

**This dissertation has been
microfilmed exactly as received**

70-4485

**SIERKA, Raymond A., 1938-
HIGH TEMPERATURE PYROLYSIS OF
SANITARY WASTES.**

**The University of Oklahoma, Ph.D., 1969
Engineering, sanitary and municipal**

University Microfilms, Inc., Ann Arbor, Michigan

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

HIGH TEMPERATURE PYROLYSIS OF SANITARY WASTES

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

RAYMOND A. SIERKA

1969

HIGH TEMPERATURE PYROLYSIS OF SANITARY WASTES

APPROVED BY

Am. W. Reid
Zac. E. Saxe
Robert F. Nelson
Leon S. Gienko

DISSERTATION COMMITTEE

ACKNOWLEDGMENTS

It is with pleasure that I acknowledge the following people and organizations, without whose help this dissertation could not have been completed:

To G. W. Reid I will always be indebted for the opportunity to do graduate work and for his advice and technical assistance in directing this work.

To my committee, Dr. Ciereszko, Dr. Streebin, Dr. Nelson and Dr. Klehr for the many hours of fruitful discussion and evaluation of this dissertation.

To Mrs. Betty Jo Todd for typing this work into manuscript form.

To the Public Health Service for their support, in the form of a Traineeship Grant, and the Food Machinery and Chemical Corporation for the equipment used throughout this study.

To my children for their interest.

And to my wife Jeanne for her love, help, and inspiration.

TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF FIGURES.	vi
LIST OF ABBREVIATIONS.	viii
Chapter	
I. INTRODUCTION	1
II. CONCEPTUAL DESIGN.	23
III. EXPERIMENTAL APPARATUS	56
IV. EXPERIMENTAL PROCEDURES.	61
V. EXPERIMENTAL RESULTS AND DISCUSSION.	66
VI. CONCLUSIONS.	112
LIST OF REFERENCES	115

LIST OF TABLES

Table	Page
1. Test Results for U.S.S. Fulton.	12
2. Summary of Sewage Properties from Navy Vessels. . .	62
3. Chemical Constituents Found in Feces - Partial Listing.	62
4. Chemical Constituents Found in Urine.	63
5. Statistical Analysis - Hot Spot Temperature as a Function of Flow Rate.	73
6. Statistical Analysis - Per Cent COD Reduced as a Function of Hot Spot Temperature.	77
7. Statistical Analysis - Effluent COD as a Function of Influent COD and Hot Spot Temperature.	78
8. Statistical Analysis - Effluent BOD ₅ as a Function of Effluent COD	86
9. Kjeldahl Nitrogen	89
10. Unsteady State Run.	104
11. COD Removed per Kilowatt of Power Supplied for Various Pyrolysis Chamber Feed Sources . .	110
12. Comparison of Sewage Effluents Pyrolyzed in the Presence and Absence of Air	111

LIST OF FIGURES

Figure	Page
1. Pyrolysis Aeration System for Shipboard Sewage Disposal	5
2. Treatment Techniques.	22
3. Process Flowsheet - Zimmerman Process	27
4. Process Flowsheet - Atomized Suspension Technique .	36
5. Process Flowsheet - Reverse Flow Reactor.	44
6. The Pyrolysis Process	50
7. Photograph of Pyrolysis Chamber and Associated Equipment	57
8. Vertical Temperature Profiles Using Nozzle #1805. .	68
9. Vertical Temperature Profiles Using Nozzle #1808. .	69
10. Vertical Temperature Profiles Using Nozzle #1811. .	70
11. Hot Spot Temperature Variations with Flow Rate.	72
12. Hot Spot Temperature Effect on Effluent COD	75
13. Hot Spot Temperature Effect on Effluent COD Reduction.	76
14. Arithmetic Probability Plot of Per Cent COD Reduced Versus Hot Spot Temperature. (600 - 1500 °F).	80
15. Arithmetic Probability Plot of Per Cent COD Reduced Versus Hot Spot Temperature.	82
16. Hot Spot Temperature Effect on Soluble COD Reductions	83

LIST OF FIGURES - Continued

Figure		Page
17.	Relationship of Soluble COD to Total COD Effluent Reductions.	84
18.	Ratio of Soluble COD to Total COD Removed as a Function of Flow Rate	85
19.	Relationship of Effluent BOD ₅ to Effluent COD . . .	87
20.	Kjeldahl Nitrogen Remaining in the Effluent as a Function of Hot Spot Temperature.	90
21.	Total Solids Changes in the Effluent as a Function of Flow Rates	91
22.	Total Volatile Solids Changes in the Effluent as a Function of Flow Rate	92
23.	Titration Curves of Sewage and Pyrolysis Chamber Effluents.	95
24.	Hot Spot Temperature Variations with Time for an Unsteady State Run.	98
25.	Outlet Condenser Water Temperature Variations with Time for an Unsteady State Run.	99
26.	COD Reductions as a Function of Time for an Unsteady State Run	101
27.	Titration Curves Unsteady State Effluents	103
28.	Effluent Color Relationship with Hexavalent Chromium Content for an Unsteady State Run . .	106
29.	Effluent pH Variations for a Pyrolyzed Solution of Glucose with Temperature.	107
30.	Titration Curves of Glucose and Sucrose Pyrolysis Chamber Effluents.	109

LIST OF ABBREVIATIONS

amp	Amperes
BOD ₅	5 day Biological Oxygen Demand Test
COD	Chemical Oxygen Demand
cc./min.	Cubic centimeters per minute
D.F.	Degrees of Freedom
°C	Degrees Centigrade
°F	Degrees Fahrenheit
kw	Kilowatts
mg./l.	Milligrams per liter
ml.	Milliliter
N	Normal
O.D.	Outside diameter
pH	Hydrogen ion concentration
psig.	Pounds per square inch gauge pressure
scf./m.	Standard cubic feet per minute
%	Per cent

HIGH TEMPERATURE PYROLYSIS OF SANITARY WASTES

CHAPTER I

INTRODUCTION

General

The United States of America has been blessed with many natural resources, not the least of which is her navigable waterways. Estuaries, rivers, and lakes have served as basic components in this nation's rise from wilderness to world power. For example, estuaries have acted as the nuclei for the birth of some of our largest metropolitan areas such as New York, Los Angeles, New Orleans, Baltimore, Boston, San Francisco, Tampa, Seattle, and San Diego. Rivers not only provided a cheap means of transportation to more equitably distribute this country's resources, coal, iron and other minerals, but also provided a mode of returning finished products to all the people. The Great Lakes, travelled by many vessels of foreign registry, opened the door for United States' entrance to world trade markets. Industry has located near the nation's waterways and uses her waters for a myriad of processing tasks.

As the nation and her economy grew, the by-products for the people were a higher standard of living, better education for all,

and more leisure time. The result of all this prosperity and industry was gross over-use of our waters and a once beautiful legacy has been reduced to a polluted resource not capable of being utilized to the fullest. At the signing of the Water Quality Act of 1965 President Johnson summed up the situation by stating, "The clear fresh waters that were our national heritage have become dumping grounds for garbage and filth. They poison our fish, they breed disease, they despoil our landscapes."

Polluted waterways that formerly helped to provide the people of this country with wealth, education, and leisure time are now living monuments to their misuse. Beaches that were once occupied by swimmers are barren and are now populated only by public-health-officials' signs warning of bacterial contamination from the indiscriminate dumping of sanitary wastes. Seafoods from the New York City area no longer are harvested, due to the discharges of untreated sewage into spawning grounds.

These wastes contain pathogenic organisms that can cause diseases such as Dysentary, Typhoid and Infectious Hepatitis. Their inorganic content, particularly nitrogen and phosphorus, act as nutrients for algal growth and promote eutrophication in lakes and other quiescent bodies of water.

Pollution results from human activities, mainly point sources at urban clusters. Other sources are dispersed pollution from land areas caused by the flush out effect of storms; and a small, but significant source, particularly in lakes and harbors, is attributable to boats.

The mobility of the marine polluter causes two immediate problems. First, it is very difficult to police his discharges; and, secondly, the congregation of vessels can lead to a concentration of waste and the overloading of the assimilative capacity of the area.

The task of treating shipboard sanitary wastes is a formidable one because of the variety of vessels, usage cycles, the lack of on-board operating personnel for pollution control equipment and the size, weight and power restrictions on design. Also, there is a changing philosophy in the degree of treatment needed to fit the circumstance. A vessel in port may require complete treatment of its sanitary wastes, while on the high seas little or no treatment is warranted. Usually immediate treatment capability is required on start up. Flexibility is the keystone of engineering design for a marine waste treatment system.

To accomplish the treatment of sanitary wastes aboard ships, Professor George W. Reid, in conjunction with the Food, Machinery and Chemical Corporation has conceived the Pyrolysis-Aeration System. This process combines recognized processes of Bio-oxidation, Pasteurization and Pyrolysis into a two stage unit which will attain or exceed the most demanding water quality requirements and will provide any intermediate level of capability in an optimal fashion.

The first stage consists of a rough screening, equalization of flow and bio-oxidation, in the reactor where sewage organisms will begin to oxidize the organics. In preparation for pyrolysis, the waste will be subjected to the high speed shearing action of revolving cutter blades in the reactor; thereby producing an effluent of

controlled particle size.

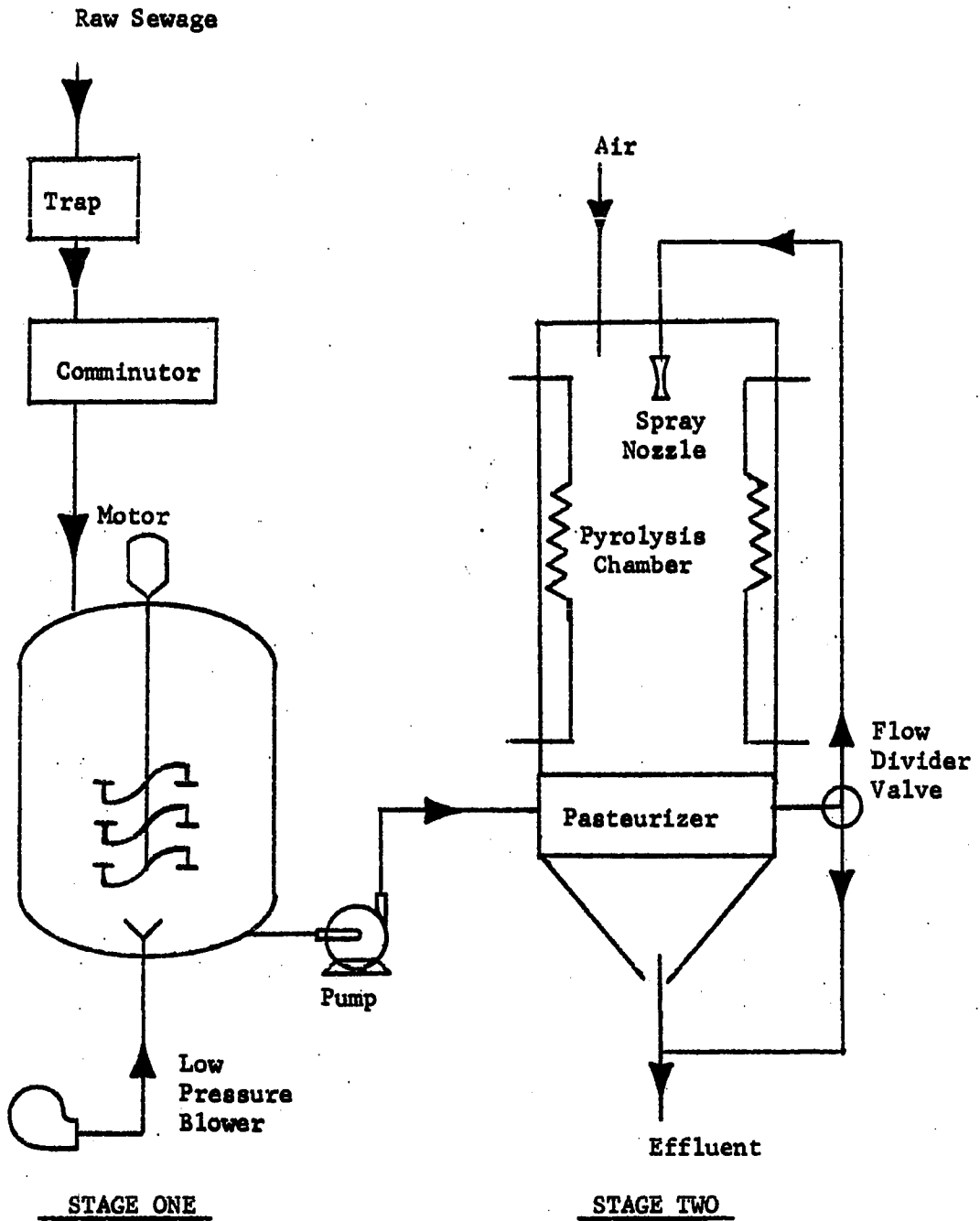
In the second stage, the partially treated waste will be pasteurized to destroy pathogenic organisms and then a portion of the stream pyrolyzed. The pyrolysis process consists of the chemical conversion of waste solids and soluble organics by radiant heat transfer in the presence of air to carbon dioxide, water and ash. This process provides complete treatment affording an effluent of essentially zero BOD and no bacteria. Figure 1 is a flow diagram of the Reid Pyrolysis-Aeration System.

Objective

This work is concerned with the Reid system, particularly the pyrolysis process. The objective is to study the chemical and biological changes in sewage as it traverses the pyrolysis chamber, as a function of system operating parameters. The data obtained is used to construct predictive mathematical models. These models may serve as the basis of engineering design for accomplishing either complete treatment or variable degrees of treatment to meet the requirements for commercial equipment design.

Three processes are involved: Biodegradation, Pasteurization, and Pyrolysis. The system is configured new and patentable, while the individual processes are well defined with a variety of engineering design configurations available satisfying each criteria, particularly the Biodegradation and Pasteurization processes. The Pyrolysis process has not been developed very extensively, and additional studies are required to validate the Reid design.

FIGURE 1

PYROLYSIS AERATION SYSTEM FOR SHIPBOARD
SEWAGE DISPOSAL

Problem Scope and Legal Background

According to Senate Document #48 entitled "Wastes From Watercraft" (1967) there are over 8,000,000 pleasure watercraft, 1,300,000 of which are equipped with toilet facilities, plying the navigable rivers and lakes in the United States. In addition, 152,000 other vessels from industry, federal and foreign governments contribute pollution by their "over the side" disposal of sewage, litter and oil. In terms of sanitary wastes alone, discharges from these vessels are equivalent to that of a city of 500,000 people.

Previously, the problem of pollution from watercraft had been masked in view of the tremendous discharge from municipalities and industry. While it had been difficult to quantify the degree of damage from vessel pollution, a clear indication of its growing contribution is seen from the tremendous increase in usage of recreational waters. Even though this type of pollution is only one source, nevertheless, if permitted to go unchecked it will negate the benefits of municipal and industrial water pollution control efforts.

Small craft, as well as large, can cause serious pollution of waterways. In 1953 Eatons Neck, a protected harbor in New York, was studied by Ingram and Diachishin (1956); and it was determined that pollution from small watercraft did adversely affect the quality of the water and endanger the health of the people participating in water contact sports. Shellfish culturing in the area had to be discontinued.

To date, concern over marine pollution has led to the enactment of laws in 29 states regulating or prohibiting the dumping of wastes from all watercraft. However, while individual states have jurisdiction over inland and some coastal waters, the Federal government supplies leadership in situations where its vessels are present in sizeable numbers.

The first Federal act which specifically prohibited the dumping of sewage by naval vessels is the Rivers and Harbors Act of 1899. Section 13; 33 USC 407 orders,

It shall be unlawful to throw discharge or deposit. . . from out of any ship, barge or other floating craft. . . any refuse matter of any kind or description whatever other than that flowing from streets and sewers and passing therefrom in a liquid state into any navigable water in the United States.

This law was followed by other legislation progressing to the Clean Water Restoration Act of 1966.

As early as 1912 Congress was concerned about water pollution, and the twentieth Congress, after much debate, made the decision to limit federal activities to the sponsoring of research and technical assistance, thus essentially surrendering police powers to state governments. In the 1930's the federal government altered its stance somewhat and began financing sewage treatment plant construction.

Finally, recognition of the enormity of the water pollution problem came in the form of the Water Pollution Control Act of 1948. This act was amended by Public Law 82-579 which extended appropriation authorizations to 1956. Subsequent amendments in 1961, 1965, and 1966 were made to enlarge the program in an effort to combat the growing problem.

The Water Quality Act of 1965 established the Federal Water Pollution Control Administration and required the formulation of water quality standards. Almost simultaneously President Johnson issued Executive Order 11258 (1965) which directed executive agency and department heads to ". . . provide leadership in the nationwide effort to improve water quality through prevention, control and abatement of water pollution from federal government activities in the United States." Furthermore, section eight of this order directed the Secretary of Health, Education and Welfare to ". . . make a comprehensive study of the problem of water pollution within the United States caused by the operation of vessels and to develop such recommendations with respect to vessels operated by any department, agency or establishment of the Federal Government." Executive Order 11288 (1966) later transferred these responsibilities from the Secretary of Health, Education and Welfare to the Secretary of the Interior.

The Clean Water Restoration Act of 1966 called for a report on water pollution caused by boats traversing the navigable waters of the United States and recommendations for legislation. This report, "Wastes From Watercraft," was submitted to Congress on August 7, 1967. The legislation was proposed to Congress in the form of Senate Bill S. 2525 and House Bill HR 13923.

The salient points of the legislation are: (1) the establishment of standards for sewage, garbage, litter and other wastes emanating from vessels, (2) the establishment of a certification program for various devices after adoption of standards,

(3) the establishment of penalties for non-compliance and (4) the placement of enforcement powers with the Secretary of the Interior and Coast Guard.

However, the catalyst for all federal activity in the field was executive order 11288. By adhering to this directive all agencies and departments initiated action to some degree. The Secretary of the Navy (1966) directed the Navy to demonstrate leadership in pollution abatement from ships and crafts and to enlist the aid and cooperation of local, state and federal governments in this task.

Other departments in the federal government, notably the Coast Guard and Geodetic Survey and the United States Corps of Engineers, had taken the early initiative by installing sewage control devices on their vessels. The Federal Water Pollution Control Administration is responsible for administering the Federal Water Pollution Control Program and is active in all areas of watercraft pollution.

Vessel Sanitary Waste Treatment Systems - State of the Art

The technology of treating sanitary wastes aboard ship presently consists of the adoption of land based systems to vessel requirements. All shipboard treatment systems experimented with to date can be categorized into one of four areas: (1) holding tanks, (2) macerator-disinfection units, (3) biological oxidation systems, and (4) incinerators. Each of these devices has been investigated to some extent demonstrating advantages and disadvantages.

Holding Tanks

By definition a holding tank is a closed container which provides a place where sewage can be stored until transferred to a treatment plant on shore. Variations in this concept include re-circulating flush toilets and chemical toilets. The former model finds extensive use in the transportation industry. Here the unit retains sewage from 80 to 100 uses before it must be emptied.

Chemical toilets operate on the principle of rendering the sewage innocuous until it can be removed. The chemical most often used is sodium hypochlorite, although recently quaternary ammonium chlorides have gained in popularity.

The basic idea of a holding tank has strong appeal due to its inherent simplicity. It can be scaled up or down in volume to fit any vessel size and can be found in boats from small cabin cruisers to the U.S.S. UNITED STATES. Other advantages of the holding tanks are a minimum of human and mechanical failure and no discharges of sewage to the water on which the watercraft floats.

The demerits of such a system lie in the lack of on-shore installations to handle the sewage. Today only the twelve states which completely prohibit the discharge of sewage from watercraft have the existing emptying tanks on land. Other disadvantages are the odor problems, the large size and weight of tanks necessary to accommodate flow, and the size limitation which permits only human wastes to be stored.

Macerator-Disinfection Devices

Macerator-Disinfection devices are the first generation of treatment systems designed for use on small watercraft. Guidelines for their design are the criteria of Ingram (1958). They are: (1) destruction of waste identity, (2) elimination of floating solids, (3) minimization of hazard to bathers, (4) minimization of hazard to shellfish beds, (5) minimization of space and weight requirements for treatment equipment, (6) minimization of operation and maintenance requirements of treatment equipment, and (7) simplification of treatment controls so that craft occupant will, with a minimum of effort, place the treatment process in operation when required.

In operation, the unit macerates toilet wastes thereby eliminating floating solids while destructing the waste's identity. Also, by application of disinfecting chemicals to kill pathogens, it minimizes danger to bathers and shellfish growing areas. After the chemical addition, contact time, varying in length from minutes to hours is provided. These units are small, light weight and operate automatically thereby theoretically meeting all the criteria of a system for small watercraft.

Jakobson (1966) evaluated a proprietary chlorinator-macerator system aboard the USS Fulton. This automatic unit was designed to service four water closets or urinals. It consisted of macerator tank, macerator, disinfection injection pump and tank, and the associated automatic controls. The disinfectant solution

for all the tests consisted of 30 lbs. of HTH in 25 gallons of sea-water, giving a free chlorine concentration of 10%. Disinfection injection rates ranged from 95 ml. to 900 ml. per flush during the two sampling periods of 20-23 January 1965 and 24-26 March 1965. These tests were conducted with residence times from 1-35 minutes. Effluent samples were evaluated for residual chlorine, coliform density, pH, BOD and settleable solids. The data demonstrated that all fecal coliforms were killed when the chlorine concentration equalled or exceeded 150 ml. per gallon flush. At the application rate of 95 ml. per 3 gallon flush, the coliform density was 265 MPN per 100 ml. sample, with a standard deviation of 27%. Macerated sewage samples without treatment yielded a geometric coliform index of 3.92×10^5 with a standard deviation of 10.4%.

Table 1 lists BOD and pH results as a function of chlorine concentrations.

TABLE 1

Disinfection Rates ml./flush	Average BOD ppm.	pH Range
900	24	9.6--9.2
600	36	7.0--8.4
300	125	6.1--8.2
150	-	7.6--9.2
95	95	7.1--8.2

From the table it can be seen that high disinfection rates did reduce the effluent BOD. The pH values reflect the use of calcium hypochlorite in the system. Due to the presence of fine

particulate solids of calcium carbonate, suspended solids are not discussed.

The United States Coast Guard has experimented with a different type of proprietary chlorinator-macerator aboard its vessels in the New York area. The unit was installed in conjunction with the Department of the Interior (1968) on buoy tenders, sea going tugboats and light ships. The program had for its objectives: (1) the determination of the unit's mechanical reliability, (2) the testing of the macerator-chlorinator under actual operating conditions, in particular, under minimum detention times in the macerator and (3) the effectiveness of the system to reduce pollution.

The first installation aboard the ARBUTUS was hampered by installation and unit problems; for instance, short circuiting of fecal solids through the macerator. This resulted in 63% of the 34 effluent samples analyzed to have a coliform index greater than 1000 MPN/100 ml. sample. Changes in the macerator-chlorinator design were made and a new unit installed aboard the FIREBUSH. However, short circuiting of fecal solids was not completely eliminated, as evidenced by large (6-12 mm. in diameter) particles in the effluent. In analyzing 227 effluent samples, 17% still showed a total coliform count of greater than 1000 MPN/100 ml.

Surveillance studies aboard the TUCHAHOE and NAVESINK showed coliform densities of less than 1000 MPN/100 ml.; however, downtime was 50% due to valve problems in the hypochlorite line. The same difficulty was experienced on the tug MANITOW where downtime was greater than 90%.

Some of the conclusions reached by the Coast Guard report were: (1) large fecal solids, not reduced sufficiently in size, mask the effect of the disinfectant, resulting in high effluent coliform index numbers, (2) during the periods of high frequency use the unit did not produce an effluent of 100 MPN/10 ml. or less, as proposed by the United States Public Health Service, (3) macerator detention times were as low as two minutes or less in maximum use periods, (4) 65 to 75% of all chlorine used is for urine flushes and (5) this proprietary chlorinator-macerator unit cannot handle heavy paper, cloth, gauze bandages or other refuse.

In summary the advantages of the macerator disinfection system are found in their small size and weight as well as their ease of installation on all sizes of ships. Counterbalancing this is their lack of ability to reduce BOD, organics, nutrients and suspended solids. Also, human errors lead to a large percentage of downtime. The need for a disinfectant, such as chlorine, presents a series of design problems encompassing safety, hauling, and storage.

Biological Waste Treatment Systems

The theory of aerobic and anaerobic biological oxidation has been known for quite a long time. Application of theory to design has resulted in many different processes. The underlying philosophy for all of them has been the minimization of energy input. As a consequence of this constraint, large land based sewage treatment systems with long hydraulic retention times have been constructed.

This philosophy has been partially voided in applying

biological oxidation theory to the treatment of shipboard sanitary wastes. New approaches have attempted to reduce the cumbersome and slow bio-oxidation processes used on land.

One of the most successful aerobic treatment schemes is the extended aeration activated sludge system. The United States Coast Guard has installed extended aeration sewage treatment plants aboard three of her ships: (1) the Hopper Dredge McFARLAND (2) the Hopper Dredge GERIG, and (3) the Pipeline Dredge GUTHRIE. On all three dredges the waste treatment plants were essentially the same design. Rotating comminutors screened all of the incoming wastes. Sludge was collected in the hopper bottoms and by means of air lift pumps, was returned to the aeration tank. Each plant had two different effluent pumps which discharged at water level. No provision was made for sludge wastage at any of the facilities. The overflow was chlorinated prior to discharge.

In two of the dredges, McFARLAND and GERIG, each had two separate treatment systems. In the dredge GUTHRIE, each of these units had provision for heat addition to accelerate the biological oxidation.

Sacks (1969) found that the effluent quality from all three ships was erratic, as seen by the BOD data which ranged from 37 to 780 mg./l. and total suspended solids from 140 to 700 mg./l. Reduction in BOD through the plants ranged from -670% to 99.5%; TSS reductions ranged from -270% to 90.4%. Chlorine residuals varied from zero to 5.0 mg./l., this was caused by faulty equipment. The maximum fecal coliform index was 22,000,000 MPN/100 ml. sample,

indicating serious bacteriological contamination. Peak flows through the system were three to five times the average.

In 1965, two sewage treatment systems were put aboard the United States Coast Guard Cutter SASSAFRAS. One system was a basic biological aerobic treatment process, while the second was one of the chlorinator-macerator types. Neither of the units performed properly and test results were reported as inconclusive. Retesting of these units was begun in 1966 while the SASSAFRAS was undergoing repairs in New York. Martin and Dewling (1966) reported that the biological plant, which consisted of aeration, settling, re-aeration and chlorine contact tanks, was not operating as an activated sludge plant. Samples of suspended solids, on a dry basis, were only 200 mg./l. Microscopic examination substantiated this premise since no higher forms of organisms, such as protozoa or rotifers, were noted. The study concluded that, while mechanically the plant operated satisfactorily, from a BOD or solids reduction viewpoint it was not satisfactory. As in the case of the first evaluation Martin and Dewling found the second test series to be inconclusive.

Schaller and Jakobson (1967) evaluated for the United States Coast Guard an aerobic treatment system designed for a 75-man ship-board complement. They found that the system, tested under land based stationary conditions, reduced BOD by 92% and suspended solids by 55%. If one pint of 15% sodium hypochlorite was injected into every 40 gallons of sewage, complete coli kill was accomplished. The system was made up of a pre-aeration disintegrator, a vacuum

aerator tower, an equilibrium base tank, a settling tank, and four pumps. In this facility, an attempt was made to reduce plant size without sacrificing reduction efficiency by use of aspiration to supply oxygen, rather than bubbling compressed air through the sewage.

Many variations of the basic aerobic biological oxidation process have been conceived and are presently being evaluated aboard ships. The currently installed aerobic biological units are limited in their future use because of their large size and weight. The advantages of biological treatment systems are that sewage aboard ship can be adequately treated; secondary treatment can be achieved; and no heat or chemical costs are incurred. Disadvantages are: the units are relatively large and heavy; proper operation requires trained personnel; the process has not been proved on ships with small crews; and immediate start-up is not possible because of the use of living organisms as the means of treatment.

Incinerators

Incinerators have been used aboard dredges and work boats not only to destroy sanitary wastes but other shipboard wastes as well. Fuel for these installations can come from electricity, fuel oil, or liquified gas.

The "Incinolet," as discussed by Blankenship (1966), is an electric incinerator which requires a minimum of 2,600 watts for operation. Through the application of heat, urine is evaporated, and sanitary solids are dehydrated and decomposed into ash. It has been estimated that approximately one teaspoon of ash remains in the unit

per fecal deposit.

Frankel (1966) describes the "Destroilet," a gas-fired combustion toilet, as a total oxidation process. The incineration is carried out by direct flame impingement on the waste loads with a 2,300 °F flame. The organics in feces and urine are completely oxidized with only an inert residue of one pound resulting from a year's use by one person.

The advantages of an incinerator are: a complete elimination of danger due to human wastes; and the light-weight system requires minimal space. Disadvantages include: high power requirements, increased fire hazard, and limitation of treatment to human wastes.

Process Description of the Reid Pyrolysis Aeration System

Process Stage One

The functions of this stage are fourfold: (1) screening of foreign materials in the influent, which could possibly damage the mechanical assembly, (2) partial biological degradation of the waste, (3) production of a given particle size distribution for solids within the waste, thus making it amenable to spraying in the pyrolysis chamber, and (4) providing surge control in the system, thereby maintaining a constant supply of feed for the operation of the pyrolysis chamber.

Removal of foreign objects is accomplished by rough screening. The total flow is then passed through a comminutor which shreds paper and large solids. After comminution the waste enters the bio-reactor where the remaining three functions, which are stated above,

will be carried out.

Particle size reduction is the result of the shearing action of the high speed cutter blades. These blades will revolve at speeds up to 10,000 RPM for a four inch diameter cutter blade, thereby reducing the solids to a maximum size of 60 microns. Detention times of five minutes reduce 50% of the particles to 60 microns while a ten minute mix period affords an 85% reduction. The unit is designed for a minimum hydraulic retention time of 20 minutes; the average is one hour. With a 20 minute retention time all solids will be reduced to 60 microns or less.

A second function of the cutter blades is to shear air bubbles as they are introduced into the reactor immediately beneath the blades. The pumping action of the blades disperses the air uniformly and quickly throughout the tank volume. The natural consequence of complete mixing, oxygen saturation of the waste fluid and an organic substrate, is a high rate biological oxidation process. Approximately 30% of the BOD load for domestic sewage is satisfied by a one-half hour reaction time in the bioreactor. Provision is made for heating the influent, thus enhancing the reaction rate in the system.

Process Stage Two

Pasteurization of the sewage by the elimination of all coliform bacteria is the first objective in stage two. The second objective is the production of an effluent that is essentially sterile, and that contains less than 150 mg./l. of suspended solids and 50 mg./l. BOD. The second stage of this system completes the treatment of

the sanitary wastes. The effluent quality can be programmed by manipulation of the system's operating variables, such as the amount of flow to be pyrolyzed and the operating conditions in the pyrolysis chamber.

All of the flow from the first stage will be pasteurized by heating the sewage to at least 161° F and maintaining this temperature for at least 15 seconds. The high temperatures eliminate all of the pathogenic organisms. The heat input for this process will come from the condensation of steam produced in the pyrolysis chamber, thereby recovering some of the electrical energy input.

A portion of the pasteurized sewage will be pyrolyzed by spraying into an electrically heated, insulated, stainless steel chamber, where temperatures as high as 1500° F will be attained.

Atomization of the sewage is accomplished by pumping the suspension through a pressure nozzle. The result is a mist of liquid with droplet diameters ranging from 10 to 100 microns. Air is introduced into the top of the chamber, thereby insuring oxidation and also providing a positive pressure in the system.

Heat is transferred to the droplets by the mechanisms of conduction and radiation. The large temperature differential, plus the high surface area per unit volume of the droplets, greatly promote heat transfer. Vaporization is completed quickly, and entrained solids are reduced to an inert ash.

After passage through the pyrolysis chamber, the vapors are condensed, and give up their heat to the pasteurizer. The condensate

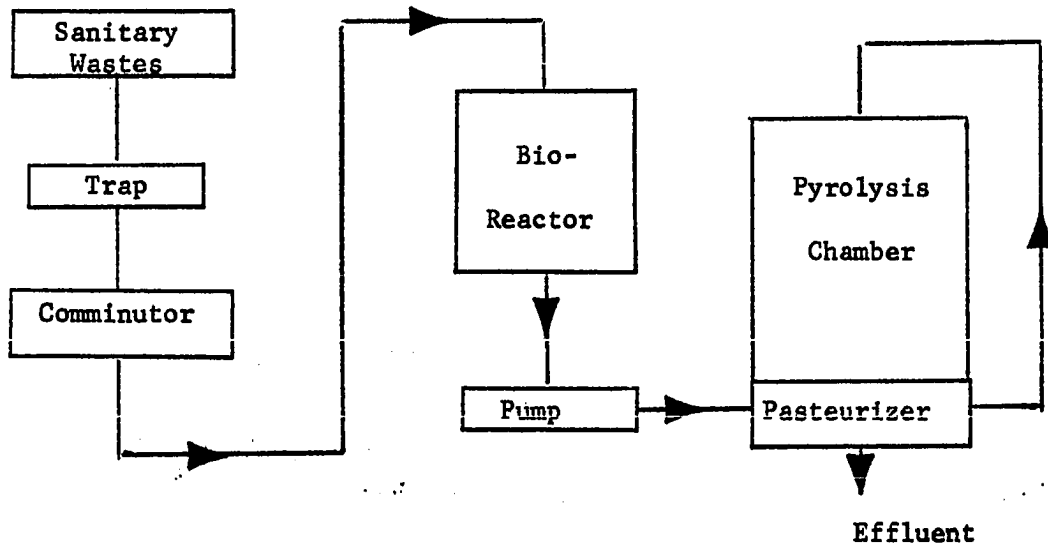
is mixed with the portion of the stream that had been pasteurized but not pyrolyzed and discharged overboard. The combined effluent will be free from pathogenic organisms, contain less than 50 mg./l. of BOD and 150 mg./l. of suspended solids. The residual BOD in the pyrolysis chamber effluent will be low molecular weight organic acids which are very susceptible to biological oxidation, and thus can be returned to the bio-reactor to complete biodegradation. The system kinetics can be improved by the addition of heat at this stage.

System Operational Analysis - Alternate Approaches

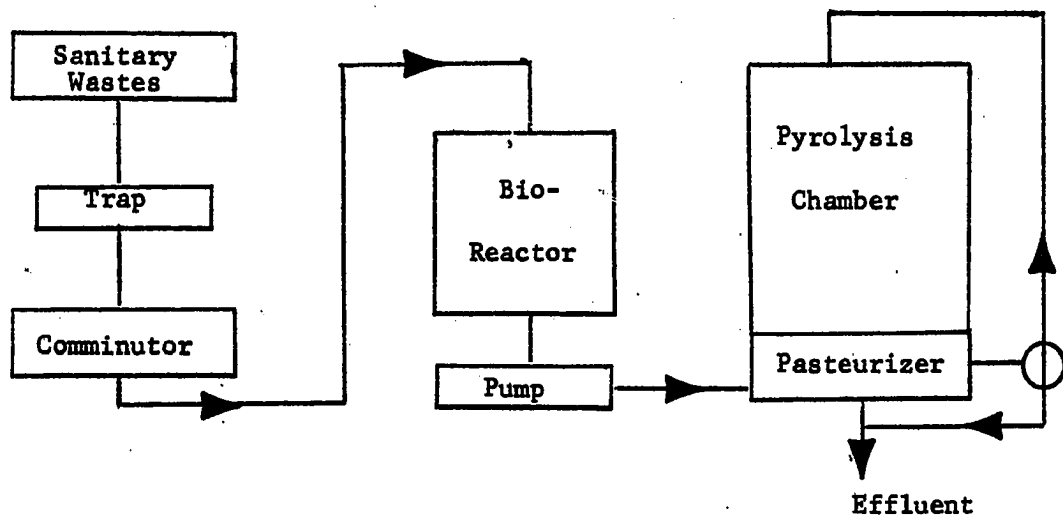
As previously discussed, the effluent quality standards are variable depending upon the geographic position of the vessels. Therefore, the Reid Pyrolysis-Aeration System was designed to provide the desired effluent quality by manipulation of system operating parameters as well as the exclusion of unit operations within the process.

Minimum treatment can be achieved by particle size reduction in the bio-reactor followed by pasteurization. Complete treatment, to drinking water standards, is attainable by pyrolysis of the entire waste stream followed by a solids removal step. Intermediate quality effluents are possible by processing the total flow through stage one and pyrolyzing only a portion of this stream. Figure 2 is a flow diagram of the possible processing route configurations.

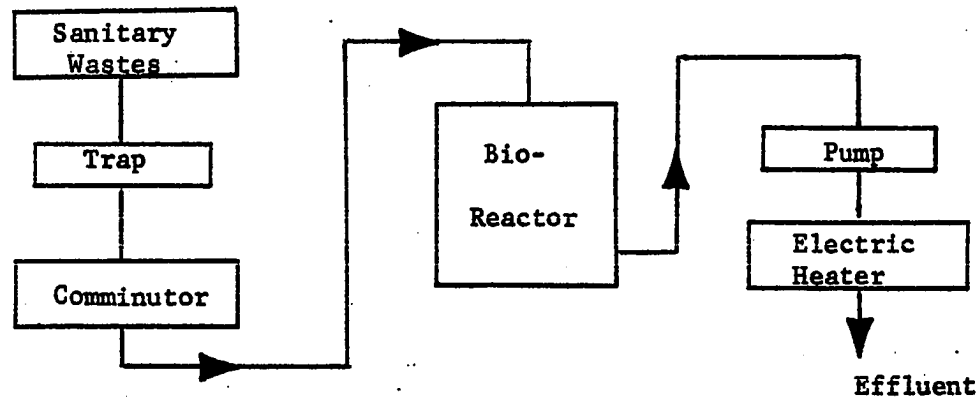
FIGURE 2 - TREATMENT TECHNIQUES



COMPLETE TREATMENT



PARTIAL TREATMENT



MINIMUM TREATMENT

CHAPTER II

CONCEPTUAL DESIGN

Introduction

The Reid Pyrolysis-Aeration System includes the processes of Biodegradation, Pasteurization and Pyrolysis. The first two operations are well understood in this application while pyrolysis is not. The intent here is to study it in depth. Studies of the Reid System of Biodegradation and Pasteurization have already been conducted and reported by Reid (1968).

To date these processes have been developed as land based treatment systems disposing their products into waterways; whereas the Reid System is specifically designed to treat and dispose of wastes generated on the waterways. Another difference in the application is the type of influent to the process. On land, the feed is a sewage sludge consisting of 95% water and approximately 5% solids while at sea the sewage to be treated has a water content of 99.9% and a solids concentration of less than 0.1%.

Effluent goals differ to some extent. In the treatment of sludges one of the main purposes is to economically reduce the volume of solids so that they may be disposed of without creating a health hazard or nuisance. COD or BOD reductions per se are

high, but the liquid effluent concentrations are still large enough to require further biological treatment before disposal. Public Health Service has proposed the following criteria for effluents from treatment systems aboard ships: (1) 50 mg./l. or less of BOD, (2) 150 mg./l. or less of suspended solids and (3) a coliform MPN of 1000 or less per 100 ml. sample.

Basically the objective for any treatment process is the reduction or the complete removal of oxygen demand that a waste would impose on a receiving body of water. To this end many novel approaches have been attempted, and they can all be classified as pyrolysis processes with the distinction of either being liquid phase or gas phase systems.

The most prominent and successful of the liquid phase processes stems from the theory of wet air combustion, with Zimmerman being the credited innovator of this process. It operates on the premise that organic matter contained in aqueous solution can be oxidized by low temperature and high pressure (500° F and 200 psig.), and the heat released by exothermic reactions is harnessed for use within the process.

The Atomized Suspension Technique represents a successful gas phase oxidation system. In this process an atomization step produces a highly dispersed stream capable of being volatilized quickly in a high temperature environment thus rendering any entrained solids subject to chemical or physical reaction. These reactions are triggered by the addition of oxidants such as air to the lower sections of the reactor. This technique is distinguished from spray drying by

the absence of air in the drying stage thereby enhancing heat and mass transfer characteristics. Products leaving the reactor are solid residues and condensible and noncondensable gases.

Improvements in the Atomized Suspension Technique have been accomplished by the Permutit Company to provide for internal recovery and reuse of energy expended in the thermal treatment operations.

These two systems are representative of the various approaches attempted to treat sanitary wastes. They will be examined in an effort to elucidate their mechanisms and patent claims.

Liquid Phase Oxidation Systems

Using as a basis the theory of wet air combustion, Zimmerman invented a process whereby sewage sludges are oxidized in the aqueous phase by dissolved oxygen at reaction temperatures, from 100° C to 372° C and pressures from 150 to 4000 lb./in.² gauge. The process has been patented with all rights held by Sterling Drug, Inc.

Wet combustion is the burning of any dissolved or suspended matter in water at temperatures ranging from 100° C to 372° C. The latter being the critical temperature at which water ceases to exist in the liquid state regardless of pressure.

The necessary condition for the oxidation of any organic in an aqueous solution is sufficient energy. In the reaction zone, energy may be supplied in the form of heat and/or pressure.

Reaction rates increase with temperature up to the critical temperature of water. Oxidations, at a given temperature, proceed until equilibrium is reached. According to Zimmerman (1958), at low

temperatures (i.e. 100°C) equilibrium for the oxidation of sewage sludges requires hours while at higher temperatures (300°C) the reactions are instantaneous.

Oxygen must be supplied to the reaction site in at least stoichiometric amounts, however elevating the partial pressure of oxygen in the system does not accelerate the process.

Process Outline

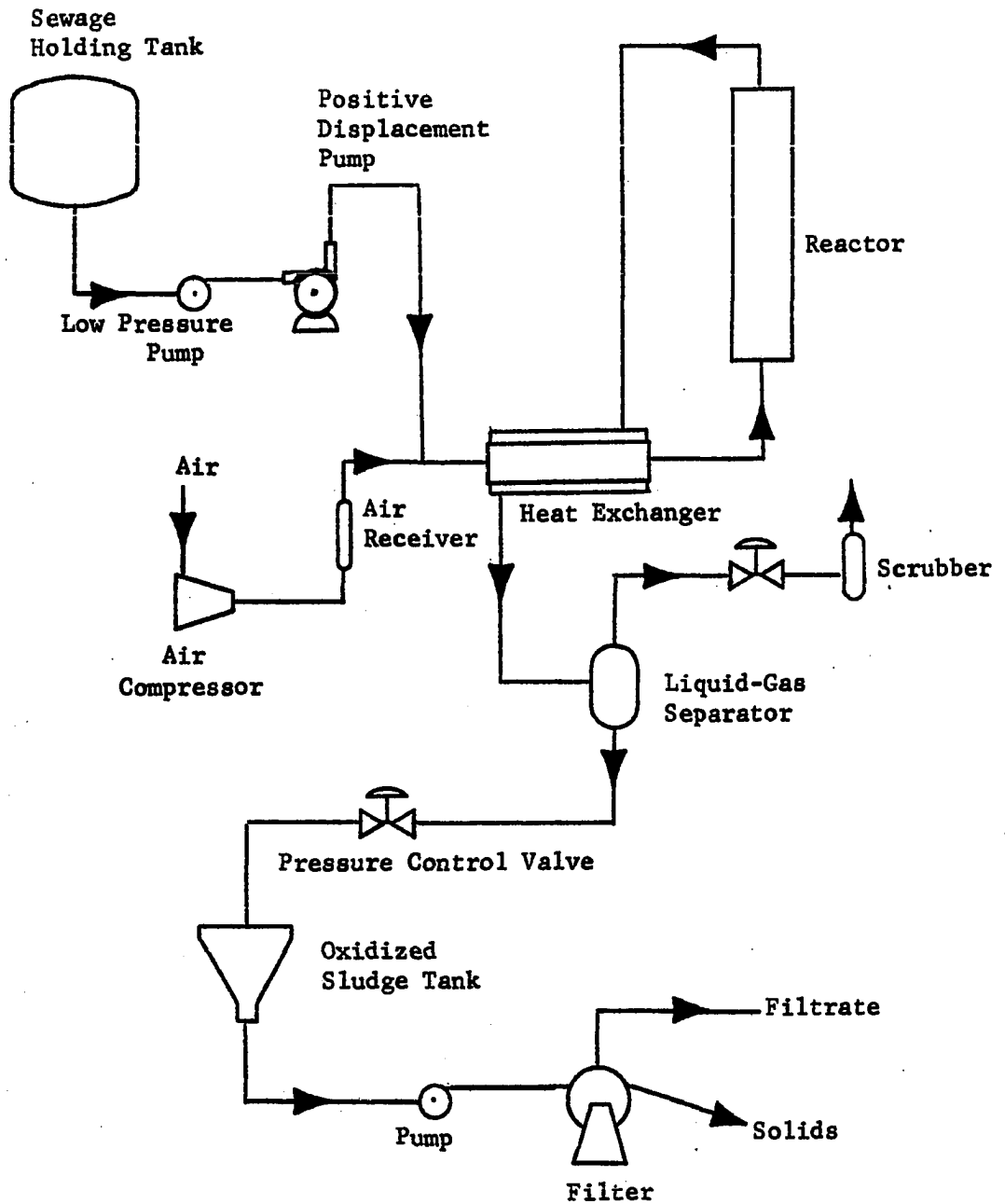
Ground raw sewage sludge is pumped from a holding tank by a low pressure pump to a positive displacement pump (Fig. 3). The pressure is raised to the operating condition and the effluent mixed with compressed air and sent to a heat exchanger. The air-sludge mixture is passed through the tube side of the exchanger and its temperature raised to approximately 300°F . The conditioned sludge next enters the bottom of the reactor. During passage through the reactor, oxidation of the organics in the liquid phase takes place. Exiting the reactor, the oxidized sludge and gases pass through the shell side of the heat exchanger relinquishing their heat. The cooled sludge passes through a separator where the gaseous products are vented through a pressure valve to a scrubber and finally discharged to the atmosphere. The liquid phase is discharged through a pressure valve to a surge tank and then by pump to a filtration system to remove the solids.

Process Variables

Temperature. In the wet air combustion process, temperature is a critical parameter. According to Zimmerman (1961) at a given

FIGURE 3

PROCESS FLOWSHEET - ZIMMERMAN PROCESS



reaction temperature sewage sludge oxidation stops as it approaches equilibrium for any given influent concentration of COD. The time to complete equilibrium attainment is a function of temperature, decreasing with increasing temperature. Oxygen concentration is not effective in changing the reaction rate, when given a sufficient quantity for combustion. These conclusions were reached after experiments on sewage sludges were performed in a rocking autoclave. Reaction time for all these experiments was one hour. The feed sources were primary sludges (2.0 and 8.9% solids), activated sludges (1.3, 1.5, 6.2% solids), and Imhoff tank sludges. The temperature range for the tests was 25° to 300° C. Autoclave effluents for all substrates at 300° C were essentially the same, which in terms of percent COD reduction, meant that as influent COD increased the percentage reductions increased. Also, the data showed that equilibrium conditions are not affected above the temperatures of 250° C, that is, equilibrium was achieved in a very short time. In terms of processing, the implication of this finding was that flow rates could be raised without decreasing oxidation efficiency for the same reactor residence time.

Pressure and Air Requirements. The pressure in a wet air oxidation reactor inadvertently controls reaction temperature. From fundamental thermodynamic considerations, it can be shown that the reactor vapor space conditions, in terms of pounds of steam per pound of dry air, fix the temperature at a given operating pressure. This is important in maintaining liquid water in the reactor.

The importance of the variable can be visualized more clearly

by an example constructed by Zimmerman (1958). If a condition of 2.0 lb. of steam per lb. of dry air were fixed in the vapor space of a reactor operating alternately at 600, 800, 1000, 1500 and 2000 psig., the reaction temperature would be 458, 486, 510, 598 °F respectively. Since COD reductions are a function of temperature, the reactor would produce successively better quality effluents with increasing pressures. The economic implications of increased pressure are larger sized compressors and more stringent safety requirements.

The effect of air rates can be appreciated by continuing with the example. If the reactor is operating at 1500 psig. with a condition of 2.0 lbs. of steam per lb. of dry air in the vapor space, the temperature would be 553° F. Assuming that the entering waste contains 8 lbs. of water per gallon of waste, for total vaporization of all liquid water to occur with a saturated vapor space condition of 2.0 lb. of steam per lb. of dry air, it would be necessary to supply 4.0 lbs. of air per gallon of waste. Therefore, since the presence of liquid water in the reactor is paramount, the maximum waste concentration should be sufficient to require less than 4.0 lbs. of air per gallon of waste entering. The addition of more than 4.0 lbs. of air per gallon of waste would cause complete vaporization and cessation of the liquid phase oxidation.

Wet Air Oxidation Effluents. From the previous sections, it is evident that any degree of oxidation can be accomplished by regulation of temperature, pressure, air rates, and influent flow rates through the process.

Hurwitz, Teletzke and Gitchel (1965) studied the chemical

characteristics of three different sewage sludges after various degrees of oxidation. The influents consisted of a raw primary sludge, a digested primary sludge, and concentrated activated sludge. All of the experiments were conducted in a closed vessel supplied with air and reacted for one hour. Reaction temperatures of 100° C to 250° C were investigated.

The liquors drained from the sludges were found to be free from suspended matter, but they contained soluble organic chemicals. Chemical oxygen demands of the liquor increased with oxidation up to 180° C and then decreased with reaction temperature. Volatile acids concentration also increased up to a 220° C oxidation temperature and then receded. The volatile acids were found to be almost exclusively acetic acid.

Teletzke, Gitchel, Diddmas, and Hoffman (1967) continued this line of research with the specific purpose of identifying basic class components of the partially oxidized liquor. Reaction temperatures from 150° C to 250° C, in 25° C increments, were investigated. All tests were carried out in a one gallon autoclave. Chemical analyses were performed on the raw sludge, oxidized slurries and the solid and liquid filtrates of the slurries, obtained by vacuum filtration.

COD's and organic matter were determined as a function of oxidation temperature for proteins, lipids, total sugars, starch, crude fibers, and volatile acids. The results verify that organic matter, as measured by the volatile matter concentration, was removed to a greater extent than the COD at any given oxidation temperature. It was ascertained that starches were the class of compounds most readily

oxidized while lipids proved to be the reverse, up to reaction temperatures of 200° C. In general, proteins and crude fibers were the most resistant class of compounds to oxidation. At temperatures in excess of 200° C, proteins were as easily removed as starch. Sugars appeared in the effluent at 150° C and 175° C and are attributed to the hydrolysis of polysaccharides, since they were not present in sewage sludges.

The distribution of these classes of compounds between the liquid and solid phases was also investigated. It was demonstrated that even at low (150° C) oxidation temperatures significant quantities of all compounds, excepting crude fibers, were found in the filtrates. Proteins, for instance, are completely solubilized by a reaction temperature of 225° C, while 79% of the lipid fraction exhibit this response at the 200° C level. At 250° C, the highest oxidation temperature investigated, 100% hydrolysis of lipids and proteins was noted while none of the other classes of compounds was found. The distribution of the residual COD between the filtrate and solids portion was 3.7% to 96.3% respectively; in the raw sludge, however, these figures were almost reversed at 95.5% to 4.5% at 250° C.

This study indicated that the major effect of low temperature oxidation is hydrolysis of macro-molecules to their constituent compounds. For example, polysaccharides hydrolyze to reducing sugars, lipids to free fatty acids, and proteins to amino acids. As the oxidation temperature is increased, some of the hydrolysis products are further degraded to carbon dioxide and water. At still higher temperatures only very stable compounds such as acetic acid remain. The amino acids either free or in polypeptide form were found in

sewage. At high degrees of oxidation, only three amino acids, namely glycine, β -alanine and γ -amino butyric acid remained. At intermediate temperatures all amino acids existed in the free state.

Process Installations. The twenty-third progress report of the committee on sanitary engineering research (1959) discussed the first commercial pilot plant of the Zimmerman process located at the Southwest Sewage Treatment Works of the Chicago Sanitary District.

The unit was designed for a flow of two tons of sludge per day (dry basis). Operating conditions were 1200 psig. and approximately 260° C. Only 80 horsepower were provided to power the unit, therefore steam recovery facilities were not installed. The plant had the capability of sludge storage and thickening and in this manner was able to evaluate primary sludge, activated sludge and mixtures of the two as feed sources.

Data gathered from plant operations during the period from September 24, 1957 to March 28, 1958 indicated that the effluent was high in ammonia, volatile acids and BOD concentrations. The ranges for these parameters were: (1) 1200 to 1910 mg./l., (2) 2790 to 4090 mg./l., and (3) 4990 to 8570 mg./l. respectively. Approximately a 79% COD and 87% volatile solids reduction in the sewage sludge was brought about under the above stated conditions. Further, the data indicated the volatile matter reductions are independent of influent sludge solids concentrations.

In a one ton per day pilot plant in Rothschild, Wisconsin, an eleven inch diameter, twenty-foot long reactor was employed to assess pressure as an operating parameter. Hurwitz and Dundas (1960)

reported that at the 1500 psig. and 1800 psig. pressure levels the reactor effluent resembled the 1200 psig. runs at the Southwest Sewage Treatment Plant. That is, ammonia and volatile acids content were relatively high; however, a lower COD in the total effluent and ash was noted for both the 1500 psig. and 1800 psig. runs when compared with the 1200 psig. experiment.

The reactor temperature averaged 273° C for the 1500 psig. runs and 277° C at the 1800 psig. condition. Influent sludge solids concentrations ranged from 2.86 to 3.57%; volatile solids were 1.91 to 2.49% and COD from 40,200 to 53,900 mg./l. The percentage COD reductions for the 1500 and 1800 psig. runs were 79.3 and 85.1% respectively. Volatile solids destruction at 1500 psig. were 88.6% while at 1800 psig. the reduction was 92.4%.

As a result of these findings, a new series of smaller plants, operating at substantially lower pressure and temperature, were built. One of these, the South-Milwaukee Plant, was reported by Teletzke (1965) to be operating at a maximum temperature of 222° C and a pressure of 485 psig. The influent sludge characteristics were 7.7% solids, 46% ash and an average COD of 60,000 mg./l. Plant throughput was 2.5 ton per day and at this rate the COD reductions are generally 40% while the insoluble organic removals were 70%.

At Rye, New York, sludge disposal for a flow of 5 MGD was accomplished by another low pressure and temperature wet air oxidation plant. The installation at the Blind Brook Plant consisted of a particle size reducer; sludge storage tank; oil fired steam generator to furnish start-up heat; centrifugal pump to transfer sludge; a

high pressure pump to transfer sludge to the reactor at elevated pressures; a 40-foot high, 36-inch diameter reactor; a vapor liquid solids separator; a diffuser to mix vapor phase products with the wastewater flow; pressure reducing valves and liquid level controllers; an ash separation tank in which the solids portion of the residue is settled; and a three-stage air compressor to supply oxygen for the reaction. This installation operates at 238°C and 750 psig. and does not attempt to recover any heat. Harding and Griffin (1965) gave 84.2% as the average organic matter reduction with the range being 53.7% to 94%. The average organic content of the oxidized sludge was 18.6%.

The average reactor liquid effluent was 8,400 mg./l. and this varied from 4,500 mg./l. to 14,000 mg./l. The color of the samples was straw to reddish brown depending upon the degree of oxidation.

A medium pressure wet air oxidation plant with operating pressures of 1200 psig. and 260°C was installed at Wheeling, West Virginia, in September, 1961. McKinley (1965) reviewed the plant's effluent characteristics from its inception until January, 1965.

During this period an average of 7.35 tons per day of dry solids were oxidized with the maximum and minimum rates being 12.2 and 4.1 tons per day respectively. The total solids content ranged from 4.0 to 9.7% with the average being 7.14%. In terms of total production, these figures represent a processing of 5,404,377 gallons of sludge containing 1,610.7 tons of dry solids. The influent had a COD range of 43.0 to 95 g./l. while the insoluble organic matter removal was 90%.

Gas Phase Oxidation Systems

Atomized Suspension Technique

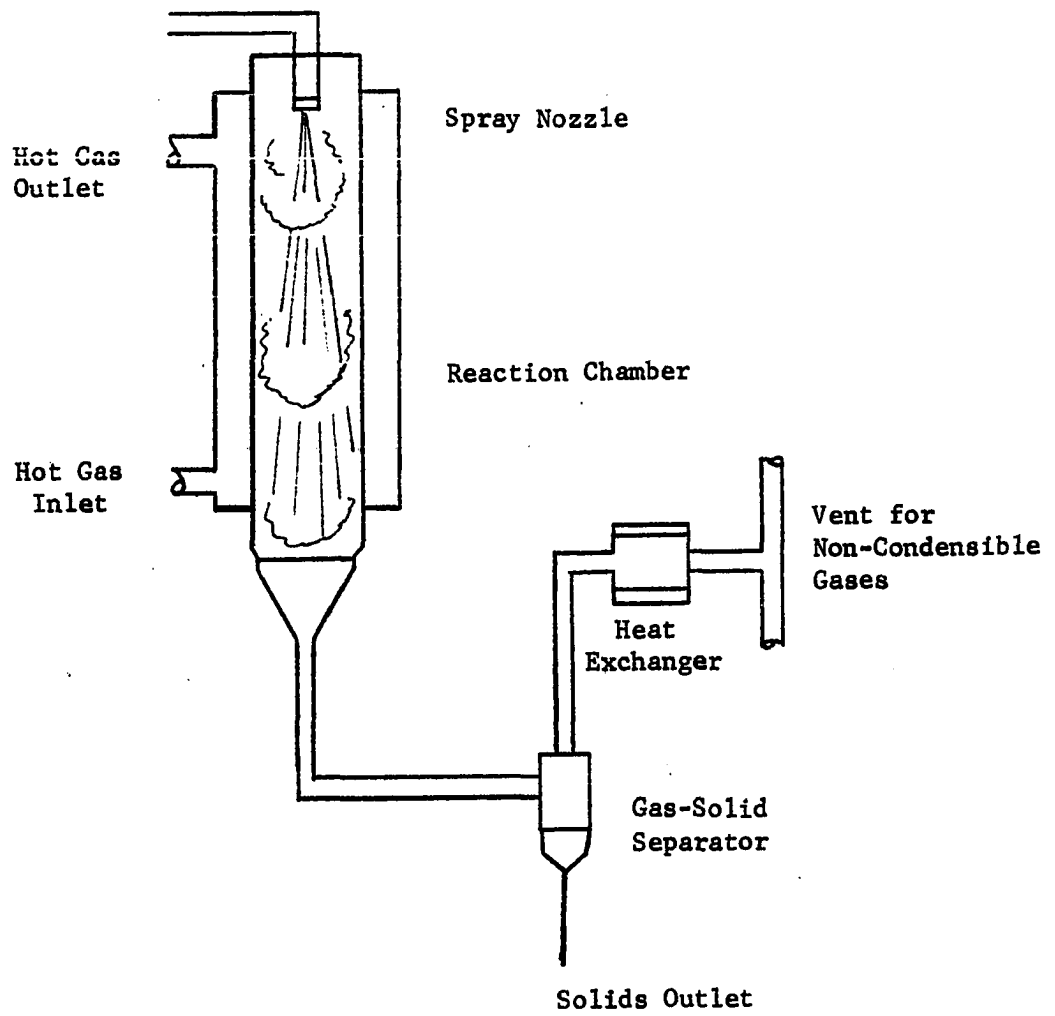
The Atomized Suspension Technique (hereafter referred to as AST) was the result of U. S. Patent 2,889,874 granted to William H. Gauvin on June 9, 1959. This invention is related "to thermal physical change or separation or thermal chemical decomposition or chemical reaction of substances."

Process Outline. A central requirement of the process is the subdivision of liquids, semi-solids, or solids into finely divided units, such as an atomized spray of liquid or finely divided particles (Fig. 4). To these droplets or particles radiant heat is supplied by the heated walls of the reactor or some suitable internal radiant heat source. Upon the addition of sufficient heat, vaporization occurs. The upper portion of the reactor is filled with vapors emanating from these substances; these vapors suspend the unvaporized liquid droplet portion of the influent thus permitting continued exposure to the radiant heat. By this phase change any degree of separation or decomposition can be attained. Chemical reactions such as oxidation are performed in the lower reaches of the reactor by injection of the proper gaseous reactants. When the desired separation, decomposition and reaction has been completed, the gaseous effluent and any residual particles are physically separated and utilized.

Application of AST to the Treatment of Sewage. The application of the principles of this invention to the treatment of sewage provides a process which exhibits superiority in the unit operations

FIGURE 4

PROCESS FLOWSHEET - ATOMIZED SUSPENSION TECHNIQUE



of evaporation, drying, and pyrolysis. This superiority is due to the increase in transfer area resulting from the atomization of the sewage and the lack of air or other foreign gas surrounding the particle that would provide an additional resistance to heat and mass transfer.

The degree of surface area increase by atomization for heat and mass transfer can be judged by calculating the amount of new surface created on production of a monodisperse spray from a volume of liquid. Assume that a given liquid is in the shape of a sphere with diameter x_0 . Further assume that this sphere is atomized to a stream of droplets all with diameter x . Therefore, the original liquid would have a surface area of πx_0^2 and a volume of $\frac{\pi}{6} x_0^3$ while the atomized liquid would have a surface area of $n\pi x^2$ with volume $\frac{n\pi}{6} x^3$. This yields a surface area increase of $\pi x_0^3 (\frac{1}{x} - \frac{1}{x_0})$ or the ratio of new to original surface of $(\frac{x_0}{x} - 1)$. It can be seen that the surface area produced is inversely proportional to the atomized drop diameter. To demonstrate the effect of the change in surface area, postulate an initial diameter $x_0 = 1$ cm. and then values of x ranging from 10 to 100 microns. This would entail a surface area increase from 10^2 to 10^3 thousandfold. Since the rate processes of heat and mass transfer are proportional to the exposed surfaces of the particles and inversely proportional to the mass volume, the process implications are readily apparent.

In theory a monodisperse spray is possible; however, in practice a distribution of droplet sizes is obtained. The pressure nozzles used for the AST reactor convert the pressure energy applied to the sewage into kinetic energy. By its design, the nozzle shapes

the liquid into a jet or sheet which disintegrates into droplets owing to its instability. The landmark work of Rayleigh (1879) demonstrated that a liquid cylinder from a nozzle is unstable and that the slightest disturbance will cause distortion and finally it breaks up into droplets. Frazer, Eisenklam and Dombrowski (1957) gave the following equation for a mean drop diameter size of the spray from pressure atomizers:

$$d \propto \left(\frac{\overline{FN} \cdot \gamma}{\Delta p \cdot \theta} \right)^{1/3} \left(\frac{\rho_l}{\rho_g} \right)^{1/6}$$

where d = a mean diameter of the spray

$\overline{FN}$ = flow number of atomizer for a standard liquid, usually H_2O

Δp = pressure differential

γ = surface tension of liquid

θ = angle of fan spray sheet

ρ_l = density of liquid

ρ_g = density of atmosphere

Consiglio and Sliepcevich (1957) found that the specific surface area of a spray is correlated by an equation of two dimensionless groups in terms of the variables; surface tension of the -1.0 power, kinematic viscosity to the -0.4 power, and volume flow rate to the 2.4 power.

Following atomization, the flow is down the inner shell of the AST reactor. The walls are maintained at a temperature far in excess of the saturation temperature of the sewage at the prevailing pressure in the system. The heat is then transferred primarily by radiation.

In the nozzle region sensible heat, as well as the heat of

vaporization, is supplied by the mechanisms of radiation and convection to the sewage droplets for the dual purpose of evaporation and heating the generated vapors to the temperature of the gas.

The evaporation of a drop of diameter d_o by conduction-convection effects is given by:

$$\left(\frac{dm}{d\theta}\right)_o = \frac{h_o A_{d_o} (t_g - t_{d_o})}{\lambda}$$

where $\frac{dm}{d\theta}$ = Evaporation Rate, lb./hr.

h_o = heat transfer coefficient for drop of diameter d_o

A_{d_o} = surface area of drop of diameter d_o

t_g = gas temperature, °C

t_{d_o} = particle temperature, °C

λ = latent heat of vaporization

The heat transfer coefficient can be calculated from the Ranz and Marshall (19) Equation:

$$\frac{h_o d_o}{k_g} = (2.0 + 0.60 \text{ Re}^{1/2} \text{ Pr}^{1/3})$$

where k_g = thermal conductivity of gas, (BTU) / (Hr)(FT)(°F)

Re = Reynolds number, $dV\rho/\mu$, dimensionless

Pr = Prandtl number, $C_p\mu/k_g$, dimensionless

This equation is corrected for the evolution of cold vapors from the droplets by multiplication of the right hand side by Spalding's (1953) transfer number:

$$B = \frac{c_p (t_g - t_d)}{\lambda}$$

Giving:

$$h_o = \frac{k_g}{d_o} \frac{\ln(1+B)}{B} (2.0 + 0.60 \text{ Re}^{1/2} \text{ Pr}^{1/3})$$

where B = Spalding's transfer number, c_p
 c_p = heat capacity (BTU)/(lb.)(°F)
 μ = absolute viscosity, (lb)/(ft.)(sec.)
 ρ = density lb./ft.³
 V = velocity, ft./sec.

The resistance to heat transfer at the drop is low, that is, h_o is large; therefore, a great portion of the vaporization will occur in the upper zone of the reactor. The transfer of heat from the walls to the gas is thus the controlling mechanism. The gas temperature down the reactor length is a function of the drop size available to receive heat transfer from the gas. Since the atomization step produces a large distribution of drop sizes, each with differing drag coefficients, their position in the column and particular temperature environment play a role when total vaporization has been accomplished.

Hoffman and Gauvin (1962) found that in spraying water in the AST reactor the larger sizes of droplets (130-170 microns) had the same lifetime, before evaporation, as the 70 micron droplets. The larger drops evaporate more quickly because they proceed to regions of higher temperatures which are further down in the reactor. They conclude that the evaporation load is distributed over the AST column because of the difference in droplet diameters produced by the nozzle, and the different times required to break the droplet into its terminal velocities and subsequent quick evaporation.

Prior to evaporation, pyrolysis is augmented due to the large surface area available for reaction and the lack of a foreign gas around the droplet. Pyrolysis in this instance is defined as

the decomposition of chemicals due to heat.

Once evaporation is completed the injection of reactant gases can be made to cause various chemical reactions. In the case of sewage, air acts as an oxidant. The availability of oxygen and heat institutes pyrolysis of the solids to an inert ash and the organics to carbon dioxide and water. Pyrolysis again is a decomposition reaction, this time in the presence of air.

The choice of whether or not to use oxygen to completely reduce the organic load of the sewage is based on the desired effluent products and economy. If oxygen is not used the most advantageous by-product is steam undiluted by a drying gas. Also, the organics in sewage cannot burn; therefore, the products of the pyrolysis will be elemental carbon and water.

Another variable is the operating pressure in the AST reactor. If higher than atmospheric pressure is maintained in the system the heat values of the steam are increased and this may be an economic consideration. Operation at these pressures have design ramifications in that the liquid boiling point is increased and pressure tends to retard gasification. This has been substantiated by Barclay, Prahocs and Gravel (1964) and leads to the belief that high pressure would inhibit drying and combustion in the oxidation of sewage. From the reactor design point of view it would mean increasing the reactor length.

The dimensions of the reactor must reflect the needs of retention time to complete the reactions and the balance between length to diameter ratios in order not to impede the transfer processes.

Sewage effluent from the AST reactor consists of solid residues which are recovered in cyclone separators, large amounts of steam which are condensed and utilized in a steam convertor, and non-condensable gases which are piped away to the atmosphere. The inventor claims that the only outside source of energy needed to operate the system is that used for pumping liquid through the atomizer.

Reverse Flow Reactor and Process

Eugene Weisburg and Stanley Lenox were granted the U. S. Patent 3,395,654 on August 6, 1968, for a process which improves upon the AST process of Gauvin and the subsequent Permutit system, named the Thermosonic Reactor System, for the treatment of sewage sludges. The improvements centered on providing a reverse flow reactor and process suitable for the economical oxidation of finely divided sewage sludges by converting them to odorless, non-noxious solids and gaseous products through thermal treatment. Basically the process is a high-temperature, low-pressure system designed to thermally process fine particles of sanitary wastes.

In the unit sludge is thickened, ground to a given particle size, and sprayed into a stainless steel chamber through a sonic nozzle. The cylinder walls are maintained at temperatures from 1000° F to 2000° F. The solids contained in the small droplets (0.1 to 100 microns) are dried and burned with the aid of an auxiliary burner at the open end of the reactor. The hot gases are then channeled upward through the annulus formed between the inner and outer walls of the reactor. The treated gases that are passed in reverse flow through

the volatilization zone transfer some of their heat by conduction and convection to the wall. The heat is then re-radiated to the droplets falling on the inside of the reactor.

This is achieved by defining a tortuous pathway between the inner and outer shell of the reactor through which all gases and solids from the volatilization and treatment zone must pass (Fig. 5). The products of the reaction release their heat to the wall of the reactor at a controlled rate as determined by the various path configurations.

The inventors offer the following pathway choices:

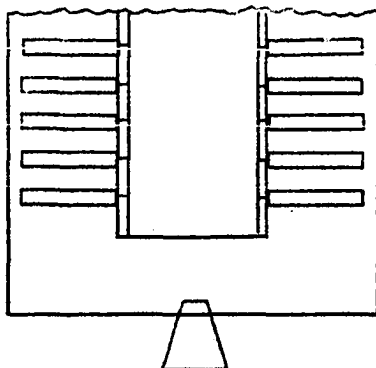
- (1) baffling elements which provide an alternating constricted and expanding flow path toward and away from the reactor wall.
- (2) a helical arrangement of baffles providing a spiral pathway for all gases and solids of the reaction, and,
- (3) baffles to provide a pathway for reaction products to flow alternately toward and away from the reactor wall.

By varying the number, spacing, shape, and pitch of the flow guides or baffles, it is proposed that control is gained over: reactor flow rates; residence times in any portion of the reactor in order to obtain the desired contact time; and the transfer of hot materials to a portion of the inner shell for heat re-use. Use of these procedures negates the addition of external heat exchangers while the desired degree of treatment is performed.

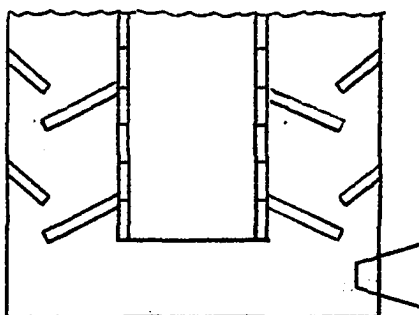
In the Weisburg and Lenox Patent, the authors present an example operation of the Reverse Flow Reactor and Process which uses

FIGURE 5

PROCESS FLOWSHEET - REVERSE FLOW REACTOR



A partial vertical cross-sectional view of the bottom portion of an embodiment of the reactor of this invention wherein annulus flow guide elements are positioned to direct hot materials along a sequentially constricted and expanded flowpath.



A partial vertical cross-section of the bottom portion of a reverse flow reactor of this invention wherein annulus flow guide elements are positioned to direct the flow of hot material alternately toward and away from the inner and the outer shells.

about a 13% solids sanitary sludge. The 70° F sludge was fed to a two fluid nozzle at a 4 gpm rate together with 100 scf/m of air. The resulting fine mist increased from 70° F at reactor entry to 212° F where volatilization of the water was completed and then to 600° F where oxidation began. The temperature in the reactor continued to rise to between 1500° F and 2000° F. These temperatures are obtained because of the exothermic release of heat from oxidation reactions and an auxiliary burner which burns fuel in excess air (500 scf/m) to insure total oxidation. The thermally treated materials enter the annulus at a velocity of 90 ft/sec and then cycle between this value and 60 ft/sec as the flow is slowed to fill the spaces provided by flow baffles. After passage through the tortuous pathway and partially releasing their heat to the reactor wall, the materials emerge at a temperature of 1050° F and a flow of 600 scf/m. The detention time in the annulus is approximately 1.5 seconds. The gases and solid ash products are odorless and innoxious.

Employing the identical reactor and operating conditions without flow baffles in the annulus gave a noxious and malodorous product at an exit temperature of 1350° F to 1400° F. These temperatures indicate minimal heat transfer to the wall. To bring about comparable heat transfer in this case without flow baffles to the baffled run would mean lengthening the reactor by 13 times. Alternately, narrowing the annulus would improve heat transfer at the expense of detention times, worsening an already intolerable problem. Sawyer and Kahn (1960) have reported that a residence time of 0.7 seconds is sufficient to destroy all odors in sanitary sludge. At lower temperatures the time

requirement increases rapidly.

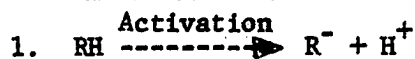
The Theory of Autoxidation of Organic Compounds in Pyrolysis

Autoxidations are defined by Waters (1948) as oxidations brought about by gaseous oxygen without electrical spark or visible flame. This definition is applicable to wet air oxidation as encountered in sanitary engineering practice.

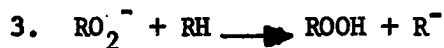
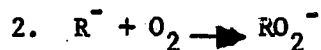
According to Ingold (1961) oxygen uptake is low during the beginning stages of autoxidation, which is known as the induction period. During this time, chain branching intermediates form thereafter causing autocatalysis. This is reflected in the increased rate of oxygen usage. The rate then reaches a maximum and begins to recede. Inhibition of autoxidation, either by prevention or retardation, is brought about by a class of compounds known as antioxidants. Their presence either lengthens the induction period or lowers the maximum rate of oxygen uptake.

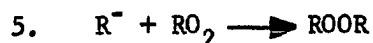
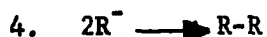
Koenig (1963), in reviewing wet air oxidation for the Advanced Waste Treatment Research Program, concluded that wet-oxidation of sewage sludges proceeds by a chain reaction propagated by a free radical process. Free radical chain processes in liquid have been described by Twigg by the following reaction equations:

Chain Initiation



Propagation



Termination

where RH represents any organic substrate, $RO_2^{\cdot}$ is the corresponding peroxyradical and ROOH is the hydroperoxide. In reaction one, chain initiation commences with the aid of radiation, initiators such as benzoyl peroxide, thermal decomposition of hydroperoxides or reaction of a metal. Reactions two or three represent chain propagation with the subsequent regeneration of $R^{\cdot}$ radicals. This reaction is extremely rapid under typical wet air oxidation conditions. Finally chain termination takes place by reactions five and six. Also termination can occur by reaction of peroxyradicals with free radical inhibitors.

Bateman (1954) described the complexity of autoxidation reactions on pure substrates by saying that the mechanisms (of autoxidations) are complex and variable and depend upon constituent conditions as well as trace impurities which may inhibit or initiate the reaction. Since this statement pertains to pure substrates only, how much more intricate and dynamic the reactions would be for a complicated waste such as sewage! However, these mechanism steps will provide a basis for interpreting the data on wet oxidation systems.

In Koenig's review (1963) he states that the oxidation reaction apparently proceeds to produce lower molecular weight oxidized compounds from the more complex and higher molecular weight compounds. Further, he states that these low molecular weight compounds are acids---acetic, formic, and so forth. This finding is in keeping with the general

theory known about the oxidation resistance of compounds containing the carboxyl group. The presence of this group enhances the resistance of the adjacent C-C bonds to oxidation. The stripping out of these low molecular weight acids in a wet oxidation reactor would not be appreciable because the reactor at best consists of a one stage separation unit of doubtful efficiency. Therefore, after formation, it is expected that these acids would stay in the effluent unoxidized and undistilled. While these acids are highly resistant to oxidation they nevertheless exhibit COD and BOD. Since evaluation of reaction completion for sewage is most often measured by these parameters therefore before data interpretation is attempted, recognition of this anomaly must be made.

Koenig further postulates these characteristics for the reaction: (1) the rate or extent of oxidation is not affected by oxygen pressure, (2) the reaction yields low molecular weight acids and carbon dioxide, (3) at first the reaction is very rapid followed by a slower rate, (4) the ultimate fraction of organics oxidized at each temperature varies, increasing with increasing temperature, (5) the ultimate fraction of organics converted at each temperature is constant regardless of the influent concentration, and (6) the fraction converted is a probability function of temperature.

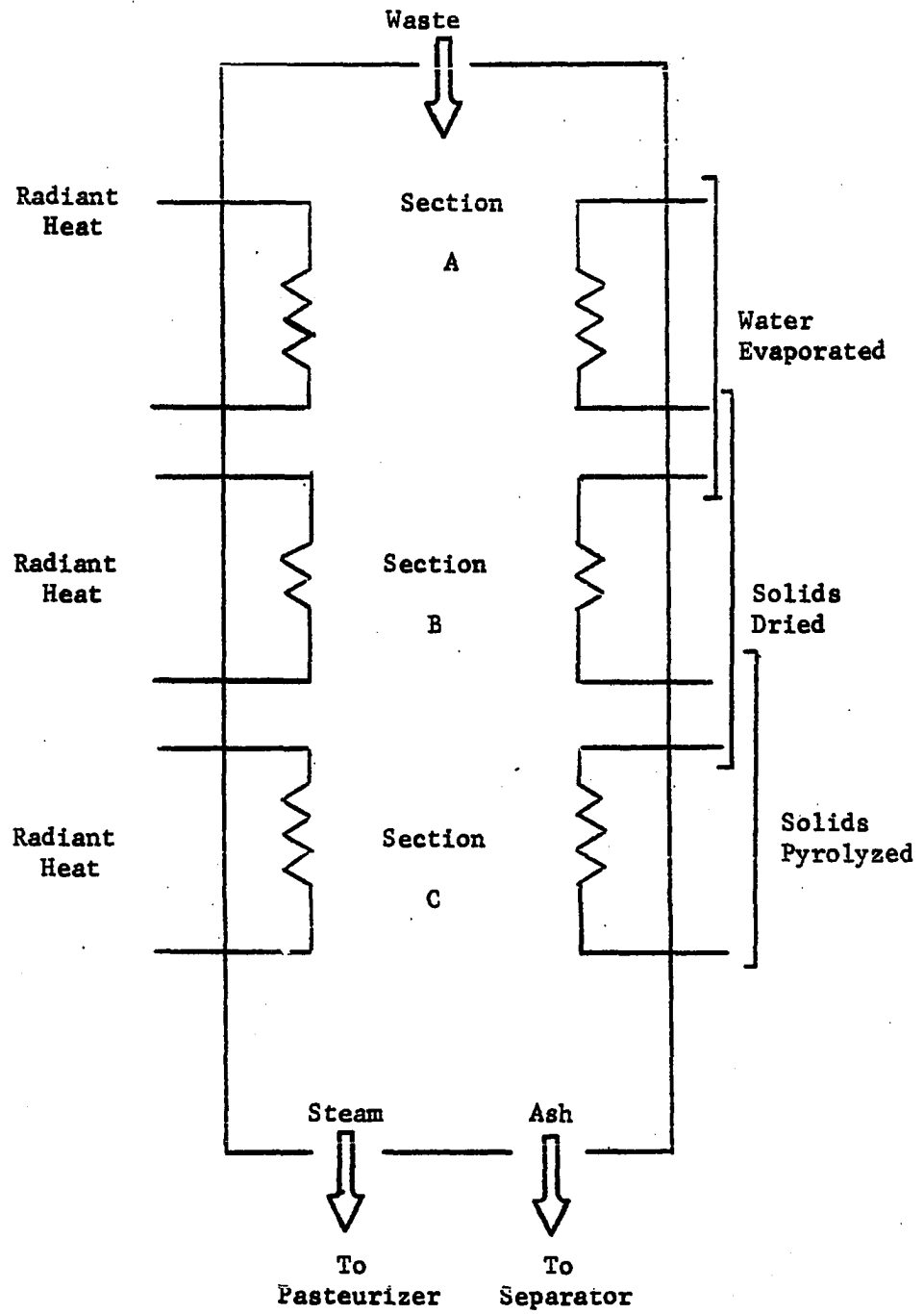
Koenig makes several hypotheses to qualitatively describe the characteristics of the reaction mechanisms enumerated above. They are as follows: (1) the overall oxidative reaction consists of a series of intermediate reactions. The reactions are responsible for partially oxidized components which are found in the effluents, (2) a chain mechanism initiated by free radicals is responsible for

the reaction, (3) the reaction rate is a function of the molecular weight of the oxidants, (4) as the oxidation temperature increases the size of the organics produced decreases, and (5) one carbon dioxide molecule is produced at the breaking of each molecule.

The Reid Pyrolysis Process

In the pyrolysis process shown schematically in Figure 6 the waste is introduced into the chamber as a liquid suspension of small-sized solids through a pressure nozzle. The pressurized, preheated sewage converts the pressure energy of the stream into kinetic energy which in turn is dissipated by the atomization process. The sewage in passing from a high pressure zone to a low pressure zone (i.e. the prevailing pressure in the pyrolysis chamber) crosses the bubble point and vaporizes part of the waste at the exit of the nozzle. Some of the enthalpy of the preheated sewage is expended in the vaporization process. A hollow cone spray is obtained from the pressure nozzle and the resultant turbulence in the air core promotes convective heat transfer. Exposure of the droplets to the radiant heaters causes the liquid portion of the waste to be converted to steam at the existing pressure in the pyrolysis chamber. Pressures can range from atmospheric down to any desired degree of vacuum. The heat is transferred in this section mainly by radiation and some convection. Referring to Figure 6 these operations are carried out in Section A. In Section B continued transfer of heat dries the solid completely. When all of the bound water in the interstices of the solids is vaporized, the solid then possesses excellent physical characteristics

FIGURE 6
PYROLYSIS PROCESS



for radiant heat absorption causing its temperature to rise rapidly. Pyrolysis of the solid to an inert ash with the aid of oxygen is completed in Section C, where temperatures up to 1500° F are attained.

The effluent from the pyrolysis chamber consists of steam, ash and small quantities of non-condensable gases. The steam is condensed in the pasteurizer to provide heat for pasteurization, to pre-heat the influent to the nozzle, or to provide a heat source for shipboard utilities. The minute amount of ash generated can be separated from the condensed phase by any number of processes and disposed of on land.

The advantages of the pyrolysis process over other shipboard sanitary treatment systems are:

- (1) the pyrolysis system can provide any degree of treatment up to and including drinking water quality effluents.
- (2) start up times are minimal in the order of minutes rather than days to weeks as is the case with bio-oxidation systems. The unit is readily secured when not in use.
- (3) the system is capable of being completely automated thus reducing the potential of human error and need for trained personnel.
- (4) operation is unaffected by the ship's pitch, roll or list as contrasted with separation processes relying on gravity.
- (5) elimination of potential hazards of fire or explosion by the presence of liquid and vapor in the pyrolysis chamber.
- (6) since no chemicals are required in the system the extra

equipment and storage is not necessary. Also the only necessity to operate the system is electricity which is readily available on board ship.

- (7) miniaturization of the system minimizes installation problems by not requiring extensive changes in existing sanitary waste piping.

Process Variables. From the discussions of the Reid Process and its advantages as a shipboard waste treatment system, it is evident several operating options are built into the system. This section outlines the process parameters and their relative importance on the quality of the pyrolysis chamber effluent.

The radiant heaters in the pyrolysis chamber must supply:

- (1) sensible heat to raise the pyrolyzate to the boiling temperature
- (2) the latent heat of vaporization (3) the superheat to pyrolyze the sewage and (4) make up for external heat losses through the system to the surroundings.

The flow rate to the unit is not constant and since the radiant heaters are of a fixed capacity, the maximum achievable temperature in the pyrolysis chamber will be a function primarily of flow rate.

Consideration of the following equations reflects the various heat requirements of the stream:

$$(1) \text{ sensible heat } Q = mc_p \Delta t$$

where Q = required heat

m = flow rate of sewage

c_p = specific heat of liquid

Δt = boiling temperature at existing pyrolysis chamber
minus preheat or pasteurization temperature

(2) latent heat of vaporization $Q = m \lambda$

where λ = heat of vaporization at the existing pyrolysis
chamber pressure, and

(3) superheat $Q = m c_{p_{\text{vapor}}} \Delta t$

where c_{p_v} = specific heat of vapor

Δt = (highest temperature in pyrolysis chamber minus
boiling temperature at the existing pyrolysis
chamber pressure)

Since the preheat temperature must be at least 161° F, the pasteurization temperature of sewage, sensible heat requirements are small. Any incremental rise in preheat temperature will further reduce this requisite. The major energy demands are in the vaporization and superheat processes. However, all of these requirements are a function of operating pressure. That is, depending upon the operating pressure in the pyrolysis chamber the physical parameters of the liquid, such as latent heat of vaporization, will take on different values. This will be reflected in the amount of heat required for the sensible, latent heat of vaporization and super heat processes.

Operating pressure determines the amount of flashing at the nozzle. As previously noted, the pressurized sewage moves from a high pressure zone to a low pressure zone and in doing so crosses

the bubble point attaining equilibrium by vaporizing some of the liquid. Further lowering of the pressure will leave the liquid superheated or at a temperature higher than the saturation temperature corresponding to the reduced pressure in the pyrolysis chamber, and the liquid will tend to convert to a vapor to regain equilibrium. The weight per cent of the stream flashing at the nozzle and at the lower pressure and saturation temperature is given by:

$$\text{Weight per cent of flow flashing} = \frac{c_p \cdot \Delta t}{\lambda}$$

where c_p = heat capacity of liquid

Δt = degrees of superheat

λ = latent heat of vaporization

From this equation the amount of superheat and/or vacuum needed to produce a specified amount of flashing can be calculated. These data will then serve as the basis for engineering design of the vacuum equipment, capital and operating costs, and the derivation of cost benefit ratios of using vacuum.

The proper choice of the pressure spray nozzle is a critical decision in the design of the pyrolysis chamber system. The nozzle controls the flow rate, spray cone angle and the atomized drop size distribution. Flow rates from a nozzle are function of line pressure and viscosity. As the line pressure increases the spray cone angle increases causing deposition of solids on the heater surfaces with the attendant loss of heat transfer capability. Increased line pressure also tends to skew the droplet size distribution toward the larger sizes. This in turn affects the heat and mass transfer

process.

Great latitude in the operation of the pyrolysis chamber is afforded by manipulation of flow rate, preheat temperature, pressure, and nozzle size. The desired effluent quality can be gained by optimizing the above parameters in the system.

CHAPTER III

EXPERIMENTAL APPARATUS

Mechanical Assembly

The pyrolysis chamber, which is used throughout the entire experimental program, is depicted by the photograph in Figure 7. The shell is constructed from a 6.357 inch internal diameter by 21.5 inch section of #304 stainless steel pipe. The unit is insulated with 8 inches of Kalo which is encased with rigid aluminum.

The electrical heaters are fastened to the top plate of the pyrolysis chamber. The calrod elements are 0.496 inch diameter by 64 inches of heated length formed into a vertical zig-zag pattern with the cold ends extending through the end flange. The vertical elements are spaced 2-1/4 inches center to center and provide a free space of diameter 5-5-1/16 inches in the core of the pyrolysis chamber. The heated portion of the pyrolysis chamber is the bottom 15-1/2 inches.

The center cover of the top plate provides the mounting for the nozzle assembly. The nozzle-deflector cone configuration may be removed as a unit. The nozzle pipe can be positioned to depths within the chamber from 1 inch to 4-1/4 inches above the calrod heating units by sliding it through the packing gland.

A 0.675 inch diameter line, 3 inches down from the top plate,

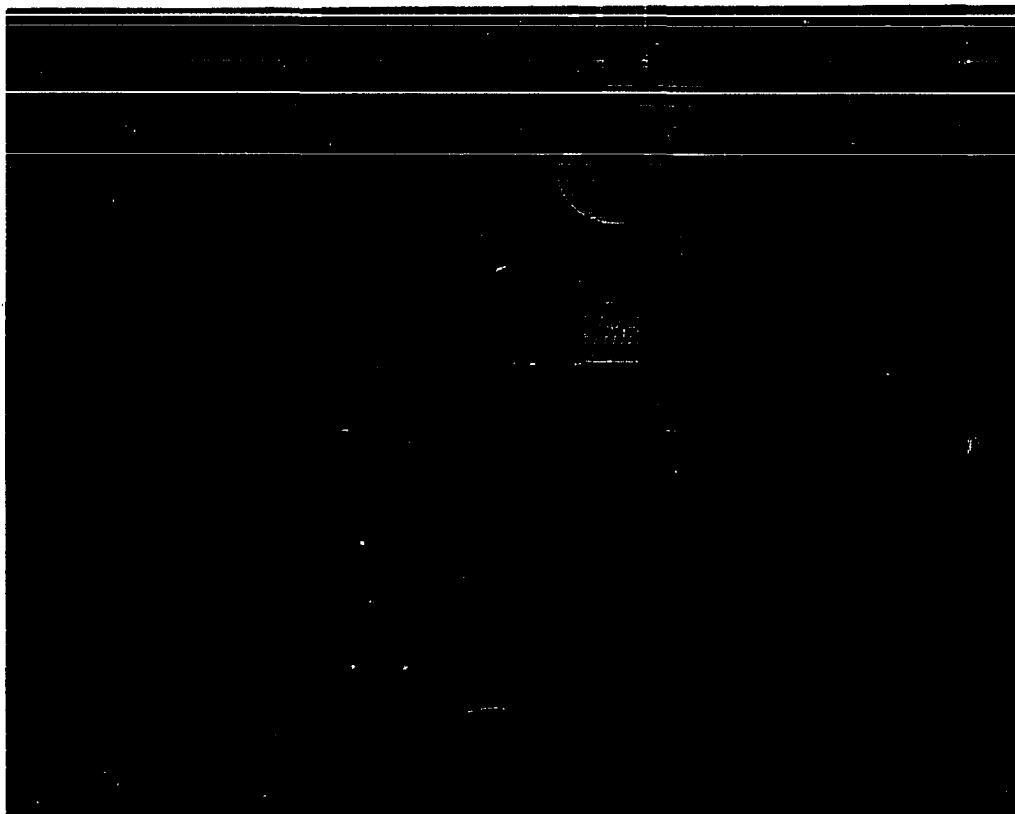


FIGURE 7

PHOTOGRAPH OF PYROLYSIS CHAMBER AND ASSOCIATED EQUIPMENT

provides entrance for the air supply. A view port, which is provided near the top of the pyrolysis chamber, is a 6 inch diameter vycor window that permits visual observation of operations inside the unit.

Three interchangeable, stainless steel, pressure nozzles with orifice diameters of 0.020 inches, 0.026 inches, and 0.035 inches were used for testing. They all produced a hollow cone mist spray. The nozzles consisted of a 2 inch base, metering center and shell with integral whirler insert.

All vapors generated in the pyrolysis chamber were condensed in a stainless steel heat exchanger. The condensor consisted of a 24-foot length of 3/8 inch O.D. by 0.035 inch wall #304 stainless steel tubing wound in coil form. The coil was housed in a 7.0 inch O.D. by 12.5 inch length #304 stainless steel shell. Tap water was used as the coolant for all runs in the pyrolysis chamber.

Electrical Assembly

The heating elements consisted of two 120 volt, 3kw heaters, one 4 pole contactor with 120 volt coil, one "off-auto" toggle switch, and one thermocouple controller. The unit is so wired that it can be operated from: (1) two 25 amp, 120 volt circuits, (2) a 50 amp, 120 volt circuit, or (3) by wiring the heaters in series from a 25 amp, 240 volt circuit. The pyrolysis chamber was wired in the 240 volt circuit for all experiments. The calrod heaters are operated by presetting the temperature controller and setting the toggle switch in the "auto" position.

Three circuits are involved for the control of electrical

energy to the pyrolysis chamber calrod heaters: (1) the thermocouple circuit, which is connected to the instrument panel directly; (2) the amplifying circuit, in which current passing through the photocell is amplified by a magnetic amplifier. A small bulb and the photocell are mounted in the same setting arm that connects the lower points. As long as the light from the bulb strikes the cell, current will flow to the calrod heater. When the temperature of the thermostat reaches the preset temperature, the light beam is interrupted causing the output of the photocell to drop to a point where the current will be reduced to a minimum, and (3) the control circuit terminal, which is isolated from the amplifying circuit and is powered separately.

The 14 gauge chromel-alumel thermocouple is encased in a 0.540 inch diameter stainless steel tube packed with magnesium oxide. The thermocouple can be positioned at any elevation within the unit. Also, it can be bent so to permit measurement of axial as well as vertical temperature profiles.

For preheating the sewage prior to atomization, an immersion calrod heater of 1.34 kw and 120 volts was used. The bulb of the thermostat is inserted opposite the heater and regulates the degree of sewage preheat by controlling the electrical current flow to the heater. The thermostat is a general purpose switching device consisting of a temperature sensitive bulb connected by a capillary to a diaphragm and a double pole, single throw, snap throw, snap action switching mechanism.

A tank, pressurized with air from 80 psig. to 100 psig. was used to deliver sewage to the pyrolysis chamber nozzles for atomization.

The requirement of high line pressure for good atomization and low flow rates necessitated the use of this method rather than conventional pumping systems.

CHAPTER IV

EXPERIMENTAL PROCEDURES

Pyrolysis Chamber Influent

Domestic sewage from the Norman Municipal Sewage Treatment Plant was the feed source for the vast majority of runs in the unit. The proximity of the plant provided a fresh and constant supply of domestic sewage which was almost totally free of industrial wastes. Norman sewage closely approximates the average waste generated aboard ship (see Table 2).

Synthetic sewage compositions were rejected as pyrolysis chamber influents because regardless of the formulation's complexity it could not possibly duplicate the vast amounts of minor constituents in human excreta. An exhaustive feces and urine analysis reported by Breeze (1961) partially reproduced in Tables 3 and 4 lends credence to this proposition. However, a few experiments using sucrose, glucose and acetic acid were performed in an attempt to understand the mechanisms of pyrolysis.

Laboratory Methods

This section describes the laboratory procedures and techniques used to generate the data which was used to evaluate the effect of the

TABLE 2

SUMMARY OF SEWAGE PROPERTIES - NAVY VESSELS*

Suspended Solids, mg./l. average	236
Biochemical Oxygen Demand, mg./l. average	102.0
Settlable Solids, ml./l.	5.4
pH, range	7.1-8.2
Total Solids, mg./l. average	33,000
Volatile and Organic Solids, mg./l. average	5,825

*Jakobson and Posner (1965)

TABLE 3

CHEMICAL CONSTITUENTS FOUND IN FECES - PARTIAL LISTING *

More Important Products Found	
Amino Acids	Methane
Ammonia	Methyl Mercaptan
Bacteria	Mucus
Carbon Dioxide	Para-oxyphenyl-propionic acid
Crystals, Phosphates, and Others	Paracresol
Detritus	Peptides
Fats	Peptones
Hydrogen	Proteoses
Hydrogen Sulfide	Skatole
Indol	Tissue remnants

*Breeze (1960)

TABLE 4

CHEMICAL CONSTITUENTS FOUND IN URINE*

More Important Products Found	
Water	Oxalic Acid
Urea	Allantoin
Hippuric Acid	Purine Basis
Uric Acid	Phenols
Creatinine	Sulfur
Indican (Indoxyl Potassium Sulfate)	Phosphate

*Breeze (1960)

operating parameters on the pyrolysis chamber effluent quality.

Chemical Oxygen Demand

Chemical oxygen demands were performed on the influents and effluents to measure the removal efficiencies of the pyrolysis chamber. Representative aliquots of the total influents and effluents as well as filtrates from these samples, after filtration through an 0.45 micron Milipore filter, were analyzed similar to the method outlined in Standard Methods for the Examination of Water and Waste Water, with one exception. The deviation was the normality of both the standard potassium dichromate and ferrous ammonium sulfate solutions. For these tests 0.125N solutions, rather than the prescribed 0.250N, were used. This procedural change was instituted due to the relatively low effluent chemical oxygen demands.

Biological Oxygen Demand

Representative samples of the influent and pyrolysis chamber effluent were analyzed by the methods suggested in the twelfth edition of Standard Methods for the Examination of Water and Waste Water. All effluent samples were seeded with fresh, raw sewage which was used as a feed source for the pyrolysis operation during that specific run. A Weston and Stack dissolved oxygen analyzer provided initial and five-day dissolved oxygen concentrations. This instrument was calibrated before use each day by the modified Winkler method.

Titration Curves

Titration Curves were obtained to evaluate the chemical change brought about in the pyrolysis chamber.

Fifty ml. samples of raw sewage and effluent from runs in the pyrolysis chamber representing all of the major operating conditions were titrated with 0.02N sulfuric acid and 0.02N sodium hydroxide. The pH of the solution was measured by a Sargent pH Meter, Model LS.

Kjeldahl Nitrogen

This analysis was made on 50 ml. influent and effluent samples to ascertain the amount of nitrogen lost to the atmosphere in the gaseous state by exposing the sewage to various temperature environments in the pyrolysis chamber.

The procedure followed is the prescribed technique found in part three of the twelfth edition of Standard Methods for the Examination of Water and Waste Water.

Solids

Total solids were measured by drying 20 ml. samples in porcelain dishes in a 103° C oven to constant weight. After drying, cooling to room temperature, and weighing, the residue was subjected to 600° C temperatures in a muffle furnace for a period of one hour; then re-weighed after cooling. The difference in weight represents the volatile solids fraction.

Total suspended solids and total volatile suspended solids were measured by filtering aliquots of samples through a 0.45 micron Milipore filter and following the above procedure. The difference in weight between the filtered samples and non-filtered samples represented the total volatile suspended content.

Temperature Profiles

Vertical temperature profiles for each run were recorded. The measurements were made after the pyrolysis chamber was at equilibrium for the pre-determined set of operating conditions. Usually a two-hour waiting period was observed to be certain of equilibrium. Temperatures were monitored at one-inch increments down the length of the chamber, approximately two inches from the inside wall of the pyrolysis chamber.

The purposes of these profiles were to provide data on the temperature of the hot spot or highest achieved temperature for each run as well as to identify the effect that operating parameters had on the heat transfer processes within the pyrolysis chamber.

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

This chapter deals with experimental results and a discussion of these data. COD is the principal determinant in the study of pyrolysis chamber performance as a function of system operating parameters. There were several reasons for this choice. First, the influents and particularly the effluents were dilute and to accurately assess operating efficiency a highly reproducible test was needed. COD determinations met this criteria. The second reason for the choice of COD is that other pyrolysis processes (i.e., Zimmerman and the Thermosonic Reactor Systems) have been studied primarily on a COD reduction basis. The review by Koenig (1963) of wet air combustion processes states that data on dilute systems is lacking and the least secure portion of reactor design is in the 200 mg./l. COD influent range.

COD, BOD, solids, nitrogen, and pH can accurately describe waste reduction efficiency, while temperature is a measure of pyrolysis which is a thermal process.

All of the data accrued throughout the study was obtained under the following range of operating conditions in the pyrolysis chamber:

(1) Pre Heat Temperature	165° F - 210° F
(2) Flow Rates	50 cc./min. - 150 cc./min.
(3) Hot Spot Temperatures	500° F - 1560° F
(4) Pyrolysis Chamber Pressure	Atmospheric Pressure

Temperature Profiles

Process control was best visualized by temperature monitoring; consequently, vertical temperature profiles were measured for each run in the pyrolysis chamber. Temperatures were recorded at one-inch intervals down the length of the chamber. Representative data for various flow rates are presented in Figures 8 to 10.

Figure 8 is a plot of the temperature in the pyrolysis chamber as a function of position, at various flow rates, for nozzle #1805. Note that the highest temperature appears at approximately three inches above the bottom plate of the pyrolysis chamber. This is the result of placing the condenser coils at the outlet of the chamber. The profiles appear as a family of curves with the temperature of the hot spot or highest temperature decreasing with flow rate. The shape of the curve indicates an increasing rate of change of temperature with distance until about the 14th inch height in the pyrolysis chamber after which the rate decreases. Quantitatively, this represents a transition from liquid in vapor to total vaporization. The phase transition is accompanied by changes in physical characteristics and heat transfer coefficients. Also, the ratio of heat transferred by radiation and conduction continually changes as the temperature increases.

FIGURE 8

VERTICAL TEMPERATURE PROFILES USING NOZZLE #1805

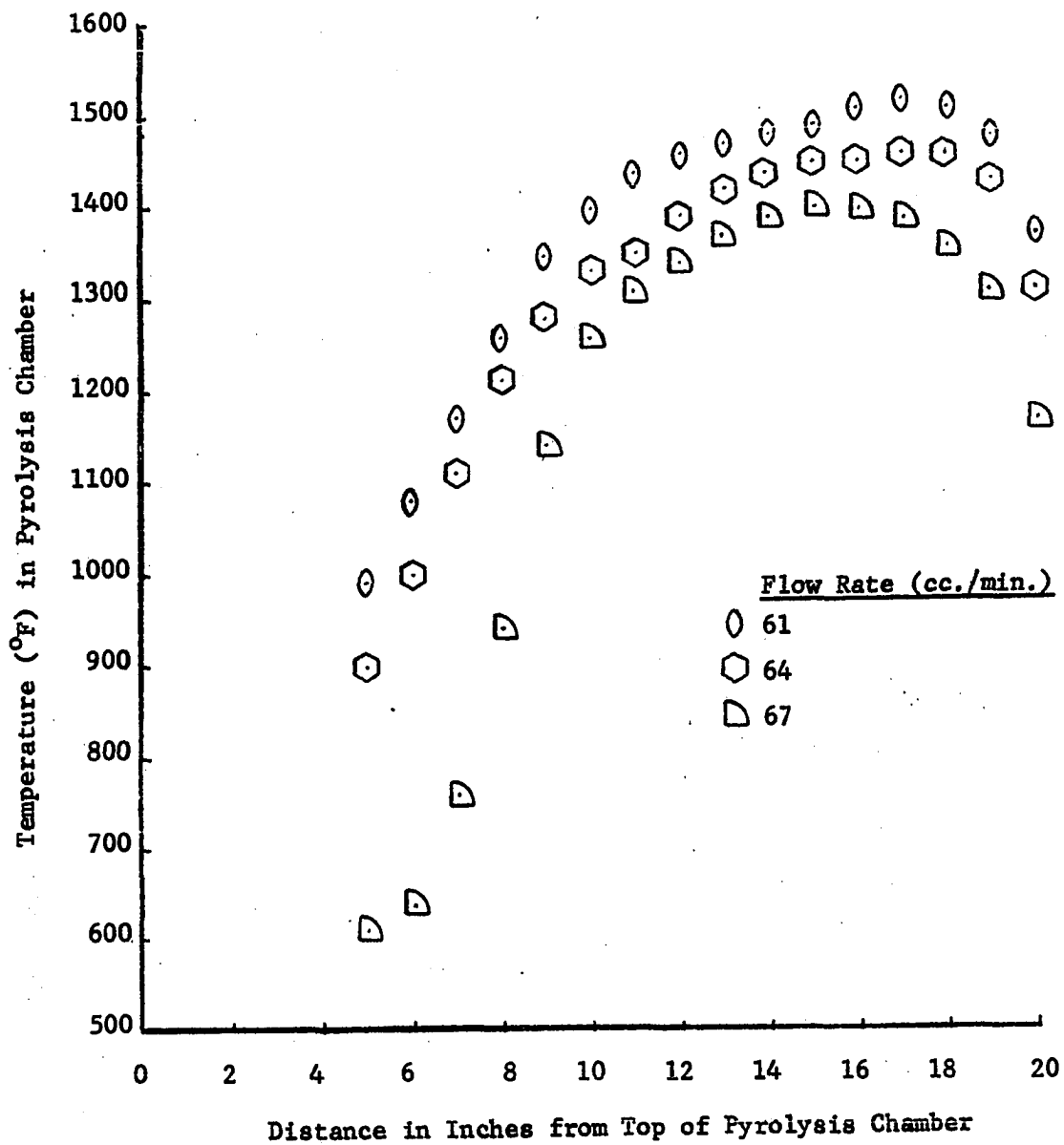


FIGURE 9

VERTICAL TEMPERATURE PROFILES USING NOZZLE #1808

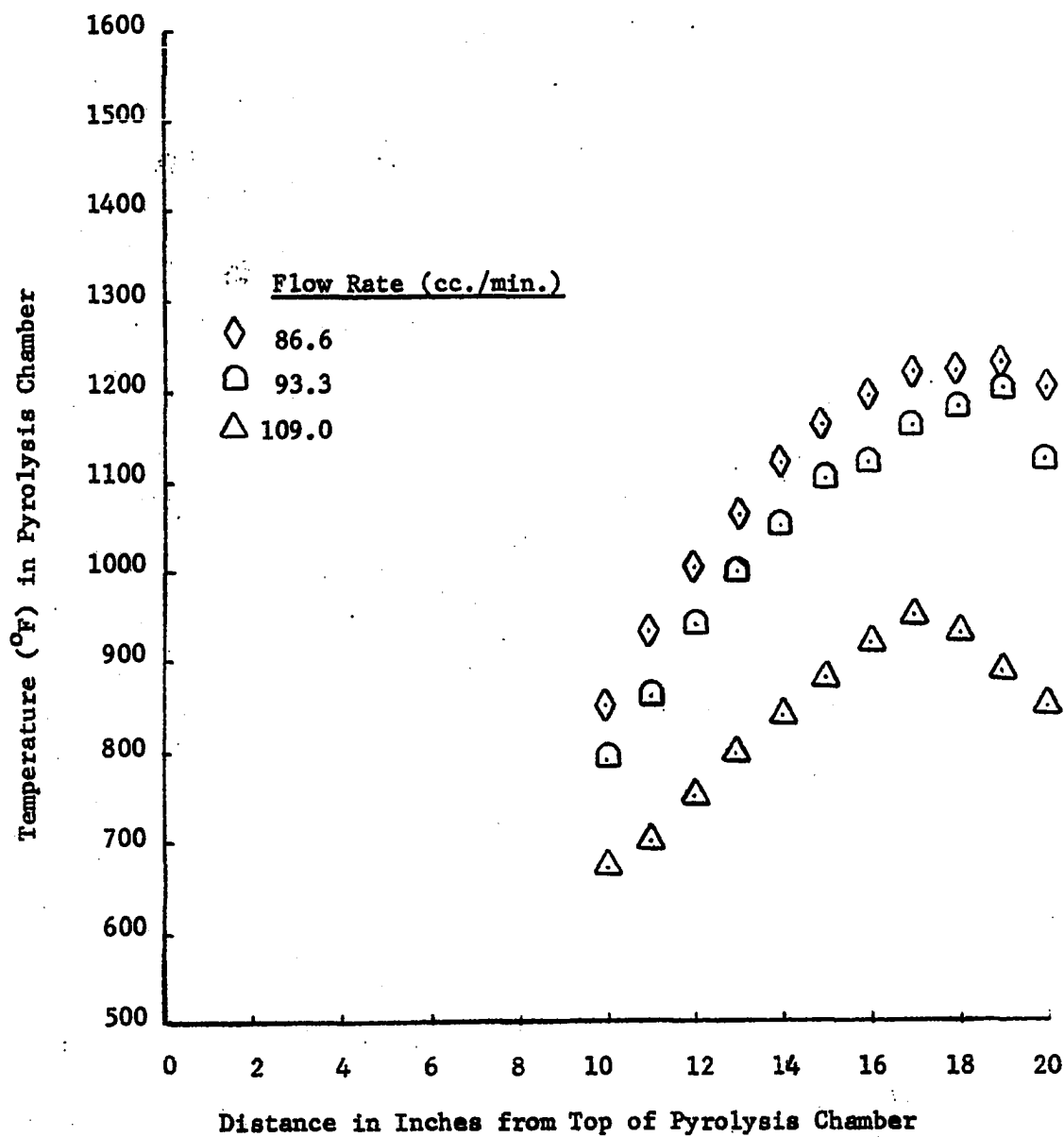


FIGURE 10

VERTICAL TEMPERATURE PROFILES USING NOZZLE #1811

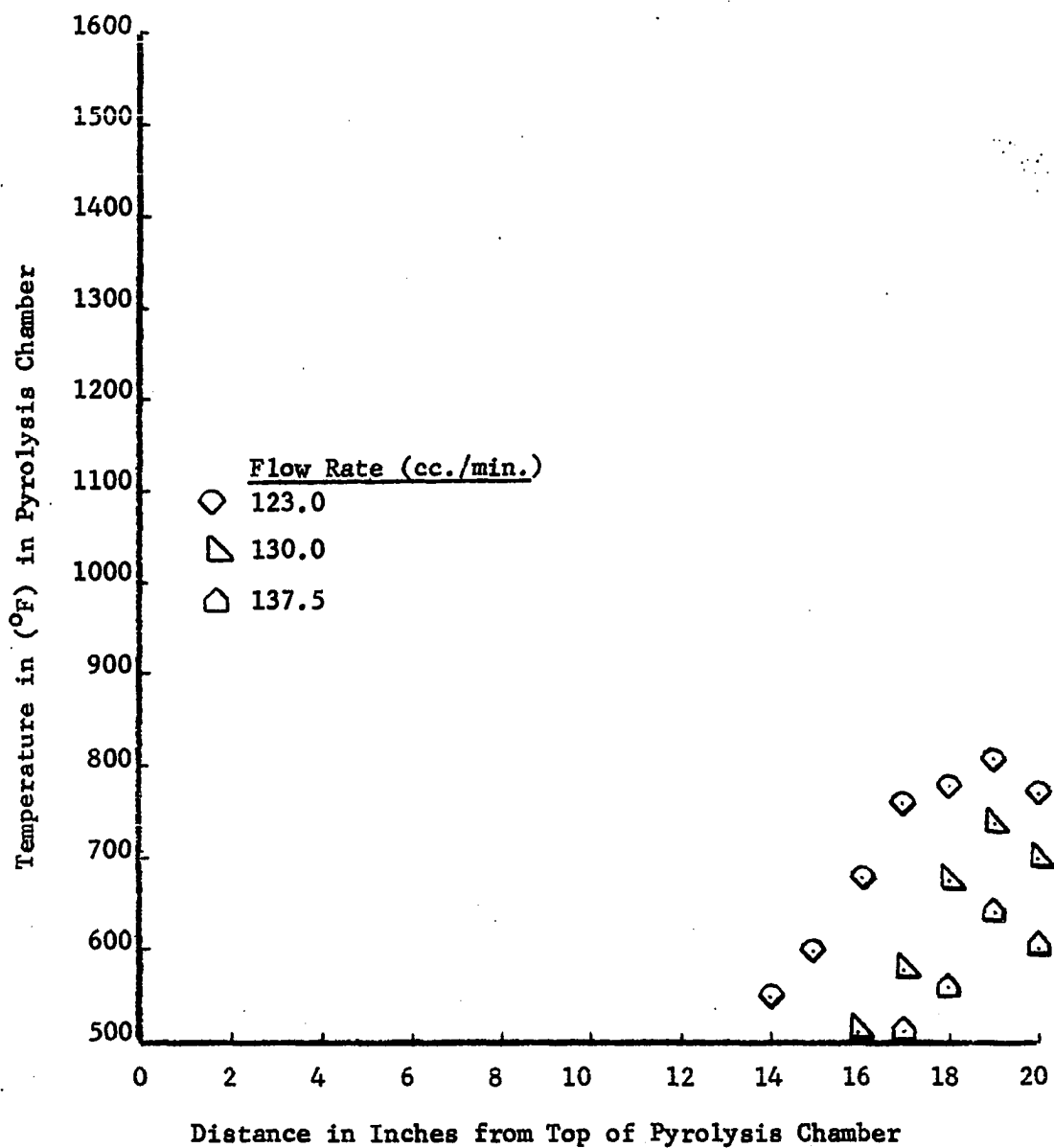


Figure 9 presents data of the same nature gathered in the pyrolysis chamber equipped with a larger capacity nozzle #1808. As in Figure 8 the family of curves retain the same identity, that is, the temperature of the hot spot decreases with increasing flow rates.

Figure 10 continues the analysis by showing data obtained with nozzle #1811, a still larger capacity jet. Here only temperature points in the lower reaches of the pyrolysis chamber were obtained because of the nature of the thermocouple system used. With the shielded thermocouple gas temperatures cannot be monitored when vaporization is not complete due to droplet condensation on the temperature sensing tip. The highest temperatures achieved for each of the flow rates again decreases with increased flow rates.

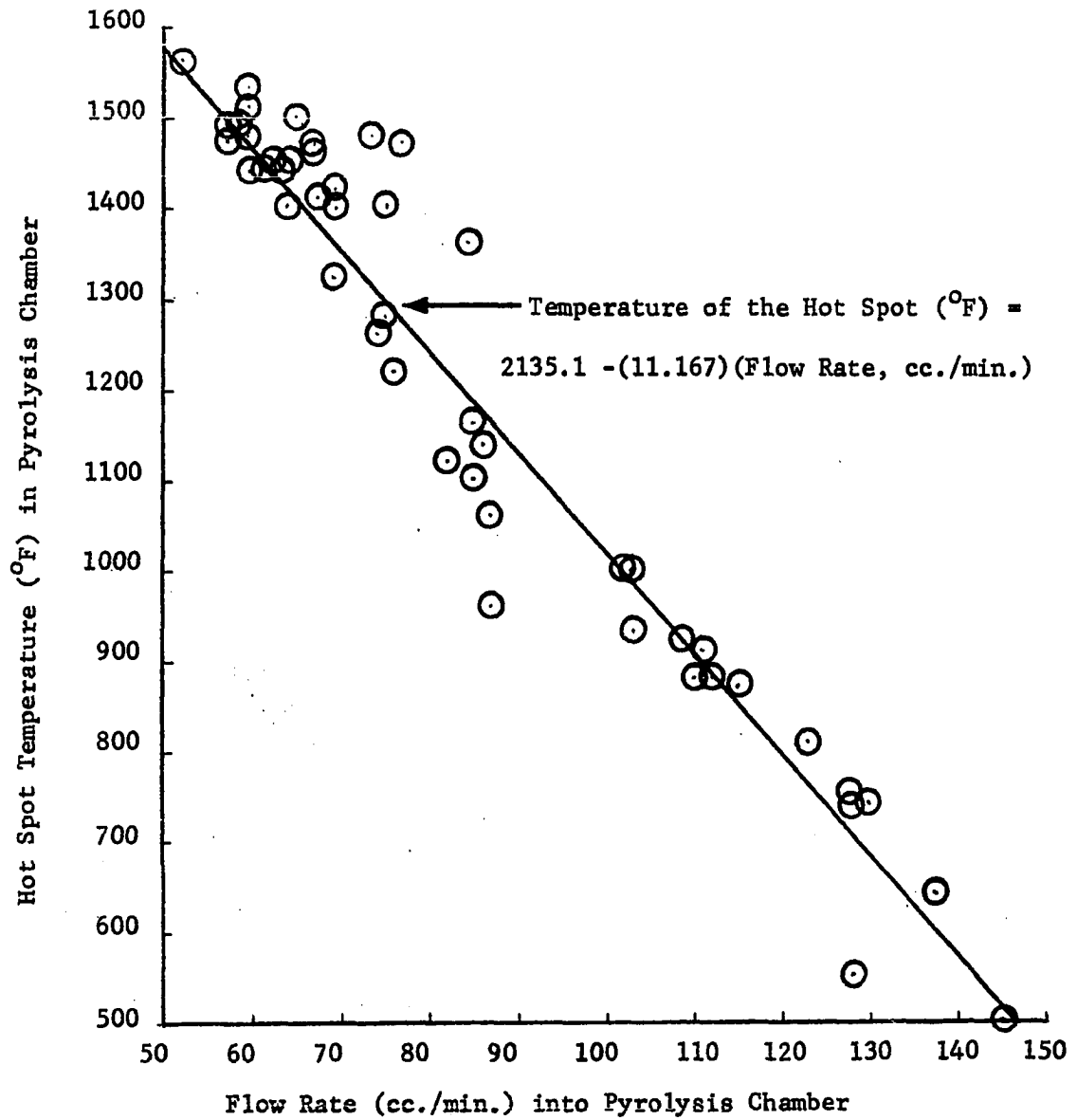
The temperatures of the hot spots for most of the runs are plotted as a function of flow rates and are represented in Figure 11. A multiple regression analysis was performed on all of the data with flow rates and pre-heat temperatures serving as independent variables and temperature of the hot spot as the dependent variable. The resulting equation took the form:

$$\text{Temperature of the Hot Spot (}^{\circ}\text{F)} = 2135.173 - (11.167)(\text{flow rate, cc./min.})$$

Pre-heat as a significant variable in the regression was ruled out by the partial F tests. This confirms the previous discussion on heat loads in the system and the suspected minor roles the pre-heat levels have on the hot spot temperatures achieved. The regression line is superimposed on the data plotted in Figure 11. Visual observation of the goodness of fit is substantiated by the statistical

FIGURE 11

HOT SPOT TEMPERATURE VARIATIONS WITH FLOW RATE



analysis for the regression found in Table 5.

TABLE 5

STATISTICAL ANALYSIS - HOT SPOT TEMPERATURE
AS A FUNCTION OF FLOW RATE

Total Sum of Squares	4,560,504.000
Sum of Squares Reduced in this Step	4,348,307.000
Coefficient of Determination	0.953
Multiple Correlation Coefficient	0.976
F for Analysis of Variance (D.F. = 1.48)	983.608
F for Analysis of Variance (D.F. = 1.48) at 1% Level of Significance	7.23
Standard Error of the Estimate	66.485
Regression Coefficient	-11.167
Standard Error of the Regression Coefficient	0.356

Chemical Oxygen Demand

Generally it is expected that effluent COD from the pyrolysis chamber would be a function of temperature and/or flow or retention time and/or influent COD. That reactions at room temperature approximately double or triple their velocity for a 10° C rise in temperature has been a well accepted empirical fact for quite some time. At the high temperatures found in the pyrolysis chamber, (i.e., up to 1560° F) the reactions proceed at instantaneous velocities requiring small fractions of a second to go to completion. Therefore, the choice of the temperature of the hot spot or maximum achieved temperature by the reaction gas as a system operating parameter is justified.

Figure 12 is a plot of effluent COD concentration in mg./l. versus temperature of the hot spot in °F. The graph shows the trend between the effluent COD and the hot spot temperature. The spread in the data is attributable to several factors such as: (1) influent concentration, (2) the large temperature range investigated (i.e., 500-1560° F), (3) variable hydraulic retention time (i.e., volume of pyrolysis chamber/flow rate), (4) the type of residual chemicals in the effluent, and (5) the COD test and its lack of ability to discern certain chemical species.

The influent COD concentration ranged from 90 mg./l. to 400 mg./l., and this variability alone can account for some of the discrepancy. The hot spot temperature also ranged from 500 to 1560° F, and it is not unlikely that kinetic mechanism changes would take place. In order to operate at various hot spots, three nozzles with different flow rates were used. This had the effect of varying hydraulic retention times. It is also assumed that the residual chemicals from high temperature hot spots would be relatively small, highly stable compounds. At low pyrolysis temperatures, a range of moderate sized components would be produced from the complex molecules found in sewage. Each of the latter types would exhibit different oxygen demands. The COD test is not sensitive to all classes of organics; for example, straight chain aliphatics, aromatic hydrocarbons, and pyridines are not oxidized to a large degree.

The data in Figure 12 were recalculated in terms of per cent COD reduced and plotted in Figure 13 as a function of hot spot temperature in the pyrolysis chamber. The curve gives evidence that

FIGURE 12

HOT SPOT TEMPERATURE EFFECT ON EFFLUENT COD

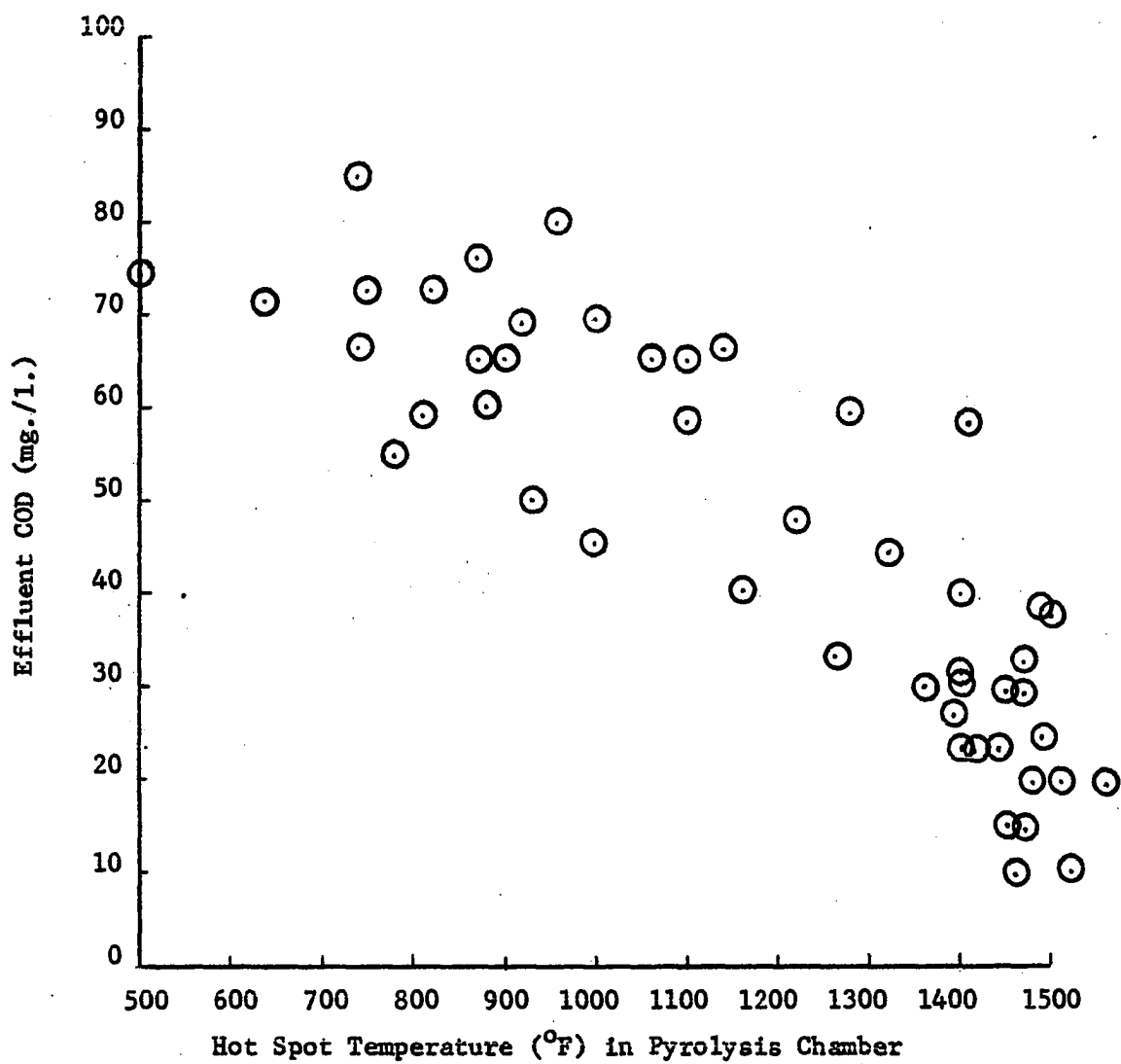
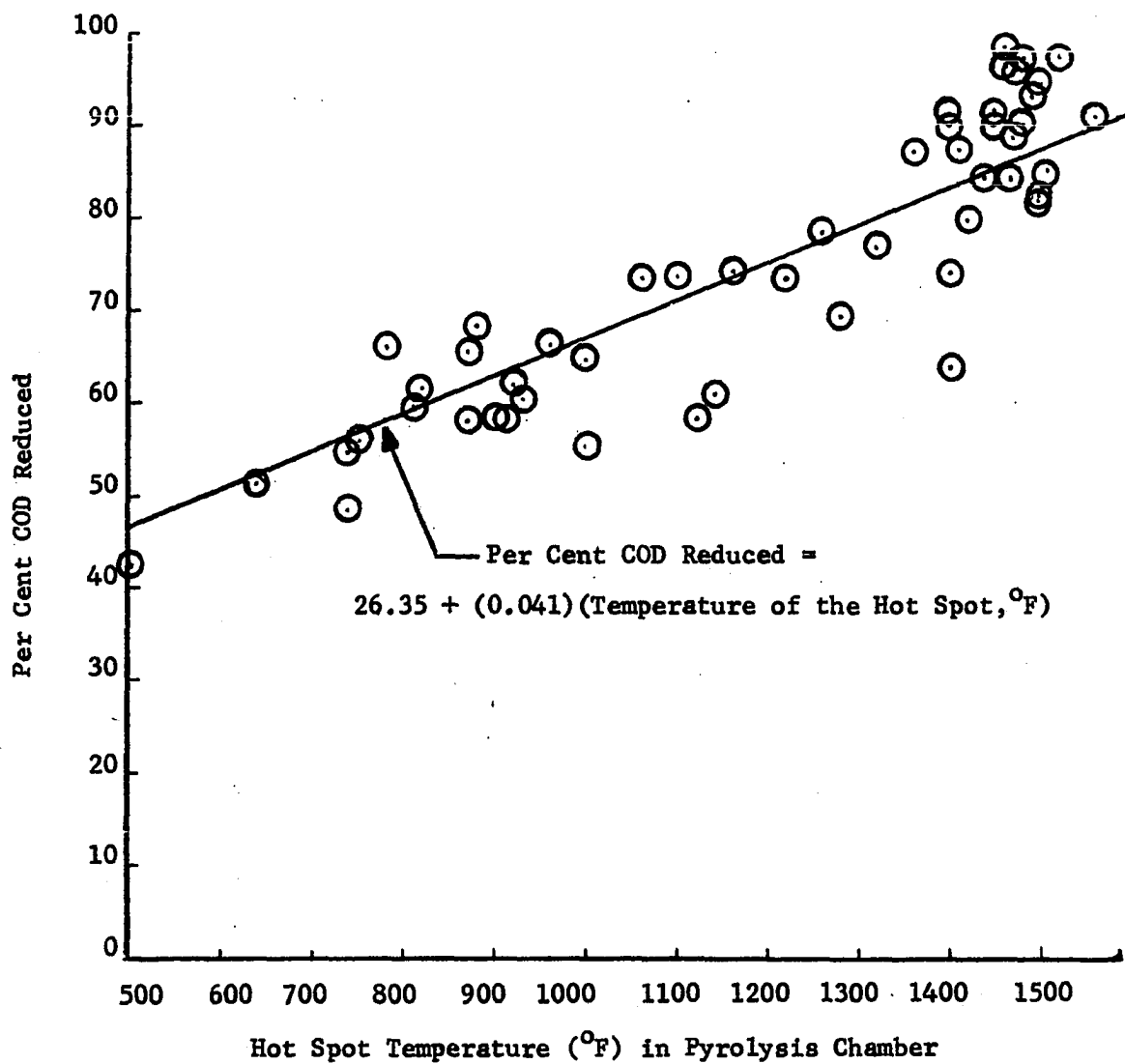


FIGURE 13

HOT SPOT TEMPERATURE EFFECT ON EFFLUENT COD REDUCTION



increasing the hot spot temperature increases the per cent COD reduced. It is apparent from the graph that the spread of the data has been substantially reduced from Figure 12. This can be ascribed to the addition of another variable in the analysis. That variable is the influent COD since the per cent COD reduced is calculated from:

$$\text{Per Cent COD reduced} = \frac{\text{Influent COD} - \text{Effluent COD}}{\text{Influent COD}} \times 100$$

The data in Figure 13 was analyzed by linear regression techniques and the following mathematical model obtained:

$$\text{Per Cent COD reduced} = 26.35 + (0.041)(\text{Temperature of the Hot Spot, } ^\circ\text{F})$$

Table 6 gives the statistical parameters obtained from the computer.

Substitution of hot spot temperatures from 500° to 1560° F into the regression equation gave the line which was replotted in Figure 13.

TABLE 6

STATISTICAL ANALYSIS - PER CENT COD REDUCED
AS A FUNCTION OF HOT SPOT TEMPERATURE

Total Sum of Squares	9641.723
Sum of Squares Reduced	7551.195
Coefficient of Determination	0.783
Multiple Correlation Coefficient	0.885
F for Analysis of Variance (D.F. = 1,48)	173.381
F for Analysis of Variance (D.F. = 1,48) at 1% Level of Significance	7.23
Standard Error of the Estimate	6.599
Regression Coefficient	0.0406
Standard Error of the Regression Coefficient	0.0031

Linear regression was applied to the data in Figure 12.

Since the per cent COD reduced versus temperature of the hot spot afforded less spread to this data, the influent COD was added as a dependent variable for the analysis. Multiple regression analysis techniques were applied by the computer and yielded the following equation:

$$\text{Effluent COD (mg./l.)} = 84.95 - (0.073)(\text{Temperature of the Hot Spot } ^\circ\text{F}) + (0.255)(\text{Influent COD, mg./l.})$$

Table 7 summarizes the statistical data for the multiple regression analysis.

TABLE 7

STATISTICAL ANALYSIS - EFFLUENT COD AS A FUNCTION
OF INFLUENT COD AND HOT SPOT TEMPERATURE

Step One - Independent Variable Selected - Hot Spot $^{\circ}\text{F}$			
Sum of Squares Reduced in this Step			15030.191
Coefficient of Determination			0.650
Partial F (D.F. = 1.48)			89.048
Cumulative Sum of Squares Reduced		0.650 of	23132.031
Multiple Correlation Coefficient			0.806
F for Analysis of Variance (D.F. = 1.48)			89.048
F for Analysis of Variance (D.F. = 1.48) at 1% Level of Significance			7.23
Standard Error of the Estimate			12.992
Variable	Regression Coefficient	Standard Error	Intercept
Hot Spot $^{\circ}\text{F}$	-0.05741	0.00608	112.285

TABLE 7 - Continued

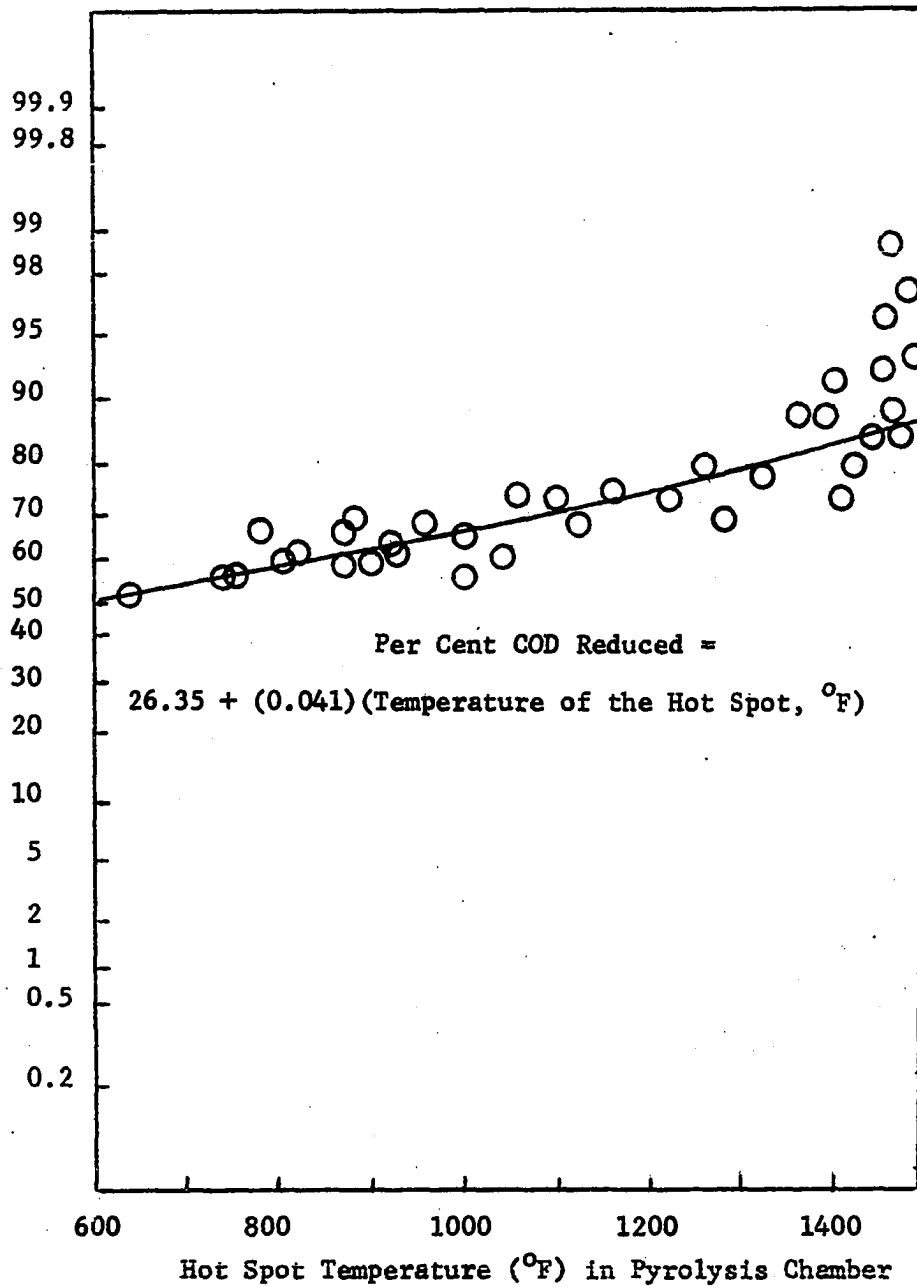
Step Two - Independent Variable Selected - Influent COD (mg./l.)			
Sum of Squares Reduced in this Step			744.562
Coefficient of Determination			0.032
Partial F (D.F. = 1.47)			4.756
Partial F (D.F. = 1.47) at 5% Level of Significance			4.05
Cumulative Sum of Squares Reduced			15774.750
Multiple Correlation Coefficient			0.826
Standard Error of the Estimate			12.512
Variable	Regression Coefficient	Standard Error	Intercept
Influent COD	0.068	0.0313	
Hot Spot °F	0.062	0.0062	104.920

From Table 7 it can be seen that the inclusion of the independent variable, influent COD, only raises the multiple correlation coefficient to 0.826 from 0.806. Other statistical parameters, such as cumulative sum of squares reduced and standard error of the estimate are also only slightly improved. The partial F test shows that the use of the second variable is significant to the regression by giving a value at (1.47) degrees of freedom of 4.756. This value is significant at greater than the 0.950 level.

The hot spot temperature - per cent COD reduced data is replotted on arithmetic probability paper in Figure 14. The vertical axis records the hot spot temperatures while the horizontal axis is used to plot the fraction of COD reduced as a probability function.

FIGURE 14

ARITHMETIC PROBABILITY PLOT OF PER CENT COD REDUCED VERSUS
HOT SPOT TEMPERATURE (600-1560 °F)



Included in the graph is the line described by the previously derived equation:

$$\text{Per Cent COD reduced} = 26.351 + (0.041)(\text{Temperature of Hot Spot, } ^\circ\text{F})$$

The data fit the model well in the lower temperature ranges. The experimental points scatter at high temperatures where the reductions are high and the graph is distorted. The temperature range 1300° F to 1560° F was replotted on an exaggerated temperature scale as seen in Figure 15. It was found that a rough family of straight lines, representing the influent concentrations, could be drawn through the data.

Several series of runs were made in the pyrolysis chamber to assess soluble COD changes with hot spot temperatures. Figure 16 is a plot of per cent COD reduced based on filtered samples as a function of hot spot temperature. The data are scattered but definitely follow the established trend of increased reductions with rising hot spot temperatures. However, the rate reduction change with temperature is not as rapid as the total effluent COD reductions. This is demonstrated in Figure 17 which is a cartesian coordinate plot with per cent COD reduced based on filtered samples on the Y axis and per cent COD reduced for the total effluent on the X axis. Figure 18 presents the data of filtered effluent COD divided by total effluent COD versus flow rate. The trend line infers that as flow rate increases some of the COD is not removed from the solids. Thus, pyrolysis is not completed at the high flow rates which is equivalent to low hot spot temperatures.

FIGURE 15

ARITHMETIC PROBABILITY PLOT OF PER CENT COD
REDUCED VERSUS HOT SPOT TEMPERATURE

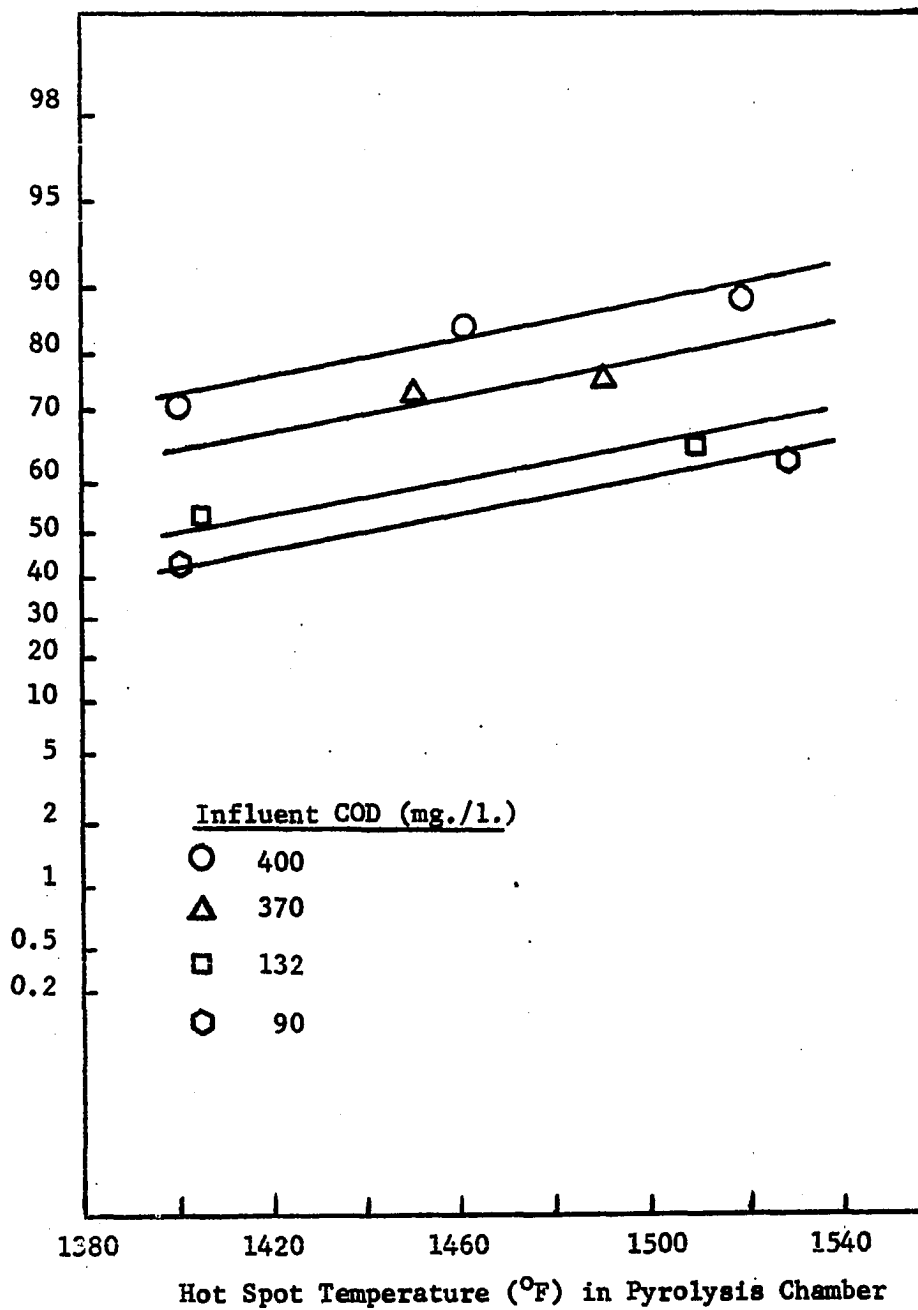


FIGURE 16

HOT SPOT TEMPERATURE EFFECT ON SOLUBLE COD REDUCTIONS

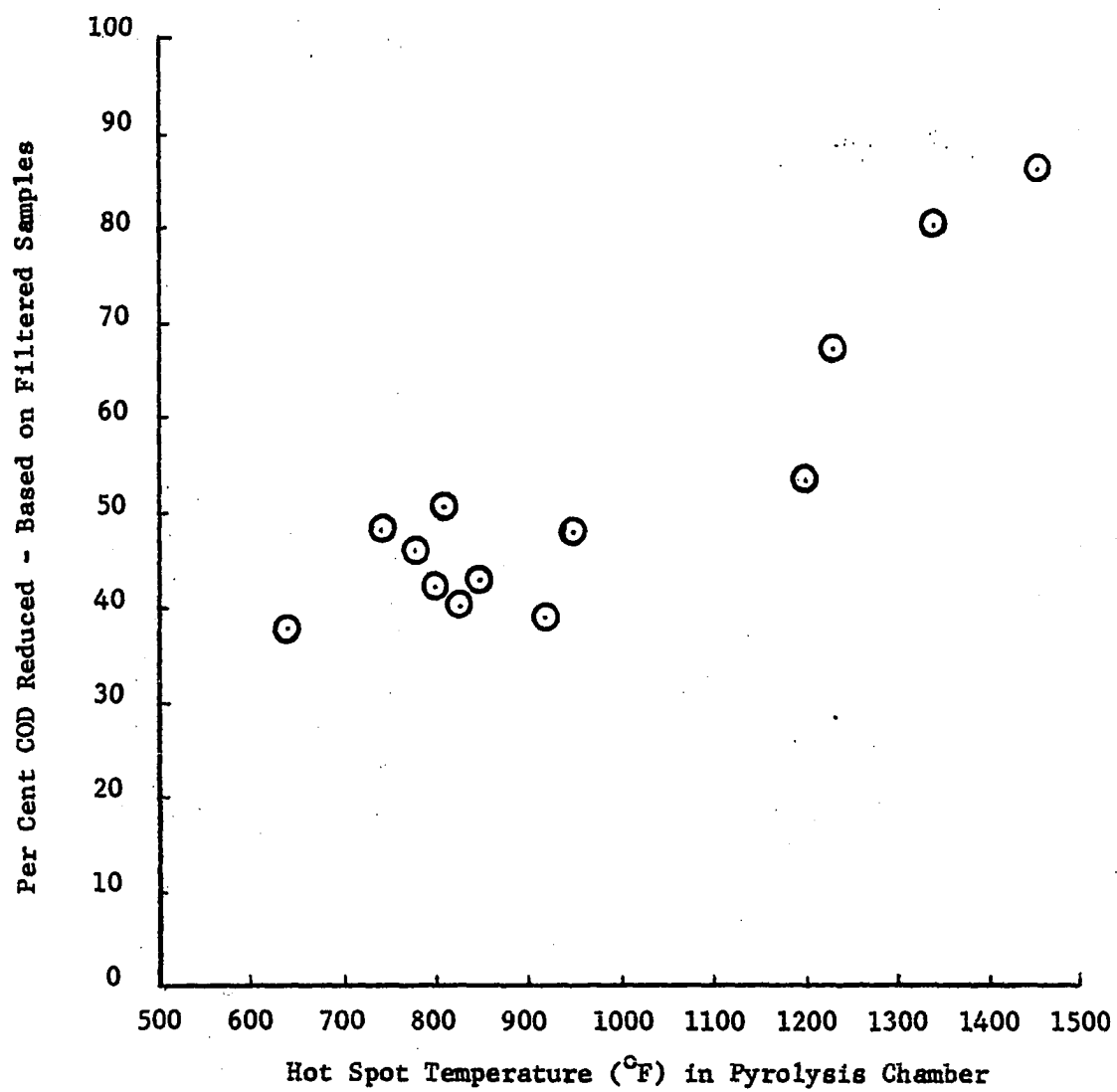


FIGURE 17

RELATIONSHIP OF SOLUBLE COD TO TOTAL COD EFFLUENT REDUCTIONS

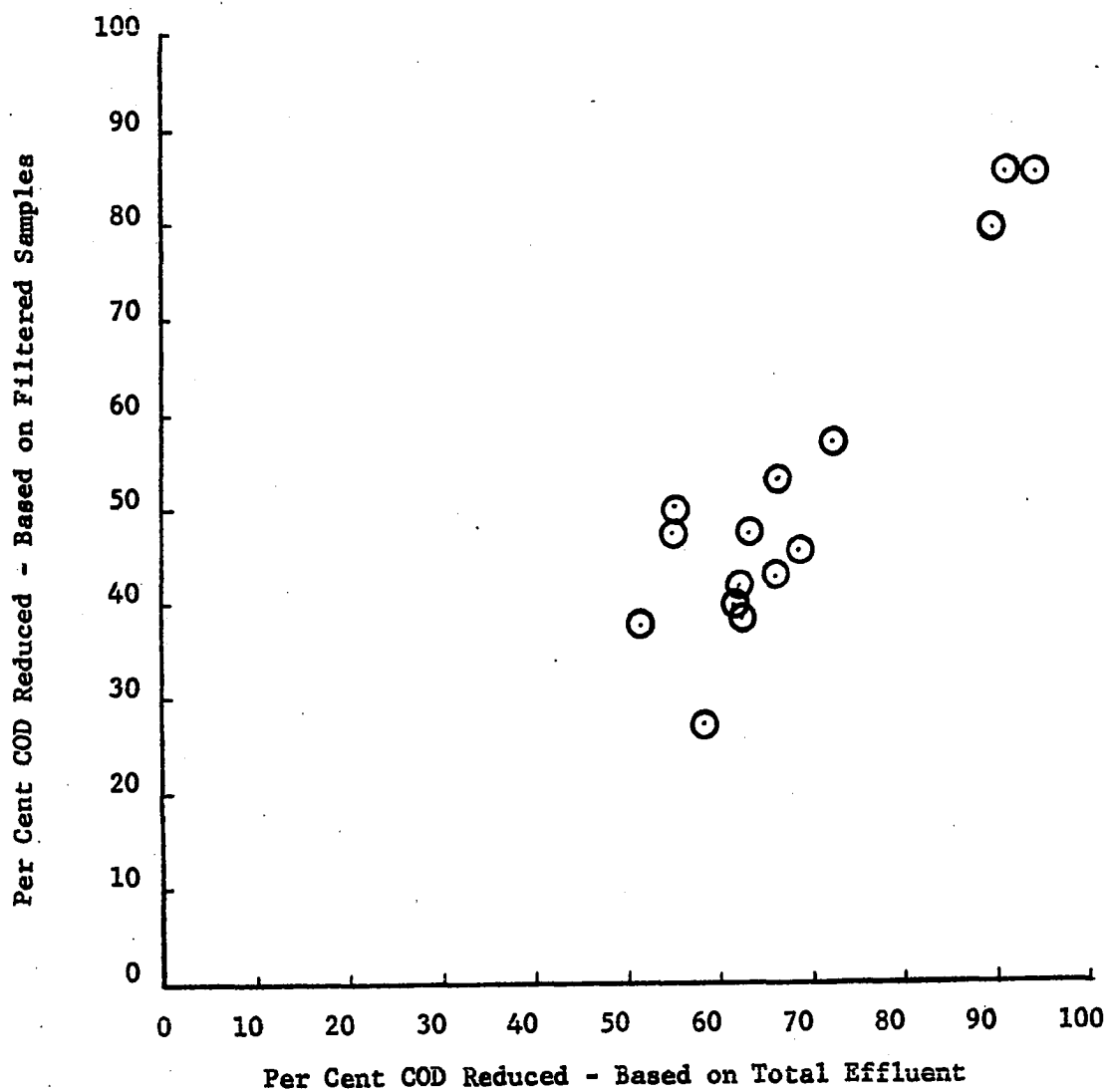
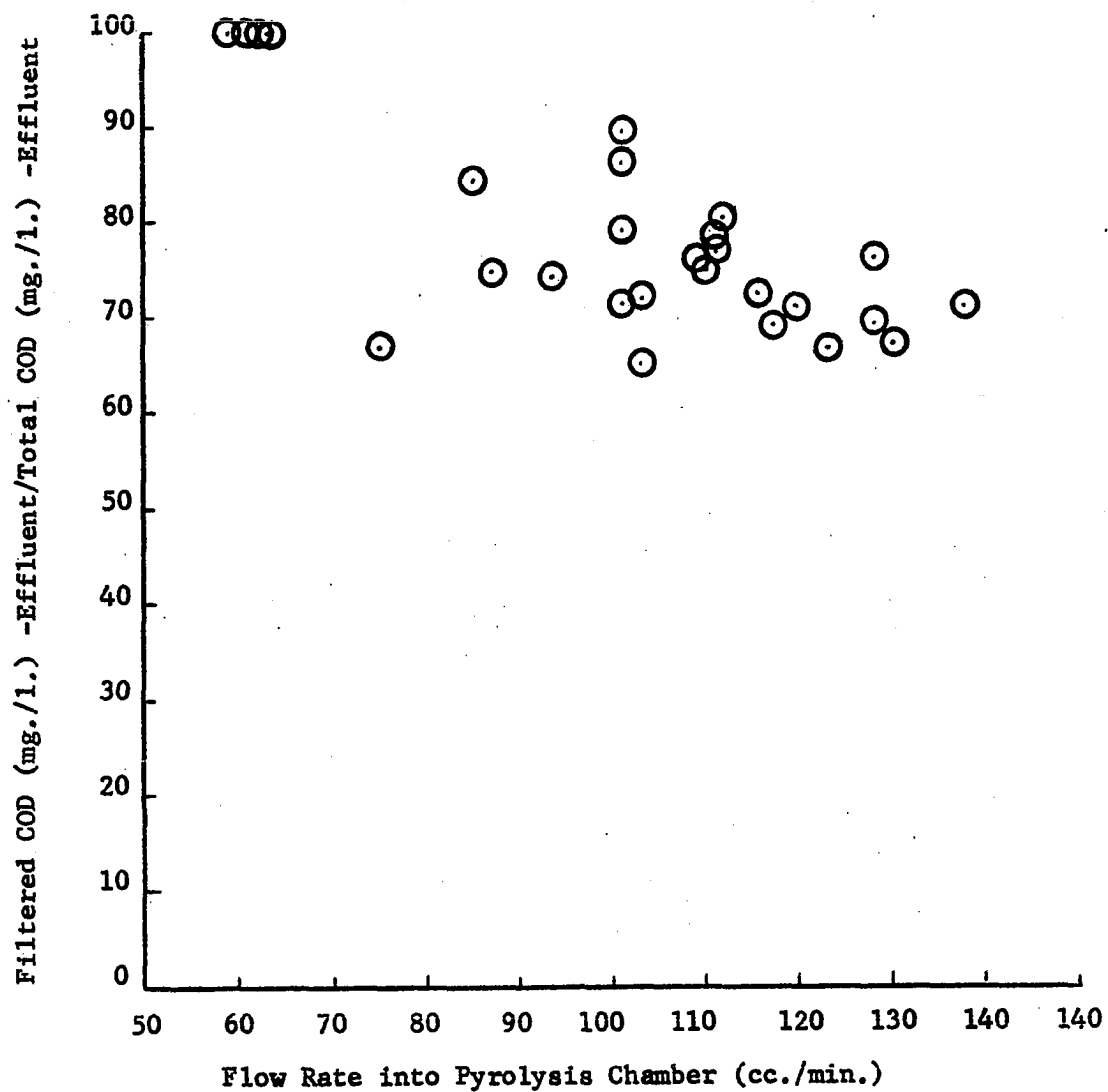


FIGURE 18

RATIO OF SOLUBLE COD TO TOTAL COD REMOVED AS A
FUNCTION OF FLOW RATE



Biological Oxygen Demands

Biological oxygen demand tests were performed on effluent samples to develop a relationship between BOD₅ and COD and to establish when the proposed criteria of 50 mg./l. would be violated.

Figure 19 presents the data of effluent BOD₅ versus effluent COD. A linear regression analysis was run on the data and the following equation produced:

$$\text{Effluent BOD}_5 \text{ (mg./l.)} = 3.876 + (0.265)(\text{Effluent COD, mg./l.})$$

Table 8 lists the statistical data on the analysis.

TABLE 8
STATISTICAL ANALYSIS - EFFLUENT BOD₅ AS A FUNCTION
OF EFFLUENT COD

Total Sum of Squares	681.932
Sum of Squares Reduced	603.366
Correlation Coefficient	0.685
Coefficient of Determination	0.467
F value for Analysis of Variance (D.F. = 25)	22.120
F value for Analysis of Variance (D.F. = 25) at 1% Level of Significance	-7.77
Standard Error of the Estimate	5.223
Regression Coefficient	0.265
Standard Error of the Regression Coefficient	0.056

Analysis of the data shows that correlation between the variables exists and is statistically significant. The data is scattered, however, particularly at the low BOD values where the test

FIGURE 19

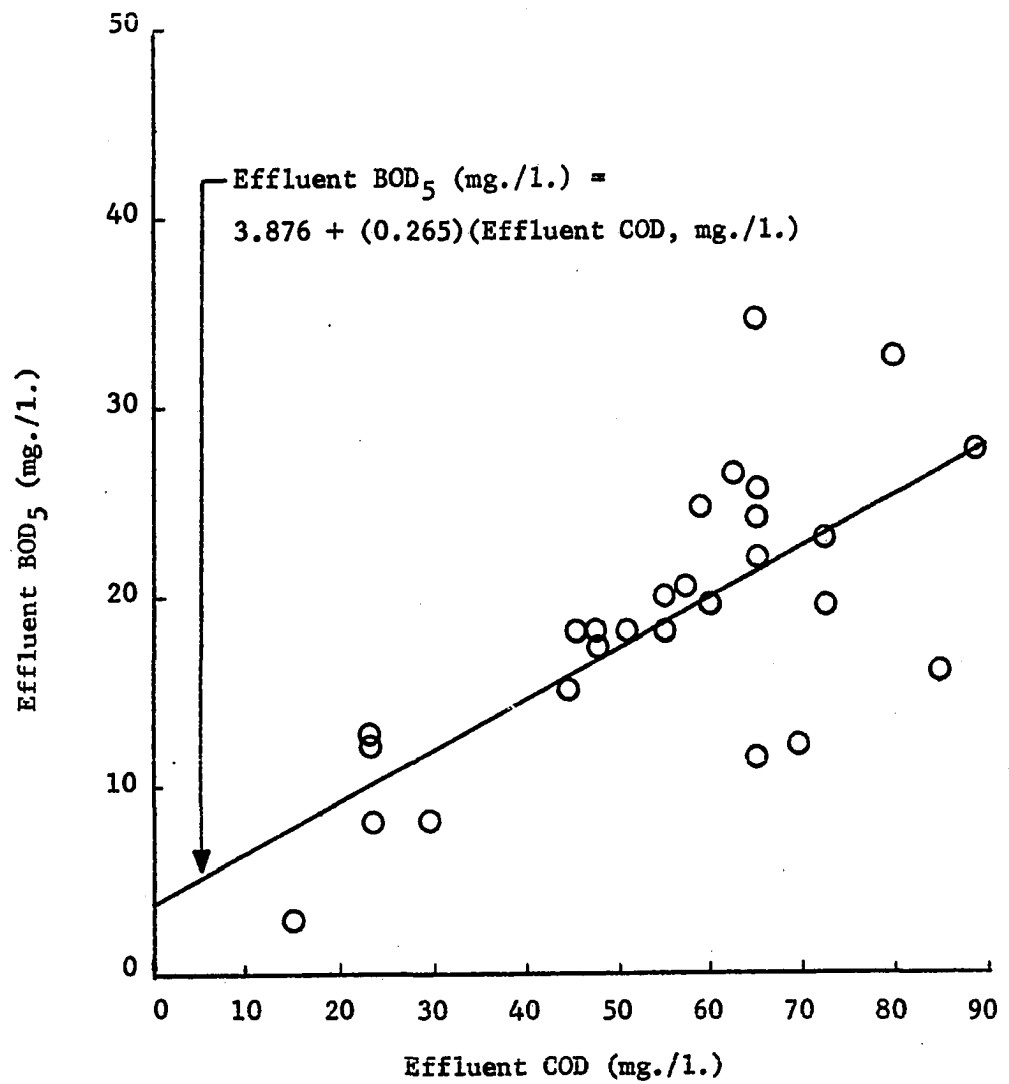
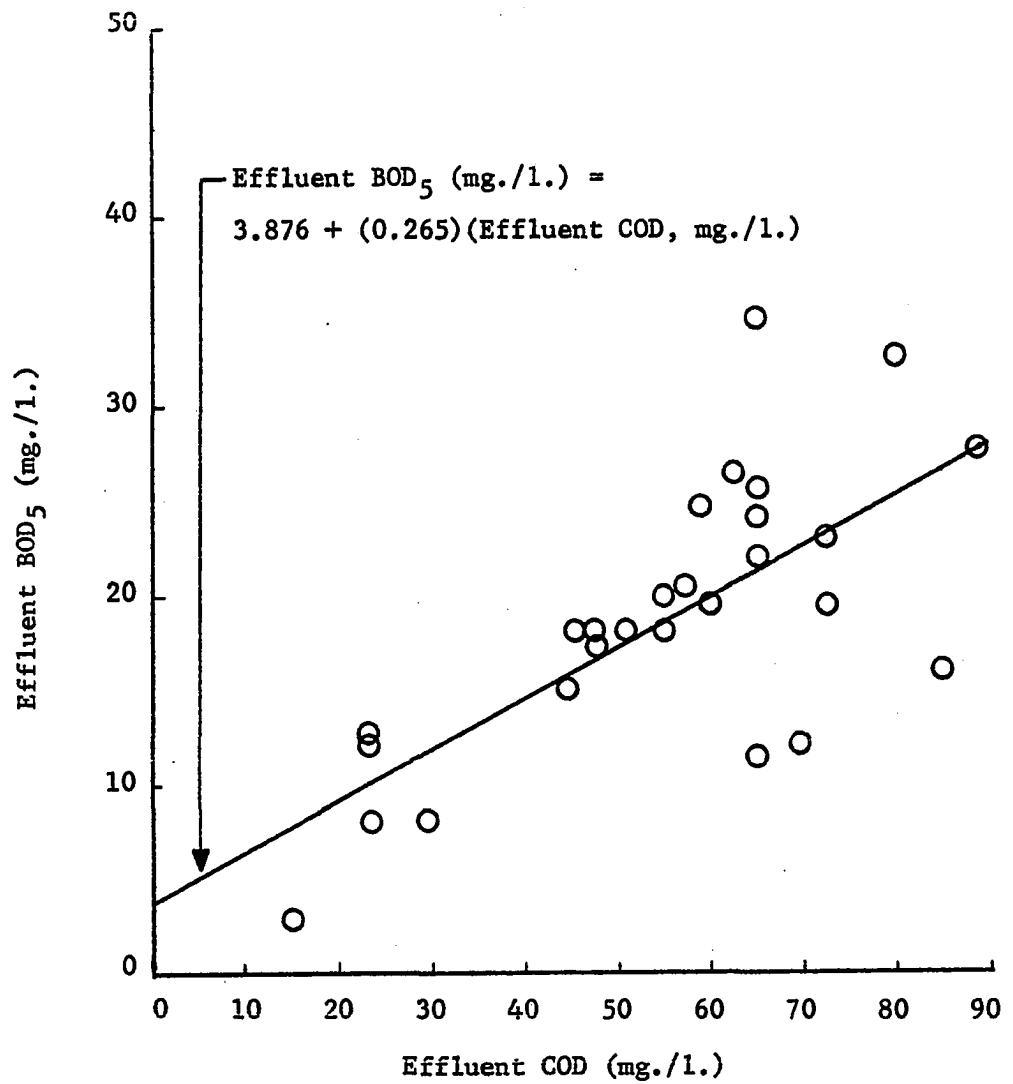
RELATIONSHIP OF EFFLUENT BOD₅ TO COD

FIGURE 19

RELATIONSHIP OF EFFLUENT BOD₅ TO COD

is not reliable. The data illustrate that none of the tested effluents exceeded the 50 mg./l. BOD₅ proposed standard for the range of operating conditions in the pyrolysis chamber.

Kjeldahl Nitrogen

The results of the Kjeldahl nitrogen determinations are reported in Table 9. A plot of per cent total Kjeldahl nitrogen remaining versus flow rate is presented in Figure 20. The data indicate a linear rise in the amount of Kjeldahl nitrogen remaining in the pyrolysis chamber effluent as flow rates are increased. This response is expected since it has been demonstrated that temperature is directly proportional to flow rate. As the temperature increases, the amount of nitrogen leaving the system as non-condensable nitrogen gas and related compounds increases.

Spot checks of the nitrate and nitrite content for representative samples processed in the pyrolysis chamber over the entire range of flow rates tested gave a concentration of less than 0.3 mg./l.

Solids Concentrations

Solids data are presented in graphical form in Figures 21 and 22. Figure 21 is a plot of per cent total solids remaining as a function of flow rate. The data are widely scattered and defy categorization into any pattern.

The lack of definition can be substantially explained by deposition of solids on the walls and heaters of the pyrolysis chamber. In the condenser a buildup of solids was also noted on the top coils of the unit. Impingement of the spray from the nozzle on

TABLE 9

KJELDAHL NITROGEN

Influent mg./l.	Effluent mg./l.	Per Cent Kjeldahl Nitrogen Remaining in Effluent	Hot Spot Tem- perature (°F)
20.1	15.1	74.2	900
20.1	18.1	90.0	910
26.8	14.6	----	1410
26.8	12.9	48.0	1440
26.8	13.5	50.1	1400
24.4	17.3	71.5	740
24.4	23.5	95.5	760
24.4	18.5	76.0	700
26.6	17.9	67.5	960
26.6	17.9	67.5	1060
26.6	18.2	68.5	1100
26.9	17.9	66.9	1280
26.9	16.2	60.1	1320
26.9	16.2	60.1	1440
19.5	13.7	70.0	930
19.5	14.8	75.9	1000
27.4	15.4	56.2	1450
27.4	14.3	56.2	1450
27.4	18.2	66.2	1440
23.5	17.1	72.9	950
23.5	15.1	64.5	1200
23.5	13.4	57.1	1230
28.0	20.7	72.9	850
28.0	22.7	81.0	830
28.0	20.1	72.0	780
19.6	15.7	75.0	640
19.6	16.3	83.0	740
19.6	15.1	77.0	810

FIGURE 20

KJELDAHL NITROGEN REMAINING IN THE EFFLUENT
AS A FUNCTION OF HOT SPOT TEMPERATURE

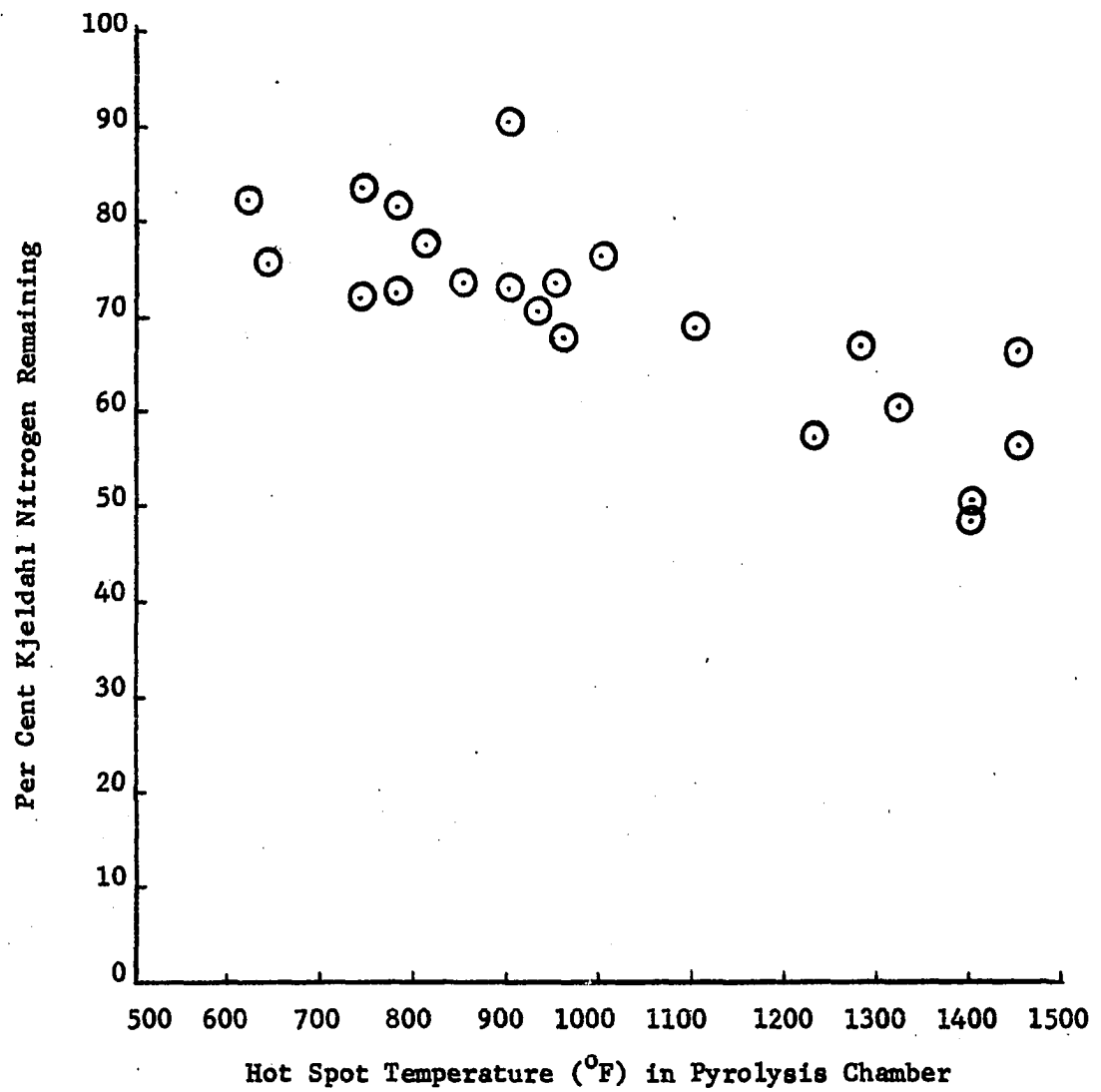


FIGURE 21

TOTAL SOLIDS CHANGES IN THE EFFLUENT AS A
FUNCTION OF FLOW RATES

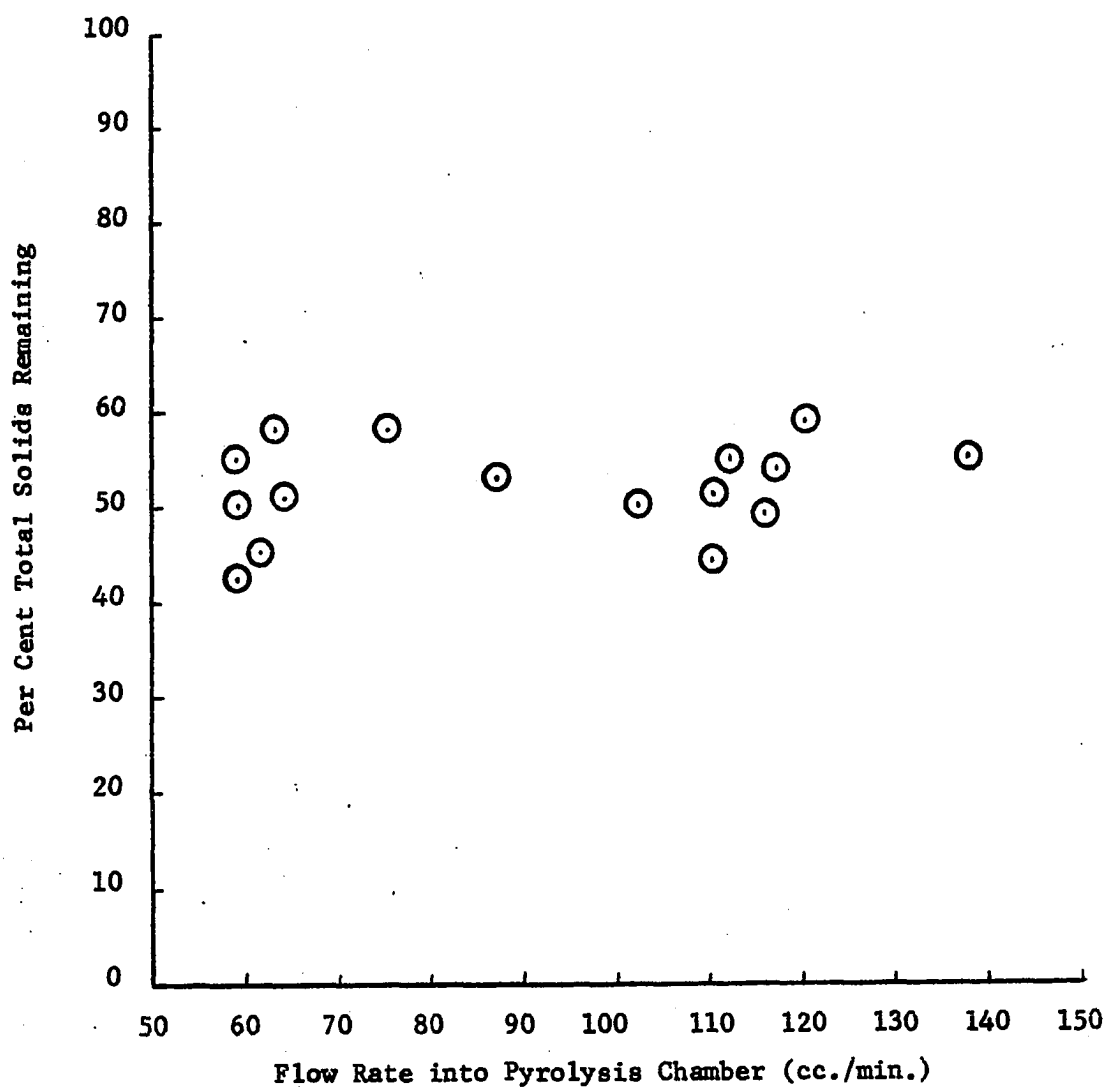
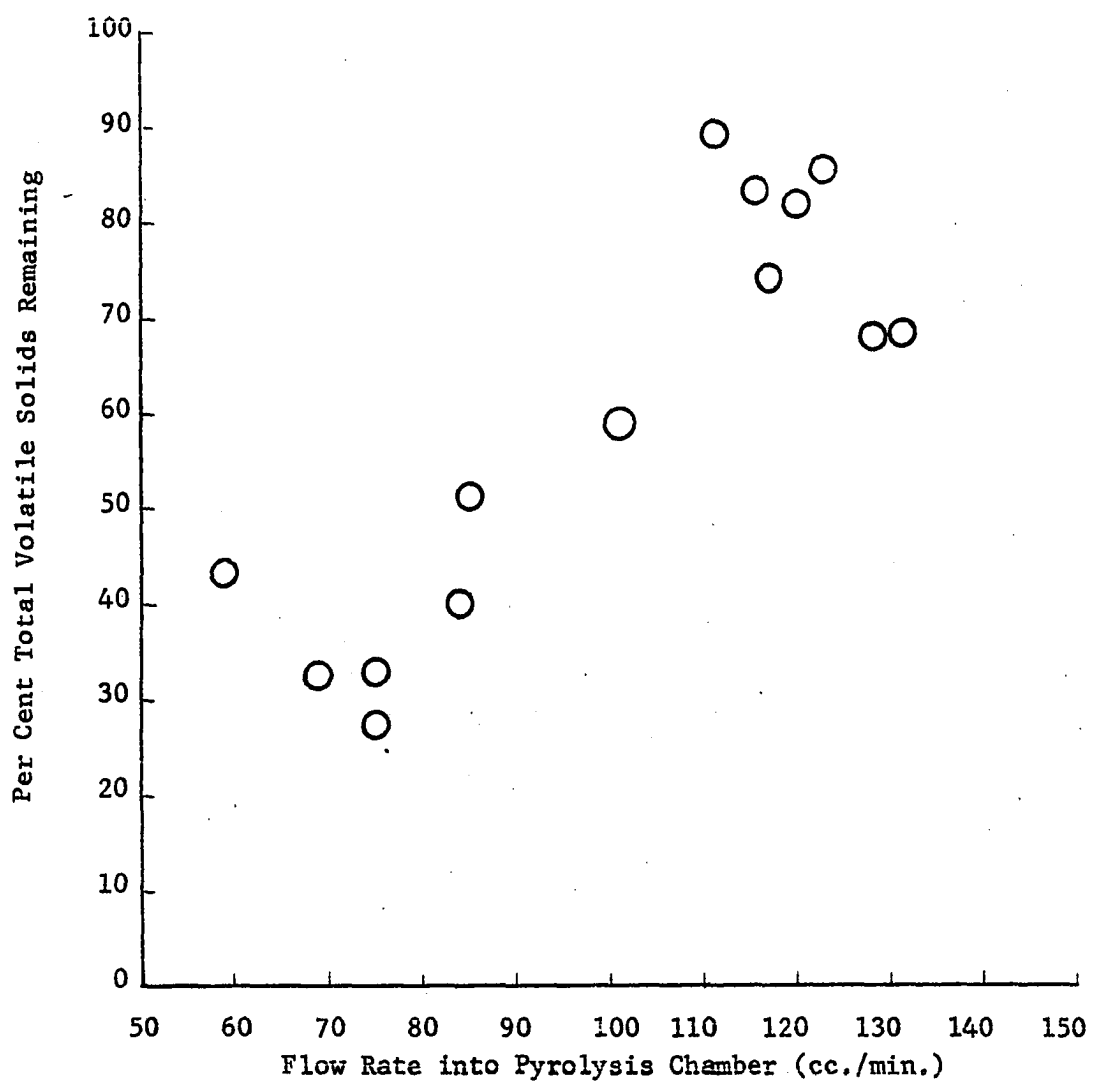


FIGURE 22

TOTAL VOLATILE SOLIDS CHANGES IN THE EFFLUENT
AS A FUNCTION OF FLOW RATE



surfaces in the unit is the result of wide-spray cone angles which take place particularly at high-flow rates. Wide spray cone angles can also be the consequence of surface active materials in sewage altering the physical properties of viscosity and surface tension of the stream.

The problem of solids buildup in the pyrolysis process can be overcome by a more judicious choice of nozzle spray cone angle and/or vessel diameter. Placement of a filter before the condenser coil will control solids from entering the condenser.

Plotting the per cent total volatile solids remaining versus flow rate affords the more predictable response as pictured in Figure 22. That is, as the flow rate was increased hot spot temperatures were reduced, thus the volatile content of the solids in the effluent also decreased.

Suspended solids concentration for all samples tested ranged from 5 to 115 mg./l. None of the results exceeds the proposed limit of 150 mg./l.

Titration Curves and pH

The influent pH for sewage used in all the runs in the pyrolysis chamber fell in the narrow band between 7.2 and 7.6. Likewise, the effluent pH ranged from 9.75 to 10.0.

The reproducibility of sewage pH values is due to the type of feed used for the experiments. The source was the Norman Municipal Sewage Treatment Plant which has only minute amounts of industrial wastes contaminating the system. Also, samples used in these

experiments were obtained at approximately the same time each day with a variance of less than one hour.

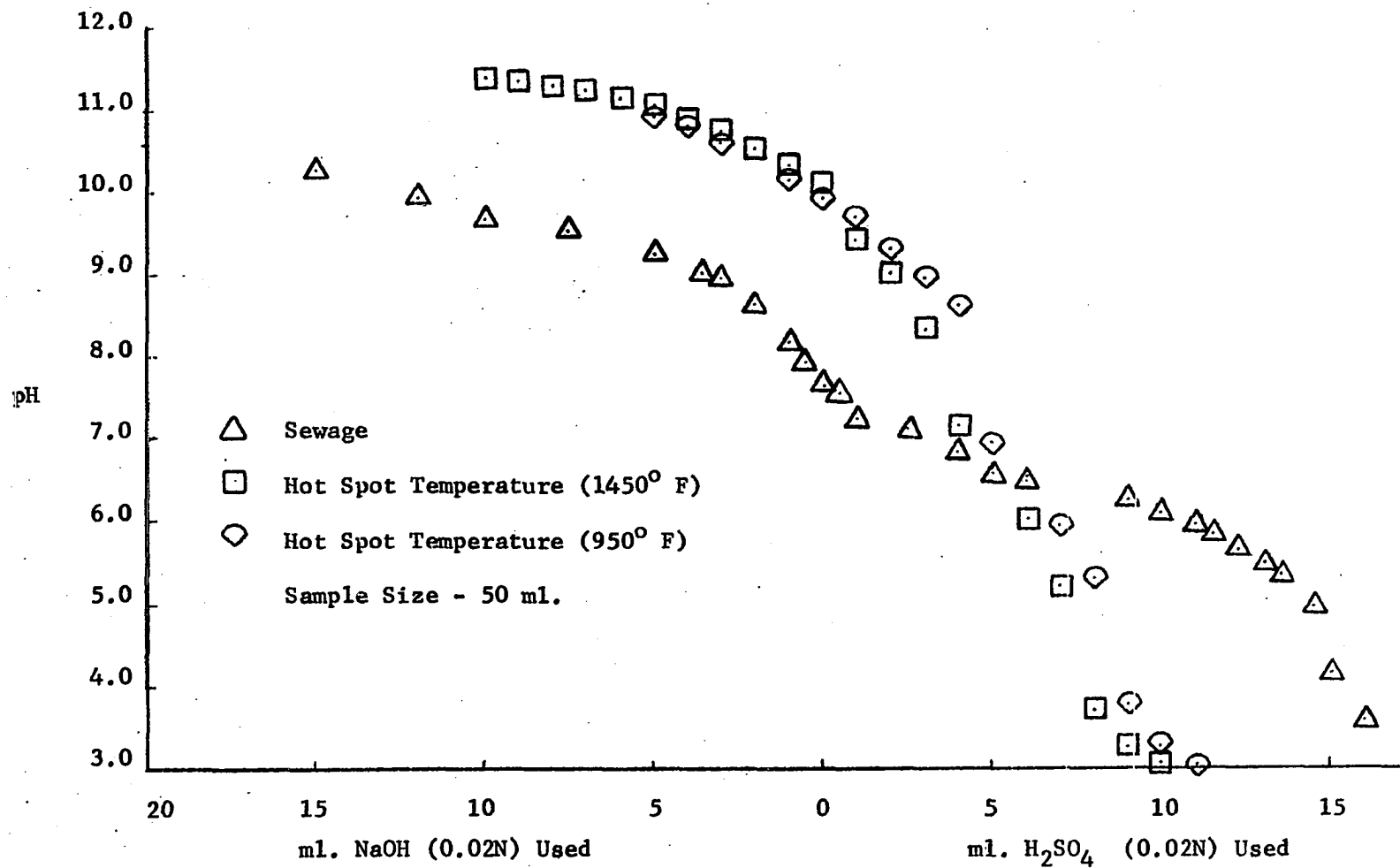
The relatively high pH values of the system effluent emanates from nitrogenous compounds. For instance, in the pyrolysis process, the amino group is removed from proteins which react to water and its electrolytes to increase the pH of the effluent.

Titrations were performed on influents and effluents to the pyrolysis system representing various operating conditions. The constant nature of the sewage was again borne out in the titration curves. Tests on a day-to-day basis revealed that the sewage varied less than 0.2 pH units along the entire length of the titration curve. Two inflection points, at pH 8.0 and 4.0, were noted for each sample of sewage. The titration curve of effluents also showed a characteristic curve with inflections at approximately pH 7.5 and pH 4.5. The amount of acid needed to reach these inflection points was found to be a function of the operating temperature in the pyrolysis chamber and the effluent.

Figure 23 depicts the titration curve data from two different runs in the pyrolysis chamber and the average curve for sewage. The hot spot temperatures for the runs were 1450° F and 950° F and effluent COD's of 15 and 65 mg./l. respectively. The amount of titrant used for the effluent with 15 mg./l. COD was 7.0 ml. at the inflection point at pH 4.5 while the 65 mg./l. effluent required 8.5 ml. at the same pH.

FIGURE 23

TITRATION CURVES OF SEWAGE AND PYROLYSIS CHAMBER EFFLUENTS



Unsteady State Runs in the Pyrolysis Chamber

The acquisition of reliable operating efficiency data as a function of temperature in the pyrolysis chamber was a slow process because of the nature of the unit. For example, to bring the pyrolysis chamber into equilibrium from a cold start up for each run required approximately 2.5 hours. Once thermal equilibrium was reached for a given set of operating conditions, a vertical temperature profile was taken. This procedure required at least an additional 1.5 hours. Sometimes small particles partially plugged the swirl ports in the nozzle, thus reducing the flow and severely altering the temperature profile within the pyrolysis chamber. When this occurred, conditions had to be stabilized before proceeding with the temperature profile. Another of the difficulties encountered in attempting to analyze temperature effects in the pyrolysis of sewage on a run-to-run basis was the slight, but sometimes significant, variability of the waste composition. In addition, it was impossible to closely control the hot spot temperature with the experimental apparatus and therefore subtle changes in mechanism and their resultant physical-chemical deviations were not always perceived. In endeavoring to remedy these problems a series of unsteady state runs were performed.

Unsteady state runs means that the operating variables, such as flow rate, pre-heat, and sewage composition are held constant; and only temperature varied from an equilibrium condition at a high level (i.e., 1300° F) gradually down to a low point in the order of 300° F. Temperature changes were brought about by shutting off

the electricity to the pyrolysis chamber calrod heaters, thus permitting temperature to drop as a result of continually spraying sewage into the unit. The temperatures monitored were the hot spots in the pyrolysis chamber and the outlet water temperature for the condenser. To reach a relatively high hot spot at equilibrium operating conditions the flow rate to the unit was maintained in the range of 60 cc./min. During the initial 14 minutes of the run samples were taken at two minute intervals and analyzed by the following tests: (1) COD, (2) pH, (3) titration curves, and (4) ammonia, nitrate and nitrite and some metals concentrations.

The results reported herein are for one run but demonstrate graphically the various responses recorded as a function of temperature. Figure 24 represents the hot spot temperatures as a function of time from the time the power was cut-off to the pyrolysis chamber calrod heaters until 12 minutes later. The thermocouple was located 18 inches down from the top of the unit. From previous unsteady state runs it was determined that the position of the hot spot temperatures in the pyrolysis chamber did not vary with time. At 12 minutes into the run, the thermocouple tip registered a temperature of 120° F indicating condensation of vapor. Figure 25 plots the corresponding outlet water temperature of the condenser versus time, and it clearly shows three regimes of fluid state within the unit. The portion of the curve from time zero to eight minutes indicates that all of the sewage is being vaporized. Evidence for this is found in the slope of the condenser water curve together with the high level of hot spot temperatures in the pyrolysis chamber. Then there is a short transition

FIGURE 24

HOT SPOT TEMPERATURE VARIATIONS WITH TIME FOR AN
UNSTEADY STATE RUN

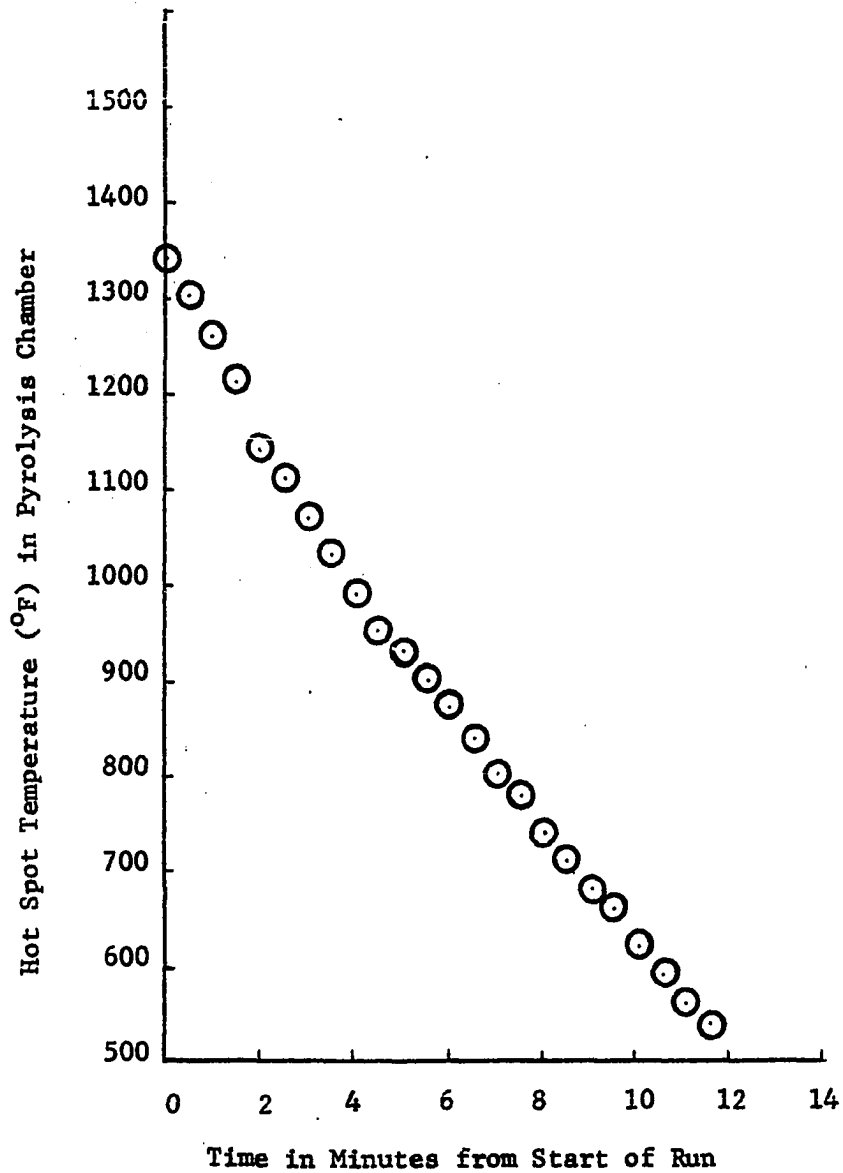
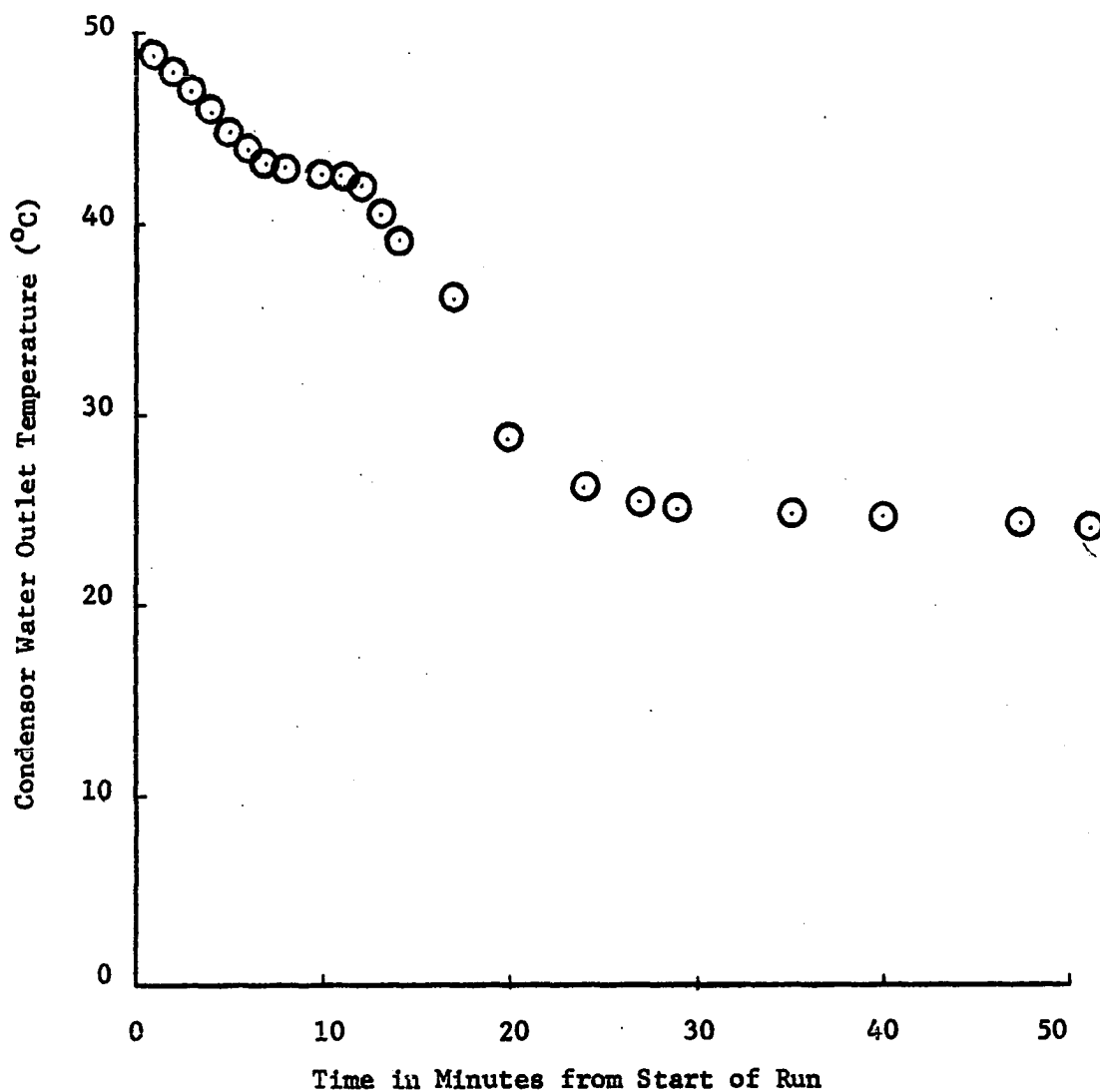


FIGURE 25

OUTLET CONDENSER WATER TEMPERATURE VARIATIONS
WITH TIME FOR AN UNSTEADY STATE RUN



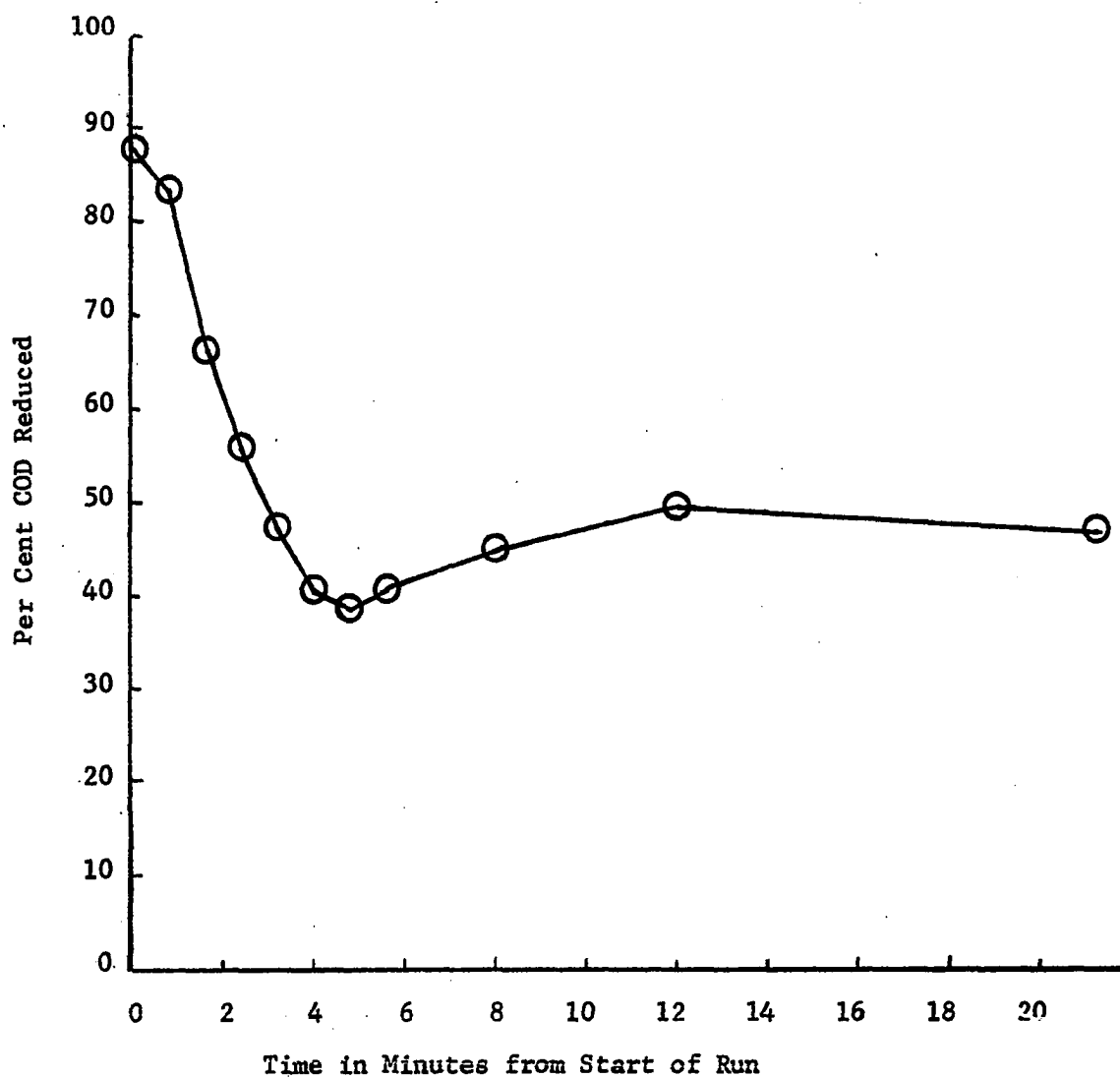
period where total vaporization terminates and a small amount of liquid is entrained in the vapor. Next from 12 to 20 minutes another straight line portion is seen and this represents a much larger portion of the liquid not being vaporized. Finally from 20 to 53 minutes the curve displays a slow rate of change of temperature with time, thus signifying that all of the spray entering the chamber remains in the liquid state. At 12 minutes into the run the temperature of the hot spot dropped drastically indicating that total vaporization had ceased. This assumption is verified from the condenser water temperature profile which coincidentally exhibits a temperature rate change.

Chemical oxygen demands tests were run on the influent, giving a concentration of 232 mg./l., and each of the effluents were obtained at two minute intervals up to 14 minutes and additional samples at 20, 30, and 53 minutes. The results are reported in Figure 26 in the form of per cent COD reduced versus time. The data demonstrates that COD reductions are highest at time zero and decline steadily to the 12 minute sample. From this point on COD reductions gradually increase with time up to the 30 minute sample. The last sample, at the 53 minute mark shows a small drop in COD reduction. The behavior of these results from time zero to 12 minutes is expected because on steady state experiments it has been proved that COD reductions are a function of temperature. The increase in per cent reduction at the lower temperatures may be explained by the degree of oxidation and its type of breakdown products available for oxygen demand measurements by the COD test.

These findings correlate well with the titration curves

FIGURE 26

COD REDUCTIONS AS A FUNCTION OF TIME FOR AN
UNSTEADY STATE RUN



measured for each sample and plotted in Figure 27. Samples 0 through 6 yielded a family of curves with the same inflection points at pH 8.0 and pH 4.5; however, the amount of titrant used in reaching these pH values increased with each sample. At the same time the effluent samples increased in COD. At sample #7 the titration curves begin to overlap and recede back toward the curve for sewage. Sample #7 was collected at the 14 minute time level in the run and corresponds to the time when total vaporization has ceased. This phase change is responsible for a different type of pyrolysis mechanism which is mirrored in the type of oxidation products obtained and the increase in COD reductions experienced at that time. The remainder of the samples follow the pattern in the titration curves and the COD reduction.

Table 10 lists the values for ammonia nitrogen and shows the constancy of this parameter for the run. The ammonia and other nitrogen bases account for the relatively high pH's in the pyrolyzed effluents. The nitrate-nitrite content ranged from 0.4 to 1.8 mg./l. with the peak value coming at sample #6. On either side of this sample concentrations were less.

All of the 11 effluent samples were colored a shade of greenish-yellow. In all other steady state runs the effluents had the identical coloring in the same pattern. The first sample was essentially colorless with a slight green tinge. Samples #1 through #6 gained in color intensity steadily then decreased until the last sample was the color of sewage except it also had a green cast of color to it. Even after filtration through a Millipore 0.45

FIGURE 27

TITRATION CURVES UNSTEADY STATE EFFLUENTS

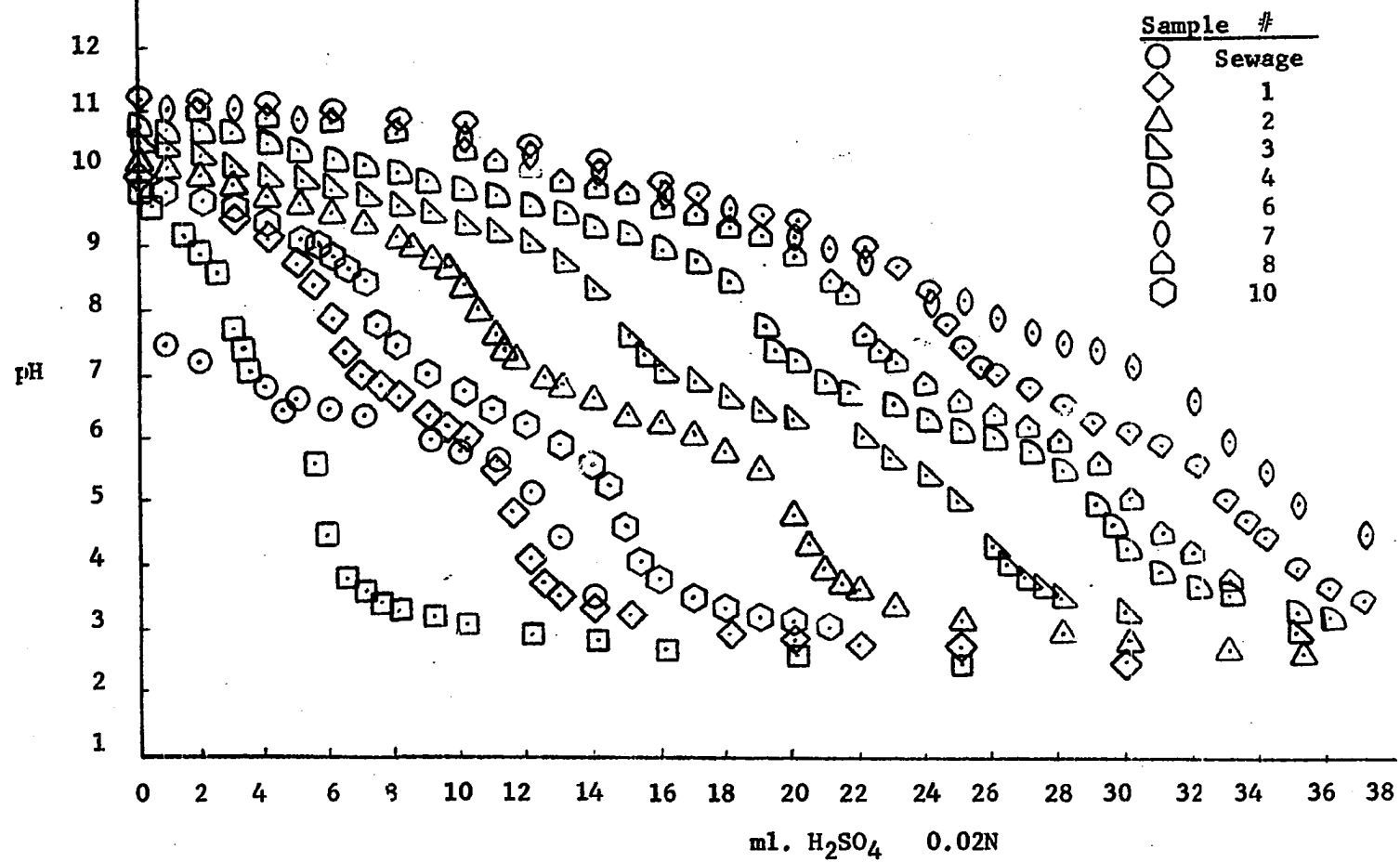


TABLE 10
UNSTEADY STATE RUN

Sample No.	0	1	2	3	4	5	6	7	8	9	10
Time of Sampling (Minutes)	0	2	4	6	8	10	12	14	20	30	53
Condenser Water Temperature ($^{\circ}$ C)	51.5	48	45.7	44	43	42.7	41	39.3	29	24.5	24.0
Hot Spot ($^{\circ}$ F)	1340	1140	990	870	740	620	360	---	---	---	---
Effluent COD	29.5	39.4	78.8	103	123	138	143	138	128	118	123
Per Cent COD Reduced	87.3	83	66	55.3	46.9	40.6	38.4	40.6	44.8	49.4	46.9
Ammonia Nitrogen (mg./l.)	22.6	23.7	24.1	22.6	23.1	23.7	23.7	22.3	22.3	22.3	18.7
Nitrate-Nitrite (mg./l.)	0.5	0.4	0.8	0.9	1.2	1.5	1.8	1.5	1.2	0.75	0.75
pH	9.8	9.9	10.2	10.5	10.8	--	11.2	11.2	11.2	10.55	9.85
Hexavalent Chromium	0.8	1.0	1.5	2.1	4.0	4.1	4.4	5.9	4.8	2.8	2.12

micron filter the color was retained. Qualitative tests for bile acids gave negative results as did tests for the metals iron and copper. When tested for chromates, the samples each contained an amount in direct proportion to their color intensity. Three of the samples, #0, #6, and #9, were scanned in the Beckman DB spectrophotometer from 740 to 320 millimicron wavelengths, and each responded with one peak at the 365 millimicron level. Each sample was then inserted into a spectrophotometer and the per cent transmittance measured at the 365 millimicron setting. Figure 28 is a semi-log plot of the log of per cent transmittance versus hexavalent chromium content in mg./l. These data prove that hexavalent chromium is responsible for the color in the effluent.

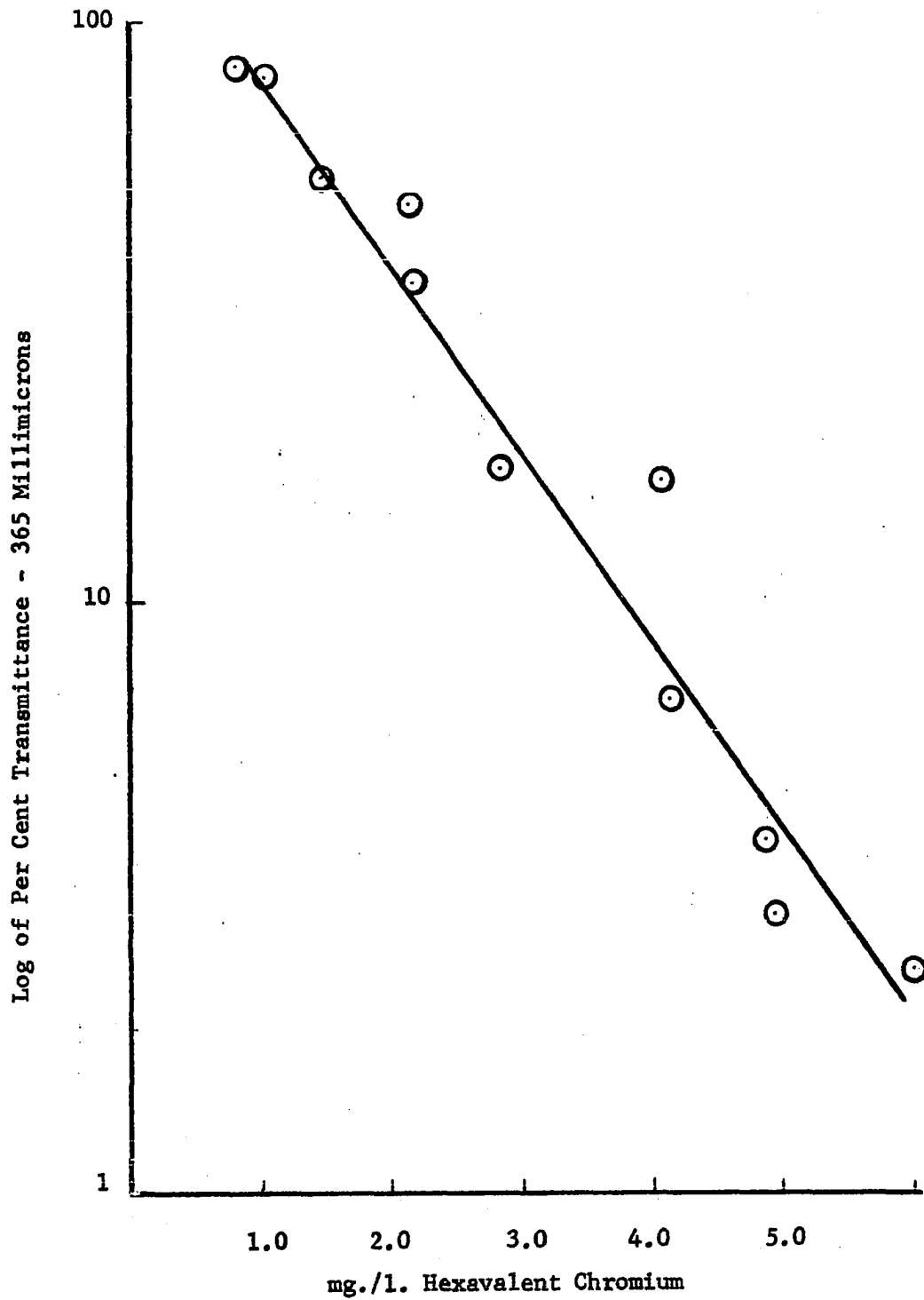
Synthetic Substrates

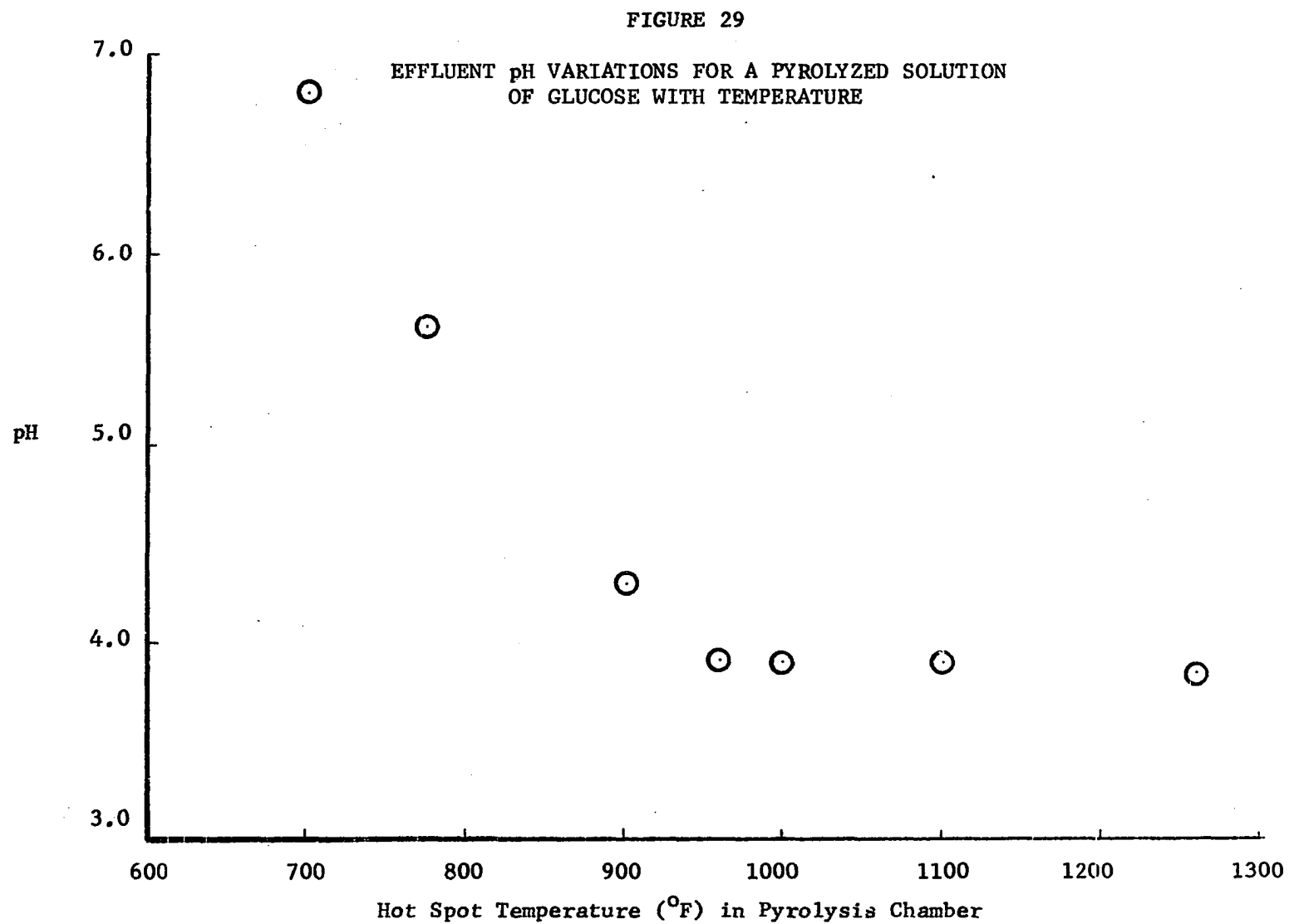
The carbohydrate compounds glucose and sucrose were chosen as suitable substrates for study because theoretically they could be completely oxidized to carbon dioxide and water. Any residual COD would be compounds containing only carbon, hydrogen, and oxygen. Glucose is the primary hydrolysis product of cellulose which represents toilet paper, fruit and vegetable fibers found in feces. Sucrose is a disaccharide intermediate between glucose and cellulose and should provide different pyrolysis products from aldehydes such as glucose.

Figure 29 is a graph of effluent pH as a function of hot spot temperature for the glucose run. The plot points out that as oxidation temperature rises the pH is reduced reflecting the production of

FIGURE 28

EFFLUENT COLOR RELATIONSHIP WITH HEXAVALENT CHROMIUM
CONTENT FOR AN UNSTEADY STATE RUN





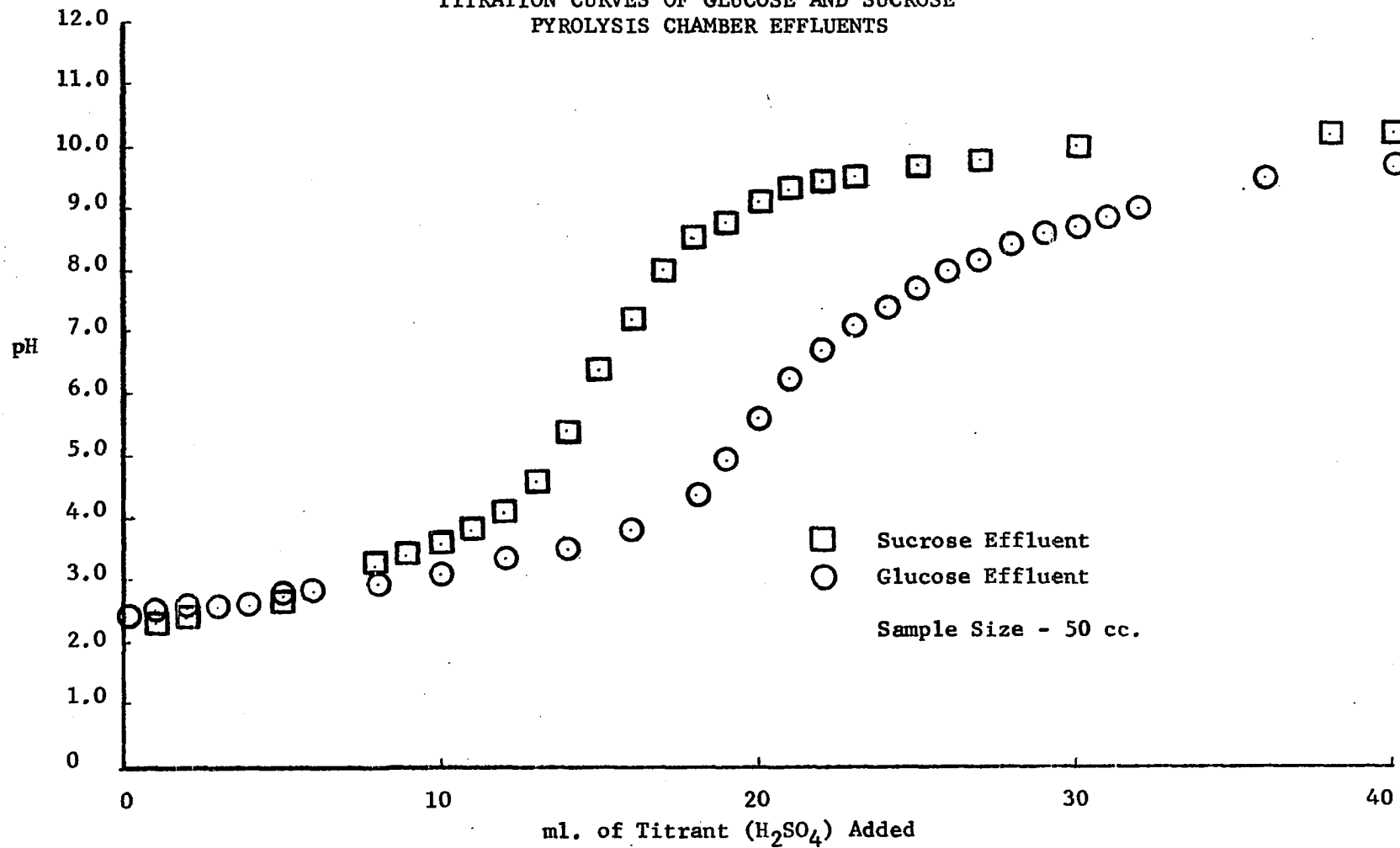
acids. Effluent COD at the hot spot temperature of 1270° F was 6,300 mg./l. representing a 60% reduction. A sucrose solution sprayed in the pyrolysis chamber was reduced in COD by 58% from its influent concentration of 10,250 mg./l. Titration curves of both effluents are presented in Figure 30. The effluent from the glucose run has an inflection point at pH 6.8 and sucrose at pH 7.1. The shape of the two titration curves indicates a difference in the acids present. The most likely acid to be found in the glucose effluent would be acetic acid; for sucrose the acids should be a mixture of acetic and formic because on hydrolysis it yields glucose and fructose.

In the case of glucose the influent had a molarity of 0.016. It is assumed that each mole of glucose will be pyrolyzed to one mole of acetic acid and four moles of carbon dioxide, the effluent COD should have been 6,760 mg./l. The experimentally measured value was 6,300 mg./l.

Since the effluents from glucose and sucrose runs more than likely contained acetic acid, a 12,800 mg./l. solution was processed through the pyrolysis chamber. The influent COD's were reduced by 85.7 and 93.6% at hot spot temperatures of 1360° F and 1440° F respectively. The pH of the influent was 3.30 and effluents measured 4.65 at the highest hot spot temperature and 4.70 at the lower hot spot temperature. The stability of the acetic acid molecule is well documented, but these runs give evidence that acetic acid as the initial feed source to the pyrolysis can be effectively oxidized to carbon dioxide and water.

FIGURE 30

TITRATION CURVES OF GLUCOSE AND SUCROSE
PYROLYSIS CHAMBER EFFLUENTS



The reductions obtained on all of these high COD, soluble substrates point out the advantage of using concentrated wastes in the pyrolysis chamber when considered in terms of COD removed per kilowatt-hour of power input. Table 11 compares the amount of COD removed per kilowatt of power supplied to the pyrolysis chamber calorod heaters for the synthetic substrates glucose, sucrose, and acetic acid as well as two sewage runs.

TABLE 11

COD REMOVED PER KILOWATT OF POWER SUPPLIED FOR VARIOUS
PYROLYSIS CHAMBER FEED SOURCES

Feed Type	Influent COD (mg./l.)	Effluent COD (mg./l.)	Flow Rate (ml./min.)	mg. COD Removed/kw-hr.*
Acetic Acid	21,800	1,835	81	8,860**
Glucose	15,720	6,300	83	7,816
Sucrose	10,250	4,300	83	4,933
Sewage	400	40	52.3	188
Sewage	100	10	52.3	47

*Based on one hour of operation

**Activated sludge plants remove 90,800 mg. COD/kw-hr.

Pyrolysis of Sewage in the Absence of Air

A series of runs was made in the pyrolysis chamber to determine the effect that air has on the effluent quality. Each run was made on the same feed source, and the only operating change made was either the addition of or removal of air from the system.

Table 12 summarizes the data. It shows that the pH of the effluent is less for the sewage processed without air than with air.

The color of the effluent for each run with air was a greenish-yellow while its companion run was always much lighter and essentially devoid of color except for a light green cast. The difference in color is probably caused by the presence of chromium in different oxidation states.

The sediment from each run was also different. Those solids pyrolyzed in the presence of air were brown while the solids from the experiments without air were all black. The COD concentrations of the effluent were very nearly identical. This is remarkable because the hot spot temperatures for the runs ranged from 580° to 1500° F.

TABLE 12

COMPARISON OF SEWAGE EFFLUENTS PYROLYZED IN THE
PRESENCE AND ABSENCE OF AIR

Run No.	COD mg./l.	With <u>air</u> COD _{out}	Without <u>air</u> COD _{out}	With <u>air</u> Hot Spot(°F)	Without <u>air</u> Hot Spot(°F)	With <u>air</u> pH	Without <u>air</u> pH
1	190	32.6	23.8	1420	1420	9.3	9.2
2	210	32.5	37.5	1500	1470	9.6	9.1
3	170	25	27.5	1500	1500	9.7	9.4
4	255	102.5	92.5	620	630	9.3	8.9
5	191	133	133	620	580	9.3	9.1

CHAPTER VI

CONCLUSIONS

- (1) The temperature of the Hot Spot or highest temperature achieved in the pyrolysis chamber is a function of flow rate (50 to 150 cc./min.) at constant heat input and yields the following regression equation:

$$\text{Temperature of the hot spot (}^{\circ}\text{F)} = 2135.173 - (11.167) (\text{Flow Rate, cc./min.})$$

with a correlation coefficient of 0.976.

- (2) COD reductions on sewage are a function of hot spot for the temperature range from 500° F to 1560° F and are independent of influent COD concentration. Regression analysis of the data produced this equation:

$$\text{Per Cent COD Reduced} = 26.351 + (0.041) (\text{Temperature of Hot Spot, }^{\circ}\text{F})$$

with a correlation coefficient of 0.885 from the pyrolysis chamber.

- (3) Effluent BOD from the pyrolysis chamber for the sewage used was found to be related to effluent COD by the

regression equation:

$$\text{Effluent BOD}_5 \text{ (mg./l.)} = 3.876 + (0.265)(\text{Effluent COD, mg./l.})$$

with a correlation coefficient of 0.685.

- (4) The amount of total Kjeldahl Nitrogen remaining in the effluent from the pyrolysis chamber decreases with increasing Hot Spot temperature.
- (5) Total volatile solids reductions for sewage after passage through the pyrolysis chamber are a function of Hot Spot increasing with increasing temperature.
- (6) Sewage can be pyrolyzed in the absence of air to essentially produce the same COD reductions as in the presence of air.
- (7) The pyrolysis process can provide any degree of waste treatment as a function of Hot Spot temperature.

Design Implications for the Pyrolysis Chamber

Several design implications for the pyrolysis chamber arise from the conclusions of this study. They are as follows: (1) Since COD (or BOD) reductions are a function of temperature and are independent of influent concentrations, variations in loading rates will not affect system performance. This is a significant finding because of the inevitable variations in usage cycles found aboard ships. (2) The more concentrated the waste the more economical the operating costs are for pyrolysis. Concentration of sanitary wastes within the ship can be accomplished by careful monitoring of flush water,

particularly in urinals. (3) Since retention time is not a direct factor in system performance, the equipment can be miniaturized as long as sufficient power input is provided to reach the desired hot spot temperature. (4) It is economically very consequential that COD reductions obtained in the pyrolysis chamber operated without air input is identical to wastes pyrolyzed in the presence of air. This obviates the need for an air compressor or blowers and the associated maintenance.

Further Application of Pyrolysis

The pyrolysis chamber was designed and tested for use as a sanitary waste treatment system aboard ship. Other applications are apparent. Pyrolysis can serve the dual purposes of waste treatment and recovery in the case of materials toxic to organisms in a bio-oxidation system. An example would be the treatment of photographic wastes, where complex organics can be oxidized to carbon dioxide, water, and residual low molecular weight chemicals. The silver can be recovered after pyrolysis in purified form by any number of solids separation devices. The recovered material helps to defray operating expenses while preventing possible contamination of a receiving stream.

In general, any waste of high strength containing toxic and/or recoverable materials is a candidate for pyrolysis processing. Injection of various gaseous reactants into the chamber can bring about any desired chemical conversions.

LIST OF REFERENCES

- Barclay, H. G., S. Frahoes, and J. J. O. Cravel. 1964. The AST Recovery Process, The Pyrolysis of Concentrated NSSC Liquids. In: The Fiftieth Annual Meeting of the Technical Section Canadian Pulp and Paper Association.
- Bateman, L. 1954. Olefin Oxidation. Quarterly Reviews (London) 8: 147-167.
- Blankenship, B. E. 1966. National Conference on Watercraft Waste Disposal. Ann Arbor, Michigan. 104p.
- Breeze, R. K. 1960. Aeronautical Systems Division Technical Report 61-161: 48-49. From: Water Recovery Systems (Wallman and Barnett), WADD TR 60-243.
- Consiglio, J. A. and C. M. Sliepcevich. 1957. Effect of Liquid Physical Properties and Flow Rates on the Surface Area of Sprays from a Pressure Atomizer. American Institute of Chemical Engineering Journal 3: 418-427.
- Frankel, D. P. 1966. National Conference on Watercraft Waste Disposal. Ann Arbor, Michigan. 104 p.
- Frazer, R. P., E. P. Eisenklam, and N. Dombrowski. 1957. Liquid Atomization in Chemical Engineering: Part 3, Pressure Nozzles. British Chemical Engineering 2: 496-501.
- Harding, J. C., and G. E. Griffin. 1965. Sludge Disposal by Wet Air Oxidation at a Five MGD Plant. Journal Water Pollution Control Federation 37: 1134-1141.
- Helfgott, T. and P. Weber. 1965. Atomized Suspension Technique Incinerates Sewage Sludges. Water Works and Waste Engineering 9: 76-79.
- Hoffman, T. W., and W. M. Gauvin. 1962. An Analysis of Spray Evaporation in a High Temperature Environment, II Calculation of the Evaporative Load Distribution. The Canadian Journal of Chemical Engineering 2: 110-117.

- Hurwitz, E., and W. A. Dundas. 1960. Wet Oxidation of Sewage Sludge. Journal Water Pollution Control Federation 32: 919-929.
- Hurwitz, E., G. H. Teletzke, and W. B. Gitchel. 1965. Wet Air Oxidation of Sewage Sludge. Water and Sewage Works 112: 298-305.
- Ingold, K. U. 1961. Inhibition of the Autoxidation of Organic Substances in the Liquid Phase. Chemical Reviews 61: 563-589.
- Ingram, W. T. and A. Diachishin. 1954. Effect of Cabin Cruiser Waste Discharge on a Small Harbor. Journal of the Sanitary Engineering Division, ASCE 80: No. 455.
- Ingram, W. T. 1956. An Investigation of the Treatment of Cabin Cruiser Wastes. Sewage and Industrial Wastes 28: 93-99.
- Jakobson, K., and M. J. Posner. 1965. Survey to Determine Quantities and Properties of Sewage from Naval Vessels. U. S. Navy Marine Engineering Laboratory Research and Development Report 356/64.
- Jakobson, K. 1966. Evaluation of a Shipboard Sewage Treatment System. U. S. Navy Marine Engineering Laboratory Evaluation Report 104/66.
- Johnson, L. B. 1965. Executive Order 11258. The White House. Washington, D. C.
- Johnson, L. B. 1966. Executive Order 11288. The White House. Washington, D. C.
- Koenig, L. 1963. Ultimate Disposal of Advanced-Treatment Waste; Part 1 Wet Oxidation. Department of Health, Education and Welfare. Public Health Service, Division of Water Supply and Pollution Control. Public Health Service Publication No. 999-WP-3: 1-34.
- Martin, L. G., and R. T. Dewling. 1966. The 2nd Evaluation of Coast Guard Sewage Systems Aboard the U. S. Coast Guard Cutter SASSAFRAS (WLB- 401). Federal Water Pollution Control Administration. Metuchen, New Jersey.
- McKinley, J. B. 1965. Wet Air Oxidation Process. Water Works and Waste Engineering 2: 97-99.
- Raleigh. 1879. Theory of Sound. In: Proceedings of the London Math Society 10: 4.

- Ranz, W. E. and W. R. Marshall, Jr. 1952. Evaporation from Drops, Parts 1 and 2. Chemical Engineering Progress 48: 141-146, 173-180.
- Reid, G. W. 1966. Compact Complete Disposal Unit for Individual Use. Personal communication from G. W. Reid to Milton Spiegle, FMC.
- Sachs, B. R. 1969. Extended Aeration Sewage Treatment Plants on U. S. Corps of Engineer Dredges. Department of the Interior, Federal Water Pollution Control Administration. Cincinnati, Ohio.
- Sawyer, C. N. and P. A. Kahn. 1960. Temperature Requirement for Odor Destruction in Sludge Incineration. Journal of Water Pollution Control Federation 32: 1274-1278.
- Schaller, C., and K. Jakobson. 1967. Evaluation of a Proprietary Sewage Treatment System Designed for Shipboard Use. Marine Engineering Laboratory Test and Evaluation Report 246/67.
- Secretary of Navy Instruction 6240.6 of June 4, 1966.
- Spalding, D. B. 1953. The Combustion of Liquid Fuels. In: Fourth Symposium (International) on Combustion: 847-864.
- Teletzke, G. H. 1964. Wet Air Oxidation. Chemical Engineering Progress 60: 33-38.
- Teletzke, G. H. 1965. Low Pressure Wet Air Oxidation of Sewage Sludges. In: Proceedings of the Twentieth Industrial Waste Conference. Engineering Bulletin of Purdue University. Engineering Extension Series 118: 40-48.
- Teletzke, G. H., W. B. Gitchel, D. G. Diddams, and C. A. Hoffman. 1967. Components of Sludge and Its Wet Air Oxidation Products. Journal Water Pollution Control Federation 39: 994-1005.
- Twenty-third Progress Report of the Committee on Sanitary Engineering Research of the Sanitary Engineering Division. 1959. Journal of the Sanitary Engineering Division, ASCE 85: 13-23.
- Twigg, G. H. 1962. Liquid-Phase Oxidation by Molecular Oxygen. Chemistry and Industry 1: 4.
- United States Congress. 1967. Wastes from Watercraft. Senate Document 48, Ninetieth Congress, 1st Session.

United States Department of the Interior. 1968. Evaluation of Macerators-Chlorinators on U. S. Coast Guard Vessels. Federal Water Pollution Control Administration Northeast Region, North Atlantic Water Quality Management Center. Edison, New Jersey.

Waters, W. A. 1948. The Chemistry of Free Radicals. 2nd ed. Oxford University Press, London. 226p.

Zimmerman, F. J. 1958. New Waste Disposal Process. Chemical Engineering 65: 117-120.

Zimmerman, F. J. 1961. Wet Air Combustion. Industrial Water and Wastes 6: 102-106.