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ANALYSIS OF DECOMPOSITION GASES AND LEACH WATER

FROM A CONTROLLED SANITARY LANDFILL

BY

ROBERT GARGANO

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

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NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey
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ABSTRACT

A sanitary landfill was simulated by placing "refuse" between two layers of soil in 6" by 24" cylinders. Canine nutriment was used to simulate the refuse. Once the refuse began to decompose, the decomposition gases were collected in a gas cell and analyzed in an Infrared Spectrophotometer. When gas samples were not taken, the decomposition gases were vented through a water trap (to prevent air from backing up into the system) into the atmosphere. Distilled water was added and withdrawn at two week intervals to leach out the pollutants.

From the Infrared analysis, the decomposition gases were determined to be carbon dioxide, methane and nitrous oxide. In general, carbon dioxide was continuously observed and after a time lag, methane was also formed continuously. The nitrous oxide was only observed at the beginning of the experiment, when the experimental system was not completely saturated with water.

The leach water was periodically analyzed for COD, (Chemical Oxygen Demand); pH; phenolphthalein acidity; and total residue. In addition, the soil pH was also determined. From the COD values, it was observed that there is an initial time lag before there is any decrease in COD. However, once the waste starts the stabilization process, the decomposition proceeds as if it were a pseudo-2/3 order chemical reaction.

The curve of pH versus time of both the leach water and the soil had the same shape curve but the pH of the soil was always found to be higher. This difference was due to the method of determining the pH of the soil. The pH curves were found to have a sinusoidal wave shape with the initial slope negative.

APPROVAL OF THESIS
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BY
ROBERT GARGANO
FOR
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PURPOSE OF INVESTIGATION

This study was undertaken to determine how the temperature of the synthesized refuse affect the efficiency of a sanitary landfill. The effects of temperature were investigated in a controlled landfill operation simulated in the laboratory.

In addition, distilled water was periodically added and withdrawn to determine the extent of the leachable pollutants.

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INTRODUCTION

The disposal of solid wastes is one of the most urgent environmental problems today. The per capita production of domestic refuse in the United States has grown from 2.75 pounds per day in 1920 to 5.3 in 1969, and it is growing at a rate of over 4 per cent per annum (9).

The most prevalent method of disposing of solid waste is by landfill. There are two types of landfill, one being sanitary which is the burial of refuse, and the other type, which is the burial of inert materials such as concrete and bricks. These two methods combined account for 40 per cent of the total solid waste disposal.

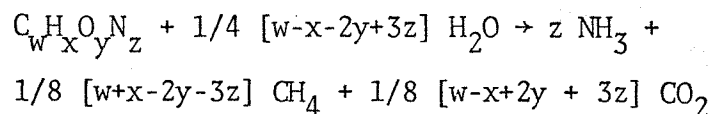
The sanitary landfill process can be described as engineered burial of refuse. After the refuse is collected and transported to a landfill location, the refuse is dumped from trucks into trenches. Each trench is approximately 20 feet wide and 6 to 10 feet deep. The refuse is then compacted by a bulldozer and covered with four to six feet of dirt (9).

In the past, after the refuse has been buried it has been forgotten. The old adage "Out of sight; out of mind" is applied. However, the ecological effects of the refuse on the soil, ground water and nearby surface waters is devastating. There is nothing sanitary about a sanitary landfill. It is at best a badly engineered refuse disposal method and at its worst

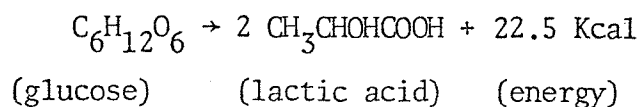
a highly efficient pollution factory manufacturing toxic gases, foul odors, high BOD loads (biological oxygen demands) and pathogenic organisms which thrive in oxygen deficient environments.

The sanitary landfill is the only form of waste disposal which contributes to all three phases of pollution: air, water and soil.

Once the refuse is buried it changes the ecological balance of the soil in three processes. These processes are: 1) the biological and chemical reactions of the refuse; 2) the diffusion of the gaseous products and 3) the leaching of pollutants from the landfill either by rainfall or ground water or both. Due to the deficiency of oxygen in the landfill the biological reactions will be of the anaerobic type. The overall reaction process can be stated as follows (3):

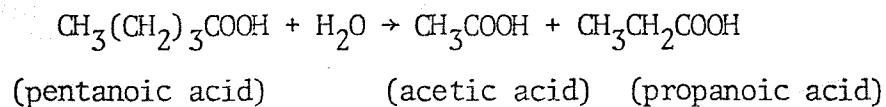
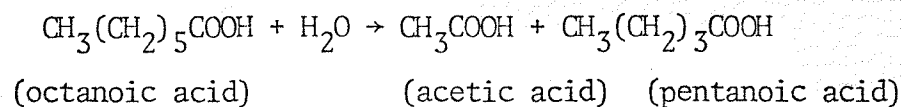


The above reaction is overly simplistic and does not show the complex and varied intermediate steps. In the first or acidifying step, bacteria metabolize the fats, proteins and carbohydrates to fatty acids. For example:



When the bacteria encounter longer chain fats, proteins and carbohydrates they cleave the chain forming either acetic or

propanoic acid and a shorter chain of either fats, proteins and carbohydrates (13). For example:



The acid forming bacteria groups responsible for this action are the anaerobic and facultative. The facultative bacteria can live in either aerobic or anaerobic environments. The acid forming bacteria bring about these initial conversions to obtain the small amounts of energy released for growth and a small portion of the organic waste is converted to cells. Although no waste stabilization (the degradation of organic compounds until almost no organisms can derive energy from further changing of the chemical structure of the compounds) occurs during the first stage of treatment, it is required to place the organic matter in a form suitable for the second stage of treatment (14).

It is in the second stage of anaerobic decomposition (or the methane formation step) that real waste stabilization occurs. During this step the organic acids are converted by the special methane forming bacteria into the gaseous end products of methane and carbon dioxide. The methane bacteria are strictly anaerobic and even small quantities of oxygen are harmful to them. The methane bacteria, besides requiring a hydrogen donor

(usually an organic compound), also needs carbon dioxide as a hydrogen acceptor. They also require a temperature in the range of 20° to 35°C (68°F to 95°F) and a pH between 5 and 9, and finally they are slow growers which limits the rate at which they can stabilize waste (12).

There are several groups of methane forming bacteria and each group is characterized by the limited number of organic compounds it can ferment (2). So far a total of eight species of methane bacteria can be distinguished by biochemical characteristics and have been described in three major genera:

A. Methanabacterium- rod shaped cells

1. Mb. formicicum- utilizes formate, carbon monoxide and hydrogen
2. Mb. omelianskii- utilizes primary and secondary alcohols and hydrogen
3. Mb. propionicum- utilizes only propionate
4. Mb. sohngeniei- utilizes acetate, butyrate

B. Methanococcus- spherical cells, not in sarcina arrangement

1. Mc. mzaei- utilizes acetate and butyrate
2. Mc. vannieli- utilizes formate and hydrogen

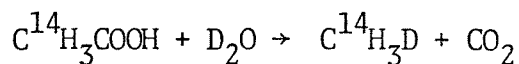
C. Methanosarcina- spherical cells in sarcina arrangement

1. Ms. methanica- utilizes acetate and butyrate
2. Ms. barkerii- utilizes methanol

Due to the extreme development of substrate specializations, the complete fermentation of so simple a compound as pentanoic

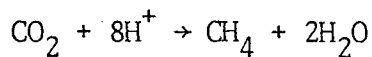
acid is an extremely complex process. First, the acidifying bacteria must oxidize it to acetic and propanoic acids which are not further attacked by this organism. A second species, *Mb. propionicum* converts the propionate (propanoic acid) to acetate, carbon dioxide and methane. However, *Mb. propionicum* cannot attack methane. Therefore, a third species such as *methanosarcina methanica* is required to ferment the acetate (2).

The methane producing bacteria have proven to be very difficult to isolate and study. Thus, relatively little is known of their basic biochemistry. The conversion of organic matter into methane, no doubt, proceeds through a long and complex series of biochemical reactions. The use of radioactive carbon (carbon 14) and hydrogen (deuterium) have indicated overall reactions. One source of methane is the direct cleavage of acetic acid:



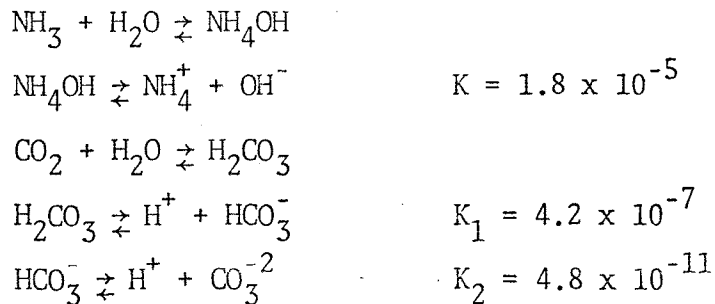
This demonstrates that the methyl group is transferred from the acetate into methane as a unit and that carbon dioxide is not needed as a hydrogen acceptor in this case.

Most of the remaining methane is formed from the reduction of carbon dioxide:

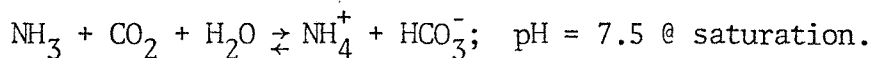


Here, carbon dioxide is the hydrogen acceptor. Since under anaerobic conditions there is always an excess of carbon dioxide, its availability is not a limiting factor. The hydrogen is obtained from the organic compounds and is removed by enzymes (2).

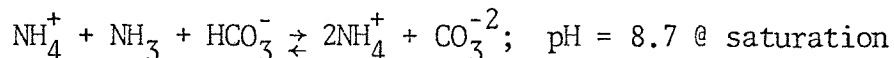
When the refuse contains proteins, ammonia gas is formed. However, detection of this product is difficult. There are two main reasons for this. Firstly, in the presence of water, both carbon dioxide and ammonia dissolve to form carbonic acid and ammonium hydroxide, respectively:



Initially there is a great excess of carbonic acid and thus the reaction:



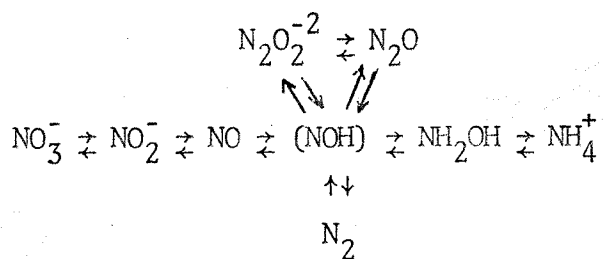
However, since ammonia is more soluble in water than carbon dioxide (one million times more than CO_2) and the ammonium hydroxide has a larger dissociation constant (10^{-5} as compared to 10^{-7} for H_2CO_3), the ammonium hydroxide reacts further:



Any further addition of ammonia will drive the pH of the water higher than 8.7. In addition, as the pH goes above 10.5 the carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and carbon dioxide equilibria will form carbonate (CO_3^{2-}) (7). Therefore, the soil should have a final pH of 8.7 whereas the leach water can have a pH of 8.7 or above since excess ammonia can be dissolved in the water driving the pH above 8.7.

The second reason for ammonia not being detected in the gas analysis is the consumption of the ammonia by bacteria. When the soil is not completely saturated with water, the bacteria have a chance to utilize the free ammonia before it can react with the carbon dioxide as previously shown.

The pathway for nitrogen assimilation and denitrification are similar:



In denitrification and assimilation several intermediates are formed; NO, N₂ and N₂O, between ammonia and nitrate nitrogen (living matter). Therefore, in a gas analysis, one would probably find either nitrogen, nitrous oxide or nitric oxide depending on the soil condition (8).

There are two methods which the soil can rid itself of the products of the preceding reactions. One is the leaching of the products by rain water or fluctuations in the ground water tables. The other is the diffusion of the gaseous products out of the soil. Gases diffuse out of the soil by two distinct processes; molecular and fluid movement due to a pressure gradient. Molecular diffusion of gases is described by Fick's first law of diffusion:

$$N_A = D_{AB} \nabla C_A \quad (1)$$

$$\begin{aligned}
 N_A &= \text{molar flux rate of A per unit area of media} \\
 D_{AB} &= \text{molecular diffusivity} \\
 C_A &= \text{concentration of A} \\
 \nabla &= \text{"del" operator which in three dimensions is:} \\
 \nabla &= \vec{i} \partial/\partial x + \vec{j} \partial/\partial y + \vec{k} \partial/\partial z
 \end{aligned}$$

The diffusivity of a gas in a porous medium (soil and refuse) is dependent on the porosity of the medium. That is, the more compacted the medium the less porosity. Hence, the free space available for molecular diffusion is smaller (7).

Since both the soil and fill are highly porous, the differential created between the gases and the atmosphere is small. The gas flow is in the laminar range. Pressure diffusion, when the fluid is flowing in the laminar range, is described by Darcy's Law. Darcy's Law states that for a given media and fluid, the flow rate is proportional to the pressure drop, or mathematically (7):

$$V = -k \nabla p \quad (2)$$

Where:

V = flow per unit area

k = Darcy's coefficient of permeability

p = pressure at a time or position

∇ = "del" operator

The combined effects of molecular and pressure diffusion are two-fold: 1) the foul odor of the decomposition gases and 2) the fire hazard due to large amounts of methane gas

escaping to the atmosphere. The gases can also create a minor air pollution problem.

The pollutants leaching from a landfill result from the transfer of water soluble nonvolatile substances from the refuse to the ground water. This is accomplished by the vertical and/or horizontal movement of water through the refuse and the intimate contact extracting the soluble matter.

When water (rain) is applied to the surface of a refuse fill a major portion seeps into the ground. The water movement in the soil (porous media) occurs under the action of gravity, pressure differences, surface tension and other forces associated with the tendency for moisture to adhere to the solid surfaces.

In the saturated portions of the medium the moisture content per unit volume is constant. Therefore, there are no net forces of the surface type. Under these conditions Darcy's Law is also applicable as it was with gas diffusion.

$$v = -kV[(p/w) +h] \quad (3)$$

Where:

v = flow per unit area

p/w = pressure head

p = potential head

k = coefficient of permeability

If the area under investigation is not saturated, there is a transfer of moisture from the moist areas to the drier areas.

In this case a modification of Darcy's Law can be applied:

$$v = -k(u) \nabla(s+h) \quad (4)$$

Where:

u = local moisture content per bulk volume of media

s = suction or capillary potential

If the progress of moisture movement in a medium of known and uniform properties is needed, it can be obtained by combining the equation of continuity (5) and the modified Darcy's Law (4):

$$\frac{du}{dt} = \nabla \cdot v \quad (5)$$

When combined, they give:

$$\frac{du}{dt} = \nabla \cdot [k\nabla(s+h)] \quad (6)$$

$$= \nabla \cdot (k\nabla s) + \frac{\partial k}{\partial z} \quad (6a)$$

Where:

z = vertical direction

If the diffusivity, D , is defined as:

$$D(u) = k \frac{ds}{du},$$

and is substituted into (6):

$$\frac{du}{dt} = v \cdot (D\nabla u) + \frac{\partial k}{\partial z} \quad (7)$$

Equation (7) gives the time rate of change of moisture content at any point as a function of the moisture content and its space derivatives. It can only be solved analytically for specific simple problems. In more general problems the equation can only be solved by numerical methods (20). From the analytical solution

of the above equation the following relationships can be obtained:

- a) moisture infiltrating into a dry medium tends to move as a fairly well defined front- the drier the medium, the sharper the front;
- b) in horizontal and vertical movement through media so fine-grained that gravity is small compared to capillary forces, the distance of an infiltration front from the origin increases as the square root of time;
- c) in vertical downward infiltration, the advancing front approaches a constant velocity and constant moisture profile;
- d) a slug of moisture having penetrated into the medium by infiltration from a saturated surface diffuses outward into the surrounding drier regions and also moves downward under gravity.

As the polluted water travels through the soil, it is purified by natural filtration. That is, the soil acts as if it were an unstratified slow sand filter. Since the water moves at a low velocity, flow can be described by Darcy's Law:

$$v = ks$$

Where:

v = velocity

k = Darcy's coefficient of permeability

s = h/l which is head loss, h, in a depth of bed, l

In this case major components of k are the density and viscosity of the water, the porosity of the bed (soil) and the size and shape of the sand (soil) grains.

For an unstratified bed:

$$s = \frac{k'}{g} v v \frac{(1-f)^2}{f^3} R^2 \quad (9)$$

Where:

k' = residue dimensionless coefficient ~ 5

g = gravity constant

v = kinematic viscosity = $\frac{\mu}{\rho}$

μ = viscosity

ρ = density

v = approach velocity

$\frac{(1-f)^2}{f^3}$ = porosity factor

$R = \frac{A}{V}$ = area of bed to volume of bed ratio

In an unstratified bed of homogeneously packed sand (soil), each component fraction of p_i of size d_i contributes its share to the total area; the individual area-volume ratio being $\frac{6}{d_i} \psi$.

For uniform porosity we have:

$$R = \frac{6}{\psi} \sum \left[\frac{p_i}{d_i} \right] \quad (10)$$

Where:

ψ = sphericity

Thus equation (9) becomes:

$$s = \frac{k}{g} v \frac{(1-f)^2}{f^3} \left(\frac{6}{\psi} \sum \left[\frac{P_i}{d_i} \right]^2 \right) \quad (11)$$

As a rate process, filtration shares the common elements of purification kinetics. The basic purification equation is:

$$\frac{dy}{dt} = k(y_0 - y) \quad (12)$$

Where:

k = reaction rate constant

y = concentration of substrate to be removed

y_0 = initial concentration of y

t = time

Equation (12) has been expanded to include important factors in filter behaviour. Among them is the identification of filtration kinetics as the kinetics of a transient operation responsible for progressive changes in the rate constant k during the course of the filter run.

$$k = k_0 + c\sigma - \phi\sigma^2 / (f_0 - \sigma) \quad (13)$$

Where:

k_0 = initial rate constant

c and ϕ describes a specific exposure

f_0 = porosity of the clean bed

σ = volume of deposited matter per unit filter volume or specific deposit

The solution to equations 12 and 13 will yield equations describing the distribution of suspended matter in the water and the specific deposit (7).

The effect of the pollutants leaching out from the landfill can be devastating to the eventual use of water as a potable supply. In Kansas City, Missouri, where a landfill was located on a bank of the Missouri River upstream from the intake of the potable water treatment plant, periodic complaints of the water quality were received at the treatment plant. The intensity of the complaints varied, climaxing in over 200 complaints on July 28, 1969. The general description given by the consumer was that of a "medicinal" or "iodine" taste and odor in the tap water. The complaints seemed to be random and it was at first thought that the proper chlorine ratio was not maintained. However, upon closer inspection of the date it was determined that complaints always were after a rainfall and on July 27, a day before the most complaints were given, over two inches of rain fell in the area. Subsequent studies identified the contaminants as leach products from the sanitary landfill located above the water treatment plant. These pollutants were leached by the rain water and carried into the stream (11). Thus, the adverse effect of water quality in the area was a direct result from the leaching of pollutants from a "sanitary" landfill.

EXPERIMENTAL APPARATUS AND PROCEDURE

Four plastic cylinders (6"ID x 24") were placed in three insulated constant temperature baths, one at 86°F, one at 74°F and the other bath contained two cylinders at 59°F. Since the 59°F constant temperature bath used tap water for cooling as the summer approached the tap water warmed to 73°F. The 74°F temperature bath also warmed up during the summer months, but only to 86°F. The 86°F temperature bath rose to only 90°F during extended heat waves in July and August.

Each cylinder was sealed with plastic covers which contained two holes, one for the exhaust gases exit and leach water entrance, and the other for the thermocouple wire heads. The hole with the thermocouple wire was sealed after the wire was in place. The bottom of each cylinder had a valve which allowed the leach water to be extracted. In each cylinder a hole was drilled at six inches from the bottom, which was used to remove soil samples during the decomposition of the refuse.

In each cylinder three inch layers of Berl Saddles were placed over the drain valve to prevent it from clogging with soil. Over the Berl Saddles a six inch layer of soil was packed. The soil was obtained from a compost pile. The soil was loam type with a pH of 6.8. Two inches of refuse was placed over the soil layer, then another six inch soil layer. Canine

nutriment (A&P Medallion Horsemeat and Meat By-Products Chunks) was used to simulate the refuse. Its approximate composition was obtained from the contents found on the label and is listed in Table 1. Finally 900 ml of distilled water (equivalent to two inches of rain) was added to saturate each cylinder.

In each cylinder four thermocouples were placed at four different levels in order to measure the temperatures at their positions. Thermocouples were placed in the middle of the refuse layer and both soil layers (6", 10.5", 15" from the bottom of the cylinders) and at the top of the cylinder just below the exhaust valve. A thermocouple was also placed in each constant temperature bath and another was used to record the room temperature.

The decomposition gases were bubbled through a water trap to prevent any outside air from backing into the system.

The experimental apparatus is shown in Figure 1.

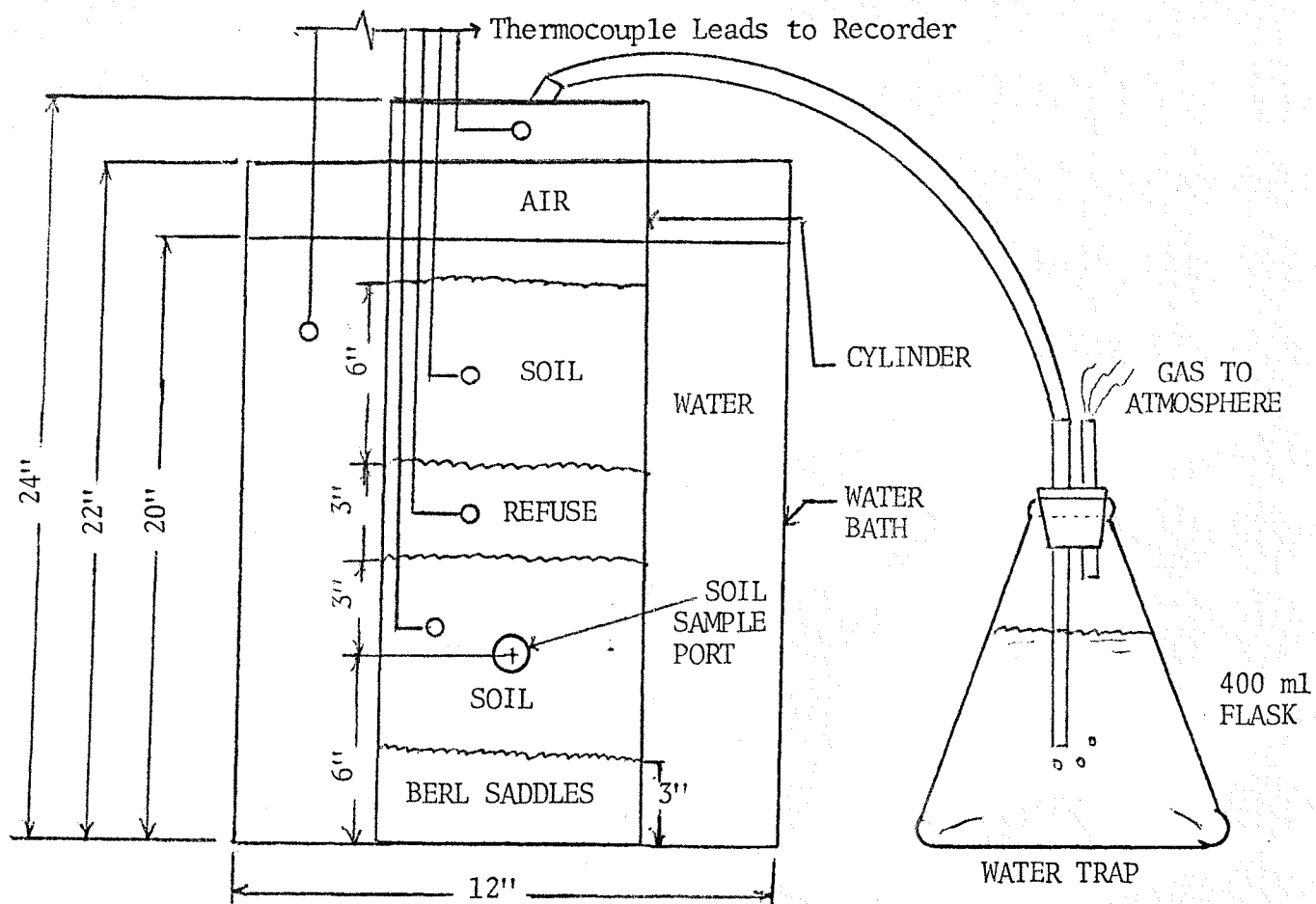
For analysis, the decomposition gases were collected in a ten centimeter gas cell with sodium chloride windows. In collecting the gases, the cell was first evacuated to 22.3 inches of mercury of vacuum. Then the tubing was removed from the water trap and placed on the gas cell. The stopcock on the cell was then opened thus pulling out the gases from the cylinder. The gas samples were then analyzed using a Beckman

TABLE 1APPROXIMATE REFUSE (CANINE NUTRIMENT) COMPOSITION

<u>COMPONENT</u>	<u>COMPOSITION (PER CENT BY WEIGHT)</u>
Crude protein	13.0
Crude fat	6.0
Crude fiber	1.5
Ash	3.0
Moisture	78.0

FIGURE 1

OVERALL SCHEMATIC OF EXPERIMENTAL APPARATUS



IR-8 Spectrophotometer.

After seven days the saturation water was withdrawn. Then another 900 ml of distilled water was added to be withdrawn after two weeks with a reapplication of 900 ml of distilled water. This procedure was repeated for 133 days after which the testing was stopped due to time restrictions.

The leach water was analyzed for pH, total residue, COD (Chemical Oxygen Demand) and total phenolphthalein acidity as defined by "Standard Methods". A detailed procedure for each test is given in the appendix along with the total phenolphthalein acidity and total residue data. At the same time the leach water was withdrawn, soil samples were taken and the pH determined.

Due to non-reproducible COD values on the 7th and 21st day leach water samples, another experimental run was started which consisted of one cylinder in the 59° to 73°F temperature bath. The cylinder for the second run was identical to the ones in the first run except both the thermocouples in the soil and refuse layers and the soil sampling holes were omitted. The saturation water was not withdrawn until the 22nd day, whereupon 900 ml of distilled water was added. As in the first, this procedure was continued until the 105th day when it was stopped due to time restrictions.

DATA

The following section contains the pertinent experimental data obtained in this investigation.

TABLE 2SOIL AND LEACH WATER ANALYSIS OF CYLINDER #1 (86-90°F)

<u>DAY</u>	<u>SOIL pH</u>	<u>LEACH WATER pH</u>	<u>COD (mg/10₂)</u>
0	6.8	7.0	-
7	6.5	6.4	-
21	6.2	7.0	-
35	7.5	7.75	47,000
50	8.9	7.8	9,780
63	8.9	7.8	5,210
77	8.7	7.7	3,030
91	8.3	7.4	1,620
105	8.7	7.6	1,150
119	8.0	7.2	870
133	8.1	-	-

TABLE 3SOIL AND LEACH WATER ANALYSIS OF CYLINDER #2 (74-86°F)

<u>DAY</u>	<u>SOIL pH</u>	<u>LEACH WATER pH</u>	<u>COD (mg/10₂)</u>
0	6.8	7.0	-
7	7.4	6.3	-
21	6.6	6.5	-
35	6.6	6.4	47,000
50	8.5	7.2	25,100
63	8.9	7.5	3,000
77	8.7	7.2	2,500
91	8.7	7.0	2,000
105	8.8	7.4	1,240
119	8.2	7.1	1,000
133	8.5	7.1	810

TABLE 4SOIL AND LEACH WATER ANALYSIS OF CYLINDER #3 (59-73°F)

<u>DAY</u>	<u>SOIL pH</u>	<u>LEACH WATER pH</u>	<u>COD (mg/10₂)</u>
0	6.8	7.0	-
7	7.6	6.3	-
21	6.5	6.6	-
35	6.8	6.3	47,000
50	7.5	6.2	26,000
63	7.5	6.2	21,500
77	7.3	6.2	15,700
91	7.8	6.4	12,900
105	8.4	7.1	6,525
119	8.0	6.9	-
133	8.1	6.9	1,485

TABLE -5SOIL AND LEACH WATER ANALYSIS OF CYLINDER #4 (59-73°F)

<u>DAY</u>	<u>SOIL pH</u>	<u>LEACH WATER pH</u>	<u>COD (mg/10₂)</u>
0	6.8	7.0	-
7	7.6	6.3	-
21	7.1	6.5	-
35	6.6	6.3	47,000
50	7.5	6.3	34,000
63	7.5	6.3	16,900
77	7.5	6.3	15,300
91	7.7	6.6	11,300
105	8.5	7.3	6,320
119	7.9	7.2	3,350
133	8.1	7.3	2,730

TABLE 6LEACH WATER ANALYSIS OF CYLINDER #5 (59-73°F)

<u>DAY</u>	<u>LEACH WATER pH</u>	<u>COD (mg/10₂)</u>
0	7.0	-
22	6.0	14,200
35	6.4	15,100
49	6.4	14,900
63	6.4	14,200
77	7.2	11,800
91	7.2	3,870
105	7.0	1,800

RESULTS AND DISCUSSION

In Figure 2 the peaks at wavenumbers 640, 670, 715, 2320 and the doublets at 3600 and 3700 indicate the presence of carbon dioxide. The peak at wavenumber 2220 indicates the presence of nitrous oxide. In Figure 3 the peaks at wavenumbers 1300 and 3000 indicate the presence of methane. The other peaks are an indication of carbon dioxide as in Figure 2 (16).

The gas analysis in Table 7 shows that carbon dioxide (CO_2) was present in all the cylinders from the first day to the last. The occurrence of carbon dioxide in the cylinders signifies that there is biological activity in the soil be it either aerobic or anaerobic. Methane gas first appeared in cylinder #1 (86-90°F) after 14 days. The time delay is due to several interacting factors. First, the aerobic bacteria must use up all the oxygen. Secondly, the acidifying bacteria must acclimate themselves to the media (canine nutriment) and develop into a colony. Thirdly, the methane bacteria also must adjust themselves to the media and develop into a colony. In the second cylinder (74-86°F) methane gas did not appear until the 24th day. The ten day difference from cylinder #1 can be explained, because cylinder #1 was at a higher temperature (12° greater) thus the aerobic organisms used up the oxygen faster, therefore going anaerobic sooner. A second reason for the difference could be that even though the soil was

FIGURE 2

Per cent Transmittance vs. Wavenumber for Typical Gas Sample with Nitrous Oxide Gas

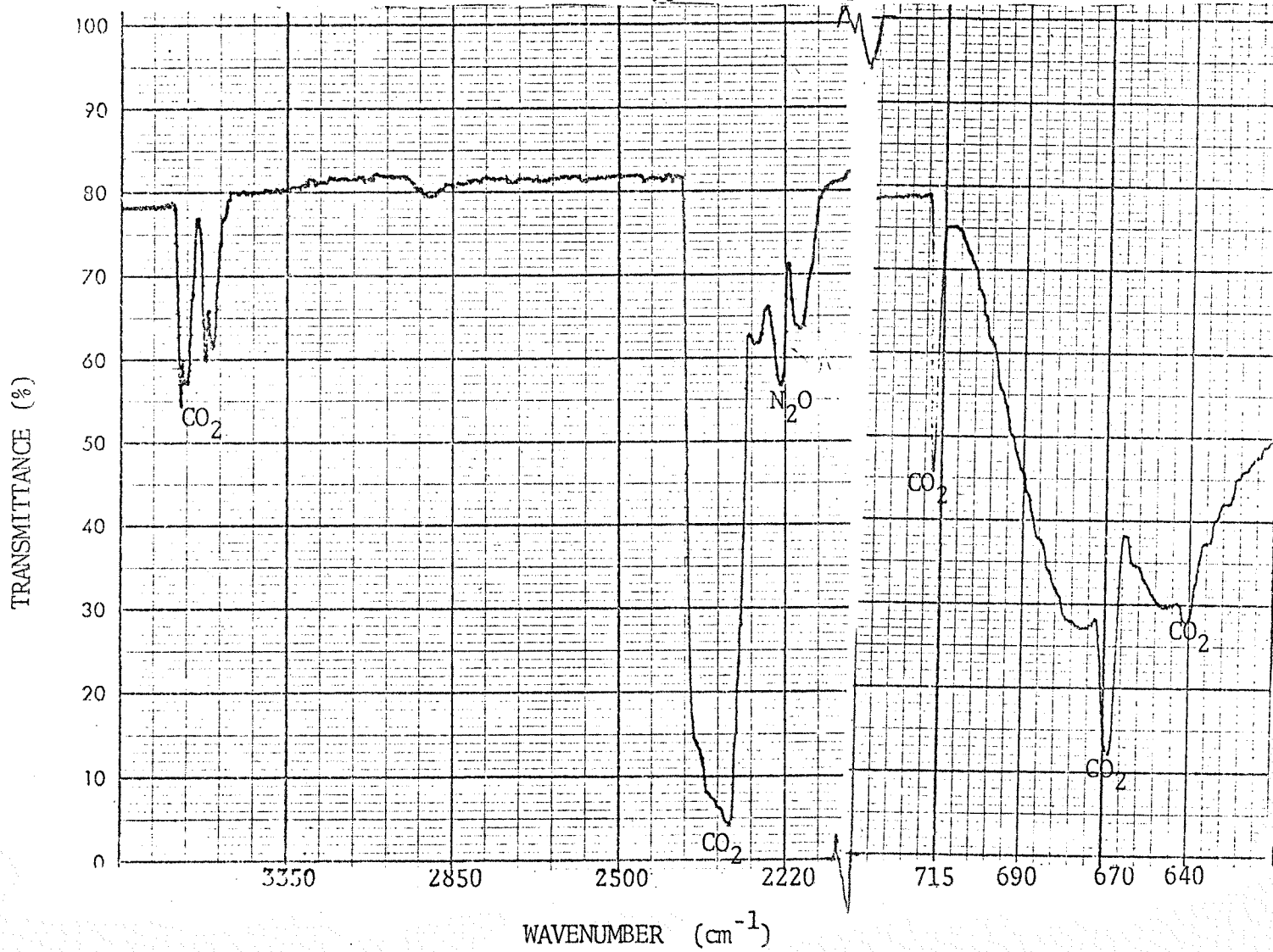


FIGURE 3

Per cent Transmittance vs. Wavenumber for Typical Gas Sample with Methane Gas

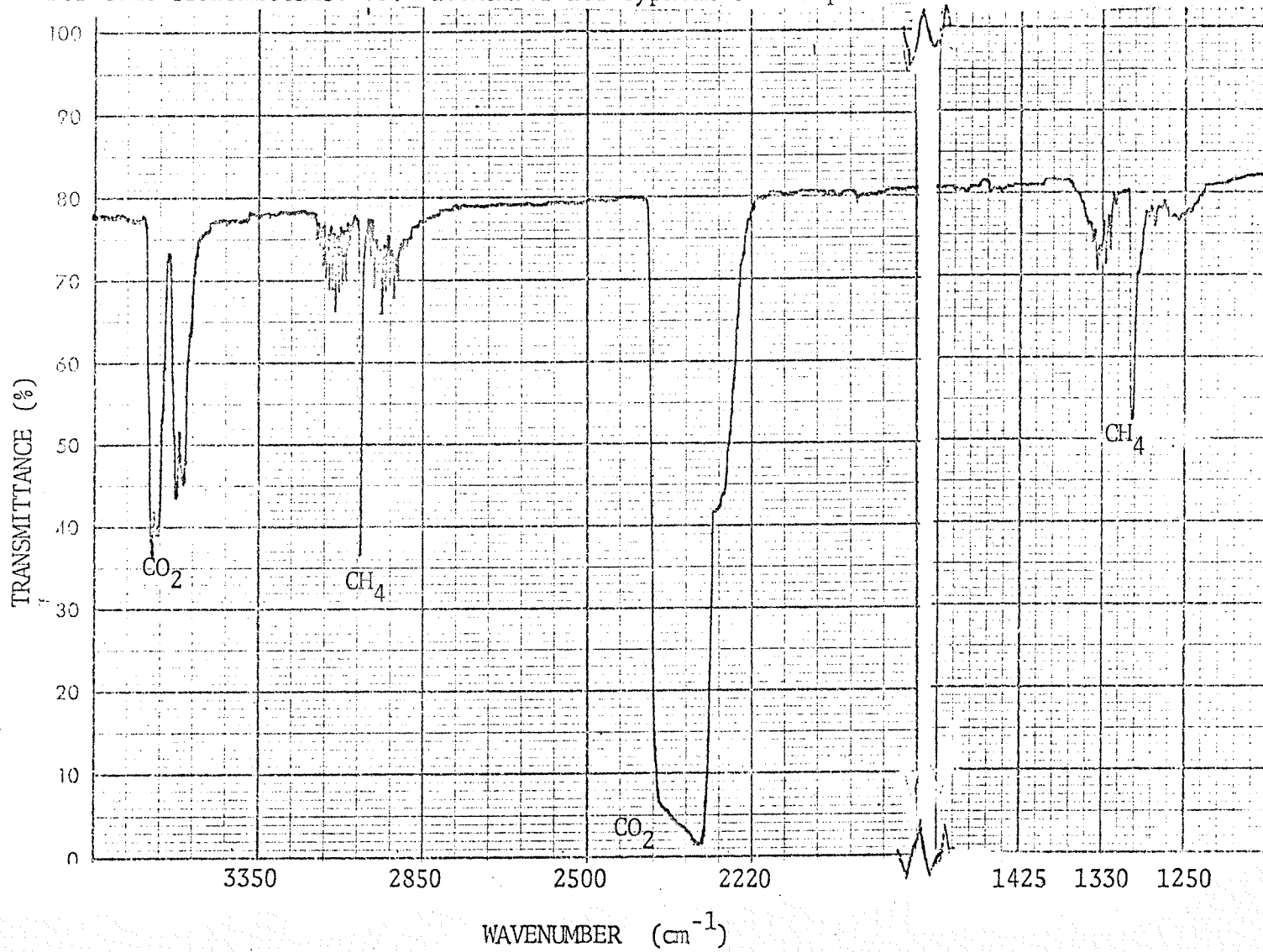


TABLE 7DECOMPOSITION GAS ANALYSIS AND DURATION OF APPEARANCE (DAYS)

	<u>CO₂</u>	<u>CH₄</u>	<u>N₂O</u>
Cylinder #1 (86-90°F)	1-133	14-133	None
Cylinder #2 (74-86°F)	1-133	24-133	None
Cylinder #3 (59-73°F)	1-133	70-133	17-24
Cylinder #4 (59-73°F)	1-133	70-133	4-25
Cylinder #5 (59-73°F)	1-105	58-105	2-4

thoroughly mixed before filling the cylinders, cylinder #1 could have received a better seeded portion of the soil.

In cylinder #3 and #4, methane gas did not appear until the 70th day. The reason for this is the low temperature at the beginning of the experiment. Methane bacteria cannot exist at temperatures lower than 68°F, thus not until after the cylinder reached and exceeded 68°F could methane be found. In cylinder #5, methane appeared on the 58th day. Since cylinder #5 was started 28 days after the first four cylinders, methane should have appeared on the 42nd day. Here the difference is due to the soil being not as well seeded as the soil used in the other cylinders. The researcher had to obtain additional soil because all the original soil was used in the first four cylinders.

Nitrous oxide only appeared in cylinder #3, #4 and #5. At first one might assume that the lower temperatures of these cylinders was beneficial to the nitrogen fixing bacteria. However, the nitrous oxide disappeared even before the cylinder bath temperature had begun to rise. The actual reason for nitrous oxide appearance was that these cylinders were not completely water saturated. For after the addition of distilled water on the 21st day to cylinder #3 and #4, the nitrous oxide disappeared from the gas analysis within four days. Also, it disappeared from cylinder #5 on the fourth day when the saturation water had a chance to diffuse through the soil.

If this explanation is correct, then why didn't the nitrous oxide disappear from cylinder #3 and #4 after the fourth day also? This can be explained since the water did not thoroughly saturate the cylinder due to channel flow. That is, the water did not saturate all the soil as it flowed through the cylinder, but flowed in paths of least resistance (channels). This was visually observed. Thus, after the cylinder was completely saturated, any ammonia which formed reacted instantaneously with the carbon dioxide to form salts thereby not allowing the bacteria time to utilize the ammonia.

Figures 4, 5 and 6 are log-log plots of COD versus time for cylinders #1 and #2, cylinders #3 and #4, and cylinder #5, respectively. Since the COD values on the 35th day for cylinder #1, #2, #3 and #4 were all the same and the COD values on the 7th and the 21st day were not reproducible, cylinder #5 was used to discover why. As was previously stated, bacteria need 1) time to develop a colony and to acclimate themselves to the waste, and 2) there is no waste stabilization in the first or acidifying stage of decomposition. Thus, Figure 6 shows the COD remaining constant during this process. It was therefore assumed that the same process should hold for the first four cylinders and hence, the dashed constant COD line.

From Figure 4, one can see that both cylinders #1 and #2 had the same decomposition reaction rate. Therefore, in this

FIGURE 4

Log of COD vs. Log of Time for Cylinders No.1 and No.2 [74-90°F]

○ Cylinder No.1 @86-90°F

□ Cylinder No.2 @74-86°F

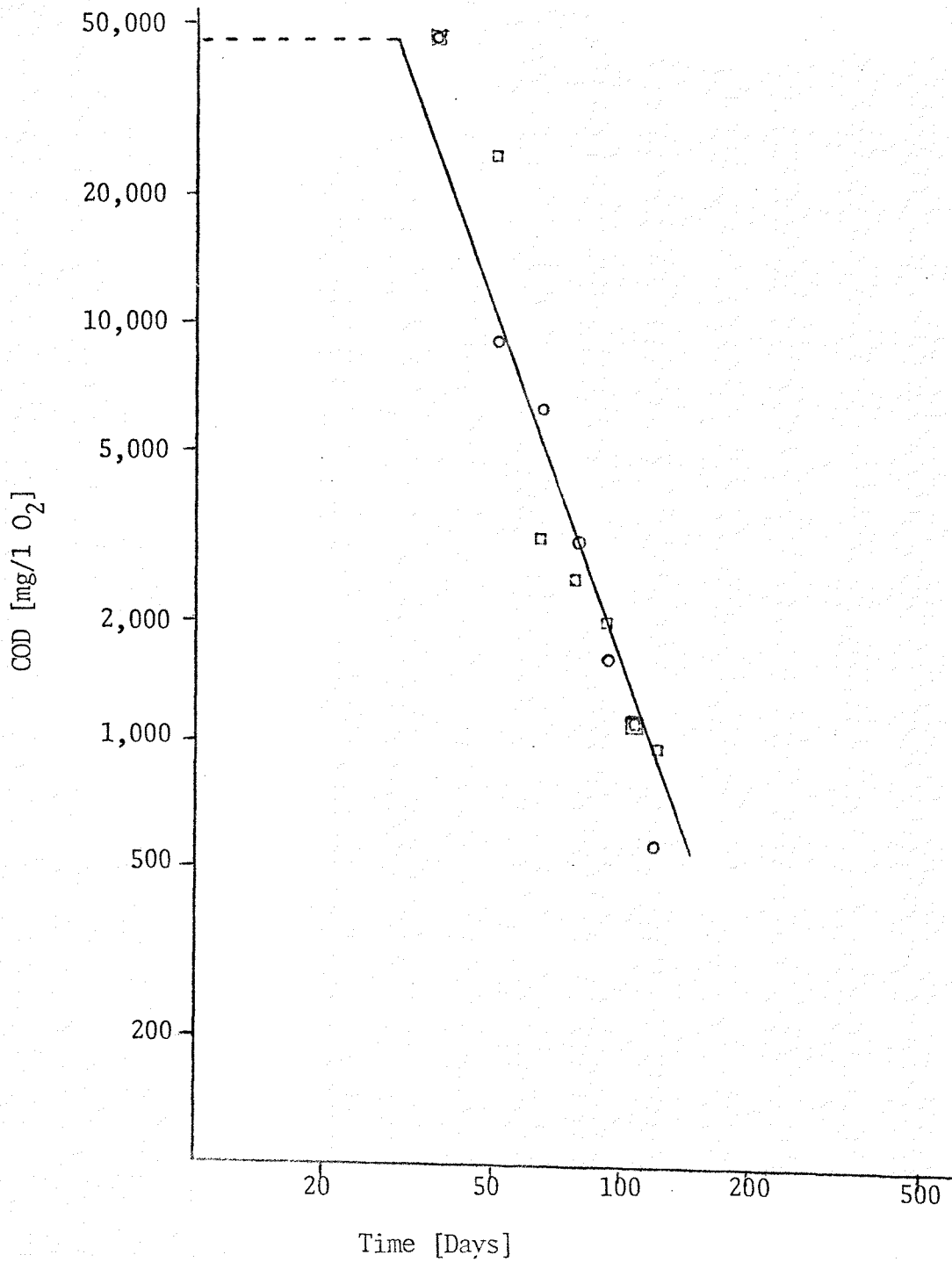


FIGURE 5

Log of COD vs. Log of Time for Cylinders No. 3 and No. 4 (59-73°F)

□ Cylinder No. 3 @ 59-73°F

○ Cylinder No. 4 @ 59-73°F

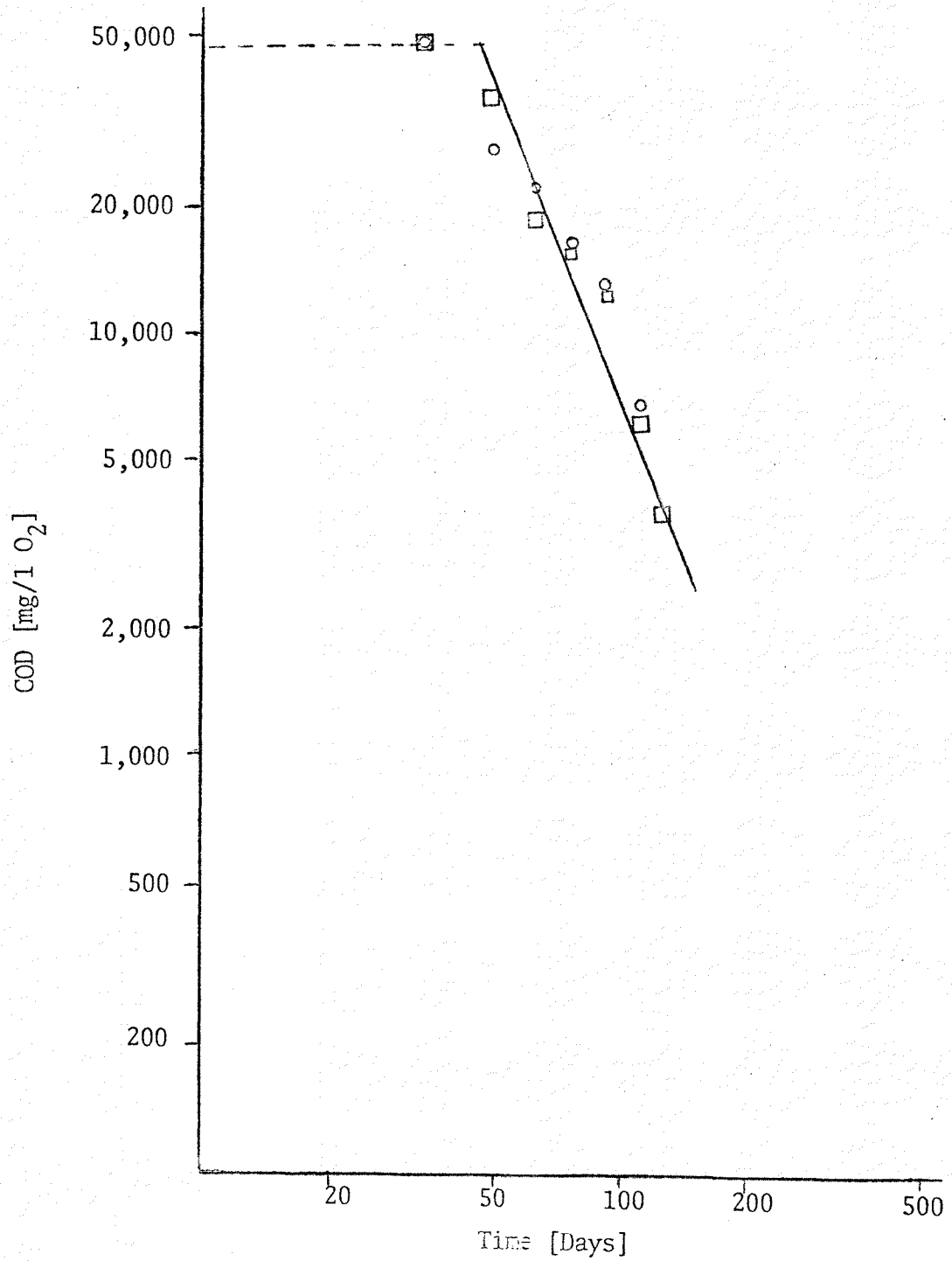
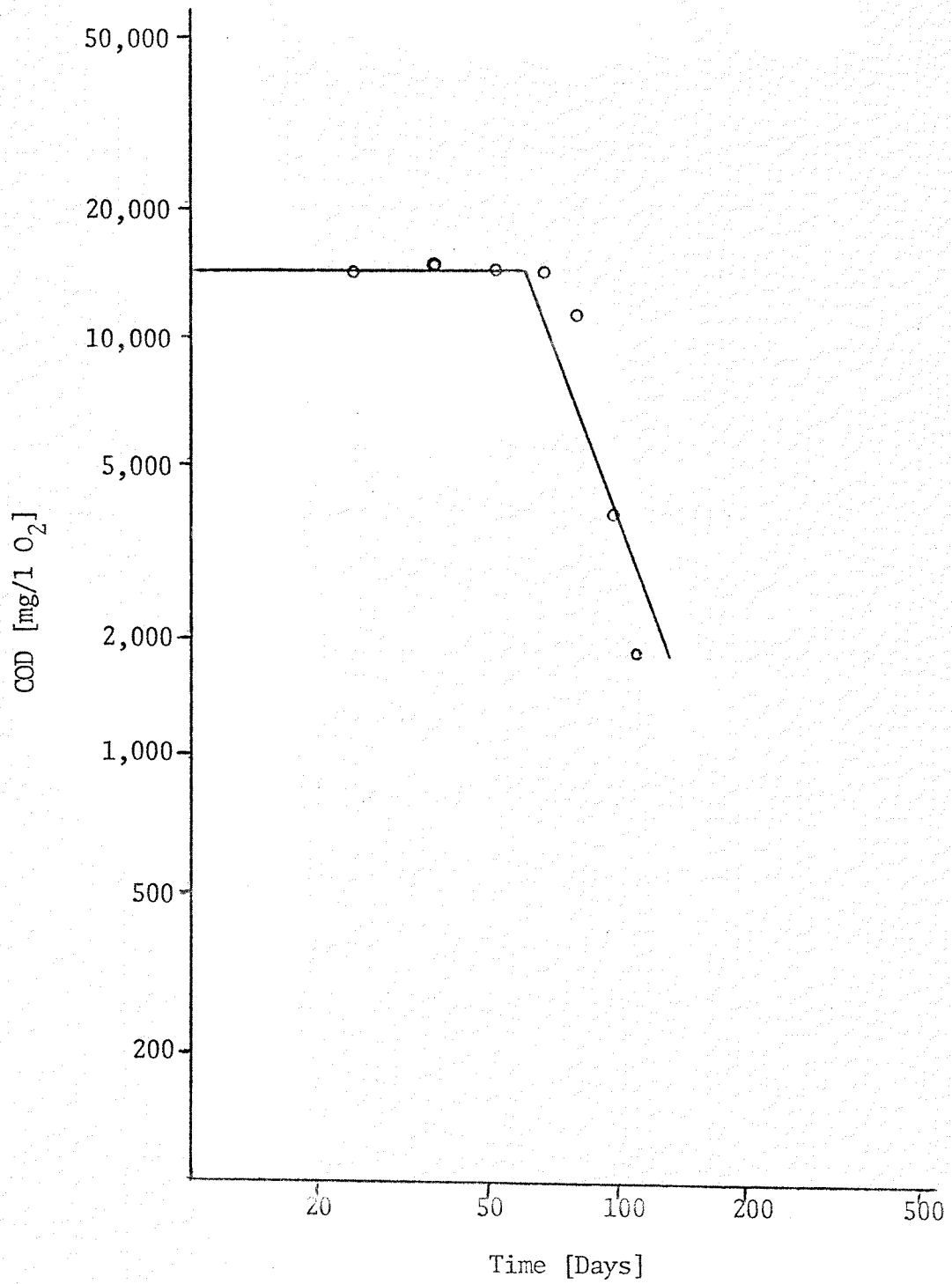


FIGURE 6

Log of COD vs. Log of Time for Cylinder No. 5 [59-73°F]



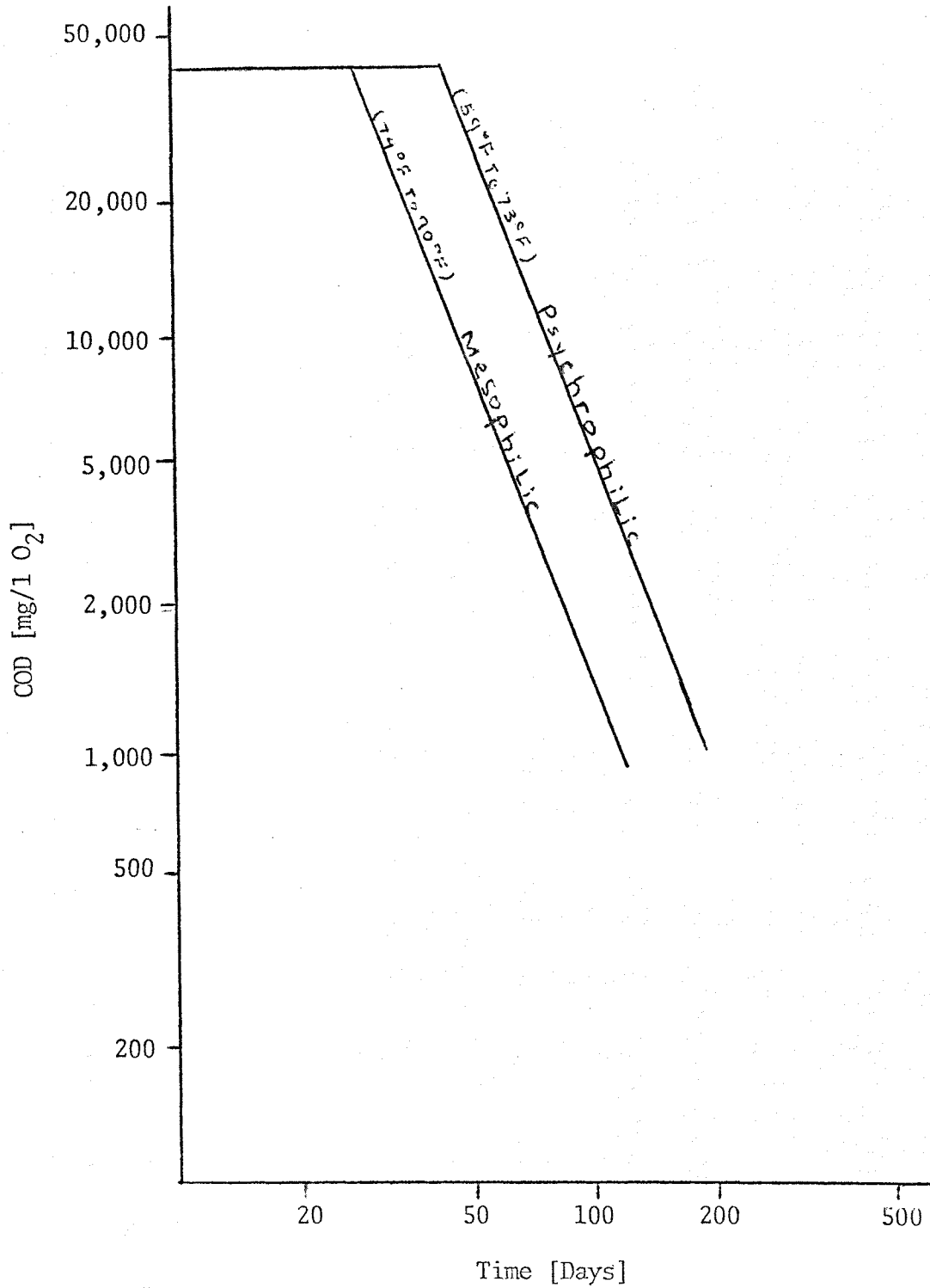
case the reaction does not follow the Arrhenius Rate Law. This law states that the rate of reaction must continuously increase with increasing temperature. Thus, other factors, such as the microbiology of the process, must be considered. There are three general classifications of biological decomposition dependent on temperature: Thermophilic (100-185°F), Mesophilic (70-106°F) and Psychrophilic (32-74°F). Obviously, there is overlapping of temperatures within the three groups (24). Since in this case the temperature range is 74-90°F, the mesophilic bacteria were the ones responsible for the decomposition.

Figure 5 has the same shape curve as Figure 4. The dashed constant COD line occurred for the same reasons as in Figure 4. In Figure 5 the reaction (decomposition) rate remained constant even though there was an increase in temperature. From the temperature range of the cylinders (59-73°F), it can be deduced that it was the psychrophilic bacteria that were responsible for the decomposition process.

Figure 7 is a composite of Figure 5 and Figure 6 (cylinder #5 was not used because as previously mentioned the soil in that cylinder was different). Here one can see that the psychrophilic bacteria need a longer acclimation period but once waste stabilization starts, they stabilize the waste at the same rate as the mesophilic bacteria.

FIGURE 7

Log of COD vs. Log of Time for the Two Temperature Ranges



The fact that the reaction rate is constant is unexpected, since the refuse (canine nutriment) is not simply one compound, but a mixture of fats, proteins and ash. However, if we assume the refuse is one compound, a pseudo-reaction order can be found. That is, assume the COD to be reacted, as one compound.

We have:

$$r_A = k c_A^n \quad (a)$$

Where:

A = COD

r_A = rate of removal of COD with respect to time

k = reaction constant

c_A = concentration of A (COD) at any time

n = order of the reaction

By definition:

$$r_A = - \frac{dc_A}{dt} \quad (b)$$

Combining (a) and (b) and transposing:

$$\frac{dc_A}{c_A^n} = -k dt \quad (c)$$

Integrating (c):

$$\frac{1}{1-n} (c_A^{1-n} - c_{A0}^{1-n}) = -kt \quad (d)$$

$$c_A^{1-n} = c_{A0}^{1-n} + (n-1) kt \quad (e)$$

Taking the log of both sides:

$$(1-n) \log c_A = (1-n) \log c_{A0} + \log (n-1) k + \log t \quad (f)$$

Since c_{A0} , n and k are constant:

$$\log k' = (1-n) \log c_{A0} + \log (n-1)k \quad (g)$$

Then (f) becomes:

$$\log c_A = \left(\frac{1}{1-n}\right) \log t + \log k' \quad (h)$$

This is an equation of a straight line with a slope of $\left(\frac{1}{1-n}\right)$ and an intercept of k' when plotted on log-log paper. From Figure 7, the slope of the line is 3. Therefore:

$$\begin{aligned} \text{slope} &= \frac{1}{1-n} = 3 \\ \therefore n &= 2/3 \end{aligned}$$

It is also possible to find k from the data but since k is not only a function of temperature which influences the bacteria group but of both the type and the total population of the bacteria, it would not yield any general results.

Figures 8 and 9 show the curves of both the leach water and soil pH. This verifies the two stage decomposition theory. Initially the curves have a negative slope (becoming more acidic) which corresponds to the acidifying stage, then the slope becomes positive (more basic) denoting the second step (methane formation and the utilization of the organic acids). Finally, the curves oscillate. This oscillation is due to the different rates of attack of the organisms on the different wastes. That is, first the acidifying organisms attack the simplest compounds, then after a build-up of acids the methane bacteria attack the acids. After all the simplest compounds have been disposed of, the acidifying

FIGURE 8

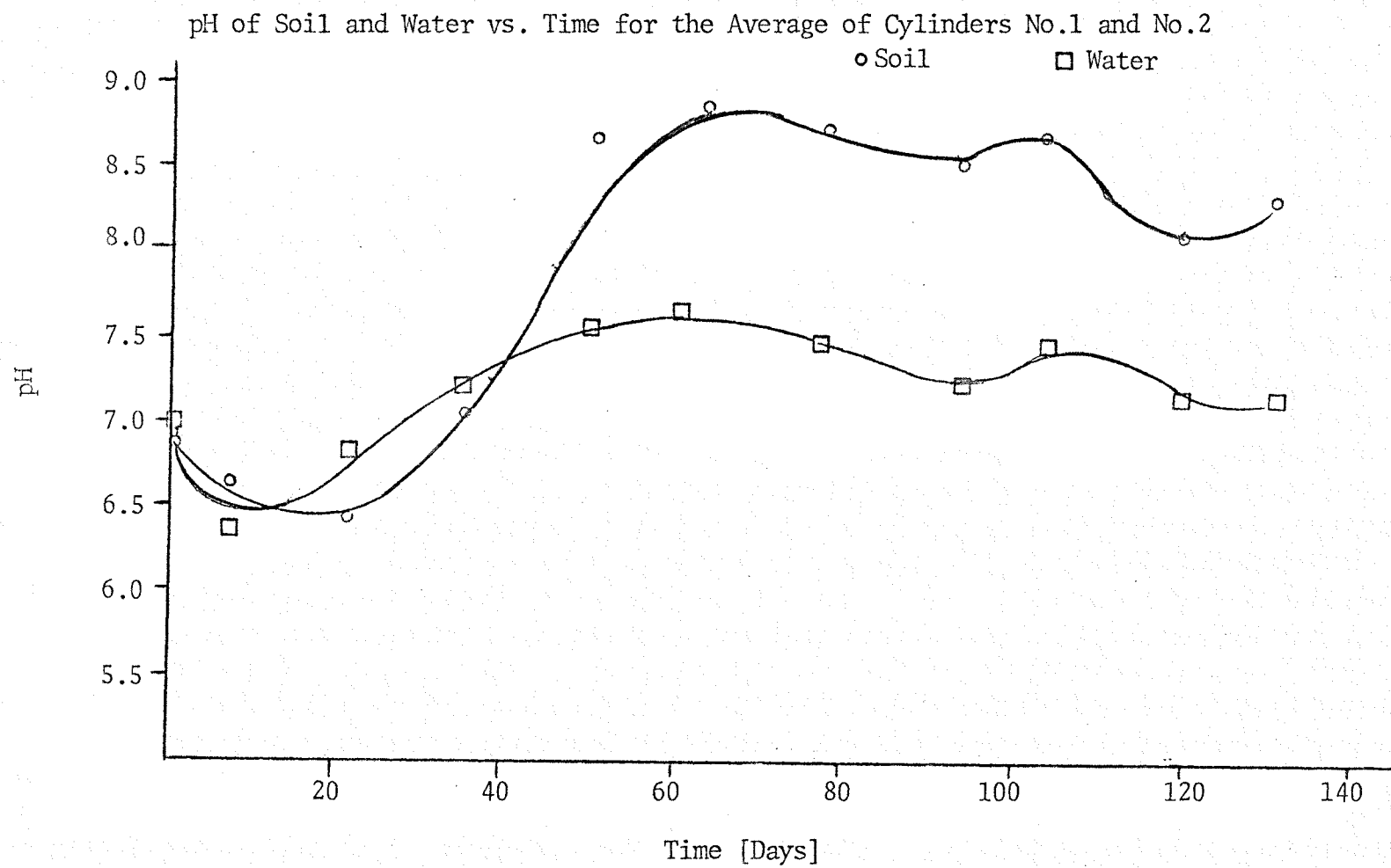
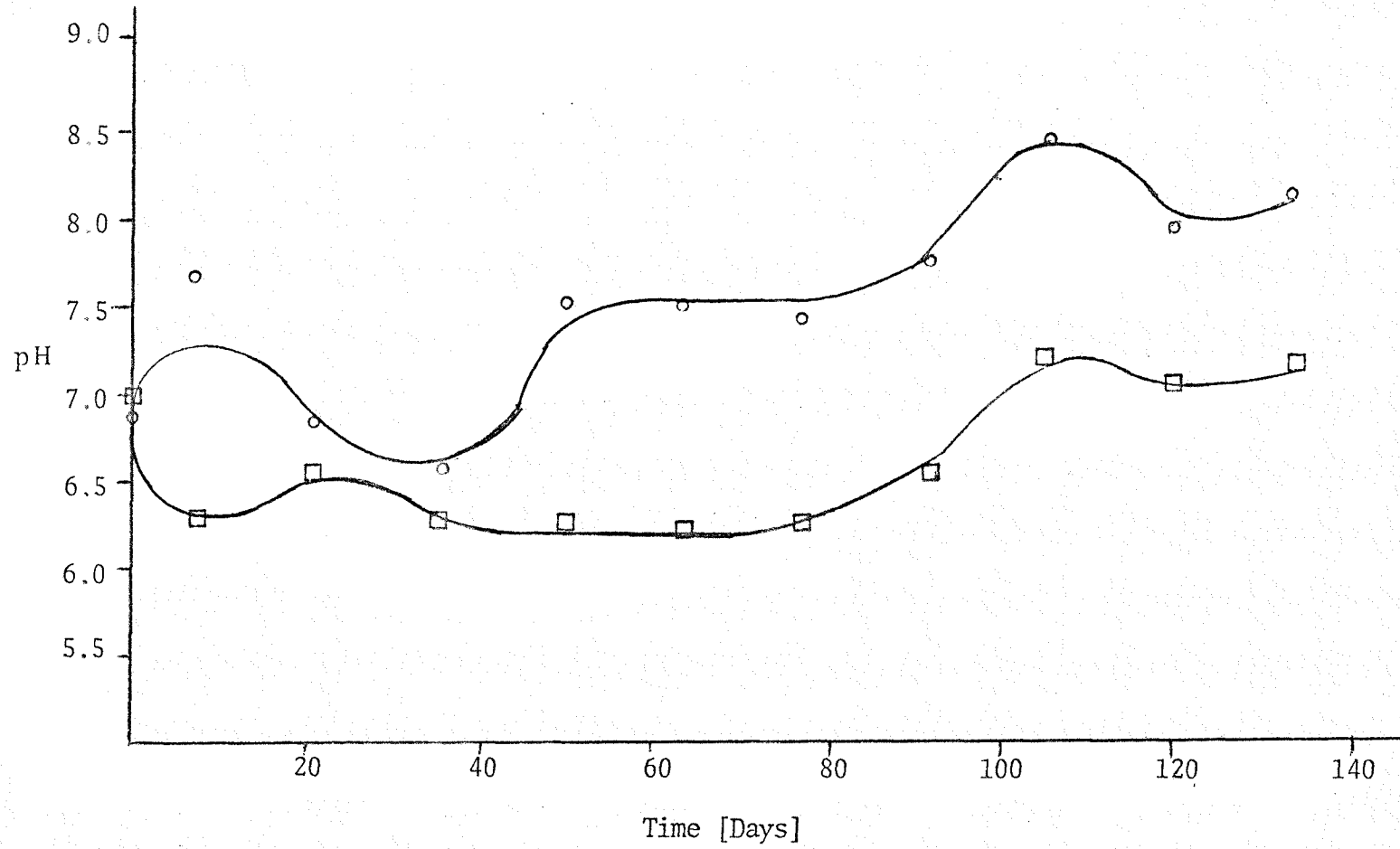


FIGURE 9

pH of Soil and Water vs. Time for the Average of Cylinders No.3 and No.4

○ Soil □ Water



bacteria attack the next simplest compounds which takes them longer than the original compounds. Therefore, the methane bacteria are utilizing the organic acids faster than the acidifying bacteria are forming them. Thus, the environment becomes less acidic. However, after the methane bacteria use up all the simple organic acids they have to attack the more complex organic acids which takes them longer. Now the organic acids are being formed faster than they can use them thereby causing an increase in acidity thus lowering the pH. This alternating acidifying-deacidifying process will continue until all the bio-degradable waste has been utilized.

In both Figures 8 and 9, the pH of the soil is always higher than the pH of the leach water. The reason for this is the method used to determine the soil pH. In the soil pH test the soil was only leached for ten minutes before the pH was taken (5). This short amount of time does not allow all the complex organic acids to be leached out. However, the leach water was left for two weeks in the cylinders thereby allowing time for all the complex compounds to be leached out.

In Figure 9 the curves do not begin to oscillate between the 30th and 80th days. This is the result of no methane being formed. The system has stabilized itself after the initial acidifying stage. After the temperature of the cylinders went above 68°F (methane bacteria cannot live below 68°F) and methane was produced, the pH of the system began to oscillate.

CONCLUSIONS

The rate of stabilization of waste in a sanitary landfill is strongly dependent upon the initial temperature condition and total bacteria population. The initial temperature of the landfill is very difficult to obtain since the landfill operation is a year-round process. However, the proper seeding of the soil can readily be accomplished.

It was found that the waste stabilization process could be fitted to a pseudo-2/3 order reaction.

The pH of the soil and leach water continuously oscillated. Therefore, any method trying to evaluate the degree of stabilization of a sanitary landfill using a pH method will not yield accurate results.

A sanitary landfill adversely affects any water coming in contact with it. The water will have abnormally high COD values. This will put an increase load on any subsequent water treatment facilities used to purify this water.

RECOMMENDATIONS

In future work the following parameters should be varied in order to obtain a greater understanding of the decomposition process in a sanitary landfill.

Air Concentration

1. Aeration of cylinders to keep the decomposition aerobic
2. Vary the quantity of air in the cylinders

Decomposition Gases

1. The Raman spectra of the decomposition gases should be obtained since nitrogen and oxygen can be detected from the spectra

Refuse

1. Use a more representative mixture of typical urban refuse
2. Vary the composition of the refuse
3. Vary the size of the refuse (whole, ground, chunks)
4. Add varying amounts of inerts (ash, rock, glass)
5. Add varying amounts of nutrients (nitrogen, phosphorus)
6. Add varying amounts of slow decomposing materials (paper, plastics)
7. Compaction

Soil

1. Vary the amount of moisture in the refuse
2. Selectively seed the soil

3. Use different types of soil (clay, sand or a mixture of the two plus gravel)
4. Add varying amounts of nutrients (nitrogen, phosphorus)

Temperature

1. Run the experiment at higher and lower temperatures
2. Cycle the temperatures to simulate seasonal changes

Experimental Apparatus

1. Use open cylinders
2. Cultivate different types of plants to study the effects of an underlying sanitary landfill

APPENDIX

TABLE IPHENOLPHTHALEIN ACIDITY (AS mg/1 CaCO₃) OF THE LEACH WATER

<u>DAY</u>	<u>CYLINDER #1</u>	<u>CYLINDER #2</u>	<u>CYLINDER #3</u>	<u>CYLINDER #4</u>	<u>CYLINDER #5</u>
7	2000	1000	350	350	-
21	5000	4000	1750	2000	400
35	4000	5500	4000	4000	2000
50	1000	750	1250	1250	3000
63	4000	2500	3500	3000	2500
77	3500	1750	3250	3250	600
91	2500	1700	2250	2000	400
105	900	500	600	400	-
119	400	500	200	370	-

TABLE IITOTAL RESIDUE (mg/l) OF THE LEACH WATER

<u>DAY</u>	<u>CYLINDER #1</u>	<u>CYLINDER #2</u>	<u>CYLINDER #3</u>	<u>CYLINDER #4</u>	<u>CYLINDER #5</u>
7	9500	11,100	3500	4000	-
21	11,000	12,000	8400	9300	2300
35	5500	9200	22,000	24,000	11,000
50	6500	6400	9600	9000	10,000
63	4200	4000	6500	6200	6900
77	2800	2100	5600	6300	5600
91	2500	2200	3600	4400	-
105	1100	1600	1500	1700	-

DETERMINATION OF CHEMICAL OXYGEN DEMAND (25)

1. General Discussion

A. Principle:

Most types of organic matter are destroyed by a boiling mixture of chromic and sulfuric acids. A sample is refluxed with known amounts of potassium dichromate and sulfuric acid and the excess dichromate titrated with ferrous ammonium sulfate. The amount of oxidizable organic matter, measured as oxygen equivalent is proportional to the potassium dichromate consumed.

B. Interferences and Inadequacies:

Straight chain aliphatic compounds, aromatic hydrocarbons and pyridine are not oxidized to any appreciable extent, although this method gives more nearly complete oxidation than the permanganate method. The straight chain compounds are more effectively oxidized if silver sulfate is added as a catalyst; however, silver sulfate reacts with chlorides, bromides or iodides to produce precipitates which are only partially oxidized by the procedure. The oxidation and difficulties caused by the presence of chlorides in the sample may be overcome by employing the following method which is a complexing technique for the elimination of chlorides from the reaction. This is accomplished by adding mercuric sulfate to the samples

before refluxing. This ties up the chloride ion as a soluble mercuric complex which greatly reduces its ability to react further.

2. Apparatus

Reflux apparatus consisting of 250-ml erlenmeyer flasks with a ground glass 24/40 neck and 300 mm socket West or equivalent condensers with 24/40 ground glass joint, and a hot plate with sufficient power to produce at least 9 watts/square inch of heating surface, or equivalent to insure an adequate boiling of the contents of the refluxing flask.

Other apparatuses, 10 ml pipette, 10 ml buret, 100 ml volumetric flask (needed for dilution of sample).

3. Reagents

- A. Standard potassium dichromate solution, 0.25N. Dissolve 12.25 g of $K_2Cr_2O_7$ (primary standard grade) in distilled water and dilute to 1000 ml. Note nitrite nitrogen exerts a COD. To eliminate this interference, sulfamic acid, in the amount of 10 ml for every 1 mg of nitrite nitrogen in the refluxing flask may be added to the dichromate solution. Thus, 0.12g of sulfamic acid per liter of dichromate solution will eliminate the interference of nitrites up to 6 mg/L, if a 20 ml sample is used.
- B. Sulfuric acid reagent, concentrated sulfuric acid containing 22 g of silver sulfate per 9 pound bottle (1 to 2 days

required for dissolution).

- C. Standard ferrous ammonium sulfate titrant, 0.10N. Dissolve 39 g of $\text{Fe}(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$ in distilled water. Add 20 ml concentrated sulfuric acid, cool, and dilute to 1000 ml. This solution must be standardized against the standard potassium dichromate daily.

Standardization: Dilute 10 ml standard potassium dichromate solution to about 100 ml. Add 30 ml concentrated sulfuric acid and allow to cool. Titrate with ferrous ammonium sulfate titrant using 10 drops of ferroin indicator (the color change is sharp, going from blue-green to reddish-brown).

$$\text{Normality} = \frac{\text{ml of } \text{K}_2\text{Cr}_2\text{O}_7 \times 0.25}{\text{ml } \text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2}$$

- D. Ferroin indicator solution: Dissolve 1.485 g of 1,10-phenanthroline monohydrate together with 0.695 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water and dilute to 100 ml. The indicator can be purchased already prepared.
- E. Silver sulfate, reagent powder (see 3B).
- F. Sulfamic acid, analytical grade (see 3A).

4. Procedure

- A. Place 0.4 g HgSO_4 in a refluxing flask. Add 20 ml sample or an aliquot diluted to 20.0 ml with distilled water and swirl to mix. Then add 10.0 ml standard potassium dichromate titrant. Carefully add 30 ml concentrated H_2SO_4 containing Ag_2SO_4 while mixing. Add boiling chips (use pumice granules

or glass beads). Swirl mixture (Caution: if mixture is not thoroughly mixed before heat is applied, mixture might be blown out of flask).

- B. Attach flask to the condenser and reflux the mixture for two hours. Cool and wash down condenser with 80 ml of distilled water.
- C. When mixture is cooled to room temperature add 10 drops of ferroin indicator and titrate excess dichromate with ferrous ammonium sulfate (end point when color goes from blue-green to reddish-brown).
- D. A blank consisting of 20 ml distilled water instead of sample together with reagents is refluxed in the same manner.

5. Calculation

$$\text{mg/l COD} = \frac{(a-b) c \times 8,000}{\text{ml sample}}$$

COD = chemical oxygen demand for dichromate

a = ml $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ used for blank

b = ml $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ used for sample

c = normality of $\text{Fe}(\text{NH}_4)_2\text{SO}_4$

TOTAL ACIDITY DETERMINATION (25)

1. General Discussion

A. Principle:

An equilibrium between carbonate, bicarbonate and carbon dioxide exists in many natural waters for potable purposes. The carbonate and bicarbonate can be estimated by titrating the alkalinity with standard acid to the bicarbonate equivalence point of pH 8.3 and then to the carbonic acid equivalence point in the pH range of 4 to 5. Acid pollutants entering a water supply in sufficient quantity will disturb the carbonate-bicarbonate-carbon dioxide equilibrium. The extent of this disturbance may be estimated by titrating with standard alkali to the end points of pH 4.5 and 8.3.

B. Interferences:

A fading and impermanent end point characterizes the phenolphthalein acidity titration performed at room temperature on samples containing iron and aluminum sulfate. Better results are obtained by titrating the samples at boiling temperatures.

2. Apparatus

- a) 10 ml buret
- b) 10 ml pipette
- c) 125 ml flask

3. Reagents

A. Sodium hydroxide 1.0N.

To prepare dissolve 40 grams in 1 liter of CO₂, free distilled water and let stand at least 48 hours in an alkali-resistant container, protected from atmospheric CO₂ with a soda lime tube.

4. Procedure

A. Sample volumes requiring less than 25 ml of titrant yield sharpest color change at the end point and therefore are recommended.

B. Methyl orange acidity: add 2 drops of methyl orange indicator to a sample diluted to 100 ml. Titrate with 1.0N NaOH to the faint orange characteristic of pH4.5.

C. Phenolphthalein acidity: add 3 drops pf phenolphthalein indicator to a sample diluted to 100 ml. Titrate with 1.N NaOH to the appearance of the faintest pink color characteristic of pH 8.3.

5. Calculation

$$\text{Acidity as mg/l CaCO}_3 = \frac{A \times N \times 50,000}{\text{ml sample}}$$

A = ml titration for sample

N = normality of NaOH

TOTAL RESIDUE DETERMINATION (25)

1. General Discussion

A. Principle

The sample is evaporated in a weighed dish on a steam bath and then is dried to constant weight in an oven at 103-105°C. The increase in weight over that of the empty dish represents the total residue.

Minimum detectable concentration: Dependent on the sensitivity of the analytical balance used for weighing.

2. Apparatus

A. Evaporating dishes

Dishes of 150-200 ml capacity of pyrex glass or similar inert substance.

B. Steam bath

C. Drying oven

D. Desiccator with a desiccant containing a color indicator of moisture concentration

E. Analytical balance, 200 g capacity, capable of weighing to 0.1 mg

3. Procedure

A. Dry dish at 103-105°C, then weigh

B. Add 100-250 mg of a well mixed sample to weighed evaporating dish

C. Dry in oven

D. Cool in desiccator; weigh

E. Return to oven and dry till difference between successful weighing is less than 0.5 mg

4. Calculation

$$\text{mg/l total residue} = \frac{\text{mg total residue} \times 1,000}{\text{ml sample}}$$

pH DETERMINATION OF SOIL (5)

1. General Discussion

The presence of a complex system of buffers in a soil sample makes pH determinations of slurries quite sensitive to concentration variations

2. Apparatus

- A. 250 ml beaker
- B. Stirring rod
- C. Analytical balance
- D. pH meter

3. Procedure

- A. Weigh out 4 grams of soil
- B. Add to it 200 ml of distilled water
- C. Stir vigorously for 3 to 5 minutes
- D. Let settle for 5 minutes
- E. Read pH with a reliable pH meter

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