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BIOLOGICAL REDUCTION OF NITRATE WASTEWATER USING FLUIDIZED-BED BIOREACTORS*

J. F. Walker, Jr., C. W. Hancher, and B. D. Patton
Chemical Technology Division
Oak Ridge National Laboratory†
Oak Ridge, Tennessee 37830

M. Kowalchuk
Goodyear Atomic Corporation
Portsmouth, Ohio

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ABSTRACT

Nitrates in food and water present a health problem by contributing to the risk of methemoglobinemia as well as contributing in the eutrophication of lakes and coastal waters. The biological reduction of these nitrates in wastewater to gaseous nitrogen, accompanied by the oxidation of a nutrient carbon source to gaseous carbon dioxide, is an ecologically sound and cost-effective method of nitrate waste disposal.

There are a number of nitrate-containing wastewater sources, as concentrated as 30 wt % NO_3^- and as large as 2000 m^3/d, in the nuclear fuel cycle as well as in many commercial processes such as fertilizer production, paper manufacturing, and metal finishing. These nitrate-containing wastewater sources can be successfully biologically denitrified to meet discharge standards in the range of 10 to 20 $gN(NO_3^-)/m^3$ by the use of a fluidized-bed bioreactor. The major strain of denitrification bacteria is Psuedomonas which was derived from garden soil. In the fluidized-bed bioreactor the bacteria are allowed to attach to 0.25 to 0.50-mm-diam coal particles, which are fluidized by the upward flow

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of influent wastewater. Maintaining the bacteria-to-coal weight ratio at approximately 1:10 results in a bioreactor bacteria loading of greater than 20,000 g/m^3.

This paper describes the results of two biodenitrification R&D pilot plant programs based on the use of fluidized bioreactors capable of operating at nitrate levels up to 7000 g/m^3 and achieving denitrification rates as high as 80 $gN(NO_3^-)/d$ per liter of empty bioreactor volume. The first of these pilot plant programs consisted of two 0.2-m-diam bioreactors, each with a height of 6.3 m and a volume of 208 liters, operating in series. The second pilot plant was used to determine the diameter dependence of the reactors by using a 0.5-m-diam reactor with a height of 6.3 m and a volume of 1200 liters. These pilot plants operated for a period of six months and two months respectively, while using both a synthetic waste and the actual waste from a gaseous diffusion plant operated by Goodyear Atomic Corporation.

INTRODUCTION

Due to tightening federal regulations regarding the discharge of nitrate waste into lakes, streams, and coastal waters, Goodyear Atomic Corporation (GAT) and National Lead of Ohio (NLO) contracted with the Oak Ridge National Laboaratory (ORNL) to develop environmental control technology for nitrates in process wastewaters. GAT and NLO, both gaseous diffusion plants used in uranium enrichment, produce approximately 360 L/d of 300,000 g/m^3 and 757,000 L/d of 2000 g/m^3 nitrate waste respectively. NLO is particularly

vulnerable to federal regulations because it discharges wastewater into the Greater Miami River which has been designated as a "State and National Resource Waterway." As result, GAT and NLO are expected to have to reach a discharge limit of approximately 10 mg/L nitrate-nitrogen by 1984.

To reach this discharge limit ORNL proposed the use of a fluidized-bed bioreactor with biomass recycle. In this process the denitrification bacteria, in the presence of a carbon source, would reduce the nitrate and produce gaseous nitrogen and carbon dioxide as by-product.

ORNL was contracted by GAT and NLO to design, build, operate and evaluate pilot plants for their specific nitrate wastewaters. The design criteria for these pilot plants can be seen in Table 1. The GAT pilot plant was operated for six months while the NLO pilot plant was operated for two months.

BACKGROUND

The general design equation for the CSTR is[1,2]

$$\tau = \left(\frac{C_{ao}V}{F_{ao}}\right) = \frac{C_{ao}X_a}{-r_a}$$

while the general design equation for the PFR is[1,2]

$$\tau = \left(\frac{C_{ao}V}{F_{ao}}\right) = C_{ao}\int_{o}^{X_a}\frac{dX_a}{-r_a}$$

Table 1. Basic Pilot Plant Design Criteria

	Goodyear Atomic Corporation	National Lead of Ohio
• Required NO_3^- Removal Rate	∿ 40 metric tons/year	∿ 550 metric tons/year
• Input NO_3^- Feed Concentration	4000 g/m^3	4000 g/m^3
• Exit NO_3^- Effluent Concentration	20 - 5 g/m^3	20 - 5 g/m^3
• Flow Rate	16 L/min	115 L/min
• Bioreactor Diameter	20 cm ID (∿8 in.)	50 cm ID (∿20 in.)
• Bioreactor Height	7.5 m (∿25 ft)	7.5 m (∿25 ft)
• Configuration	two reactors in series	single reactor

If we assume the reaction rate follows nth order kinetics ($-r_a = kC_a^n$) and divide the design equation for the CSTR by the design equation of the PFR we have[1,2]

$$\frac{\left(\frac{V\ C_{ao}^{n-1}}{Q}\right)_{CSTR}}{\left(\frac{V\ C_{ao}^{n-1}}{Q}\right)_{PFR}} = \frac{\left[\frac{X_a}{(1 - X_a)^n}\right]_{PFR}}{\frac{-1}{1-n}\left[(1 - X_a)^{1-n} - 1\right]_{PFR}}$$

where

τ = Space time

C_a = Concentration of reactant A

F_a = Molar flow rate of substance A

V = Volume

X_a = Fraction reactant A converted into product

n = Order of reaction

Q = Volumetric flow rate

o = Entering condition.

From this equation it can be shown that if the reaction order is positive, the volume required in the CSTR is larger than the volume required in the PFR at all conversion levels. The higher the fraction conversion involved, the greater the disparity between the sizes of the CSTR and the PFR.[2] This means a reduced capital cost due to the smaller volume required by the PFR. Another advantage of the PFR over the CSTR is that it provides a higher surface for biomass

growth increasing biomass concentrations from 10 to 20 fold.[3] As a result of these advantages it is possible to attain much higher reaction rates (10 to 100 fold) in the PFR than in the CSTR. This means the liquid residence time required in the FBR is much less (30 to 60 min) than that required in the CSTR (10 to 20 days) to obtain the same effluent concentration.[3]

Other studies using fluidized beds in denitrification have been reported. Bosman and Hendricks demonstrated the removal of nitrate in pilot plants using fluidized beds for processing wastewaters with nitrogenous concentrations in excess of 1000 mg/L as N while using molasses as a carbon source. The important design and process parameters studied were reactor hydraulics, fluidization characteristics of the medium, and process reaction rates.[4] Gregory and Sheiham also found that for selected large-scale applications a fluidized-bed bioreactor was more economical than ion exchange or blending to reduce nitrate concentrations.[5]

BIOLOGICAL DENITRIFICATION

Biological denitrification as referred to in this paper is the biological reduction of nitrate or nitrite to gaseous nitrogen accompanied by the oxidation of a nutrient carbon source to carbon dioxide.[6] With ethanol as the carbon source, this reaction in unbalanced form may be written as:

$$NO_3^- + C_2H_5OH \rightarrow CO_2 + N_2 + H_2O + OH^- + XC_5H_7O_2N,$$

where $C_5H_7O_2N$ is the approximated composition of the biomass. The observed molar ratio of carbon consumed to nitrogen (as nitrate) reacted is approximately 1.3 to 1.5, while the biomass yield is roughly 0.1 g/g nitrate consumed.[7]

Under normal conditions the process of biological denitrification takes place in soil under anaerobic conditions by various strains of facultative bacteria, such as Pseuslomonas denitrificans and Pseudomonas stutzeri. The denitrification bacteria used in this FBR research were a mixed culture derived from garden soil with the major strain being Pseudomonas. These bacteria were allowed to attach to 30-60 mesh anthracite coal particles (density = 1.5 g/cm^3) for use in fluidized-bed bioreactors.

PROCESS DESCRIPTION

Process Flowsheets

The GAT pilot plant (Fig. 1) contained two bioreactors, each with a 0.2-m diam and a height of 6.4 m operating in series. The concentrated feed solution (Table 2) was pumped into a holding tank where it was mixed with water and phosphoric acid. From this holding tank the wastewater was pumped into the first bioreactor, at a velocity of approximately 0.9 cm/sec, fluidizing the bacteria-laden coal particles. As biomass grew on the coal particles, they became less dense, floated to the top of the bioreactor, and exited with the liquid effluent. The excess biomass and wastewater were separated from the recycled coated particles using a vibrating-screen filter;

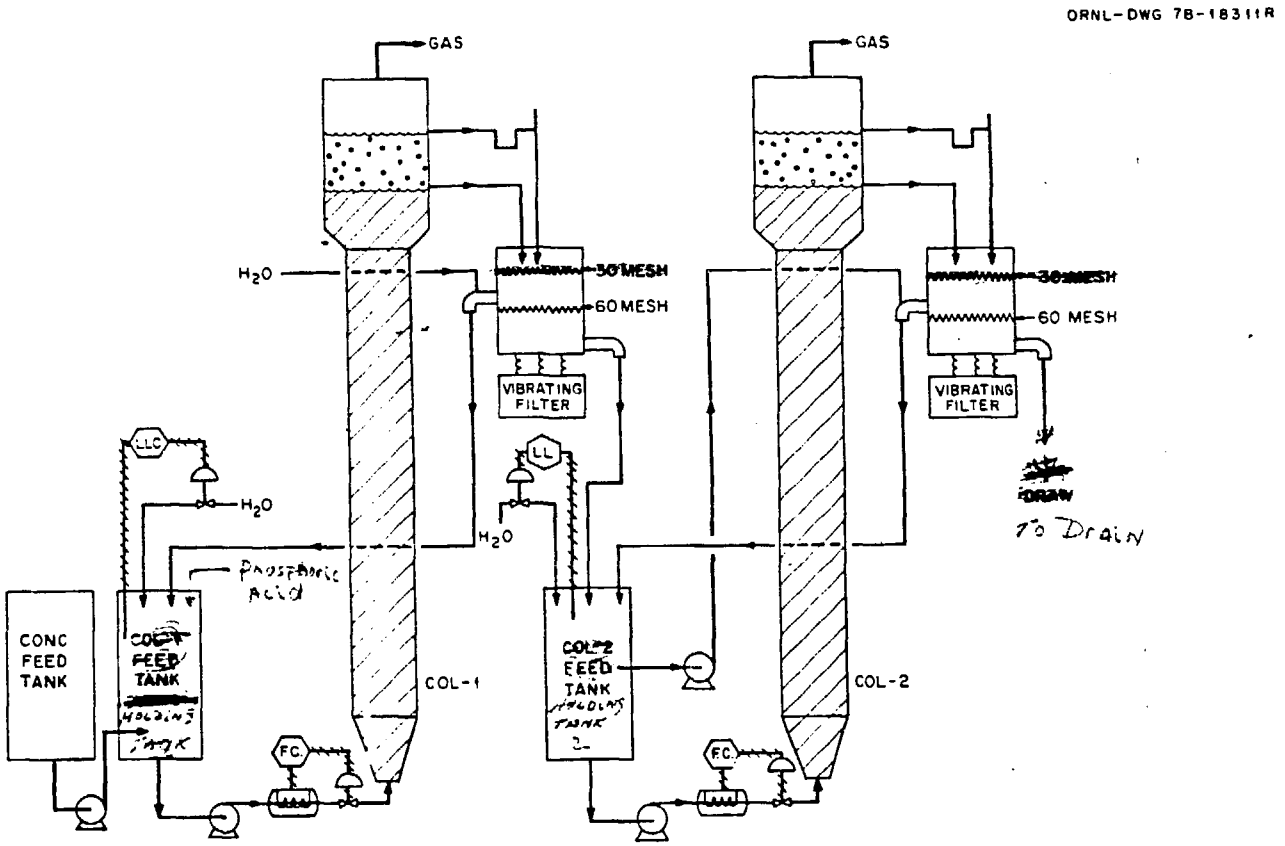

Fig. 1. Goodyear Atomic Corporation Pilot Plant Flowsheet

Table 2. Concentrated Feed Solution for the 20-cm-diam Bioreactor

30 % Nitrate (g/L)	
HNO_3	300
NH_4OH	120
ETOH	200
$MgSO_4$	1
Dow-Antifoam "A"	1
Trace metal solution	0.1

Trace Metal Solution Mix (g/L)	
H_3BO_3	1
$ZnSO_4 \cdot 7H_2O$	0.4
$NH_4MO_7O_{24} \cdot 4H_2O$	0.2
$MnSO_4 \cdot 7H_2$	0.25
$CuSO_4 \cdot 5H_2O$	0.45
$FeSO_4 \cdot 7H_2O$	0.25
KI	10
Fe-chelate	200

the recycle stream was returned to the first holding tank, and subsequently to a second holding tank. From this second holding tank, the wastewater was pumped through an identical bioreactor to a second vibrating filter. The wastewater and excess biomass from the second vibrating filter was discharged to a sanitary sewage drain, while the coated coal particles were recycled to the second holding tank.

The NLO pilot plant (Fig. 2) contained a single 0.5-m-diam bioreactor with a height of 6.4 m. In the NLO pilot plant the concentrated feed was pumped to one of two holding tanks where it was mixed with water and phosphoric acid. The wastewater was pumped from these holding tanks, mixed with dilution water, and entered the bioreactor at a velocity of approximately 0.9 cm/sec. The effluent from the bioreactor overflow entered a weir box which split and directed the wastewater to two separate vibrating screen filters. The excess biomass and the wastewater from these filters again exited via the sanitary drain, while the coal particles were recycled to the holding tanks.

Process Equipment

Bioreactors. The bioreactors used in the GAT and NLO pilot plants were similar in design. Each consisted of a tapered bottom to enhance flow distribution and prevent plugging by maintaining a high inlet velocity. The tapered section was followed by a cylindrical section, a tapered top section to enhance solid-liquid disengagement, and a liquid-gas disengaging space (Fig. 3). The bioreactors and their sections are discussed in detail below.

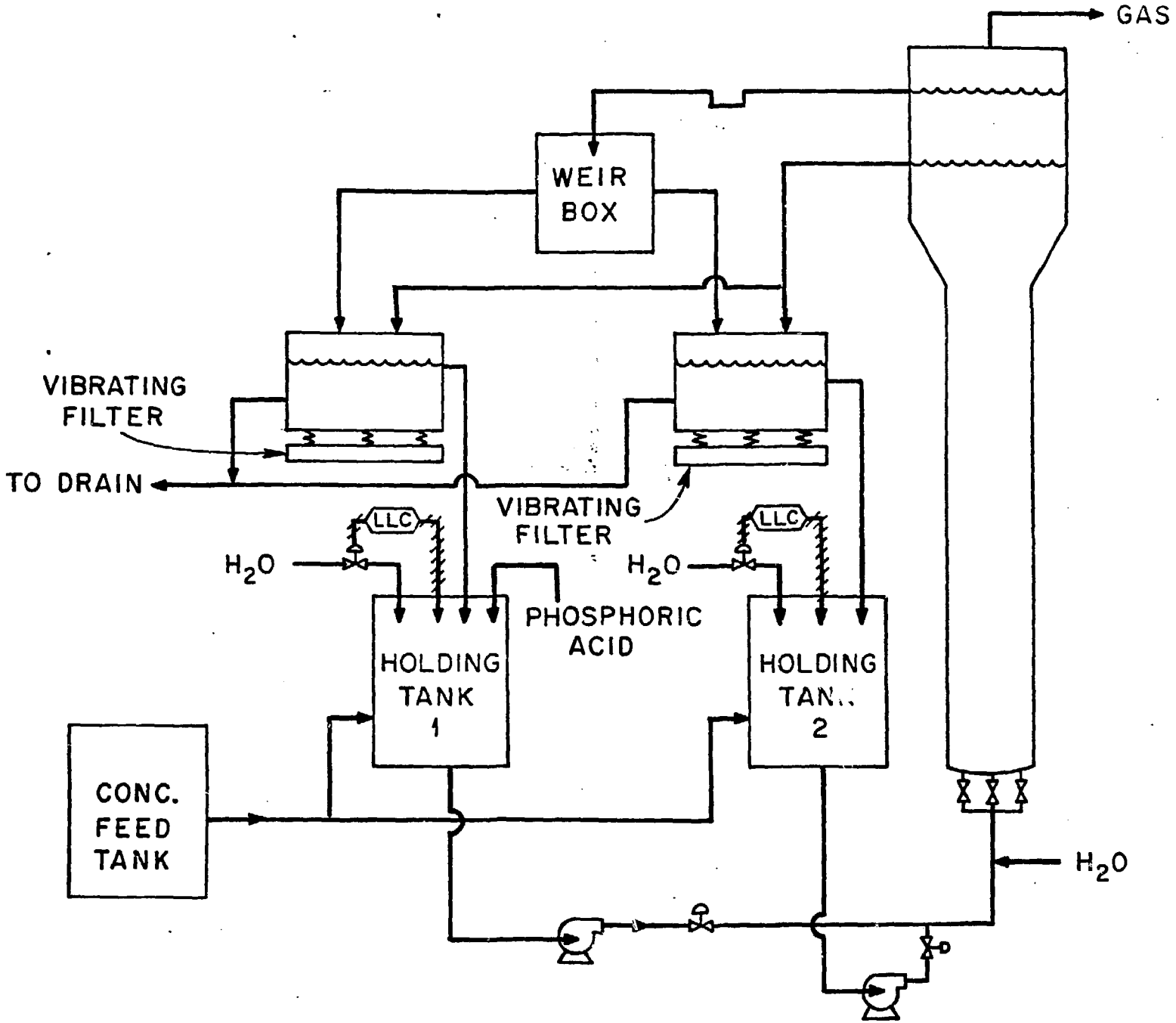

Fig. 2. Flowsheet for the National Lead of Ohio Pilot Plant

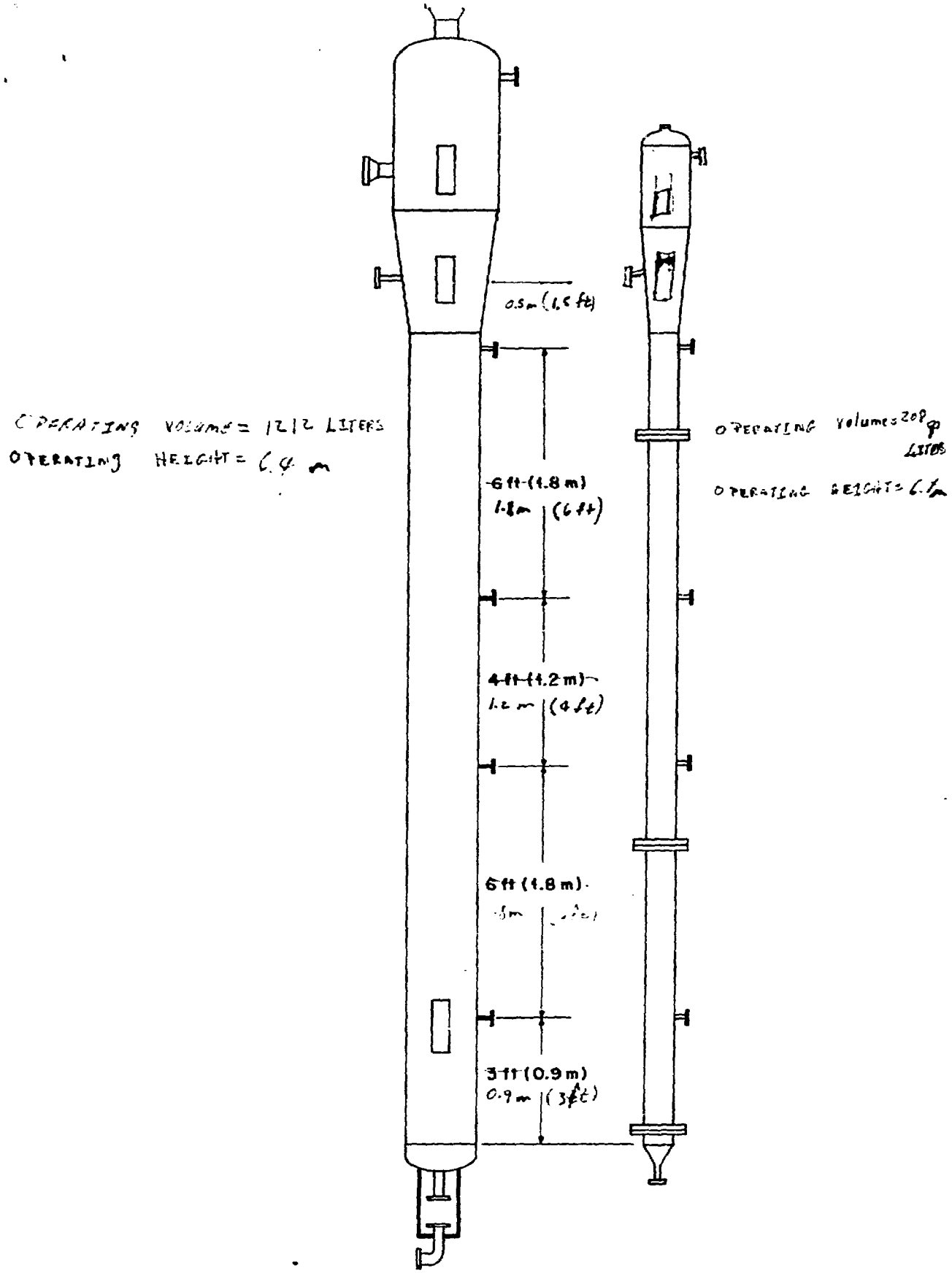

Fig. 3. Comparison of the 20-cm-diam and the 50-cm-diam bioreactors

(1) To enhance flow distribution the 0.2-m-diam reactor's bottom tapered from 0.027-m ID to 0.211-m ID over a distance of 0.165-m. Similarly, the 0.5-m-diam reactor had a bottom rounded from 0.051-m OD to 0.489-m OD over a distance of 0.076-m. In addition, the 0.5-m-diam reactor contained a valve which allowed it to be fed from either a single 0.051-m tube in the center or from five separate 0.019-m tubes evenly spaced across the bottom cross-sectional area.

(2) Both reactors contained a 5.9-m long cylindrical section.

(3) The reactors contained a top liquid-solid disengaging section 0.914-m long, tapering from either 0.218- to 0.356-m or 0.508- to 0.742-m OD.

(4) The 0.356-m OD liquid-gas disengaging space on the 0.2-m-diam column was 0.61-m long, while this disengaging space on the 0.5-m-diam reactor was 0.742-m OD and 1.295-m long.

(5) The 0.2-m-diam column was constructed of 304 L stainless steel, while the 0.5 m column was constructed of carbon steel.

Analytical Methods and Measurements

Biomass Loading. The biomass-coated coal particles were washed with water to remove any non-attached biomass. The sample was then air dried at 105°C for 24 h, cooled in air, and weighed. The dried sample was soaked in 4 m NaOH for 4 h to remove the attached biomass. The cleaned coal particles were water-washed, dried at 105°C for 25 h, cooled, and reweighed. The attached biomass

was reported on a dry weight basis. Based on the approximated biomass composition of $C_5H_7O_2N$, the biomass was 58% carbon.

Liquid samples taken from the GAT and NLO processes were analyzed for nitrate-nitrogen, nitrite-nitrogen, ammonia-nitrogen, ethanol, and phosphate. These analyses were performed by either the ORNL Analytical Chemistry or the ORNL Environmental Sciences Division. All analyses were performed by EPA approved methods found in Standard Methods for Examination of Water and Wastewater, 14th edition.

RESULTS

Comparison of Operating Performance of the GAT and NLO Pilot Plants.

The operating conditions used in the GAT and NLO pilot plants can be seen in Table 3. These bioreactors were operated under similar conditions of temperature, pH, unit cross-sectional flow rate (m^3/m^2), and bacteria loading. Feed conditions varied however, with the NLO pilot plant being operated with an inlet NO_3^- concentration ranging from 500 to 2900 g/m^3, and the GAT pilot plant being operated with an inlet NO_3^- concentration ranging from 500 to 10,000 g/m^3. This was due to the fact that the concentrated nitrate wastewater at GAT contained approximately 300,000 g/m^3 of nitrate, while the NLO concentrated wastewater contained approximately 2000 g/m^3 of nitrate. It was also found that if the first bioreactor in the NLO pilot plant was fed at low NO_3^- concentrations (e.g., <1000 g/m^3), the inlet into the second bioreactor did not contain enough NO_3^- to sustain the bacteria in the second column. Under these circumstances, the bacteria would disengage from the coal and be washed out of the bioreactor.

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OPERATING CONDITIONS

INLET pH = 6.5 to 7.0

OPERATING TEMPERATURE = ~27 to 31°C

UNIT CROSS SECTIONAL FLOW RATE = ~0.9 cm/s

BACTERIA LOADING = 10 to 20% ON A DRY WEIGHT BASIS

INLET NO_3^- FEED CONCENTRATIONS = NLO: 500 to 2900 g/m^3

GAT: 500 to 10,000 g/m^3

Table 3. Pilot Plant Operating Conditions

As can be seen in Table 4, the denitrification rates for the 20-cm column, the 50-cm column, and the two 20-cm columns operating in series showed no significant differences. (Data from the GAT pilot plant were taken so the first column in the series and both columns operating in series could be analyzed as separate systems.)

pH Profile in Fluidized-Bed Bioreactor. Fig. 4 shows a typical pH profile along the length of the 50-cm-diam bioreactor. As can be seen, the pH at the entrance to the bioreactor was approximately 7.0, and steadily rose to a pH of ∿7.7 at the exit of the bioreactor. When operating two bioreactors in series, it will probably be necessary to readjust the feed pH into the second column to about 7.0. It has been observed that the pH has a marked effect on the efficiency of the denitrification process. In studies using packed columns to treat high nitrate wastes, the denitrification process ceased at a pH of 9.2.[8]

Effect of Nitrate Concentration on Denitrification Reaction Rates. There are many models used in correlating data from biological systems. One of the more common is the Monod equation[2,9]

$$\mu = \frac{\mu_{max}\, S}{K_S + S}$$

where

μ = specific growth rate = $\frac{1}{X}\frac{dX}{dt}$

X = cell concentration

μ_{max} = maximum specific growth rate

S = concentration of growth limiting substrate

K_S = saturation constant.

Table 4. Comparison of Denitrification Rates for 20- and 50-cm Bioreactors at Different Feed Concentrations

Feed/Effluent Concentrations of NO_3 (g/m^3)			Denitrification Rate [$KgN(NO_3)/d \cdot m^3$]		
20-cm	50-cm	two 20-cm in series	20-cm	50-cm	two 20-cm in series
860/27	860/34	1715/40	26	24	23
1006/110	1100/27	2080/5	28	27	29
2027/1000	1741/455	4011/1430	32	30	33
2668/1340	2500/1025	5730/2110	38	38	43

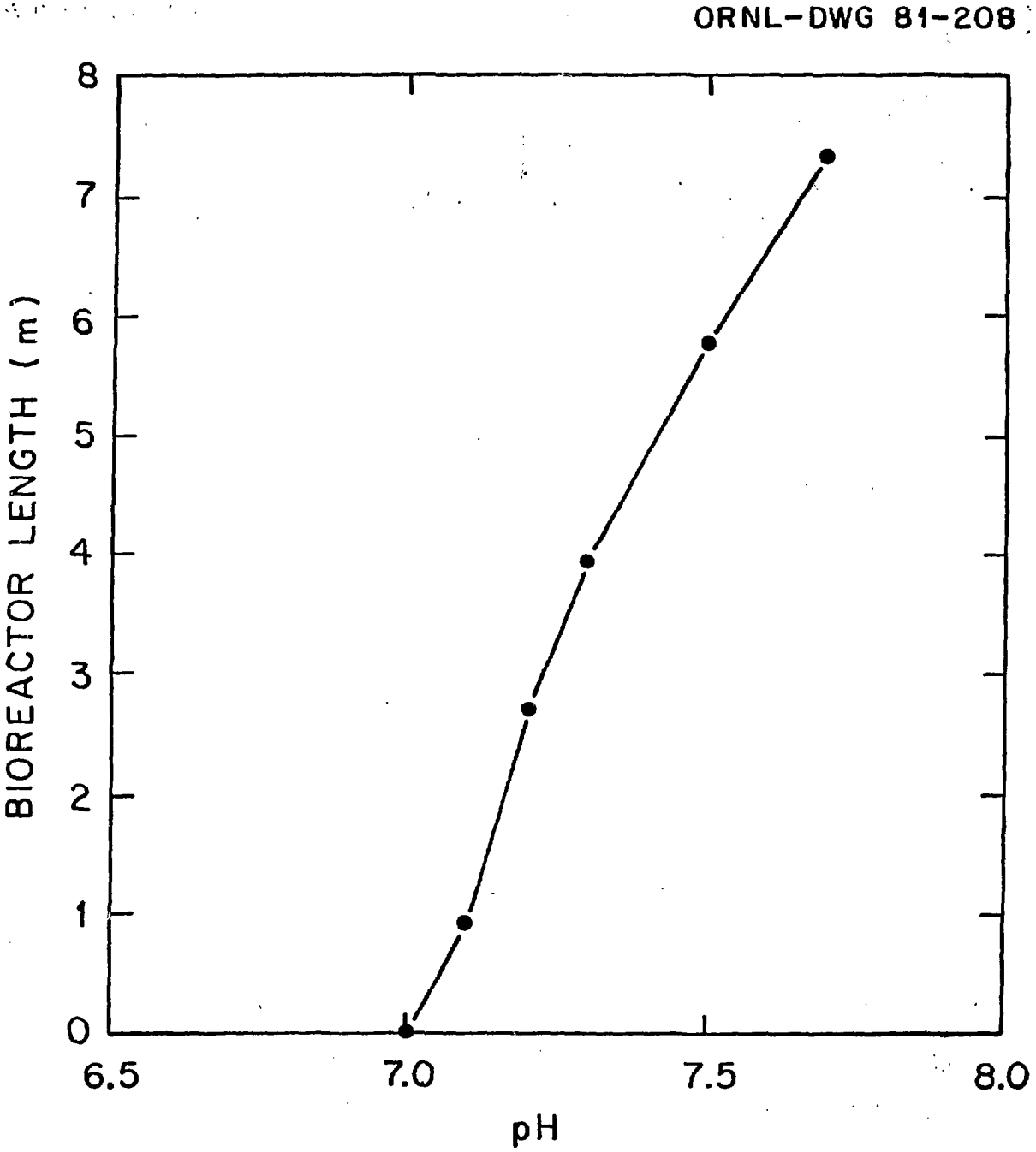

Fig. 4. Typical pH Profile in the 50-cm-diam Fluidized-Bed Bioreactor

Figure 5 shows a typical Monod reaction.

Studies on the 20- and 50-cm-diam bioreactors indicated that the denitrification rate [$KgN(NO_3^-)/d \cdot m^3$], based on the empty reactor volume, increases with increasing nitrate concentrations reaching rates as high as 78 $KgN(NO_3^-)/d \cdot m^3$. It was observed that at low nitrate concentrations (approximately <500 g/m^3 for the single column and <1000 g/m^3 for the two columns in series) this is a statistically significant linear relationship. At higher concentrations there is more scatter in the data. This indicates that at these low nitrate concentrations the system may be modeled by the Monod equation. By comparing a graph of the actual data taken from the 50-cm-diam bioreactor (Figs. 6 and 7) with a graph of a typical Monod reaction (Fig. 5) it can be in the region of first-order kinetics the denitrification rates seem to follow the Monod equation. In the region of zero-order kinetics there seems to be a deviation from Monod kinetics. Due to time and monetary restrictions, the maximum specific growth rate and the saturation constant were not calculated.

Figure 8 gives an indication of the relative standard deviation of the denitrification rates at various average (arithmetic average between inlet and outlet values) nitrate concentrations. It should be noted that the 20-cm-diam bioreactors, operated either as a single column or as two columns in series, followed the same general pattern. At low nitrate concentrations the denitrification rate increased rapidly with average nitrate concentration; at the higher average nitrate concentrations the increase in rate was much more gradual.

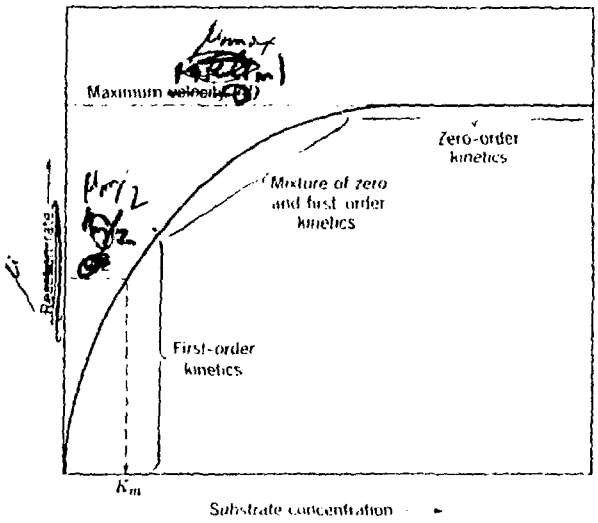

Fig. 5. Typical Monod Reaction

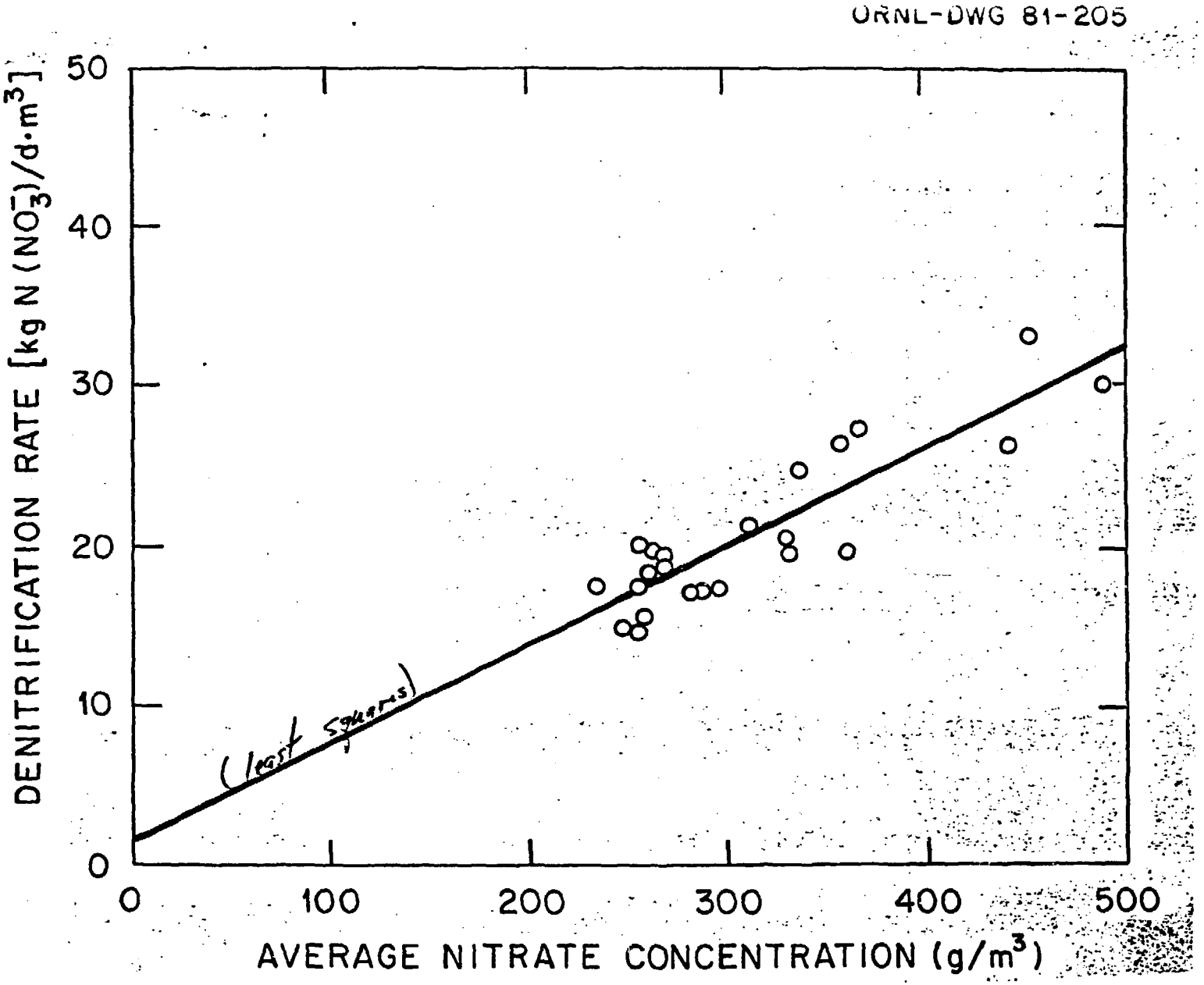

Fig. 6. Denitrification Rates for Average Nitrate Concentrations Below 500 g/m^3 in the 50-cm-diam Bioreactor

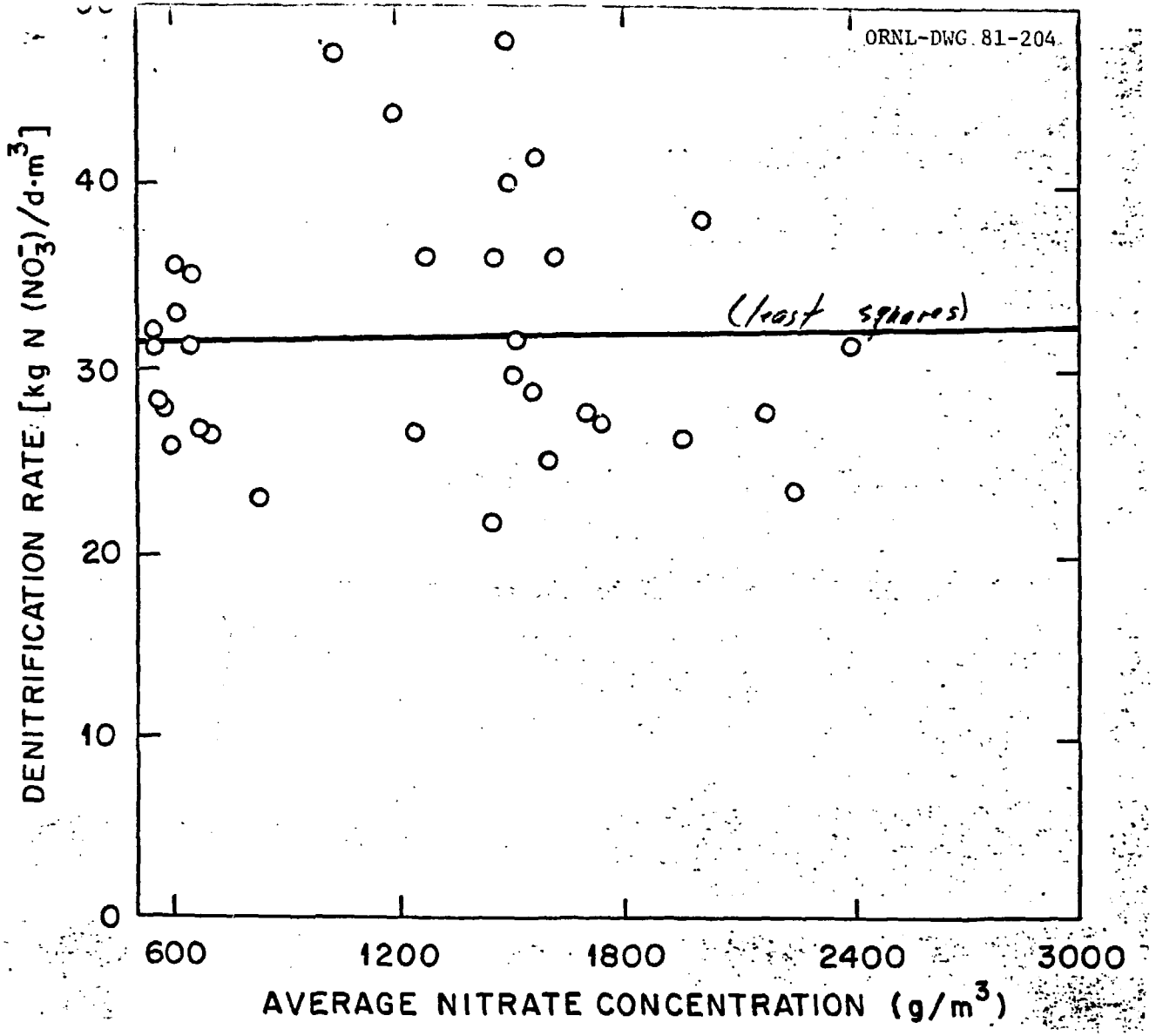

Fig. 7. Denitrification Rates for Average Nitrate Concentrations Greater than 500 g/m^3 in the 50-cm-diam Bioreactor

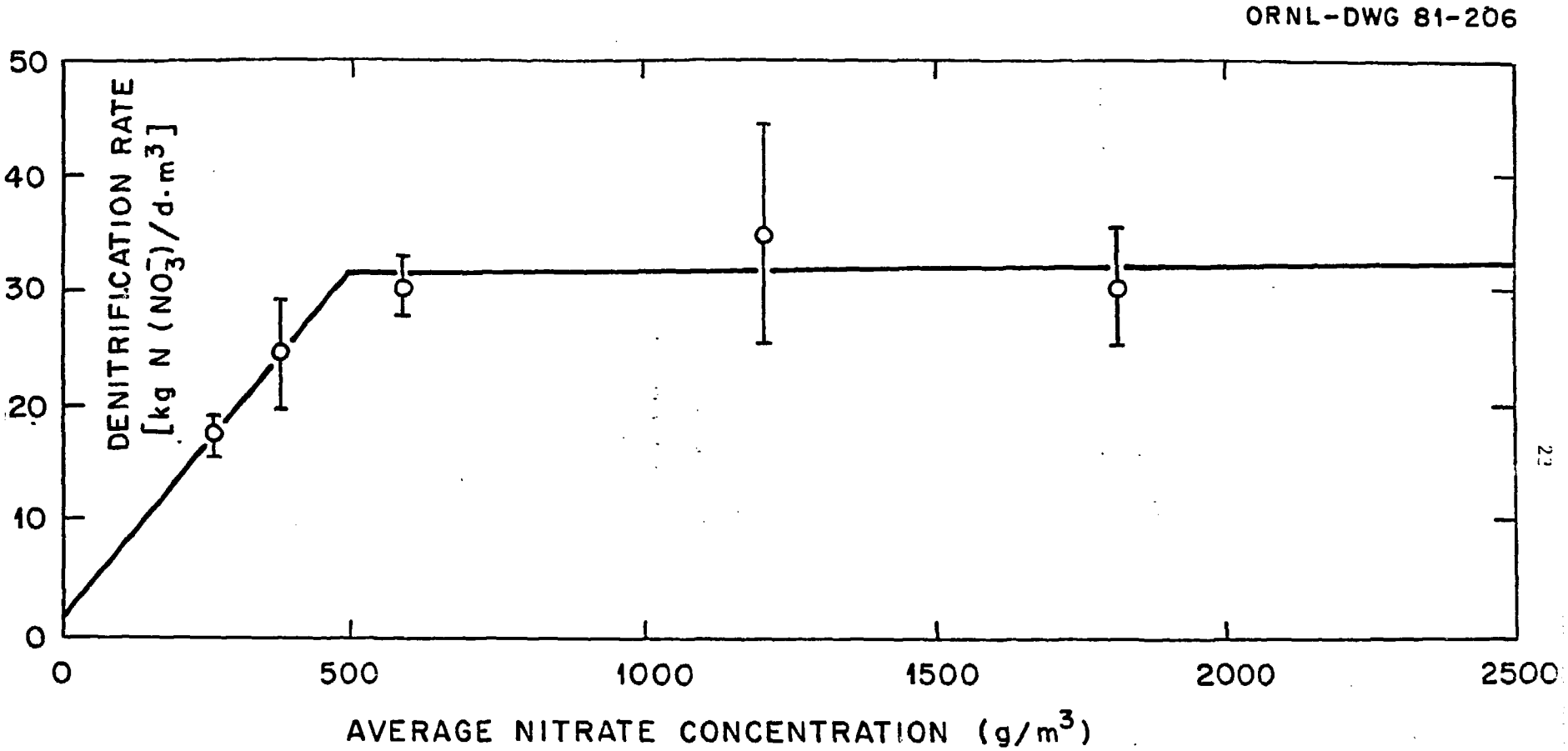

Fig. 8. Denitrification Rates vs Average Nitrate Concentrations for the 50-cm-diam Bioreactor

USE OF DENITRIFICATION RATE DATA IN ESTIMATING BIOREACTOR SIZES

Experimental evidence has shown that the volume required for these bioreactors can be estimated by assuming that flow in the bioreactor behaves according to plug-flow models. Thus, the required hydraulic residence time (or space time) τ can be calculated from the following familiar design equation:[1,2]

$$\tau = - \int_{C_{NO_3,\ feed}}^{C_{NO_3,\ effluent}} \frac{dC_{NO_3}}{-r_{NO_3}}$$

where C_{NO_3} and r_{NO_3} represent the concentration of nitrate and the rate of denitrification, respectively. This equation can be solved for τ if the denitrification kinetics are known and the influent and effluent nitrate concentrations are specified.

The rate of denitrification has been shown to be primarily a function of nitrate concentrations in the feed. Two models have been used to correlate data and investigate the dependence of rate on feed concentrations. The expressions

$$r_{NO_3} = aC_{NO_3} + b$$

and

$$r_{NO_3} = a + b \ln C_{NO_3}$$

where a and b are experimentally determined constants provided a description of the biodenitrification kinetics which occurred in the 0.5 m diameter column. Either of these rate equations can be combined with the design equation above and used to predict the hydraulic residence times needed to achieve effluent requirements under varying influent nitrate loadings. Using the linear rate equation leads to the following expression:

$$\tau = \ln\left(\frac{C_{NO_3,\text{feed}} + b/a}{C_{NO_3,\text{effluent}} + b/a}\right) \Big/ a \quad .$$

If the logarithmic rate expression is used it is more convenient to solve for the hydraulic residence time by numerical integration. The coefficients in these expressions were obtained using data obtained during operation of the 0.5 m diam reactor. This reactor had a length of 6.4 m, a volume of 1212 L, and was operated at flow rates ranging from approximately 100 L/min to approximately 150 L/min, inlet nitrate concentrations ranging from approximately 500 g/m^3 to approximately 2500 g/m^3, and a carbon to nitrogen ratio of approximately 1.4. Under these operating conditions the following equations were developed. The linear rate expression

$$r_{NO_3} = 0.061\ C_{NO_3} + 1.651$$

where r_{NO_3} has the units [Kg(N-as nitrate)/d$\cdot$m^3] and C_{NO_3} has the units (g/m^3), gave the best correlation for inlet nitrate concentrations of 500 g/m^3 and

below. For inlet concentrations of 700 g/m^3 and lower the logarithmic expression

$$r_{NO_3} = -66.81 + 15.23 \ln C_{NO_3}$$

provided the best correlation. These equations were obtained using a method of least squares and have correlation coefficients (R^2) of 0.78 and 0.77 respectively. For inlet concentrations greater than 700 g/m^3 the 0.5-m diameter column provided a mean removal rate of 31.9 $\pm$ 8.0 [Kg(N-as nitrate)/ d•m^3]. Above inlet nitrate concentrations of 700 g/m^3 only removal rates at or below this mean were used to develop the following rate expression:

$$r_{NO_3} = 0.00131\ C_{NO_3} + 24.34$$

This rate expression provided a reasonably conservative correlation for inlet nitrate concentrations greater than 700 g/m^3 using the 0.5-m diam column data.

While the above models have been used in preliminary data evaluations, other models are being investigated at ORNL. If the above models are employed, the parameters should be evaluated under operating conditions established for a particular application and with consideration for site-specific variables.

Using the relationship

$$V = \tau \cdot Q$$

where V and Q are the reactor volume and the volumetric flow rate to be processed, respectively, the essential volume of the reactor can be defined.

The diameter to be used in generating the required volume is calculated from the relationship

$$v = Q/A = Q/(\pi D^2/4)$$

where v is the superficial liquid velocity in the column, and A and D are the column cross-sectional area and diameter, respectively. Values of v are chosen to provide at least a minimum fluidization of the column and yet avoid washout of the bacteria-coated support particles. When using anthracite coal praticles in the 30- to 60-mesh size range, ORNL has found that a value of v of 0.84 cm/sec satisfies the above requirements.

This approach to specifying the diameter can be used since the rate of denitrification has been shown to be independent of the column diameter in the range of diameters studied. This independence has been verified in 5-cm, 10-cm, 20-cm, and 50-cm diam columns.

After the volume and diameter of the cylindrical geometry have been specified, the length can be readily determined. The required length can be dividied among two or more reactors if the total length is impractical for use in a single reactor.

The above procedures were developed after analyses of data taken under the following operating conditions were performed:

Feed nitrate concentrations: 0-10,000 g/m^3

Feed pH: 7.0 (average)

Feed temperature: 28-32°C

Biomass loading: 15% dry weight of coal.

Students from the Massachusetts Institute of Technology School of Chemical Engineering Practice performed residence-time distribution studies at ORNL on the 50-cm-diam bioreactor in order to characterize the non-ideal flow within the bioreactor. The axial dispersion model which describes mass transport in the axial direction in terms of an apparent longitudinal diffusivity D_L superimposed on the plug-flow velocity v was used. The axial dispersion for a fluidized substance flowing through a tube is described by the equation of continuity[1] as:

$$D_L \frac{\partial^2 C}{\partial z} - v \frac{\partial C}{\partial z} = \frac{\partial C}{\partial t}$$

For the case where one injects a perfect pulse of tracer to the reactor and assumes that there is no dispersion outside the reactor boundaries, the solution to this partial differential equation for distance L from the entrance is given by the following expression:[10]

$$E(\theta) = \sum_{i=1} \alpha_i \exp\left[\frac{0.5\ Pe^2 - (\lambda_i + 0.5\ Pe^2)\theta}{Pe}\right]$$

where

$$\alpha_i = \frac{\lambda_i (0.5\ Pe \sin \lambda_i + \lambda_i \cos \lambda_i)}{(0.5\ Pe)^2 + Pe + \lambda_i^2}$$

θ = dimensionless time = $t/\bar{t}$

Pe = Peclet number, $\frac{vL}{D_L}$

and λ_i is a particular solution to the equation:

$$\lambda_i^2 - Pe\,\lambda_i C_0 + \lambda_i - 0.5\,Pe = 0$$

A variety of mathematical techniques can be used to derive the dispersion parameter (Pe^{-1}) from experimental concentration-vs-time (C - t) curves. For example, the technique used in this analysis relates Pe^{-1} to the variance σ_θ^2 of a C-t curve.

Given discrete values of a C-t curve, one can approximate σ_θ^2 as:

$$\sigma_\theta^2 = \frac{\sum_{i=1}^{\infty} tC\,\Delta t}{t \sum_{i=1}^{\infty} C\,\Delta t} - 1$$

If it is assumed that there is no dispersion outside the system boundaries, it has been shown[1] that:

$$\sigma_\theta^2 = \frac{2}{Pe}\left[1 - \frac{1}{Pe}(1 - e^{-Pe})\right]$$

From Figure 9 it can be seen that an inverse Peclet number of 0.1154 and 0.0884 was obtained at axial velocities of 130 and 115 L/min respectively from the 50-cm-diam bioreactor.[11] Since the inverse Peclet number is zero for an ideal PFR and infinity a single CSTR respectively, it can be seen that the 50-cm-diam column approaches plug-flow although there is some dispersion.

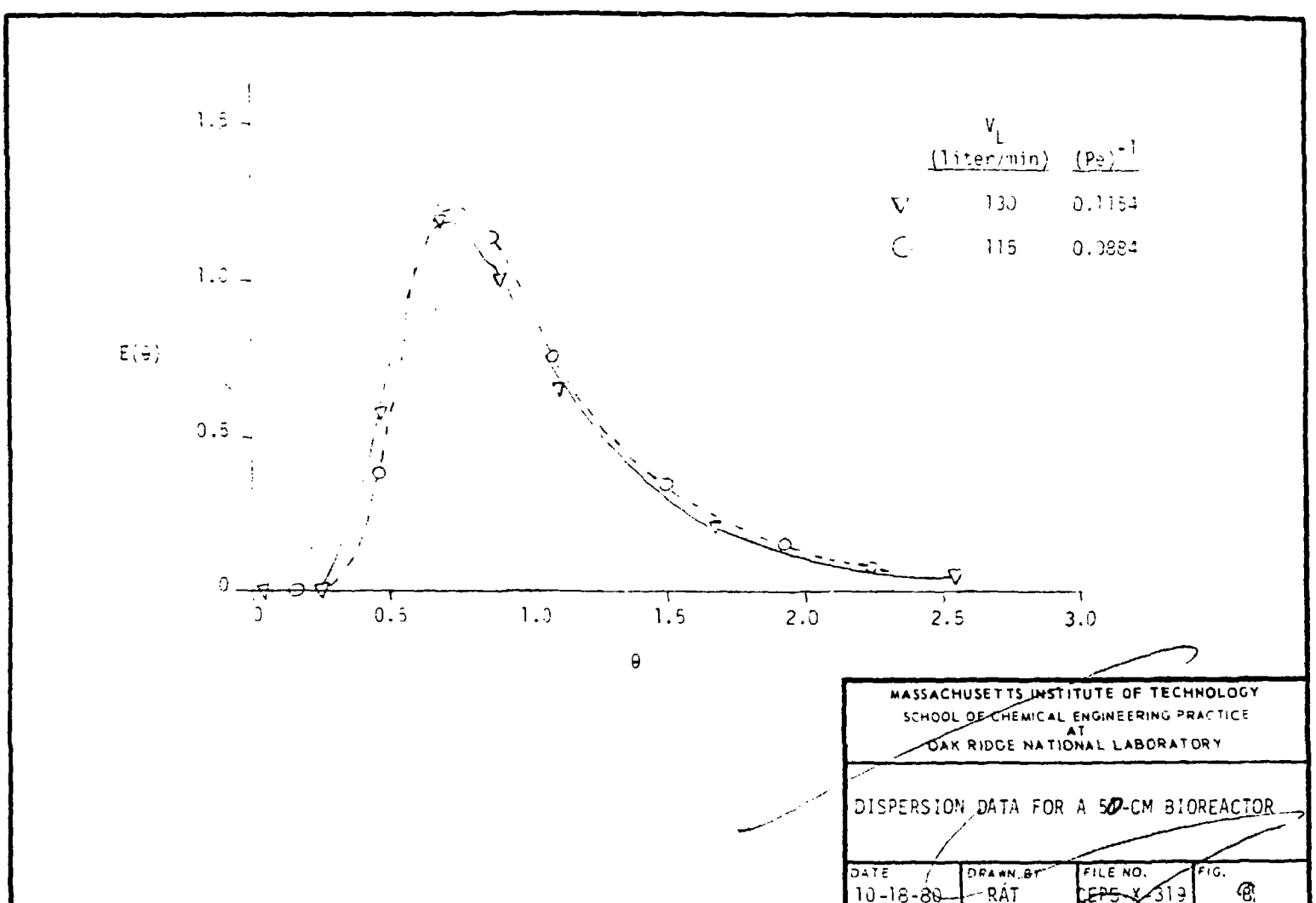

Fig. 9. Dispersion Data for a 50-cm Bioreactor

RESPONSE TO (OR PERTUBATIONS) IN OPERATING CONDITIONS

The 50-cm bioreactor was shut down in order to determine the length of time necessary to reach steady-state operation under normal operating conditions after four days of downtime. It was found that steady-state was reached approximately 31 h after startup. This was determined by the rate of off-gas produced and the nitrate reduction rate. In Figure 10 it can be seen that the rate of off-gas produced increased steadily until the bioreactor reached steady-state at 31 hours; at this time the gas production rate became essentially constant. An analysis of the off-gas produced by the bioreactor showed it consisted of approximately 81% N_2, 18% CO_2, and 1% O_2. It should also be noted that the gas-production rate provided an excellent monitor for the denitrification process. Any perturbations in the process were immediately detected by a decrease in the gas production rate.

Effluent Quality Attainable

At feed concentrations in the range of 0 to 500 g/m^3 nitrate, the 6.4 m high fluidized-bed bioreactors, with a hydraulic residence time (τ) of approximately 11 minutes, demonstrated the ability to produce an effluent stream within the EPA expected discharge level of 10 g/m^3 nitrate (N) in wastewater. It was further demonstrated that the fluidized-bed biological denitrification system is able to attain low nitrogen discharge levels from highly concentrated nitrate wastewater by operating bioreactors in series.

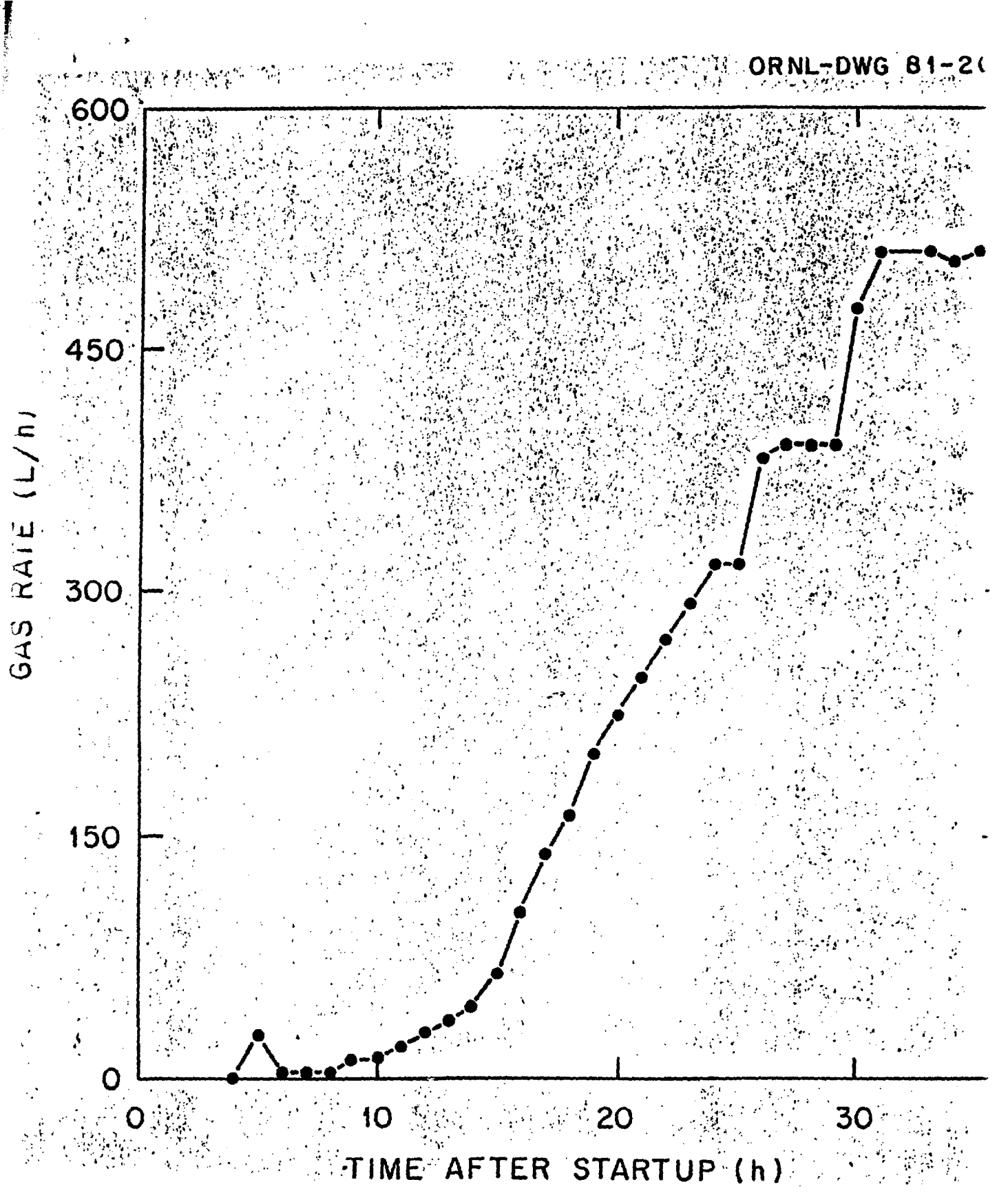

Fig. 10. Effect on Gas Production Rate of a 96-hr Shutdown

The bioreactor effluent also contains organic carbon concentrations which can be reduced to required levels using standard sanitary sewage procedures. These carbon sources include the following: (1) biomass not attached to particles, (2) soluble organic biomass degradation products, (3) dissolved carbon dioxide, and (4) excess organic feed nutrients.[12]

Mixed Carbon Source

The denitrification process requires a molar ratio of carbon consumed to nitrogen (as nitrate) reacted of about 1.3 to 1.5. The 20-cm bioreactor used ethanol alone as well as ethanol plus sucrose to meet this carbon requirement. No difference was detected in the denitrification rates due to a mixed carbon source. It is possible, however, that use of mixed-substrates might result in a more diverse and thus more stable biological population under long-term operations.

Biomass Control

Operating experience has shown that a biomass loading of no more than 5 to 10% by dry weight (0.1 g biomass per 1 g coal) is satisfactory. If this biomass loading is exceeded the rate is decreased due to a reduced reaction surface area. The particles also tend to clump together and these floating particles became difficult to control.[3] The excess biomass generated must be removed periodically to insure optimum bioreactor operation. To control biomass in these pilot plants, a Sweco vibrating screen filter with a 60-mesh screen was used to separate excess biomass from the coal particles.

The NLO pilot plant was first equipped with Sweco filters which contained a 30-mesh screen followed by a 60-mesh screen. This caused operational problems because the process had to be shutdown and the filters dismantled to clean the 60-mesh screen. Due to these difficulties the 30-mesh screen was removed and the filters operated with only the 60-mesh screen. It was observed that the single 60-mesh screen adequately removed excess biomass from the coal particles. This alleviated the problem, thus allowing the screens to be cleaned with the process in operation.

CONCLUSIONS

The denitrification pilot plants were designed and built to heat the specific nitrate wastewaters of GAT and NLO. Rough design procedures were defined for these pilot plants and operating conditions were developed and tested. These pilot plants demonstrated long-term stable operation and the ability to obtain acceptable nitrate discharge levels in the range of 10 $gNO_3\text{-}N/m^3$.

Denitrification rates as high as 78 $[KgN(NO_3^-)/d \cdot m^3]$ were obtained with a hydraulic residence time of approximately 11 minutes. Plug-flow with dispersion models were used to describe hydraulic behavior.

Upon completion of testing, these modular pilot plants were shipped to GAT where they are to be erected for on-site usage.

REFERENCES

1. C. G. Hill, Jr., An Introduction to Chemical Engineering Kinetics and Reactor Design, Wiley, New York, 1977.
2. O. Levenspiel, Chemical Reaction Engineering, 2nd ed., pp. 253-300, Wiley, New York, 1972.
3. W. W. Pitt, C. W. Hancher, and B. D. Patton, "Biological Reduction of Nitrate Wastewater Using a Fluidized-Bed Bioreactor," 9th Annual Hydrometallurgical Meeting, Toronto, Nov. 11-13, 1979.
4. J. Bosman and F. Hendricks, "The Technology and Economics of the Treatment of a Concentrated Nitrogenous Industrial Effluent by Biological Denitrification using a Fluidized Bed Reactor," Biological Fluidized Bed Treatment of Water and Wastewater Conference, Manchester, England, April 14-17, 1980.
5. R. Gregory, and I. Sheiham, "Biological Denitrification of Surface Water. Economics of a Remedy for Nitrate in Drinking Water," Biological Fluidized Bed Treatment of Water and Wastewater Conference, Manchester, England, April 14-17, 1980.
6. C. D. Scott and C. W. Hancher, "Use of a Tapered Fluidized Bed as a Continuous Bioreactor," Biotech. Bioeng., 18, 1393 (1976).
7. C. W. Hancher, P. A. Taylor, and J. M. Napier, "Operation of a Fluidized-Bed Bioreactor for Denitrification," Biotech. Bioeng. Symp. No. 8, 361-378 (1978).
8. D. J. R. Dodd, and D. H. Bone, "Nitrate Reduction by Denitrifying Bacteria in Single- and Two-Stage Continuous Flow Reactors," Water Research, 9, 323 (1975).

9. S. Ailoa, A. E. Humphrey, and N. F. Millis, Biochemical Engineering, 2nd ed., pp. 115-117, Academica Press, Inc., New York and London, 1973.

10. H. A. Thomas and J. E. McKee, "Longitudinal Mixing in Aeration Tanks," Sewage Works J., 16(1) 42 (1944).

11. S. J. Roadcap, R. A. Trevino-Lozano, and S. Znaimer, "Residence Time Distribution Studies in Fluidized-Bed Bioreactors," ORNL/MIT-319, January 1981.

12. B. D. Patton, C. W. Hancher, W. W. Pitt, and J. F. Walker, Jr., "Design of Fluidized-Bed Biological Denitrification System," ORNL/TM-7628.