NITRIFICATION & DENITRIFICATION FACILITIES

PREPARED
FOR
ENVIRONMENTAL PROTECTION AGENCY
TECHNOLOGY TRANSFER PROGRAM

DESIGN SEMINAR
FOR
WASTEWATER TREATMENT FACILITIES

ATLANTA, GEORGIA
MAY 8, 9, & 10, 1972

NITRIFICATION & DENITRIFICATION

FACILITIES

PREPARED
FOR
ENVIRONMENTAL PROTECTION AGENCY
TECHNOLOGY TRANSFER PROGRAM

DESIGN SEMINAR
FOR
WASTEWATER TREATMENT FACILITIES

ATLANTA, GEORGIA
MAY 8, 9, & 10, 1972

CHAPTER 1

FACTORS AFFECTING NITRIFICATION KINETICS*

Harry E. Wild, Jr., Clair N. Sawyer, and Thomas C. McMahon

The nitrification phenomenon has been studied intensively by soil scientists for the past century. With the advent of biological wastewater treatment systems, chemists and engineers were impressed by the fact that the same phenomenon occurred in their treatment plants. Originally, in the absence of biological methods of assessing degrees of purification, chemical analyses served as the major means of evaluation. Experience soon taught the lesson that highly nitrified effluents were immune to putrefaction. As a result, waste treatment plants prior to 1930 were designed as standard or conventional plants intended to accomplish a relatively high degree of nitrification, at least during the summer months.

With the development and widespread application of the BOD test, it became apparent to many designing engineers that high degrees of waste treatment, in terms of BOD removal, could be accomplished, at marked savings in capital and operating costs, by designing to avoid nitrification. Thus, from 1940 until the late 1960's the main objective in the United States was to design to minimize nitrification.

*Paper presented at the Boston Meeting of the WPCF, October 1970. Published in Jour. WPCF, Vol 43, p. 1845, (1970).

Many of the newly designed high-rate or modified plants, and some older plants suffering from overloads, were plagued with denitrification and resultant "rising sludge" problems in the final clarifiers. These problems stimulated numerous studies on how to control nitrification, since it was a physical impossibility to accomplish high degrees of nitrification, in most cases, without expansion of the plant facilities.

Although the NOD of unnitrified effluents was well understood, sanitary engineers generally dismissed this matter from their minds on the basis of three premises:

1. Nitrification is caused by special organisms, the population of which is minimal in surface waters.

2. The reaction constant for nitrogenous oxidation is small in relation to the constant for carbonaceous matter.

3. Oxidation of ammonia to nitrates simply converts dissolved oxygen to a form from which it is still available to prevent formation of anaerobic conditions.

The philosophy that unnitrified effluents are not damaging to receiving streams has been undermined by biologists and conservationists who point out that nitrates will not satisfy the oxygen requirements of fish and many other aquatic organisms and by the river and stream investigations of Gannon[1] and the Michigan Water Resources Commission, as reported by Courchaine[2].

As a result of the studies conducted in Michigan, many states are now requiring that NOD be considered as well as BOD in any analysis of pollutional loads that streams can bear. This will undoubtedly mean that many plants of the future will be designed to accomplish extensive nitrification, at least during the warmer months of the year when oxidation rates are highest and stream flows are apt to be minimal.

With regard to eutrophication of surface waters, nitrogen in the fixed forms of ammonium and nitrate ions is considered to be one of the major nutrients supporting blooms of green and nonnitrogen fixing blue-green algae. Its removal from wastewaters is being requested in some areas and considered in many others. Where discharge is to lakes or reservoirs with significant detention times, seasonal removal will not suffice and 365-day per year performance will be expected. Removal through nitrification followed by denitrification represents the most promising method at this time. It has the advantage of returning nitrogen to the atmosphere in its natural form.

Nitrification and Population Dynamics

It seems certain at this time that nitrification will play a greater and greater role in wastewater treatment in the future because of anticipated increased NOD removal requirements and possible use of systems employing nitrification-denitrification for nitrogen removal.

It is conceivable that NOD removal will be a seasonal requirement in most locations and will occur during the warm months of the year. If so, then conventional designs of biological systems, similar to those used prior to 1930 or any which are capable of maintaining conditions so that the reciprocal growth rate of the nitrifying bacteria is less than the mean cell residence time or sludge retention time as described by Jenkins and Garrison[3], will be required. In simple terms, this means that nitrification in plants can be maintained only when the rate of growth of nitrifying bacteria is rapid enough to replace organisms lost through sludge wasting. When they can no longer keep pace, the ability to nitrify decreases and may become extinct.

It has been quite well established that no treatment plants, including those of the extended aeration type, are capable of accomplishing complete nitrification on a year-round basis in our northern states. In situations where nitrogen removal is required and the nitrification-denitrification route is preferred, it will be mandatory to accomplish nitrification in a separate biological system where the reciprocal growth rate can be kept less than the mean cell residence time at all times. This will mean that a large part of the normal BOD will have to be removed before the wastewater enters the nitrification unit. Such a system is shown as Figure 1. It is believed that a BOD of 40 or 50 mg/L can be tolerated in the feed to the nitrification

unit; consequently either high-rate activated sludge or trick-ling filter systems should be acceptable for the first stage of treatment.

Nitrification Kinetics

The response of both nitrite and nitrate forming bacteria in pure culture to various environmental conditions has been extensively studied. The effect of pH upon the respiration rate of Nitrosomonas as reported by Meyerhof[4] and Engel and Alexander[5], is shown on Figure 2 and the effect upon Nitrobacter, as reported by Meyerhof[6] is shown as Figure 3.

Early studies on nitrification in wastewater treatment were mainly related to its control to prevent "rising sludge" problems in the activated sludge process. These brought dissolved oxygen under close scrutiny, since it was the only environmental condition that could be considered readily controllable under normal operating conditions. Bragstad and Bradney[7] reported that dissolved oxygen must be kept below 0.5 mg/L to control nitrification. Recently, Downing et al[8] and Jenkins and Garrison[3] have reported on other aspects affecting nitrification and Zanoni[9] investigated the effect of temperature on the velocity constant for nitrification in treated effluents.

Our study was prompted by three major considerations:

1. A paper by Borchardt[10] which indicated that temperature had little effect on nitrification in the range of 15 to 35 deg C (see Figure 4), in opposition to published data[11].

2. A lack of information on sludges in systems
    receiving feed stock containing relatively
    low BOD.

3. A considered need to establish a quantitative
    basis for evaluating the ability of nitrifying
    sludges to convert ammonia to nitrate, under
    various temperature and pH conditions.

Method of Study

The investigations to be described were conducted at
Marlborough, Massachusetts, where a 10-gpm pilot nitrification
unit, receiving settled high-rate trickling filter effluent,
was operated, open to the weather from October 1969 through
April 1970. All observations on the effects of dissolved
oxygen were made in the pilot plant. The studies on the in-
fluence of temperature and pH were made in the laboratory
using return sludge from the nitrification unit and settled
trickling filter effluent in the apparatus shown as Figure 5.
The batch studies on pH and temperature were conducted with
dissolved oxygen levels above 2 mg/L to ensure that it would
not be an inhibiting factor.

Experimental Results

Pilot Plant

The results of measuring the dissolved oxygen in the
aeration tank of the pilot plant and the resulting effluent
quality are indicated on Figure 6. The dissolved oxygen

concentration was measured twice daily and found not to have a significant variance during any given day. The effluent ammonia nitrogen concentration was taken from a 24-hour composited sample.

The wide range of dissolved oxygen concentration resulted from breakdowns in one of the two available compressors and a varying demand for air at other locations.

Figure 6 indicates that there was apparently no inhibition of nitrification occurring at dissolved oxygen levels exceeding 1.0 mg/L.

Laboratory

The laboratory studies were concerned with determining the effect of temperature and pH under carefully controlled conditions. The procedure used involved collection of samples of return sludge from the nitrification pilot plant and of settled trickling filter effluent, determination of suspended and volatile suspended solids in the return sludge, and the adjustment of portions of each to definite pH and temperatures before making the desired mixtures in the aeration units. In most instances, the trickling filter effluent was supplemented with a dilute aqueous solution of ammonium chloride in order to give runs of sufficient duration to obtain three or more experimental values.

The rate of nitrification was determined by measuring residual ammonia nitrogen on grab samples of mixed liquor which were filtered immediately after collection. Dissolved oxygen,

pH, and temperature were monitored continuously during the course of each study. Dilute sodium hydroxide was added to control pH as needed. The system of study may have involved some slight loss of ammonia at pH levels above 8.5 but such losses were too insignificant to be detected from a plotting of the data.

It was assumed that the relative population of nitrifiers in the total MLVSS concentration for the duration of the study remained constant. It is felt that this assumption was justified due to the long duration of the pilot studies run under the same conditions, employing settled trickling filter effluent as feed stock.

Mixed Liquor Volatile Suspended Solids. The nitrification studies were conducted with MLVSS concentrations within the range of 800 to 6,000 mg/L.

A sample of two of the experiments run at the same pH and temperature conditions but with two different mixed liquor volatile suspended solids is shown on Figure 7. It was observed that the time to completely nitrify the same amount of ammonia nitrogen per gram of MLVSS was constant given the same environmental conditions. This allows direct comparisons to be made for different MLVSS concentrations in the study and permits subsequent data to be expressed in terms of mg of ammonia nitrogen per mg of MLVSS.

Ammonia. The augmented ammonia nitrogen concentrations for the studies varied from 6 to 60 mg/L. The ammonia nitrogen concentration had to be augmented on many occasions because the

time required for complete nitrification of low levels was so short that only one or two samples could be analyzed prior to attaining the zero level. Two sample results are shown on Figure 8. Both of the experiments were conducted at the same pH and temperature conditions. As can be seen from the figure, the slopes of the lines are parallel and constant for all residual concentrations of ammonia nitrogen regardless of the initial concentration. This would indicate that nitrification is not inhibited at concentrations normally found in a domestic wastewater system. This also allows adjustment of other data for different ammonia nitrogen concentrations by constructing a line parallel to the experimental line at the desired concentration.

BOD. A special study was made to determine the effect of variable BOD upon the rate of nitrification. This was accomplished by nitrifying three different samples. The temperature and pH for all three units were the same. The wastewater in the first unit was primary effluent with a BOD of 110 mg/L, the second unit contained settled trickling filter effluent with a BOD of 45 mg/L, and the third unit contained nitrification effluent from the pilot plant with a BOD of 5 mg/L. All samples were augmented with enough ammonium chloride to give a reasonable duration for the test.

Figure 9 shows the results of this special study. Within the limits of the study, there was no apparent inhibition of

nitrification for the various BOD concentrations. It should be realized that this study was undertaken to determine the reaction of the nitrifiers to a shock loading of BOD and that any sustained high BOD loading would eventually cause nitrification to cease, due to the washing out effect wasting of sludge would have on the nitrifiers. This is concluded because of the low growth rate exhibited by the nitrifiers as compared to those organisms utilizing carbonaceous BOD and the established fact that an increased BOD loading in a conventional system leads to greater sludge production.

pH. The pH range investigated in these studies was from 6.0 to 10.5. The samples were adjusted to the desired pH level and maintained at that level for the duration of the experiment. The ammonia nitrogen weight per MLVSS weight ratio of the grab samples was plotted against time and all the other variables were noted. The time plot allowed calculation of the exact time of complete nitrification, i.e., complete oxidation of ammonia. A sample graph is presented on Figure 10. This graph shows two sample results both of which were obtained at a temperature of 20 deg C. The pH of one sample was 8.5 and the other 6.5. The figure also shows an adjusted line to compensate for different initial concentrations of ammonia.

Three factors are immediately evident from the preceding figure.

1. There was no apparent initial uptake of ammonia
    nitrogen by the nitrifiers.

2. There was no lag time involved in the rate
    of nitrification.

3. The rate was uniform and constant for the entire
    length of the experiment. This indicates that
    the nitrifiers work at maximum efficiency at
    all times independent of the residual concen-
    tration of ammonia nitrogen.

Our studies indicate an optimum pH for nitrification to
be 8.4. Figure 11 indicates that 90 percent of the maximum
rate occurs in the range of 7.8 to 8.9 and that outside the
ranges of 7.0 to 9.8 less than 50 percent of the optimum rate
occurs.

Temperature. The temperature studies covered the range
from 5 deg C to 30 deg C, and nitrification occurred at all
temperatures investigated. The rate of nitrification increased
with temperature throughout the full range. Figure 12 indicates
the straightline relationships for two sample experiments run at
different temperatures but the same pH. One adjusted line is
shown to offset the initial ammonia concentration difference.
There was no lag period observed nor any decrease in the rate of
nitrification as the residual ammonia concentration decreased.

The relationship of the rate of nitrification at all
temperatures studied to the rate at 30 deg C is indicated on
Figure 13. Since 30 deg C is a very high wastewater temperature
for all but the most southerly states in the United States, a

summary of relative rates in terms of other maximum temperatures is as shown in Table 1, based upon the data of Figure 13.

Table 1. Relative Rates of Nitrification
at Various Temperatures

Temperature deg C					
30	25	20	15	10	5
100	80	60	48	27*	12*
	100	75	60	34	16*
		100	80	45	21

*Abnormal temperatures for maximums stated.

These data indicate, on the basis of temperature alone and the most adverse conditions considered possible, that up to five times the detention time may be needed to accomplish complete nitrification in the winter as is needed in the summer. However, temperature effects can be overcome to a considerable degree by increasing mixed liquor suspended solids and adjustment of pH to more favorable levels. Optimum design for complete nitrification will depend upon the best combination of aeration tank capacity, mixed liquor suspended solids, and pH for winter operating conditions. Under summer conditions, operation will be possible at less favorable pH levels and lower mixed liquor solids.

Discussion

When all of the above information is evaluated, rates of nitrification can be computed. The rate of nitrification has been defined as the weight ratio of ammonia nitrogen oxidized per day to the mixed liquor volatile suspended solids.

The rates for any pH within the range of 6.0 to 10.5 are shown on Figure 14. All of the rates are for a temperature of 20 deg C. As can be seen from the figure, the rate varies from a maximum of 0.185 g NH_3-N nitrified per day per g MLVSS at a pH of 8.4 to a minimum of 0.020 g NH_3-N nitrified per day per g MLVSS at a pH of 6.0.

The results obtained in this study with respect to pH show good correlation with the results indicated in the previous section of the paper on work performed by others.

Our results on temperature effects are opposed to what was observed at Ann Arbor, Michigan, and reported by Borchardt[10] as shown on Figure 4. Borchardt's low temperature observations were made in extended aeration studies by measuring the ammonia and nitrate nitrogen in the effluent of the units. It is felt by the authors that the apparent effects of temperature were observed because the units were not being stressed to their limit of nitrification at the higher temperatures and complete nitrification was being obtained in less time than the detention time of the units. As the temperature decreased, the time required to obtain complete nitrification approached the detention time of the units and when the temperatures dropped low enough, the time required for complete nitrification exceeded the detention time and this lesser percent of nitrification was noted. Our results are from units which were stressed to their capacity at all times, and indicated an immediate drop in efficiency as the temperatures decreased, which is in agreement with results reported by Sawyer and Rohlich[11].

Figure 15 gives the expected rate of nitrification compared to temperature for various selected pH conditions. This figure allows the computation of the time required for complete nitrification at any MLVSS concentration, ammonia nitrogen concentration, temperature, and pH.

The curve at the optimum pH of 8.4 was determined from information gathered during the course of the study. The curves for 75 percent and 50 percent of the optimum rates were computed from the rates experienced at pH 8.4 The pH values for the 75 percent and 50 percent curves were obtained from Figure 11.

From a practical standpoint, Figure 15 indicates that if the nitrification system were run at 50 percent of the optimum conditions, the time required to completely oxidize the ammonia nitrogen would double or the MLVSS would have to be carried at twice the level necessary for complete nitrification under optimum conditions.

Summary

The preceding may be briefly summarized as follows:

1. The ammonia nitrogen concentration did not inhibit nitrification in concentrations of less than 60 mg/L.

2. pH did affect the rate of nitrification. Optimum pH was found to be 8.4.

3. Temperature did affect the rate of nitrification. The rate increased through the range of 5 deg C to 30 deg C, in reasonable agreement with the van't Hoff-Arrhenius law.

4. The time required for nitrification is directly proportional to the amount of nitrifiers present in the system.

5. Instantaneous increases or decreases in BOD concentration from 50 mg/L to 5 or to 110 mg/L did not affect the rate of nitrification. However, it would be expected that a change in the average BOD concentration of the feed would affect that percentage of MLVSS which is composed of nitrifiers, and as a result would affect the time to achieve complete nitrification.

Acknowledgments

Special appreciation is extended to Mr. John Hartley, Superintendent, and the staff of the Marlborough Easterly Treatment Plant. Their work on the installation and help in operation of the nitrification pilot plant contributed immeasurably to the success of the project.

REFERENCES

1. Gannon, J. J. "River BOD Abnormalities". Bull. 05168-1-F, The University of Michigan, Office of Research Administration, Ann Arbor, Michigan.

2. Courchaine, Robert J., "Significance of Nitrification in Stream Analysis - Effects on the Oxygen Balance." This Jour., 40, 835 (1968).

3. Jenkins, D. and Garrison, W. E., "Control of Activated Sludge by Mean Cell Residence Time". This Jour. 40, 1905 (1968).

4. Meyerhof - Arch. f. die ges Physiologie, 166, 255 (1917).

5. Engel, M. S. and Alexander, M., "Growth and Autotrophic Metabolism of Nitrosomonas Europaea". J. Bact., 76, 217 (1958).

6. Meyerhof - Arch. f. die ges Physiologie, 164, 416 (1916).

7. Bragstad, R. E. and Bradney, L., "Packing House Waste and Sewage Treatment at Sioux Falls, South Dakota". Sewage Works J., 9, 959 (1937).

8. Downing, A. L., Painter, H. A., and Knowles, G., "Nitrification in the Activated Sludge Process". Jour. Inst. Sewage Purif. (Brit.) Part 2, 130 (1964).

9. Zanoni, A. E., "Secondary Effluent Deoxygenation at Different Temperatures", This Jour., 41, 640 (1969).

10. Borchardt, J. A., "Nitrification in the Activated Sludge Process", Bull. "The Activated Sludge Process". The University of Michigan, Division of Sanitary and Water Resources Engineering", Ann Arbor, Mich.

11. Sawyer, C. N. and Rohlich, G. A., "The Influence of Temperature upon the Rate of Oxygen Utilization by Activated Sludge". Sewage Works J., 11, 946 (1939).
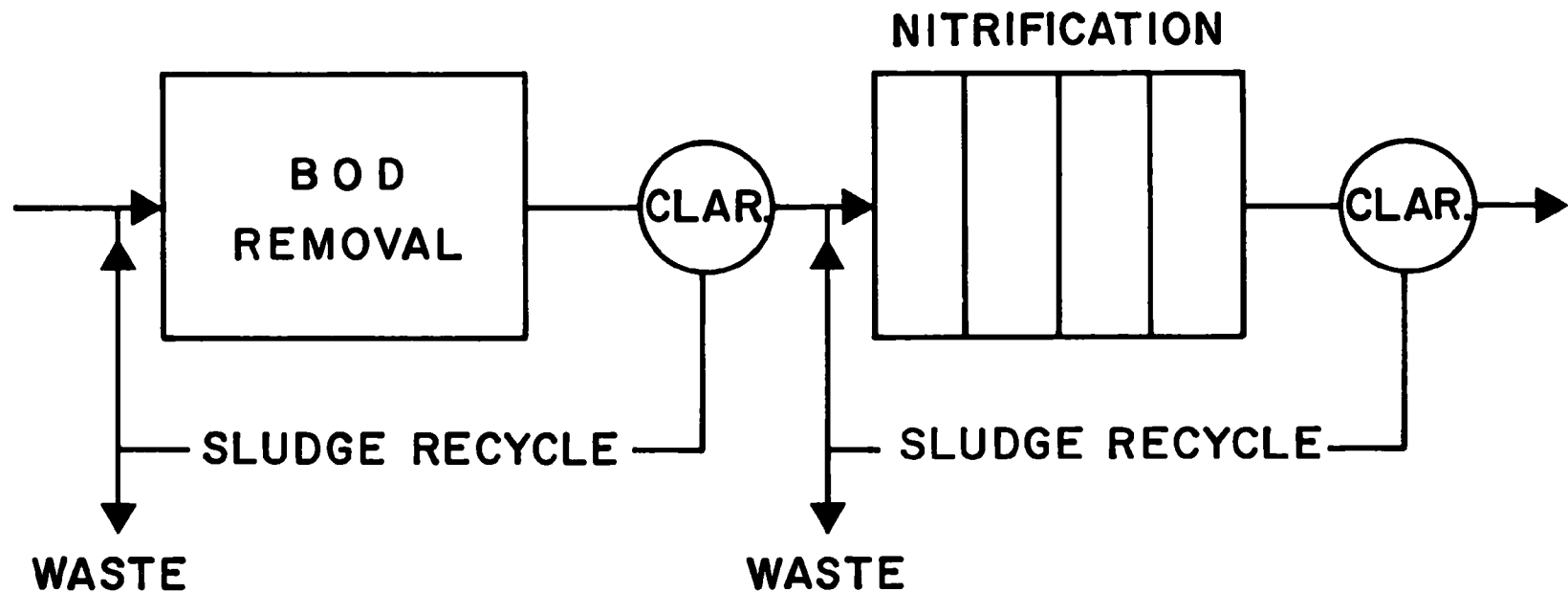
FIG. I   TWO STAGE BIOLOGICAL SYSTEM REQUIRED
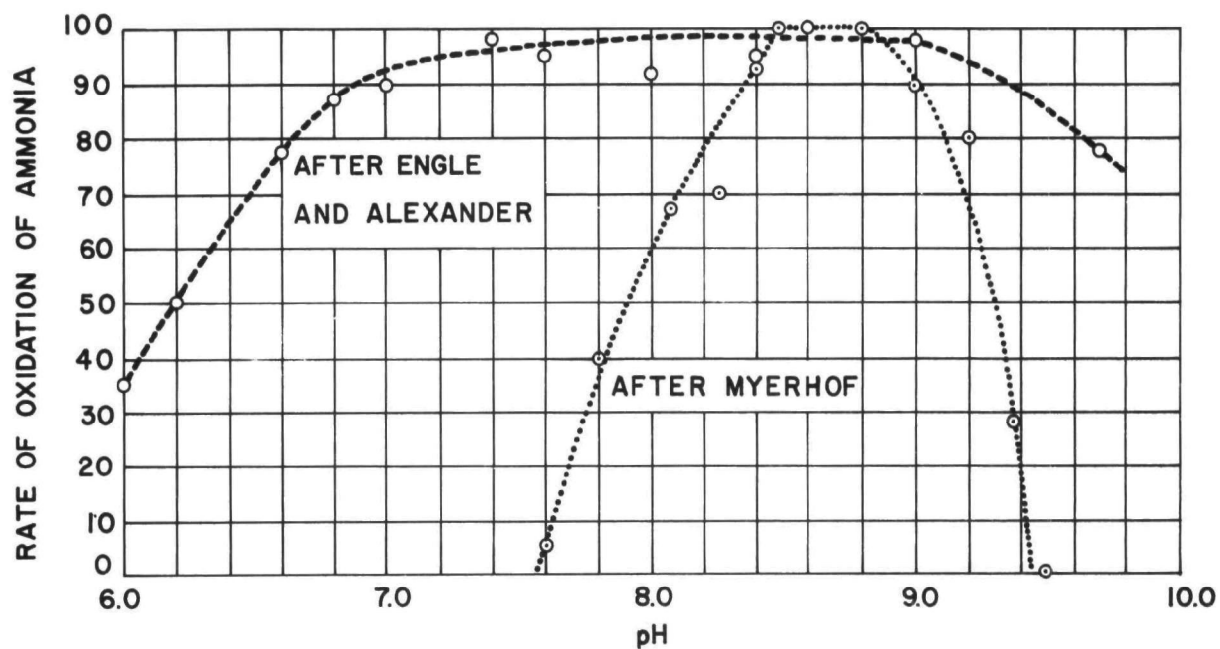TO GUARANTEE COMPLETE NITRIFICATION

FIG. 2   THE EFFECT OF pH ON OXIDATION OF
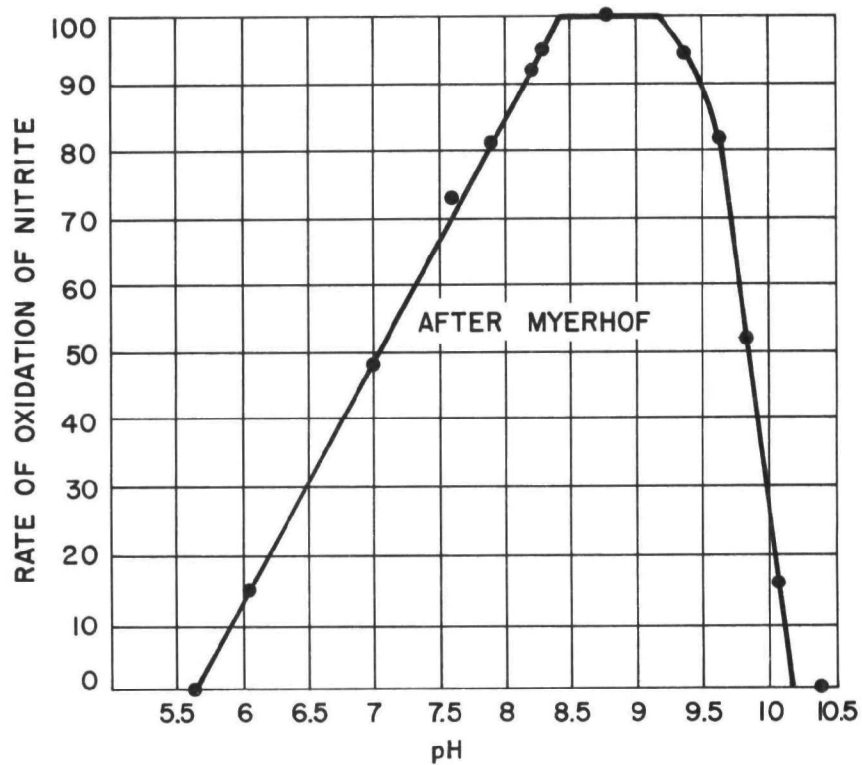AMMONIA BY NITROSOMONAS
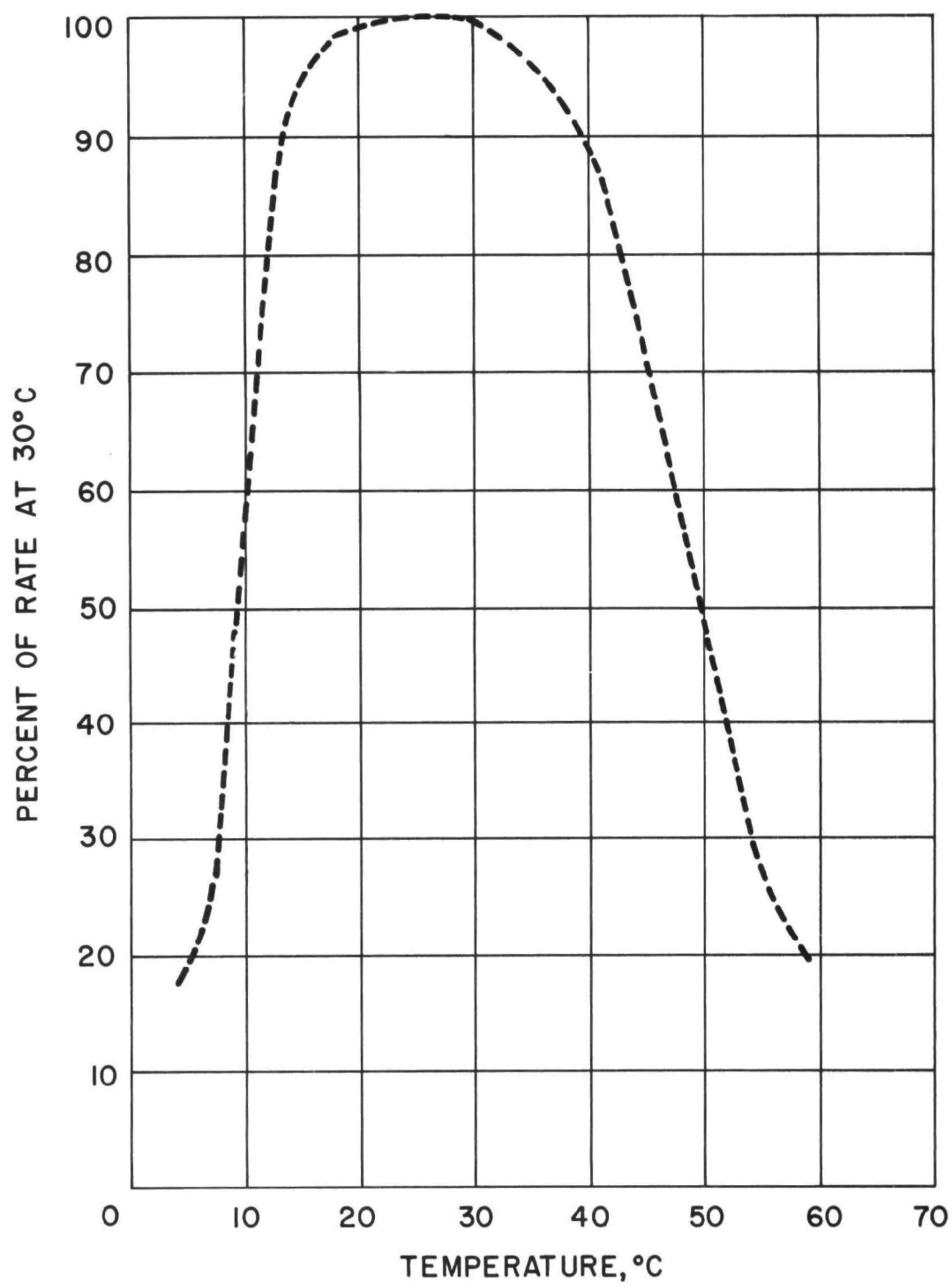

FIG. 3   RATE OF OXIDATION OF NITRITE
BY NITROBACTER

FIG. 4 EFFECT OF TEMPERATURE ON
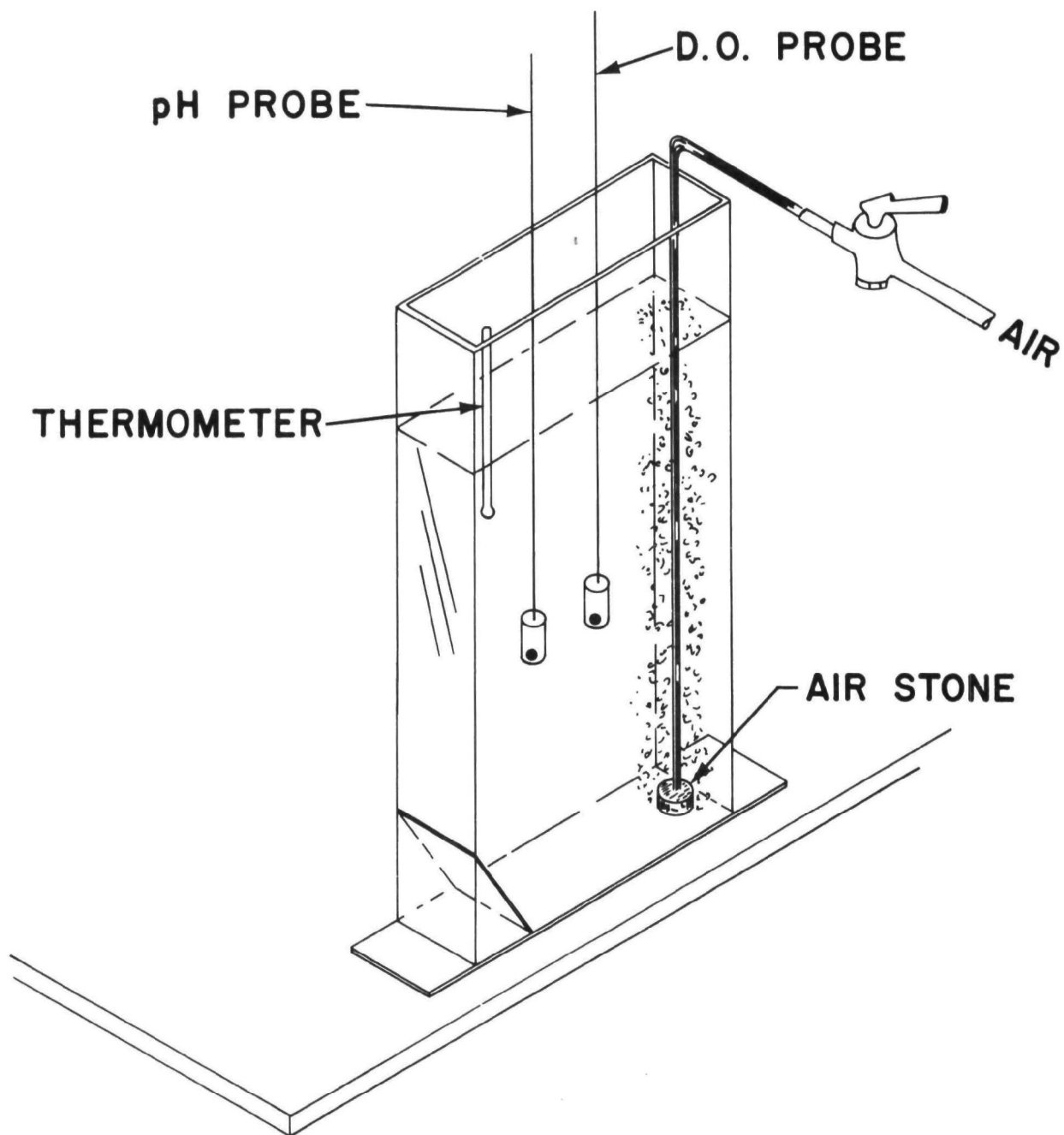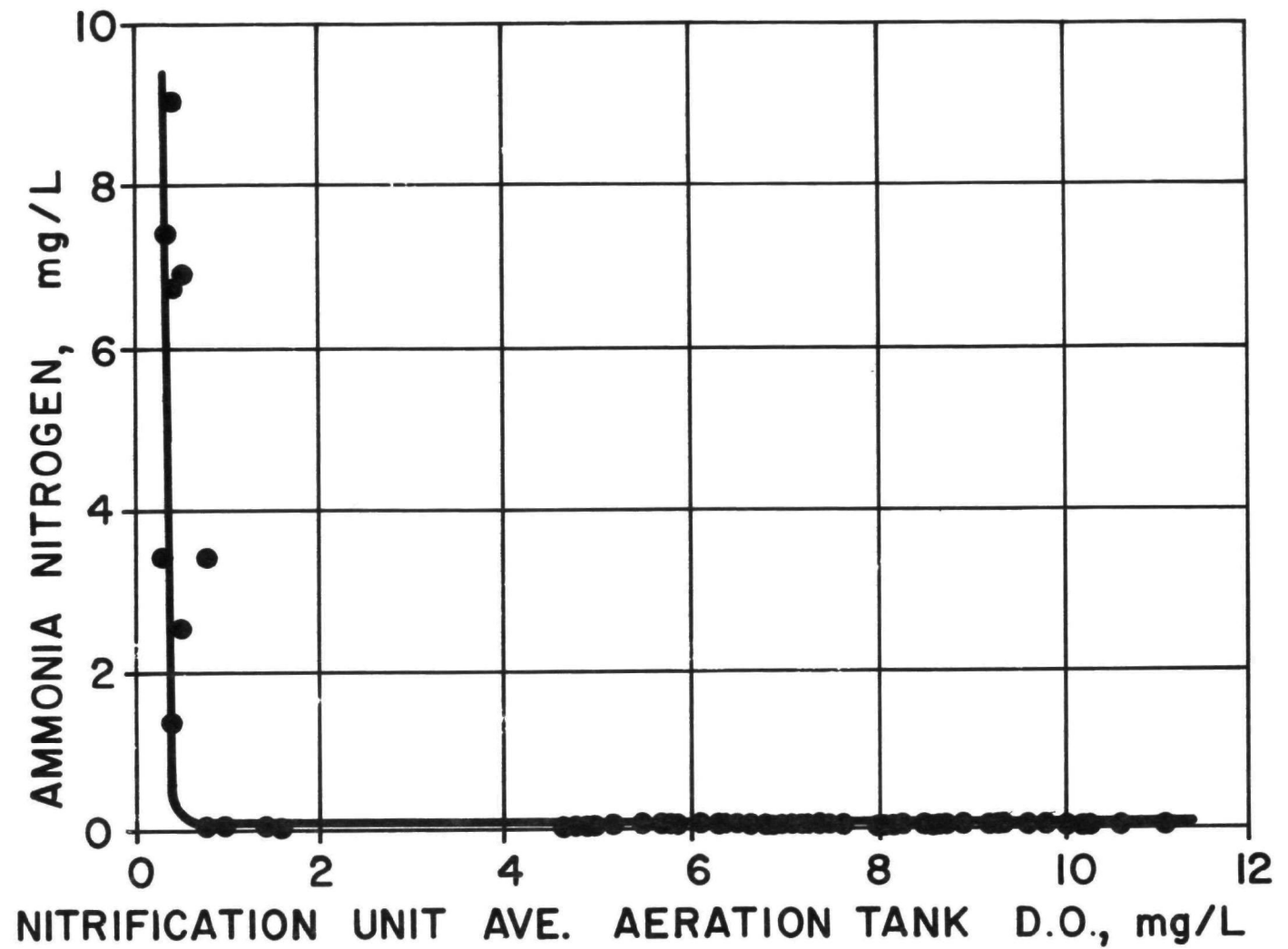NITRIFICATION AS REPORTED BY
BORCHARDT (10)

pH PROBE

D.O. PROBE

THERMOMETER

AIR

AIR STONE

FIG. 5   LABORATORY   AERATION   UNIT

METCALF & EDDY

FIG. 6   RELATIONSHIP OF RESIDUAL
AMMONIA TO DISSOLVED OXYGEN
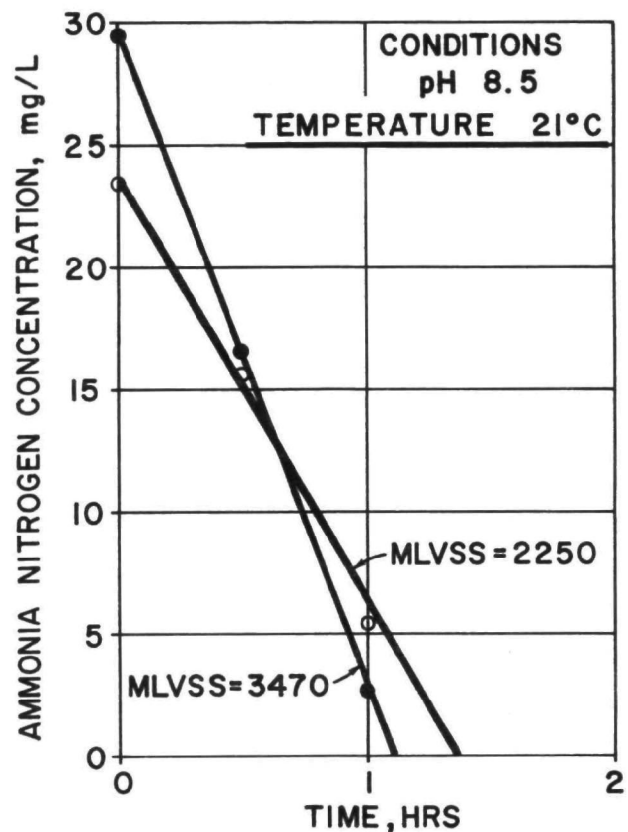
FIG. 7   EFFECT OF VARIATION
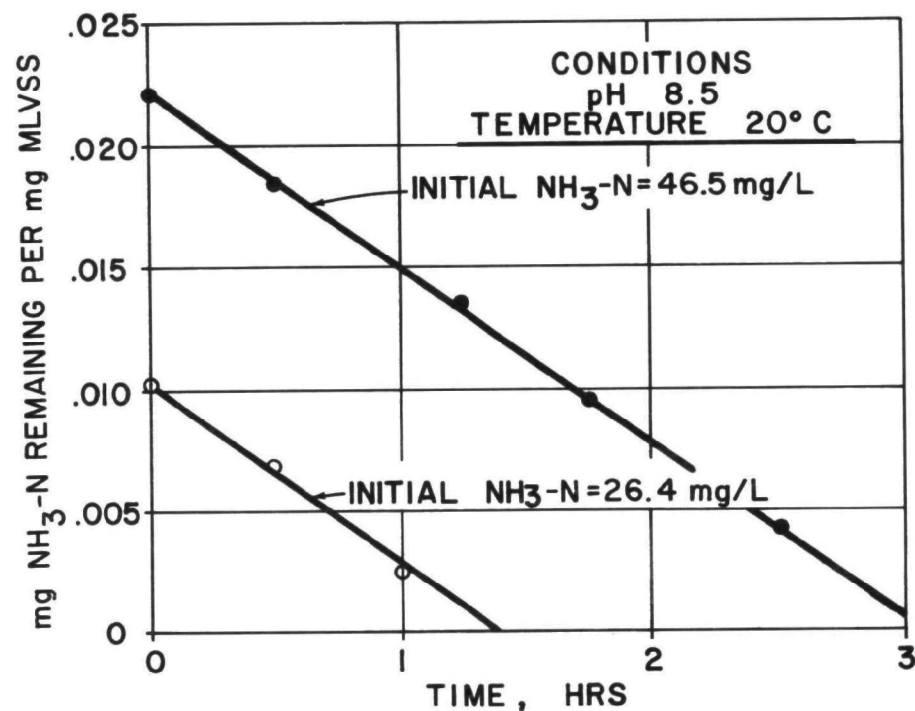IN MIXED LIQUOR VOLATILE
SUSPENDED SOLIDS

FIG. 8   EFFECT OF VARIATION
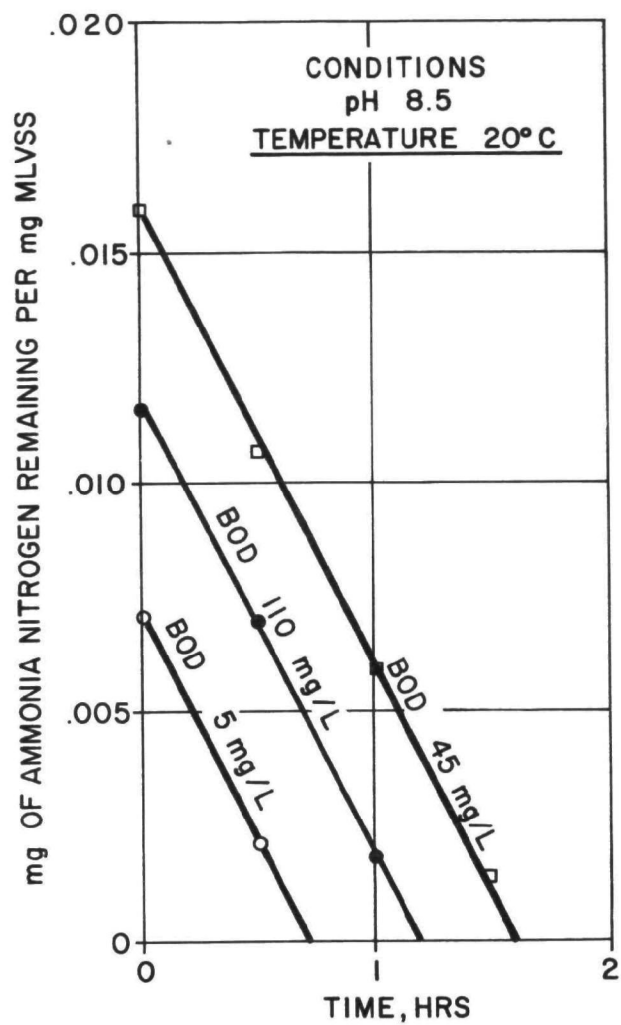IN AMMONIA CONCENTRATION

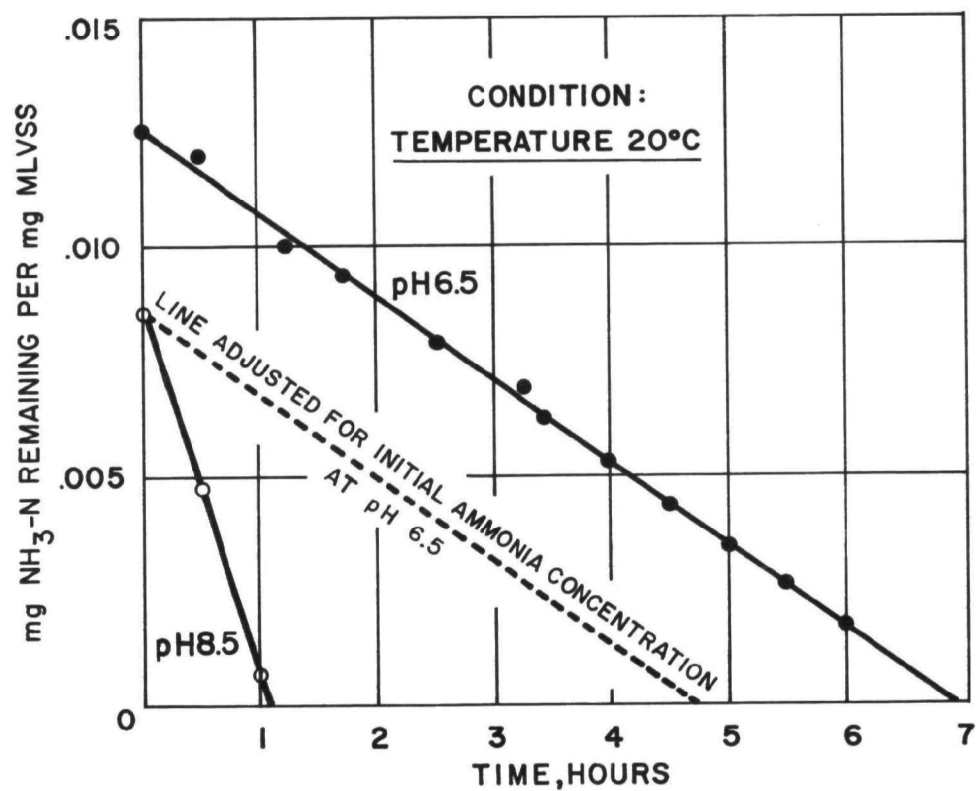FIG. 9   EFFECT OF VARIATION
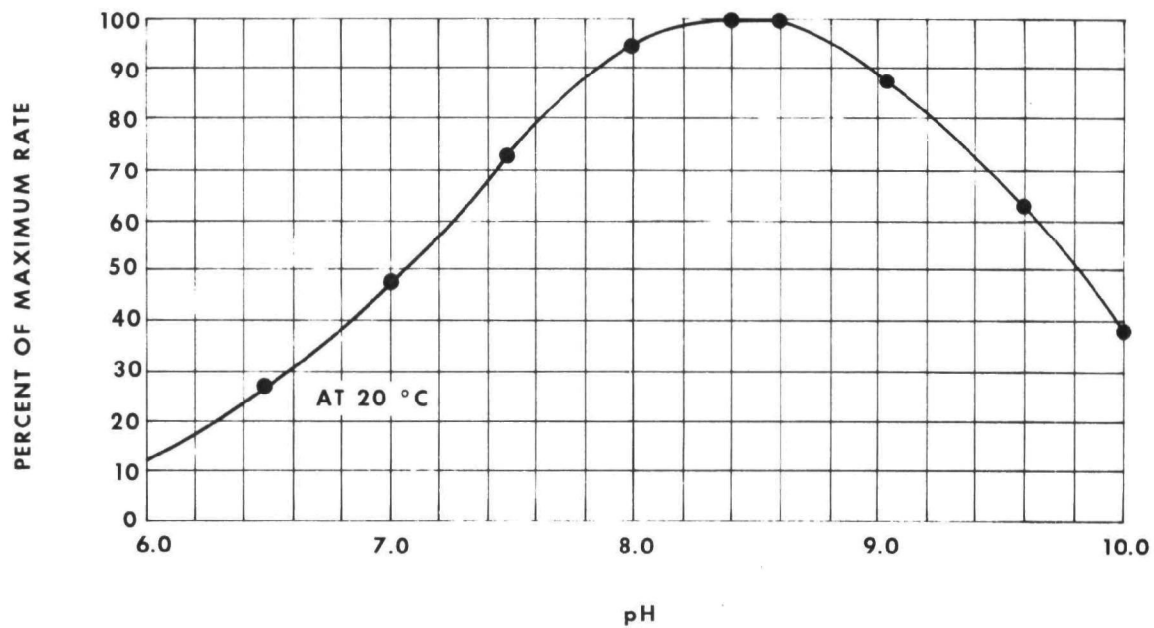IN BOD

FIG. 10   EFFECT OF VARIATION IN pH

FIG. 11 PERCENT OF MAXIMUM RATE OF NITRIFICATION
AT CONSTANT TEMPERATURE vs pH
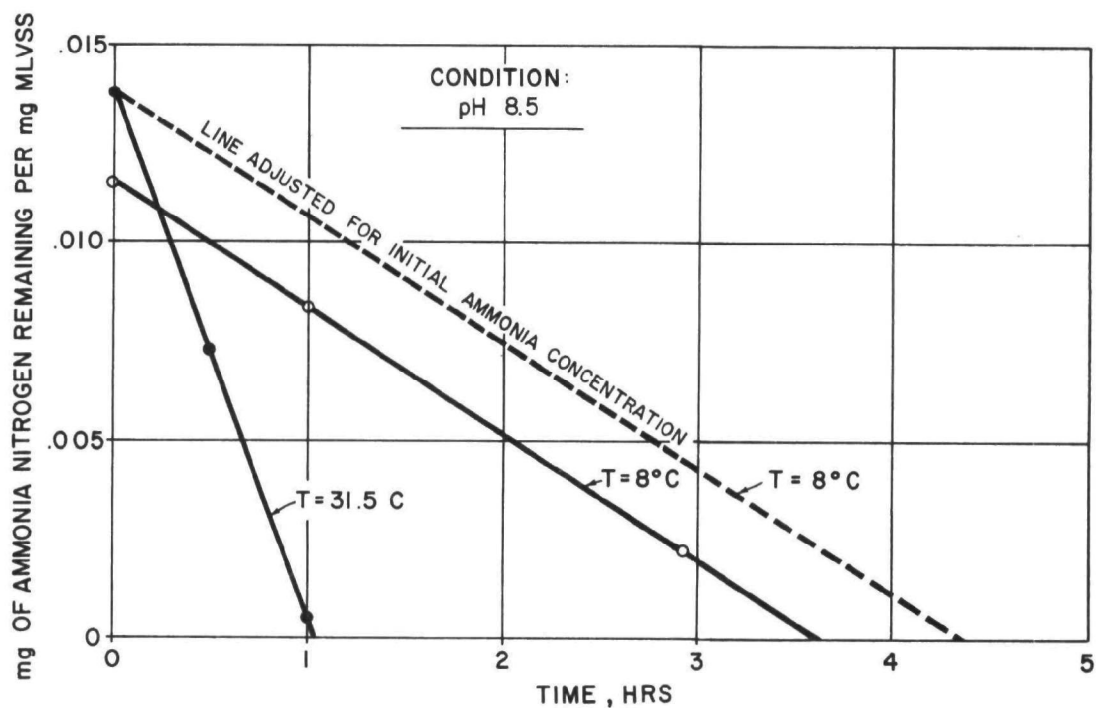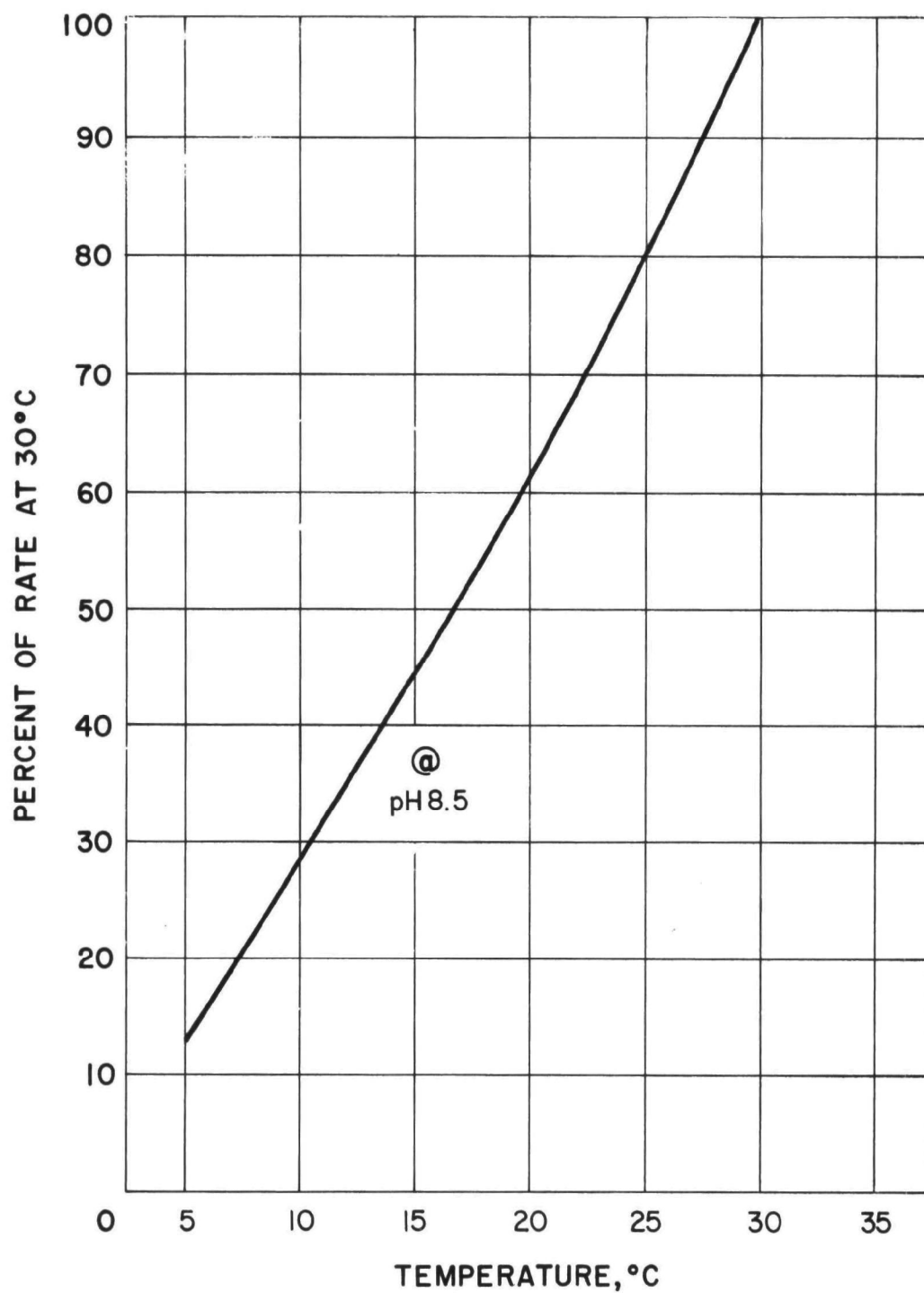

FIG. 12 EFFECT OF VARIATION IN TEMPERATURE

FIG. 13   RATE OF NITRIFICATION
AT ALL TEMPERATURES
COMPARED TO THE RATE
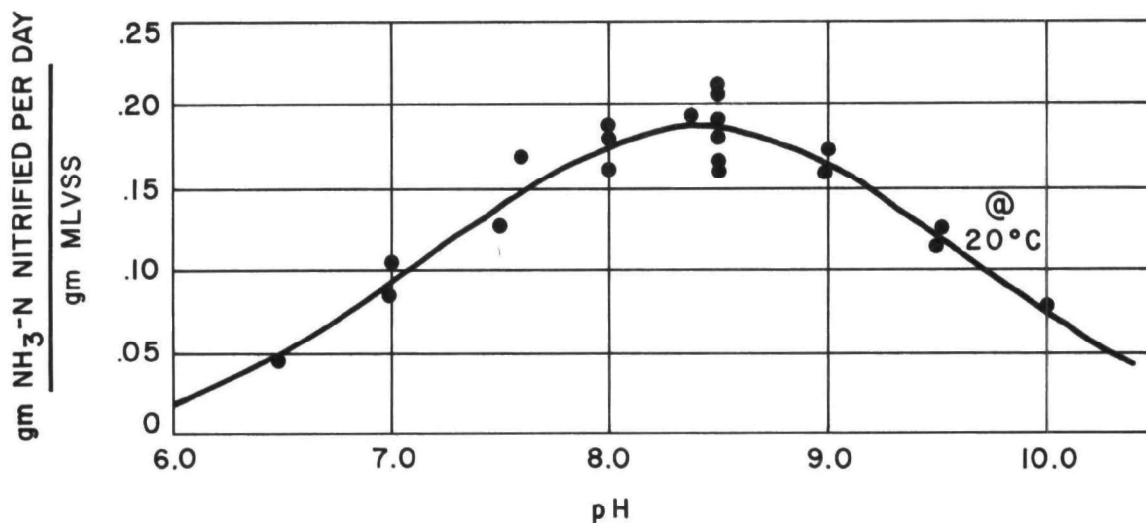AT 30 DEGREES C

FIG. 14   RATE OF NITRIFICATION vs pH AT
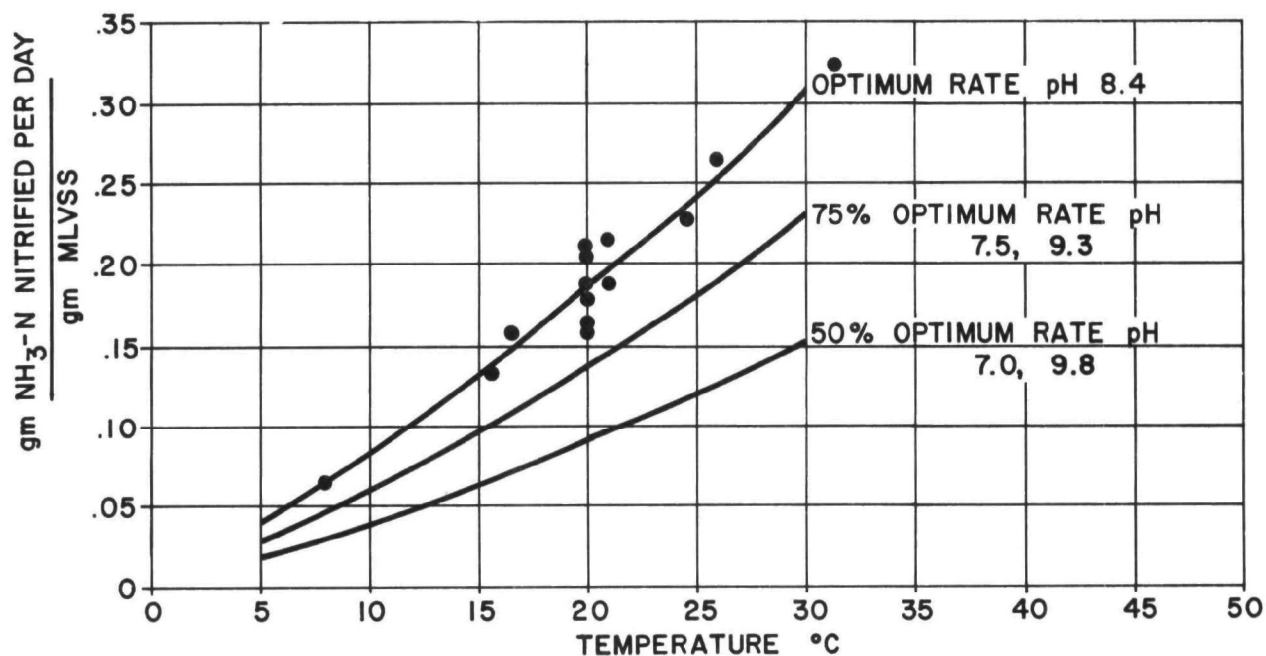CONSTANT TEMPERATURE

FIG. 15   RATE OF NITRIFICATION vs TEMPERATURE
AT VARIOUS pH LEVELS

CHAPTER 2

NITRIFICATION AND DENITRIFICATION

Nitrification and denitrification have been well recognized phenomena in wastewater treatment for many years. The former occurred to the greatest degree during the warmer months of the year and was considered highly beneficial in most instances because of the oxygen resource that the nitrates provided. Because of additional capital and operating costs required to produce nitrates, American engineers, in general, attempted to design or use processes which minimized nitrification.

The problems of "rising sludge" in conventional activated sludge and standard rate trickling filter plants were shown to be due to denitrification. The common way of controlling the problem was to limit nitrification.

The Michigan studies on the significance of nitrogenous oxidation (NOD) in creating oxygen sag in receiving streams and other studies showing the role of ammonia and nitrate nitrogen in stimulating algal blooms have demonstrated the need for information on how wastewater treatment plants can be designed to accomplish nitrification and denitrification. Figure 2-1 shows the facilities required to accomplish both in a controlled manner.

A three-stage biological system is considered necessary in northern climates where wastewater temperatures drop below

65 deg F (18 deg C). The first stage is necessary to remove carbonaceous BOD_5 to levels of about 50 mg/L. The second stage is needed to accomplish nitrification and should be designed to employ the plug-flow principle as closely as possible. The third stage accomplishes denitrification. A source of carbonaceous BOD must be added to reduce the nitrates to nitrogen gas in a reasonable period of time.

CARBONACEOUS
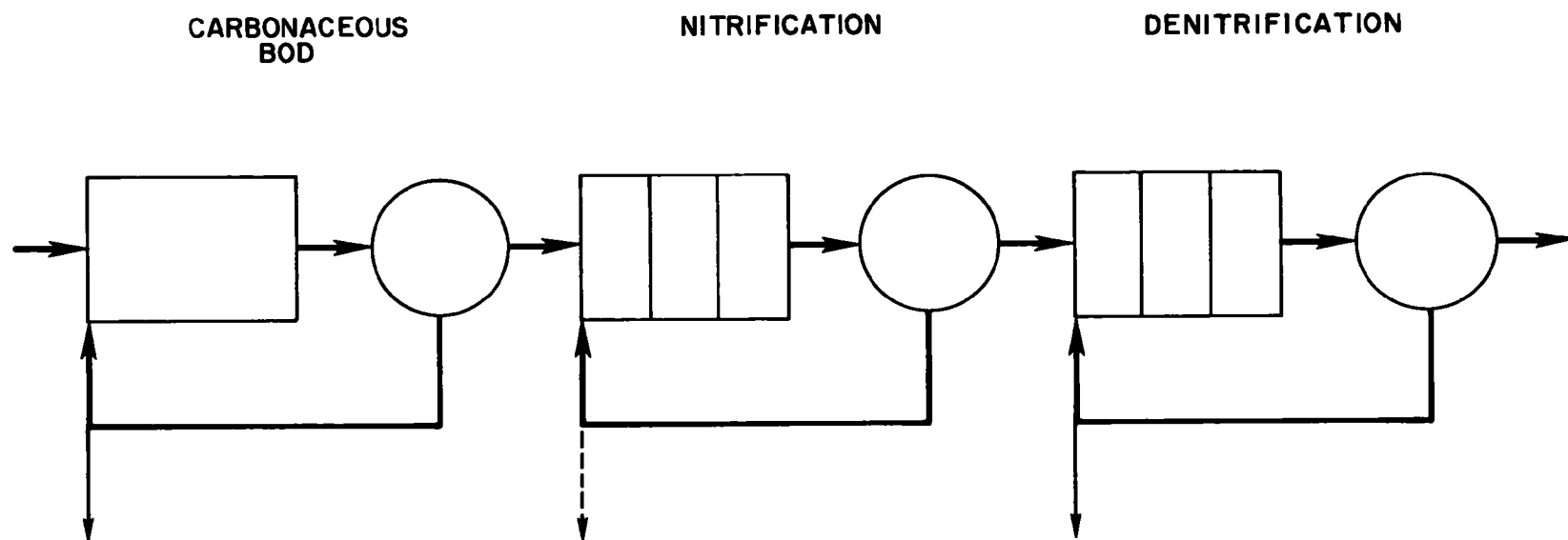BOD

NITRIFICATION

DENITRIFICATION

FIG. 2-1 MODEL SYSTEM FOR NITRIFICATION AND DENITRIFICATION

CHAPTER 3

DESIGN CRITERIA OF NITRIFICATION SYSTEMS

Discussed below are the design criteria which appear to be reasonable at this time (Oct., 1972). It must be emphasized that these criteria are based solely upon pilot plant experience.
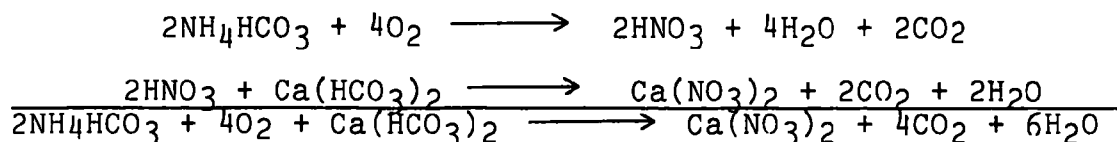
NITRIFICATION TANKS

Tank Layout

Because the rate of oxidation of ammonia is essentially linear (zero order reaction), short circuiting must be prevented. The tank configuration should ensure that flow through the tank follows the plug-flow mixing model as closely as possible. This can be accomplished by dividing the tank into a series of compartments with ports between them. Three compartments is a minimum number as shown on Figure 3-1. Tanks can be designed for either diffused air or mechanical aeration systems.

Since the oxidation rate of the process varies widely with temperature, special provisions may be necessary to incorporate the necessary flexibility in the oxygen supply system, as discussed hereinafter.

pH Control

Nitrification tanks should be sized to permit complete nitrification under the most adverse combination of ammonia load and temperature expected and at a pH as near optimum as feasible. The range of 7.6 - 7.8 is recommended in order to allow carbon dioxide to escape to the atmosphere.

The nitrification process destroys alkalinity and the pH may fall to levels which will inhibit nitrification

$$2NH_4HCO_3 + 4O_2 \longrightarrow 2HNO_3 + 4H_2O + 2CO_2$$

$$\underline{2HNO_3 + Ca(HCO_3)_2 \longrightarrow Ca(NO_3)_2 + 2CO_2 + 2H_2O}$$
$$2NH_4HCO_3 + 4O_2 + Ca(HCO_3)_2 \longrightarrow Ca(NO_3)_2 + 4CO_2 + 6H_2O$$

unless excess alkalinity is present in the wastewater or lime is added to maintain favorable pH levels. Theoretically, 7.2 pounds of total alkalinity are destroyed per pound of ammonia nitrogen oxidized to nitrate. One-half of this is due to loss of alkalinity caused by ammonia and the remainder is due to destruction of natural alkalinity, as shown in the equations above.

Whether or not lime additions will be required depends upon the alkalinity of the wastewater and the desired pH of operation. For operation under the most adverse temperature conditions and at operating pH, sufficient lime must be added initially to raise the pH into the desired range and then 5.4 pounds of hydrated lime per pound of ammonia nitrogen will be required to maintain the pH. An actual titration test should be conducted to obtain design criteria. In Boston sewage, about 250 pounds of hydrated lime are needed per million gallons to raise the pH initially to optimum pH range and an additional 700 pounds to hold it there during the course of oxidation of the ammonia. The total hydrated lime requirements are estimated to be about 115 mg/L. Additional amounts of lime may be required if chemicals, such as alum, have been added previously for phosphorus removal.

Marked reductions in lime requirements will result in any system that can be designed to operate at pH levels of 7.8 or less because carbon dioxide resulting from destruction of alkalinity and organic matter will be washed out of the liquid phase by air contact. The pH of such systems will vary somewhat with the rate of aeration (ventilation).

The type and sensitivity of the pH control system will depend on the character of the wastewater and the variations in the ammonia load fed to the system. A proposed system for pH control under the most demanding situation is shown as Figure 3-2. In many situations, a lesser degree of control will be feasible, in some none will be needed.

MLSS and MLVSS Concentrations

Designs based upon MLSS concentration alone should be avoided since MLSS will not truly reflect the biological mass in the system. The ratio of MLVSS to MLSS may vary depending on the nonvolatile suspended solids (including residual chemical precipitates) in the feed. The fraction of the MLVSS attributable to nitrifying organisms is as yet unknown. However, for nitrification systems receiving normal secondary effluents, MLVSS concentrations of 1,500 to 2,000 mg/L appear to be safe for design.

Tank Capacity

The choice of the "design peak" load depends upon the circumstances of the specific project, and need not necessarily

be the absolute maximum expected load. For many projects, the use of a peak load factor of 1.5 represents a reasonable peak at low temperature conditions.

Figure 3-3 shows the permissible volumetric loading of the nitrification tanks at a pH of 8.4 and at various temperatures and mixed liquor volatile suspended solids concentrations, based upon the nitrification kinetics studies at Marlborough, Massachusetts[1].

Figure 3-4 shows the corrections that must be applied to the permissible loadings when the pH is different from 8.4. In plants with well buffered wastewater, it may be more economical to provide the additional tankage to permit operation at a lower pH, rather than to add an alkaline material. The following is a sample calculation for computing the tank size:

Sample Calculation for Tank Volume

Given: Design Flow - 10 mgd.

Average NH_3-N concentration to nitrification

tanks - 15 mg/L.

Minimum temperature - 10 deg C.

Operating pH - 7.8.

MLVSS concentration = 1,500 mg/L.

Computed:

1. NH_3 load

a. Average - 10 x 8.34 x 15 = 1,250 lb/day.

b. Maximum - 1,250 x 1.5 = 1,870 lb/day.

2. Tank volume at 10 deg C, MLVSS = 1,500 mg/L.

   a. From Figure 3-3, volumetric loading

      = 8.2 lb/1,000 cu ft.

   b. Tank volume = $\dfrac{1,870}{8.2}$ x 10^3

      = 228,000 cu ft.

3. Tank volume adjusted to pH 7.8 (See Fig. 6-4)

   $\dfrac{228,000}{.88}$ = 260,000 cu ft.

4. Check detention period

   $\dfrac{260,000 \text{ x } 24 \text{ x } 7.48}{10 \text{ x } 10^6}$ = 4.65 hr.

Oxygen Requirements

Stoichmetrically, each pound of ammonia nitrogen that is nitrified requires 4.6 pounds of oxygen. (The amount of ammonia nitrified is usually slightly more than the amount of nitrate measured because some denitrification occurs.) Usually, it is assumed that all of the ammonia fed will be nitrified. An additional oxygen allowance must be made for carbonaceous BOD that escapes from the secondary treatment process.

Nitrification appears to be uninhibited at dissolved oxygen concentrations of 1.0 mg/L or more. Design based on maintaining 3.0 mg/L of dissolved oxygen in the mixed liquor under average loading conditions includes a reasonable factor of safety. Under peak loading the dissolved oxygen concentration may be permitted to fall somewhat but not below 1.0 mg/L.

Sample Calculation for Oxygen Requirements

Given: Design Flow - 10 mgd.

Average NH_3-N concentration - 15 mg/L.

Average BOD - 30 mg/L.

Computed:

1. NH_3 load

   a. Average = 1,250 lb/day.

   b. Maximum = 1,870 lb/day.

2. BOD load = 2,500 lb/day.

3. Oxygen requirement:

   a. NH_3 oxidation -
      1,870 x 4.6 =   8,650

   b. BOD requirements
      2,500 x 1.5   <u>3,750</u>

   c. Total   12,400 lb/day.

To design the aeration system, the total oxygen require-
ment must be corrected to actual operating conditions by the
use of well-known equations incorporating such factors as:

1. Critical wastewater temperature.

2. Minimum dissolved oxygen concentration.

3. Coefficient of wastewater oxygen uptake rate (alpha).

4. Coefficient of wastewater dissolved oxygen satura-
   tion (beta).

5. Altitude of plant.

The rate of nitrification will vary significantly with
temperature and pH, and compensation for this must be made

in the design of the plant. During the summer, the following
methods can be used to match the oxygen demand rate to the
oxygen supply rate:

1. Reduce MLSS concentration.

2. Reduce pH by reducing chemical supply.

3. Reduce tankage in service while increasing
    oxygen supply to the tanks remaining in service.

Miscellaneous

Although the nitrification process will handle the normal
variations in ammonia load found in raw wastewater, experience
at the Washington, D.C. pilot plant indicates that nitrification
in the carbonaceous removal units must be carefully controlled
to ensure stable operation. Experience at South Lake Tahoe,
California, indicates that the addition of 2-8 mg/L of chlorine
to the effluent of the carbonaceous aeration tank will effectively
prevent nitrification.. In addition, excessive amounts, of car-
bonaceous BOD and suspended solids that escape from the carbonaceous
treatment process, such as those associated with "bulking"
sludge caused by filamentous growths, must not be so great that
sludge wasting from the nitrification process causes a washout
of the nitrifying organisms. Carbonaceous BOD concentrations
higher than 50 mg/L in the nitrification influent may interfere
with winter operation.

Foam spray systems have not been found to be necessary
where the MLSS concentration was greater than 2,000 mg/L.

The substances listed below have been shown[2] to have an inhibiting effect on the nitrification process in concentrations greater than those shown:

Halogen substituted phenolic compounds - 0.0 mg/L.

Thiourea and thiourea derivatives - 0.0 mg/L.

Halogenated solvents - 0.0 mg/L.

Heavy metals - 10 to 20 mg/L.

Cyanides and all compounds from which hydrocyanic
   acid is liberated on acidification - 20 mg/L.

Phenol and cresol - 20 mg/L.

SETTLING TANKS

Design information on settling tanks serving nitrification systems is generally limited to pilot plant research studies. The criteria given herein represent what has been determined to date, Oct. 1972.

Surface Loadings. The maximum permissible hydraulic surface loading appears to be approximately 1,000 gpd/sq ft. Average surface loadings should be in the range of 400 to 600 gpd/sq ft. It may be necessary to reduce this loading somewhat if the MLSS concentration is greater than 2,500 mg/L, because of limiting sedimentation tank solids loadings.

Mulbarger[3] noted at the Manassas, Virginia, pilot plant that settling improved in the nitrification settling tanks when alum was added to upstream processes, probably due to carryover of alum floc. It has also been noted that the periodic addition of waste sludge from the carbonaceous treatment process

improves settling. In cases where nitrification units follow, addition of waste sludge from them may facilitate a more rapid buildup of nitrifying organisms.

Number of Tanks. Because of the relatively slow growth and settling rates of nitrifying sludges, it is desireable to provide more than two settling tanks to ensure that the sludge is kept within the system when a tank is down for maintenance and repair. Four tanks is a desirable minimum number.

Depth. Depths of 12 to 15 feet are recommended.

Sludge Collection Equipment. Experiences to date have shown no evidence of rising sludge problems, probably due to complete nitrification and very low residual BOD_c levels. Use of rapid removal suction-type sludge collection equipment is not mandatory although it may be desirable in large circular tanks. The settling tanks should be equipped with skimmers and provision should be made to use the scum system to pump floating sludge, should it ever occur, to the nitrification tank influent.
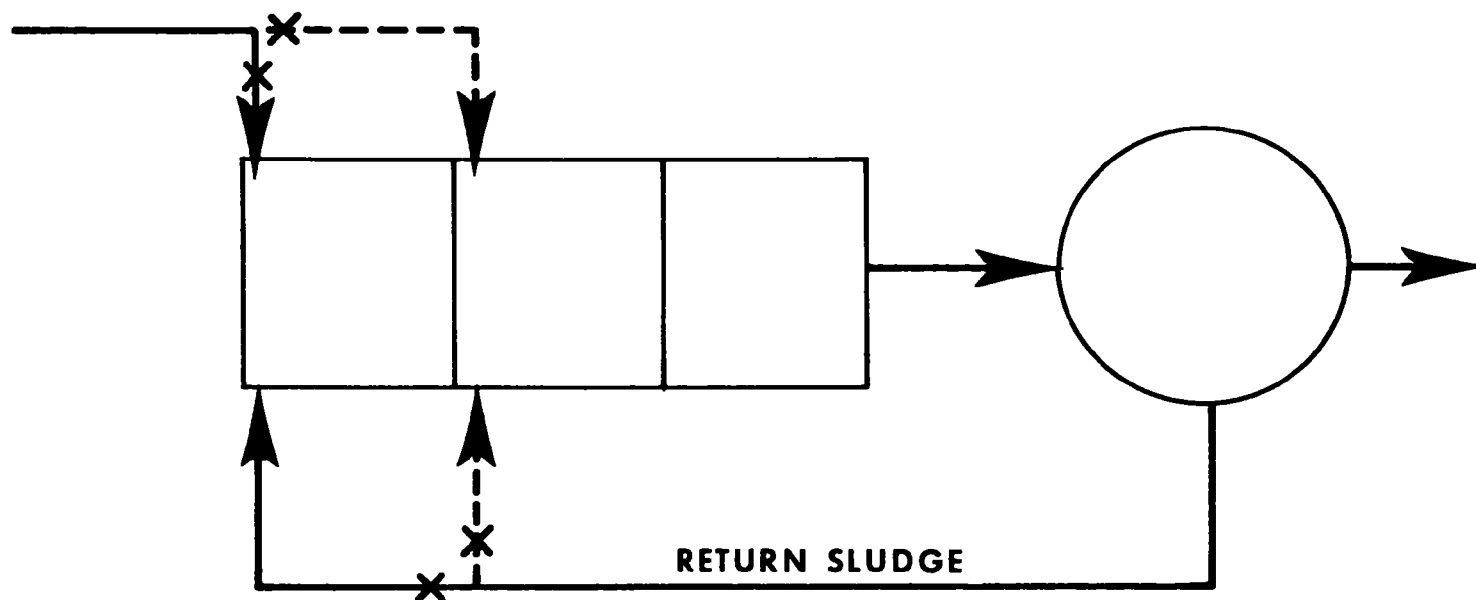
Sludge. It is recommended that capacity be provided for a return sludge rate of 50 to 100 percent of average flow since the nitrification sludge is lighter and does not compact as well as carbonaceous sludges.

Continuous sludge wasting was not normally necessary at the pilot plants at Washington, D.C., and Malborough, Massachusetts. However, periodic adjustments of MLSS concentration are necessary and provisions should be made to dispose of waste

nitrification sludge with the waste sludge from the carbon-
aceous treatment process.

References

1.   See Chapter 1.

2.   Drew, E.A., Chief Engineer, Middle Regional Drainage
      Scheme, England.

3.   Mulbarger, M.C., "The Three Sludge System for Nitrogen
      and Phosphorus Removal." Paper presented at the 44th
      Annual Conference of the Water Pollution Control Federation,
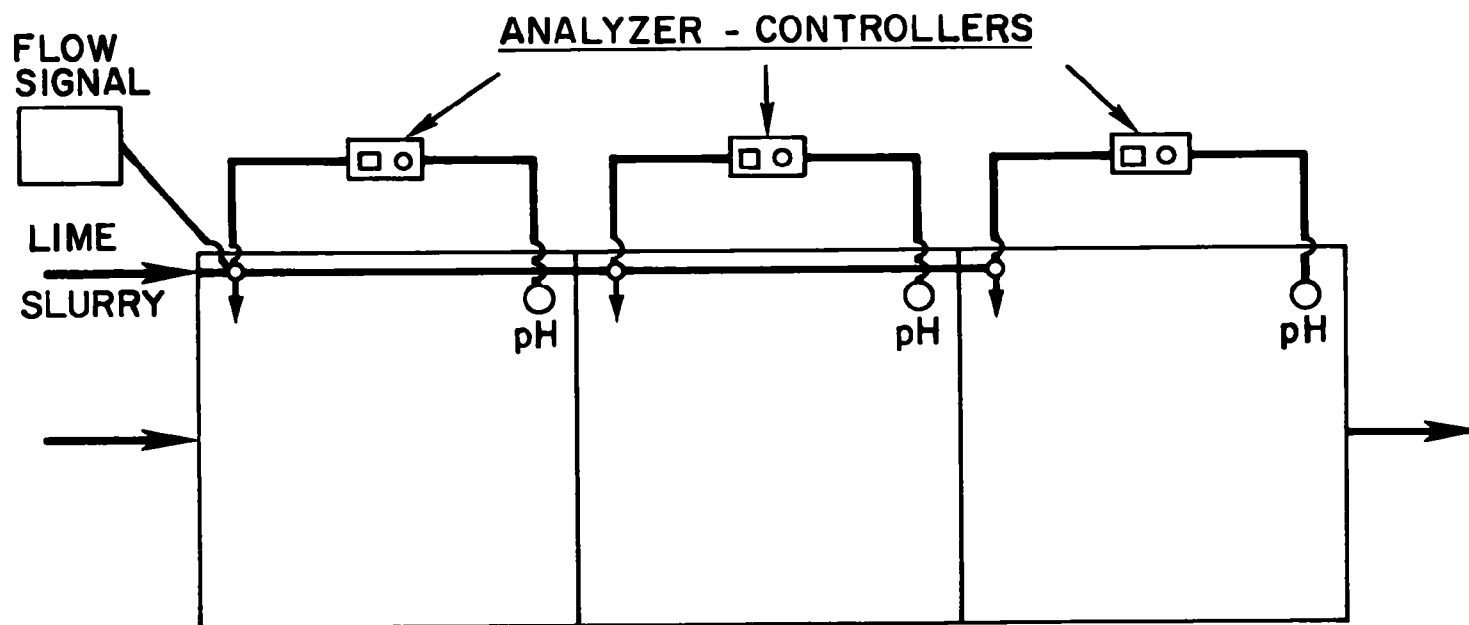   San Francisco, California (Oct 71)

MODEL NITRIFICATION SYSTEM

FIG. 3-1

FLOW
SIGNAL

ANALYZER - CONTROLLERS

LIME

SLURRY

pH

pH

pH

FIG. 3-2 pH CONTROL FOR NITRIFICATION SYSTEM
PLAN VIEW

BASED UPON NITRIFICATION RATES
OBSERVED AT MARLBORO, MASS

pH 8.4

2500 mg/L MLVSS
2000 mg/L MLVSS
1500 mg/L MLVSS
1000 mg/L MLVSS

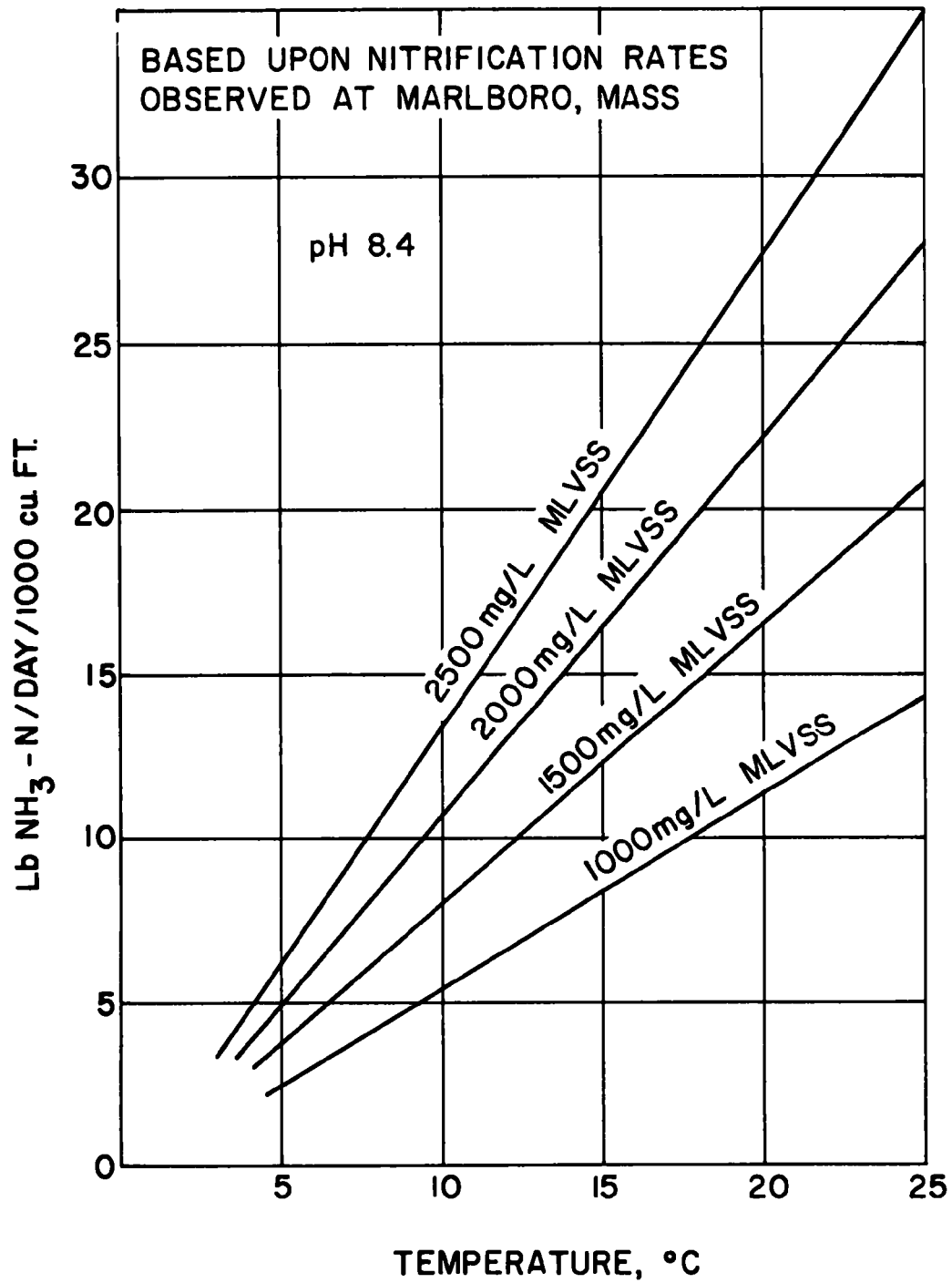Lb NH$_3$ - N / DAY / 1000 cu FT.

TEMPERATURE, °C

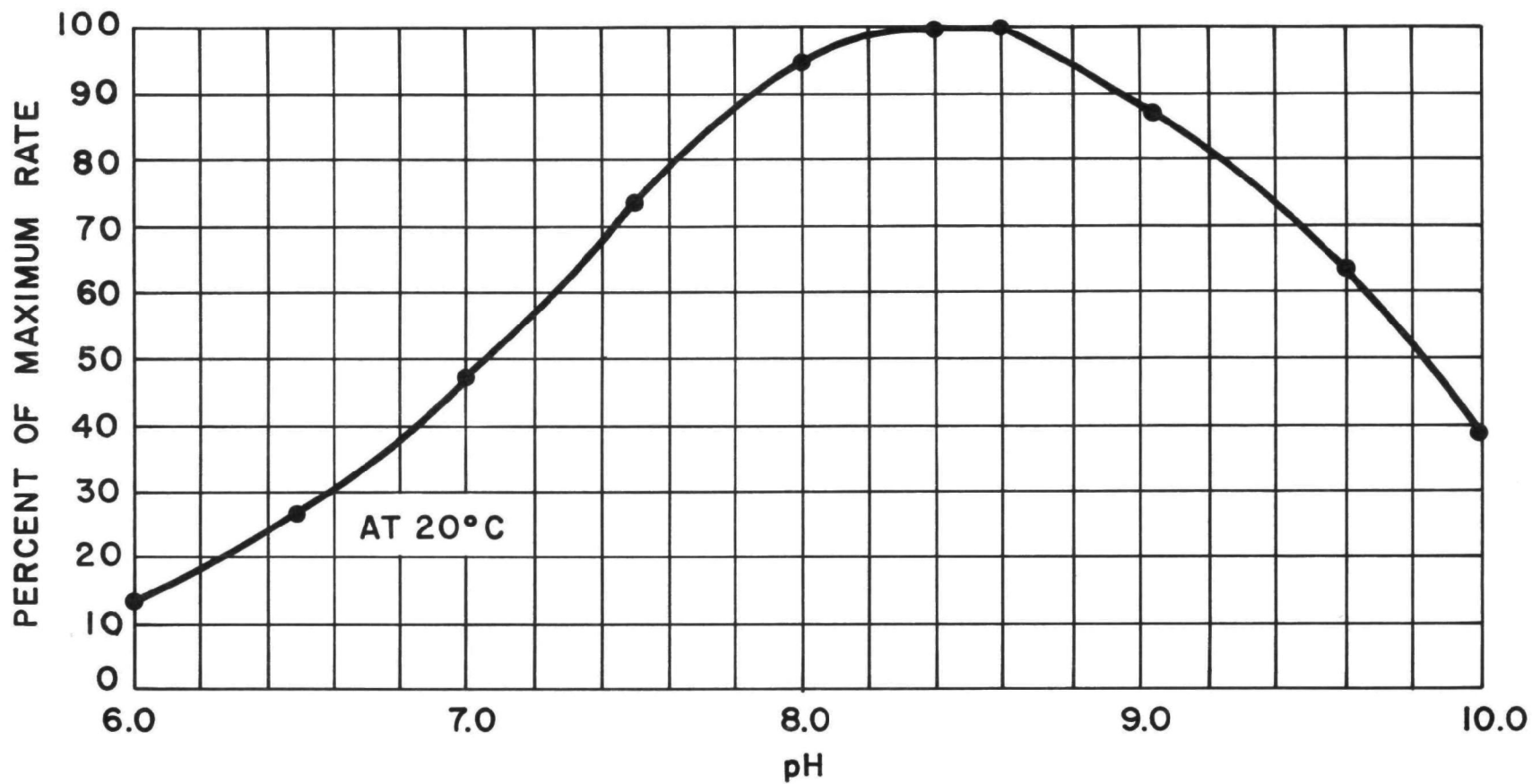FIG. 3-3 PERMISSIBLE NITRIFICATION TANK LOADINGS

FIG. 3-4 PERCENT OF MAXIMUM RATE OF NITRIFICATION
AT CONSTANT TEMPERATURE vs pH

DENITRIFICATION BY SUSPENDED GROWTH SYSTEMS

Only pilot plant data is available at the present time
to serve as the basis of suspended growth denitrification systems.
In our opinion, the most valid information which can serve as a
basis of rational design comes from the pilot plant studies at
Manassas, Virginia, as reported by Mulbarger[1] and the invest-
igations at Washington, D.C.[2] Figure 4-1 shows the kinetics
of the denitrification reaction in relation to temperature for
a given pH range, as reported by Mulbarger and as observed at
Washington, D.C. The data from which the figure was developed
were obtained in laboratory studies in a manner comparable to
those shown on Figure 15 of Chapter 1 and are considered to be
fully as reliable. The reasons for the difference between the
two curves has not been fully determined but points to the need
for additional kinetic studies on other wastewaters.

Denitrification Tank

The tank layout should assure that the plug-flow mixing
model is followed as closely as possible, because nitrates are
not adsorbed by biological growths and detention periods may be
quite short. Whether covered tanks are required to minimize
absorption of oxygen from the atmosphere is a matter of conjec-
ture. There is some evidence to indicate that properly designed
denitrification units can be made to seal themselves by forma-
tion of a floating scum. In any event, airtight or walk-in

covers are to be avoided, because nitrogen and carbon dioxide are both released during the denitrification reaction.

pH

Studies by Mulbarger[1] have indicated that optimum pH for the denitrifying organisms is in the range of 6.5-7.5, the same as for most saprophytic bacteria. Figure 4-3 shows the corrections that must be applied to the permissible tank loadings when the pH is different from the optimum range.

Although the pH of the effluent from the nitrifying units may exceed 7.5 at some time during a year, this is no particular problem because carbon dioxide generated from oxidation of carbonaceous matter in the denitrification unit reduces the pH into the favorable range below 7.5 very quickly. There is no need for addition of chemicals to control pH.

MLSS and MLVSS

The limited experience available has shown that denitrifying sludges have settling properties comparable to good activated sludges. It seems reasonable to assume, therefore, that mixed liquor solids in the range of 2,000 to 3,000 mg/L can be maintained without excessive rates of returning sludge. The volatile matter in the denitrifying sludges at Manassas and Washington, D.C. is about 65 percent.

Size

Reference to Figure 4-1 will show that the minimum temperature to be allowed for will play a great role in determining the size of the denitrification tanks, as well as the MLVSS that can be carried in the system. Figures 4-2 and 4-3 may be used to compute the size of the denitrification tanks as follows:

Sample Calculation for Denitrification Tank Volume

(Calculation based upon kinetic data from Manassas, Va.)

Given: Design Flow = 10 mgd.

Average NO_3-N + NO_2-N concentration = 15 mg/L.[1]

Minimum temperature = 10 deg C.

Expected operating pH = 7.7.

MLVSS = 2,000 mg/L.

Computed:

1. NO_3-N plus NO_2-N loading

   a. Average = 10 x 8.35 x 15

          = 1,250 lb/day.

   b. Peak   = 1,250 x 1.5

          = 1,870 lb/day.

2. Tank loading at 10 deg C, optimum pH (from Fig 4-2)

   = 26.8 lb/1,000 cu ft.

3. Tank volume at MLVSS = 2,000, optimum pH

$$= \frac{1,870 \times 10^3}{26.8}$$

   = 70,000 cu ft.

---

1. For this example problem, assume complete conversion is desired.

4. Tank volume at pH 7.7 (See Fig 4-3)

$$= \frac{70,000}{.90}$$

$$= 77,500 \text{ cu ft.}$$

5. Check detention period

$$= \frac{77,500 \times 7.48 \times 24}{10 \text{ mgd}}$$

$$= 1.39 \text{ hours.}$$

Such a system would have over twice the tankage needed at 20 deg C. For this reason good design will allow for idle operation of part of the capacity during the warm months of the year. A design similar to that shown for the nitrification system in Figure 3-1 is recommended.

Carbonaceous Matter

Effluents from nitrifying units are exceptionally free of oxidizable carbonaceous matter (BOD_c). For this reason denitrification is very slow unless a readily oxidizable source of carbonaceous matter is added. Methyl alcohol (Methanol) is the cheapest commercial source of carbonaceous matter at this time. Glucose (corn sugar) is the next cheapest source. Methanol is preferable because it is more completely oxidized than glucose and, consequently, produces less sludge for disposal.

In some areas, nitrogen deficient industrial wastes, such as brewery wastes, might be available and suitable for use. All such waste materials should be employed before considering

methanol because it is produced from natural gas which is not
an unlimited resource.

When methanol is used for denitrification the basic
reaction involved is:

$$5CH_3OH + 6H^{+1} + 6NO_3^- \longrightarrow 5CO_2 + 3N_2 + 13H_2O$$

$$(5 \times 32) = 160 \quad (6 \times 14) = 84.$$
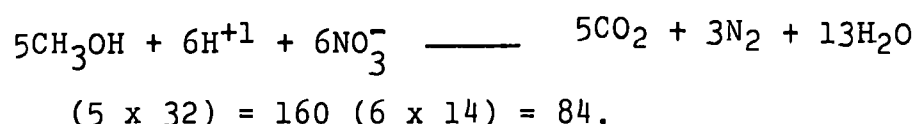
From the above equation and weight relationships, it might be
concluded that each pound of nitrate nitrogen would require
about 2 pounds of methanol for its reduction. This is true
but some of the methanol is used to produce new cell growth
(sludge) as follows:

$$(CH_3OH)_x \longrightarrow CO_2 + (CH_2O)_x + H_2O$$
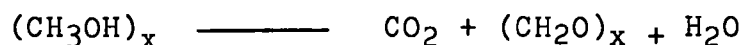
Also, nitrified effluents normally carry some dissolved oxygen
into the denitrification tank and some may enter the mixture
as a result of agitation. This increases the amount of methanol
required. An equation commonly used to estimate methanol
requirements is:

Methanol, lb/day = 2.47 lb NO_3-N + 1.53 lb NO_2-N + 0.87 lb D.O.

Reports indicate that from 3.0 to 4.0 pounds of methanol
per pound of nitrate nitrogen are required to consume dissolved
oxygen and leave sufficient to reduce the nitrate to nitrogen gas.

The amount of methanol fed must be very closely controlled
by a system such as shown on Figure 4-4 to ensure that enough
is fed to reduce the nitrates and to avoid an excess. Any excess
is not only a waste of chemical but it creates an undesirable
residual BOD.

Equipment

The contents of the denitrification tanks are mixed with underwater mixers comparable to those used in flocculation tanks in water treatment plants. The energy provided must be sufficient to keep the MLSS in suspension but controlled to prevent pickup of atmospheric oxygen as much as possible, unless the tanks are covered or some other method is used to exclude contact with the air.

Power requirements of 1/4 to 1/2 hp per thousand cubic feet have been found to be adequate.

Nitrogen Release

The denitrification reaction results in the formation of carbon dioxide and nitrogen gas. Both have limited solubility in water, especially the latter. Because of the gentle mixing used in the denitrification tanks, the mixed liquor leaving the tanks is supersaturated with nitrogen, and possibly carbon dioxide. As a result, gas bubbles tend to form and adhere to the MLSS and inhibit settling in the final clarifier. Supersaturated conditions can be relieved by employing an aeration tank or aerated open tanks. It is recommended that from 5 to 10 minutes detention be provided at peak flow. Such a facility will also provide the ability to remove small amounts of excess methanol.

Settling Tanks

The limited experience available indicates that the settling properties of denitrification sludge, following relief

of supersaturation, are very similar to conventional activated sludge.

Tank depths of 12 to 15 feet are recommended and surface overflow rates should not exceed 1,200 gal/sq ft/day at peak flows. MLSS concentrations greater than 2,500 mg/L may require larger tanks due to the higher settling tank solids loadings.

A suction type sludge collector is recommended for large circular tanks. Long rectangular tanks should be equipped with mid-tank sludge drawoff systems.

Skimming facilities should be provided on the settling tanks and provisions should be made for returning the scum to the denitrification tank when desired.

Sludge

Return

Capability of returning sludge to the denitrification tank of up to at least 50 percent and preferably of up to 100 of average flow is recommended.

Waste

Provision should be made for periodic wasting of sludge from the denitrification systems similar to that employed for carbonaceous systems. Normally, the sludge should be wasted to mix with primary and/or waste activated sludge and be disposed of with them. However, the waste sludge line should be designed to transport sludge to the nitrification tank when

desired. In the event nitrifying sludge is lost from the nitrifying system, it is normally captured by the denitrifying system. It can be returned to its normal home, at least in part, by using denitrifying sludge to reseed the nitrification tank.

Quantity of Waste Sludge

It is reported that about 0.2 pounds of sludge will be generated for each pound of methanol fed. This would correspond to about 0.7 lb/lb of nitrate nitrogen reduced.

Effluent Quality

Based upon pilot plant studies operating under steady state conditions the following effluent quality is predicted from a nitrification-denitrification system designed for operation at 10°C wastewater temperatures. At warmer temperatures improved quality can be expected.

	mg/L
Suspended Solids	10
BOD	5
Organic-N	1.0
NH_3-N	0.5
NO_3-N	0.5
Total -N	2.0

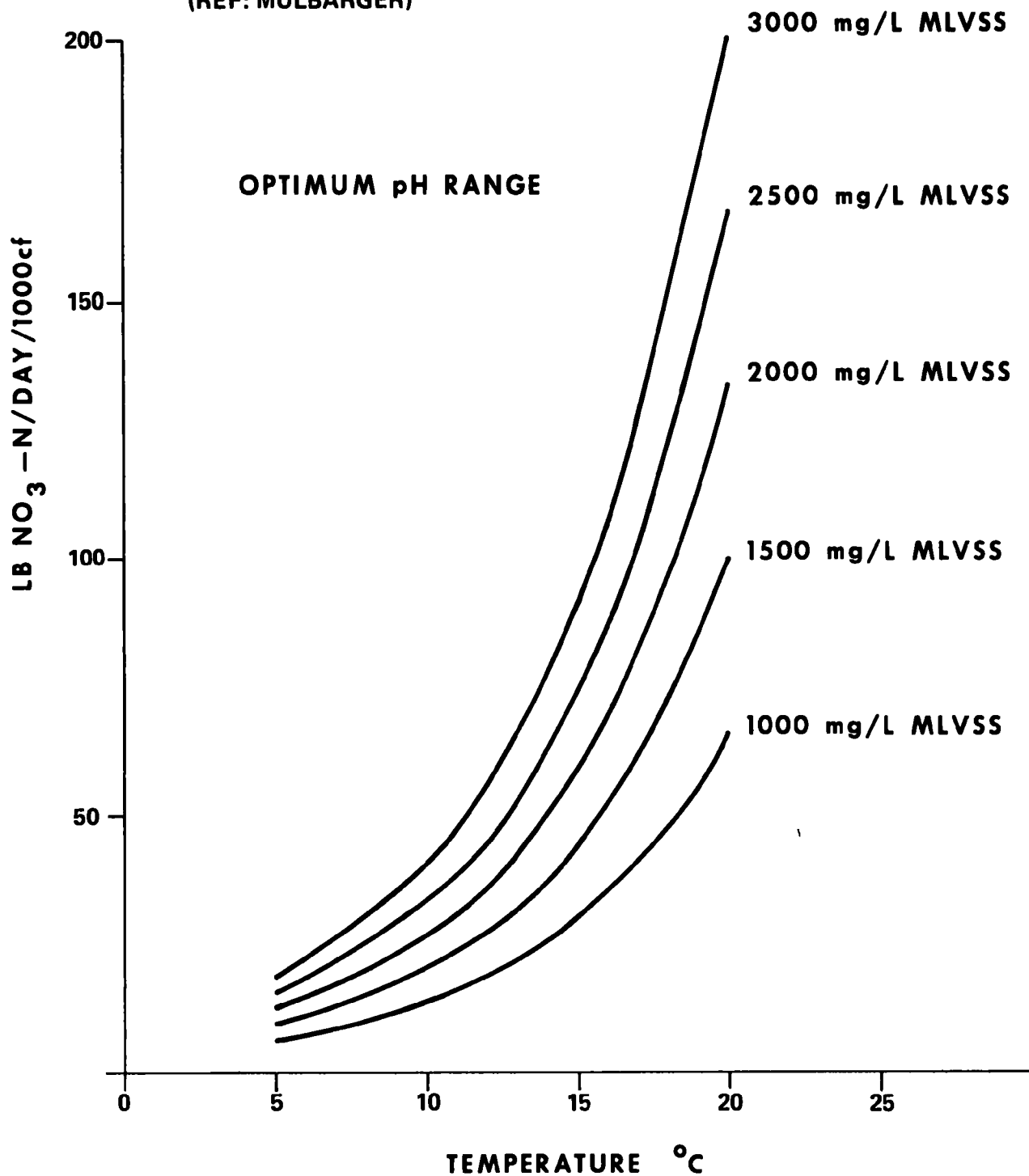Thus, it appears that 90 percent removals of total nitrogen can be achieved in actual practice.

Reference

1. Mulbarger, M.C., "The Three Sludge System for Nitrogen and Phosphorus Removal." Paper presented at the 44th Annual Conference of the Water Pollution Control Federation, San Francisco, California (Oct 71)

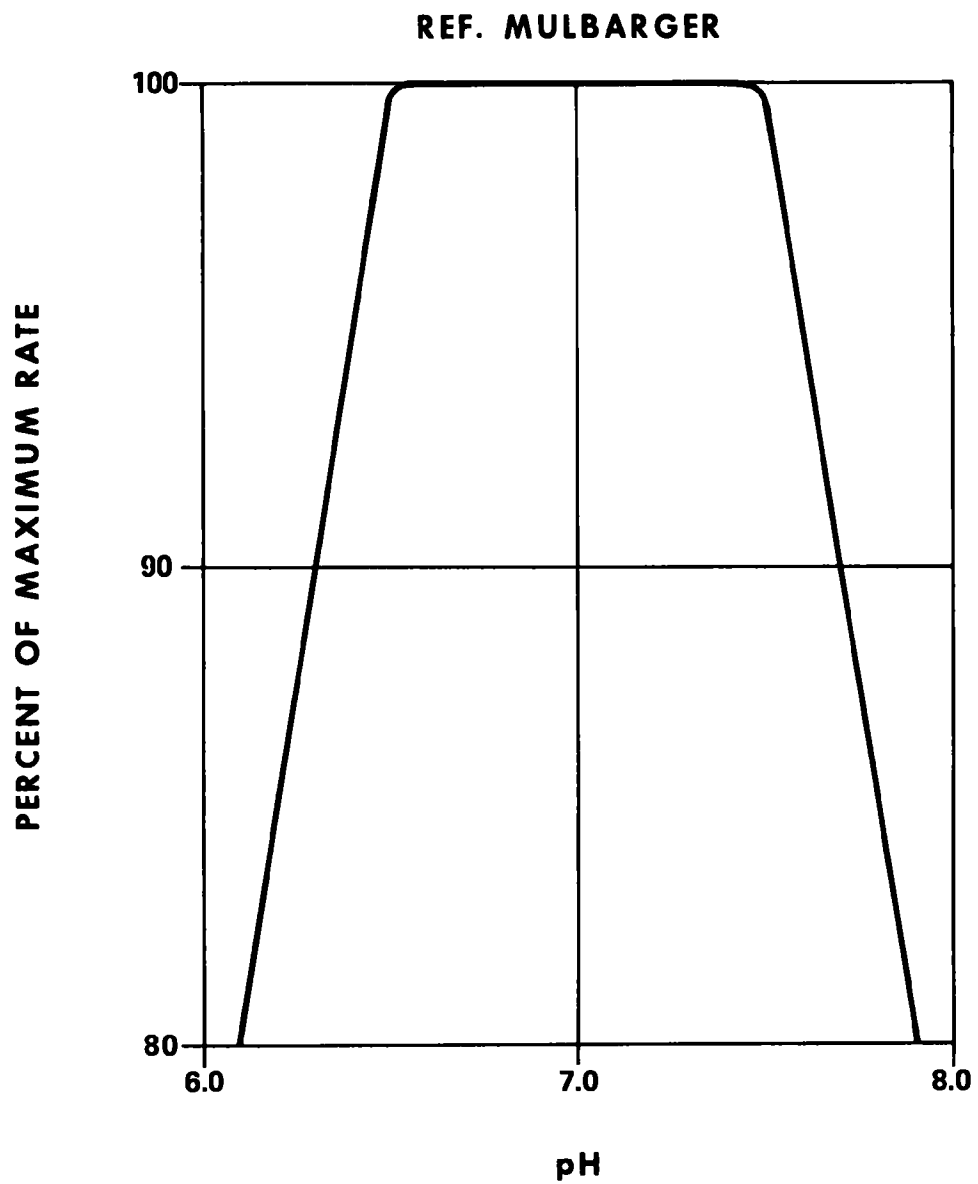2. Stamberg, J., Private Communication.
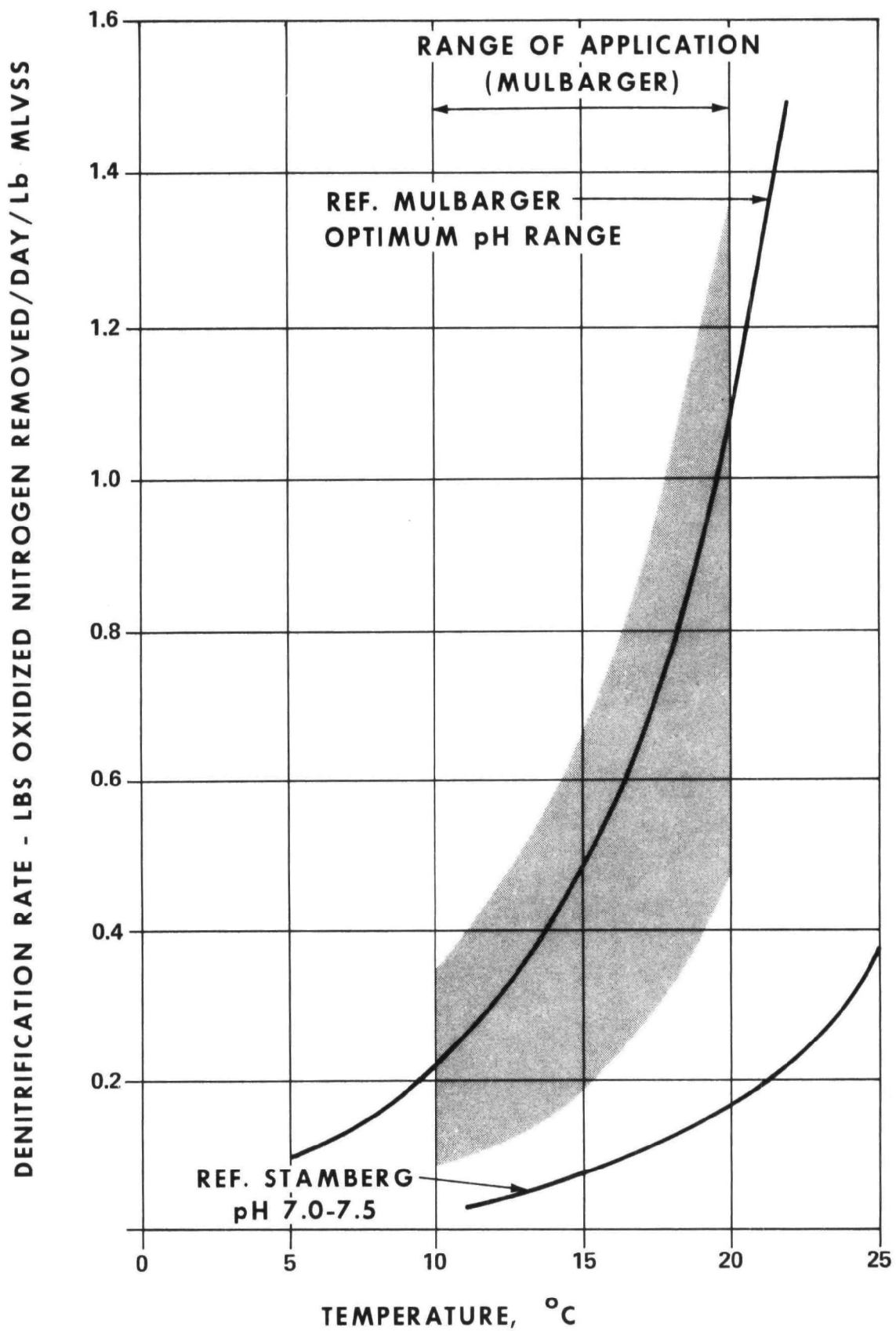
FIG. 4-1 EFFECT OF TEMPERATURE
UPON RATE OF DENITRIFICATION

METCALF & EDDY

BASED ON DENITRIFICATION RATES
OBSERVED AT MANASSAS, VA.
(REF: MULBARGER)

3000 mg/L MLVSS

OPTIMUM pH RANGE

2500 mg/L MLVSS

2000 mg/L MLVSS

1500 mg/L MLVSS

1000 mg/L MLVSS

LB NO$_3$ –N/DAY/1000cf

TEMPERATURE °C

PERMISSIBLE DENITRIFICATION TANK LOADING

FIG. 4-2

REF. MULBARGER

FIG. 4-3 PERCENT OF MAXIMUM RATE
OF DENITRIFICATION VS pH
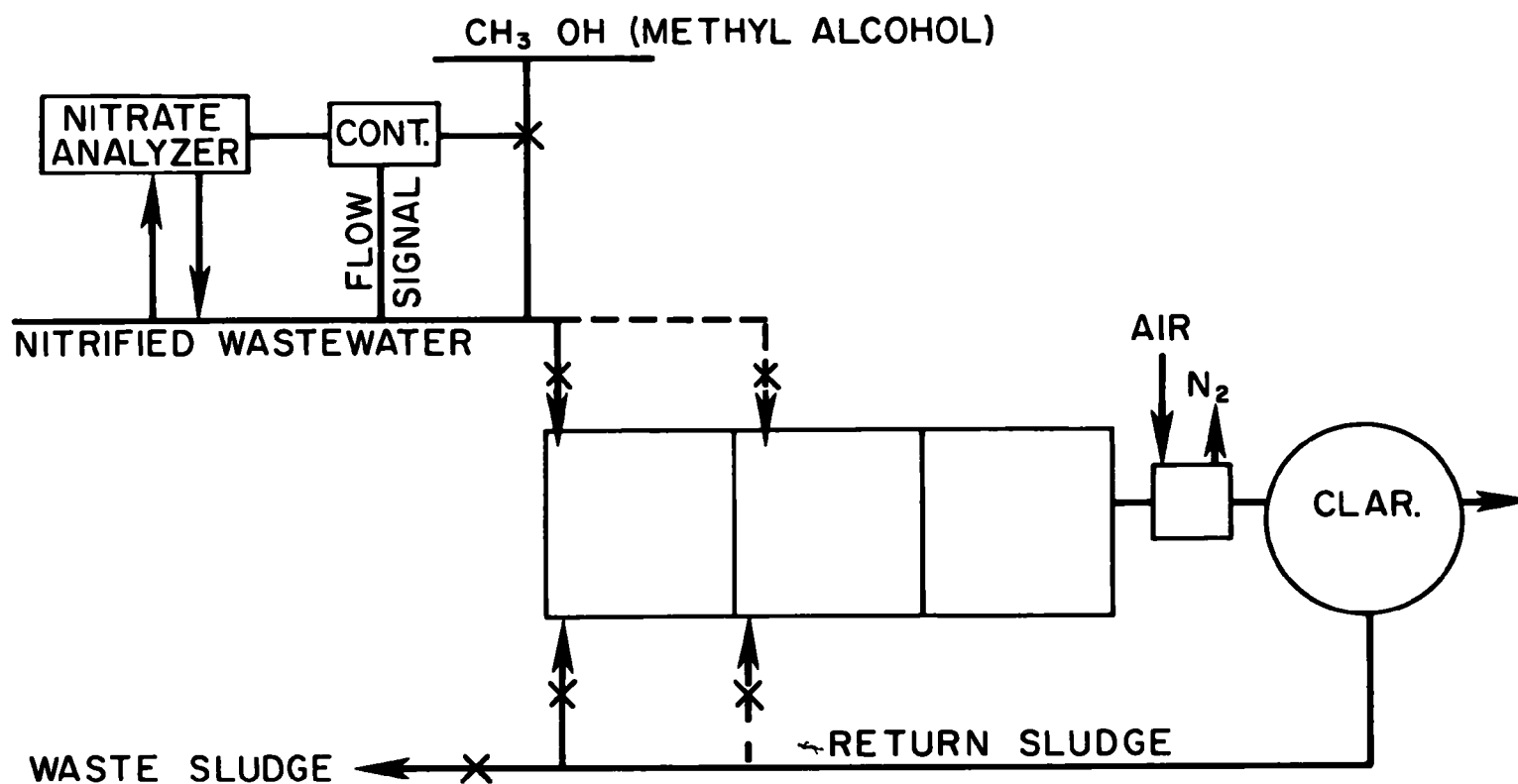
**MODEL SYSTEM FOR FEEDING METHYL ALCOHOL
TO DENITRIFICATION TANK**

FIG. 4-4