gallons.

TABLE C-3

CONTINUOUS-FLOW RUN OF NOVEMBER 27, 1972

(Test No. 72332)

Results of Chemical Analysis

Sampling Time, PST	Sample Station	COD, mg/ℓ 0	Percent Reduction in COD
1500	Influent	1975	----
	Compartment 1	945	52.2
	Compartment 2	626	68.3
	Compartment 3	586	70.3
	Compartment 4	529	73.2
1600	Influent	1715	----
	Compartment 1	850	50.4
	Compartment 2	559	67.4
	Compartment 3	508	70.4
	Compartment 4	407	76.3
1645	Influent	1809	----
	Compartment 1	692*, 670*	61.7
	Compartment 2	551	69.5
	Compartment 3	483	73.3
	Compartment 4	393	78.3

---

[*] These were entirely independent assays performed on separate days.

TABLE C-4

CONTINUOUS-FLOW RUN OF NOVEMBER 30, 1972

(Test No. 72335)

Results of Chemical Analysis

Sampling Time, PST	Sample Station	COD, mg/ℓ O	Percent Reduction in COD
1300	Influent	1363	----
	Compartment 1	461	66.2
	Compartment 2	432	68.3
	Compartment 3	405	70.3
	Compartment 4	365	73.2
	Vapor Cond.	651	
1600	Influent	927	----
	Compartment 1	393	57.6
	Compartment 2	351	62.1
	Compartment 3	300	67.6
	Compartment 4	273	70.6
1700	Influent	900	----
	Compartment 1	527	41.5
	Compartment 2	351	61.0
	Compartment 3	273	69.7
	Compartment 4	262	70.9
	Vapor Cond.	930	

C.2 BATCH TESTS ON COMBINED SHIPBOARD WASTEWATER

As a supplement to the two continuous-flow tests on combined shipboard wastewater, several batch tests were conducted in which aliquots of the same feed used in the continuous tests were reacted in a one-gallon laboratory autoclave with comparable quantities of compressed air, at the same temperature and under the same oxygen over-pressure as in the continuous tests. Tables C-5 and C-6 present summaries of pertinent conditions for two uncatalyzed batch tests; the results of chemical analysis of samples removed periodically from the batch reactor are included in the tables.

The percentage reduction in COD achieved in these uncatalyzed batch tests is comparable to the reduction achieved in the same total elapsed time in the four-compartment continuous reactor. For example, compare the results shown in Table C-3 (for the effluent from compartment 4 of the continuous reactor) with the data of Tables C-5 and C-6 for the COD of the sample taken from the batch reactor at the end of 60 minutes after injection of wastewater: The mean from Table C-3 is 75.9% reduction in COD; and the corresponding value from Table C-6 is 74.2.

Rate parameters can also be derived from the batch experiments, and these constants agree closely with those observed in the continuous tests. The method of obtaining these rate parameters is described in following paragraphs.

In batch experiments wet oxidation almost always proceeds in a surprisingly straightforward manner--the over-all reaction is actually a series of apparently interconnected rate-limiting steps, each of which is a pseudo-first-order with respect to the COD content of the liquid phase and rate-determining over a range of percentage reduction in COD. (Further discussion of this point appears in Section 2 of the main report.) For example, Figures C-1 and C-2 are plots of the logarithm of effluent concentration, $\log_{10}$ COD, versus reaction time, t, for the two uncatalyzed batch tests. Plotted in this semi-logarithmic manner, the trend in COD clearly falls along two intersecting, straight lines with progressively diminishing slopes. This same trend has been observed in over 400 batch experiments. Occasionally, there are three intersecting lines, but usually the correlation is highly significant when all of the data is fitted to two lines. In the language of chemical kinetics, the conformance of rate data to graphical correlation like that exhibited in Figures C-1 and C-2 is indicative of a chemical reaction governed by a pseudo first-order rate-limiting step. The change in slope of the trend line indicates a change in the rate-limiting step: Generally, this transition in the rate-limiting step occurs after 2/3 of the organics have been destroyed; the transition can, however, be delayed by the use of catalyst until as much as 90% of the organic has been destroyed. Destruction beyond the transition point in the curve occurs much slower than oxidation up to that point. The secret of successful waste disposal by wet oxidation is to create an environment that delays (or eliminates) the transition to the slower rate-limiting process.

TABLE C-5

SUMMARY OF BATCH TEST ON SIMULATED COMBINED SHIPBOARD WASTEWATERS

Batch Test No.:	238
Test Conditions:	
Mean Temperature, °F:	474
Ratio of Oxygen Supplied to Oxygen Demanded:	1.2
Initial Partial Pressure of Oxygen, psi:	20
Speed of Agitator, rpm:	1500
Source of Oxygen:	Compressed Air
Catalyst:	None

Results:

Sample	COD, mg/ℓ O	% Red. in COD
Influent	1092	----
5 min. after injection	789	27.8
10 min. after injection	559	48.8
15 min. after injection	470	57.0
40 min. after injection	357	67.3
60 min. after injection	299	72.6
80 min. after injection	256	76.6
100 min. after injection	213	80.5
120 min. after injection	166	84.8

TABLE C-6

SUMMARY OF BATCH TEST ON
SIMULATED COMBINED SHIPBOARD WASTEWATERS

Batch Test No.: 239

Test Conditions:

Mean Temperature, °F	474
Ratio of Oxygen Supplied to Oxygen Demanded:	1.3
Initial Partial Pressure of Oxygen, psi:	45
Speed of Agitator, rpm:	1500
Source of Oxygen:	Compressed Air
Catalyst:	None

Results:

Sample	COD, mg/ℓ O	% Red. in COD
Influent	1986	----
5 min. after injection	1409	29.1
[illegible]0 min. after injection	1011	49.1
15 min. after injection	831	58.2
40 min. after injection	583	70.7
60 min. after injection	513	74.2
80 min. after injection	471	76.3
100 min. after injection	419	78.9
120 min. after injection	370	81.4

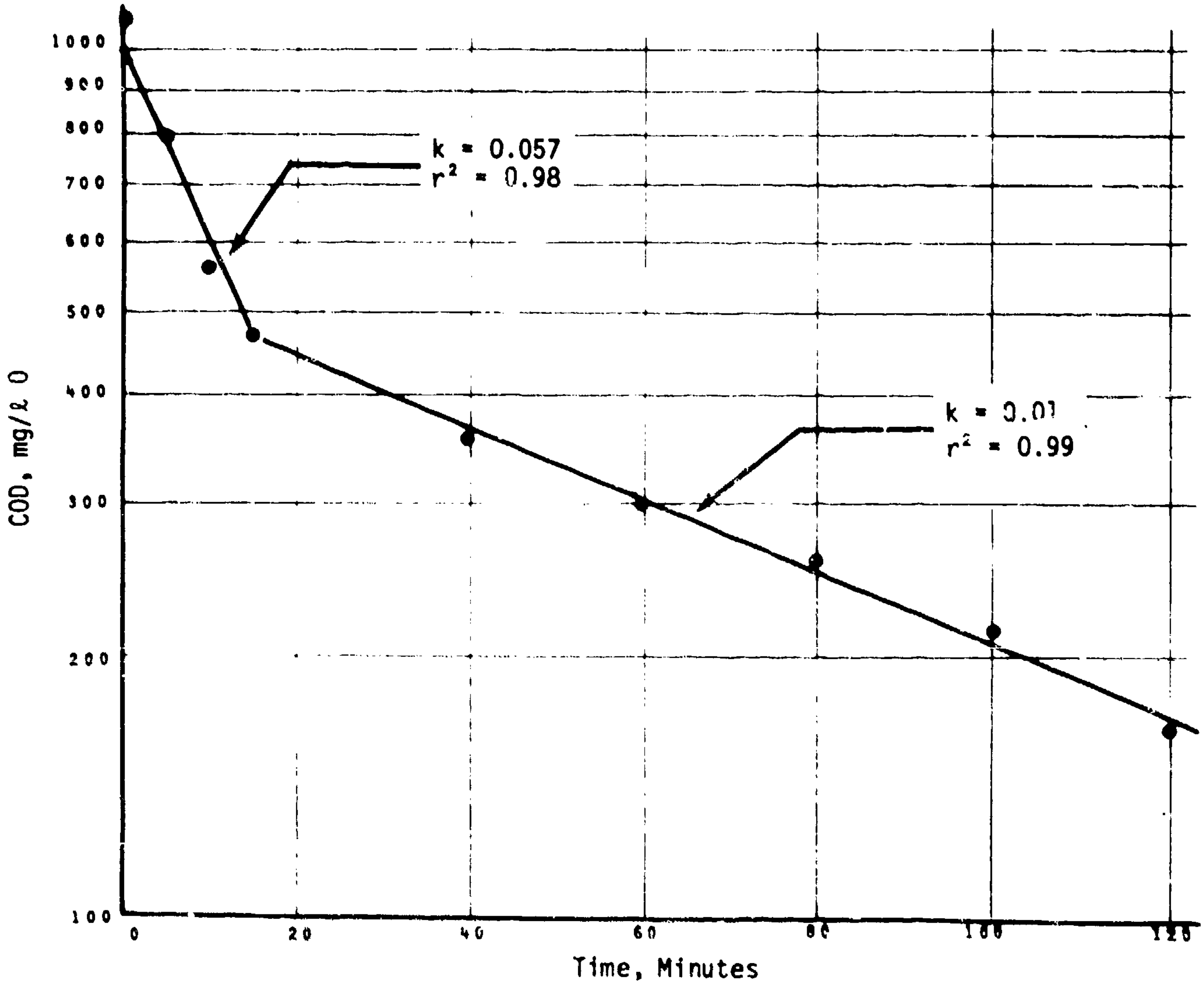

FIGURE C-1. DECREASE IN COD OF LIQUID PHASE OBSERVED FOR INCREASED REACTION TIME--BATCH TEST NO. 238, SIMULATED COMBINED SHIPBOARD WASTEWATERS

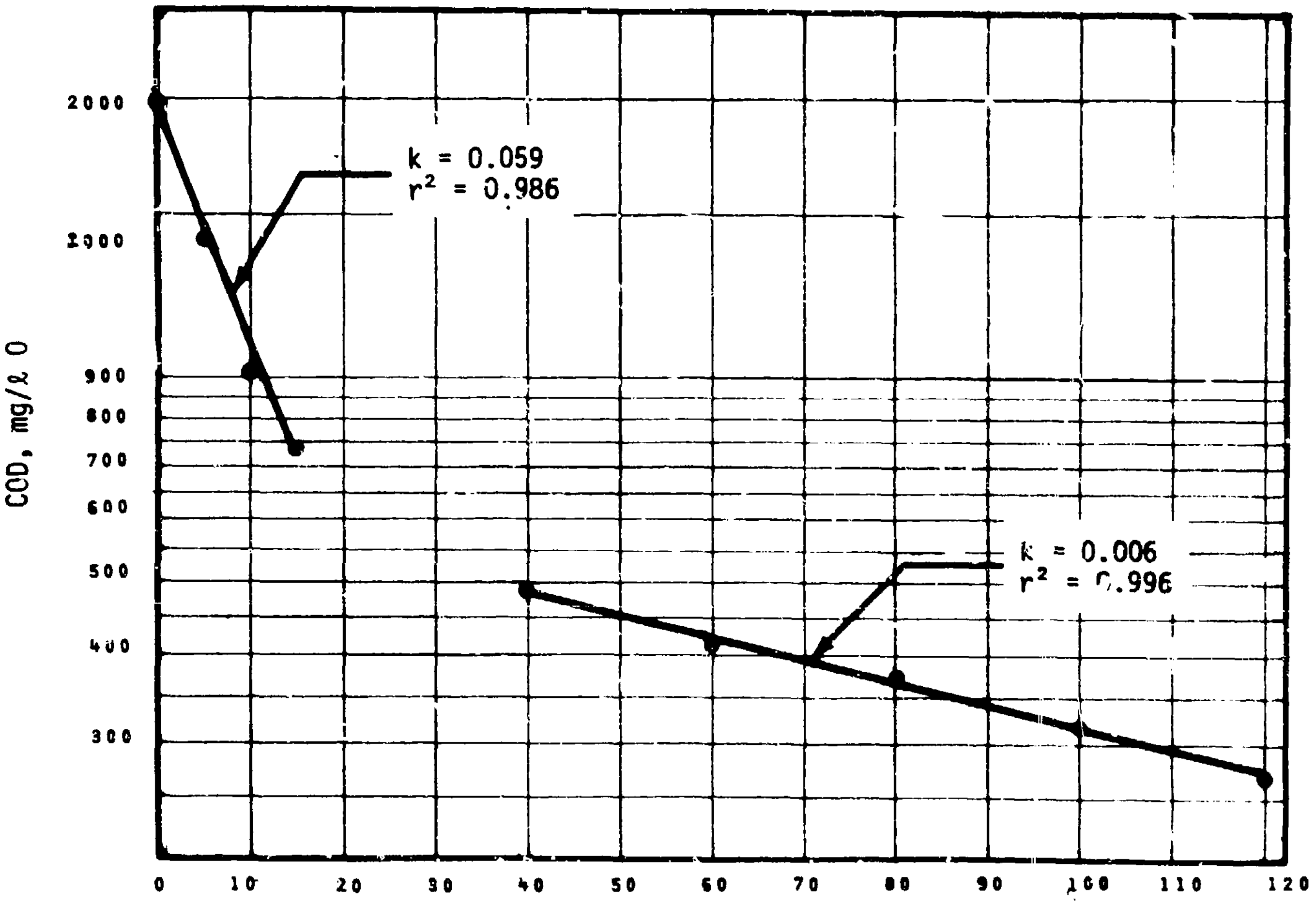

FIGURE C-2. DECREASE IN COD OF LIQUID PHASE OBSERVED FOR INCREASED REACTION TIME--BATCH TEST NO. 239, SIMULATED COMBINED SHIPBOARD WASTEWATERS

From plots like those of Figures C-1 and C-2, one can calculate the pseudo first-order reaction rate constant k:

$$k = 2.303\ b \qquad (5)$$

where b is the slope of the trend line, $\Delta(\log_{10} \text{COD})/\Delta t$. The lines shown in Figures C-1 and C-2 are the "least-squares" fit of the datum points indicated by the black circles. The so-called coefficient of determination r^2 is indicated for each line. The statistical parameter r^2 is the fraction of the variance which can be accounted for by the natural regression of a straight line whose slope is b. In other words, if $r^2 = 1$, the fit of the data is perfect. In most cases, correlation of wet-oxidation data by the method depicted in Figures C-1 and C-2 results in fits whose unaccounted-for variance $(1-r^2)$ is less than acceptable error in routine chemical analysis.

Table C-7 lists k values determined from the continuous tests. Compare the k values for the 27 November run with those shown on Figures 2 and 3 for uncatalyzed batch tests:

Continuous Test

Compartment 1	Compartment 2	Compartment 3	Compartment 4
$k_{avg.} = 0.076$	$k_{avg.} = 0.028$	$k_{avg.} = 0.007$	$k_{avg.} = 0.013$
55% Reduction	68% Reduction	71% Reduction	76% Reduction

Batch Tests

$k_{avg.} = 0.058$	$k_{avg.}$ 0.003
|← 0 - 60% Red. →|	|← 60 - 85% Reduction →|

The continuous-flow run of 30 November was conducted in the presence of a carbon substance known to be catalytic, at least in batch tests. Table C-8 summarizes such a batch test, one conducted in the presence of carbon. The percentage reduction in COD achieved in the batch test is considerably greater than that achieved in the continuous test (91 percent compared to 71 percent). Figure C-3 is the semi-logarithmic plot of $\log_{10}$ COD versus t for this batch run. Compare the k values obtained in the continuous test of 30 November with those obtained in the batch test.

TABLE C-7

REACTION RATE PARAMETERS FOR CONTINUOUS-FLOW RUNS ON COMBINED SHIPBOARD SEWAGE

Test No.	Time of Sampling, PST	Sample Station							
		Compartment 1		Compartment 2		Compartment 3		Compartment 4	
		-r	k	-r	k	-r	k	-r	k
72332	1500	63.6	0.067	21.0	0.034	2.7	0.005	3.9	0.007
	1600	53.4	0.062	13.1	0.034	3.4	0.007	6.8	0.017
	1645	69.0	0.10	9.3	0.017	4.5	0.009	6.1	0.015
72335	1300	60.1	0.13	2.1	0.005	1.9	0.005	2.9	0.008
	1600	35.6	0.091	3.0	0.008	3.7	0.012	2.0	0.007
	1700	24.9	0.047	12.5	0.035	5.6	0.020	0.8	0.003

TABLE C-8

SUMMARY OF BATCH TEST ON SIMULATED COMBINED SHIPBOARD WASTEWATERS

Batch Test No.: 240

Test Conditions:

Mean Temperature, °F	482
Ratio of Oxygen Supplied to Oxygen Demanded:	2.1
Initial Partial Pressure of Oxygen, psi:	35
Speed of Agitator, rpm:	1500
Source of Oxygen:	Compressed Air
Catalyst:	168 in.^{2} Carbon

Results:

Sample	COD, mg/ℓ O	% Red. in COD
Influent	1022	----
5 min. after injection	686	32.9
10 min. after injection	663	35.2
15 min. after injection	621	39.3
20 min. after injection	489	52.2
25 min. after injection	390	61.9
60 min. after injection	96	90.6
80 min. after injection	90	91.2
100 min. after injection	76	92.6
120 min. after injection	70	93.2

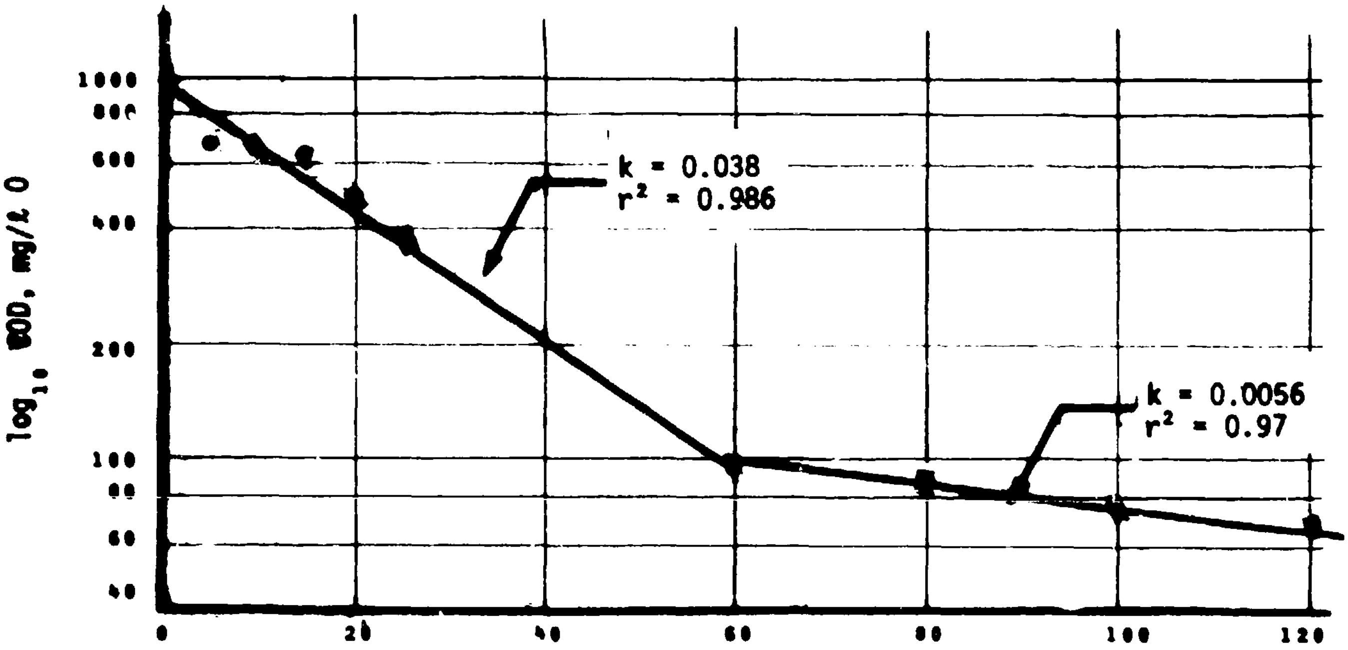

FIGURE C-3. DECREASE IN COD OF LIQUID PHASE OBSERVED FOR INCREASED REACTION TIME--BATCH TEST NO. 240, SIMULATED COMBINED SHIPBOARD WASTEWATERS

	Compartment 1	Compartment 2	Compartment 3	Compartment 4
Continuous Test	$k_{avg.} = 0.089$	$k_{avg.} = 0.016$	$k_{avg.} = 0.012$	$k_{avg.} = 0.006$
	55% Reduction	64% Reduction	69% Reduction	72% Reduction

Batch Test	k = 0.04 ← 0 - 90% Reduction →	k=0.005 ← 90-100% → Red.

Using the means of the k values from the continuous-flow test as a basis for the comparison results in a wide disparity. However, compare the continuous-flow k values from the sampling at 1700 with the k values from the batch test:

	Compartment 1	Compartment 2	Compartment 3	Compartment 4
Continuous Test	k = 0.047	k = 0.035	k = 0.020	k = 0.003
	42% Reduction	61% Reduction	70% Reduction	71% Reduction

Batch Test	k = 0.04 ← 0 - 90% Reduction →	k=0.005 ← 90-100% → Red.

The agreement is better between the late in the day samples and the batch test, indicating perhaps that the system is sluggish in obtaining a steady state.

In this preliminary continuous run, there were only superficial areas of carbon present in the reactor. (There was not adequate material on hand to line all of the reactor shell with carbon.) In the batch test, the ratio of area of catalyst to volume of wastewater is generally about 0.72 cm^{-1}; whereas in the continuous run, the corresponding ratio was about 0.015 cm^{-1}. The continuous run took place in the presence of about one-fifth as much carbon to solution as the batch test.

C.3 CONTINUOUS-FLOW TESTS ON SHIPBOARD SEWAGE IN A CARBON-LINED REACTOR

Two series of tests were conducted in a 4-compartment reactor which was lined with porous carbon platelets. In batch tests, carbon was found to accelerate the rate and extent of wet oxidation. In the first series, acidified shipboard sewage was treated in the carbon-lined reactor per se; whereas, in the second series, additional catalytic agents were also used.

C.3.1 TESTS WITHOUT ADDITIONAL CATALYSTS

These tests were conducted in December 1972. In this series of tests, as was the case with the test of 30 November, each compartment of the reactor contained 15 to 20 sq. in. of a carbonaceous catalyst.

In the November test, the performance of the carbon catalyst was disappointing; considerably less reduction in COD occurred in the continuous run than under comparable batch conditions. In the second monthly report, the poor performance in the continuous test was attributed to the fact that the continuous reactor contained substantially less carbon than the batch reactor. However, in subsequent continuous-flow tests, the percentage reduction in COD was comparable with that achieved in batch tests; and in some continuous runs, certain aspects of the catalyzed process exceeded expectations based on batch tests. In retrospect, therefore, we must conclude that the poor initial performance was due to some other factor--possibly temporary catalytic poisoning from a refractory cement (used in making a water-tight seal around the periphery of the partition walls which divide the interior of the autoclave into compartments). Once the acid-soluble constituents of the cement were purged from the system, the performance of the reactor improved.

These tests serve to delineate the effect of most principal process variables on the efficacy of wet oxidation applied to shipboard wastewaters. Percentage reduction in COD ranged from about 60 percent in some runs to nearly 90 percent in others. Efficacy was greatest when wet oxidation was conducted in the presence of a carbonaceous catalyst and in tap water rather than in saline water.

a. General Operating Conditions.

In Table C-9, the principal operating conditions are listed for the series of continuous-flow tests. Reactor pressure and the temperature of individual compartments were held constant in all tests as was also the speed of stirring. There was some variation in the rates of flow of reactants: the nominal range is listed in Table C-9 and specific values are cited in following discussion for particular tests.

Air flow was held constant in most tests and, in all cases, was excessive: These preliminary tests were conducted in equipment originally assembled for the treatment of waste much more concentrated than shipboard wastewater. Until proper flow meters were obtained, it was not possible to regulate the flow of air in the desired range, 0.3 - 1.0 cfm.

TABLE C-9

SUMMARY OF OPERATING CONDITIONS

Continuous-Flow Runs of December 1972

Reactor Temperature	
Compartment 1, °F	470-480
Compartment 2, °F	450-455
Compartment 3, °F	430-435
Compartment 4, °F	415-420
Reactor Pressure	
Total, psi	600, max.
Steam, psi	550, max.
Air Flow	
Total Flow Rate, scfm:	4 - 6
Pct. supplied to Compartment 1:	33
Pct. supplied to Compartment 2:	27
Pct. supplied to Compartment 3:	20
Pct. supplied to Compartment 4:	20
Agitator Speed, rpm:	800
Influent Flow Rate, Liters/Minute:	0.4 - 0.5
Residence Time, Min./Compartment:	12 - 15

b. Descriptions of Individual Tests

In following paragraphs, brief summaries are presented for each test. The objectives and general conclusions are stated, and the chemical analysis of the effluents and influent is listed with the calculated percentage reduction in COD. Detailed discussion of the tests and analysis of the data are presented in the following section.

(1) Continuous-Flow Test No. 72343 (8 December 1972)--Establishment of Maximum Efficacy

Extensive batch tests demonstrated that the maximum reduction in COD is achieved from acidic non-saline influent. (Results from typical batch tests are included in Section 2.) On 8 December, 1972, a continuous-flow test was conducted in which the influent consisted of macerated feces and urine in tap water containing about 6 g/ℓ H_2SO_4. Feed to the autoclave was initiated at 0930; the test was terminated at 1630; during the 8-hour period, 200 liters (approximately 52 gallons) of influent were treated.

Influent and effluent streams were sampled at 1300, 1400, 1530 and 1630. Chemical analysis for COD and the calculated percentage reduction in COD are summarized in Table C-10. The influent was prepared in two batches. The first batch which was treated during the interval from 0930 to 1410 was more amenable to treatment than the second batch. There is a distinct possibility that no sulfuric acid was added to the second batch of influent--if this were the case, the drop in efficacy is understandable. An alternative explanation would be that the second batch contained an excessive amount of urine--certain uric species retard wet oxidation.

Exiting vapors from the reactor passed through an efficient water-cooled condenser. Approximately 11.7 liters of condensate were collected during the course of the run--5.85% of the influent volume. The weighted-mean percentage of input COD contained in the vapor condensate was about four percent. In view of the excessive air flow in this and the other tests described in this report, the amount of vapor condensate is excessive and unrepresentative of the ultimate process.

(2) Continuous-Flow Test No. 72346 (11 December 1972)--Treatment of Typical Saline Sewage

Aboard watercraft utilizing sea water to flush toilets, combined shipboard wastewaters may average 6,000 - 7,000 mg/ℓ total chloride. To demonstrate the effect of salinity on the extent and rate of wet oxidation feces were macerated in urine and diluted in a mixture of one part sea water and two parts tap water. The resulting saline body sewage was used as influent in a continuous-flow test. Chemical analysis of influent and effluents is summarized in Table C-11. Comparison with results from the preceding test (72343), which was performed under otherwise identical conditions on non-saline influent, dramatically demonstrates the effect of salinity on wet oxidation. Over-all reduction in COD was nearly 90 percent in the absence of excessive chloride, and only 65 percent in the case of influent containing 7,000 ppm Cℓ.

TABLE C-10

CHEMICAL ANALYSIS AND PERCENTAGE REDUCTION IN COD

Continuous-Flow Test No.	72343, 8 December
Mean Residence Time, Min./Compartment	14
Volume of Influent Treated, ℓ	200
Volume of Vapor Condensate Collected, ℓ	11.7
Percent of Influent Volume Condensed from Vapor	5.85
Percent of Influent COD Condensed from Vapor	4

Time of Sampling, PST	Sampling Station	COD, mg/ℓ	% Red. in COD	Solute Concentration, mg/ℓ			
				H_2SO_4	Cℓ*	Amm. N	pH
1300	Influent	2386		6000	420		
	Comp. 1	495	79.3		387		
	Comp. 2	421	82.4		318		
	Comp. 3	339	85.8				
	Comp. 4	266	88.9				
	Vapor Cond.	1175			17		
1400	Influent	2222		6000			
	Comp. 1	479	78.4				
	Comp. 2	414	81.4				
	Comp. 3	344	84.5				
	Comp. 4	255	88.5				
	Vapor Cond.	1794					
1530	Influent	2036		6000 (?)			1.42
	Comp. 1	473	76.8			338	1.47
	Comp. 2	402	80.3			351	1.45
	Comp. 3	371	81.8				
	Comp. 4	307	84.9				
	Vapor Cond.	1336					3.07
1630	Influent	1655		6000 (?)			
	Comp. 1	385	76.7				
	Comp. 2	365	78.0				
	Comp. 3	338	79.6				
	Comp. 4	300	81.9				
	Vapor Cond.	1191					

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[*] Assay of composited hourly samples.

TABLE C-11

CHEMICAL ANALYSIS AND PERCENTAGE REDUCTION IN COD

Continuous-Flow Test No.	72346, 11 December
Mean Residence Time, Min./Compartment	14
Volume of Influent Treated, ℓ	122
Volume of Vapor Condensate Collected, ℓ	6
Percent of Influent Volume Condensed from Vapor	4.9
Percent of Influent COD Condensed from Vapor	5.3

Time of Sampling, PST	Sampling Station	COD, mg/ℓ	% Red. in COD	Solute Concentration, mg/ℓ			
				H_2SO_4	Cℓ*	Amm. N	pH
1300	Influent	1780		6000	6992		
	Comp. 1	769	56.8		6071		
	Comp. 2	730	59.0		5924		
	Comp. 3	708	60.0		5764		
	Comp. 4	685	61.5		5719		
	Vapor Cond.	1833			52		2.94
1430	Influent	1796		6000			
	Comp. 1	639	64.4			265	1.48
	Comp. 2	615	65.8			262	1.48
	Comp. 3	564	68.6			260	1.48
	Comp. 4	544	69.7			256	1.48
	Vapor Cond.	2014					

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[*] Assay of Composited Hourly Samples.

(3) Continuous-Flow Test No. 72347 (12 December 1972)--Treatment of Moderately Saline Sewage

In view of the strong dependency of rate on salinity exhibited in wet oxidation, an additional run was conducted in which the influent consisted of macerated feces and urine diluted in a less saline mixture of one part sea water and five parts tap water. The chemical analysis of influent and effluents is summarized in Table C-12. The level of reduction in COD was 73 percent compared to 89 percent for non-saline water and 65 percent for influent containing twice as much sodium chloride as was the case in the present test.

(4) Continuous-Flow Test No. 72349 (14 December 1972)--Treatment of High Urinous Sewage

Previous batch tests have indicated that certain uric species retard wet oxidation. To establish the effect on continuous-flow wet oxidation, influent was prepared that contained 5 to 6 liters of urine to each 150 grams of feces. (According to the published statistics, an adult excretes daily about 100 - 150 grams of feces and 1000 - 1300 grams of urine.) The influent in this test might be typical of mid-day sewage; i.e., high in urine compared to the daily average. The results summarized in Table C-13 indicate that the extent and rate of wet oxidation are less (77% reduction compared to 90%) in the treatment of excessively urinous wastewater than in the case of influent containing feces and urine in the per-capita-day ratio.

(5) Continuous-Flow Test No. 72350 (15 December 1972)--Effect of Recycling

The vapor-phase condensate from the preceding test (72349) was mixed with macerated feces, urine and tap water and used as influent in a continuous-flow test. The data of Table C-14 indicate that recycling vapor condensate probably would not seriously affect the rate and extent of wet oxidation. Moreover, as previously mentioned, the amount of vapor condensate in this series of tests is excessive; and, therefore, the quantity of condensate that need be recycled would be much less than was the case in this test.

(6) Continuous-Flow Test No. 72353 (18 December 1972)--Effect of Less Residence Time

The results of the preceding tests were analyzed, and an additional test was planned in which the flow of air was reduced to as low a level as possible with the existing regulator, and the flow of influent was increased so that the residence time was about 12 minutes per compartment. Chemical analysis of influent and effluents is presented in Table C-15. Assays of effluent from the third compartment indicate that 80% of the influent COD was destroyed in about 36 minutes. In the December 8 run, assays of effluent from the second compartment indicated about 82% of the influent COD was destroyed in about 32 minutes.

TABLE C-12

CHEMICAL ANALYSIS AND PERCENTAGE REDUCTION IN COD

Continuous-Flow Test No.	72347, 12 December
Mean Residence Time, Min./Compartment	14
Volume of Influent Treated, ℓ	184
Volume of Vapor Condensate Collected, ℓ	12.3
Percent of Influent Volume Condensed from Vapor	6.7
Percent of Influent COD Condensed from Vapor	7.0

				Solute Concentration, mg/ℓ			
Time of Sampling PST	Sampling Station	COD, mg/ℓ	% Red. in COD	H_2SO_4	Cℓ*	Amm. N	pH
1300	Influent	1609		6000	3388		
	Comp. 1	540	66.4		3127		
	Comp. 2	498	69.0		3024		
	Comp. 3	471	70.7		2922		
	Comp. 4	442	72.5		2444		
	Vapor Cond.	1645			46		
1400	Influent	1700		6000			1.40
	Comp. 1	629	63.0			211	1.43
	Comp. 2	533	68.6			200	1.44
	Comp. 3	482	71.6			217	1.45
	Comp. 4	442	74.0			212	1.45
	Vapor Cond.	1855					2.85
1530	Influent	1292		6000			
	Comp. 1	470	63.6				
	Comp. 2	410	68.3				
	Comp. 3	369	71.4				
	Comp. 4	349	73.0				
	Vapor Cond.	1083					
1630	Influent	1276		6000			
	Comp. 1	482	62.2				
	Comp. 2	441	65.4				
	Comp. 3	392	69.3				
	Comp. 4	324	74.6				
	Vapor Cond.	1620					

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*Assays of Composited Hourly Samples

TABLE C-13

CHEMICAL ANALYSIS AND PERCENTAGE REDUCTION IN COD

Continuous-Flow Test No.	72349, 14 December
Mean Residence Time, Min./Compartment	14
Volume of Influent Treated, ℓ	132
Volume of Vapor Condensate Collected, ℓ	11.6
Percent of Influent Volume Condensed from Vapor	8.8
Percent of Influent COD Condensed from Vapor	8.2

Time of Sampling, PST	Sampling Station	COD, mg/ℓ	% Red. in COD	Solute Concentration, mg/ℓ			pH
				H_2SO_4	Cℓ*	Amm. N	
1400	Influent	1678		6000	443		1.45
	Comp. 1	580	65.4		437		1.50
	Comp. 2	455	72.9		339		1.50
	Comp. 3	408	75.7		321		1.50
	Comp. 4	377	77.5		284		1.54
	Vapor Cond.	1063			6		3.07
1500	Influent	1549		6000		97	1.43
	Comp. 1	521	66.4			405	1.48
	Comp. 2	492	68.2			409	1.50
	Comp. 3	468	69.8			405	1.50
	Comp. 4	435	71.9			393	1.50
	Vapor Cond.	1633					
1600	Influent	1764		6000			1.44
	Comp. 1	578	67.2				1.48
	Comp. 2	510	71.1				1.50
	Comp. 3	475	73.1				1.50
	Comp. 4	422	76.1				1.50
	Vapor Cond.	1578					
1700	Influent	1321		6000			1.45
	Comp. 1	499	62.2				1.50
	Comp. 2	431	67.4				1.50
	Comp. 3	385	70.9				1.48
	Comp. 4	350	73.5				1.49
	Vapor Cond.	1587					

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*Assays of Composited Hourly Samples

TABLE C-14

CHEMICAL ANALYSIS AND PERCENTAGE REDUCTION IN COD

Continuous-Flow Test No.	72350, 15 December
Mean Residence Time, Min./Compartment	14
Volume of Influent Treated, ℓ	65
Volume of Vapor Condensate Collected, ℓ	4.5
Percent of Influent Volume Condensed from Vapor	6.9
Percent of Influent COD Condensed from Vapor	9.4

Time of Sampling, PST	Sampling Station	COD, mg/ℓ	% Red. in COD	Solute Concentration, mg/ℓ			
				H_2SO_4	Cℓ	Amn. N	pH
1215	Influent	1812		6000	529		1.39
	Comp. 1	530	70.8		466		1.49
	Comp. 2	495	72.7		398		1.48
	Comp. 3	440	75.7		370		1.49
	Comp. 4	390	78.5		364		1.49
	Vapor Cond.	2466			34		

TABLE C-15

CHEMICAL ANALYSIS AND PERCENTAGE REDUCTION IN COD

Continuous-Flow Test No.	72353, 18 December
Mean Residence Time, Min./Compartment	12
Volume of Influent Treated, ℓ	157
Volume of Vapor Condensate Collected, ℓ	6.5
Percent of Influent Volume Condensed from Vapor	4.2
Percent of Influent COD Condensed from Vapor	3.1

Time of Sampling, PST	Sampling Station	COD, mg/ℓ	% Red. in COD	Solute Concentration, mg/ℓ H_2SO_4	Solute Concentration, mg/ℓ Cℓ*	Solute Concentration, mg/ℓ Amm. N	pH
1300	Influent	1672			398		1.37
	Comp. 1	474	71.6		227		1.39
	Comp. 2	437	73.9		307		1.39
	Comp. 3	417	75.0		233		1.39
	Comp. 4	340	79.7		233		1.39
	Vapor Cond.	1291			17		3.09
1400	Influent	1546					1.39
	Comp. 1	450	70.9			142	1.38
	Comp. 2	402	74.0			146	1.40
	Comp. 3	322	79.2			142	1.40
	Comp. 4	301	80.5			145	1.39
	Vapor Cond.	1272					3.05
1500	Influent	1704					1.40
	Comp. 1	446	73.8				1.40
	Comp. 2	382	77.6				1.40
	Comp. 3	321	81.2				1.40
	Comp. 4	387	83.2				1.40
	Vapor Cond.	1138					2.99

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*Assays of Composited Hourly Samples

c. Rate of Wet Oxidation

Table C-16 presents a summary of rate parameters for the foregoing continuous-flow tests as calculated from chemical analysis of the hourly samples. Table C-17 is a compilation of k-values for the seven runs. Three general levels of process efficacy are apparent:

(1) Wet oxidation of non-saline wastewaters in the absence of carbon.

(2) Wet oxidation of non-saline wastewaters in the presence of carbon.

(3) Wet oxidation of saline wastewaters in the presence of carbon.

The rate of wet oxidation is greatest in the second case: About 3/4 to 4/5 of the organic matter contained in non-saline wastewaters is destroyed in the presence of carbon by a rate process which is two and one-half times faster than in the absence of carbon; and the remaining COD, representing 1/5 to 1/4 of the original organic matter, oxidizes at a rate which is at least 50 percent faster than in any other observed environment.

Based on the typical values listed in Table C-17, 90 percent of the influent COD would be reduced by a 60-minute treatment in a four-compartment reactor containing the small amount of carbonaceous catalyst used in Run 72332 (a ratio of area of catalyst to volume of wastewater equal to 0.015 cm^{-1}). In 40 minutes, nearly 83 percent would be destroyed.

Something in sea water, however, retarded wet oxidation. In the treatment of wastewaters containing a level of salinity commensurate with that present in combined shipboard wastewaters, wet oxidation proceeds by a series of chemical reactions which is slower than in non-saline water. Even more importantly, the transition to the slow rate-limiting process occurs earlier when saline liquors are oxidized than when the influent is non-saline: About two-thirds of the organic matter is destroyed by a chemical reaction which is two and one-half times slower than in non-saline influent; whereas the remaining COD is reduced at a rate which is one-fourth of that limiting final oxidation in non-saline influents. Consequently, in a 60-minute treatment in a four-compartment reactor, about 74 percent of the COD is reduced; and, in a total residence time of 40 minutes, about 62 percent is reduced.

TABLE C-16

CALCULATED REACTION RATE PARAMETERS

Continuous-Flow Runs of December 1972

Test No.	Time of Sampling, PST	Compartment	-r, mg/ℓ O min.$^{-1}$	k, min.$^{-1}$
72343	1300	1	126.2	0.25
		2	5.2	0.012
		3	5.9	0.017
		4	5.3	0.020
	1400	1	116.3	0.24
		2	4.6	0.011
		3	5.0	0.015
		4	6.5	0.025
	1530	1	104.3	0.22
		2	5.0	0.012
		3	2.2	0.006
		4	4.7	0.015
	1630	1	84.7	0.22
		2	1.4	0.004
		3	1.9	0.006
		4	2.8	0.010
72346	1300	1	67.4	0.088
		2	2.8	0.004
		3	1.6	0.002
		4	1.7	0.002
	1430	1	77.1	0.12
		2	1.7	0.003
		3	3.7	0.006
		4	1.5	0.003
72347	1300	1	71.3	0.13
		2	3.0	0.006
		3	1.9	0.004
		4	2.1	0.005
	1400	1	71.4	0.114
		2	6.8	0.013
		3	3.7	0.008
		4	2.9	0.007
	1530	1	54.8	0.116
		2	4.3	0.010
		3	2.9	0.008
		4	1.5	0.004
	1630	1	52.9	0.110
		2	2.9	0.007
		3	3.5	0.009
		4	5.0	0.015

TABLE C-16

(Continued)

Test No.	Time of Sampling, PST	Compartment	-r mg/ℓ O min.$^{-1}$	k, min.$^{-1}$
72349	1400	1	73.2	0.126
		2	8.9	0.019
		3	3.4	0.008
		4	2.3	0.006
	1500	1	68.5	0.132
		2	2.1	0.004
		3	1.7	0.004
		4	2.4	0.006
	1600	1	79.0	0.137
		2	4.8	0.009
		3	2.5	0.005
		4	3.9	0.009
	1700	1	54.8	0.110
		2	4.8	0.011
		3	3.3	0.009
		4	2.6	0.007
72350	1300	1	85.5	0.161
		2	2.5	0.005
		3	4.0	0.009
		4	3.6	0.009
72353	1300	1	91.4	0.193
		2	3.0	0.007
		3	1.6	0.004
		4	6.4	0.019
	1400	1	83.7	0.186
		2	3.9	0.010
		3	6.6	0.020
		4	1.8	0.006
	1500	1	96.0	0.215
		2	5.2	0.014
		3	5.0	0.016
		4	2.8	0.010
72332	1500	1	63.6	0.067
		2	21.0	0.034
		3	2.7	0.005
		4	3.9	0.007
	1600	1	53.4	0.062
		2	19.1	0.034
		3	3.4	0.007
		4	6.8	0.017
	1645	1	69.0	0.10
		2	9.3	0.017
		3	4.5	0.009
		4	5.1	0.015

TABLE C-17

COMPARISON OF VALUES FOR REACTION RATE CONSTANT

Preliminary Continuous-Flow Runs of November and December 1972

Run No.	Pertinent Conditions	Observed Reaction Rate Constant				Transition in Rate Limiting Step, % Red. in COD
		k_i, min.$^{-1}$		k_ℓ, min.$^{-1}$		
		Range	Typical	Range	Typical	
72332	No Carbon; Non-Saline Influent		0.10		0.015	50 - 60
72343	Small Amount of Carbon; No Salinity	0.22 - 0.25	0.24	0.011 - 0.025	0.020	80
72346	Small Amount of Carbon; Typical Salinity	0.09 - 0.12	0.1	0.002 - 0.006	0.005	55 - 65
72347	Small Amount of Carbon; Moderate Salinity	0.11 - 0.13	0.12	0.004 - 0.015	0.010	65
72349	Small Amount of Carbon; High Urinous Influent	0.11 - 0.14	0.13	0.004 - 0.019	0.010	65
72350	Small Amount of Carbon; Recycled Condensate		0.15		0.01	70
72353	Small Amount of Carbon; No Salinity; Reduced Residence	0.19 - 0.22	0.20	0.004 - 0.020	0.02	70 - 75

C.3.2 TESTS WITH BARBER-COLMAN CO. CATALYSTS

This series of continuous-flow tests is the first in this program in which Barber-Colman Co. catalysts were used. A number were known to us from previous work. Particularly promising ones are Barber-Colman Company catalysts 22,368 and 10,480. In continuous-flow tests in the same four-compartment reactor on wastewaters from a citrus processing plant, over 95 percent reduction in COD was achieved by the use of catalyst 10,480. The pertinent operating conditions were identical to the December series of continuous-flow tests on simulated shipboard sewage.) The Barber-Colman catalysts are very effective in the presence of carbon and on relatively mild acidic liquors. For instance, the citrus wastewaters were treated at pH 3.8--the natural acidity.

a. Modification of System

On completion of the test series described in Section C.3.1, the four-compartment reactor was disassembled and lined with additional catalytic carbon. The amount of carbon was greatly increased. Presently, the area of carbon per volume of solution (the so-called specific area in cm^{-1}) is 0.16, 0.22, 0.17 and 0.18 in compartments 1, 2, 3 and 4, respectively. The available surface for catalysis has been increased by a factor of ten. In the batch tests described in Section C.2; the second monthly report, however, the specific area was 0.72 cm^{-1}. In other words, in the batch tests, there is about four times as much carbon surface as in the continuous-flow tests.

b. Description of the Individual Continuous-Flow Tests

During January and February, 1973, two continuous-flow tests were conducted in the reassembled reactor. Barber-Colman Company catalysts were used in all tests. The first test was performed to demonstrate the use of Barber-Colman catalyst 22,368 on non-saline wastewater of reduced acidity. The catalyst (BC-22,368) achieves the same level of oxidation with one-sixth as much acid as identical tests without the catalyst. In the other tests, Barber-Colman Company catalyst 10,480 was used. Nearly 75 percent reduction in COD was obtained in continuous-flow wet oxidation of saline influent in the presence of the catalyst (10,480); whereas in the absence of the catalyst in otherwise identical tests employing six times as much acid, about 65 percent reduction was achieved.

(1) Treatment of Non-Saline Sewage With Barber-Colman Co. Catalyst 22,368--Test Number 7302(

A non-saline body sewage was prepared as influent for the test by macerating accumulated feces (equivalent to the daily excretions of four people) with three liters of urine and diluting the mixture with water containing 100 mℓ concentrated sulfuric acid to a total volume of 47.5 gallons. The influent contained organic matter exhibiting a COD of about 1265 mg/ℓ 0 and was acidified with one-sixth as much acid (1 g/ℓ H_2SO_4) as in previous tests.

During the first portion of the test, the reactor was operated with Barber-Colman Company catalyst 22,368 in all compartments. Immediately after sampling the compartments at 1430, the catalyst was removed.

The operating conditions for the test and other pertinent data are summarized in Table C-18. Chemical analysis of hourly samples is summarized in Table C-19.

The test indicates that with the use of Barber-Colman Company catalyst 22,368 nearly 90 percent reduction in COD was achieved using one-sixth as much acid as would otherwise be needed. (See Test No. 72343, Section C.3.1.b(1).

(2) Treatment of Saline Sewage With Barber-Colman Co. Catalyst 10,480--Test Number 73029

A saline body sewage was prepared as influent for this test by blending fifteen gallons of Newport Bay water, one liter of urine, 50 mℓ conc. H_2SO_4, and macerated feces (equivalent to two day's per-capita excretions) with 12.5 gallons of influent from Test No. 73026 and diluting the mixture with tap water to a total volume of 40 gallons. The influent had a COD of about 1765 mg/ℓ 0 and contained 1 g/ℓ H_2SO_4; it was comparable to the influent of Test No. 73026 but contained sea water. (The influent assayed about 7200 g/ℓ Cℓ.)

Pertinent operating data for the test are listed in Table C-20. Chemical analysis of influent and effluents is given in Table C-21. During this test, the Barber-Colman Company catalyst 10,480 was present in all compartments. The flow of air was varied intentionally during the test, and the amount of oxygen supplied ranged from twice to four times the COD.

(3) Treatment of Non-Saline, pH 2 Sewage in Presence of Barber-Colman Company Catalyst 10,480 (Test No. 73051)

Feces (equivalent to the daily excretions of three to four people) were macerated with 3 - 3.5 liters of urine and diluted to 45 gallons with tap-water containing 270 mℓ concentrated sulfuric acid. The resulting mixture, which was about pH 1.8, was used as influent in Test No. 73051. The test was conducted in a four-compartment, carbon-lined reactor.

The operating conditions for the test and other pertinent data are summarized in Table C-22. Barber-Colman Company Catalyst 10,480 was present in all compartments throughout the test.

TABLE C-18

OPERATING CONDITIONS
AND OTHER PERTINENT DATA

Test No. 73026

Reactor Temperature, °F	
Compartment 1	480-470
Compartment 2	465-460
Compartment 3	445-440
Compartment 4	435-425
Reactor Pressure, psi	
Total	605-585
Steam	550-500
Air Flow, scfm	0.60
Influent Flow, Liters/Minute	0.533
Agitator Speed, rpm	770
Total Volume of Vapor Condensate, ℓ	5
Total Volume of Influent Treated, ℓ	131

TABLE C-19

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENTS

Test No. 73026

Time of Sampling, PST	Sampling Station	COD, mg/ℓ	% Red. in COD	-r mg/ℓ min.$^{-1}$	k, min.$^{-1}$	pH
1330	Influent	1240				2.2
	Comp. 1	255	79.4	71.4	0.279	2.2
	Comp. 2	--				2.2
	Comp. 3	174	86.0			2.1
	Comp. 4	122	90.2	4.4	0.036	2.4
	Vapor Cond.	225				3.4
1430	Influent	1244				2.4
	Comp. 1	317	74.5	67.2	0.211	2.4
	Comp. 2	230	81.5	6.4	0.027	2.4
	Comp. 3	170	86.3	4.4	0.025	2.4
	Comp. 4	115	90.8	4.7	0.040	2.4
	Vapor Cond.	560				
1530	Influent	1439				2.4
	Comp. 1	414	71.2	73.7	0.173	2.4
	Comp. 2	324	77.5	6.6	0.020	2.4
	Comp. 3	275	80.9	3.6	0.013	2.4
	Comp. 4	211	85.3	5.5	0.026	2.5
	Vapor Cond.	869				2.8
1630	Influent	1140				
	Comp. 1	409	64.1	52.6	0.129	2.4
	Comp. 2	327	71.3	6.0	0.018	2.4
	Comp. 3	280	75.4	3.5	0.012	2.4
	Comp. 4	163	85.7	10.0	0.061	2.6
	Vapor Cond.	851				2.8

TABLE C-20

PERTINENT OPERATING CONDITIONS AND OTHER DATA

Test No. 73029

Reactor Temperature, °F	
Compartment 1	480-470
Compartment 2	463-460
Compartment 3	447-440
Compartment 4	435-415
Reactor Pressure, psi	
Total	605-580
Steam	550-500
Air Flow, scfm	0.6-0.3
Influent Flow, Liters/Minute	0.533
Agitator Speed, rpm	780
Total Volume of Vapor Condensate, ℓ	3.7
Total Volume of Influent Treated, ℓ	136

TABLE C-21

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENTS

Test No. 73029

Time of Sampling, PST	Sampling Station	COD, mg/ℓ	% Red. in COD	-r mg/ℓ O min.$^{-1}$	k, min.$^{-1}$	pH	Oxygen Supplied/ Oxygen Demanded
1130	Influent	1882				2.3	4.0
	Comp. 1	528	71.9	97.4	0.184	2.6	
	Comp. 2	481	74.4	3.4	.007	2.7	
	Comp. 3	396	79.0	6.3	.016	2.6	
	Comp. 4	329	82.5	5.7	.017	2.7	
1230	Influent	1855				2.3	3.5
	Comp. 1	807	56.5	75.4	0.093	2.7	
	Comp. 2	642	65.4	12.0	.019	2.8	
	Comp. 3	559	69.9	6.1	.011	2.7	
	Comp. 4	492	73.5	5.7	.012	2.8	
1330	Influent	1624					4.1
	Comp. 1	608	62.6	73.1	0.120	2.8	
	Comp. 2	527	67.6	5.9	.011	2.8	
	Comp. 3	448	72.4	5.9	.013	2.8	
	Comp. 4	416	74.4	2.7	.007	2.8	
1430	Influent	1701				2.4	2.4
	Comp. 1	557	67.3	82.3	0.148	3.0	
	Comp. 2	492	71.1	4.7	.010	3.0	
	Comp. 3	470	72.4	1.6	.003	2.8	
	Comp. 4	438	74.3	2.7	.006	2.9	

TABLE C-22

OPERATING CONDITIONS AND OTHER PERTINENT DATA

Test No. 73051

Reactor Temperature, °F	
Compartment 1	473-480
Compartment 2	455-460
Compartment 3	430-435
Compartment 4	395-405
Reactor Pressure, psi	
Total	550-605
Steam	515-550
Air Flow, scfm	0.4
Influent Flow, Liters/Minute	0.5
Agitator Speed, rpm	800
Total Volume of Vapor Condensate, ℓ	2.25
Total Volume of Influent Treated, ℓ	146
Mean Over-All Residence Time, Minutes	57

Chemical analysis of hourly samples is summarized in Table C-23. From 1300 to 1645--from commencement of sampling to termination of the test--the final effluent was impounded, allowed to settle overnight and assayed for COD. Based on chemical analysis of the composited effluent, the mean of the influent assays, and the mean of vapor-condensate assays, the over-all reduction in COD was about 89 percent:

Total Amount of COD Treated:	330.4 g
Total Amount of COD Condensed from Vapor:	1.7 g
Percent of COD Contained in Vapor Condensate:	1.1 %
Percent of COD Contained in Liquid Effluent:	9.5 %

In this test, the air flow was sufficient to maintain a mean ratio of O_2 : COD of 2.35. In other words, more than twice as much oxygen was supplied as was required according to the chemical oxygen demand (COD).

(4) Treatment of Non-Saline, pH 5 Sewage in the Presence of Barber-Colman Company Catalyst 10,480 (Test No. 73054)

Feces and urine equivalent to 3 pcd (per-capita-day) excretions were macerated and diluted with tapwater to a total volume of 42 gallons. The above mixture, which was used as influent in Test No. 73054, contained no sulfuric acid.

The operating conditions for the test and other pertinent data are summarized in Table C-24. Barber-Colman Company Catalyst 10,480 was present in all compartments throughout the test.

Chemical analysis of influent and effluent samples is summarized in Table C-25 Effluent was impounded from 1130, when the first samples were taken, until 1430, at which time the test was terminated.

Comparison of the test results with those from the previous test indicate that the catalyst performs better in the presence of a mineral acid such as H_2SO_4 than in the presence of organic acids alone.

TABLE C-23

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENT

Test No. 73051

Time of Sampling, PST	Sampling Station	COD, mg/ℓ	% Red. in COD	$-r$ mg/ℓ O min.$^{-1}$	k, min.$^{-1}$	pH
1300	Influent	2815				1.9
	Comp. 1	730	74.1	141.[illegible]	0.194	1.9
	Comp. 2	664	76.4	4.5	0.007	2.0
	Comp. 3	452	83.9	14.6	0.032	2.0
	Comp. 4	391	86.1	4.7	0.012	2.2
	Vapor Cond.	1610				3.6
1400	Influent	2568				1.8
	Comp. 1	521	79.7	138.8	0.266	1.8
	Comp. 2	373	85.5	10.1	0.027	2.0
	Comp. 3	322	87.5	3.5	0.011	2.0
	Comp. 4	No Samples				
	Vapor Cond.	1669				4.0
1500	Influent	2070				1.8
	Comp. 1	454	78.1	109.6	0.241	2.0
	Comp. 2	374	81.9	5.5	0.015	2.0
	Comp. 3	291	85.9	5.7	0.020	2.0
	Comp. 4	239	88.5	4.0	0.017	2.0
	Vapor Cond.	1612				3.3
1600	Influent	1950				1.7
	Comp. 1	418	78.6	103.9	0.248	1.9
	Comp. 2	340	82.6	5.3	0.016	1.8
	Comp. 3	253	86.5	5.3	0.020	1.9
	Comp. 4	207	89.4	4.4	0.021	2.0
	Vapor Cond.	1612				3.9
1645	Influent	1911				1.7
	Comp. 1	382	80.0	103.7	0.271	1.8
	Comp. 2	316	83.5	4.5	0.014	1.8
	Comp. 3	233	87.8	5.7	0.025	1.9
	Comp. 4	199	89.6	2.6	0.013	1.9
	Vapor Cond.	1810				3.9
Composited Effluent:		219	90.3			

TABLE C-24

OPERATING CONDITIONS AND OTHER PERTINENT DATA

Test No. 73054

Reactor Temperature, °F	
Compartment 1	470-480
Compartment 2	450-460
Compartment 3	437-443
Compartment 4	415-420
Reactor Pressure, psi	
Total	565-605
Steam	500-550
Air Flow, scfm	0.4
Influent Flow, Liters/Minute	0.5
Agitator Speed, rpm	800
Total Volume of Vapor Condensate, ℓ	2.2
Total Volume of Influent Treated, ℓ	129
Mean Over-All Residence Time, Minutes	55

TABLE C-25

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENT

Test No. 73054

Time of Sampling, PST	Sampling Station	COD, mg/ℓ	% Red. in COD	-r mg/ℓ O min.$^{-1}$	k, min.$^{-1}$	pH
1130	Influent	1880				6.3
	Comp. 1	632	66.4	87.3	0.138	5.0
	Comp. 2	556	70.4	5.4	0.010	4.5
	Comp. 3	504	73.2	3.7	0.007	3.9
	Comp. 4	388	79.4	9.4	0.024	3.6
	Vapor Cond.	1520				4.6
1230	Influent	1860				6.4
	Comp. 1	672	63.9	83.1	0.124	5.0
	Comp. 2	528	71.6	10.1	0.019	4.8
	Comp. 3	476	74.4	3.7	0.008	4.8
	Comp. 4	386	79.2	7.3	0.019	4.6
	Vapor Cond.	1700				5.8
Composited Effluent:		332	80.6			

C.4 TESTS PERFORMED IN UNLINED REACTORS

Several series of continuous-flow tests were conducted in titanium reactors which were unlined. That is to say, the wetted wall of the reaction chamber was not lined with porous carbon.

Tests were performed in two reactors: the 4-compartment reactor described in Section 3 of the main report and the two-compartment reactor built for the Coast Guard as a part of this program and described in Section 5.

C.4.1 CONTINUOUS-FLOW TESTS ON SHIPBOARD SEWAGE IN AN UNLINED 4-COMPARTMENT REACTOR

These were the first tests on shipboard sewage in which Barber-Colman Company Catalyst 10,480 was used in a titanium reactor which was not carbon lined, and the first tests conducted at an agitator speed above 800 rpm.

a. Modifications to the System

At the conclusion of the test series reported in Section C.3.2, the reactor was disassembled and the carbon lining was removed. The carbon was in excellent condition, there was no sign of chemical attack, and there was also no indication that any titanium component was undergoing corrosion.

Requisite adjustments were made to enable the speed of the four agitators to be increased to 1200 rpm. (A new Magnadrive agitator was installed in the first compartment.)

A high-pressure metering pump was installed so that additives like sulfuric acid could be introduced directly into the reaction chambers of the autoclave and influent could be pumped unacidified into the reaction zone.

Provisions were made to enable influent to be pumped directly to the first compartment from the blow-case pumps. (In other words, the external heat exchanger was by-passed. The internal heat exchanger was also circumvented. Heretofore, in all continuous-flow tests influent was introduced into the reactor by pumping the slurry through an external heat exchanger, into an internal heat exchanger (located in the fourth compartment of the reactor), and then to the first compartment.

b. Descriptions of Individual Tests

During March 1973, eight additional continuous-flow tests were conducted in which wet oxidation was investigated under a variety of conditions:

(1) At three levels of temperature: 412, 435 and 460 - 470°F.

(2) With and without Barber-Colman Company Catalyst 10,480.

(3) In saline and nonsaline water.

(4) At influent flow rates resulting in residence times of 15, 17.5, 20 and 30 minutes per compartment.

(5) At two levels of air supply: 0.6 and 0.2 scfm.

(6) Utilizing several methods of influent and additive addition.

In this series of tests, the agitator speed was maintained at 1200 rpm, whereas in previous tests, the speed was 800 rpm. Percentage reduction in COD ranged from 66 to 94 in the four-compartment reactor, which was not lined with carbon or any other substance.

Each test is summarized in a following subsection. An over-all summary is presented as Table C-26.

(1) Wet Oxidation Without Internal Heat Exchanger--Continuous-Test No. 73064

In this test, feces and urine were blended, in tap water, acidified with sulfuric acid, and pumped to the first compartment directly from the external heat exchanger. In previous tests, the influent passed through two heat exchangers--one located externally and the other internally in the fourth compartment of the autoclave. In past tests, passage of influent through the internal heat exchanger has resulted in the temperature of the fourth compartment being substantially cooler than the other compartments. There are no indications that the over-all process is less effective when the fourth compartment is colder than the others; moreover, efficient heat exchange is essential for practical wet oxidation. Notwithstanding, the use of the internal heat exchanger was discontinued to facilitate the investigation of the operating variables and analysis of the test data. In other words, the present series of tests were performed under more nearly isothermal conditions. The mean temperatures and other operating conditions are tabulated for the test in Table C-27. The temperature gradient in the reactor was about 30 - 35°F from compartment 1 to compartment 4; whereas in previous tests--like Test No. 73054 the average temperature gradient has been about 50 - 55°F.

Barber-Colman Company Catalyst 10,480 was present in each compartment of the reactor which did not contain any internal lining of carbon.

The agitator speed was 1200 rpm, whereas in past tests, the speed was generally 800 rpm.

Chemical analysis of influent and effluents is presented in Table C-28.

TABLE C-26

CONTINUOUS-FLOW TESTS PERFORMED IN UNLINED 4-COMPARTMENT REACTOR

Test No.	Mean Temp., °F First Compart.	Catalyst	Flushing Liquid*	Mean Residence Time, Minutes	Mean % Red. in COD	Air Supply			Method of Influent Addition*	Influent COD, mg/ℓ O
						O_2:COD	scfm	Minimum Over-Pressure, psi		
73064	468	10,480	TW	30	76.1	4	0.5	75	ET	1832
				45	79.1					
				60	82.4					
73068	435	10,480	TW	30	73.0	4	0.6	235	ET	2209
				45	76.8					
				60	80.2					
73072	435	10,480	$\frac{2}{3}$TW, $\frac{1}{3}$SW	30	69.1	3	0.6	215	ET	2539
				45	70.6					
				60	71.8					
73075	412	10,480	TW	35	59.4	4	0.6	290	NT	2171
				55	64.0					
				70	66.4					
73079	465	10,480	TW	30	86.7	2	0.2	50	NT	2150
				60	89.1					
				90	91.6					
				120	94.1					
73082	465	10,480	TW	20	78.0	1.1	0.2	75	NP	3365
				40	82.0					
				60	83.5					
				80	85.5					
73086	460	None	$\frac{2}{3}$TW, $\frac{1}{3}$SW	20	69.6	1.3	0.2	75	NTR	2738
				40	70.4					
				60	73.3					
				80	75.1					
73089	460	None	$\frac{2}{3}$TW, $\frac{1}{3}$SW	20	72.0	1.4	0.2	75	NTR	2627
				40	75.6					
				60	78.7					
				80	80.8					

* Tap Water is denoted by "TW"; Sea Water by "SW". The various methods of addition are denoted by the following letter symbols:

P - Additive Pump
N - No Heat Exchanger
E - External Heat Exch.
I - Internal Heat Exch.
T - Additives in Head Tank
R - Condensate recycled.

TABLE C-27

OPERATING CONDITIONS AND OTHER PERTINENT DATA

Test No. 73064

Reactor Temperature, °F	
Compartment 1	475-460
Compartment 2	455-450
Compartment 3	445-435
Compartment 4	440-435
Reactor Pressure, psi	
Total	600
Steam	525
Air Flow, scfm	0.5
Influent Flow, Liters/Minute	0.5
Agitator Speed, rpm	1200
Total Volume of Vapor Condensate, ℓ	2
Total Volume of Influent Treated, ℓ	84
Mean Over-All Residence Time, Minutes	60
Catalyst	10,480

TABLE C-28

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENTS

Test No. 73064

Time, PST	Sampling Station	COD, mg/ℓ O	% Red. in COD	-r, mg/ℓ O min.$^{-1}$	k, min.$^{-1}$	pH
1100	Influent	1853				1.5
	Comp. 1	627	66.2	74.8	0.119	1.7
	Comp. 2	385	79.2	15.4	0.040	1.7
	Comp. 3	322	82.6	4.2	0.013	1.7
	Comp. 4	270	85.4	4.0	0.015	1.7
	Vapor Cond.	1001				3.2
1130	Influent	1797				1.5
	Comp. 1	639	64.4	70.6	0.110	1.6
	Comp. 2	421	76.6	13.9	0.033	1.6
	Comp. 3	353	80.4	4.5	0.013	1.7
	Comp. 4	294	83.6	4.5	0.015	1.7
	Vapor Cond.	977				3.2
1200	Influent	1313				1.6
	Comp. 1	647	64.3	71.1	0.110	1.7
	Comp. 2	449	75.2	12.6	0.028	1.7
	Comp. 3	365	79.9	5.6	0.015	1.6
	Comp. 4	306	83.1	4.5	0.015	1.7
	Vapor Cond.	1001				3.2
1300	Influent	1866				1.6
	Comp. 1	607	67.5	76.8	0.126	1.7
	Comp. 2	429	77.0	11.3	0.026	1.7
	Comp. 3	405	78.3	1.6	0.004	1.7
	Comp. 4	341	81.7	4.9	0.014	1.7
	Vapor Cond.	969				3.1

(2) Low-Temperature (410-440°F) Wet Oxidation of Non-Saline Sewage--Continuous-Flow Test No. 73068

In this test macerated feces and urine were suspended in acidified tap water and fed to the four-compartment reactor which was maintained at lower temperature (410 - 440°F) than in past tests. Pertinent operating conditions are listed in Table C-29. Barber-Colman Company Catalyst 10,480 was present in all compartments. As was the case in the preceding test, the internal heat exchanger was by-passed to obtain a smaller thermal gradient.

Chemical analysis of influent and effluents is summarized in Table C-30. The mean percentage reduction in COD (based on four consecutive hourly samples) is 80.2 (for 60 minute's residence) which is not greatly different than the mean (82.4%) for otherwise comparable treatment at 470°F (c.f., Test No. 73064). In both tests (Nos. 73064 and 73068), the ratio O_2 : COD was about 4; i.e., four times as much oxygen was supplied as required, according to COD analysis. Because the temperature was substantially less in Test No. 73068, the combined overpressure of gases (nitrogen, oxygen, carbon dioxide, carbon monoxide, etc.) was greater (235 psi) in that test than in Test No. 73064. As the concentration of dissolved oxygen (DO) obeys Henry's Law, the DO in Test No. 73068 probably was greater than in Test No. 73064.

(3) Low-Temperature (410-440°F) Wet Oxidation of Saline Sewage--Continuous-Flow Test No. 73072

In this test, all operating conditions (which are listed in Table C-31) were essentially the same as in the previous one (Test No. 73068); the influent in this test, however, was saline: Feces were macerated in urine and a mixture of one part Newport Bay water and two parts acidified tap water. Barber-Colman Company Catalyst 10,480 was present in all compartments. No internal heat exchanger was used.

Chemical analysis of influent and effluents is presented in Table C-32. As in the past, the percentage reduction in COD is less for treatment of saline wastewater than for treatment of non-saline wastewater under otherwise comparable conditions.

(4) Low-Temperature (400-410°F) Wet Oxidation (Without Any Heat Exchanger)--Continuous-Flow Test No. 73075

In this test, wet oxidation was conducted at about the lowest practical temperature (400 - 410°F). Influent was pumped directly to the first compartment from the blow-case pumps. (Neither the external nor the internal heat exchanger was used.) The rate of influent flow was slightly less than in the preceding tests of this series. (Operation at reduced flow and direct feeding were necessary to obtain a low, nearly isothermal reactor temperature.) The influent consisted of macerated feces and urine in acidified tap water. Barber-Colman Company Catalyst 10,480 was present in each compartment. The operating conditions are listed in Table C-33.

Chemical analysis of influent and effluents is presented in Table C-34. The mean percentage reduction (based on three consecutive hourly samplings) is 66.4 (for a total mean residence time of 68 minutes). Efficacy at 410°F

TABLE C-29

OPERATING CONDITIONS AND OTHER PERTINENT DATA

Test No. 73068

Reactor Temperature, °F	
Compartment 1	440-425
Compartment 2	428-420
Compartment 3	416-408
Compartment 4	416-408
Reactor Pressure, psi	
Total	600, max.
Steam	365, max.
Air Flow, scfm	0.6
Influent Flow, Liters/Minute	0.5
Agitator Speed, rpm	1200
Total Volume of Vapor Condensate, ℓ	3
Total Volume of Influent Treated, ℓ	135
Mean Over-All Residence Time, Minutes	60
Catalyst	10,480

TABLE C-[illegible]

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENTS

Test No. 73068

Time, PST	Sampling Station	COD, mg/ℓ O	% Red. in COD	-r, mg/ℓ O min.$^{-1}$	k, min.$^{-1}$	pH
1030	Influent	2260				1.6
	Comp. 1	633	72.0	102.3	0.162	1.6
	Comp. 2	546	75.8	5.4	0.010	1.6
	Comp. 3	487	78.5	3.8	0.008	1.6
	Comp. 4	405	82.1	6.2	0.015	1.6
	Vapor Cond.	1651				3.1
1130	Influent	2290				1.6
	Comp. 1	645	71.8	103.5	0.160	1.7
	Comp. 2	558	75.6	5.4	0.010	1.7
	Comp. 3	503	78.0	3.6	0.007	1.7
	Comp. 4	429	81.3	5.6	0.013	1.7
	Vapor Cond.	1572				3.1
1230	Influent	2339				1.6
	Comp. 1	664	71.6	105.3	0.159	1.6
	Comp. 2	574	75.4	5.6	0.010	1.6
	Comp. 3	507	78.3	4.4	0.009	1.6
	Comp. 4	430	81.6	5.8	0.013	1.6
	Vapor Cond.	1356				3.2
1330	Influent	1946				1.6
	Comp. 1	672	65.5	80.1	0.119	1.6
	Comp. 2	623	68.0	3.0	0.005	1.7
	Comp. 3	503	74.2	7.8	0.015	1.7
	Comp. 4	436	77.6	5.0	0.0115	1.7
	Vapor Cond.	1396				3.2
Composited Effluent:		434				1.6

TABLE C-31

OPERATING CONDITIONS AND OTHER PERTINENT DATA

Test No. 73072

Reactor Temperature, °F	
Compartment 1	445-425
Compartment 2	425-420
Compartment 3	420-415
Compartment 4	415-410
Reactor Pressure, psi	
Total	600
Steam	385
Air Flow, scfm	0.6
Influent Flow, Liters/Minute	0.5
Agitator Speed, rpm	1200
Total Volume of Vapor Condensate, ℓ	3
Total Volume of Influent Treated, ℓ	144
Mean Over-All Residence Time, Minutes	60
Catalyst	10,480

TABLE C-32

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENTS

Test No. 73072

Time, PST	Sampling Station	COD, mg/ℓ O	% Red. in COD	-r, mg/ℓ O min.$^{-1}$	k, min.$^{-1}$	pH	Cℓ
1100	Influent	2536				1.6	5592
	Comp. 1	859	66.1	105.5	0.123	1.7	5482
	Comp. 2	769	69.7	5.6	0.007	1.7	5208
	Comp. 3	712	71.9	3.7	0.005	1.7	5044
	Comp. 4	655	74.2	4.3	0.007	1.7	4989
	Vapor Cond.	878				4.1	219
1200	Influent	2509				1.6	5757
	Comp. 1	1128	55.0	86.9	0.111	1.7	5702
	Comp. 2	780	68.9	21.6	0.028	1.7	5263
	Comp. 3	729	70.9	3.3	0.005	1.7	5154
	Comp. 4	670	73.3	4.4	0.007	1.7	5200
	Vapor Cond.	2064				3.9	319
1300	Influent	2536				1.6	5921
	Comp. 1	1152	54.6	87.0	0.076	1.6	5866
	Comp. 2	800	68.5	21.9	0.027	1.6	5428
	Comp. 3	754	70.3	3.0	0.004	1.5	5263
	Comp. 4	721	71.6	2.5	0.003	1.6	5428
	Vapor Cond.	2201				3.8	219
1400	Influent	2575				1.6	6031
	Comp. 1	1219	52.7	85.3	0.070	1.7	5702
	Comp. 2	776	69.9	27.5	0.035	1.7	5702
	Comp. 3						
	Comp. 4	761	70.5			1.7	
	Vapor Cond.	2365				3.9	219

TABLE C-33

OPERATING CONDITIONS AND OTHER PERTINENT DATA

Test No. 73075

Reactor Temperature, °F	
Compartment 1	425-400
Compartment 2	410-400
Compartment 3	400-395
Compartment 4	395-390
Reactor Pressure, psi	
Total	600
Steam	310
Air Flow, scfm	0.6
Influent Flow, Liters/Minute	0.5
Agitator Speed, rpm	1200
Total Volume of Vapor Condensate, ℓ	2
Total Volume of Influent Treated, ℓ	121
Mean Over-All Residence Time, Minutes	68
Catalyst	10,480

TABLE C-34

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENTS

Test No. 73075

Time, PST	Sampling Station	COD, mg/ℓ O	% Red. in COD	-r, mg/ℓ O min.$^{-1}$	k, min.$^{-1}$	pH
1200	Influent	1986				1.6
	Comp. 1	939	53.1	58.8	0.063	1.7
	Comp. 2	882	55.7	3.2	0.004	1.6
	Comp. 3	786	60.7	5.6	0.007	1.6
	Comp. 4	728	63.6	3.9	0.005	1.6
	Vapor Cond.	1675				3.5
1300	Influent	2393				1.6
	Comp. 1	921	61.5	82.7	0.090	1.6
	Comp. 2	862	64.0	3.3	0.004	1.6
	Comp. 3	765	68.0	5.7	0.007	1.6
	Comp. 4	722	69.8	2.9	0.004	1.6
	Vapor Cond.	2414				3.5
1430	Influent	2134				1.6
	Comp. 1	931	56.4	67.6	0.073	1.6
	Comp. 2	888	58.4	2.4	0.003	1.6
	Comp. 3	782	63.4	6.2	0.008	1.7
	Comp. 4	730	65.8	3.5	0.005	1.7
	Vapor Cond.	1835				3.4
Composited Effluent:		651				1.6

(5) Nearly Isothermal (450°F) Wet Oxidation (Without Any Heat Exchanger)--Continuous-Flow Test No. 73079

In this test, macerated feces and urine were suspended in acidified tap-water and fed directly from the blow-case pumps to the first compartment whose temperature fluctuated continuously from 480 to 450°F with the frequency of influent addition.* (The remainder of the reactor was 445°F or greater; see Table C-35 for a listing of temperatures and other pertinent operating conditions.) The rate of influent addition was considerably less in this test than in any other. (As in the previous test, reduced flow and direct feeding were essential to achieve the desired environment--in this case, a fairly hot, nearly isothermal reactor.)

Chemical analysis of influent and effluents is presented in Table C-36. Note that the mean percentage reduction in COD achieved in the first compartment in this test--30 minutes' residence time--is significantly greater than that achieved in other tests in which a residence time of 30 minutes was achieved in two compartments; e.g., Test No. 73064 (Tables I and III) in which the residence time per compartment was about 15 minutes.

(6) Direct Addition of Acid--Continuous-Flow Test No. 73082

In this test, sulfuric acid was added directly to the first compartment by a high-pressure metering pump, and unacidified influent--macerated feces and urine in tap-water--was pumped directly to the first compartment. The rates of addition for influent and additive were set to yield a combined flow of 0.4 ℓ/minute. Thus, in this test, the residence time was about 20 minutes per compartment. Flow rate and other pertinent operating data are summarized in Table C-37. Barber-Colman Company Catalyst 10,480 was present in all compartments.

Chemical analysis of influent and effluents is presented in Table C-38.

(7) Nearly Isothermal (450°F) Wet Oxidation of Saline Sewage--Continuous-Flow Test No. 73086

In this test, feces and urine were macerated with one part saline (Newport Bay) water and two parts acidified tap-water and fed to the first compartment directly from the blow-case pumps. No catalyst was present. Vapor condensate was recycled continuously to the influent head tank. Pertinent operating conditions are listed in Table C-39.

Chemical analysis of influent and effluents are presented as Table C-40. The mean percentage reduction in COD is 75.1 percent, based on five hourly samplings. The percentage reduction is remarkably high for a saline influent, especially in view of the fact that the agitator in the second compartment did not operate during the test: Note that the values of k

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*Temperature fluctuation in the first compartment always occurs, but is greater when the influent is colder. A typical temperature tracing for the first compartment was included in Section 3 of the main report.

TABLE C-35

OPERATING CONDITIONS AND OTHER PERTINENT DATA

Test No. 73079

Reactor Temperature, °F	
Compartment 1	480-450
Compartment 2	465-455
Compartment 3	460-450
Compartment 4	450-440
Reactor Pressure, psi	
Total	600
Steam	550
Air Flow, scfm	0.2
Influent Flow, Liters/Minute	0.3
Agitator Speed, rpm	1200
Total Volume of Vapor Condensate, ℓ	5.5
Total Volume of Influent Treated, ℓ	100
Mean Over-All Residence Time, Minutes	117
Catalyst	10,480

TABLE C-36

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENTS

Test No. 73079

Time, PST	Sampling Station	COD, mg/ℓ O	% Red. in COD	-r mg/ℓ O min.$^{-1}$	k, min.$^{-1}$	pH
1230	Influent	2059				1.5
	Comp. 1	267	87.0	58.1	0.218	1.7
	Comp. 2	22[illegible]	89.0	1.3	0.006	1.7
	Comp. 3	186	91.0	1.4	0.007	1.7
	Comp. 4	141	93.2	1.8	0.012	1.7
	Vapor Cond.	139				3.3
1330	Influent	2119				1.6
	Comp. 1	289	86.4	59.4	0.206	1.7
	Comp. 2	236	88.9	1.7	0.007	1.7
	Comp. 3	172	91.9	2.2	0.012	1.7
	Comp. 4	130	93.9	1.6	0.012	1.7
	Vapor Cond.	455				3.4
1430	Influent	1703				1.6
	Comp. 1	281	83.5	46.2	0.164	1.7
	Comp. 2	229	86.6	1.7	0.007	1.6
	Comp. 3	168	90.1	2.1	0.012	1.7
	Comp. 4	123	92.8	1.8	0.014	1.7
	Vapor Cond.	515				3.3
1530	Influent	2396				1.5
	Comp. 1	277	88.4	68.8	0.248	1.7
	Comp. 2	216	91.0	2.0	0.009	1.7
	Comp. 3	174	92.7	1.4	0.008	1.7
	Comp. 4	135	94.4	1.5	0.011	1.7
	Vapor Cond.	198				3.3
1630	Influent	2475				1.5
	Comp. 1	273	88.2	70.8	0.242	1.7
	Comp. 2	248	90.0	1.4	0.006	1.7
	Comp. 3	194	92.2	1.8	0.009	1.7
	Comp. 4	99	96.0	3.7	0.037	1.7
	Vapor Cond.	277				3.3

Composited Effluent: 123

TABLE C-37

OPERATING CONDITIONS AND OTHER PERTINENT DATA

Test No. 73082

Reactor Temperature, °F	
Compartment 1	475-450
Compartment 2	455-445
Compartment 3	445-435
Compartment 4	440-435
Reactor Pressure, psi	
Total	600
Steam	525
Air Flow, scfm	0.2
Influent Flow, Liters/Minute	0.37
Additive Flow, Liters/Minute	0.03
Agitator Speed, rpm	1200
Total Volume of Vapor Condensate, ℓ	6
Total Volume of Influent Treated, ℓ	126
Mean Over-All Residence Time, Minutes	78
Catalyst	10,480

TABLE C-38

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENTS

Test No. 73082

Time, PST	Sampling Station	COD, mg/ℓ O	% Red. in COD	$-r$ mg/ℓ O min.$^{-1}$	k, min.$^{-1}$	pH
1200	Influent	3380				8.3
	Comp. 1	754	77.7	128.1	0.170	1.5
	Comp. 2	710	79.0	2.1	0.003	1.5
	Comp. 3	616	81.8	4.7	0.008	1.5
	Comp. 4	548	83.8	4.0	0.007	1.5
	Vapor Cond.	1260				3.7
1300	Influent	3430				8.3
	Comp. 1	748	78.2	130.8	0.175	1.4
	Comp. 2	702	79.5	2.2	0.003	1.4
	Comp. 3	660	80.8	2.1	0.003	1.4
	Comp. 4	568	83.4	5.3	0.009	1.4
	Vapor Cond.	1240				3.3
1400	Influent	3560				8.2
	Comp. 1	760	78.7	136.6	0.180	1.5
	Comp. 2	674	81.1	4.1	0.006	1.4
	Comp. 3	628	82.4	2.3	0.004	1.4
	Comp. 4	576	83.8	3.0	0.005	1.4
	Vapor Cond.	1260				3.3
1500	Influent	3379				8.2
	Comp. 1	780	76.9	126.8	0.163	1.5
	Comp. 2	546	83.8	11.2	0.020	1.5
	Comp. 3	524	84.5	1.1	0.002	1.5
	Comp. 4	439	87.0	4.9	0.011	1.5
	Vapor Cond.	1340				3.7
1600	Influent	3074				8.3
	Comp. 1	662	78.5	117.7	0.178	1.5
	Comp. 2	414	86.5	11.9	0.029	1.5
	Comp. 3	370	88.0	2.2	0.006	1.5
	Comp. 4	317	89.7	3.1	0.010	1.5
	Vapor Cond.	1123				3.3
Vapor Composite:		1379				3.3
Effluent Composite:		479				1.5

TABLE C-39

OPERATING CONDITIONS AND OTHER PERTINENT DATA

Test No. 73086

Reactor Temperature, °F	
Compartment 1	475-445
Compartment 2	455-445
Compartment 3	450-445
Compartment 4	445-435
Reactor Pressure, psi	
Total	600
Steam	525
Air Flow, scfm	0.2
Influent Flow, Liters/Minute	0.4
Agitator Speed, rpm	1200
Total Volume of Influent Treated, ℓ	141
Mean Over-All Residence Time, Minutes	78
Catalyst	None

TABLE C-40

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENTS

Test No. 73086

Time, PST	Sampling Station	COD, mg/ℓ O	% Red. in COD	-r mg/ℓ O min.$^{-1}$	k, min.$^{-1}$
1200	Influent	2733			
	Comp. 1	885	67.6	89.3	0.101
	Comp. 2	851	68.9	1.6	0.002
	Comp. 3	764	72.0	4.3	0.005
	Comp. 4	695	74.6	4.0	0.006
1300	Influent	2759			
	Comp. 1	844	69.4	92.5	0.110
	Comp. 2	828	70.0	0.8	0.001
	Comp. 3	734	73.4	4.7	0.006
	Comp. 4	684	75.2	2.9	0.004
1400	Influent	2766			
	Comp. 1	784	71.7	95.7	0.122
	Comp. 2	770	72.2	0.7	0.001
	Comp. 3	709	74.4	3.1	0.004
	Comp. 4	670	75.8	2.3	0.003
1500	Influent	2700			
	Comp. 1	1323	51.0	66.5	0.050
	Comp. 2	1233	54.3	4.3	0.003
	Comp. 3	721	73.3	25.7	0.036
	Comp. 4	670	75.2	3.0	0.004
	Vapor Cond.	N.S.			
1600	Influent	2733			
	Comp. 1	1304	52.3	69.0	0.053
	Comp. 2	1233	54.9	3.4	0.003
	Comp. 3	721	73.6	25.7	0.035
	Comp. 4	687	74.9	2.0	0.003
	Vapor Cond.	N.S.			
Composited Effluent:		681	75.1	pH = 1.55; 6229 mg/ℓ Cℓ	

(the pseudo-first-order reaction rate constant) tabulated in Table C-40 for compartment 2 are much less (3 to 5 times less) than the corresponding values for compartments 3 and 4. In other words, the reaction is proceeding three to four times as fast in the agitated compartments as in the unagitated one--(compartment 2).

(8) Nearly Isothermal (450°F) Wet Oxidation of Saline-Sewage--Continuous-Flow Test No. 73089

This is a repeat of Test No. 73086, in which the agitator in compartment 2 did not function. The operating conditions are summarized in Table C-41, and chemical analysis of influent and effluents is presented in Table C-42.

Sampling commenced at 1200--two and one-half hours after start-up--as past performance has established that two hours is adequate to reach steady state. Immediately after the 1200 sampling, the agitator again failed to function and the test was terminated.

Note that the percentage reduction in COD achieved in this test is greater than that obtained in Test No. 73086, primarily because all agitators were operative. The performance in this test is particularly good for treatment of a saline influent.

TABLE C-41

OPERATING CONDITIONS AND OTHER PERTINENT DATA

Test No. 73089

Reactor Temperature, °F	
Compartment 1	475-445
Compartment 2	435-450
Compartment 3	450-445
Compartment 4	445-440
Reactor Pressure, psi	
Total	600
Steam	525
Air Flow, scfm	0.2
Influent Flow, Liters/Minute	0.4
Agitator Speed, rpm	1200
Total Volume of Influent Treated, ℓ	66
Mean Over-All Residence Time, Minutes	79
Catalyst	None

TABLE C-42

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENTS

Test No. 73089

Time, PST	Sampling Station	COD, mg/ℓ O	% Red. in COD	-r, mg/ℓ O min.$^{-1}$	k, min.$^{-1}$
1200	Influent	2627			
	Comp. 1	735	72.0	91.4	0.124
	Comp. 2	640	75.6	4.5	0.007
	Comp. 3	560	78.7	4.0	0.007
	Comp. 4	504	80.8	3.3	0.006

C.4.2 CONTINUOUS-FLOW TEST ON SHIPBOARD SEWAGE IN UNLINED TWO-COMPARTMENT REACTOR

On May 4, 1973, a continuous-flow test of the acid circuit was performed in the newly assembled 2-compartment reactor built as a part of the program. This reactor is described in detail in Section 5 of the main report.

Accumulated feces and urine were macerated in IRWD tap water and 480 mℓ concentrated sulfuric acid. The mixture was diluted to 40 gallons. The operating conditions are listed in Table C-43. Table C-44 presents the chemical analysis of the hourly samples (taken after steady state was achieved).

C.5 SUMMARY TABLES

Table C-45 is a compilation of data from all tests; the percentage reduction is listed for each test with the pertinent operating conditions and the coefficient of variation. In Table C-46 and C-47, the mean reaction rate constants and the coefficients of variation are listed for tests performed in the carbon-lined and unlined reactors, respectively.

TABLE C-43

OPERATING CONDITIONS AND OTHER PERTINENT DATA

Test No. 73124

Reactor Temperature, °F	
Compartment 1	475-445
Compartment 2	450
Reactor Pressure, psi	
Total	600
Steam	525
Air Flow, scfm	0.2
Influent Flow, Liters/Minute	0.4
Agitator Speed, rpm	1200
Mean Over-All Residence Time, Minutes	40
Catalyst	None

TABLE C-44

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENTS

Test No. 73124

Time, PDT	Sampling Station	mg/ℓ O	% Red. in COD	$-r$ mg/ℓ O min.$^{-1}$	k, min.$^{-1}$
1300	Influent	3346			
	#1	1569	53.1	86.3	0.055
	#2	1460	56.4	5.8	0.004
1400	Influent	3161			
	#1	1370	56.7	86.9	0.063
	#2	1292	59.1	4.1	0.003
1500	Influent	3141			
	#1	1339	57.4	87.5	0.065
	#2	1260	59.9	4.2	0.003
1600	Influent	3112			
		1342	56.9	85.9	0.064
		1249	59.9	4.9	0.004
Composited Condensate		1748			

TABLE C-45

A COMPILATION OF THE CONTINUOUS-FLOW TESTS

Test Number	Weighted Mean Temp., °F	Over-pressure Less Steam, psi	Aqueous Carrier	Agitator Speed, rpm	Air Flow, scfm	Catalyst	H_2SO_4 g/ℓ	Mean Residence Time, Min	Mean % Red. in COD	Coefficient of Varia-tion, Pct of Mean	Influent COD, mg/ℓ O	Effluent pH	O_2/COD
72332	454	50	TW	800	0.9	None	6	30	68.4	2	1633	1.5	7
								45	71.3	2			
								60	75.9	3			
72336	454	50	TW	800	0.9	None	6	30	63.8	6	1063	1.5	12
								45	69.2	2			
								60	71.6	2			
72343	446	50	TW	800	1	Carbon Felt	6	30	81.9	1	2075	1.5	7
								45	86.2	1			
								60	88.7	<1			
72346	446	50	$\frac{2}{3}$TW, $\frac{1}{3}$SW	800	1	Porous Carbon, 0.002 cm^{-1}	6	30	62.4	7	1788	1.5	8
								45	64.3	9			
								60	65.6	9			
72347	446	50	$\frac{5}{6}$TW, $\frac{1}{6}$SW	800	1	Porous Carbon, 0.02 cm^{-1}	6	30	67.8	2	1409	1.5	10
								45	70.8	1			
								60	73.5	1			
72349	445	50	TW	800	1	Porous Carbon, 0.02 cm^{-1}	6	30	69.9	4	1576	1.5	9
								45	72.4	4			
								60	74.8	3			
72360	446	50	TW	800	1	Porous Carbon, 0.02 cm^{-1}	6	30	72.7	ID†	1812	1.5	8
								45	75.7	ID†			
								60	78.5	ID†			
72363	446	50	TW	800	1	Porous Carbon, 0.02 cm^{-1}	6	30	75.2	3	1641	1.4	9
								45	78.5	4			
								60	81.1	2			

TABLE C-45
A COMPILATION OF THE CONTINUOUS-FLOW TESTS
(CONTINUED)

Test Number	Weighted Mean Temp., °F	Over-pressure Less Steam, psi	Aqueous Carrier	Agitator Speed, rpm	Air Flow, scfm	Catalyst	H_2SO_4 g/ℓ	Mean Residence Time, Min.	Mean % Red. in COD	Coefficient of Variation, Pct of Mean	Influent COD mg/ℓ O	Effluent pH	O_2/COD
73026	453	50	TW	800	0.6	Porous Carbon, 0.2 cm^{-1} plus 22,368	1	30	81.5	ID†	1266	2.4	7
								45	86.3	ID†			
								60	90.8	ID†			
	453	50	TW	800	0.6	Porous Carbon, 0.2 cm^{-1}	1	30	71.3	ID†			
								45	75.4	ID†			
								60	85.7	ID†			
73029	453	50	$\frac{2}{3}$TW, $\frac{1}{3}$SW	800	0.6	Porous Carbon, 0.2 cm^{-1} plus 10,480	1	30	68.0	4	1766	2.8	5
								45	71.6	2			
								60	74.1	<1			
73051	443	50	TW	800	0.4	Porous Carbon, 0.2 cm^{-1} plus 10,480	3	30	83.4	2	2263	2.0	3
								45	86.9	1			
								60	89.2	<1			
73054	448	50	TW	800	0.4	Porous Carbon, 0.2 cm^{-1} plus 10,480	0	30	71.6	ID†	1870	4.8	3
								45	74.4	ID†			
								60	79.2	ID†			
73064	454	50	TW	1200	0.5	10,480	6	30	76.1	2	1832	1.7	4
								45	79.1	1			
								60	82.4	1			
73068	420	250	TW	1200	0.6	10,480	6	30	73.0	6	2209	1.7	9
								45	76.8	3			
								60	80.2	3			
73072	422	250	$\frac{2}{3}$TW, $\frac{1}{3}$SW	1200	0.6	10,480	6	30	69.1	1	2539	1.7	3
								45	70.6	<1			
								60	71.8	2			

TABLE C-45

A COMPILATION OF THE CONTINUOUS-FLOW TESTS

(CONTINUED)

Test Number	Weighted Mean Temp., °F	Over-pressure Less Steam, psi	Aqueous Carrier	Agitator Speed, rpm	Air Flow, scfm	Catalyst	H_2SO_4 g/ℓ	Mean Residence Time, Min	Mean % Red. in COD	Coefficient of Varia-tion, Pct of Mean	Influent COD mg/ℓ O	Effluent pH	O_2COD
73075	402	330	TW	1200	0.6	10,400	6	36	59.4	7	2171	1.7	4
								53	64.0	6			
								66	66.4	5			
73079	457	50	TW	1200	0.2	10,480	6	30	86.7	2	2150	1.7	2
								60	89.1	2			
								90	91.6	1			
								120	94.1	1			
73082	448	50	TW	1200	0.2	10,480	8	20	78.0	1	3365	1.5	1.1
								40	82.0	4			
								60	83.6	3			
								80	85.5	3			
73086	450	75	$\frac{2}{3}$TW, $\frac{1}{3}$GW	1200	0.2	None	6	20	69.6*	3	2738	1.6	1.3
								40	70.4*	2			
								60	73.3	1			
								80	75.1	<1			
73089	461	75	$\frac{2}{3}$TW, $\frac{1}{3}$GW	1200	0.2	None	6	20	72.0	ID	2627		1.4
								40	75.6	ID			
								60	78.7	ID			
								80	80.8	ID			
73124	460	180	TW	1200	0.2	None	6	20	56.0	4	3200		1.0
								40	58.8	3			
								60	72.2	ID			
								80	74.2	ID			
								100	74.7	ID			
								120	76.3	ID			

TABLE C-45

A COMPILATION OF THE CONTINUOUS-FLOW TESTS

(CONTINUED)

Test Number	Weighted Mean Temp., °.	Over-pressure, Less Steam, psi	Aqueous Carrier	Agitator Speed, rpm	Air Flow, scfm	Catalyst	H_2SO_4 g/ℓ	Mean Residence Time, Min	Mean % Red. in COD	Coefficient of Variation, Pct of Mean	Influent COD mg/ℓ O	Effluent pH	O_2/COD
73141	450	180	TW**	1200	0.2	24,130	0	20	27.3	30	6288	9.2	0.5
								40	44.2	6			
								60	54.5	4			
								80	58.9	8			
								100	66.2	4			
								120	72.7	2			

+ ID denotes insufficient data to compute the coefficient of variation

* Average of first three hourly samples

**Effluent from previous tests.

TABLE C-46

MEAN RATE CONSTANTS FOR CONTINUOUS-FLOW TESTS CONDUCTED IN CARBON-LINED REACTOR

Test No.		Compart. 1	Compart. 2	Compart. 3	Compart. 4
72346	Mean k, min^{-1}	0.104	0.004	0.004	0.002
	$100s/\bar{k}$, pct†	22	20	71	28
72347	Mean k, min^{-1}	0.118	0.009	0.007	0.008
	$100s/\bar{k}$, pct†	7	35	31	64
72349	Mean k, min^{-1}	0.126	0.011	0.006	0.007
	$100s/\bar{k}$, pct†	9	58	36	20
72350	Mean k, min^{-1}	0.161	0.005	0.009	0.009
	$100s/\bar{k}$, pct†	ID*	ID*	ID*	ID*
72353	Mean k, min^{-1}	0.198	0.010	0.013	0.012
	$100s/\bar{k}$, pct†	8	34	62	57
73029	Mean k, min^{-1}	0.136	0.012	0.011	0.011
	$100s/\bar{k}$, pct†	29	44	52	48
73051	Mean k, min^{-1}	0.244	0.016	0.022	0.016
	$100s/\bar{k}$, pct†	13	46	36	26
73054	Mean k, min^{-1}	0.131	0.014	0.008	0.022
	$100s/\bar{k}$, pct†	8	44	9	16
	Mean Coef. variation	14	40	42	37

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*ID denotes insufficient data to compute the coefficient of variation
†Coefficient of variation

TABLE C-47

MEAN RATE CONSTANTS FOR CONTINUOUS-FLOW TESTS CONDUCTED IN UNLINED REACTOR

Test No.		Compart. 1	Compart. 2	Compart. 3	Compart. 4
72332	Mean k, min^{-1}	0.076	0.028	0.007	0.013
	$100s/\bar{k}$, pct†	27	35	29	41
72335	Mean k, min^{-1}	0.089	0.015	0.012	0.006
	$100s/\bar{k}$, pct†	46	103	61	44
73064	Mean k, min^{-1}	0.116	0.032	0.011	0.015
	$100s/\bar{k}$, pct†	7	20	44	3
73068	Mean k, min^{-1}	0.150	0.009	0.010	0.013
	$100s/\bar{k}$, pct†	14	29	37	11
73072	Mean k, min^{-1}	0.095	0.024	0.005	0.006
	$100s/\bar{k}$, pct†	27	50	12	41
73075	Mean k, min^{-1}	0.075	0.004	0.007	0.005
	$100s/\bar{k}$, pct†	18	16	8	12
73079	Mean k, min^{-1}	0.216	0.007	0.010	0.017
	$100s/\bar{k}$, pct†	16	17	24	65
73082	Mean k, min^{-1}	0.173	0.012	0.005	0.008
	$100s/\bar{k}$, pct†	4	96	52	29
73086	Mean k, min^{-1}	0.111	0.002	0.017	0.004
	$100s/\bar{k}$, pct†	9	50	95	31
73089	Mean k, min^{-1}	0.124	0.007	0.007	0.006
	$100s/\bar{k}$, pct†	ID*	ID*	ID*	ID*
	Mean Coef. variation	19	46	40	31

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*ID denotes insufficient data to compute the coefficient of variation

†Coefficient of variation

APPENDIX D

EVALUATION OF WET OXIDATION
OF SHIPBOARD LAUNDRY WASTEWATER,
BILGE WATER AND GALLEY WASTE

In this appendix, results are presented from continuous-flow tests and supplemental batch experiments on three types of shipboard wastewaters: effluent from the laundry, bilge and galley. These tests were performed as a part of U.S. Navy Contract No. N00174-73-C-0140.

D.1 WET OXIDATION OF LAUNDRY WASTEWATER

D.1.1 COMPOSITION OF SYNTHETIC LAUNDRY WASTEWATER

The organic content of wastewater from a shipboard laundry is derived from body sweat, urine and detergents and differs from the common household variety in that it contains more salt (sodium chloride). (Soiled clothing aboard ship generally is caked with salt crustations.)

The influent (simulated shipboard laundry wastewater) for this series of tests was formulated in accordance with instructions from Mr. Paul Schatzberg, Naval Ship Research and Development Center ,Annapolis, Maryland and contained

1500 mg/ℓ sodium chloride
1000 mg/ℓ urea
700 mg/ℓ lactic acid
10,000 mg/ℓ sodium lauryl sulfate (SLS)

in 50 gallons of Irvine Ranch Water District (IRWD) tapwater*. The influent had a mean COD of 4955 mg/ℓ O; the corresponding mean TOC was 1445 mg/ℓ C according to a Beckman model 915B TOCA (total organic carbon analyzer). The influent was pH 8.5.

D.1.2 CONTINUOUS-FLOW TEST

No additives--sulfuric acid or Barber-Colman Co. catalysts--were used in the continuous-flow test, which was conducted in a 4-compartment, WETOX PLAG reactor. That is to say, simulated laundry wastewater was treated by the WETOX process--in which wet oxidation is accomplished at relatively low temperatures by constantly stirring the wastewater in the presence of air (oxygen). The PLAG reactor is a tubular, horizontal autoclave in which both the liquid and gas phases are partitioned into compartments, each containing an agitator and air inlet.

In the PLAG (partitioned liquid and gas) reactor, the barrier walls between the compartments are solid circular plates of commercial-grade titanium metal, which are fastened securely around the periphery of the autoclave shell to form water-tight chambers. Effluent liquid, suspended solids, steam,unused oxygen and other gases must exit from each compartment into the next by flowing through a tubular-elbow opening in the partition that extends beneath the liquid level in the adjacent compartment directly in the path of the impeller. Thus, in each compartment, the incoming liquid is intimately mixed with the accompanying volatile species and oxygen.

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*IRWD tapwater, much of which is derived from the Colorado River, is generally regarded as extremely hard and has a high dissolved-salts content.

The cylindrical portion of the reactor interior was lined with unglazed ceramic tile and porous carbon. Individual pieces of tile were approximately 1 in. wide by 5 in. long x 1/4 in. thick and were cemented to the autoclave shell with Pennwalt H.E.S. acid-proof motar. An equally sized piece of Union Carbide porous carbon was substituted for every fourth piece of tile. The tile was an ordinary household bathroom-grade manufactured by Pomona Tile Co.

The reactor was filled with water and preheated to 475°F. At 1020 PDT, the flow of influent commenced. Samples were first taken at 1100, and hourly thereafter. Constantly blowing air through the continuously stirred liquid produced so much suds and foam that sampling the individual compartments was accomplished successfully only once. The test was terminated at 1340. During the course of the tests, three hourly samples were taken and assayed for pertinent constituents. A summary of the chemical analysis is presented in Table D-1.

The mean operating conditions for the continuous-flow test were

Pressure, psi	600
Temperature, °F	
Compart. 1	465
2	450
3	440
4	440
Air Flow, scfm	0.5
Mean Influent Flow, ℓ/hr	30
Space-Time, min/compartment	14
Space-Velocity, hr^{-1}	1.1
Oxygen Supply, O_2/COD	1.4
Relative Reaction Time (Combined Mean Space Time), min	55
Stirring Speed, rpm	1000

In Table D-2, mass balances are presented for COD, TOC and sodium lauryl sulfate. The tabulated data indicate that little or no destruction occurred. There is little change in the level of COD or TOC after nearly an hour of continuous-flow wet oxidation.

Sodium lauryl sulfate (SLS) appears to be an extremely refractory substance. In fact, as the data of Table I indicate, SLS is not completely "burned" in either of the wet- or dry-combustion methods generally used for the chemical analysis of organic matter in wastewaters. Fifty percent of the mass of SLS*

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*Sodium lauryl sulfate, $NaCH_3(CH_2)_{11}SO_4$

TABLE D-1

CHEMICAL ANALYSIS OF INFLUENT AND EFFLUENT

Continuous-Flow Wet Oxidation of Simulated Laundry Wastewater

Time Sampled PDT	Sampling Station	COMBINED ORGANIC SUBSTANCES		Sodium Lauryl Sulfate**, mg/ℓ SLS	pH
		COD mg/ℓ O	TOC mg/ℓ C		
1100	Influent	4840	1515	-	8.5
	Compart. 1	4410	1460	18,855	7.1
	2	3550	1250	17,430	6.9
	3	3950	1240	15,465	6.9
	4	3835	1230	12,785	6.8
1200	Influent	5045	1430	-	8.5
	Effluent	4080	1300	13,075	6.2
1300	Influent	4980	1395	-	8.5
	Effluent	3945	1330	12,500	6.4
	Vap. Conds.*	14,505	3955	-	8.4

* Sample of impounded condensate for entire test.

**Determined by standard method for Methylene Blue Active Substances (MBAS)

TABLE D-2

MASS BALANCES--CONTINUOUS-FLOW WET OXIDATION OF SIMULATED LAUNDRY WASTEWATER

	COD		TOC		Sodium Lauryl Sulfate	
	mg O	Pct of Input	mg C	Pct of Input	mg SLS	Pct of input
Added to reactor	490,545	100.	143,255	100.	990,000	100
Remaining in						
Effluent	267,220	54.5	87,000	60.7	864,380	87.3
Condensate	58,020	11.8	15,815	11.0	-	-
Reactor	108,310	22.1	35,265	24.6	350,355	35.4
Unaccounted for	56,995	11.6	5175	3.7	0	0

is carbon; lactic acid* is 40 percent carbon; and urea** is 20 percent carbon. The theoretical total-organic-carbon (TOC) content of the influent is, therefore, 5480 mg/ℓ C, over 90 percent of which is due to SLS. In the TOC analyzer (marketed by Beckman), organic matter is burned to CO_2 which is detected by infrared spectroscopy. Apparently only about one third of the available carbon in the influent forms CO_2 in the TOC analysis. The theoretical COD also should be greater than the actual. The standard COD method is a form of wet oxidation in which organic substances are reacted with dichromate in 50-pct sulfuric acid. Apparently SLS is also not converted completely to CO_2 in the COD method.

Chemical analysis for SLS was also attempted by the MBAS (methylene-blue-active-substances) method. More SLS was detected than added. The apparent incongruity is due to the presence of some other species that forms MBAS. (A great many organic (and inorganic) compounds are detected by the method.) In fact, chemical analysis of the influent for MBAS detected matter equivalent to three times the added amount of SLS†; but after wet oxidation (for even as short a period as 5 minutes) the MBAS concentration decreased to a level commensurate with that of the added SLS. Apparently the interfering substances were destroyed readily by wet oxidation.

In any event, despite the incompleteness of chemical analysis, all evidence indicates that the detergent was not destroyed in the continuous-flow test. The levels of COD and TOC are relatively unchanged, and the MBAS detected in the effluent is in reasonably close agreement with the calculated head.

D.1.3 SUPPLEMENTAL BATCH EXPERIMENTS

In view of the poor results experienced in the continuous-flow test, several small-scale laboratory experiments were performed. Published data†† indicate that lauryl sulfate is destroyed by wet oxidation: 81-percent reduction in organic carbon in 30 min @ 300°C and 91 pct in 30 min @ 350°C. Quite possibly wet oxidation of SLS can be

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* α-hydroxypropionic acid, $CH_3CH(OH)CO_2H$

**NH_2CONH_2

† The source of the sodium lauryl sulfate (SLS) was Procter and Gamble Co. Orvus Extra Granules, a relatively pure detergent, which is 80 percent sodium alkyl sulfate, principally SLS. The remaining 20 percent is unknown to us.

††The Report of the Director of Water Pollution Research UK Ministry of Technology, (Water Pollution Research 1968, p. 131, published by Her Majesty's Stationery Office, 1969)

effected only at extremely high temperatures*. On the other hand, the continuous-flow test was conducted without either sulfuric acid or any proprietary catalyst: the two additives which have proved to be most beneficial in accelerating wet oxidation at relatively low temperatures. Consequently, supplemental batch tests seemed requisite in establishing the efficacy of the WETOX process.

Four batch experiments were conducted in a one-gallon, stirred autoclave. In each experiment, 1500 mℓ of the same influent used in the continuous-flow test was sealed in the autoclave. An excess of oxygen was added--either as compressed air or oxygen gas--and the reactants were heated to 475°F.

Compressed air was used in two of the tests; and oxygen gas in the other two. No difference in efficacy was observed which could be attributed to the particular gaseous reactant; however, the use of oxygen gas caused the reacting liquid to be less sudsy and greatly aided sampling.

After the reactants reached 450°F, the autoclave and its contents were permitted to react for one to two hours. During the reaction period, samples of the liquid phase were removed periodically and assayed for total organic carbon (TOC) and methylene-blue-active substances (MBAS). The results are of these assays and a summary of the test conditions for each experiment are presented in the following:

a. <u>Batch Test No. 372</u>

Conditions: No acid
No catalyst
460-480°F for 150 minutes
Unlined titanium cylinder
Compressed air
900 rpm

Results:

Elapsed Time Above 450° F, Minutes	TOC mg/ℓ C	Percent Reduction
0	1600	-
15	1315	18
45	1285	20
105	1175	27
150	1225	23

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*Wet oxidation at extremely high temperatures is impractical. At 300°C, the pressure exerted by confined steam is 1245 psia; and at 350°C the corresponding pressure is 2395 psia. The weight of a shipboard wet-oxidation system for treatment at 300-350°C would be prohibitive.

b. Batch Test No. 374

Conditions: Barber-Colman Co. catalyst 10,480
6/gℓ H_2SO_4
465-475°F for 90 minutes
Unlined titanium cylinder
Compressed air
900 rpm

Results:

Elapsed Time Above 450°F, Minutes	TOC mg/ℓ C	Percent Reduction
0	1550	-
5	1120	28
45	985	36
90	1110	28

c. Batch Test No. 375

Conditions: Barber-Colman Co. catalyst 10,480
6 g/ℓ H_2SO_4
470-480°F for 150 minutes
Tile-and-porous-carbon lined cylinder
Oxygen gas
900 rpm

Results:

Elapsed Time Above 450°F, Minutes	TOC mg/ℓ C	TOC Pct. Reduc.	MBAS,as mg/ℓ SLS
0	2060	-	-
5	1455	29	10,820
30	1090	47	10,750
60	1140	45	8820
90	1325	36	8320
120	1374	33	8105

d. Batch Test No. 376

Conditions: Barber-Colman Co. catalyst 10,480
No H_2SO_4
475°F
Tile and porous carbon lined cylinder
Oxygen gas
900 rpm

Results:

Elapsed Time Above 450°F, Minutes	mg/ℓ C	Percent Reduction	MBAS, as mg/ℓ SLS
0	4525	-	-
5	5135	-	15,230
30	4410	2	14,460
60	4305	5	13,980
90	4290	5	11,675
120	4065	10	12,060
150	4345	4	12,300
180	4060	10	12,300
210	4080	10	12,060

D.1.4 CONCLUSIONS - LAUNDRY WATER

Less than 10 to 30 percent of the input COD and total organic carbon (TOC) is reduced by WETOX treatment of laundry water--wet oxidation at 475°F of constantly stirred wastewater. Chemical analysis for methylene-blue-active-substances (MBAS) indicates the sodium lauryl sulfate (SLS), the principal constituent of most modern detergents, is virtually unoxidized in acid or neutral solutions with or without any of the catalysts used to date. This compound is exceedingly refractory. While other investigators* have achieved 81 to 91 percent oxidation at extremely high temperatures and pressures, the conditions are impractical for shipboard use.

Based on the effectiveness of catalyzed ammoniacal circuits for the destruction of photographic film, some trials might be warranted. In the case of Mylar or tri-acetate film base materials, relatively poor oxidation has been achieved using neutral or acid circuits. Even if such a system did successfully remove sodium alkyl sulfate, it would be difficult to devise a practical shipboard flow sheet for the destruction of laundry water.

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*<u>Water Pollution Research - 1968</u>, p. 131, published by Her Majesty's Stationery Office, 1969.

D.2 WET OXIDATION OF BILGE WATER

D.2.1 FORMULATION OF A SIMULATED BILGE WATER

According to recently published data*, water from the bilge generally contains 0.1 percent or less of oil and not more than 400 mg/ℓ particulate matter. Fifty gallons of simulated bilge water was prepared by adding

185 mℓ automotive diesel fuel,
75 grams wet-oxidation residual solids, and
180 grams sodium chloride

to 50 gallons of Irvine Ranch Water District tapwater.

D.2.2 CONTINUOUS-FLOW TEST

Simulated bilge water was treated in a 2-compartment PLOG (partitioned liquid, open gas) WETOX reactor. The compartments in PLOG reactors are formed by segments of circular plates of titanium, over which the liquid flows; the space above the liquid level is open throughout the interior of the reactor.

The first compartment of the reactor was lined with Pomona-brand unglazed tile; the second compartment was unlined--the autoclave shell was constructed of commercial-grade titanium.

Automatically controlled, separate vents for the vapor and liquid phases were located in a small settling basin adjacent to the rear (second) compartment. The temperature of the settling basin appears to have been essentially the same as that of the liquid phase of the rear compartment.

In WETOX continuous-flow reactors, compressed air is fed continually to each compartment in proportion to the input COD. The incoming air is introduced through small openings in the floor of each compartment beneath the liquid. Rising bubbles of gas are mixed thoroughly with the agitating liquid and become saturated with steam (and volatile organic species). As air and wastewater are added to the reactor, its total pressure increases until it exceeds the desired maximum and a pressure-regulated valve is actuated. Each time the valve opens, steam (water-saturated gas and vapors) passes from the reactor through the vapor vent generally located in the rear.

All exiting gas (vapors and steam) was passed through a 100-ft. coil of copper tubing submerged in water maintained at 70-75°F. The volume of vapor condensate was measured and the COD of a representative sample was determined. The resulting data are included in Table D-3.

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*Cdr. J. R. Gauthey and F. J. Ventriglio, "The Naval Ship Systems Command Research and Development Program on Pollution Abatement", ASME publication 73-ENAs-41, preprint of an oral presentation delivered at the Intersociety Conference on Environmental Systems, San Diego, July 16-19, 1973.

TABLE D-3

CHEMICAL ANALYSIS
WET OXIDATION OF SIMULATED BILGE WATER
(Continuous-Flow Test No. 73253)

Time Sampled, PDT	Sampling Station	COD mg/ℓ O
1300	Influent	1222
	Compart. 1	269
	2	250
1400	Influent	1025
	Compart. 1	223
	2	204
1500	Influent	1455
	Compart. 1	238
	2	196
1600	Influent	1233
	Compart. 1	228
	2	198
	Composited Effluent	195*
	Composited Vapor Condensate	5395

	Mean COD, mg/ℓ O	Coefficient of Variation, Pct.
Influent	1234	12
Compart. 1	240	11
2	212	17

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*The corresponding TOC was 65 mg/ℓ C

The amount of vapor condensate collected during the test is commensurate with the air flow and temperature of the exiting vapor.

The duration of the test was about five hours, during which, the following operating conditions were maintained:

Pressure, psi	600
Temperature, °F	475
Air Flow, scfm	0.3
Mean Influent Flow, liters/hour	22
Space-Time, min./compartment	20
Space-Velocity, hr^{-1}	1.5
Oxygen Supply, O_2/COD	5*
Relative Reaction Time (Combined Mean Space-Time), min	40
Stirring Speed, rpm	1200

Table D-3 presents a summary of the chemical analysis performed on samples taken during the test.

During the test, 107 liters (28.3 gallons) of influent were pumped to the reactor, and 19 liters of vapor condensate (3.8 liters/hour) were collected. Based on the assays recorded in Table D-3, and the measurements cited above, a mass balance for COD was assembled--see Table D-4. The results indicate that little if any of the influent COD was wet oxidized. Most of the COD (78 percent of the input) was volatilized from the reactor. Seven percent of the input COD is unaccounted for and possibly was destroyed by wet oxidation, but the experimental error may have exceeded 7 percent (based on the coefficient of variation listed at the bottom of Table D-3).

D.2.3 PAST BATCH TESTS

Past batch-test results had been interpreted to indicate that bilge water was destroyed by wet oxidation. For example, in Batch Test No. 34 (Feb. 22, 1972), actual bilge water from a U.S. Coast Guard patrol boat was acidified with six g/ℓ H_2SO_4 and subjected to wet oxidation at 470°-475°F. Samples were taken of the liquid phase 10, 15, 25 and 40 minutes after injecting 400 mℓ of bilge water into a preheated 500 mℓ of water.

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*Based on the assay COD, which is about one-third of the theoretical oxygen demand; therefore, based on stoichiometry of the oxygen supply was about 1.3 times the ultimate demand.

TABLE D-4

COD BALANCE - WET OXIDATION OF BILGE WATER

		% of Input
COD Added		
1235 mg/ℓ x 107 ℓ	= 132,145 mg 0	
COD Condensed from Vapor		
5395 mg/ℓ x 19 ℓ	= 102,505 mg 0	78
COD Remaining in Reactor		
230 mg/ℓ 0 x 9.2 ℓ		
200 mg/ℓ 0 x 9.3 ℓ	= 3,976 mg 0	3
COD Passed in Liquid Let-Down		
220 mg/ℓ 0 x 69.5 ℓ	= 15,290 mg 0	12
Unaccounted for COD	= 10,374 mg 0	7

Chemical analysis for COD established the following:

Elapsed Time After Injection of Bilge Water, Minutes	COD mg/ℓ O	Percent Reduction In COD
0	15,690**	
10	2,950	81
15	2,500	84
25	1,860	88
40	1,445	91

Based on the assays of samples of the liquid phase taken during wet oxidation, one concludes that over 90 percent of the input COD has been destroyed. Conceivably the bulk of the COD resided in the vapor phase during the experiment and thus escaped detection. The final (chilled) effluent was not assayed for COD; consequently, one can only speculate concerning the apparent incongruity.

D.2.4 DISCUSSION OF THE TEST RESULTS

Diesel fuel is derived from crude petroleum by distillation or simple cracking. It is a mixture of hydrocarbons and boils over the range, 250-350°C (482-662°F). Occasionally diesel fuel is "doped" with ethyl nitrate to improve ignition quality, but the practice is not common. The liquid-phase oxidation of hydrocarbons has been investigated extensively and found to occur slowly by so-called chain reactions involving free radicals.* The initiation of the chain is generally extremely slow, unless a so-called initiator is present. Often appreciable oxidation begins only after the reactants have been contacted for several hours. During this so-called induction period, only superficial oxidation takes place.

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*N.M. Emanuel, E.T. Denisov, and Z.K. Maizus, Liquid-Phase Oxidation of Hydrocarbons, Plenum Press, New York, N.Y., 1967, 350 pp.

**Calculated initial COD of diluted bilge water immediately after injection into the preheated water. The sample of bilge water was received in a pail and consisted of a 1/4-in. layer of oil on top of 6-3/4 inches of brackish water. There were signs of rust flakes and rust-preventive chromates in the sample. Note that the sample obtained from the Coast Guard was nearly 20 times stronger in COD than the simulated bilge water used in the continuous-flow test described in Section D.2.2.

In the continuous-flow reactor, the behavior of diesel fuel is readily understandable when examined in terms familiar to common chemical-engineering operations like steam distillation or steam stripping[†]:

As diesel fuel is virtually immiscible in water, there are present in the reactor three coexisting phases--the two immiscible liquids and the vapor phase. Because the temperature of the reactor is essentially constant, it follows from the Gibbs Phase Rule that the total vapor pressure is fixed and equal to the sum of the separate vapor pressures of the two pure components*.

The composition of the condensate will be equal to that of the vapor; or in equation form,

$$\frac{\text{mass of immiscible substance}}{\text{mass of condensed steam}} = M_{im} P_{im}/M_W P_s \qquad \text{(D-1)}$$

where M_{im} is the molecular (formula) weight of the immiscible substance;

M_W is the molecular (formula) weight of water;

P_{im} is the vapor pressure of the immiscible substance; and

P_s is the steam pressure.

Let us assume that the reactor temperature is 450°F and that the mean vapor pressure of the diesel fuel is comparable to that of n-eicosane**, $C_{20}H_{42}$,

then $P_s = 423$ psia; $M_W = 18$; $P_{im} = 0.8$ psia; and $M_{im} = 282$; it follows that

$$W_{im}/W_s = 0.0296 \qquad \text{(D-2)}$$

In the continuous-flow test described in Section D.2.2, 19 liters of condensate were collected during the 5-hour test.

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†R.W. Ellerbe, "Steam-Distillation Basics", Chemical Engineering, March 4, 1974, pp 105-112.

*S. Glasstone, Text-Bock of Physical Chemistry, D. Van Nostrand Co., Inc., New York, N.Y., 1940, pp 724-725.

**Computed from data contained in Table 10-10, page 10-36, Lange's Handbook of Chemistry, 11th Edition, McGraw-Hill Book Co., 1973.

Assuming that the specific gravity of the condensate is unity, solving Equation D-2 gives a maximum value for W_{im} of 546 grams. In other words, the air flow and reactor temperature were sufficient to steam-strip 546 grams of diesel fuel from the reactor. Actually less than 145 grams of diesel fuel were fed to the reactor during the duration of the test. Steam stripping was potentially great enough to account for much more than the observed vaporization.

In the batch test described in Section D.2.3, approximately 11.4 grams of diesel fuel were heated to 470°F. The Phase Rule also applies in this case; and

$$W_{im}/W_s = M_{im}\ P_{im}/M_w\ P_s \qquad \text{(D-3)}$$

$$= (282\ \text{g})\ (1.14\ \text{psi})/(18\ \text{g})\ (514.7\ \text{psi})$$

$$= 0.0347$$

In the batch experiment, the one-gallon autoclave contained about one liter of liquid and 0.1 cu ft. of vapor phase. From a steam table, one can compute the mass of confined steam to be 49 grams and, from Equation D-3, estimate the amount of volatilized diesel fuel (as eicosane) to be 1.7 grams. In other words, in the batch test, about 15 percent of the diesel fuel was present in the vapor phase. The remaining 85 percent was dispersed in the liquid phase and during the test was oxidized extensively. Chemical analysis of liquid-phase samples taken during the batch test indicate that 75 percent of the input COD was destroyed apparently by wet oxidation. In the continuous-flow test, on the other hand, the bulk of the diesel fuel was swept out of the reactor before it could be oxidized.

D.2.5 CONCLUSIONS--WET OXIDATION OF BILGE WATER

Nearly four-fifths of the input COD reported in the vapor condensate in a continuous-flow test on simulated bilge water (0.1 percent diesel fuel in water). In practice, the vapors from wet oxidation aboard ship would be burned by mixing them with the main-engine exhaust.

Therefore, the effluent COD--which was 10 to 15 percent of the input COD--is probably a more practical index of process efficacy than the over-all percentage reduction in COD. Viewed in this light, WETOX treatment of bilge water significantly reduced the level of organic matter entrained or dissolved in the wastewater. Treated water contained about one-tenth as much organic matter as untreated water.

D.3 WET OXIDATION OF GALLEY WASTE

The contents of three 6-pound, 12-ounce cans of beef stew were macerated in forty gallons of IRWD tapwater and used as influent in a continuous-flow test in which no acid or catalyst was added. According to the label on the cans, the stew consisted of beef, potatoes, carrots, beef broth, water, peas, tomato, modified food starch, corn flour, salt, flavorings, caramel color and spice.

The test was conducted in the 2-compartment PLOG reactor described in Section D.2.2. The mean operating conditions were as follows:

Pressure, psi:	600
Temperature, °F:	470
Air Flow, scfm:	1
Mean Influent Flow, ℓ/hr:	22
Space-Time, min/compartment.	20
Space-Velocity, hr^{-1}.	1.5
Oxygen Supply, O_2/COD:	1.3
Relative Reaction Time (Combined Mean Space-Time), min:	40
Stirring Speed, rpm:	1200

The duration of the test was nearly six hours and six sets of hourly samples were taken and analyzed for COD. The results of chemical analysis are presented in Table D-5.

During the test, 126 liters (33.2 gallons) of influent were fed to the reactor and 32 liters of condensate (5.4 ℓ/hr) were collected. Based on the assays of Table D-5 and the above measurements, the mass balance for COD presented in Table D-6 was constructed.

In the treatment of simulated galley waste, about 60 percent of the input COD was destroyed by wet oxidation. Ten percent of the input COD, however, has been volatilized and can possibly be burned in the exhaust gases. Therefore, the level of destruction might be considered to be about 67-70 percent.

No acid or catalyst was added to the influent, and it is quite possible that a greater level of destruction could be achieved than the results of the continuous-flow test indicate.

TABLE D-5

CHEMICAL ANALYSIS
WET OXIDATION OF SIMULATED GALLEY WASTE
Continuous-Flow Test No. 73254

Time Sampled, PDT	Sampling Station	mg/ℓ O
1000	Influent	12,782
	Compart. 1	6574
	2	4238
1100	Influent	11,405
	Compart. 1	7104
	2	4673
1200	Influent	13,545
	Compart. 1	6020
	2	5050
1300	Influent	11,406
	Compart. 1	7287
	2	5485
1400	Influent	13,487
	Compart. 1	7780
	2	5842
1500	Influent	19,258
	Compart. 1	8985
	2	6751
	Composited Effluent	5773
	Composited Vapor Condensate	5720

Station	Mean COD, mg/ℓ O	Coefficient of Variation, Pct
Influent	13,647	22
Compart 1	7291	13
Compart 2	5340	20

TABLE D-6
COD BALANCE
WET OXIDATION OF SIMULATED GALLEY WASTE

			% of Input
COD Added			
13,647 mg/ℓ 0 x 126ℓ	=	1,719,522 mg 0	
COD Condensed From Vapor			
5720 mg/ℓ 0 x 32ℓ	=	183,040 mg 0	11
COD Remaining In Reactor			
8985 mg/ℓ 0 x 9.2ℓ			
6751 mg/ℓ 0 x 9.3ℓ	=	145,466 mg 0	8
COD Passed In Liquid Let-Down			
5340 mg/ℓ x 75.5ℓ	=	403,170 mg 0	23
COD Destroyed			
(Determined by difference)		987,866 mg 0	58

APPENDIX E

BATCH EXPERIMENTS ON
FECES AND URINE
IN PRESENCE OF
BARBER-COLMAN CO. CATALYST 10, 480

In this Appendix, results are presented from batch experiments which were conducted on concentrated mixtures of feces, urine and toilet paper in the presence of Barber-Colman Co. catalyst 10,480. The COD of the influent was formulated to be representative of that derived from an advanced sanitation system, one in which the volume of flushant is an order of magnitude less than utilized aboard present-day ships. There are a number of systems under development which generate such sewage, for example, those employing vacuum-flush, oil-flush or water-flush-and-recycle toilets.

E.1 TEST PROCEDURE

The tests were conducted in a one-gallon autoclave which was equipped with a mechanical stirrer. The standard procedure was to preheat 1000 to 1500 mℓ water to the desired temperature and then inject a measured volume of macerated waste into the reactor from a pressurized bomb. Generally, nitrogen was used to inject the waste followed immediately by a known quantity of air or oxygen. On introduction of the sewage, the temperature of the reactor cooled some 80-100 degrees Fahrenheit, but recovered to the desired level within 4 to 7 minutes. During each test periodic samples of the liquid phase and suspended solids were removed from the reactor through a water-cooled condenser and subjected to chemical analysis. All the samples taken were analyzed for chemical oxygen demand (COD). The COD was determined on unfiltered samples and is, consequently, the combined oxygen demand of the liquid phase and suspended solids (the overall COD of the slurry).

The liquid-phase samples were also examined by gas-liquid chromatography using a Hewlett-Packard research gas chromatograph, model 5754 B. Partitioning was effected on a 6 foot x 1/8" OD column packed with 50/80 mesh Porapak Q. The samples were analyzed isothermally with the column oven maintained at 170°C. Compounds eluting from the column were detected by a dual flame ionization detector. A semiquantitative analysis is reported. Quantitative analysis and positive identification of several unknown peaks is in progress. In most cases, the concentration of the various organic compounds is directly proportional to the peak height which is reported in the tables.

E.2 TEST RESULTS

E.2.1 BATCH EXPERIMENTS IN UNLINED TITANIUM

Three experiments were conducted in which the reaction took place in the bare titanium containers that is, no carbon liner or ceramic tile or brick was present. The percentage reduction in COD achieved in these tests was less than that obtained in other tests in which the titanium reaction chamber was lined with porous carbon or a ceramic substance.

The liquid phase in batch experiments conducted in unlined (bare) titanium was stirred continuously by an impeller rotating at 1000 rpm in the presence of three vertical baffles of thin titanium sheet (5.5 in. high and 0.75 in. wide) spaced 120 degrees apart.

a. Batch Test No. 301.

In the first test of the series, 700 mℓ of macerated feces, urine and toilet paper was injected into a preheated reactor containing 1 liter of water and 6 mℓ of concentrated sulfuric acid. Wet oxidation was monitored for 120 minutes after injection of the sewage.

During the period of wet oxidation, the reactor was maintained at a mean temperature of 480°F. The ratio, O_2:COD, was initially 0.9. Periodic samples of the liquid phase were removed and assayed.

Examination of Figure E-1--a semilogarithmic plot of COD vs time*--indicates that, under the conditions of this experiment (Barber-Colman Co. catalyst 10,480 and 6 g/ℓ H_2SO_4 in an unlined titanium reactor), 88 percent reduction in COD was achieved in about one hour, but virtually no further reduction occurred during the next hour of monitored reaction.

The straight lines shown in Figure E-1 are the "least-squares fits" of the datum points. The coefficient of determination (r^2)--fraction of variance not accounted for in the regression of the straight line--is indicated for each line. The rate constant (k) is also indicated for each line. The values of k are smaller than those observed in many catalyzed wet-oxidation experiments. The rate constant for late-stage oxidation (k = 0.002) is extremely small and poorly defined (r^2 = 0.55).

The pH of the liquid samples ranged from 3 to 5. Generally Barber-Colman Co. catalyst 10,480 is most effective when the liquid phase is pH 1.5 or less. The acid requirement (to achieve the same pH) of macerated feces and urine is greater than that of primary sewage sludge.

b. Batch Test No. 302.

In this experiment, 700 mℓ of macerated feces, urine and toilet paper was added to a preheated autoclave that contained 1000 mℓ of water and 12 mℓ concentrated sulfuric acid--twice as much acid as the previous Batch Test No. 301. The mean temperature of the reactor was 472°F over the period of wet oxidation. The initial O_2: COD ratio was 1.14.

The results are summarized in Figure E-2. Under these conditions (Barber-Colman Company catalyst 10,480; 13 g/ℓ H_2SO_4; unlined titanium), about 90 percent reduction in COD was achieved in about one hour, but again in the subsequent one hour's wet oxidation no further reduction occurred. The initial rate constant (k = 0.091) is greater than in the previous test, but the late stage value of k is about the same and even less certain (r^2 = 0.48). Based on the two tests, one concludes that increasing the acidity (and oxygen supply) has not increased the percentage reduction in COD and that the wet-oxidation process does not proceed to completion but stops after about 90 percent of the initial COD has been reduced.

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*In this series of plots, percentage reduction in COD has been included as an alternative ordinate on each graph.

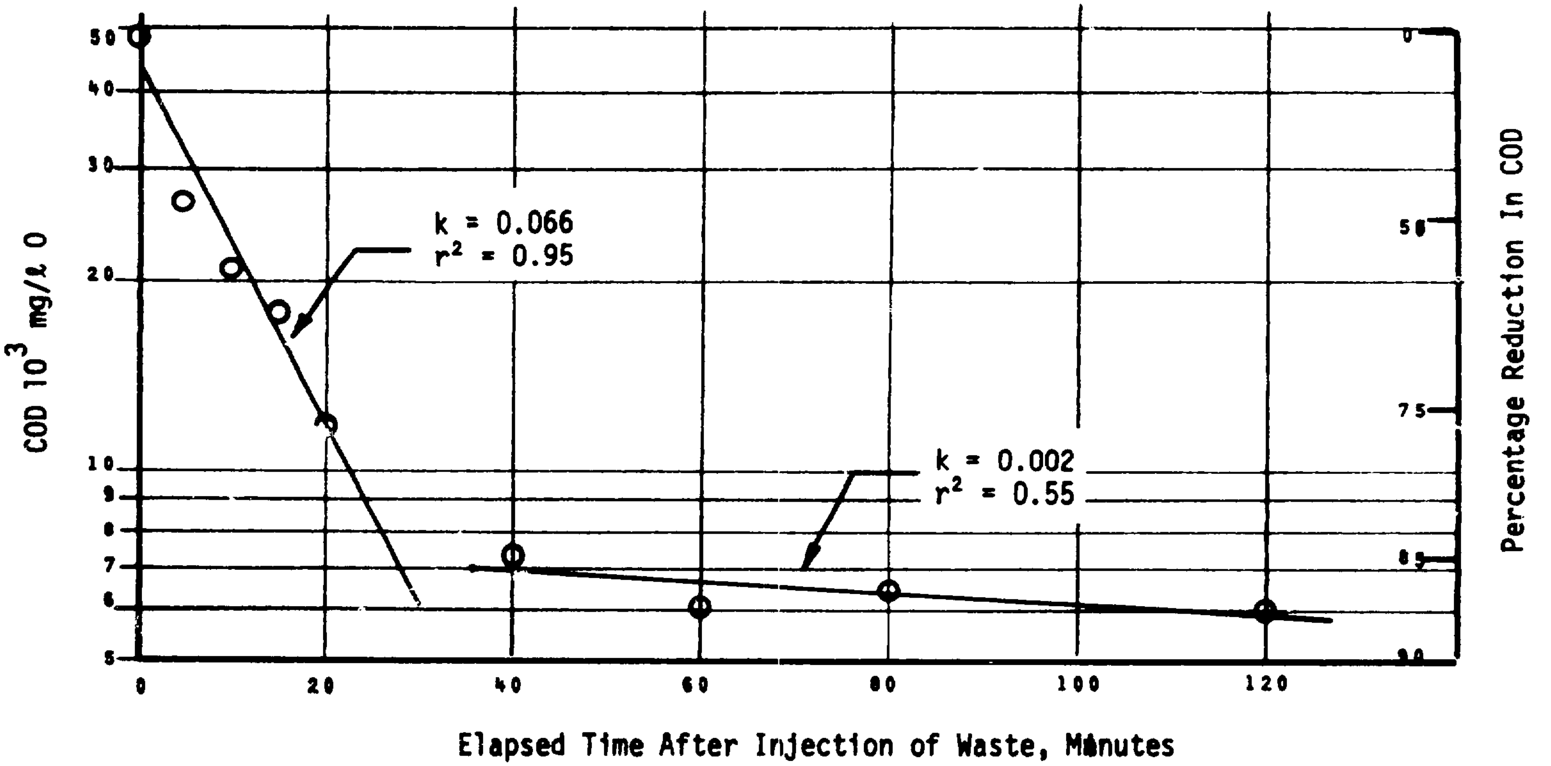

FIGURE E-1. SEMI-LOGARITHMIC PLOT OF DECREASE IN COD WITH INCREASING REACTION TIME FOR BATCH TEST NO. 301 (Wet oxidation of macerated feces, urine, and toilet paper in presence of Barber-Colman Co. catalyst 10,480; 6 g/ℓ H_2SO_4; unlined titanium.)

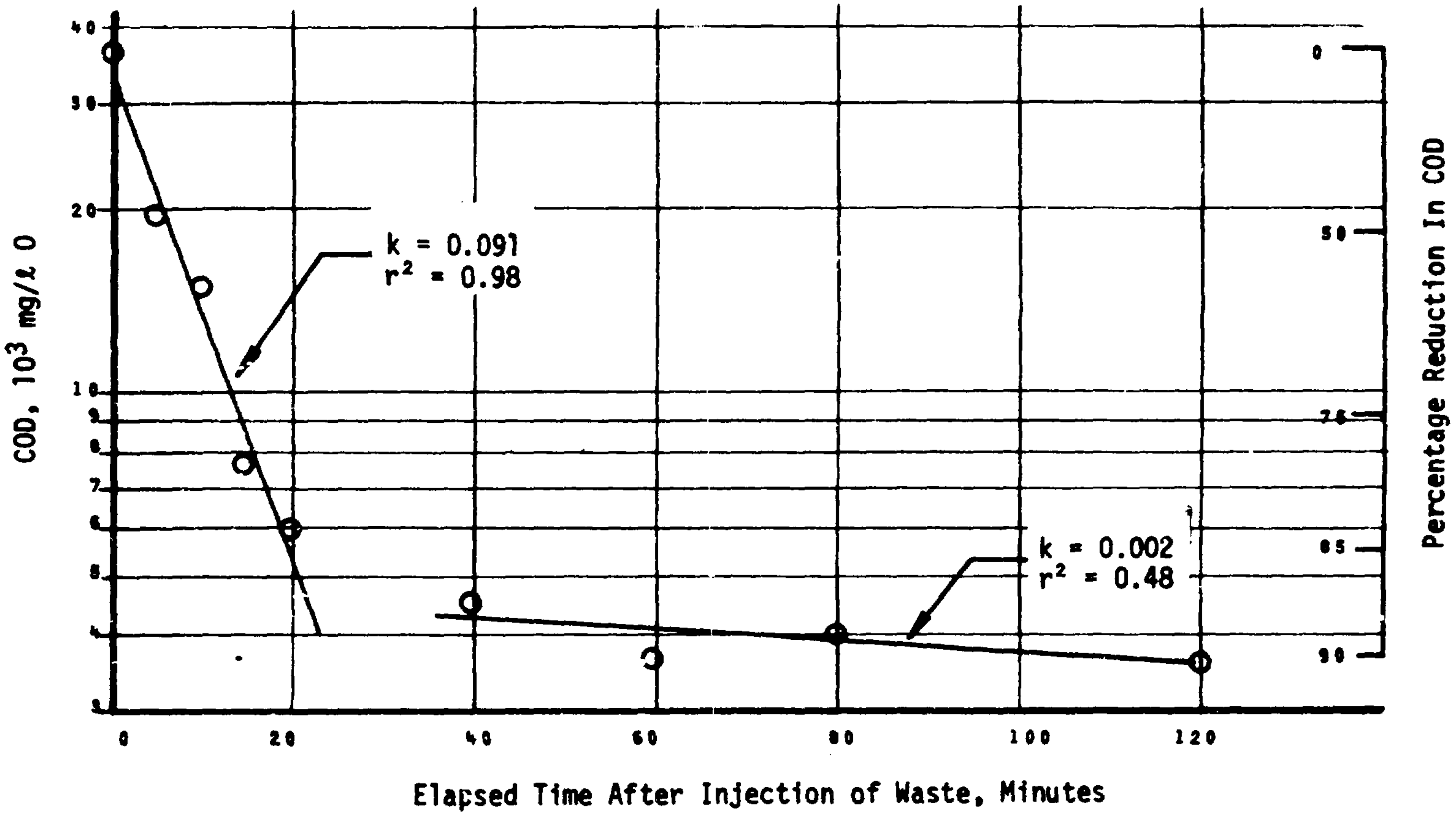

FIGURE E-2. SEMI-LOGARITHMIC PLOT SHOWING DECREASE IN COD WITH INCREASING REACTION TIME FOR BATCH TEST NO. 302
(Wet oxidation of macerated feces, urine and toilet paper in presence of Barber-Colman Co. catalyst 10,480; 13 g/ℓ H_2SO_4; unlined titanium.)

Table E-1 presents a summary of chromatographs for each of the liquid-phase samples from Batch Test No. 302. In evaluating these data one should be aware that in all of the earlier samples (the 5-, 10-, 15- and 20-minute ones) there were discernible solids which contained organic matter and probably were not present in the 2-microliter aliquot injected into the chromatograph oven. In other words, the chromatographic analysis is that of the true liquid phase, and therefore does not constitute an over-all analysis until solubilization of the organic solids is complete. In the experiments described in this memo, solubilization of organic matter was consummated at some period between 20 and 40 minutes after injection of the sewage into the preheated autoclave. The chromatographic results indicate that the sewage is degraded after one hour of wet oxidation to a solution containing formaldehyde, acetone and acetic acid (principally the latter). None of these organic species appears to have been significantly diminished by further oxidation.

The acidity of the 120-minute sample was determined by titration of an aliquot with standardized NaOH. The sample was initially pH 2.65 and titration to pH 4.5* consumed NaOH equivalent to 2.65 g/ℓ H_2SO_4 indicating that apparently more than 10 g/ℓ H_2SO_4 was consumed in wet oxidation and related reactions.

c. Batch Test No. 305.

This experiment is a repeat of the previous Batch Test No. 302. The mean temperature during the reaction period was 460°F; the initial ratio, O_2:COD, was 1.3. The same volume (700 mℓ) of the same concentrated sewage was injected into a preheated 1000 mℓ of water and 12 mℓ of concentrated sulfuric acid. The results of the experiment are presented in Figure E-3.

Again, as in the previous case, at the end of one-hour's reaction about 90 percent of the initial COD had been reduced, but unlike the previous tests some discernible further reduction in COD occurred during the second hour of wet oxidation. In fact the late-stage rate constant ($k = 0.008$) is in the range ($0.008<k<0.018$) normally observed in acidic wet oxidation. (Note, however, that the difference in behavior did not significantly affect over-all reduction in COD: at the end of two hours in Batch Test No. 305 the percent reduction was 93 compared to 90 percent in Batch Test No. 302.)

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*Titration of acidic organic solution to pH 4.5 is generally considered sufficient to neutralize any strong mineral acids such as sulfuric acid that might be present. Titration to pH 7 results in neutralization of the organic acids. In the above experiment, organic acids were present equivalent to 0.015 gram-equivalents per liter.

TABLE E-1

CHROMATOGRAPHIC ANALYSIS OF THE LIQUID PHASE

Batch Test No. 302

SAMPLE TIME	DIVISIONS OF PEAK HEIGHT							
COMPOUND	5	10	15	20	40	60	80	120
Formaldehyde	9	17	16	11	6	4	4	4
Acetaldehyde	45	56	7	2	<1	<1	<1	<1
Unknown #1	1	3	1	<1	<1	<1	-	-
Unknown #2	2	<1	-	-	-	-	-	-
Acetone	<1	3	9	8	6	5	4	3
Unknown #3	21	24	6	2	<1	<1	-	-
Acetic Acid	54	82	>100	114	87	~110	95	89
Unknown #4	2	1	-	-	-	-	-	-
Propionic Acid	1	1	<1	<1				

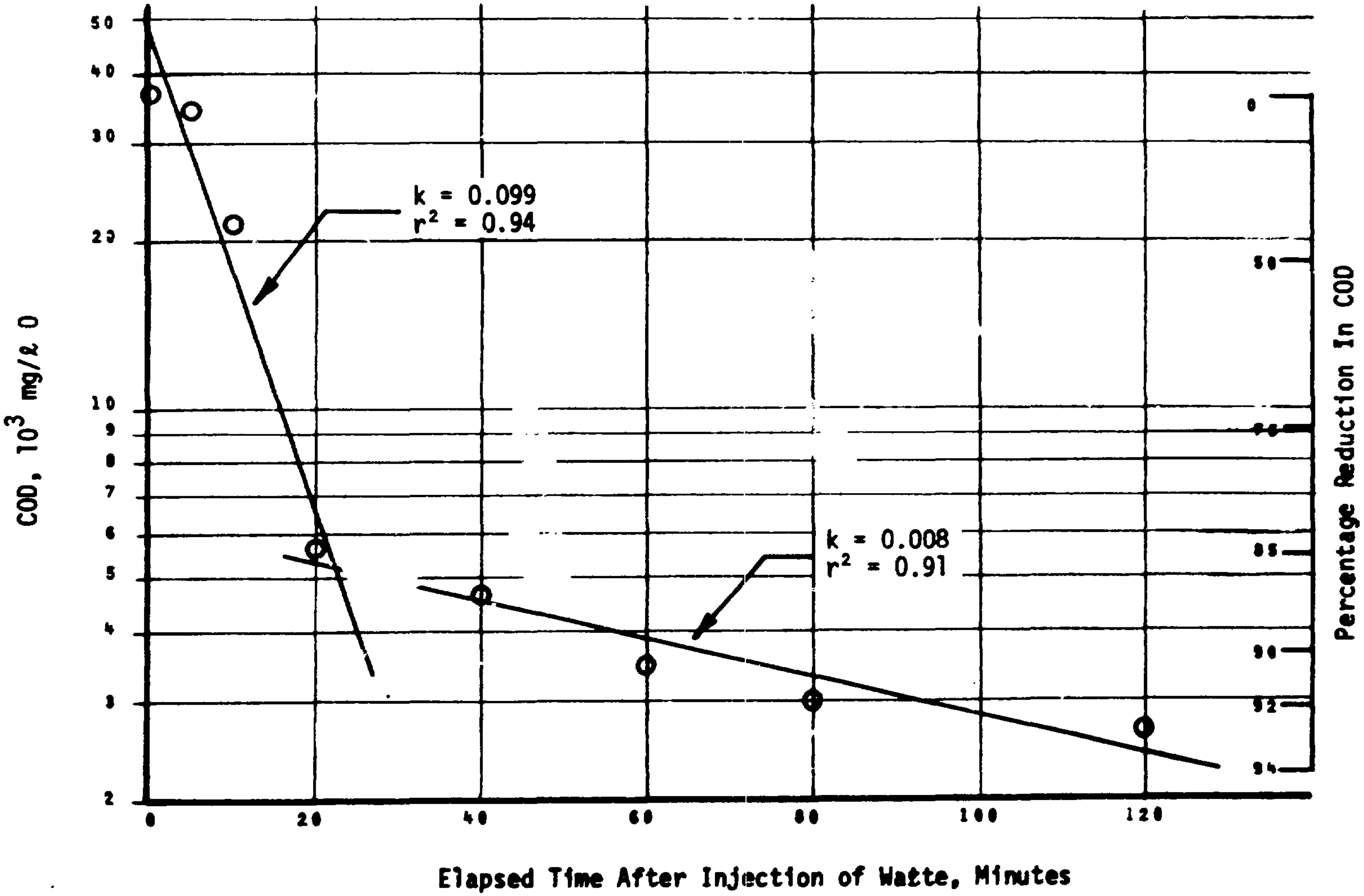

FIGURE E-3. SEMI-LOGARITHMIC PLOT SHOWING DECREASE IN COD WITH INCREASING REACTION TIME FOR BATCH TEST NO. 305
(Wet oxidation of macerated feces, urine and toilet paper in presence of Barber-Colman Co. catalyst 10,480; 13 g/ℓ H_2SO_4; unlined titanium.)

Chromatographic analysis of the liquid phase in Batch Test No. 305 is presented in Table E-2. Compare Table E-2 with Table E-1: there is less acetone and formaldehyde in the second-hour samples from Test No. 305 than in the samples from Test No. 302--there is also significant propionic acid in the samples from Test No. 305; and the amount of propionic acid fluctuates (as the concentration of propionic acid decreases the concentration of acetic acid increases).

E.2.2 BATCH EXPERIMENTS IN CARBON-LINED TITANIUM

In the past, Barber-Colman Company catalyst 10,480 has been found to perform best in the presence of porous carbon. The following tests indicate that in the wet oxidation of macerated feces a substantial improvement can be obtained by conducting the reaction in a carbon-lined reactor.

a. Batch Test No. 303.

In this experiment a 10 1/4 in. long tube (with a 4-1/8 in. OD and a 5/16-in. thick wall) of porous carbon was inserted in the titanium liner which was filled with 1000 mℓ of water and 12 mℓ concentrated sulfuric acid; 700 mℓ of concentrated sewage was injected into the preheated autoclave. The mean temperature of the reactor was 474°F over the period during which wet oxidation occurred. The initial ratio, O_2:COD, was 1.2. The liquid phase was stirred constantly by an impeller rotating at 1000 rpm. A single vertical baffle of thin titanium protruded through the porous carbon liner 3/4 inch into the agitating slurry.

The results of the experiment are summarized in Figure E-4. Conducting wet oxidation in a carbon-lined reactor has significantly increased the percentage reduction in COD--in 10 to 15 minutes 90 percent of the initial COD has been reduced; whereas, in the absence of carbon under otherwise identical conditions (Barber-Colman Co. catalyst 10,480; addition of 13 g/ℓ H_2SO_4), about 60 minutes of reaction is required to achieve the same percentage reduction. Moreover, at the end of the second hour 97 percent reduction in COD has been achieved.

The initially observed reaction rate constant is twice as great for the experiment in the carbon-lined titanium reactor as in the bare titanium reactor: $k = 0.182\ \text{min}^{-1}$ compared to $k = 0.091$-0.099. Moreover, the late-stage rate constant is greater ($k=0.011$) and well-defined ($r^2=0.92$).

Table E-3 summarizes the chromatographic analysis for the test in the carbon-lined reactor. Unlike the chromatographs presented for the previously discussed experiments, which were performed in the absence of carbon, from the beginning the liquid phase from the carbon-lined reactor contained mainly acetic acid, formaldehyde and acetone. Moreover, the quantities of all organic species detected are progressively less in each successive sample--wet oxidation is slowly but steadily taking place.

TABLE E-2

CHROMATOGRAPHIC ANALYSIS OF THE LIQUID PHASE

Batch Test No. 305

SAMPLE TIME / COMPOUND	DIVISIONS OF PEAK HEIGHT							
	5	10	15	20	40	60	80	120
FORMALDEHYDE	3	11	8	9	4.5	3.5	3	2
ACETALDEHYDE	27	42	4	4	1	<1	<1	<1
UNKNOWN #1	<1	1.5	1	<1	<1	-	-	-
UNKNOWN #2	1	2	1	<1	-	-	-	-
ACETONE	-	1	1	4	3	2	2	1
UNKNOWN #3	11	18	3	3	<1	<1	-	-
ACETIC ACID	39	46	53	89	77	81	56	73
UNKNOWN #4	1	1	-	-	-	-	-	-
PROPIONIC ACID	1.5	2	3	<1	2	-	3	-

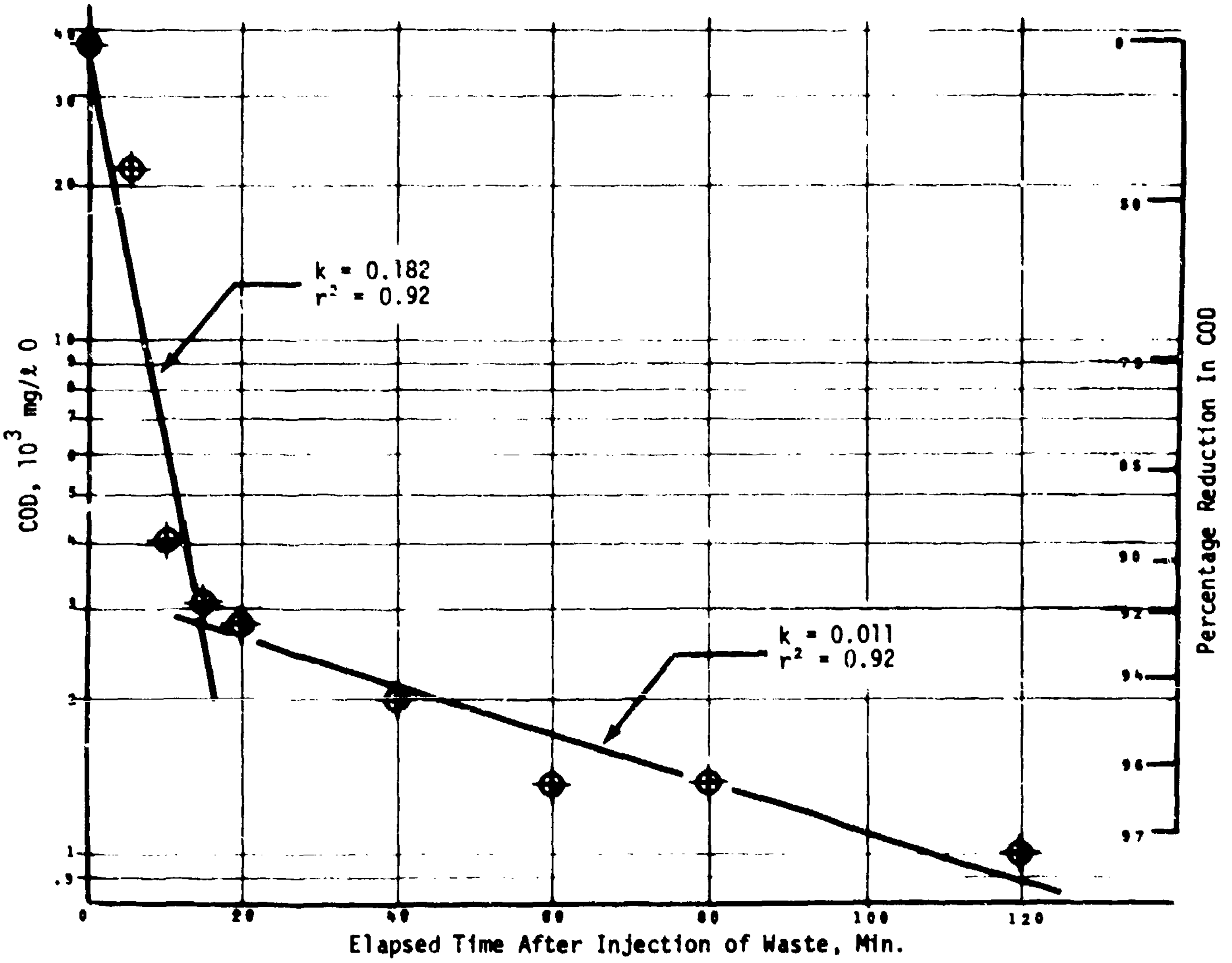

FIGURE E-4. SEMI-LOGARITHMIC PLOT SHOWING DECREASE IN COD WITH INCREASING REACTION TIME FOR BATCH TEST NO. 303
(Wet oxidation of macerated feces, urine and toilet paper in presence of Barber-Colman Co. catalyst 10,480; 13 g/ℓ H_2SO_4; carbon-lined titanium.)

TABLE E-3

CHROMATOGRAPHIC ANALYSIS OF THE LIQUID PHASE

Batch Test No. 303

SAMPLE TIME / COMPOUND	DIVISIONS OF PEAK HEIGHT						
	5	10	15	20	40	60	80
FORMALDEHYDE	15	10	7	6	2.5	1	1
ACETALDEHYDE	23	<1	-	-	-	-	-
UNKNOWN #1	2	1	<1	<1	-	-	-
UNKNOWN #2	2	-	-	-	-	-	-
ACETONE	2	7	6	5.5	3	2.5	2
UNKNOWN #3	14	<1	-	-	-	-	-
ACETIC ACID	82	85	74	67	50	38	32
UNKNOWN #4	1	-	-	-	-	-	-
PROPIONIC ACID	2.5	1	<1	<1	-	-	-

b. Batch Test No. 306

From the preceding experiments, one concludes that acetic acid is not oxidized appreciably in a bare titanium reactor but is oxidized in a carbon-lined reactor (in the presence of Barber-Colman Co. catalyst 10,480). To verify that acetic acid is indeed oxidized by Barber-Colman Co. catalyst 10,480 in a carbon-lined reactor the following experiment (Batch Test No. 306) was performed: A dilute solution of acetic acid and ammonium acetate was prepared by diluting 7 mℓ glacial acetic acid and 2.5 mℓ concentrated ammonium hydroxide to one liter with distilled water to form a pH 5.3 standard acetate solution containing about 500 ppm N and exhibiting a COD of about 9000 mg/ℓ O. The porous carbon liner was inserted in the titanium cylinder and placed in the one-gallon autoclave which then was filled with one liter of water and 6 mℓ concentrated sulfuric acid. After preheating the autoclave and its contents to about 425°F, 800 mℓ of the standard acetate solution was injected from a pressurized bomb into the carbon-lined reaction chamber, followed immediately by an excess of oxygen gas. During the period of wet oxidation the reactor mean temperature was 459°F and the liquid phase was stirred continuously by an impeller rotating at 1000 rpm. Periodically samples were removed from the liquid phase and assayed for COD.

Figure E-5 is a semilogarithmic plot of COD versus the elapsed time after injection of the standard acetate solution into the preheated reactor. The decrease in log COD is directly proportional to the elapsed reaction time. In other words, under the imposed experimental conditions, the wet oxidation of acetate is a simple (or pseudo) first-order chemical reaction. The reaction rate constant (k=0.014) compares closely with that for the late-stage oxidation observed in Batch Test No. 303 (k=0.011).

Table E-4 summarizes the chromatographic analysis of the liquid-phase samples from the experiment. The absence of any species in most samples except acetate indicates that acetate burns directly to carbon dioxide and water and does not degrade to something else, e.g., formic acid or formaldehyde. (The initial presence of the substance denoted as Unknown #3 possibly signifies that there is a side reaction.)

E.2.3 BATCH EXPERIMENTS IN CERAMIC-LINED TITANIUM.

The experiments described in the preceding sections indicate that Barber-Colman Co. catalyst 10,480 is more effective in porous-carbon-lined reactor than in one of bare titanium. The following series of batch tests demonstrate that a reaction chamber with rough walls of extensive surface area and not carbon per se is the essential component for thorough wet oxidation.

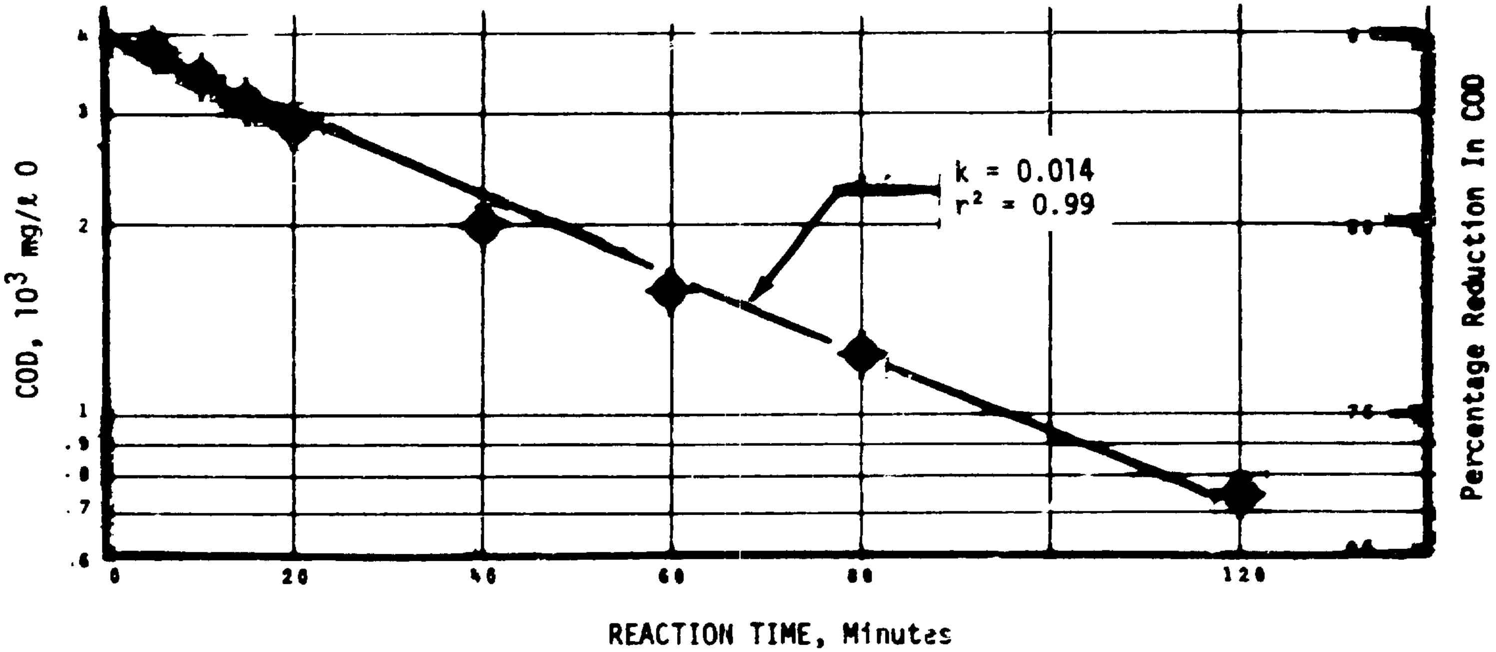

FIGURE E-5. SEMI-LOGARITHMIC PLOT SHOWING DECREASE IN COD WITH INCREASING REACTION TIME FOR BATCH TEST NO. 306
(Wet oxidation of acetate solution in presence of Barber-Colman Co. catalyst 10,480 13 g/ℓ H_2SO_4; carbon-lined titanium).

TABLE E-4

CHROMATOGRAPHIC ANALYSIS OF THE LIQUID PHASE

Batch Test No. 306

SAMPLE TIME COMPOUND	DIVISIONS OF PEAK HEIGHT							
	5	10	15	20	40	60	80	120
FORMALDEHYDE	<1	<1	<1	<1				
ACETALDEHYDE	<1	<1	-	-				
UNKNOWN #1	<1	-	-	-				
UNKNOWN #2	-	-	-	-			<1	
ACETONE	-	-	-	-				
UNKNOWN #3	1.5	1	<1	<1				
ACETIC ACID	>95	83	86	76	47.0	37.5	26.5	12.5
UNKNOWN #4	-	-						
PROPIONIC ACID	-	-						

a. Batch Test No. 307.

In this test, the titanium cylinder was lined with segments of Hermosa tile, a well-known brand of bathroom-and-kitchen glazed porcelain tile. Segments of tile (4 1/4" high x 1/4" thick x 1" wide) were wedged around the inner periphery of the titanium cylinder. (The unglazed side was exposed to the reacting slurry.) Three vertical baffles of thin titanium metal were positioned 120 degrees apart on top of the tile array.

The reactor was filled with one liter of water and 12 mℓ concentrated sulfuric acid and preheated to 407°F; 600 mℓ macerated feces, urine and toilet paper were injected into the reaction chamber which was stirred by an impeller rotating at 1000 rpm. Oxygen gas was introduced immediately after the waste; the initial ratio O_2:COD was 1.2 During the period of wet oxidation the reactor was maintained at a mean temperature of 476°F.

Chemical analysis of samples which were taken periodically from the liquid phase indicates that more than 90 percent of the initial COD was reduced in the first ten minutes after injection of the waste; and more than 96 percent reduction in COD was achieved in 80 minutes of wet oxidation. Compare these results with those from Batch Test No. 303, which was performed in a carbon-lined reactor but under otherwise identical conditions (Compare Figures E-4 and E-6)--the results from the two experiments are identical.

In Figure E-6 the logarithm of the COD is plotted versus the elapsed time after injection of waste into the preheated autoclave. Compare Figure E-6 with Figure E-4 which is the corresponding plot for Batch Test No. 303--the otherwise analogous experiment performed in a carbon-lined reactor:

	Batch Test No.	
	303	307
Initial rate constant, k, min^{-1}	0.18	0.25
Late-Stage rate constant, k, min^{-1}	0.011	0.011
Transition in rate, % red. in COD	92	92

Table E-5 summarizes the chromatographic analysis of the liquid phase during Batch Test No. 307. Comparison with Table E-3--the corresponding data for Batch Test No. 303--indicates that although the 80-minute samples were found to be comparable in COD the sample from the test performed in a tile-lined reactor contains a greater quantity (1/3 more) of residual organic species, possibly indicating that carbon has eroded from the liner in Batch Test No. 303.

b. Batch Test No. 308

A second experiment was conducted in a titanium reaction chamber lined with Hermosa tile, in which the initial concentration of waste and of sulfuric acid were decreased. The results were slightly inferior.

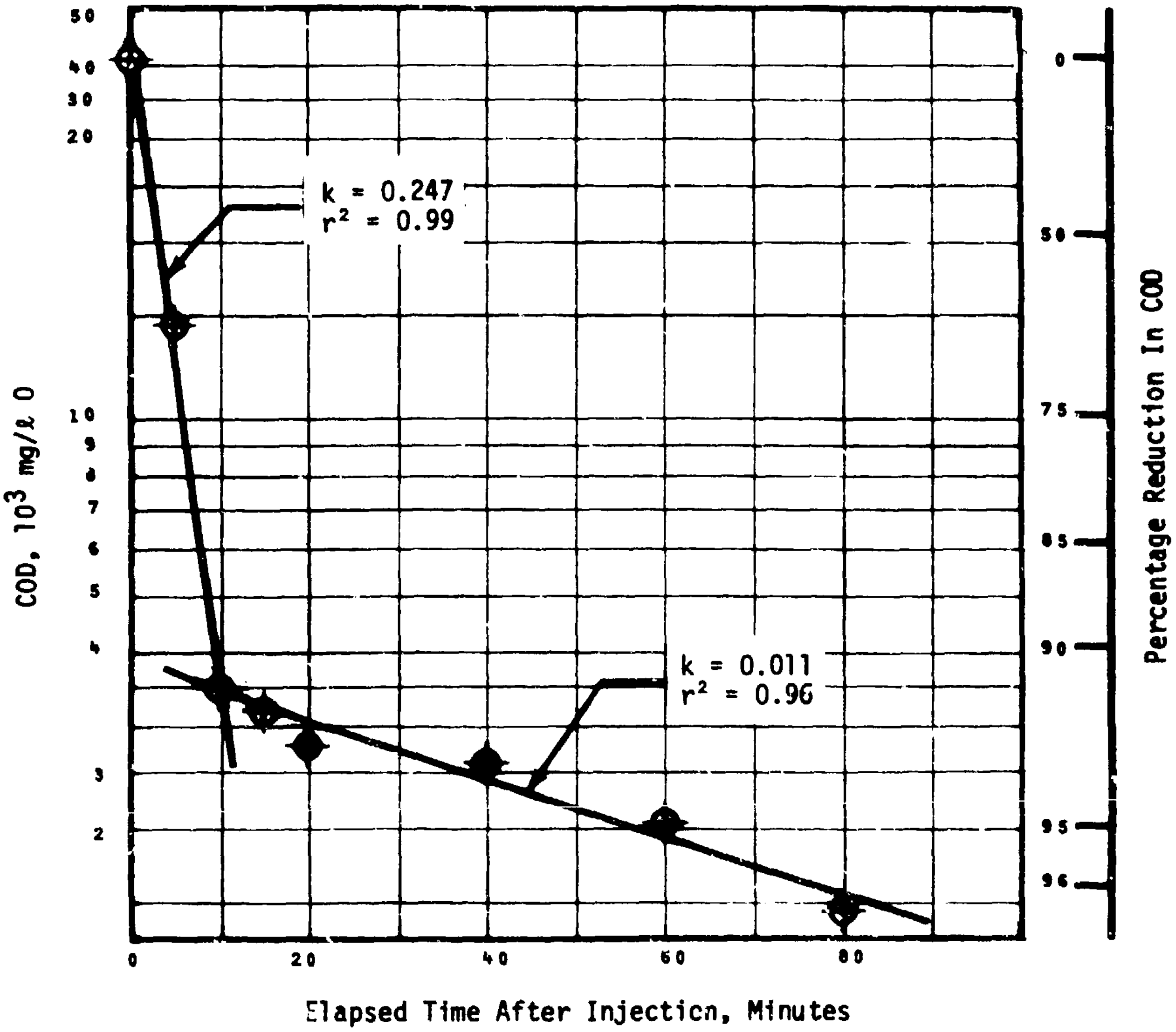

FIGURE E-6. SEMI-LOGARITHMIC PLOT SHOWING DECREASE IN COD WITH INCREASING REACTION TIME FOR BATCH TEST NO. 307
(Wet oxidation of macerated feces, urine and toilet paper in presence of Barber-Colman Co. catalyst 10,480; 13 g/ℓ H_2SO_4; Hermosa tile-lined titanium.)

TABLE E-5

CHROMATOGRAPHIC ANALYSIS OF THE LIQUID PHASE

Batch Test No. 307

COMPOUND \ SAMPLE TIME	DIVISIONS OF PEAK HEIGHT						
	5	10	15	20	40	60	80
FORMALDEHYDE	3	9	8	7	6	4	3
ACETALDEHYDE	<1	<1	<1	<1	<1	<1	-
UNKNOWN #1	<1	<1	<1	<1	<1	<1	-
UNKNOWN #2	-	-	-	-	-	-	-
ACETONE	1	7	7	7	6	5	4
UNKNOWN #3	<1	-	-	-	-	-	-
ACETIC ACID	7	56	57	51	53	48	45
UNKNOWN #4	-	-	-		-		
PROPIONIC ACID	2	-	-				

In this test, 250 mℓ of concentrated sewage was injected into a preheated autoclave that contained 6 mℓ concentrated sulfuric acid, 1300 mℓ water and Barber-Colman Co. catalyst 10,480. The pertinent conditions were:

Agitator speed, rpm	1000
Initial O_2:COD ratio	1.2
Mean Temperature, °F	466

Chemical analysis of unfiltered liquid-phase samples indicates that the percentage reduction in COD is less than in the previous test: At the end of 10 minutes, 85 percent of the initial COD has been reduced; whereas in the presence of stronger acid in the previous test nearly 92 percent was reduced. Overall reduction in COD at the end of 80 minutes was 93.4 percent compared to 96.4 percent when wet oxidation was performed in the presence of twice as much sulfuric acid. If one were only interested in percentage reduction in COD, very little has apparently been gained by operation at the higher level of acid. On the other hand, consider effluent purity: Discharge from the treatment of the stronger acid would contain 50 percent less residual organic matter.

Figure E-7 is a plot of log COD vs. t--the rate constants observed in Batch Test No. 308 are one-half as great as those in Batch Test No. 307. In a continuous-flow reactor twice as much organic would be burned in the same period in the stronger acid slurry.

The chromatographic analysis for Batch Test No. 308 is summarized in Table E-6. Wet oxidation in weaker acid resulted in effluent which contained essentially the same residual organic species--formaldehyde, acetone and acetic acid--in the same relative amounts (principally acetic acid) as formed during wet oxidation in stronger acid.

c. Batch Test No. 304.

This experiment was conducted in a titanium cylinder lined with segments of the same Duro acid-proof brick used to line the interior of the Laguna 6-compartment, continuous-flow reactor. The results are slightly inferior to those obtained in otherwise identical tests performed in carbon-lined or Hermosa-tile-lined reaction chambers. Inferior performance is attributed to the fact that the Duro brick is much more dense than the tile or carbon and, therefore, presents less surface area for wet combustion.

The test was conducted in the same one-gallon autoclave in the same manner as previously described tests. The experimental conditions and reactants are listed on the following page.

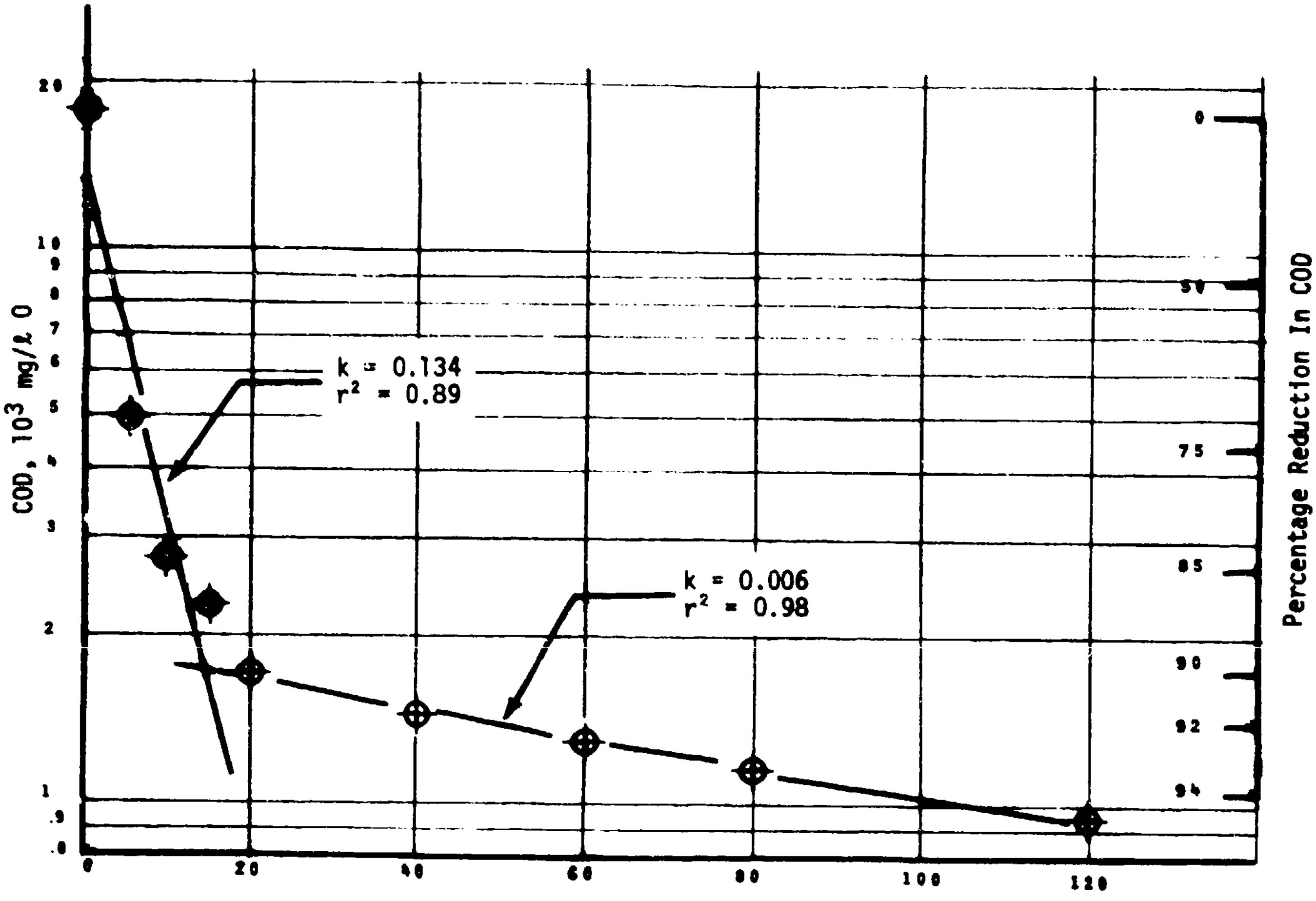

FIGURE E-7. SEMI-LOGARITHMIC PLOT SHOWING DECREASE IN COD WITH INCREASING REACTION TIME FOR BATCH TEST NO. 308
(Wet oxidation of macerated feces, urine and toilet paper in presence of Barber-Colman Co. catalyst 10,480; 6 g/ℓ H_2SO_4; Hermosa tile-lined titanium.)

TABLE E-6

CHROMATOGRAPHIC ANALYSIS OF THE LIQUID PHASE

Batch Test No. 308

COMPOUND \ SAMPLE TIME	DIVISIONS OF PEAK HEIGHT							
	5	10	15	20	40	60	80	120
FORMALDEHYDE	6.5	5	3	2.5	2	1	1	1
ACETALDEHYDE	4.5	1	<1	<1	<1	-	-	-
UNKNOWN #1	<1	<1	-	-	-	-	-	-
UNKNOWN #2	-	-	-	-	-	-	-	-
ACETONE	2	2	2	2	2	1	1	1
UNKNOWN #3	3	1	<1	<1	-	-	-	-
ACETIC ACID	27	26	30	27	26	22	24	18
UNKNOWN #4	-	-	-			-		-
PROPIONIC ACID	-	-	-			-		-

Influent	700 mℓ macerated feces, urine and toilet paper
O_2:COD	1.1
Initial (preheated) water	1000 mℓ
H_2SO_4	12 mℓ
Agitator speed	1000 rpm
Catalyst	Barber-Colman Co. [illegible]30
Mean temperature	473°F

The results from chemical analysis of unfiltered liquid-phase samples indicate that although 88 percent reduction in COD was obtained in the first 10 minutes--just as in Batch Test No. 303 which was performed in a carbon-lined reactor--subsequent reduction in COD was less than in the previously cited experiment. Figure E-8, the plot of log COD vs. t, shows that, although the initial rate constant (k=0.21) is comparable to that observed for wet oxidation in carbon (k=0.18), the late-stage rate constant is less (k=0.008 compared to k=0.011 for wet oxidation in carbon).

E.3 ACID CONSUMPTION IN ACIDIC WET OXIDATION

In most of the foregoing tests, twice as much sulfuric acid was used as in standard WETOX treatment of primary sewage sludge, because the first experiments of the series consumed more acid than in analogous tests on sewage sludge. The data presented in Table E-7 indicate that acid consumption continued to be equally as great in the later tests, but varied from about 7 to 14 g/ℓ H_2SO_4. One plausible explanation is that the acid is being primarily consumed in acid hydrolysis of the toilet paper and that the amount of paper varied in the batches of waste used in the research.

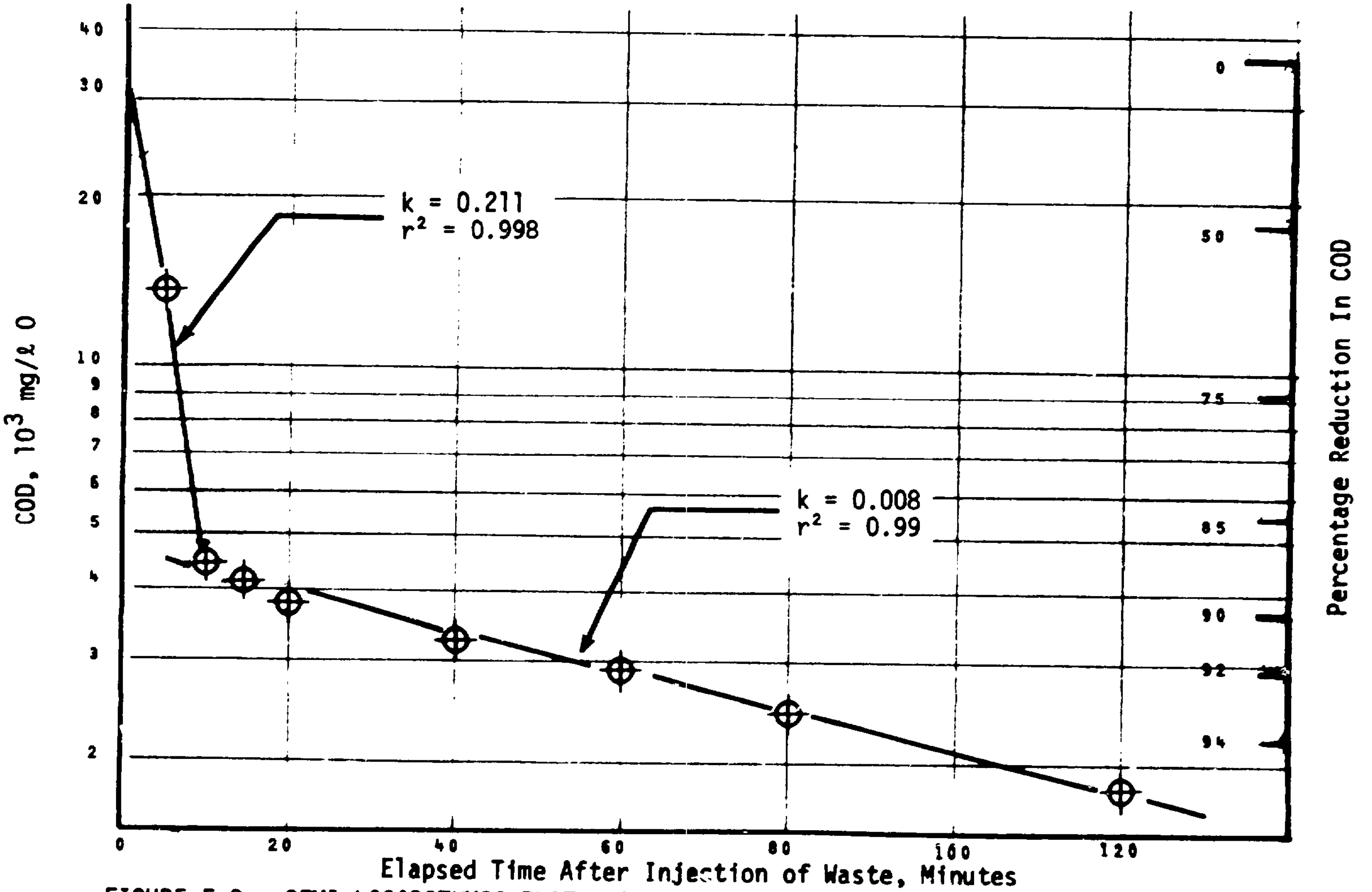

FIGURE E-8. SEMI-LOGARITHMIC PLOT SHOWING DECREASE IN COD WITH INCREASING REACTION TIME FOR BATCH TEST NO. 304
(Wet oxidation of macerated feces, urine and toilet paper in presence of Barber-Colman Co. catalyst 10,480; 13 g/ℓ H_2SO_4: Duro acid-proof brick-lined titanium.)

TABLE E-7

ACID CONSUMPTION

DURING ACIDIC WET OXIDATION

Batch Test No.	pH, Final Effluent	Initial Acid Added, g/ℓ H_2SO_4	Residual Mineral Acid, Final Effluent, g/ℓ H_2SO_4
(Tests on Primary Sewage Sludge)			
299	2.3	6	2.4
300	2.2	6	2.3
(Tests on Feces, Urine and Toilet Paper, Macerated 3 Apr. 1973)			
302	3.1	13	1.7
303	2.5	13	3.0
304	2.8	13	3.0
305	2.5	13	4.0
(Test on Standard Ammonium Acetate)			
306	2.0	6	6
(Tests on Feces, Urine and Toilet Paper, Macerated 9 Apr. 1973)			
307	4.5	13.8	0
308	3.4	7.1	0.8
312	1.8	13	5.0
(Test on Feces, Urine and Toilet Paper, Macerated 23 Apr 1973)			
315	1.7	13	6.2

APPENDIX F

DERIVATION OF RELATIONSHIPS BETWEEN PERCENTAGE REDUCTION IN COD AND INCREASED RESIDENCE TIME (OR NUMBER OF COMPARTMENTS

The relationships established in this appendix substantiate the use of time as a variable in the multiple (linear) regression analysis discussed in Section 3.3. The formulas also establish quantitatively the effect of prolonging treatment beyond a short two-compartment reactor.

The nature of wet oxidation is such that for most wastes the initial, faster rate of reaction is dominant only in the first compartment of the multiple-chambered reactor; whereas , in the subsequent compartments, wet combustion is governed by the late-stage, slower rate of oxidation. At steady state, the concentration of the reactants are invariant in each of the n compartments; and the concentration (C) in the nth compartment is related to the concentration in the adjacent (n-1) compartment by the expression:

$$C_{n-1}/C_n = 1 + k_\ell \tau_n \qquad \text{(F-1)}$$

Equation F-1 is merely a statement of mass balance, which is derived in Appendix G. It probably should be noted that in Equation F-1 and the ensuing expressions,

$n \geq 2$; i.e., the expression is only good for compartments, in which the late-stage, slower reaction is rate-controlling;
k_ℓ = the late-stage, slow reaction rate constant; and
τ = the mean residence time in the indicated compartment

If one multiplies each term in Equation F-1 by $-100C_n/C_o$, where C_o is the influent concentration, and then adds 100 to each side of the equation, the resulting expression is

$$[100 - 100(C_{n-1}/C_o)] = [100 - 100(C_n/C_o)] - 100(k_\ell C_n \tau_n/C_o), \qquad \text{(F-2)}$$

which can be rewritten as

$$\begin{bmatrix}\text{\% red, end of} \\ \text{n-1 compartments}\end{bmatrix} = \begin{bmatrix}\text{\% red, end of} \\ \text{n compartments}\end{bmatrix} - 100(k_\ell C_n \tau_n/C_o) - 100C_n/C_o \qquad \text{(F-3)}$$

For a reactor with compartments of approximately equal capacity, the residence time is the same for all compartments ($\tau_n = \tau$); and, because the late-stage oxidation process is first order with respect to COD (or C, as we have abbreviated it in this Appendix),

$$C_n = C_\ell^o \cdot \exp(-k_\ell \cdot n\tau) \qquad \text{(F-4)}$$

In Equation F-4,

C_ℓ^o is the initial concentration (COD) of the organic species which degrade by the late-stage oxidation; and
$n\tau$ is the over-all residence time (excluding the reaction time in compartment 1).

Substitution of Equation F-4 in Equation F-3 yields the relationship:

$$\Delta(\%\text{red.}) = 100(C_\ell^\circ/C_0)nk_\ell\tau\cdot\exp(-nk_\ell\tau) \qquad \text{(F-5)}$$

Equation E-6 can be written in the simpler form:

$$\Delta(\%\text{red.}) = 100(C_\ell^\circ/C_0)xe^{-x} \qquad \text{(F-5a)}$$

In the wet oxidation of most wastewaters including those generated aboard ship, the reaction rate constant k_ℓ is quite small, typically less than 0.15 min^{-1}. Moreover, we generally are concerned with residence times (τ) of the order of 15 to 20 minutes per compartment and values of n from 2 to 6. Consequently, since the exponent x, or $nk_\ell\tau$, is typically less than 0.2, the product xe^{-x} is nearly equal to x alone*; and equation F-5 becomes

$$\Delta(\%\text{red.}) = 100(C_\ell^\circ/C_0)k_\ell\tau\cdot n \qquad \text{(F-6)}$$

---

*The quantity xe^{-x} can be expressed as an infinite series,

$$xe^{-x} = x - x^2 + x^3/2! - x^4/3! + \ldots$$

For small values of x, the first term of the series generally suffices as an approximation. For example, 0.2exp(-0.2) = 0.24; 0.16exp(-0.16) = .019; and 0.14exp(-0.14) = 0.16.

APPENDIX G

ESTIMATION OF CONTINUOUS-FLOW PERFORMANCE FROM BATCH-TEST RESULTS

The application of the methods described in this appendix are illustrated in Section 3.4 and in Section 6.4.1.

The following references pertain to the same subject:

O. Levenspiel, Chemical Reaction Engineering, Second Edition, John Wiley and Sons, Inc., New York, N.Y., 1972, 578 pp.

R. E. Johnstone and M. W. Thring, Pilot Plants, Models, and Scale-up Methods in Chemical Engineering, Chap. 15, "Chemical Reactors", pp 182-196, McGraw-Hill Book Co., Inc., New York, N.Y., 1957.

D. Turner and K. Denbigh, Chemical Reactor Theory, An Introduction, Cambridge University Press, London, 1971.

A. R. Cooper and G. V. Jeffreys, Chemical Kinetics and Reactor Design, Oliver & Boyd, Edinburgh, 1971.

The continuous-flow tests described in this report were conducted in a pressurized version of the multi-stage, continuous stirred tank reactor (CSTR) widely used in chemical engineering. In a CSTR, the reactants pass continuously through a series of interconnected vessels (or, in our case, isolated compartments of a multiple chambered reactor). The flow of reactants is much slower than the speed of mixing in the constantly stirred chambers or tanks, and incoming fluid immediately blends with the much larger agitating mass already present in the vessel. At steady state, the concentrations of the reactants in individual compartments are invariant. Rate of reaction and extent (percentage reduction) depend on the mass flow through the reactor.

Mass balance dictates that for any reactor INPUT MINUS OUTPUT EQUALS AMOUNT DESTROYED. For the nth compartment of a CSTR, mass balance generally can be expressed* by an equation like the following:

$$C_{n-1} - C_n = r_n \tau_n \qquad \text{(G-1)}$$

where

C = concentration of the reactant in the indicated compartment

n = number of the compartment from inlet end

r = rate of wet oxidation

τ = residence time of reactants in the indicated compartment**

Knowing the chemical characteristics of a system--specifically possessing the data to construct a plot of rate (r) vs concentration (c)--one can establish the efficacy of a CSTR. Both algebraic and graphical solutions are widely used.

G.1 GRAPHICAL SOLUTION ACCORDING TO JONES

Graphical methods seem especially appropriate for general discussion; that which follows is attributed to R. W. Jones and is commonly used to predict large-scale, continuous-flow performance in a CSTR from the results of small laboratory batch experiments.

---

* An exception is discussed in Section G.3.

**See Appendix B for the derivation of an expression for calculating residence time which depends on the mass flow rate of influent to the reactor and the capacity of a compartment for liquid:

$$\tau_n = m_n/\dot{m}, \qquad \text{(G-2)}$$

where m_n is the capacity of compartment n for liquid (expressed in grams); and $\dot{m}$ is the mass flow rate of reactant through the reactor (grams of reactant per unit of time).

The essence of the Jones method is the relationships:

$$[r_n] / [C_{n-1} - C_n] = 1/\tau_n = \tan \alpha_n \quad \text{(G-3)}$$

The first equality is merely a restatement of equation (1); the second is the basis for a geometric construction which provides a means for the graphical determination of the efficacy of the CSTR. The graphical solution is obtained by constructing at the bottom of the r-vs-C plot, beginning at the point C_0, a set of right triangles each obeying equation G-3 for the appropriate value of τ_n. That is to say, the triangles have sides equal to the absolute values of $[r_n]$ and $[C_{n-1} - C_n]$; and the angles between the hypotenuse and the abscissa are equal to α.

A hypothetical Jones' Plot for a typical treatment of waste in a WETOX reactor is shown in Figure G-1.

The general procedure for constructing the plot is as follows:

(1) Lay off a line of slope $1/\tau_1$ from the point $C = C_0$, $r = 0$.

(2) Extend the line until it intersects the rate curve.

(3) Drop a vertical line from the point of intersection to the bottom of the graph, thus locating the value of C_1, the concentration in the first compartment of the CSTR.

(4) Repeat the procedure, using the value of τ_2 to determine the slope of the next line and starting from the point $C = C_1$, $r = 0$; thus determining the value of C_2.

(5) Repeat for successive compartments using the appropriate values for τ_n.

G.2 ALGEBRAIC SOLUTION

Graphical solutions like the Jones Method discussed in Section 2.2, however, are not always appropriate in the wet oxidation of biological waste, because the scale of the initial destruction is so out of proportion to the late-stage oxidation. Consequently, instead of the Jones Method, the following solution is presented based on algebraic manipulation of Equation G-1:

$$C_{n-1} - C_n = r_n \tau_n \quad \text{(G-1)}$$

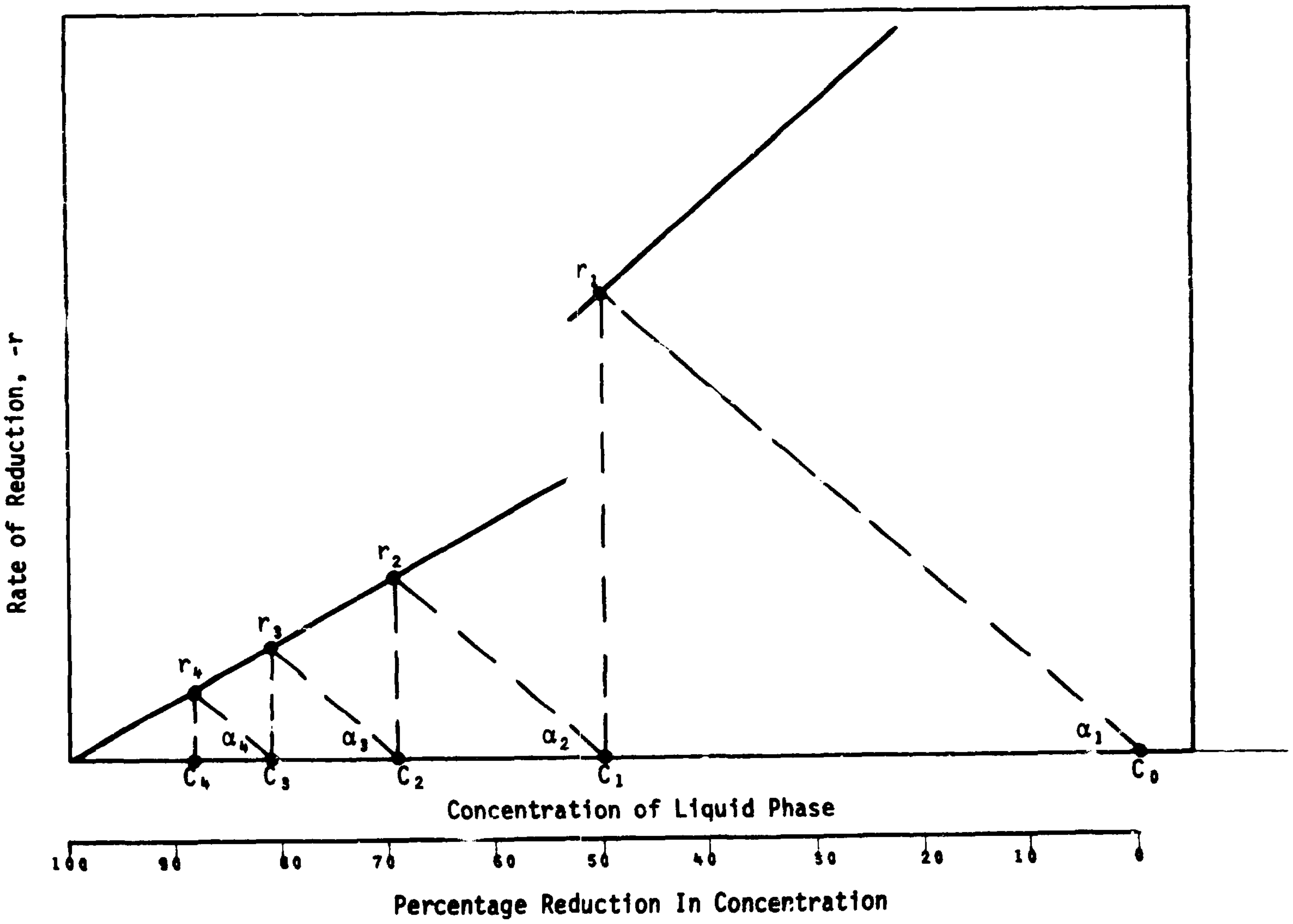

FIGURE G-1. HYPOTHETICAL JONES PLOT ILLUSTRATING RUDIMENTS OF THE CONSTRUCTION

Equation G-1 expresses the mass balance for the CSTR in terms of the nth compartment. Since wet oxidation occurs as a series of pseudo first-order chemical reactions, it follows that the rate of reaction r_n is directly dependent on the concentration C_n; i.e.,

$$r_n = \left(\frac{dC}{dt}\right)_n = -k_n C_n \tag{G-4}$$

where k_n is the pseudo first-order reaction rate constant for the chemical reaction taking place in compartment n.

Equations G-1 and G-4 can be combined to yield the expression:

$$f = \frac{C_n}{C_{n-1}} = (1 + k_n \tau_n)^{-1} \tag{G-5}$$

in which f is the fraction of the COD in the influent to compartment n remaining in the effluent from compartment n. Likewise, if f_n is the fraction of the COD contained in the feed (or influent to the first compartment) which remains in the effluent from the nth compartment, then

$$f_n = C_n/C_o \tag{G-6}$$

The foregoing Equation G-5 can be written in the alternative form:

$$f_n = \frac{C_n}{C_{n-1}} \cdot \frac{C_{n-1}}{C_{n-2}} \cdots \frac{C_2}{C_1} \cdot \frac{C_1}{C_o} = \Pi\ (1 + k_n \tau_n)^{-1} \tag{G-7}$$

where $\Pi\ (1 + k_n \tau_n)^{-1}$ is the product of successive f-values; i.e.,

$$f_n = (1 + k_1 \tau_1)^{-1} (1 + k_2 \tau_2)^{-1} \cdots (1 + k_{n-1} \tau_{n-1})^{-1} (1 + k_n \tau_n)^{-1}. \tag{G-8}$$

The related expression for f_d, the fraction of the initial COD which has been destroyed by treatment in n compartments, is

$$f_d = 1 - \Pi\ (1 + k_n \tau_n)^{-1} \tag{G-9}$$

These parameters define the wet-oxidation process and can be used to evaluate process efficacy in pilot-plant development.

G.3 SPECIAL CASE CAUSED BY THE DISCONTINUITY IN THE RATE CURVE

The foregoing methods are those generally described in standard texts. They suffice for all situations discussed in this report save one. The exception is that in which graphically (in the Jones plot) the slant line with slope $1/\tau_1$ either passes between the two segments of the rate curve or intersects the lower segment. An example appears in Section 6.4.1 of the main report. There is obvious confusion in constructing a Jones plot when the slant line passes through the region of the discontinuity in the rate curve: one has no idea where to terminate the line. In cases in which the standard method is applied and the slant line intersects the lower segment of the rate curve, although it is not obvious, the resulting solution is in error.

Simply stated, the problem lies in Equation G-1. The formula is incomplete. It is not a mass balance for the above cases; because, as we shall see, it does not give proper credit for the extensive destruction accomplished by the initial (fast) reaction(s). The derivation of a satisfactory expression follows.

Physicochemically the situations described above have a commonality: The late-stage, slow reaction is the dominant one in all compartments. The incoming raw waste is mixed into a preponderance of acetate and related species and held for more than ample residence time to effect virtually complete transformation of the raw waste to acetate. Only a minute quantity of raw waste exists at any time in the chamber.

As always, INPUT MINUS OUTPUT EQUALS AMOUNT DESTROYED. When the flow of influent and the nature of wet oxidation are such that the late-stage rate of reaction dominates in all compartments, the proper mass balance is

$$\rho_0 v C_0 - \rho_0 v C_1 = \rho_0 v \cdot \Delta C_i + r_1 \rho_T V_1 \qquad \text{(G-10)}$$

Expressed in words, Equation G-10 states that input minus output equals the quantity destroyed by the initial (fast) reaction plus the quantity burned by the late-stage (slow) reaction. The symbols denote the following:

ρ is the density of the liquid at room temperature

ρ_T is the density of the liquid at the operating temperature of the reactor

v is the volumetric flow rate of the liquid as measured at room temperature

C_0 is the concentration of the influent

C_1 is the concentration at steady state in the first compartment

ΔC_ℓ is the change in concentration caused by the destruction effected by the initial (fast) reaction

r_1 is the rate of reaction (per volume of liquid) for the late-stage oxidation taking place in the first compartment

V_1 is the capacity for liquid of the first compartment (measured in cm^3)

All concentrations are in terms of TOC or COD as measured at room temperature.

Rearrangement of terms in Equation G-10 yields

$$C_0 - C_1 - \Delta C_\ell = r_1 \rho_T V_1 / \rho_0 v \qquad \text{(G-11)}$$

Noting that the term ΔC_ℓ is an incremental change in concentration from C_0, the influent concentration, to some lesser concentration C_ℓ°, we can reduce Equation G-11 to a form which is analogous to that of Equation G-3:

$$[r_1]/[C_\ell^\circ - C_1] = 1/\tau_1 = \tan \alpha_1 \qquad \text{(G-12)}$$

Equation G-12 is a restatement of the essence of the Jones method (suitable for cases involving a discontinuity in the rate curve). The modified procedure for constructing the Jones plot is made clear from Figure G-2 and the following instructions:

(1) Drop a vertical line from the lowest point on the upper segment of the rate curve

(2) Extend the vertical line until it intersects the abscissa at $C = C_\ell^\circ$

(3) Lay off a line of slope $1/\tau_1$ from the point C_ℓ°

(4) Extend the slant line of slope $1/\tau_1$ until it intersects the lower portion of the rate curve

(5) Drop a vertical line from the point of intersection to the bottom of the graph, thus locating the value of C_1.

(6) Repeat the procedure beginning with step 3 but using the value of τ_2 to determine the slope of the next slant line and starting at $C = C_1$, $r = 0$; thus determining the value of C_2

(7) Repeat for successive compartments using the appropriate values for τ_n

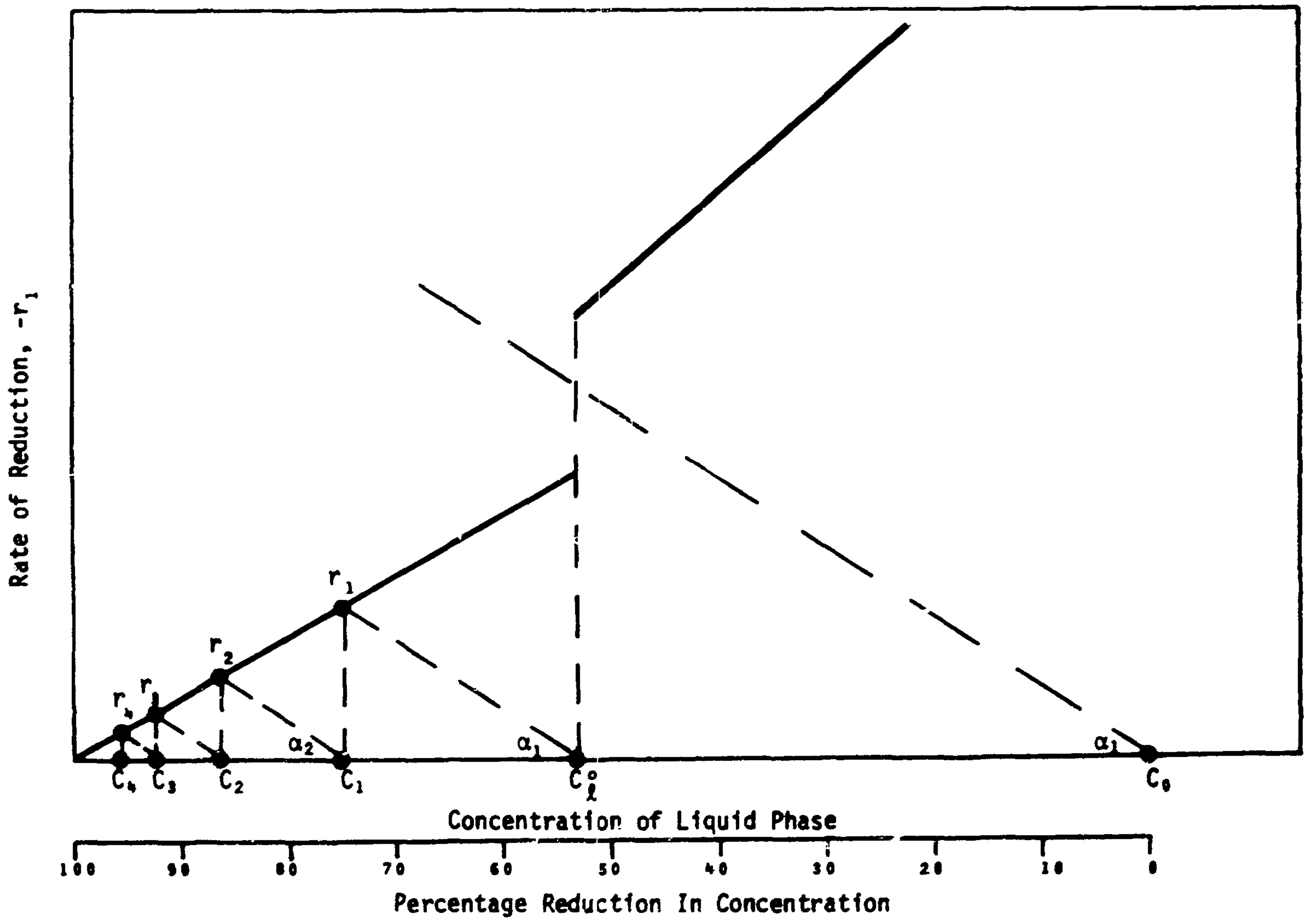

FIGURE G-2. GRAPHICAL SOLUTION FOR CASE INVOLVING DISCONTINUITY IN RATE CURVE

Application of the foregoing method results in a better solution than the conventional method; and, for this reason, its use is recommended. Unfortunately, there are certain underlying implications associated with it which may not be entirely justifiable. Specifically, by the use of the modified method, we are in effect assuming that wet oxidation in reality is the simultaneous decomposition of two species (or groups of substances). The two differ markedly in chemical reactivity, but both form carbonaceous gases as their sole end-products. (Moreover, for successful curve-fitting, the concentrations of condensed intermediates must be either invariant and/or very small compared to the concentration of the reactants.) Ploos van Amstel[*] made the same basic assumptions in his model for the wet oxidation of hydrolyzed activated (sewage) sludge. He found that the model fitted his data; we find that it fits our data. That is to say, the trend in COD is correlated by the use of such a model--two parallel reactions forming a common product[†].

The initial concentration of one of the two reactive groups is C_ℓ° and the associated rate constant is k_ℓ, which we have been calling the late-stage oxidation rate constant. The rate constant that we have called k_i in this report is (in this model) the sum of two rate constants, k_ℓ and k_0, where k_0 is the rate constant for the decomposition of the other group of reactive species. In constructing a Jones plot for the case in which the slant line $1/\tau_1$ does not intersect the upper rate curve, the upper segment of the rate curve should be redrawn to form the loci from the expression:

$$r = (k_i - k_\ell)[COD] \qquad (G\text{-}13)$$

One can then proceed with the procedure outlined on page G-8.

---

[*] J.J.A. Ploos van Amstel, The Oxidation of Sewage Sludge in the Liquid Water Phase at Elevated Temperatures and Pressures, Doctorate Thesis, Technische Hogeschool Te Eindhoven, 1971, p. 74

[†] For a basic derivation, see E.S. Swinbourne, Analysis of Kinetic Data, Appleton-Century-Crofts, New York, N.Y., 1971, pp. 87-88.

APPENDIX H

DERIVATION OF FORMULA FOR ESTIMATING CONCENTRATION OF DISSOLVED OXYGEN

Henry's Law is deceptively simple. To make use of it, one must convert to common engineering units. The formulas derived in this appendix are applied in Sections 3.5.8 and 3.5.10.

Henry's law is obeyed between 212° and 572°F below an oxygen partial pressure of 1500-2000 psia* and furnishes the basis for a useful expression for concentration of dissolved oxygen.

According to Henry,

$$X_{O_2} = H^{-1} P_{O_2} \qquad \text{(H-1)}$$

That is to say, X_{O_2}, the mol fraction of oxygen dissolved in a liquid, is directly proportional to P_{O_2}, the partial pressure of the oxygen gas in equilibrium with the liquid phase. The constant of proportionality in equation (H-1) is the reciprocal of the so-called Henry's Law constant H. Since

$$X_{O_2} \equiv \frac{\text{moles } O_2 \text{ in liquid phase}}{[\text{moles } O_2 \text{ in liquid}] \text{ plus } [\text{moles liquid}],} \qquad \text{(H-2)}$$

for dilute solutions, the moles of liquid are essentially the moles of water. Moreover, as oxygen is sparingly soluble in dilute aqueous solutions, we can neglect the term. "moles O_2 in liquid" in the denominator of equation (5) and that equation becomes

$$X_{O_2} \simeq \text{moles } O_2/\text{moles } H_2O. \qquad \text{(H-3)}$$

Consider a system containing 1000 grams of water; equation (H-3) becomes

$$X_{O_2} \simeq \frac{\text{moles } O_2/1000 \text{ g solv.}}{\text{moles } H_2O/1000 \text{ g } H_2O} = \frac{m}{1000/18} \qquad \text{(H-4)}$$

In other words, mol fraction can be replaced by molality (m). (The term, 1000/18 is the moles of water in 1000 grams of water.) Substitution of equation (H-4) in equation (4) yields

$$m = (1000/18)\ H^{-1}\ P_{O_2} \qquad \text{(H-5)}$$

---

*D.M. Himmelblau, "Solubilities of Inert Gases in Water, 0° C to Near the Critical Point of Water", Journal of Chemical and Engineering Data, Vol. 5, No. 1, pp 10-15 (January 1960)

To convert the molality expression (equation (H-5)) to one of molarity and then to concentration, we multiply first by the appropriate density ρ, and in turn by 32,000 mg O/gm-mole. The resulting expression is

$$DO = \frac{32 \times 10^6}{18} \rho H^{-1} P_{O_2} \qquad \text{(H-6)}$$

where DO is the concentration of dissolved oxygen in mg/ℓ O.

The density of water at elevated temperatures can be computed from Equation (B-5) in Appendix B.

Himmelblau offers several expressions for computing the Henry's Law constant. In this program, the following one was used:

$$H = 7.09 \times 10^7 (1/T) - 10.94 \times 10^4 \qquad \text{(H-7)}$$

where T is the absolute temperature in degrees Kelvin, i.e., °C plus 273.2.

APPENDIX I

DEMONSTRATION OF THE CLOSED-LOOP SANITATION SYSTEM

Appendix I is a reprinted report originally submitted to the U.S. Navy under Contract No. N00174-73-C-0140.

BARBER-COLMAN COMPANY
Resource Recovery Systems Division
1032 McGaw Avenue
Santa Ana, California 92705

INTERIM PROGRESS REPORT

30 JULY 1973

WET OXIDATION OF SIMULATED SHIPBOARD WASTE WATER

This document contains information resulting from research conducted by the Barber-Colman Company under U.S. Navy Contract No. N00174-73-C-0140.

RRS Report No. 73-001

1.0 INTRODUCTION AND SUMMARY

Under Contract No. N00174-73-C-0140 (Items 006-008), the Barber-Colman Company is investigating for the U.S. Navy Ships Research and Development Center, Annapolis, Maryland, the feasibility of wet oxidation for the onboard treatment of combined shipboard wastewaters. A system is desired that can treat effectively waste from all areas of the ship: the heads, showers, laundry, and galley as well as substantial amounts of bilge water and solid waste such as paper and garbage. No discharge of treated wastewater is contemplated. Treatment must be effected in an odorless, noiseless, water-tight (spill-proof) system of minimal weight and volume, at relatively low temperatures and pressures. The system must require a minimal expenditure of power, be virtually automatic and fail-safe, and compatible with existing plumbing and ship construction. Treatment should consume only small amounts of relatively common, non-hazardous chemicals.

The process demonstrated in this report, using batch, semi-continuous and continuous testing methods, fulfills the above stated system objective. The process utilizes wet oxidation of concentrated sanitary waste at 450°F and 600 psig. The wet oxidation process is conducted under basic conditions--pH 8. to 9. -- using ammonia to control the pH of the solution. Barber-Colman Company catalysts Nos. 24,130 and 42,167 were used to improve the process efficacy.

The oxidation autoclave effluent, after filtration in this closed loop system, can be recycled as a flushant. It is sterile and free of objectionable color or solids. While it has a faint odor of ammonia, it does not have a sewage odor.

Initial work was performed on feces and urine on a semi-batch basis with the addition of fresh fecal material at the end of the oxidation period. This test series demonstrated that the process was practical as evaluated on the basis of COD build-up, ammonia concentration and catalyst stability.

Continuous tests were performed in a six-compartment WETOX reactor with recycling to simulate the shipboard configuration.

Sufficient ammonia is present from the urine and amino acid decomposition to maintain the required NH_4^+ ion concentration; hence, only air, water and catalysts are required for system operation.

A flow diagram is presented showing the proposed shipboard configuration, method of removing excess water and salt accumulated from the urine. The calculated system weight is included for a 45-man complement ship to treat sanitary sewage.

2.0 SEMI-BATCH WET OXIDATION OF MACERATED FECES AND URINE

From April 24-27, 1973, two experiments (Tests No. 316 and 318) were conducted in which macerated feces and urine were subjected to wet oxidation in a simulated "closed-loop" system in the presence of Barber-Colman Company catalysts 24,130 and 42,167. Brief summaries of the tests, which were conducted on Barber-Colman Company funds, are presented below.

2.1 EXPERIMENTAL PROCEDURE

Feces were accumulated over several days and macerated with spent toilet tissue and urine to yield several liters of concentrated body waste with a chemical oxygen demand of 90,000 to 120,000 mg/ℓ O. A JABSCO (Model No. 17460-0003) Self-Priming Macerator Pump was used to prepare the concentrated sewage. Macerated sewage was passed through the pump several times to chop and blend the waste thoroughly.

The standard operating procedure in each experiment was to preheat 1290 mℓ of distilled water and 10 mℓ of an ammoniacal additive solution containing the catalyst in a one-gallon autoclave which was stirred by a turbine-disc impeller rotating at a fixed speed (1000 RPM). When the autoclave was heated to 380-390°F, 250 mℓ of concentrated macerated sewage was injected into the reactor from a pressurized bomb. Nitrogen was used to inject the sample followed immediately by a known quantity of oxygen. On introduction of the sewage, the temperature of the reactor cooled an average of 37°F, but recovered to 450-470°F within 5 to 15 minutes.

These tests were semi-batch in nature and additional injections of sewage into the reactor were made during each test. When additional macerated feces and urine were injected into the reactor (which contained sewage that had undergone wet oxidation), the general procedure was to vent a portion of the non-condensable gases that were present in the autoclave headspace through a water-cooled condenser. This was done so that the autoclave pressure did not become excessive. Then, the autoclave was allowed to cool (approximately 10-70°F) so that the heat released during the rapid, initial oxidation of the injected feces influent did not cause excessive reactor temperatures. Additional injections of sewage were also made from a pressurized bomb using nitrogen followed immediately by oxygen. Oxygen was added after each injection so that initially the ratio added O_2/COD remaining in the autoclave ranged from approximately 0.8 to 1.2. No additional catalyst was added. The temperature of the reactor dropped with each additional injection of sewage, but recovered quite rapidly to the desired operating temperature (450-470°F). This operating temperature was maintained and monitored continuously throughout each test. Total pressure was also recorded periodically during each test.

In both experiments, the liquid phase was contained in a cylindrical container of commercial-grade titanium metal which was inserted into the stainless-steel autoclave to protect it from corrosion. In Test No. 316, the titanium cylinder was lined with segments of Hermosa tile, a well-known brand of bathroom-and-kitchen glazed porcelain tile. Segments of the tile (4-1/4" high x 1/4" thick x 1" wide) were wedged around the inner periphery of the titanium cylinder with the unglazed side exposed to the reacting slurry. Three vertical baffles of thin titanium metal were positioned 120 degrees apart on top of the tile array. In Test No. 318, an alundum sleeve manufactured by Norton Company (Identification Number-AN298) was inserted inside the titanium liner. Due to the size of the alundum sleeve (7-1/4" high x 4-1/2" O.D. x 3/8" wall thickness) no baffles were used during this experiment (Test No. 318).

In Test No. 316, Barber-Colman Company catalyst 24,130 was present while in Test No. 318, catalyst 42,167--a modified version of catalyst 24,130--was used. In both experiments, the catalyst was placed in the autoclave before preheating commenced. No additional catalyst was added to the autoclave during either test.

During each test, periodic samples of the liquid phase and suspended solids were removed from the reactor through a water-cooled condenser and subjected to chemical analysis. All the samples taken were analyzed for chemical oxygen demand (COD). The COD was determined on unfiltered samples and is, consequently, the combined oxygen demand of the liquid phase and suspended solids (the over-all COD of the slurry). Selected samples were analyzed colorimetrically by the direct Nesslerization method for ammonia nitrogen content. COD and ammonia nitrogen analyses were performed in accordance with the procedures set forth in the 13th edition of Standard Methods for the Examination of Water and Wastewaters.

The liquid-phase samples were also examined by gas-liquid chromatography using a Hewlett-Packard research gas chromatograph, Model 5754 B. Partitioning was effected on a 6 foot x 1/8" O.D. column packed with 50/80 mesh Porapak Q. The samples taken in Test No. 316 were analyzed isothermally with the column oven maintained at 170°C. Later, it was found that a more complete analysis could be obtained by temperature programming; that is, by varying the temperature of the column oven; and the samples taken in Test No. 318 were analyzed by temperature programming the oven from 170°C-200°C at 60°C/minute with a post injection delay of three minutes and an upper limit hold of six minutes. Compounds eluting from the column were detected by a dual flame ionization detector. A semiquantitative analysis is reported. Quantitative analysis and positive identification of several unknown peaks is in progress. In most cases, the concentration of the various organic compounds is directly proportional to the peak height which is reported in the tables presented.

The solids that remained in the reactor at the end of each test were separated from the remaining liquid phase by filtration and were dried at 105°C. A weighed portion of the dried solids was then fired at 550°C for 18 hours and the percentage of weight lost on ignition at 550°C was determined. This figure can be used to qualitatively indicate whether the solids remaining after wet oxidation are largely organic or inorganic in nature.

2.2 RESULTS - TEST NO. 316

During Test No. 316, a total of six injections of 250 mℓ each of concentrated sewage were made into the heated autoclave. Injection 1 was allowed to react for 115 minutes before the second injection was made. Injections 2 - 5 reacted for approximately 40 - 70 minutes each, while the sewage that entered the autoclave in the sixth (and final) injection was allowed to react for four hours. The total elapsed time for Test No. 316 was slightly over nine hours.

In Table I, the results of the COD analyses performed on the samples taken during Test No. 316 are presented along with the percent reduction in COD that had occurred at the time of sampling. The percent reduction in COD has been computed on a mass balance basis according to the following equation:

% reduction in COD =

$$(100)\left[1 - \left(\frac{\text{mg of COD in reactor at sampling}}{\text{mg of COD added to reactor minus mg of COD removed in prior sampling}}\right)\right]$$

Table I indicates that, when the reactor was last sampled after six injections of concentrated feces and urine had been made, a 94 percent reduction in COD had been achieved.

Table II presents a summary of the chromatographic analyses performed on each liquid-phase sample taken during Test No. 316. These results indicate that the sewage is degraded by wet oxidation to a solution containing formaldehyde, an unidentified compound, and acetic acid (principally the latter).

When the solids that remained in the reactor at the conclusion of Test No. 316 were dried and fired at 550°C, an 8.7% loss of weight on ignition occurred. This indicates that these solids are largely inorganic in nature.

TABLE I - COD ANALYSES RESULTS, TEST NO. 316

INJECTION	TIME AFTER INJECTION (MINUTES)	COD (mg/ℓ O)	PERCENT REDUCTION IN COD
1	40	2850	85.5
	115	2535	88.0
2	41	4462	88.4
3	40	6604	87.4
4	40	6180	90.4
5	10	12,147	83.7
	40	7501	90.3
6	40	7454	91.4
	180	6730	92.6
	240	6180	93.6

TABLE II-CHROMATOGRAPHIC ANALYSIS OF THE LIQUID PHASE, TEST NO. 316

	DIVISIONS OF PEAK HEIGHT									
INJECTION-MINUTES AFTER INJECTION	1-40	1-115	2-41	3-40	4-40	5-10	5-40	6-40	6-180	6240
COMPOUND										
FORMALDEHYDE	4.5	4	5.5	5.5	6	7	6	7	6	17
ACETALDEHYDE	-	-	-	-	<1	4	<1	<1	<1	<1
UNKNOWN #1	1	<1	<1	<1	<1	<1	<1	<1	<1	<1
UNKNOWN #2	-	-	-	-	-	-	-	-	-	-
UNKNOWN #3	15.5	12	30	46.5	60	60	68	81	41	31
ACETONE	-	-	-	-	-	5.5	-	-	-	-
ACETIC ACID	22.5	21	46	62.5	75	72	82	92	102	95
UNKNOWN #4	-	-	-	-	-	-	-	-	-	-
PROPIONIC ACID	-	-	-	-	-	-	-	-	-	-

2.3 RESULTS - TEST NO. 318

In this experiment, a total of four additions of sewage were made to the reactor and the total reaction time was just over four hours.

Table III summarizes the results of COD analyses and the percentage reduction in COD that was achieved at the various times that samples were removed from the autoclave during this test. Table IV indicates that after the first addition of sewage to the reactor, a total of seven samples were taken over the eighty minute period in which reaction occurred. The reactor was sampled frequently after this first influent injection so that a reaction rate constant could be determined. The initial rate constant of Test No. 318 (k = 0.154) is comparable to that obtained for the acidic wet oxidation of feces and urine in a ceramic-lined titanium cylinder.

From Table III, it is noted that a 91 percent reduction in COD was achieved by the end of Test No. 318. This compares with a 94 percent reduction in COD that was observed for Test No. 316. Thus, in terms of percent reduction in COD, process efficacy is not apparently increased by the use of Barber-Colman Company catalyst 42,167. Therefore, since catalyst 24,130 is the least expensive of the two catalysts examined in these tests, it should be used in further tests in preference to catalyst 42,167.

The ammonia nitrogen content of two samples withdrawn from the reactor near the end of Test No. 316 is presented in Table IV. The results listed in Table IV indicate that an accumulation of ammonia nitrogen has occurred. The organic nitrogen initially present in feces and urine is converted during wet oxidation to ammonia nitrogen.

Reference to Table IV reveals that a build-up of ammonia nitrogen has taken place during Test No. 318. The ammonia-nitrogen content appears to reach a maximum after the first injection of sewage has been made, then drops and remains at a constant level after each additional injection.

The results of the chromatographic analyses performed on the liquid phase of Test No. 318 are presented in Table V. As observed in Test No. 316 (Table II), forty minutes of wet oxidation degrades sewage to a solution containing mainly formaldehyde, an unidentified compound, and acetic acid. However, by performing the chromatographic analysis with the column oven temperature programmed, small amounts of propionic and butyric acid are also detected in the liquid phase. As in Test No. 316, acetic acid is the compound that remains in the greatest quantity.

A 7.55% weight loss on ignition at 550°C was observed for the solids remaining in the reactor at the end of this test. As in Test No. 316, this residue that remains after wet oxidation of feces and urine is of an inorganic nature.

The pH of most of the samples taken in these tests was measured using indicator papers. All samples tested had pH values in the range of 8 - 9.

TABLE III - COD ANALYSES RESULTS, TEST NO. 318

INJECTION	TIME AFTER INJECTION (MINUTES)	COD (mg/ℓ O)	PERCENT REDUCTION IN COD
1	5	4738	69.5
	10	3340	79.3
	15	3138	81.4
	20	2796	84.2
	40	2214	88.2
	60	2116	89.5
	80	1981	90.9
2	40	4267	89.1
3	45	5741	88.9
4	80	5648	90.9

TABLE IV - AMMONIA NITROGEN CONTENT OF SAMPLES TAKEN DURING TESTS NO. 316 AND 318

TEST NO.	INJECTION	TIME AFTER INJECTION (MINUTES)	mg/ℓ (NH_3) N
316	6	180	3920
		240	2780
318	1	80	6500
	2	40	5500
	3	45	5490
	4	80	5550

TABLE V - CHROMATOGRAPHIC ANALYSIS OF THE LIQUID PHASE, TEST NO. 318

	DIVISIONS OF PEAK HEIGHT									
INJECTION-MINUTES AFTER INJECTION / COMPOUND	1-5	1-10	1-15	1-20	1-40	1-60	1-80	2-40	3-45	4-60
FORMALDEHYDE	5	5	3.5	2	1.5	2	2.5	1.5	4	3.5
ACETALDEHYDE	2	<1	<1	-	-	<1	-	-	<1	-
UNKNOWN #1	<1	<1	<1	<1	<1	<1	<1	-	<1	<1
UNKNOWN #2	-	-	-	-	-	-	-	-	-	-
UNKNOWN #3	13	13	10	3.5	4.5	6.5	7.5	5.5	33	30
ACETONE	2	<1	-	-	-	-	-	-	-	-
ACETIC ACID	20.5	23	19	17	16.5	20	21.5	35	61	82
UNKNOWN #4	<1	-	-	-	-	-	-	-	-	-
PROPIONIC ACID	2	2	1.5	1.5	1	1	1	1	2	8
BUTYRIC ACID	2.5	3.5	3	2.5	2.5	3	2.5	3	6	8

2.4 CONCLUSIONS - SEMI-BATCH TESTS

The use of an ammoniacal circuit for wet oxidation of feces and urine can be catalyzed to equal the performance of the sulfuric acid containing circuit. The end products of the effluent are similar to the acid circuit and the solids remaining are predominantly inorganic.

In a batch type reactor, the ammonia nitrogen tends to build up from the decomposition of urea and amino acids. It was believed that excess ammonia concentration would be lost to the vapor phase in a continuous reactor. Our concern was that perhaps all the ammonia would be lost, making it difficult to run the system at a pH in the 8 to 9 range.

While the tests were of short duration, no sign of corrosion of the titanium or deterioration of the "acid proof" mortar was observed.

3.0 CONTINUOUS WET OXIDATION OF SIMULATED SHIPBOARD SEWAGE - VAULT WASTE FEED

In conducting a continuous test on the destruction of large quantities of feces and urine, logistics becomes quite a problem. The best available source located was the campsite latrines in nearby U.S. Forest Service campgrounds. This feed material is not ideal because of its age and contamination with hypodermic syringes, tennis shoes, etc. It does, however, seem to behave almost as well as fresh material and it is available in quantity. Two 40-gallon garbage cans full of feed material were provided by the Forest Service for this test.

3.1 OPERATING PROCEDURE

The test was conducted utilizing a 6-compartment WETOX reactor, as shown in the flow chart (Figure 1), in series with an external heat exchanger, a dual blow-case pump and a stirred head tank.

A 6-compartment WETOX reactor was assembled by joining in series a 2-compartment and a 4-compartment horizontal autoclave. Each day for five consecutive days influent was passed continuously through the preheated WETOX reactor for 7 to 8 hours daily. Each evening, the reactor was depressurized and cooled; the following morning, it was reheated.

The campaign was initiated by preparing approximately 40 gallons of weakly ammoniacal carrier solution containing Barber-Colman Company catalyst 24,130. About fifteen gallons of the ammoniacal carrier solution was pumped to the WETOX reactor (via an external heat exchanger and a small internal heat-exchanging coil in the 2-compartment autoclave). The WETOX reactor and the carrier solution were then preheated to the operating temperature.

Approximately 6.5 gallons of Forestry Service vault waste was added to the remaining approximately 35 gallons of carrier solution; and the mixture was pumped to the WETOX reactor from a continuously stirred head tank. All vapor condensate was recycled continuously to the head tank. All effluent--liquid and suspended solids--was impounded and periodically pumped (in 20-35 gallon batches) to the head tank. Each time effluent was pumped to the head tank, additional vault waste was added--generally in the ratio: 1 part vault waste to 4 parts recycled effluent.

Generally, the WETOX reactor was sampled just before recycling effluent and adding additional vault waste. A 6-compartment WETOX reactor--operating under the conditions imposed in the test described in this report--requires about three hours to reach a steady state.

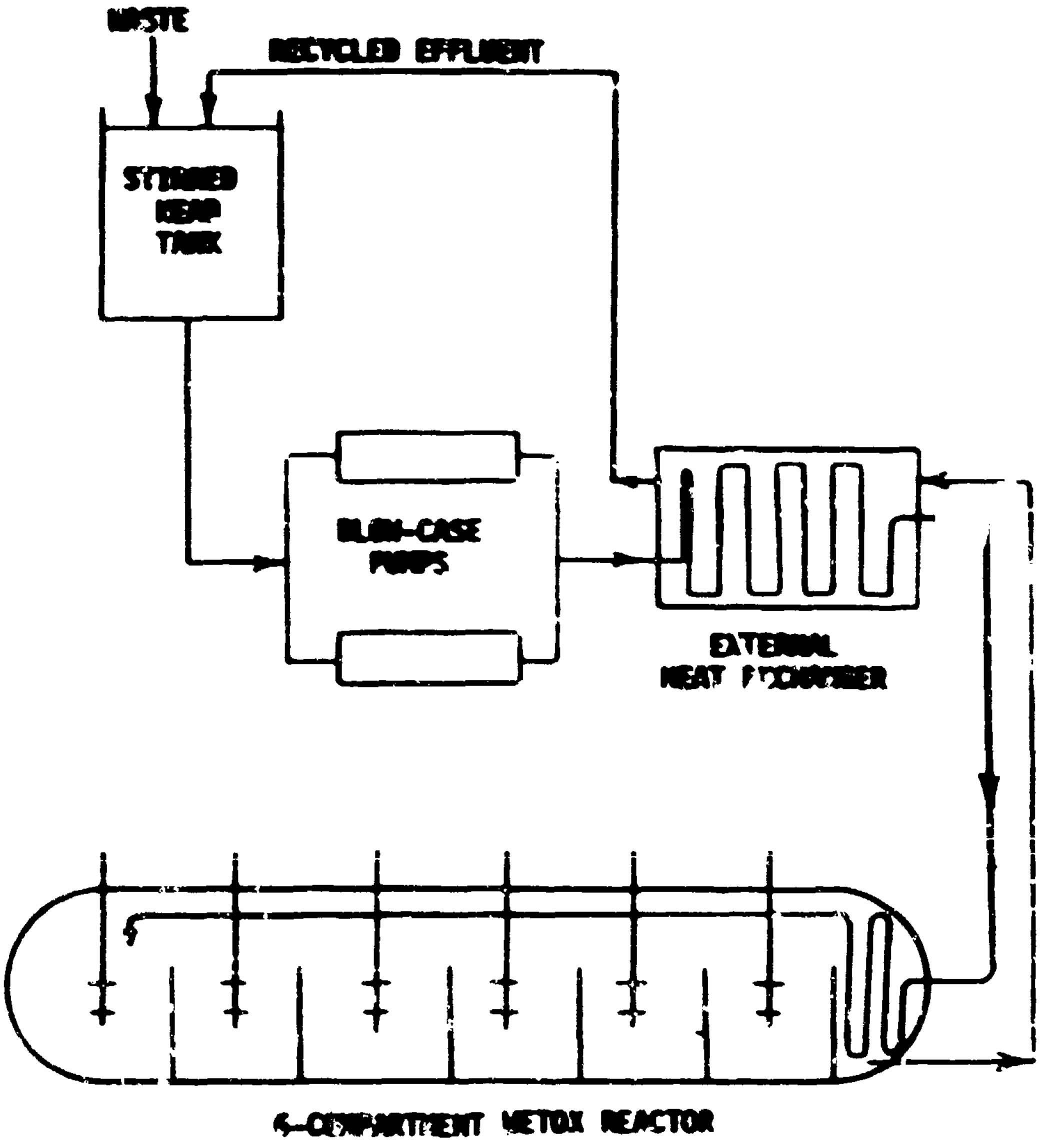

FIGURE 1. FLOWCHART FOR CLOSED-LOOP SANITATION SYSTEM

During the 5-day campaign, the following variables were held constant:

Reactor Temperature	440 - 465°F
Reactor Pressure	
Total	580 - 600 psi
Steam	382 - 444 psi, max.
Influent Pumping Rate	367 mℓ/min.
Agitator Speed	1000 - 1200 rpm
Air Flow	0.4 - 0.6 scfm

Operated at the above conditions, the mean residence time in each compartment was about 22 minutes; and the ratio O_2/COD--the ratio of oxygen added to oxygen demanded by waste--varied from 0.9 to 1.5.

3.2 EXPERIMENTAL RESULTS

A chronological summary is presented for the 5-day campaign in the Appendix of this report (73128, 73129, 73130, 73131 and 73134). At commencement, the total volume of liquid in the closed-loop system was about 46 gallons. During the first day, an additional 11.5 gallons were added; and 40 percent of the accumulating effluent was recycled. At the end of the second day, all of the circulating load had been recycled at least once. Effluent amounting to 1.4 times the volume of liquid in the system had been recycled by the end of the third day; 1.7 times, at the end of the fourth day; and at the conclusion of the test on the fifth day, effluent equivalent to 1.8 times the volume of the circulating load had been recycled through the reactor.

At the conclusion of the test, less than one gallon of influent remained in the head tank; and about 58 gallons of effluent had been impounded. The volume of liquid in process was estimated, and the following balance sheet was prepared.

Liquid Accountability (1630, 73134)

In the Reactor:	48.2 ℓ
In the Heat Tank, Pumps, Piping & Heat Exchanger:	5. ℓ
Impounded Effluent:	218. ℓ
Removed as Samples:	18.3 ℓ
	289.5 ℓ (76.5 gal.)

According to the Chronology (Run 73134), the accumulated volume of liquid in the system at the conclusion of the test was 81.3 gallons--the tally presented above accounts for 94 percent of the added volume--4.3 gallons (18.2 liters) are unaccounted for. There was no large spillage during the campaign. Each evening, however, the reactor was depressurized rather rapidly; and, apparently, about 1 gal on of steam was lost each night during the shut-down operation.

Based on the final assays at the end of the 5-day campaign and on the liquid balance, the mass balance for COD was:

COD Added:		6.091 kg	
COD Untreated -			
Removed in Sampling:	.060 kg		
Unused Influent:	.049		
		.109	
COD Treated:		5.982 kg	
COD Remaining -			
In the Reactor:	.124		2.07 pct
In Effluent:	.520		8.69 pct
		.644 kg	10.76 pct

$$\text{Percentage Reduction in COD} = 100 \left[\frac{\text{COD treated minus COD Remaining}}{\text{COD Treated}}\right] = 89.2$$

3.3 CONCLUSIONS - FIVE-DAY CAMPAIGN, FOREST SERVICE VAULT WASTE

The continuous wet oxidation of simulated shipboard waste (diluted vault waste) appears practical in a catalyzed ammoniacal circuit. As summarized in Table VI, the COD of the effluent remains nearly constant as does the percentage reduction per pass.

In this campaign, the vapor phase condensate was returned to the head tank for re-treatment. Occasionally, very high COD values were noted; e.g.(73131). Normally, this part of the effluent would be exhausted into the propulsion engine or auxiliary engine exhaust stack. In this campaign, the vapor phase would amount to 10 - 15 percent of the total effluent. If it had been removed from the system, the percentage reduction of COD would have been well above 90 percent.

No operational problems were encountered treating this type of waste in the WETOX reactor. The catalyst was stable and no additions other than air and vault waste were required during the campaign.

TABLE VI

SUMMARY, 5-DAY CAMPAIGN, SIMULATED SHIPBOARD SEWAGE (VAULT WASTE)

Run No.	COD Final Effluent mg/ℓ	COD Vapor Phase Condensate, mg/ℓ	% Reduction, COD
73128	977	-	85.1
	1560	-	74.0
73129	1505	-	76.6
	1920	2650	74.5
73130	1610	3728	76.3
73131	1680	2289	81.1
	2253	6844	79.1
73134	2153	3319	82.2

4.0 CONTINUOUS WET OXIDATION OF SIMULATED SHIPBOARD WASTE--PRIMARY SEWAGE SLUDGE

A second, four-day campaign was performed under the identical operating procedures outlined in Section 3, except that primary sludge from the Orange County Sanitation District and urine were blended to simulate the on-board waste.

The campaign was started using the final effluent from the above described 5-day vault waste tests.

At the completion of this test, the circulating volume of the system had been recycled through the WETOX reactor four to five times. The COD remaining in the final volume of liquid in the system was about 15 percent of that initially in the system.

During this campaign, the air flow was adjusted each day to maintain a constant ratio of O_2/COD as the concentration of residual COD in the system increased. The mean air flow and related values are:

Day	SCFM Air	Mean Value g/min. O_2	O_2/COD
73135	0.84	6.0	0.92
73136	0.86	6.1	0.93
73137	0.95	6.8	1.04
73138	1.2	8.2	1.05

4.1 RESULTS

A chronological tabulation is presented for each day of the campaign in the Appendix of this report. The amount and time is noted for each addition of waste to the system as well as the time and chemical analysis of samples taken from the system.

The carrier solution (and catalyst) used in preparing influent for the campaign had been used previously at least twice. By the end of the first day (73135), the entire volume of carrier solution had passed once more through the reactor; twice by the end of the third day (73137); and three times at the conclusion of the campaign on 73138.

There is no sign of deterioration in the efficacy of the catalyst and/or its carrier solution after five treatment cycles (four recycles).

The final liquid and vapor phase effluent analyses from each day's campaign are summarized in Table VII.

TABLE VII

SUMMARY, 4-DAY CAMPAIGN, SIMULATED SHIPBOARD WASTE PRIMARY SEWAGE SLUDGE FEED

Run No.	Final Liquid Phase Effluent COD, mg/ℓ	Vapor Phase Condensate, COD, mg/ℓ	% Reduction COD (Combined Liq. + Vapor)	NH_3-N mg/ℓ Liquid/Vapor	Liquid pH/ Vapor pH
73135	3182	6,943	80.3	920/2700	8.4/7/4
73136	3840	14,962	73.8	1720/2720	8.8/7.8
73137	3910	8,960	79.6	1500/2800	8.6/7.9
73138	2356	21,015	80.5	1200/2800	8.4/7.8

Influent COD: 15,000 - 22,400 mg/ℓ COD. See Appendix.

Throughout the campaign, a physical inventory of the liquid volume of the system was maintained. The statistics, which are included in the chronology, indicate that during each day's operation, the volume of the system diminished by about three gallons. The loss of liquid is the result of inadequate condensation of expelled vapors. In the present campaign, the rate of gas flow through the reactor was four to five times greater than in the previous test; and the condenser normally used with the WETOX reactor proved inadequate. (The deficiency has been corrected and another campaign is underway in which complete vapor condensation is being achieved.)

Data from the present campaign are representative of a shipboard system in which a portion of the vapor condensate is injected into the exhaust gas of either diesel or turbine propulsion units for evaporation to the air. This condensate contains no inorganic salts or high molecular weight compounds likely to form particulate material or char layers in the exhaust injection region. The energy required to evaporate the excess water ranges from 4,500 BTU/hr. to 6,800 BTU/hr. in alternative sanitation systems under development at Barber-Colman Company. This requirement is insignificant when compared to the sensible heat available even in the exhaust gas of the auxiliary diesels.

Liquid balance during the campaign was such that at the end of the first day the system contained essentially the same volume as initially present. (During the first day, nine gallons of sludge were added.) At the end of the second day, the system contained five gallons more than were initially present; at the conclusion of the third day, seven additional gallons had accumulated; and during the fourth day, no additional liquid was accumulated. Thus, at the end of the four-day campaign, the system contained about 25 percent more liquid than at start-up.

Mass balance for COD was computed for the first two days as well as for the four-day campaign. The results are presented in Tables VIII and IX.

4.2 CONCLUSIONS - FOUR-DAY CAMPAIGN - SEWAGE SLUDGE/URINE, SIMULATED SHIPBOARD WASTE

In this campaign, the vapor phase condensate was not recycled. Sewage sludge, in contrast to vault waste, produces a higher COD vapor phase condensate. No practical reason is apparent that would preclude the discharge of this product into the engine exhaust stream.

As evidenced by Run 73138, an increase in air flow promptly reduced the liquid phase COD and caused a remarkable increase in the vapor phase COD.

It appears possible to control rather easily the volume of liquid expelled in the vapor phase to maintain the system in hydraulic equilibrium. By increasing the air flow in Test 73138, no additional liquid was accumulated.

The NH_3 nitrogen appears to remain very nearly constant in the vapor phase. It is suspected that if the air feed rate is increased, the liquid phase NH_3 content will decrease because of the greater mass of vapor phase condensate with its constant NH_3 content. Again, Run 73138 demonstrates this point.

The system appears to maintain pH without additions.

TABLE VIII

COD Balance (1600, 73136)

COD Added			
As Sewage Sludge	4.256 kg		
In Initial Circulating Load	.334		
		4.59 kg	
COD Untreated			
In Unused Influent	0.203		
Removed In Samples	0.069		
		.272	
COD Treated		4.318	
COD Remaining			
In Reactor	0.219		5.1 pct
In Effluen	0.436		10.1 pct
		.655	
Percentage of Initial COD Not In the System At Conclusion of the Second Day			84.8 pct

TABLE IX

COD BALANCE (1540, 73138)

COD Added			
As Sewage Sludge	8.818 kg		
In Initial Circulating Load	.334		
		9.152 kg	
COD Untreated			
In Unused Influent	.102		
Removed In Samples	.152		
		.254	
COD Treated		8.898	
COD Remaining			
In Reactor	.611		6.8 pct
In Effluent	.682		7.7 pct
		1.293	
Percentage of Initial COD Not In the System At the Conclusion of the Fourth Day			35.5 pct

APPENDIX

TITLE **PAGE**

Chronological Summary of Five-Day Campaign

Chronological Summary of Four-Day Campaign

CHRONOLOGY--73128*

Time, PDT	Volume of Vault Waste, Added gal (ℓ)	COD Added mg O	Volume of Effluent Recycled, gal (ℓ)	Accumula- tive Vol. of influ. Fed To Reac. gal (ℓ)	Sampling Station	COD of Sample, mg/ℓ O	% Red. in Influent COD
1030	6.5(24.6)	784,233					
1300					Influent	6544	
					CG Compart 1	2646	59.6
					2	1939	70.4
					BS Compart 1	1413	78.3
					2		
					3	1084	83.4
					4	977	85.1
1305	5(18.9)	603,310	20(75.7)	15.3(58)			
1600					Influent	6003	
					CG Compart 1	3303	45.0
					2	2045	65.9
					BS Compart 1	1618	73.0
					2	1711	71.5
					3	1610	73.2
					4	1560	74.0
1630				36.2(137)			
	11.5(43.5)	1,387,533	20(75.7)	36.2(137)			

---

*Mean Air Flow for 73128: 0.4 scfm air; 2.7 g/min O_2; O_2/COD = 1.17.

CHRONOLOGY--73129*

Time, PDT	Volume of Vault Waste, Added gal (ℓ)	COD Added mg O	Volume of Effluent Recycled, gal (ℓ)	Accumulative Vol. of Influ. Fed To Reac. gal (ℓ)	Sampling Station	COD of Sample, mg/ℓ O	% Red. in Influent COD
0800	5(18.9)	603,310	20(75.7)	36.2(137)			
1300				55.5(210)	Influent	6432	
					CG Compart. 1	2700	58.0
					2	2382	63.0
					BS Compart. 1	1975	69.3
					2	1747	72.8
					3	1861	71.1
					4	1505	75.6
1305	6(22.7)	723,972	22(83.3)				
1600				71.3(270)	Influent	7520	
					CG Compart. 1	3200	57.4
					2	2784	63.0
					BS Compart. 1	2310	69.3
					2	2090	72.2
					3	1980	73.7
					4	1920	74.5
					Vapor Condensate	2656	
1630				74.0(280)			
	22.5(85.2)	2,714,815	62(235)	74.0(280)			

---

*Mean Air Flow, for 73129: 0.5 scfm air; 3.4 g/min O_2; O_2/COD = 1.33

CHRONOLOGY--73130*

Time, PDT	Volume of Vault Waste, Added gal (ℓ)	COD Added mg O	Volume of Effluent Recycled, gal (ℓ)	Accumulative Vol. of Infl. Fed To Reac. gal (ℓ)	Sampling Station	COD of Sample, mg/ℓ O	% Red. in Influent COD
0800				74.0(280)			
1115	6.5(24.6)	784,303	35(132)	75.6(286)			
1600				102 (386)	Influent	6800	
					CG Compart. 1	2848	58.1
					2	2720	60.0
					BS Compart. 1	2100	69.1
					2	2000	70.6
					3	1840	72.9
					4	1610	76.3
					Vapor Condensate	3728	
1630				105(398)			
	29(110)	3,499,118	97(367)	105(398)			

The Forestry Service Vault Waste used in this series of tests was received in two containers--a 35-gal. plastic drum and a 20-gal garbage can--Test Nos. 73128 thru 73130 were run on a 30-gal. portion from the 35-gal drum, which assayed 31,879 mg/ℓ O-COD. The remaining 25 gal. Vault Waste was blended and macerated to form undiluted influent for the subsequent tests in the series; this second portion assayed 52,694 mg/ℓ O-COD.

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*Mean Air Flow, for 73130: 0.5 scfm air; 3.7 g/min O_2; O_2/COD - 1.48

CHRONOLOGY--73129*

Time, PDT	Volume of Vault Waste, Added gal (ℓ)	COD Added mg O	Volume of Effluent Recycled, gal (ℓ)	Accumulative Vol. of Influ. Fed To Reac. gal (ℓ)	Sampling Station	COD of Sample, mg/ℓ O	% Red. in Influent COD
0800				105([illegible]			
1015	5(18.9)	997,234	20(75.7)	111(421)			
1300					Influent	8880	
					CG Compart. 1	5504	38.0
					2	4448	49.9
					BS Compart. 1	4150	53.2
					2	2960	66.7
					3	2180	75.4
					4	16[illegible]	81.1
					Vapor Condensate	2289	
1305	3(11.4)	598,340	12(45.4)	127(482)			
1630				146(553)	Influent	10,799	
					CG Compart. 1	3557	67.1
					2	3047	71.8
					BS Compart. 1	3047	71.8
					2	2719	74.8
					3	2561	76.3
					4	2253	79.1
					Vapor Condensate	6844	
	37(140)	5,094,692	123(488)	146(553)			

---

*Mean Air Flow, for 73131: 0.5 scfm; 3.3 g/min O_2; O_2/COD = 0.91

CHRONCLOGY--73134*

Time, PDT	Volume of Vault Waste, Added gal (ℓ)	COD Added mg O	Volume of Effluent Recycled, gal (ℓ)	Accumulative Vol. of Influ. Fed To Reac. gal (ℓ)	Sampling Station	COD of Sample, mg/ℓ C	% Red. in Influent COD
0800				146(553)			
0915	5(18.9)	997,234	20(75.7)				
1630				189(715)	Influent	12,126	
					CG Compart. 1	3127	74.2
					2	3032	75.0
					BS Compart. 1	2613	78.5
					2	2313	80.9
					3	2253	81.4
					4	2154	82.2
					Vapor Condensate	3319	
	42(160)	6,091,926	149(564)	189(715)			

1630,73134 The portion of this closed-loop test conducted on Forestry Vault Waste was concluded. Less than one gallon of influent remained and 58 gallons of effluent from which the solids were settled and filtered off the following day. Settled solids were filtered, washed and dried at 110°C overnight.
Settled effluent from 73134 assayed 2373 mg/ℓ O-COD
Settled solids from 35 gallons effluent weighed 450 grams (dried @ 110°C)

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*Mean Air Flow, for 73134: 0.6 scfm air; 4.1 g/min O_2; O_2/CCD = 0.92

<u>CHRONOLOGY--73135</u>

Time, PDT	Amount of Sludge Added To System gal	Amount of Sludge Added To System mg O-COD	Volume of Effluent Recycled gal	Accumulative Vol. of Influent Fed To Reactor gal	Accumulative Vol. of Liquid In System, gal Actual	Accumulative Vol. of Liquid In System, gal Added	Sampling Station	COD of Sample, mg/ℓ O	% Red. in Influent COD	NH$_3$-N, mg/ℓ N	pH
0800	5	1,418,750			40	40					
1300				19.8			Influent	17,877			7.6
							CG Compart. 1	4916	72.5	1200	
							2	4661	73.9	1280	
							BS Compart. 1	3631	79.7	1280	
							2	3522	80.3	1320	
							3	3362	81.2	1320	
							4	3182	82.2	1280	8.6
							Vapor Condens.	6129		2720	7.7
1310	4	1,138,000	16.8		40.5	44					
1630				40.4	39.2		Influent	17,717			7.8
							CG Compart. 1	5623	68.8	720	
							2	4917	72.2	820	
							BS Compart. 1	4340	75.5	960	
							2	3911	77.9	880	
							3	3731	78.9	1000	
							4	3492	80.3	920	8.4
							Vapor Condens.	6943		2700	7.8

CHRONOLOGY--73136

Time, PDT	Amount of Sludge Added To System gal	Amount of Sludge Added To System mg O-COD	Volume of Effluent Recycled gal	Accumulative Vol. of Influent Fed To Reactor gal	Accumulative Vol. of Liquid In The System gal Actual	Accumulative Vol. of Liquid In The System gal Added	Sampling Station	COD of Sample, mg/ℓ O	% Red. in Influent COD	NH_3-N mg/ℓ N	PH
0800				40.4	39.2	44					
0955	6	1,702,500	25			51*					
1300				58.1			Influent	21,067			7.8
							CG Compart. 1	8539	59.5	1040	
							2	6144	70.8	1120	
							BS Compart. 1	5203	75.3	1280	
							2	4501	78.6	1280	
							3	4050	80.8	1120	
							4	3871	81.6	1280	8.4
							Vapor Condens.	15,004		2720	7.8
1600				75.3			Influent	14,683			7.6
							CG Compart. 1	6065	58.7	1280	
							2	5107	65.2	1280	
							BS Compart. 1	4389	70.1	1400	
							2	4150	71.7	1400	
							3	4149	71.7	1720	
							4	3840	73.8	1720	8.6
							Vapor Condens.	14,962		2720	7.8
1630					48						

*Includes water from 4 liters of urine added 0955,73136

CHRONOLOGY--73137

Time, PDT	Amount of Sludge Added To System gal	Amount of Sludge Added To System mg O-COD	Volume of Effluent Recycled gal	Accumulative Vol. of Influent Fed To Reactor gal	Accumulative Vol. of Liquid In System gal Actual	Accumulative Vol. of Liquid In System gal Added	Sampling Station	COD of Sample mg/l O	% Red. in Influent COD	NH3-N mg/l N	pH
0800			35	75.3	45	51					
0845	5	1,418,750				57*					
1400							Influent	16,320			7.8
							CS Compart. 1	5200	68.1	1400	
							2	5360	67.2	1820	
							BS Compart. 1	3536	78.3	1820	
							2	3424	79.0	1600	
							3	3136	80.8	1600	
							4	1444	91.2	1720	9.0
1406	5†	1,571,627	20	100.4		63**	Vapor Condens	10,880		3200	
1600				111.8			Influent	19,200			7.9
							CS Compart. 1	8560	55.4	1200	
							2	7960	58.5	1720	
							BS Compart. 1	5680	70.4	1800	
							3	4950	74.2	1900	
							4	3910	79.6	1820	8.6
							Vapor Condens.	8960		5500	7.9
					52.8						

*Includes 4 liters urine added 0845, 73137

**Includes 3 liters urine added 1406, 73137

†Sludge added (1406, 73137 and subsequently) assayed 83,046 mg/l O-COD; whereas previously added sludge assayed 74,967 mg/l O-COD.

CHRONOLOGY--73138

Time, PDT	Amount of Sludge Added To System gal	Amount of Sludge Added To System mg/ COD	Volume of Effluent Recycled gal	Accumulative Vol. of Influent Fed To Reactor gal	Accumulative Vol. of Liquid In The System gal Actual	Accumulative Vol. of Liquid In The System gal Added	Sampling Station	COD of Sample, mg/ℓ O	% Red. in Influent COD	NH_3-N mg/ℓ N	pH
0800	5	1,571,627	20	114.9		68.4*					
1300							Influent	22,400			8.1
							CS Compart. 1	11,360	49.3	1.00	
							2	9160	59.1	1800	
							RS Compart. 1	3089	86.2	1800	
							3	2643	88.2	1600	
							4	2356	89.5	1200	6.4
							Vapor Condens.	21,015		2060	7.8
1630				153.2	51.5						
	30	8,818,254	116.5	153.2	51.5	68.4					

*Includes 2 liters urine added 0800, 73138

1840, 73138 Physical inventory conducted: 1 gal unused influent; 12.5 gal liquid in reactor and 38 gal eff .ent impounded. Settled effluent assayed mg/ℓ O-COD, pH 7.95, and 1080 mg/ℓ N.

APPENDIX J

EVALUATION OF
CONTINUOUS-FLOW TESTS
AMMONIACAL WET OXIDATION

With the data presented in Appendix I, the supplementary experiments and analysis presented herein constitute the support of the closed-loop sanitation system reccommended in Sections 4 and 6 of the main report.

In a recent report (Appendix I) prepared and disseminated to the U.S. Navy under Contract No. N00174-73-C-0140, pilot-plant results were presented from continuous-flow tests in which simulated shipboard sewage was demonstrated to be treated effectively in a closed-loop sanitation system: Body waste was conveyed in an aqueous carrier solution (with a catalyst) through a wet-oxidation reactor in which the putrid, pathogenic sewage was destroyed--mainly by burning to carbon dioxide and water but secondarily by forming innocuous water-soluble ammonium acetate. Effluent from the reactor (the ammonium acetate), in practice, would be recycled to the shipboard toilets and urinals as flushant. The tests demonstrated that the effluent (and catalyst) can be recycled without apparent loss of efficacy. Buildup of ammonium acetate in the circulating effluent is fairly slow, and effluent could be reused as flushant many times before replacing a portion with fresh carrier solution (and catalyst). Spent effluent would be stored aboard ship in a holding tank; ultimate disposal of spent effluent would be accomplished ashore.

In this appendix, data from the pilot-plant tests and supplemental laboratory research are examined to establish the nature of the wet-oxidation processes.

J.1 SUPPLEMENTAL BATCH EXPERIMENTS

In addition to the continuous-flow tests described in the Navy reports, batch experiments were conducted on aliquots of the same waste--Forestry Service vault waste and OCSD primary sewage sludge. These supplemental experiments establish the rate of wet oxidation.

J.1.1 EXPERIMENTAL PROCEDURE.

The batch experiments were performed in the same manner as those described elsewhere in this report, e.g., Section 2.3, and Appendices C and E. In each test, 1000 mℓ H_2O, or 0.1-N NH_4OH, containing Barber-Colman Co. catalyst 24,130 was preheated in a stirred 1-gal autoclave. When the desired temperature (about 450°F) was reached, 500 mℓ waste was injected into the preheated reactor, followed immediately by oxygen gas. The oxygen was metered from a pressure cylinder of known volume and temperature and was added in sufficient quantity to yield an initial ratio of O_2:COD of about unity. The temperature of the reactor was maintained constant over a two-hour period after injection of the waste during which the liquid phase was sampled periodically.

a. Analytical Methods.

Samples of the liquid phase were assayed for chemical oxygen demand (COD) and total organic carbon (TOC) by the procedures specified in Methods For Chemical Analysis of Water and Wastes 1971, published by Environmental Protection Agency, Water Quality Office, Cincinnati, Ohio.

Ammoniacal-nitrogen content was determined by a specific ion electrode (Orion Model 95-10) using the manufacturer's recommended method.

The liquid portion of each sample was also examined by gas-liquid chromatography using a Hewlett-Packard research gas chromatograph, model 5754 B. Partitioning was effected on a 6 foot x 1/8" OD column packed with 50/80 mesh Porapak Q: A 2-microliter aliquot of each sample was injected into the chromatograph with the column oven at 170°C, and the temperature of the oven was programmed to increase at 60° C/minute to 200°C three minutes after injection. Compounds eluting from the column were detected by a dual flame ionization detector. A semiquantitative analysis is reported in this memo. Quantitative analysis and positive identification of several unknown peaks is in progress. In most cases, the concentration of the various organic compounds is directly proportional to the peak height which is reported in the tables presented in this memo.

b. Interpretation of Analytical Results.

In the chemical and chromatographic analysis of experiments like those presented in this section, one must bear in mind the limitations of the different analytical methods:

1) Chromatographic analysis is effected routinely in our laboratory on a 2-microliter aliquot which is taken generally by inserting a syringe with a 0.005- to 0.010-in. ID needle into the supernatent liquid above the settled solids (that form in the liquid-phase slurry after its removal from the autoclave). In other words, only the water-soluble and colloidal organic species are analyzed by chromatography. Much of the organic matter contained in early samples escapes analysis.

2) Total organic carbon is determined on a 50-microliter aliquot of samples exhibiting a COD of 4000 mg/ℓ O or less, and on the same aliquot of suitably diluted samples exhibiting COD greater than 4000 mg/ℓ O. The aliquot is withdrawn with a syringe from an agitating portion of the liquid-phase slurry originally taken from the autoclave. The bore of the needle in the TOC syringe is considerably larger than in the chromatograph syringe. Stated simply, water-soluble, colloidal and particulate matter are assayed in the TOC method; large particles probably escape analysis.

3) Chemical oxygen demand is determined on a 10- to 50-mℓ aliquot of the liquid-phase slurry or a diluted portion. The aliquot is reacted in boiling 50-percent sulfuric acid for two hours in the presence of dichromate and a silver catalyst. The organic solids are digested completely and converted to soluble species which in turn are oxidized to carbon dioxide and water. Extensive research has established that virtually all of the organic compounds formed in the wet oxidation of natural waste are reactive in the standard COD method. In other words, the COD test determines the organic content of the entire liquid-phase slurry--solids, colloidal, and water-soluble species.

J.1.2 BATCH TEST ON VAULT WASTE.

Batch Test No. 329 was conducted on the same lot of Forestry Service vault waste denoted in Navy (Contract N00174-73-C-0140) Progress Report No. 1 as "the second portion," i.e., vault waste which was received in a metal 20-gal garbage can and assayed 52,694 mg/ℓ O (COD). The experiment was performed in the manner described in the earlier section on the experimental procedure. The vault waste was injected into 1000 mℓ preheated 0.1-N NH_4OH. The initial ratio O_2:COD was 1.0 and the mean temperature was 451°F during the reaction period.

The results of chemical and chromatographic analyses are presented in Table J-1. The data indicate that at the end of 60 to 80 minutes of wet oxidation the original waste has been destroyed and the effluent exhibits a COD equivalent to about one tenth of that originally present in the system. Subsequent treatment beyond 60 minutes results in little additional destruction.*

The effluent contains at least six water-soluble chemical species which are detected by a flame ionization detector in the helium gas eluted from a porous-polymer chromatographic column. Four of the six compounds have been identified tentatively as acetic acid, formaldehyde, propionic acid and butyric acid. (Further discussion of the chromatographs for this and the other experiments is presented in a later section.)

In Figure J-1, a graph is presented in which the decreases in COD and in TOC observed in Test No. 329 are plotted for increasing reaction time. The trend is the same for both indices of organic concentration: There is a rapid initial decrease (a sharp descent, which is linear for the logarithm) followed by an abrupt change to a slower rate of decrease (which is also linear with respect to the logarithm of the concentration variable). The corresponding rate constants for the decrease in TOC are smaller--about one-half the magnitude of those for COD-reduction--and the abrupt change from a rapid decline in TOC to a slower one occurs a bit later than in the corresponding COD plot. These similarities between COD and TOC are understandable; because the ratio COD:TOC is consistent over most of the monitored reaction:

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*The COD listed in Table J-1 for the 120-min. sample is obviously not the true value: It does not agree with either the chromatographic or TOC analyses. The chromatograph indicates that there are no great differences in the kinds and numbers of compounds present in the samples taken at 80 and 120 minutes; likewise the TOC's of these two samples are comparable. Moreover, the peak height registered for acetate in the 120-min. sample is equivalent to a concentration of about 1000 mg/ℓ O (COD) indicating that the COD must be greater than the 990 reported in Table J-1.

TABLE J-1

CHEMICAL AND CHROMATOGRAPHIC ANALYSES OF THE LIQUID PHASE

Batch Test No. 329--Vault Waste

	Elapsed Time After Injection of Waste, Minutes							
	5	10	15	20	40	60	80	120
Pct. Red. in COD	29	57	72	74	84	88	90	94
COD, mg/ℓ O	12,400	7600	4880	4603	2720	2160	1680	990
TOC, mg/ℓ C	4760	3360	2860	2730	1090	915	810	[illegible]
Ratio, COD:TOC	2.6	2.3	1.7	1.7	2.5	2.4	2.1	1.5
NH_3-N, mg/ℓN	780	880	1050	1150	1150	1400	2050	2400
Formaldehyde*	2.5	6	5	2	1.5	3.5	4	3.5
Acetaldehyde*	4	1.5	<1	<1	<1	<1	<1	<1
Unknown #1*	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†	<1	<1	<1
Unknown #2*	<1	<1	<1	n.d.†	n.d.†	<1	<1	<1
Unknown #3*	2	8	10	4	5	11	10	10
Acetone*	2	1	<1	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†
Unknown #5*	9.5	6	4.5	2	2	5	11.5	10
Acetic Acid	16	22	23	17	20	25	22	22
Unknown #4*	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†
Propionic Acid*	8.5	8	6.5	3.5	3	3	3.5	3.5
Butyric Acid*	2	1.5	1	1	1	1.5	2.5	2

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*Divisions of peak height

†n.d. denotes not detected

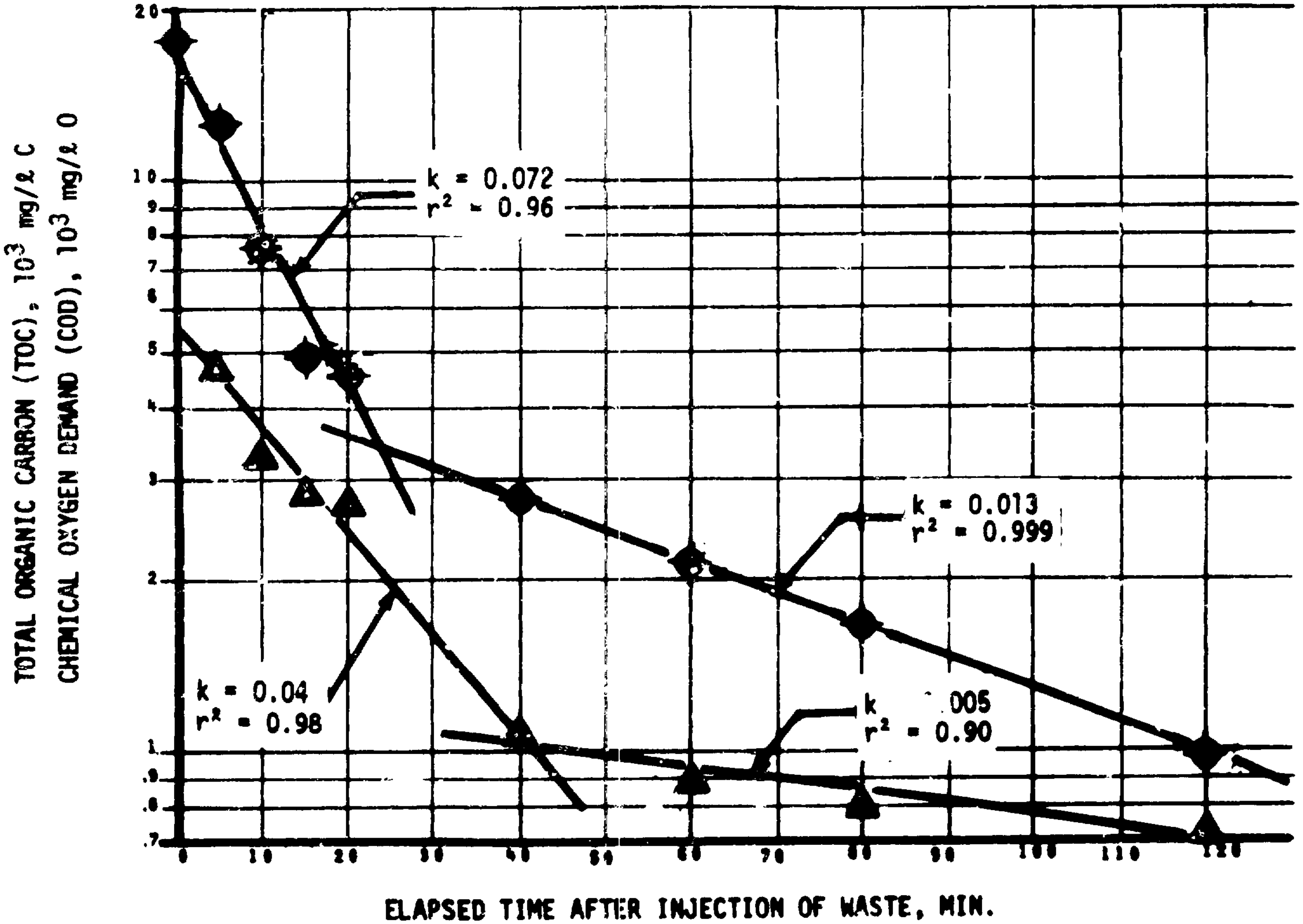

FIGURE J-1. SEMI-LOGARITHMIC PLOT SHOWING DECREASE IN COD (◆) AND IN TOC (▲) WITH INCREASING REACTION TIME OBSERVED IN AMMONIACAL WET OXIDATION OF FORESTRY SERVICE VAULT WASTE (BATCH TEST NO. 329) PERFORMED 5/14/73

t, min	5	10	15	20	40	60	80	120
COD:TOC	3	2	2	2	2	2	2	2*
% Red in COD	29	57	72	74	84	88	90	94**

J.1.3 BATCH TEST ON SEWAGE SLUDGE

Batch Test No. 333 was conducted on a portion of the same lot of JCSD primary sewage sludge used in the latter part (Test Nos. 73137 and 73138) of the continuous-flow campaign described in Navy (Contract N00174-73-C-0140) Progress Report No. 2. The experimental procedure is described in an earlier section of this report. The sludge was injected into 1000 mℓ preheated 0.1-N NH_4OH. The initial ratio O_2:COD was 1.2; and the mean temperature was 470°F over the 2-hr. reaction period.

The results of the chemical analyses, which are summarized in Table J-2 for the experiment on sewage sludge, are in most respects similar to those obtained in similar ammoniacal wet oxidation of vault waste. The percentage reduction in COD is the same at the end of a comparable period of reaction; and, as can be seen in Figure J-2, the rate constants associated with the reduction in COD and TOC are the same in the wet oxidation of vault waste as in the wet oxidation of primary sewage sludge. In other words, the age of the waste did not affect the rate or extent of destruction: In the ammoniacal system, vault waste--body sewage deposited over a period of 6 months to 1 year in a concrete-lined latrine--oxidizes as rapidly and completely as primary sewage sludge which was 3 to 4 days old.

The ratio COD:TOC is the same in effluent samples from ammoniacal wet oxidation of sewage sludge as in effluent from similar treatment of vault waste. The magnitude of the COD and TOC is proportionately greater in effluent samples from the test on sludge than from the test on vault waste, because the initial concentration of organic matter was greater in the test on sludge.

J.2 COMPARISON OF BATCH AND CONTI JUS-FLOW TESTS

The preceding batch tests were, of course, performed in order to compare the results with those from the continuous-flow tests described in Appendix I.

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* As pointed out in a previous footnote this value is probably about two.

**This value is probably 90.

TABLE J-2

CHEMICAL AND CHROMATOGRAPHIC ANALYSES
OF THE LIQUID PHASE
Batch Test No. 333 Sewage Sludge

	Elapsed Time After Injection of Waste, Minutes						
	10	15	20	40	60	80	120
Pct. Red. in COD	34	62	73	80	86	88	89
COD, mg/ℓ O	18,229	10,508	7404	5572	3781	3423	3105
TOC, mg/ℓ C				1770	1690	1490	1430
Ratio, COD:TOC				3.2	2.2	2.3	2.2
NH_3-N, mg/ℓN	940	940	1150	1150	1500	1350	1350
Formaldehyde*	9.5	9.5	14	9	9.5	9	4.5
Acetaldehyde*	24	<1	<1	n.d.†	<1	<1	<1
Unknown #1*	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†
Unknown #2*	3	2	3	1.5	1.5	1.5	<1
Unknown #3*	23	22.5	37	21	28	26	10
Acetone*	4	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†
Unknown #5*	<1	1	4.5	1.5	2.5	2	<1
Acetic Acid	30	36.5	31	38	35	45	36.5
Unknown #4*	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†	n.d.†
Propionic Acid*	12	9	6	5	5	5	3
Butyric Acid*	3	3	1.5	1.5	2	3	3

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*Divisions of peak height

†n.d. denotes not detected

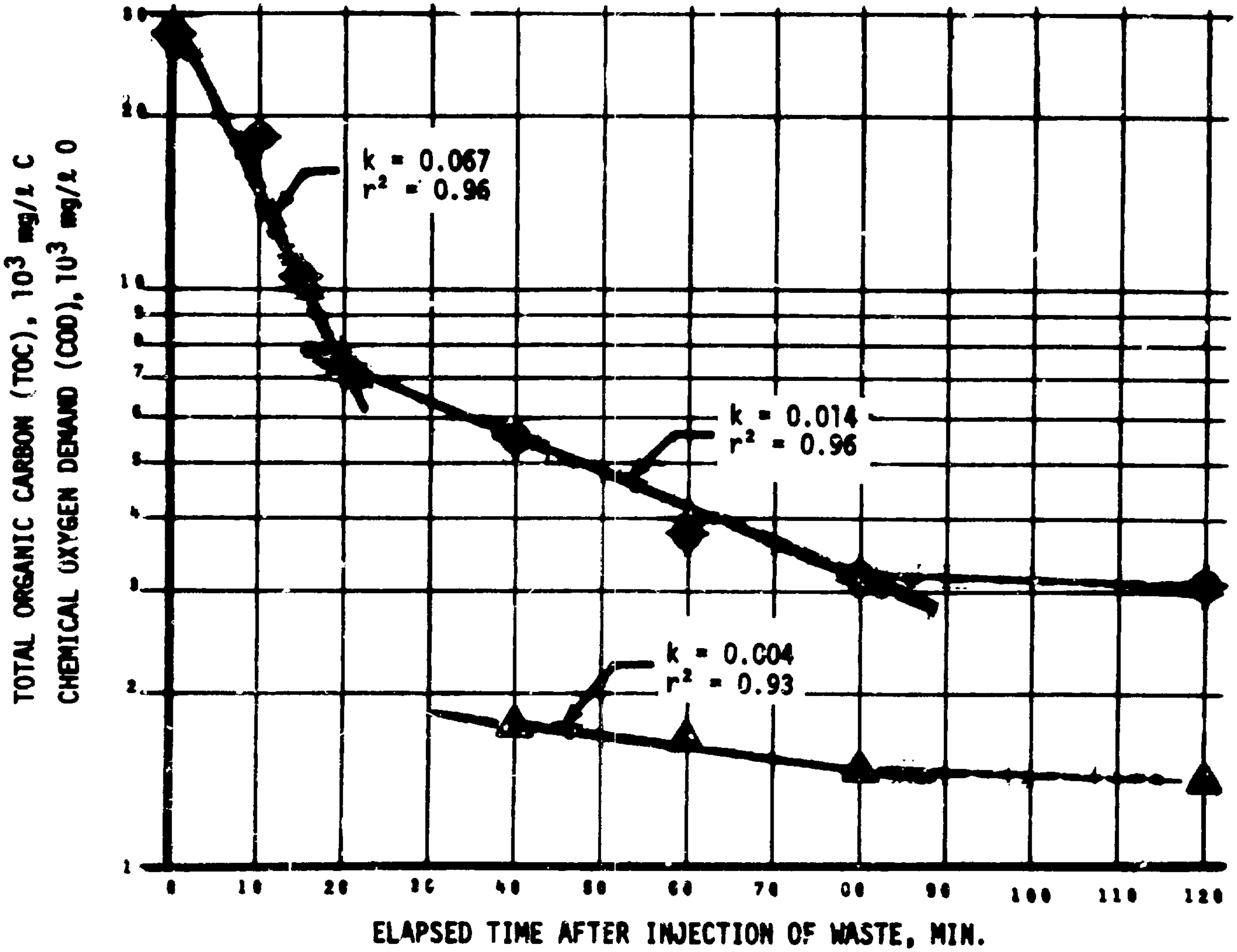

FIGURE J-2. SEMI-LOGARITHMIC PLOT SHOWING DECREASE IN COD (◆) AND IN TOC (▲) WITH INCREASING REACTION TIME OBSERVED IN AMMONIACAL WET OXIDATION OF PRIMARY SEWAGE SLUDGE (BATCH TEST NO. 333 PERFORMED 5/18/73).

J.2.1 RATE OF REACTION

As in past tests, the rate of reduction in COD was calculated for the continuous-flow tests from the expression:

$$-r_n = (C_{n-1} - C_n)\ \tau_n \qquad \text{(J-1)}$$

in which r is the rate of reduction in COD:C and τ are, respectively, the COD and mean residence time of the liquid slurry in a compartment; and n is a subscript denoting the location of a compartment with reference to the inlet end of the horizontal reactor. (See Section 3.4, main report.)

Likewise pseudo-first-order rate constants were calculated from the formula:

$$r_n = -k_n\ C_n, \qquad \text{(J-2)}$$

in which k is a rate constant for the COD-reduction process.

Past research has demonstrated that generally values of k calculated from continuous-flow tests correlate with k-values determined from batch experiments. In the case at hand, a 5-day continuous-flow campaign was conducted on Forestry Service vault waste, and a 4-day campaign on sewage sludge. The supplemental batch experiments, which were previously described, establish rate constants for the processes comprising wet oxidation under the imposed conditions. The most likely values of these rate parameters were presented in Figures J-1 and J-2; they are reproduced below:

	vault waste	sewage sludge
Initial rate constant, min^{-1}	0.072	0.067
Late-Stage rate constant, min^{-1}	0.013	0.014

For comparison, the rate parameters for the continuous-flow tests are compiled in Table J-3. Mean values are presented in Table J-4.

In comparing the rate constants computed for the continuous-flow tests with those from the batch tests, consideration must be given to the fluctuations in catalyst and recycled COD that occurred during the continuous campaign. Mean values for the relative catalyst level and percentage of recycled COD are listed in Table J-4. Initially the system contained sufficient catalyst to achieve effective reduction in COD; however, with each addition of waste to the closed loop, the volume of liquid in the system grew, because the waste was almost wholly water--the catalyst was diluted. Periodically, additional catalyst was added to compensate for the increased volume.

Note in Table J-3 that the rate constants for the reduction in COD occurring in the first compartment are, in general, proportional to the level of catalyst present in the reactor at the time of sampling. Note, however, that

TABLE J-3

COMPILATION OF RATE PARAMETERS CALCULATED FOR CONTINUOUS-FLOW TESTS ON SEWAGE SLUDGE AND VAULT WASTE IN 0.1-N NH_4OH

Day of Test	SAMPLE Time PDT	Compartment	Rate($-r_n$) mg/ℓ 0 min^{-1}	Rate Constant k, min^{-1}	Catalyst, Pct of Initial	Recycled COD, Pct of Influent	% red. in Influent COD
73128*	1300	1	173	.065	100	0	59.6
		2	34	.018			70.4
		3	23	.016			78.3
		4					
		5					83.4
		6	6	.006			85.1
	1600	1	120	.036		11	45.0
		2	61	.030			65.9
		3	19	.012			73.0
		4					71.5
		5	5	.003			73.2
		6	3	.002			74.0
73129*	1300	1	166	.060	80	16	58.0
		2	15	.006			63.0
		3	18	.009			69.3
		4	10	.006			72.8
		5					71.1
		6	21	.013			76 6
	1600	1	192	.060	65	16	57.4
		2	20	.007			63.0
		3	21	.009			69.3
		4	10	.005			72.2
		5	5	.003			73.7
		6	3	.002			74.5

TABLE J-3 (CONTINUED)

COMPILATION OF RATE PARAMETERS

Day of Test	SAMPLE Time PDT	Compart-ment	Rate($-r_n$) mg/ℓ 0 min $^{-1}$	Rate Constant k, min $^{-1}$	Catalyst, Pct of Initial	Recycled COD, Pct of Influent	% red. in Influent COD
73130*	1600	1	176	.062	50	24	58.1
		2	6	.002			60.0
		3	27	.013			69.1
		4	4	.002			70.6
		5	7	.004			72.9
		6	12	.008			76.3
73131**	1300	1	150	.027	20	11	38.0
		2	51	.012			49.9
		3	13	.003			53.2
		4	52	.018			66.7
		5	36	.016			75.4
		6	27	.016			81.1
	1630	1	322	.090	100	11	67.1
		2	25	.008			71.8
		3					71.8
		4	14	.005			74.8
		5	7	.003			76.3
		6	16	.007			79.1
73134**	1630	1	400	.128		15	74.2
		2	5	.002			75.0
		3	18	.007			78.5
		4	13	.006			80.9
		5	3	.001			81.4
		6	5	.002			82.2

TABLE J-3 (CONTINUED)

COMPILATION OF RATE PARAMETERS

Day of Test	SAMPLE Time PDT	Compart-ment	Rate($-r_n$) mg/ℓ O min^{-1}	Rate Constant k, min^{-1}	Catalyst, Pct of Initial	Recycled COD, Pct of Influent	% red. in Influent COD
73135†	1300	1	576	.117	200	12	72.5
		2	12	.003			73.9
		3	45	.012			79.7
		4	5	.001			80.3
		5	7	.002			81.2
		6	10	.003			82.2
	1630	1	542	.098	200	15	68.8
		2	29	.006			72.2
		3	25	.006			75.5
		4	19	.005			77.9
		5	8	.002			78.9
		6	13	.004			80.3
73136†	1300	1	557	.065	150	16	59.5
		2	116	.019			70.8
		3	41	.008			75.3
		4	31	.007			78.6
		5	21	.005			80.8
		6	10	.002			81.6
	1600	1	383	.063	150	16	58.7
		2	46	.009			65.2
		3	32	.007			70.1
		4	10	.003			71.7
		5					71.7
		6	16	.004			73.8

TABLE J-3 (CONTINUED)

COMPILATION OF RATE PARAMETERS

Day of Test	SAMPLE Time PDT	Compartment	Rate($-r_n$) mg/ℓ 0 min^{-1}	Rate Constant k, min^{-1}	Catalyst, Pct of Initial	Recycled COD, Pct of Influent	% red. in Influent COD
73137+	1400	1	494	.095	75	17	68.1
		2					67.2
		3	80	.023			78.3
		4	5	.001			79.0
		5	13	.004			80.8
		6	90	.062			91.2
	1600	1	473	.055	75	16	55.4
		2	29	.004			58.5
		3	100	.018			70.4
		5					74.2
		6	56	.014			79.6
73138+	1300	1	491	.043	70	16	49.3
		2	107	.012			59.1
		3	267	.087			86.2
		5					88.2
		6	15	.006			89.5

* Tests 73128, 73129 and 73130 were conducted on the first portion of the vault waste which had a COD of about 32,000 mg/ℓ 0.

**Tests 73131 and 73134 were performed on the second portion of the vault waste which assayed about 53,000 mg/ℓ 0.

+ Tests 73135, 73136, 73137 and 73138 were performed on sewage sludge assaying from 75,000 to 63,000 mg/ℓ 0.

TABLE J-4

MEAN VALUES OF RATE PARAMETERS FROM CONTINUOUS-FLOW TESTS ON VAULT WASTE AND SEWAGE SLUDGE

Percentage Reduction in COD

Compartment	Mean Value	Standard Deviation
1	59.3	10.0
2	65.7	6.9
3	73.2	7.4
4	74.8	4.5
5	77.5	5.0
6	80.5	5.2

Reaction Rate Constant, k, min^{-1}

Compartment	Mean Value	Standard Deviation
1	0.071	0.029
2	0.010	0.008
3	0.016	0.021
4	0.005	0.005
5	0.004	0.004
6	0.010	0.015

Percentage Recycled COD In Influent

Mean,	14.1%
Std. Dev.,	5.1%

Percentage Level of Catalyst

Mean	102%
Std. Dev.	52%

the fluctuation in the level of catalyst had little effect on the over-all percentage reduction in COD achieved in a 6-compartment CSTR--although less reduction occurred in the initial compartments whenever the level of catalyst dropped substantially, proportionately more reduction took place in the later compartments. (See, for example, the 73131 data at 1300.). As can be seen from Table J-4, during the 9 days of continuous tests, the mean level of catalyst was 102 percent of the design level.

As the campaigns progressed, effluent from previous tests was recycled as a part of the influent in successive tests. Because effluent COD is largely due to the presence of oxidation-resistant compounds, the rate of reduction associated with influent containing substantial recycled effluent is less than the rate of reduction for influent containing no recycled effluent. In the campaigns performed for the Navy, however, circumstances were such that the relative amount of recycled effluent was consistent throughout the tests--also the amount of recycled COD was not substantial (14% of the total COD)--therefore, there are no discernible fluctuations attributable to recycled COD.

Compare the mean rate constants for the continuous-flow tests, which are listed in Table J-4, with the values listed for the batch experiments, which were described earlier. The reaction in the first compartment of the continuous reactor proceeded at the same rate initially observed in the batch tests; and the rate in the second, third, and sixth compartments of the CSTR is comparable to the late-stage rate of the batch tests. On the other hand, the mean rates for the fourth and fifth compartments are less than either rate observed in the batch tests.

J.2.2 COMPARISON OF CHROMATOGRAPHS

Chromatographs were prepared from a set of samples taken 1630, 73131, during the continuous-flow test on the same vault waste used in the previously described batch experiment.

The final effluent for the continuous-flow test* is compared on the following page with the 120-min. sample for the batch test:

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*The over-all mean residence time in the 6-compartment CSTR was about 129 minutes

	Divisions of Peak Height	
	Batch Test	Continuous-Flow Test
Formaldehyde	3.5	4
Acetaldehyde	<1	<1
Unknown #1	<1	<1
Unknown #2	<1	<1
Unknown #3	10	17
Unknown #5	10	10.5
Acetic Acid	22	26
Propionic Acid	3.5	6
Butyric Acid	2	2

The continuous-flow effluent contains disproportionately more of Unknown #3 and propionic acid than effluent from the batch test,*otherwise the composition of the two effluents are identical.

A comparison is presented below of the chromatographs obtained for the vapor condensate and final effluent from the continuous test. The tabulated data indicate than unknown #3 is a substance comparable in volatility to formaldehyde. (Based on published retention times on Porpak Q and its behavior in the continuous-flow test, Unknown #3 may be propionaldehyde.)

	Divisions of Peak Height	
	Final Effluent	Vapor Condensate
Formaldehyde	4	19
Acetaldehyde	<1	1
Unknown #1	<1	<1
Unknown #3	17	50
Acetone	n.d.	<1
Unknown #5	10.5	13
Acetic Acid	26	9
Propionic Acid	6	4
Butyric Acid	2	3
COD, mg/ℓ 0	2253	6844

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*The effluent from the continuous-flow test assayed 2253 mg/ℓ 0 in COD; whereas the 120-minute sample from the batch test is estimated to contain about 1500 mg/ℓ 0.