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The Biodenitrification Development Program

J. F. Walker, Jr.
M. V. Helfrich
T. L. Donaldson

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Chemical Technology Division

THE BIODENITRIFICATION DEVELOPMENT PROGRAM

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THE BIODENITRIFICATION DEVELOPMENT PROGRAM

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ABSTRACT

Oak Ridge National Laboratory (ORNL) conducted a pilot-plant program in support of the fluidized-bed biodenitrification system currently under construction by Westinghouse, Inc., at the Feed Materials Production Center (FMPC) in Fernald, Ohio. Two 0.1-m-diam bioreactors in series, each with ~6.1 m of active bed height, and a single 12.2-m-high, 0.1-m-diam fluidized-bed bioreactor were operated to simulate the larger bioreactors (four 1.2-m-diam bioreactors each with 12.2 m of active bed height to be operated in series) under construction at Fernald. These pilot systems were used to verify the Fernald design as well as to identify and attempt to solve any problems that might affect the full-scale system.

Results of studies with FMPC wastewater having nitrate levels as high as 10 g/L indicate that the Fernald bioreactors probably cannot operate on untreated wastewater because of its high calcium concentration. When the pilot-plant system was tested with raw wastewater having calcium concentrations ranging from 100 to 450 mg/L, the bioreactors ceased to function within 5 weeks after startup due to the buildup of calcium carbonate on the bioparticles. However, Fernald wastewater has been softened at ORNL and successfully biodenitrified.

During biodenitrification, the pH in the bioreactors typically increases from ~7.0 in the feed to ~9.0 in the effluent without pH control. As reported by various other investigators, the optimum pH for biodenitrification ranges from ~7.0 to 7.5, and the denitrification rate falls sharply in the bioreactors as the pH exceeds 8.0. Adjustment of the pH with phosphoric, acetic, and sulfuric acids at several points in the bioreactors has successfully increased the overall denitrification rates.

The results obtained to date indicate that the biodenitrification rate used in the design of the Fernald bioreactors, 32 kg $(NO_3\text{-}N)/d \cdot m^3$, may be achieved or exceeded; however, pH adjustment within the bioreactors may be necessary.

The temperature rise may be as high as 4°C in each bioreactor due to the exothermic nature of the biodenitrification reaction. Under limiting adiabatic conditions, the overall temperature rise through four columns could be 15–20°C. Thus, some kind of temperature control will probably be necessary to achieve optimal performance.

1. INTRODUCTION

Design of the Feed Materials Production Center (FMPC) biodenitrification facility at Fernald, Ohio, has been based on pilot work performed at Oak Ridge National Laboratory (ORNL). Since design of the FMPC facility involves extrapolation of the ORNL results to both significantly larger-scale equipment and to actual rather than synthetic wastewaters, design verification studies were performed by ORNL (May—August 1985) to reduce uncertainties associated with the process. Results of the design verification studies indicated a high probability of serious problems associated with the process which could preclude operation of the full-scale system as originally designed. As a result, a development program was initiated to provide answers to the remaining questions regarding the Fernald biodenitrification system. The Biodenitrification Development Program was subdivided into three major tasks:

1. Operation on synthetic feed to establish a mature culture of biomass and to determine if the design denitrification rate could be met using a synthetic feed;
2. Operation on softened FMPC wastewaters to determine if the design denitrification rate could be obtained using softened FMPC wastewaters as well as to determine if there were any contaminants in the FMPC wastewaters which might inhibit biodenitrification; and
3. Operation on unsoftened FMPC wastewaters to determine if the biodenitrification system could operate in the presence of high concentrations of calcium.

During these major tasks, several additional items were examined, including (1) the effect of the pH on the denitrification rate, (2) the use of various acids for pH adjustment, (3) the effects of the exothermic denitrification reaction on the temperature of the wastewater within the bioreactor, and (4) the correlation between the biomass-to-coal ratio and the biodenitrification rate along the length of the bioreactor.

The results from the Design Verification Program (May—August 1985) and Task 1 of the Biodenitrification Development Program (September—December 1985) were presented in an earlier report.[1] These results indicated that the Fernald biodenitrification system could not operate, as originally designed, on actual wastewaters which contained high concentrations of calcium (>100—450 mg/L) but could achieve the FMPC design rate of 32 kg $N/m^3 \cdot d$ using a synthetic feed prepared from sodium nitrate. However, intrareactor pH adjustment would probably be necessary.

This report covers Task 2 and Task 3 of the Biodenitrification Development Program, which were performed by ORNL.

2. BIOLOGICAL DENITRIFICATION USING FLUIDIZED-BED BIOREACTORS

In biological denitrification, bacteria are utilized to remove nitrate from wastewaters by converting the nitrate to gaseous nitrogen. This is accomplished under anoxic conditions, with the NO_3^- serving as the terminal electron acceptor for microbial respiration in the absence of molecular oxygen. A carbon source such as methanol or acetate must also be present to act as an electron donor.

The bacteria responsible for denitrification are facultative and utilize the same biochemical pathways during both aerobic and anaerobic respiration; the major differences are in the enzymes which catalyze the terminal electron transfer and their sites in the electron transport chain.[2]

The general equation for biological denitrification is presented below:

$$NO_3^- + \text{carbon source} \xrightarrow{\text{microorganisms}} N_2 + CO_2 + H_2O + OH^- + \text{cells.} \qquad (1)$$

As can be seen, hydroxide ions are produced. This production of hydroxide ions may cause the pH within the bioreactor to rise. Several literature studies have shown the denitrification rate to be a function of the pH. These studies have generally shown the optimum pH for biological denitrification to be in the 6.5 to 8.0 range. Outside of this range there is a sharp decrease in the rate of denitrification.[2–5] Also, since denitrification is an exothermic reaction, there may also be a temperature rise within the bioreactor.

In the fluidized-bed bioreactor process developed at ORNL, bacteria are allowed to grow and attach to 30-to 60-mesh anthracite coal particles to form "bioparticles". The wastewater is pumped up through a bed of bioparticles at a velocity sufficient to fluidize the bed. As the wastewater flows past the bioparticles, the nitrate is degraded with N_2 and CO_2 gas being produced and vented to the atmosphere.

3. BACKGROUND AND PROCESS DESCRIPTION

A schematic diagram that includes the wastewater sources at the FMPC, the present treatment scheme, and the proposed treatment scheme is presented in Fig. 1. At the present, the wastewaters are collected in a general sump for neutralization and solids separation before being pumped into the clearwell and released to the environment.

In the proposed treatment scheme, the wastewater, presently being released from the clearwell, will be diverted to an 8.5 x 10^6-gal lined lagoon. The wastewater from the lagoon will be treated in a biodenitrification facility, which will utilize four bioreactors operating in series. Each of these bioreactors will have a 1.3-m (4-ft) diam and an active bed height of 12 m (40 ft). This facility is designed to produce an effluent containing <100 mg/L of nitrate, at flow rates ranging from 600 to 800 L/min (150 to 200 gal/min), with inlet nitrate concentrations up to 10 g/L.

The purpose of the Biodenitrification Development Program was to simulate the operation of one of the 12-m-high bioreactors at the FMPC facility. During Tasks 2 and 3 of the program, two separate pilot biosystems were operated to accomplish this. The first of these pilot facilities utilized two 10-cm (4-in.)-diam, 6-m (20-ft)-high, glass bioreactors operated in series, and the second facility utilized a single 10-cm-diam, 12-m-high PVC bioreactor. The two-reactors-in-series system, which operated from December 10 to January 27 of Task 2, was already present at ORNL and was utilized until the single 12-m bioreactor system could be built to more closely simulate the bioreactors in the FMPC facility. The pilot system with the single 12-m-high bioreactor operated from February 11 through April 7 of Task 2 and for all of Task 3. Both of these pilot systems had sample ports located every 1 to 1.3 m along the length of the bioreactor, so that parameters of interest could be followed through the entire bioreactor.

A schematic diagram of the two-bioreactors-in-series system is presented in Fig. 2. As can be seen, the wastewater from the FMPC clearwell water (~6000 mg NO_3^-/L) was mixed with either softened raffinate or a concentrated sodium nitrate solution to give a nominal inlet nitrate concentration ranging from ~7000 to 10,000 mg NO_3^-/L. A carbon source and nutrients were added to the wastewater before it was pumped into the bottom of the bioreactor. The volume and flow of N_2 and CO_2 gases produced

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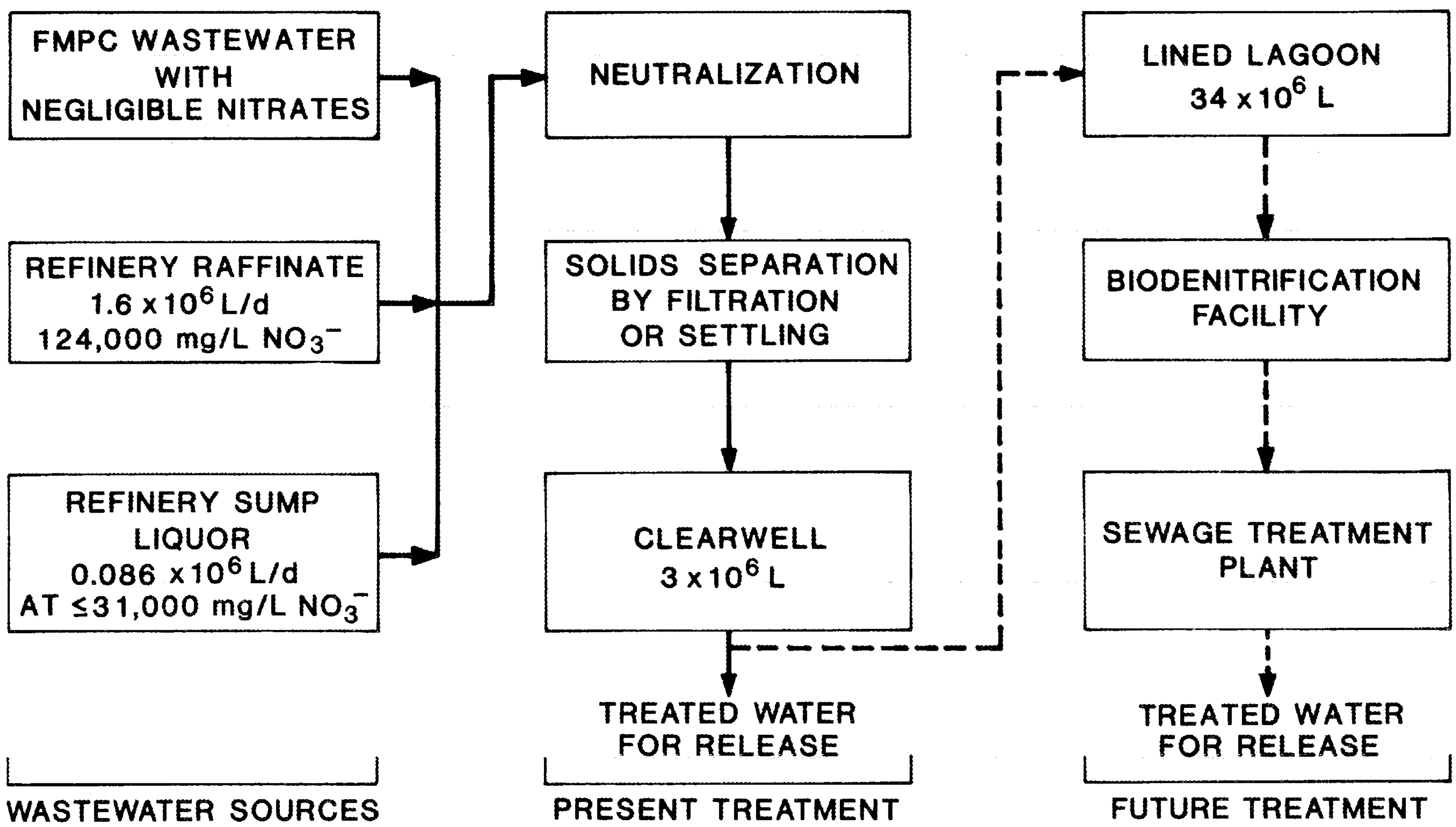

Fig. 1. Schematic flow design of present and proposed FMPC wastewater treatment schemes.

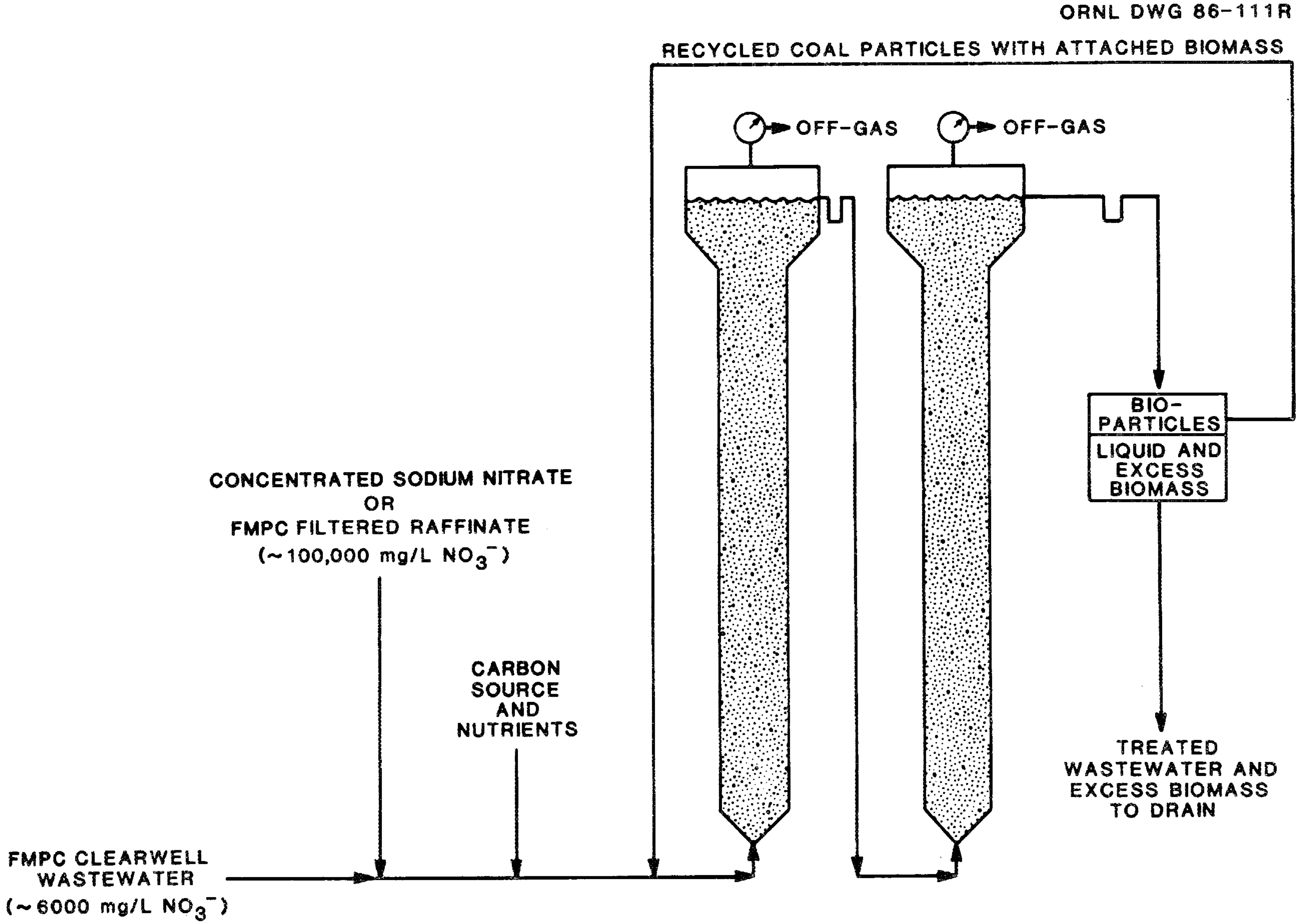

Fig. 2. Schematic diagram of the two-bioreactors-in-series pilot facility.

in the first reactor were continuously monitored and recorded by a wet-test meter, equipped with an electronic pickup, before being vented to the atmosphere. The wastewater and entrained bioparticles overflowed the first bioreactor and were pumped into the second bioreactor. The process was repeated in the second bioreactor, with the liquid and entrained bioparticles passing to a vibrating screen filter which served as a liquid/solid separator. The filter was designed to remove the excess biomass from the bioparticles and to recycle the bioparticles to the inlet of the first bioreactor. The excess biomass and broken coal particles left the system with the effluent from the second bioreactor and were treated in the ORNL nonradiological waste treatment facility.

In the second pilot facility, minor modifications were made to improve the operability of the biosystem; however, the process was essentially identical to the first, except for the change to a single tall bioreactor.

Since Task 2 of the Bioreactor Development Program called for the operation with softened wastewaters from the FMPC, jar tests were run on various combinations of clearwell and raffinate mixtures. From the information generated in these tests, a pilot softening facility was designed and operated. A simplified flow diagram for this facility, which was designed to remove up to 1500 mg/L of calcium at flowrates up to 4 L/min, is presented in Fig. 3. In this softening process, the wastewater (clearwell/raffinate mixtures), sodium hydroxide, and commercial grade soda ash were brought together in a 10-L rapid-mixing tank, which was designed to thoroughly mix the softening chemicals. Enough sodium hydroxide was added to raise the pH to 11.5, and the amount of soda ash added varied with the calcium concentration in the wastewater. From the rapid-mix tank, the wastewater flowed by gravity to an ~100-L flocculating tank. This tank was designed for the addition of a polymer to aid in solids settling; however, from operational experience it was found that a flocculating agent was not required. From the flocculating tank, the wastewater flowed by gravity to an ~200-L settling tank, where it was forced up through a sludge blanket. The softened wastewater from this tank was pumped to the biosystem for treatment (removal of nitrates), while the solids were periodically removed from the bottom for disposal.

ORNL DWG 86-635

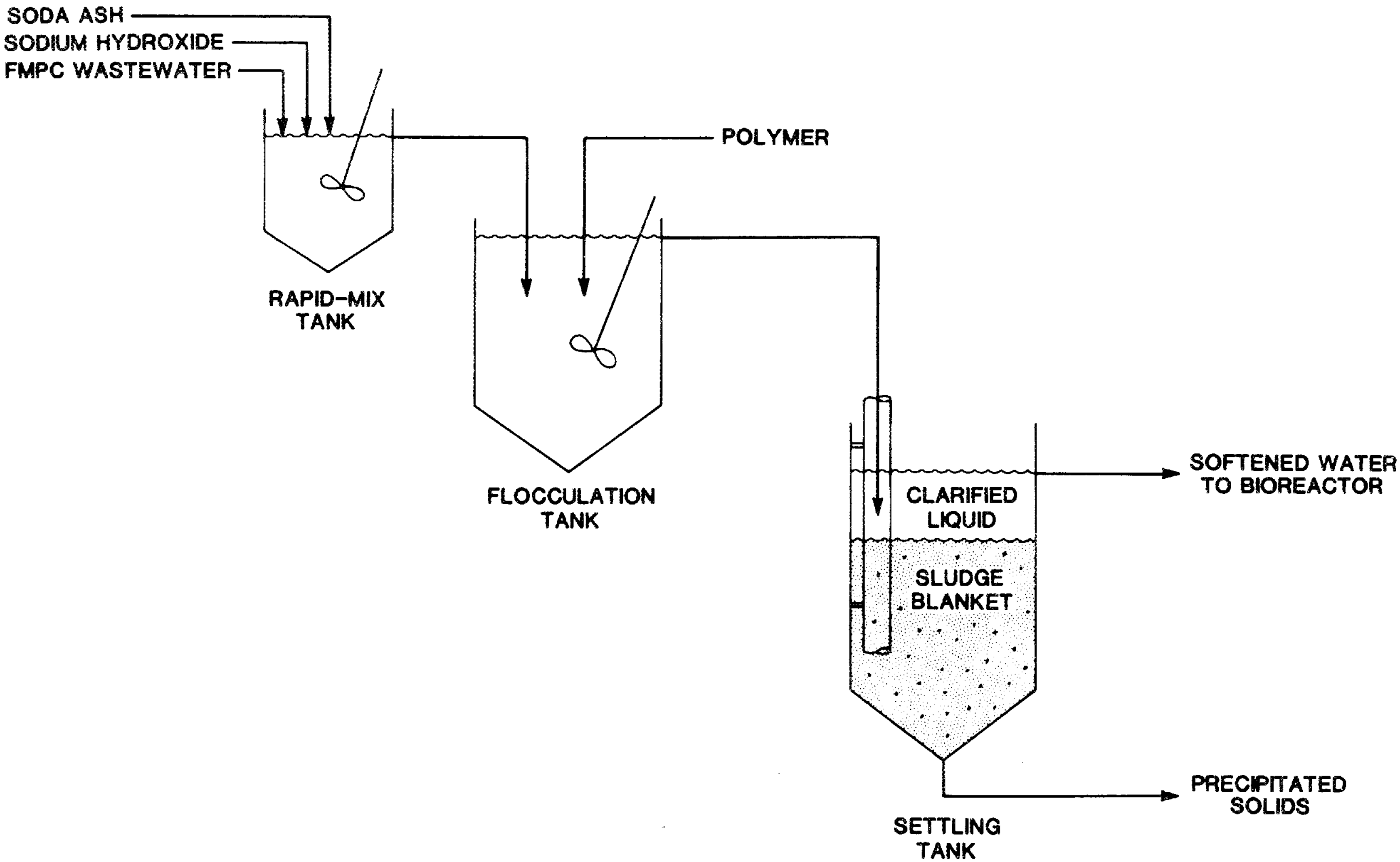

Fig. 3. Schematic diagram of the pilot softening unit used to soften the feed to the biodenitrification system during Task 2.

4. EXPERIMENTAL METHODS

During the experimental portion of this program, liquid, solid, and gas samples were taken and subjected to various chemical analyses. A summary of the samples taken, the analyses performed, and the frequency of analysis is presented in Table 1, while the analytical procedures used are presented in Table 2.

In addition to these analyses, the temperatures along the length of the bioreactor, the inlet and effluent pH, and the off-gas rate were continually monitored.

Table 1. Summary of analyses for the Biodenitrification Development Program

Sample	Sample point	Analysis	Frequency
Wastewater	Influent and bioreactor profile	NO_3^-	3 to 5 x/week
		pH	3 to 5 x/week
		NO_2^-	intermittent
		TOC	1 to 5 x/week
		PO_4^{3-}	
		Ca^{2+}	intermittent
Bioparticles	Bioreactor profile	Biomass loading	intermittent
		Precipitate characterization	intermittent
Off-gas	Gas vent line	CO_2	intermittent
		N_2	
		O_2	
		Combustibles	
Wastewater	Softener inlet and effluent	Ca^{2+}	intermittent
Wastewater	Raw clearwell and raffinate	Metals	intermittent
		NO_3^-	
		NO_2^-	
		TOC	
		Organics	

Table 2. Summary of analytical procedures

Analysis	Method
Nitrate	HACH cadmium reduction [a,b]
Nitrite	HACH ferrous sulfate[a]
pH	pH electrode[c]
Total organic carbon	Combustion - infrared[c]
Phosphate	HACH orthophosphate[a]
Calcium	EDTA titrimetric method[c]
Biomass loading	Wt % biomass
Off-gas analysis	Mass spectrometer or gas chromatograph[c]
Metals	Ion-capture argon plasma spectrograph[d]
Precipitate identification	Electron-excited X-ray fluorescence scan[d]

[a]Source: (Ref. 6) Water Analysis Handbook, 1985 ed., HACH Systems for Analysis, Loveland, Colo.

[b]This test measures the quantity of nitrogen from both nitrate and nitrite, which is present in the wastewater.

[c]Source: (Ref. 7) Standard Methods for the Examination of Water and Wastewater, 15th ed., American Public Health Association, Washington D.C., 1981.

[d]Source: (Ref. 8) Oak Ridge National Laboratory, Analytical Chemistry Division.

5. CORRELATION BETWEEN OFF-GAS AND DENITRIFICATION RATE

The primary reason for continually monitoring and recording the off-gas rate was to develop a correlation between the off-gas rate and the rate of denitrification calculated from the inlet and effluent nitrate concentrations, as shown below.

Volumetric Biodenitrification Rate ($kg\ N/m^3 \cdot d$) = [nitrate in - nitrate out (mg/L)] / reactor volume (L) * (14 mg N/62 mg NO_3^-) * (1440 min/d) * (1 kg/10^6 mg) * (10^3 L/m^3) * [volumetric flow rate (L/min)].

As can be seen from the denitrification stoichiometry for overall nitrate removal, which is presented in Appendix A for both methanol and ethanol carbon sources, for each mole of nitrate consumed, 0.47 mol N_2 and 0.76 mol CO_2 are generated. From a material balance, comparing the quantity of CO_2 generated and its solubility in water, it can be shown that essentially all of the CO_2 generated can be dissolved in the wastewater. Since nitrogen is only slightly soluble in water, it can be assumed that most of the off-gas would be in the form of nitrogen. This was confirmed by several analyses of the off-gas taken during the course of the program. A summary of these off-gas analyses is presented in Table 3.

Table 3. Summary of off-gas analyses taken during the Biodenitrification Development Program

Component	Mean concentration (%)	Standard deviation (5 samples)
N_2	93.0	4.1
O_2	2.6	2.1
CO_2	3.4	2.1
H_2	>0.01	
CH_4	a	
NO	a	
NO_2	a	
CO	a	

[a]Indicates that none of the component was detected.

Using the above assumptions, a material balance for nitrogen indicates that 4 L/h of off-gas should be generated for every kilogram of nitrogen consumed per day per cubic meter (kg $N/d \cdot m^3$) of reactor volume. Presented in Fig. 4 is a graph of the off-gas rate vs the denitrification rate for the entire period of operation of the 12-m bioreactor. From the least squares fit (which was forced through the origin), it can be seen that the slope indicates that for this entire period of operation, an average of 3.8 L/h of off-gas was generated per kg $N/d \cdot m^3$. This is in good agreement with the value from the material balance (4 L/h) presented above.

It should be noted that during portions of this operational period, a lot of scatter occurred in the nitrate axial profile data, while at other

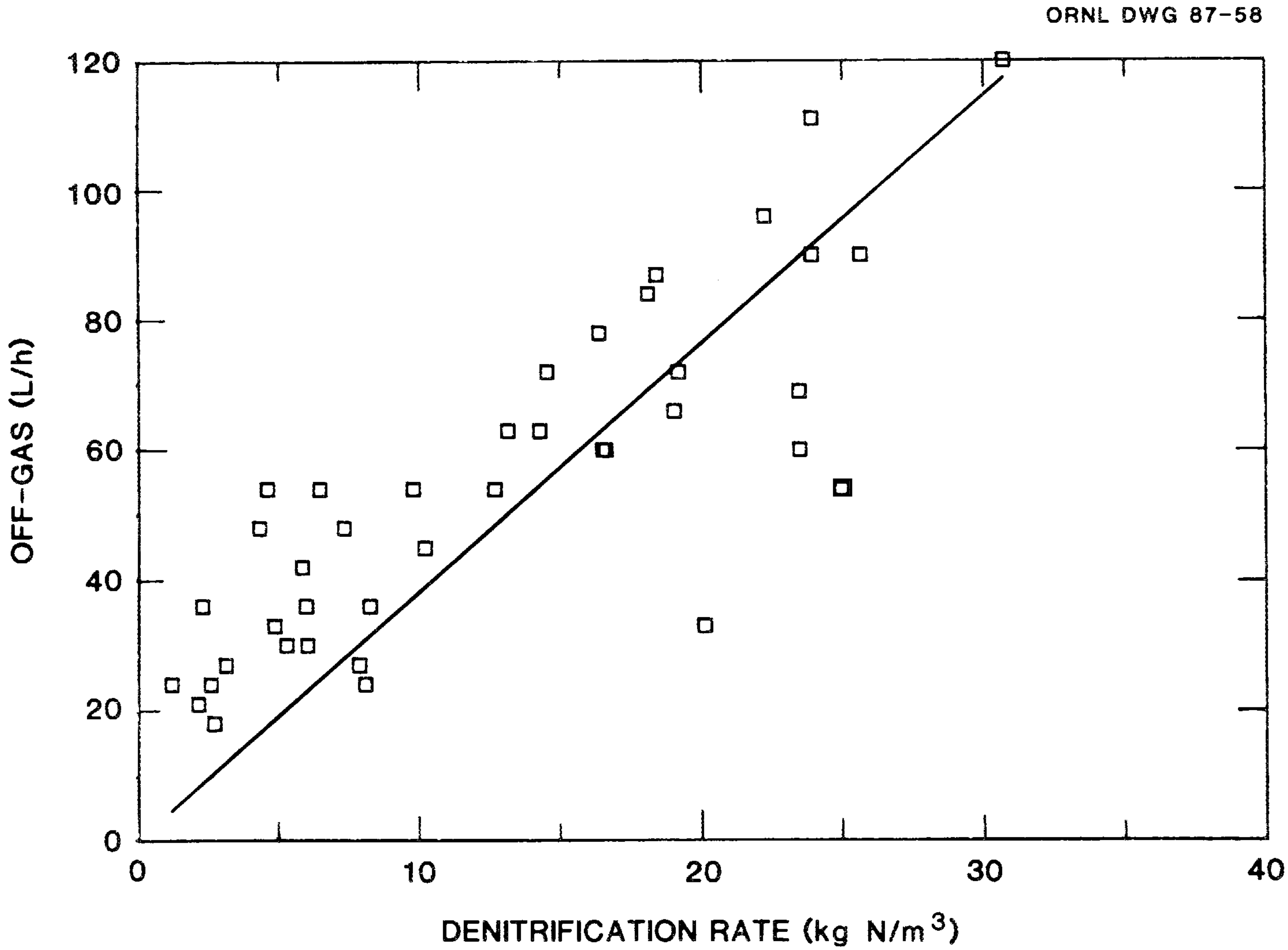

Fig. 4. Comparison of the off-gas rate with the denitrification rate as calculated from the inlet and effluent nitrate concentrations for the entire period of operation of the 12-m bioreactor.

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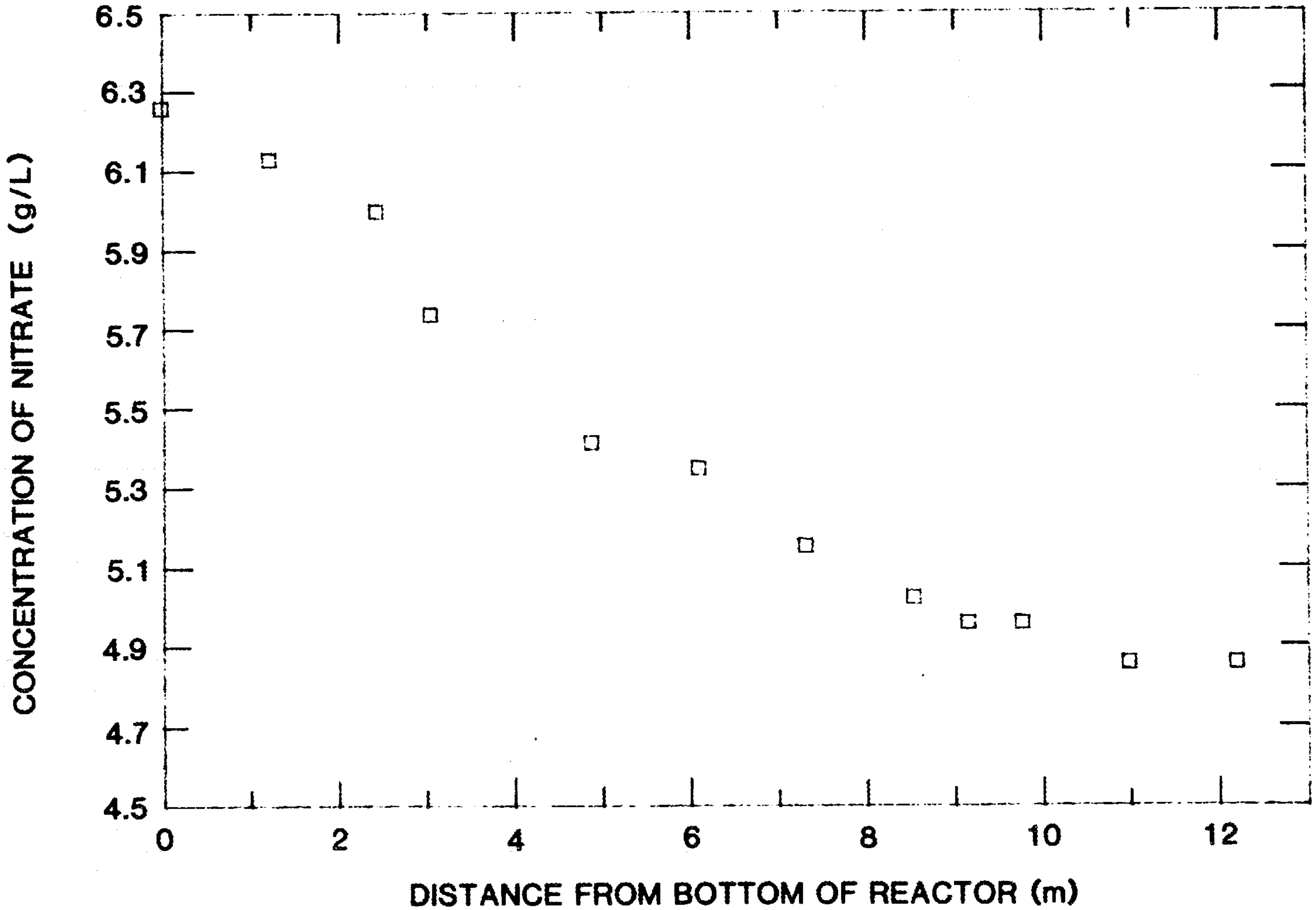

Fig. 5. Nitrate profile from the 12-m bioreactor on May 1, 1986, which shows little scatter in the data during a period of high denitrification.

ORNL DWG 87-56

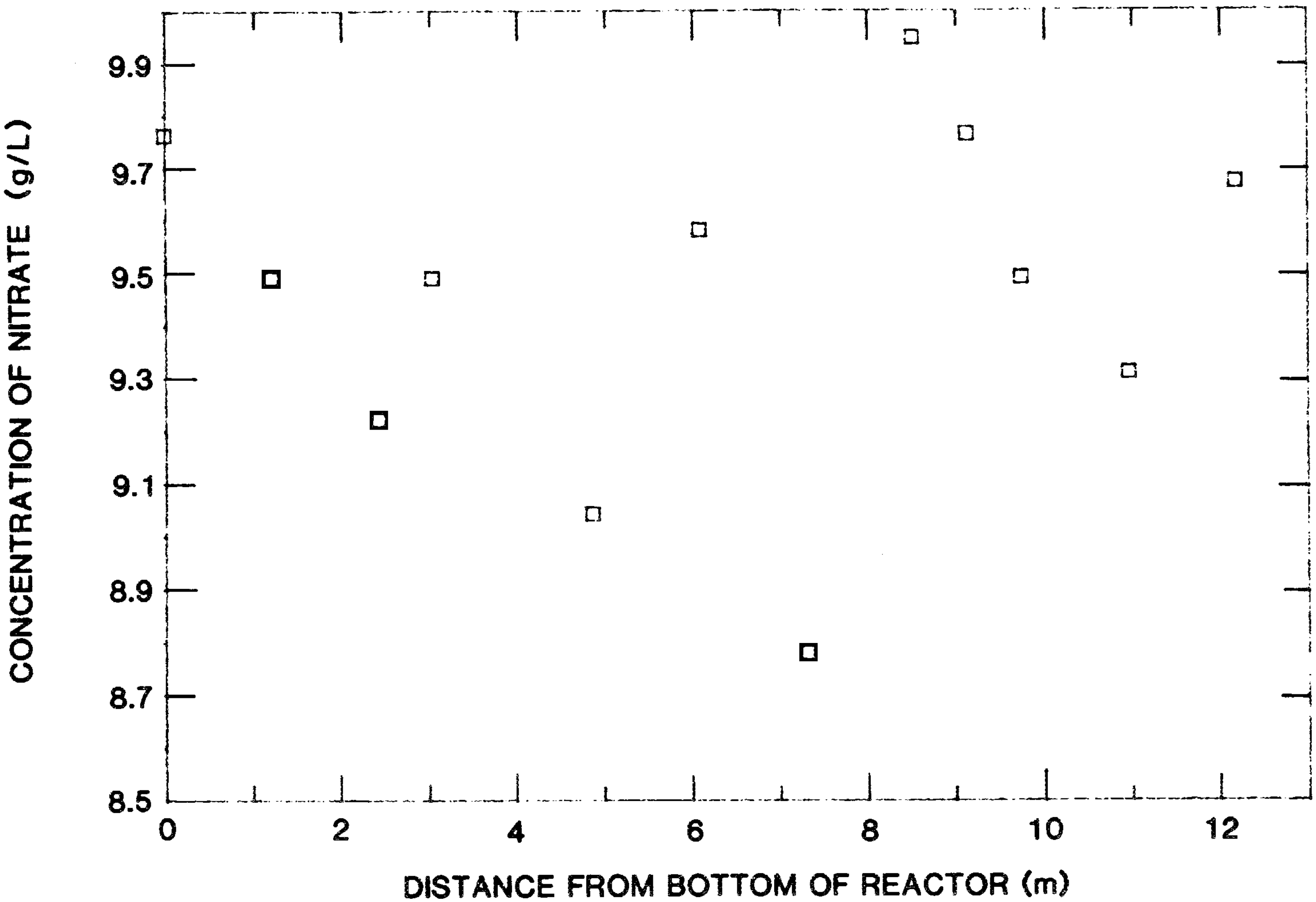

Fig. 6. Nitrate profile for the 12-m bioreactor on March 19, 1986, which shows considerable scatter in the data during a period of low denitrification.

times, very little scatter appeared. This can be seen graphically by comparing Figs. 5 and 6, which represent two extremes for the operational period. In general, during periods of lower denitrification (10 kg N/d·m^3) there seemed to be more scatter in the nitrate profile samples than during periods of higher denitrification. This is believed to be due, in part, to the experimental error inherent in measuring the smaller changes in nitrate concentrations. By observing Fig. 6, it can be seen that most of the scatter present is within the ± 5% experimental error attributable to the analytical procedure. From visual observations of the bioreactors, it is apparent that there are erratic flow patterns within the bioreactors which may also contribute to the scatter in the nitrate profile samples.[9]

During periods with little scatter in the nitrate profile data, the off-gas generation and denitrification rates, as calculated from the nitrate profile data, correlated well. During periods with a lot of scatter in the nitrate profiles, the denitrification rate, calculated from the off-gas generation, provided a better indication of bioreactor performance than did the denitrification rate, which was calculated from the profile data. Therefore, throughout this report the off-gas data will be used to provide a continuous overall denitrification rate, and the bioreactor profile data will be used to examine the relationship between the denitrification rate and various parameters of interest within the bioreactor. A complete record of the off-gas data for both Tasks 2 and 3 is presented in Appendix B.

6. BIODENITRIFICATION DEVELOPMENT PROGRAM TASK 2 (DECEMBER 10, 1985–APRIL 17, 1986)

Task 2 consisted of the operation of the biodenitrification system utilizing softened clearwell water as the feed source, with the primary objective being to demonstrate that the FMPC design denitrification rate, with the maintenance of a stable biomass/coal ratio on softened water, was achievable. During Task 2, the two-bioreactors-in-series system was operated from December 10, 1985, until January 27, 1986, and the single bioreactor system was operated from February 11 until April 17, 1986. During Task 2, the FMPC wastewaters were treated in a pilot softening unit that had been designed, constructed, and tested during Task 1. This softening unit consistently reduced the level of calcium to <10 mg/L.

A chronological order of events for Task 2 of the Biodenitrification Development Program is presented in Table 4. From this table, Task 2 can be split into three operational periods:

1. Operation on softened FMPC wastewater with the two 6-m bioreactors in series, using methanol as the carbon source;
2. Operation on softened FMPC wastewater with the single 12-m bioreactor system, using methanol as the carbon source; and
3. Operation on softened FMPC wastewater, using ethanol as the carbon source.

These three operational periods are discussed further in Sect. 6.1.

Table 4. Chronological order of events for Task 2 of the Biodenitrification Development Program (December 10, 1985—April 17, 1986)

Date	Event
December 10:	Softened clearwell, at 1 L/min, was mixed with 3 L/min of ORNL process water and pumped into the bioreactor. The concentration of calcium leaving the softener was assayed to be 2.7 mg/L.
December 11:	The softened clearwell flow rate was raised from 1 to 2 L/min. The concentration of calcium leaving the softener assayed at <1 mg/L.
December 12:	The flow rate of the softened clearwell water was raised from 2 to 3 L/min.
December 13:	The flow rate of the softened clearwell water was raised from 3 to 4 L/min.
December 19:	A load of clearwell water was received at ~1300 h.
December 20:	A load of clearwell water was received at 1500 h. The system had to be shut down at ~1900 h because solids from the vibrating screen filter had clogged the return line to the feed pot.
December 23:	A load of clearwell water was received. The calcium concentration entering the bioreactor assayed at 2.7 mg/L.
December 26:	The second bioreactor clogged from the carryover of bacteria peeling off the lines from the first bioreactor.

Table 4 (continued)

Date	Event
December 31:	A load of clearwell water was received.
January 1:	The methanol line feeding the bioreactor began leaking.
January 2:	The methanol line feeding the bioreactor ruptured, and the bioreactor was without a carbon source for ~8 h.
January 3:	A load of clearwell water was received at ~0800 h.
January 5:	The pH at the inlet of the second bioreactor fell to 2.9 for ~1 min.
January 6:	At ~1500 h, raffinate was introduced to the softening unit at a flow rate of ~450 mL/min. At ~1520 h, the raffinate addition was stopped.
January 7:	The addition of raffinate to the softening unit was initiated at ~1000 h to give a feed mixture of 88% softened clearwell and 12% softened raffinate.
January 8:	A malfunction in the softening unit caused the calcium concentration to climb to ~350 mg/L for several hours.
January 9:	The raffinate addition was stopped at ~1000 h. A buildup of calcium carbonate was observed in the feed lines to the bioreactor.
January 13:	A sample of the raffinate sent to analytical chemistry for analysis identified no components which were toxic to the bacteria. The flow of methanol to the biosystem was stopped at ~1700 h.
January 14:	The flow of methanol into the system was again started at ~0800 h.
January 16:	The bioreactors were reinoculated.
January 17:	A load of clearwell water was received at ~1200 h.
January 18:	During the evening hours the pH control system failed, the pH into the first bioreactor climbed to 11.5, and the pH into the second bioreactor climbed to 10.7.

Table 4 (continued)

Date	Event
January 20:	The biosystem was reinoculated.
January 21:	The biosystem was reinoculated.
January 23:	The system was switched to a synthetic feed in an attempt to improve the denitrification rate.
January 27:	The contents of the two 20-ft bioreactors were emptied into a 500-gal tank and operated as a batch reactor.
February 10:	The coal and biomass were transferred from the 500-gal tank to the 40-ft bioreactor.
February 11:	The 40-ft bioreactor was started on softened clearwell water at a reduced flow rate and in a partial recycle.
February 13:	The flow rate was raised to 4 L/min, and the bioreactor was taken off recycle.
February 19:	The addition of 10% phosphoric acid at the 20-ft level was initiated.
February 20:	The initiation of 10% phosphoric acid at the 10-ft level was initiated.
February 24:	The denitrification rates dropped to a very low value for a reason which could not be determined. The most probable reason was a possible contamination in the process water.
February 25:	The bioreactor was reinoculated.
March 5:	The bioreactor was again reinoculated, and the biosystem flow rate was reduced to 1 L/min in an attempt to give the bacteria more time to attach.
March 6:	The biosystem flow rate was raised to 2 L/min.
March 7:	The biosystem flow rate was raised to 3 L/min.
March 10:	Jar tests indicated that the raffinate was not toxic to the bacteria.
March 11:	Raffinate was introduced into the softener at a flow rate of ~400 mL/min at ~1250 h.

Table 4 (continued)

Date	Event
March 12:	The raffinate flow rate was reduced from 400 mL/min to 200 mL/min, and the wastewater entering the bioreactor assayed at 5.2 mg/L of calcium.
March 13:	A load of clearwell water was received at ~1130 h, and the addition of raffinate was stopped at ~2000 h.
March 14:	A process of filtering all raffinate which was to be treated in the biosystem with a 10-μm filter was initiated.
March 17:	The addition of filtered raffinate into the softening system at 30 mL/min was initiated.
March 18:	A load of clearwell water was received at ~1230 h.
March 19:	A load of clearwell water was received.
March 21:	The raffinate flow rate was increased to 115 mL/min in small increments during the day.
March 24:	The raffinate flow rate was increased to 200 mL/min, and the wastewater entering the biosystem assayed at 4 mg/L of calcium.
March 25:	A load of clearwell water was received at ~1400 h.
March 26:	The raffinate flow rate was increased to 300 mL/min.
March 28:	The pH at the inlet of the bioreactor climbed to ~11 for ~12 h during the off shift. The bioreactor was reinoculated with coal fines and 1 gal of Portsmouth coal and bacteria.
March 29:	The bioreactor was reinoculated.
March 31:	The flow rate to the bioreactor was reduced to 2 L/min, the raffinate flow rate was reduced to 30 mL/min, and the bioreactor was placed in total recycle during the day and in a once-through mode of operation at night.
April 1:	The carbon source was switched from methanol to ethanol at ~1600 h.
April 3:	The raffinate flow rate was increased to 60 mL/min, and the system was switched from a recycle mode to a once-through

Table 4 (continued)

Date	Event
	mode of operation at 4 L/min.
April 4:	The system flow rate was reduced to 2 L/min.
April 8:	The system flow rate was raised to 4 L/min, and two loads of clearwell water were received.
April 9:	The first 6 ft of the bioreactor was not fluidized because of the heavy buildup of biomass in the bottom of the bioreactor. Two loads of clearwell water were received, and the wastewater entering the bioreactor assay at 2.6 mg/L of calcium.
April 10:	Approximately 7.5 gal of coal and biomass was removed from the bottom of the bioreactor and reintroduced through the feed pump to shear off the excess biomass.
April 11:	A new load of clearwell water was received.
April 17:	The supply of raffinate ran out at ~1200 h, and raw clearwell water was introduced into the bioreactor. The addition of phosphoric acid at the 20-ft level was initiated.

6.1 OPERATION ON SOFTENED FMPC WASTEWATER, USING METHANOL AS THE CARBON SOURCE, IN THE TWO-BIOREACTOR SYSTEM (December 10, 1985–January 27, 1986)

On December 10, the feed to the two-bioreactors-in-series system was switched from a synthetic sodium nitrate solution to softened clearwell water. With the introduction of the softened clearwell water, there was an immediate increase in the rate of denitrification, as indicated by the off-gas record presented in Fig. 7. As can be seen, for several days prior to the addition of the softened clearwell water, the system had been operating at an off-gas generation level of ~100 L/h (25 kg N/d•m^3). With the addition of the softened clearwell water, the off-gas rate jumped to ~170 L/h (42.5 kg N/d•m^3) before leveling off at ~145 L/h (36 kg N/d•m^3). This represents a 45% increase in the denitrification rate, which can be attributed, at least in part, to the buffering capacity of the softened clearwell water. The effects of this buffering capacity, which caused a smaller pH rise even though denitrification rates were higher, can be seen in Fig. 8.

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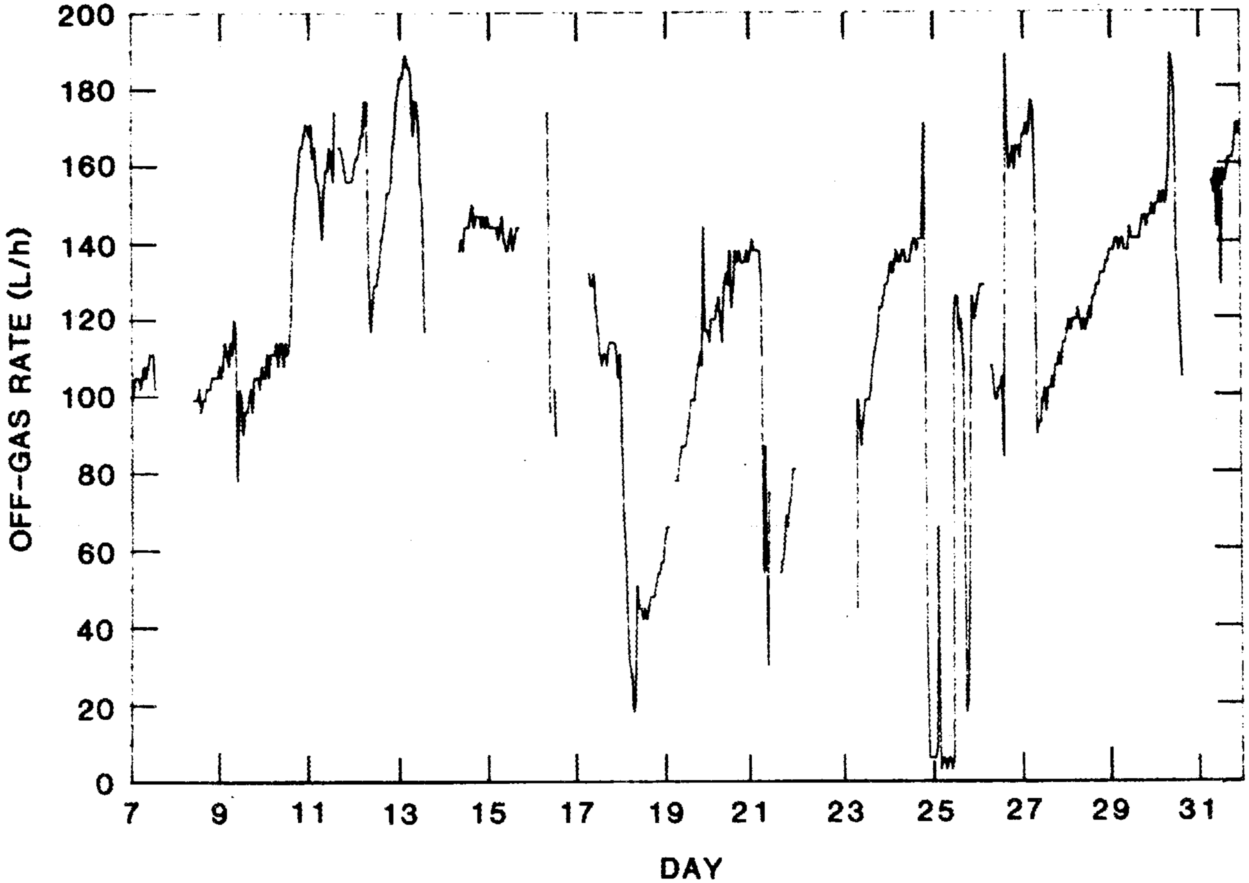


OFF-GAS RATE VS TIME
DECEMBER 7 - DECEMBER 31

Fig. 7. Off-gas record for bioreactors-in-series system from December 7–31, 1985, which shows an increase in the denitrification rate after the addition of softened clearwell water on December 10, 1985.

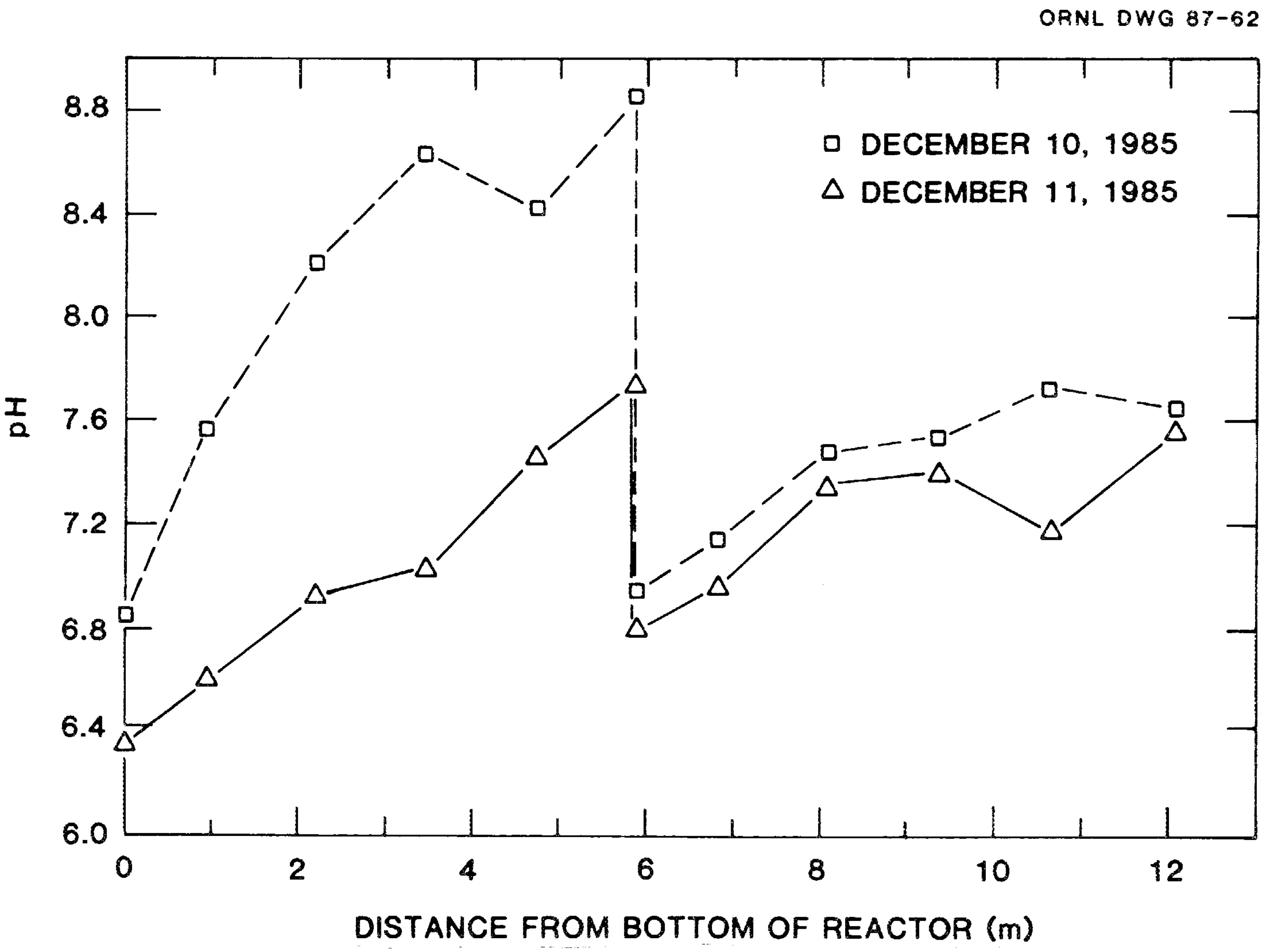


Fig. 8. Comparison of the pH profiles from the two-reactors-in-series pilot facility for December 10 and 11, 1985, which shows the buffering capacity of the softened clearwell water.

Figure 8 presents a comparison of the pH profiles taken from the bioreactors the day before and the day after the addition of the softened clearwell water. As can be seen, on the day before the addition of the softened clearwell water, the pH in the first bioreactor rose from ~6.8 to ~8.9, while on the day after the addition, the pH rose from ~6.4 to ~7.6. Likewise, in the second bioreactor, the pH rose from ~6.8 to ~7.6 the day before the addition and from ~6.8 to ~7.4 the day after the addition of the softened clearwell water. The less-dramatic pH rise in the second bioreactor can be attributed to acid addition halfway up the second bioreactor, which is the 9-m level on Fig. 8. These pH profiles, which are characteristic of the period while operating with softened clearwell water in the two-bioreactors-in-series system, also indicate feed pH values as low as 6.5 may be utilized without adversely affecting the system denitrification rate.

Presented in Figs. 9 and 10 are typical nitrate vs reactor-height profiles during this period of operation. As can be seen, nitrate is being degraded over the entire height of both bioreactors. The high biodenitrification in the bottom 3 m of bioreactor and the very low rates in the top 3 m, which were seen in Task 1, were not as pronounced during this period of operation.

By again observing Fig. 7, it can be seen that from December 18 through December 31, there were approximately six separate incidents, mostly operational problems, which caused at least a 50% drop in the off-gas rate. Following each of these incidents, the off-gas rate recovered and seemed to level out in the range of 140 to 170 L/h (35–42.5 kg N/d·m^3), which exceeds the FMPC design denitrification rate.

As presented in Fig. 11, a graph of the off-gas rate vs time for the remainder of this operational period, two points are of particular interest. The first of these represents the addition of softened raffinate. On January 6, softened raffinate was introduced into the feed tank of the biosystem at a flowrate of 460 mL/min for ~20 min. Because the feed tank had a capacity of 500 gal, the softened raffinate was present in the feed to the bioreactor for ~8 h. Following this introduction, the off-gas rate fell from ~120 L/h (30 kg N/d·m^3) to ~80

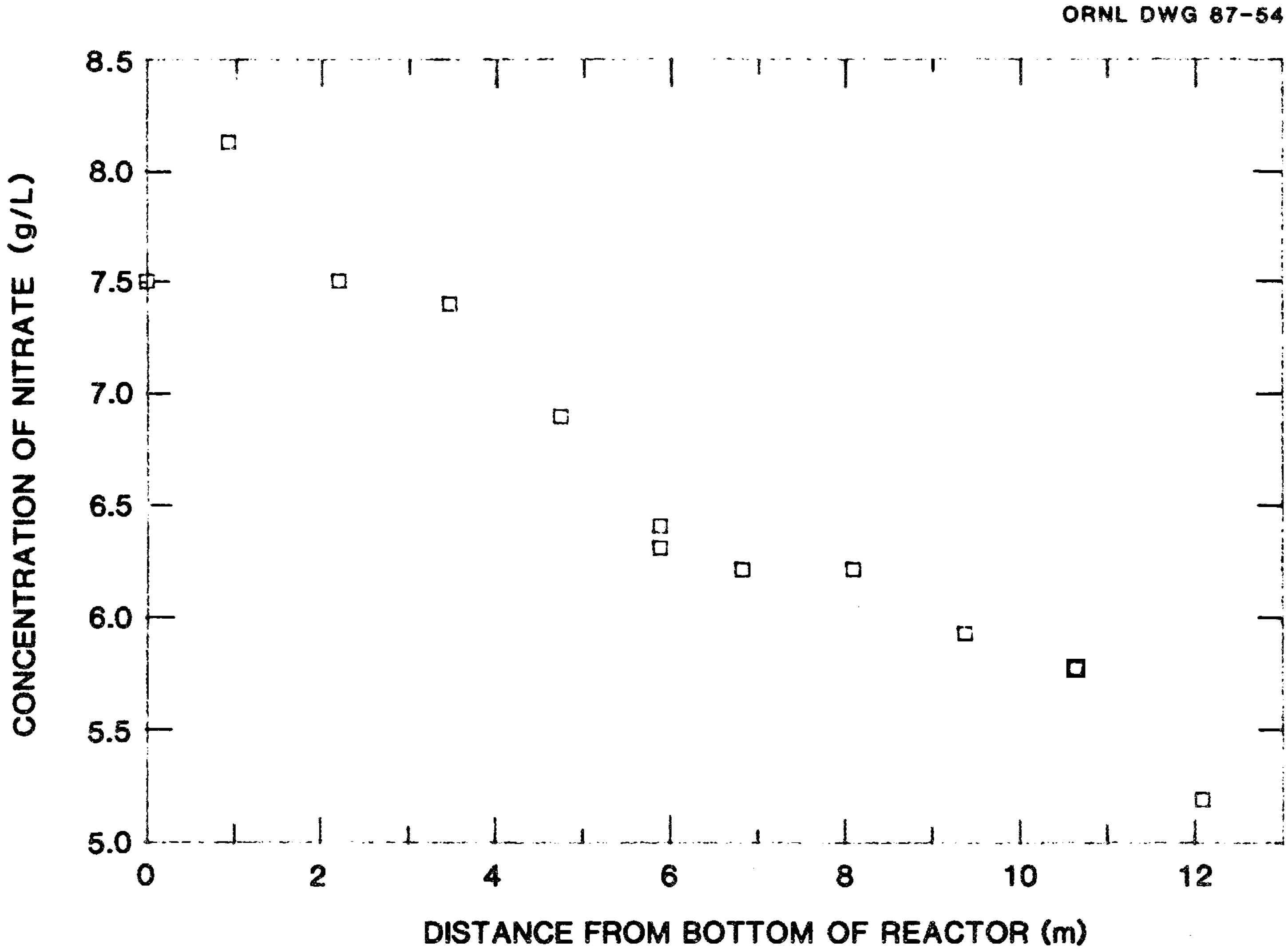


Fig. 9. Nitrate profile from the two-reactors-in-series system on December 11, 1985, which shows nitrate being degraded over the entire height of both reactors.

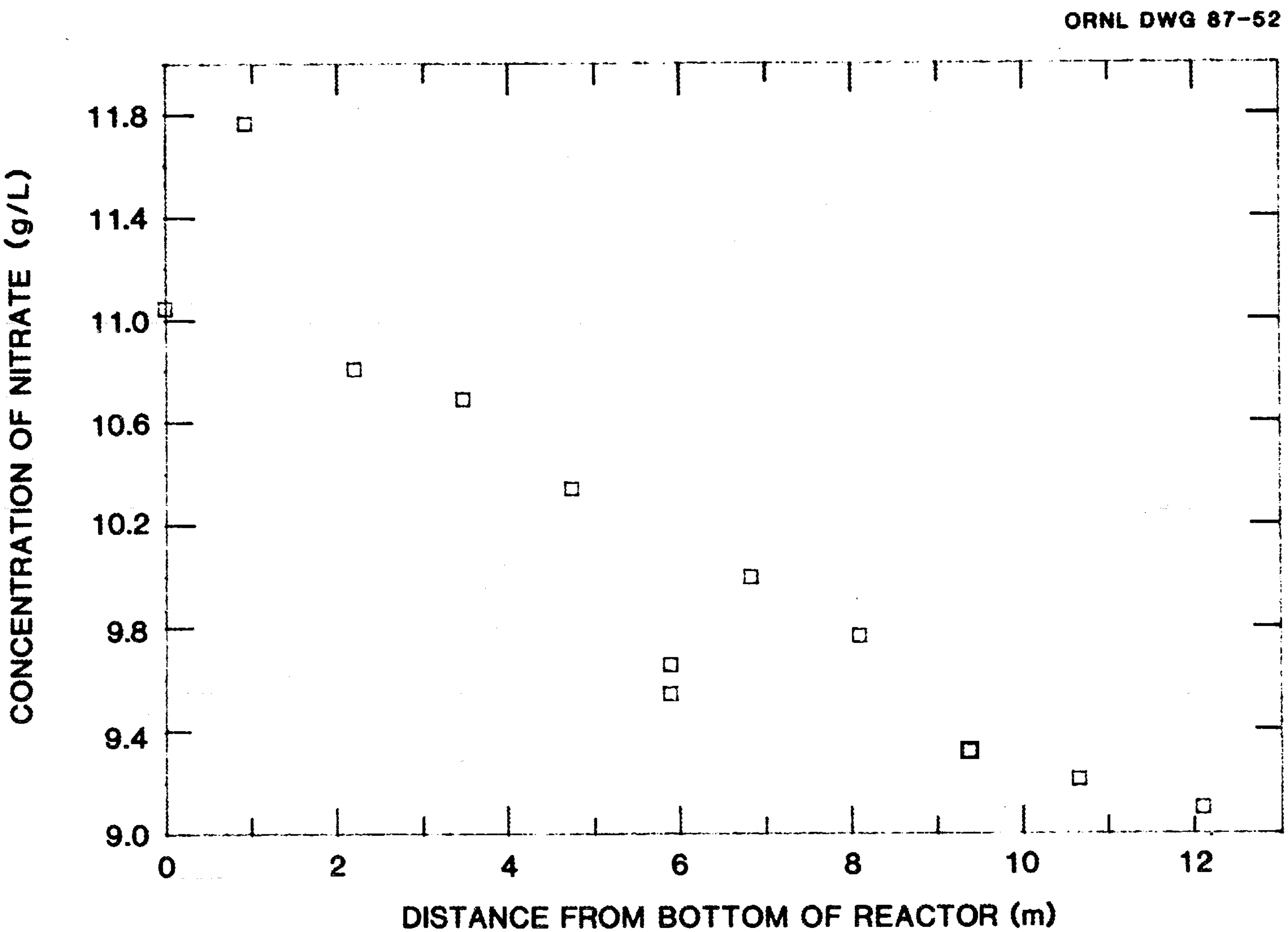
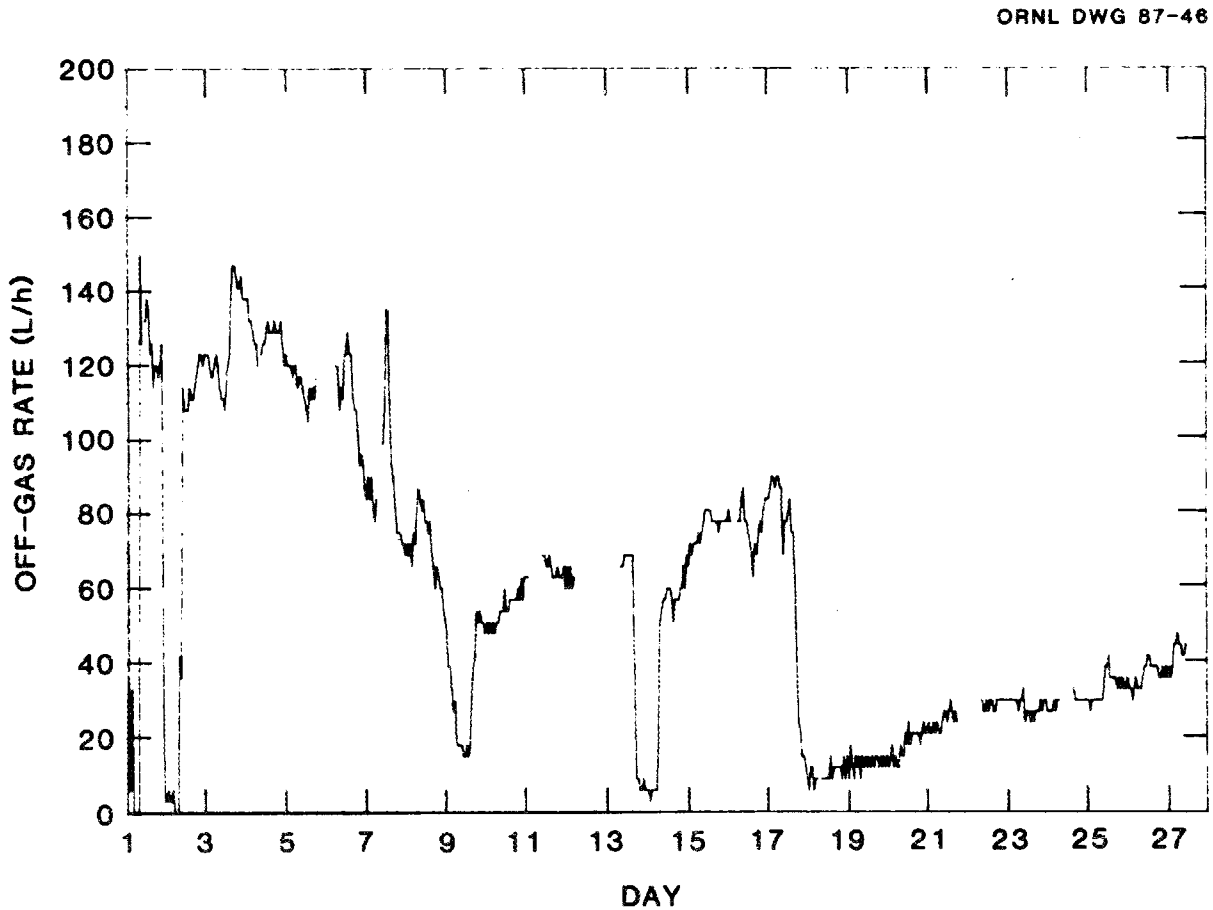


Fig. 10. Nitrate profile for the two-reactors-in-series system on December 27, 1985, which shows denitrification occuring in both bioreactors.



OFF-GAS RATE VS TIME
JANUARY 1 - JANUARY 27

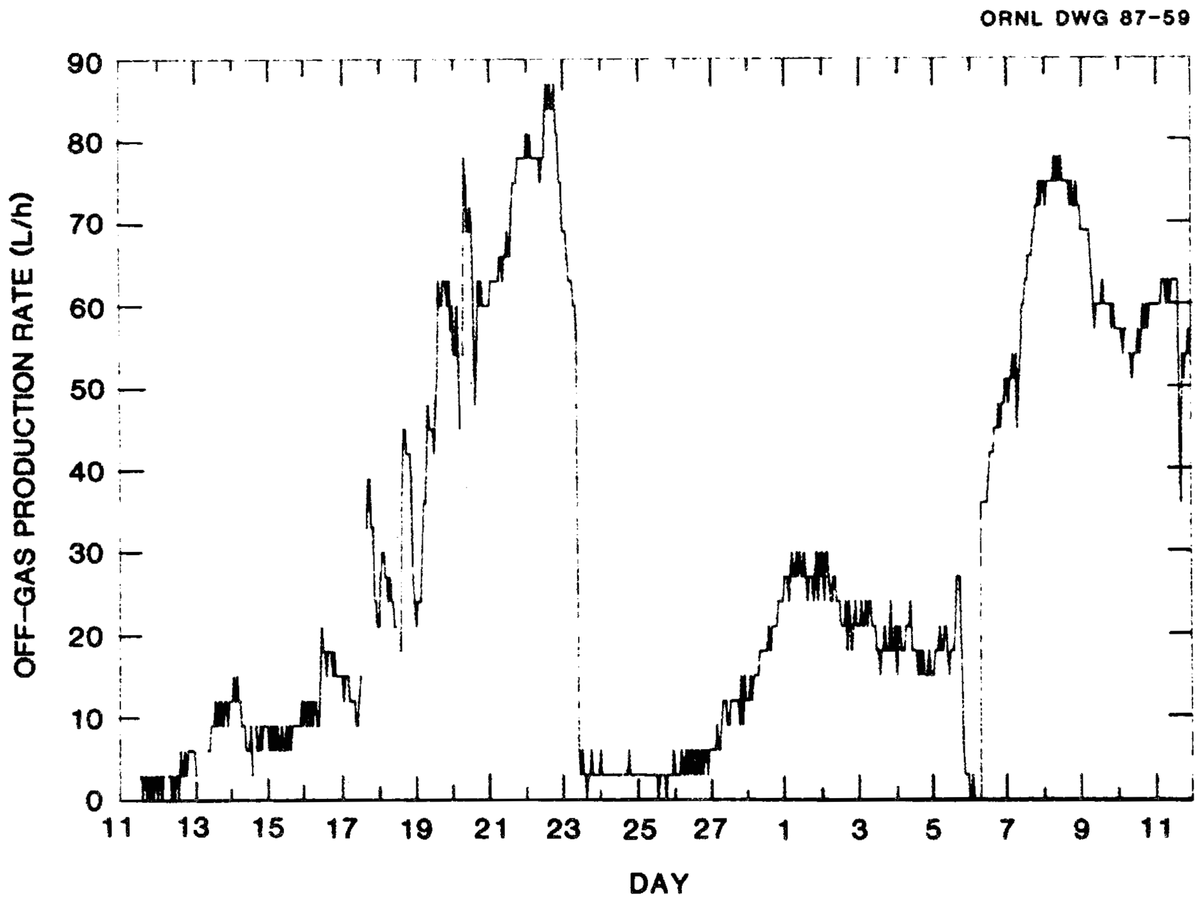
Fig. 11. Off-gas record for the two-reactors-in-series system from January 1–27, 1986, which shows a drop in the denitrification rate after the addition of softened raffinate on January 6–7.

L/h (20 kg N/d•m^3) over a period of ~12 h. The off-gas rate then climbed to ~150 L/h (37.5 kg N/d•m^3), and the raffinate was reintroduced. Following this reintroduction, the off-gas rate fell from ~150 L/h to ~15 L/h (3.8 kg N/d•m^3) over a period of 3 d. When the introduction of softened raffinate was stopped, the off-gas rate quickly climbed to the 70 to 80 L/h (~20 kg N/d•m^3) level, where it remained for several days. It should also be noted that sometime during the night of January 8, the softener malfunctioned and the calcium concentration rose to ~350 mg/L for several hours. This high calcium concentration may also have contributed to the drop in the denitrification rate.

The second point of interest occurred on January 16. During the off shift, a controller malfunction in the pH control system caused the pH in the bioreactor feed to rise to ~11.5 and remain for ~12 h. Following this upset, the off-gas rate fell to ~10–25 L/h (< 4 kg N/d•m^3) and remained there for the remainder of the operational period (~10 d). During this period, the bioreactors were inoculated several times in an attempt to increase the denitrification rate. On January 27, the contents of the two 6-m bioreactors were emptied into a 2000-L (500-gal) tank, ending this operational period with the two 6-m bioreactors.

6.2. OPERATION ON SOFTENED FMPC WASTEWATER, USING METHANOL AS THE CARBON SOURCE, IN THE SINGLE 12-m BIOREACTOR SYSTEM (February 10, 1986—March 31, 1986)

On February 10, the bioparticles that had been removed from the two bioreactors were transferred to the single 12-m bioreactor. Since a synthetic feed had been used to feed the bacteria while they were in the storage tank, the 12-m bioreactor was started on synthetic feed for a period of acclimation before switching to clearwell water. As can be seen in Fig. 12, the off-gas rate climbed steadily and reached ~90 L/h (23 kg N/d•m^3) after ~12 d. On February 23, the off-gas rate fell from the 90 L/h mark to essentially zero. The most probable cause was a contamination in the process water, such as a high concentration of residual chlorine, but this could not be verified. Following this upset, the bioreactor was reinoculated and again started on a synthetic feed. The off-gas rate climbed very slowly and by March 1 had leveled out at ~30 L/h (8 kg N/d• m^3).



OFF-GAS RATE VS TIME
FEBRUARY 11 - MARCH 11

Fig. 12. Off-gas record for the 12-m bioreactor system from February 11—March 11, 1986, which shows an unidentified drop in the denitrification rate on February 23, which required a reinoculation of the column.

On March 5, softened clearwell water was introduced into the bioreactor. Following this introduction, the off-gas rate climbed from the 30 L/h level to ~75 L/h (19 kg N/d·m^3) before leveling out at ~60 L/h (15 kg N/d·m^3). This 100% increase in the off-gas rate, as in the preceding operational period, seemed to be associated with the buffering capacity of the softened clearwell water. This can be seen in the typical pH-vs-reactor-height profiles presented in Fig. 13. As can be seen for the profile taken on March 5, immediately preceding the introduction of the softened clearwell water, the pH typically rose from ~7.2 to ~9. After the introduction of the softened clearwell water, represented by March 10, the pH typically rose to $\leq$8.

Since two previous additions of softened raffinate to the biosystem had caused a sharp drop in the denitrification rate, jar tests were run to determine if some component in the raffinate was toxic to the bacteria. These tests indicated that the raffinate was not toxic; therefore, the remainder of the operational period was devoted to acclimation of the bioreactor to softened raffinate. The softened raffinate was fed to the bioreactor at a rate of ~30 mL/min for ~1 week in order to allow time for acclimation before increasing the flow rate to ~200 mL/min. During this time, the off-gas rate was at a level of ~30–40 L/h (7.5–10 kg N/d·m^3), which is substantially below the FMPC design rate.

On March 21, the pH in the bioreactor feed rose to ~11.5 for ~15 h. As in the previous operational period, all bioactivity ceased and the bioreactor had to be reinoculated. While operational experience has shown that the microorganisms will tolerate extreme pH (as low as 2 and as high as 12) for a few minutes, these two incidents indicate that extreme pH will not be tolerated for extended periods.

6.3 OPERATION ON SOFTENED FMPC WASTEWATER, USING ETHANOL AS THE CARBON SOURCE, IN THE SINGLE BIOREACTOR SYSTEM (APRIL 1–APRIL 17)

On April 1, the carbon source to the 12-m bioreactor was changed from methanol to ethanol. This was done to determine if the FMPC design denitrification rate could be achieved in the 12-m bioreactor using ethanol as the carbon source. Presented in Fig. 14 is the off-gas record from April 1 to April 17, while the bioreactor was operating on a softened 95%

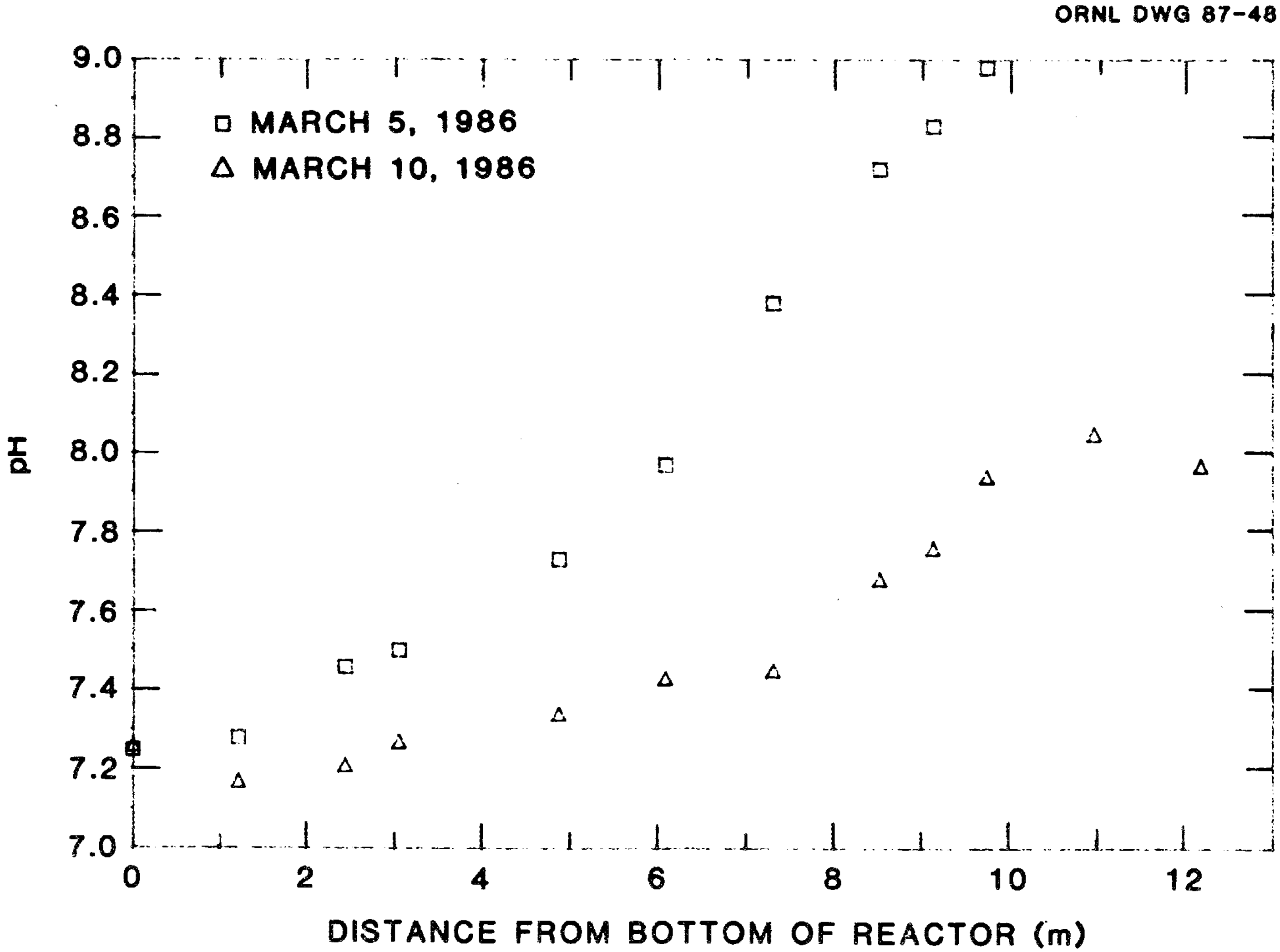


Fig. 13. Comparison of the pH profile for operation on synthetic and clearwell wastewater in the 12-m bioreactor system, which shows the buffering capacity of the softened clearwell water.

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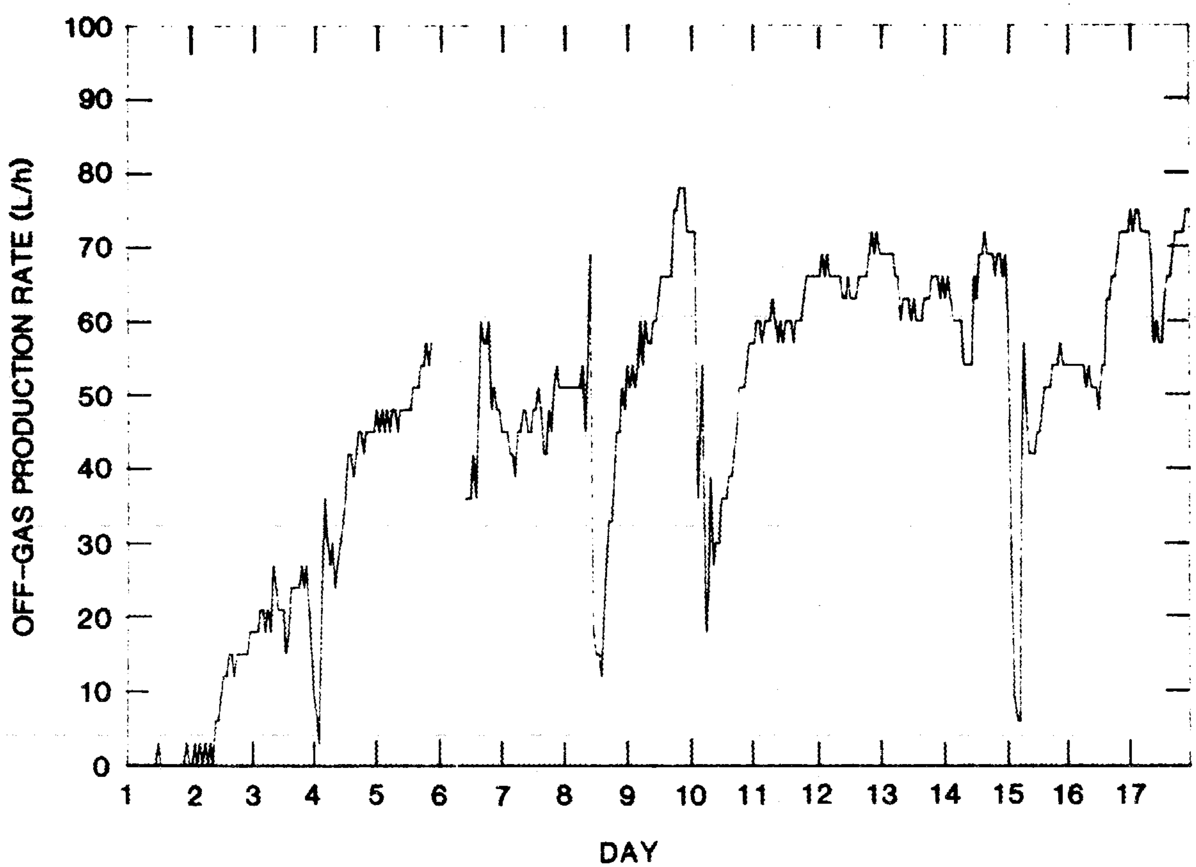


OFF-GAS RATE VS TIME
APRIL 1 - APRIL 17

Fig. 14. Off-gas record for the 12-m bioreactor system from April 1–17, 1986, which shows a slow climb in the off-gas rate when the system was operating on a mixture of clearwell water and raffinate with ethanol as a carbon source.

clearwell—5% raffinate mixture using ethanol as the carbon source. As can be seen, the off-gas rate slowly climbed to the 70 to 80 L/h (18–20 kg N/d•m^3) level and remained there for most of the operating period. Typical nitrate-and-pH-versus-reactor axial profiles for this period are presented in Figs. 15 and 16, respectively. These profiles are similar to those recorded for earlier periods, while operating on softened clearwell water with methanol as the carbon source. As can be seen in Fig. 15, the high denitrification rate in the lower portion of the bioreactor, typical of operation on synthetic feeds, was again not present. This can again be attributed to the buffering capacity of the softened wastewater, as shown in the axial pH profile presented in Fig. 16.

Also, by comparing Fig. 14 and Table 4, it can be seen that when new loads of clearwell water were introduced into the system, there was a sudden and sharp decrease in the off-gas rate. With a few exceptions, this was true of most loads of clearwell water received throughout the Biodenitrification Development Program. It should also be noted that other changes in the bioreactor feed, such as a change in the acid used for pH adjustment, produced a similar decrease in the off-gas rate. These drops in rate were generally short-lived, and the rate usually returned to its previous level within a couple of days. This phenomenon highlights the importance of maintaining constant feed conditions to maintain high denitrification rates.

7. BIODENITRIFICATION DEVELOPMENT PROGRAM TASK 3 (April 17–May 22, 1986)

Task 3 consisted of the operation of the biodenitrification system utilizing raw unsoftened FMPC wastewater. The original purpose for Task 3 was to determine the ability of the biodenitrification system to operate with the high levels of calcium present in the FMPC wastewater. However, because no raffinate had been processed at the FMPC for several months, the calcium concentration had dropped from 450 mg/L, at the beginning of the program, to ~20 mg/L, at the initiation of Task 3. Due to the low calcium concentration present in the FMPC wastewater and to the fact that the FMPC design denitrification rate had not been reached for the

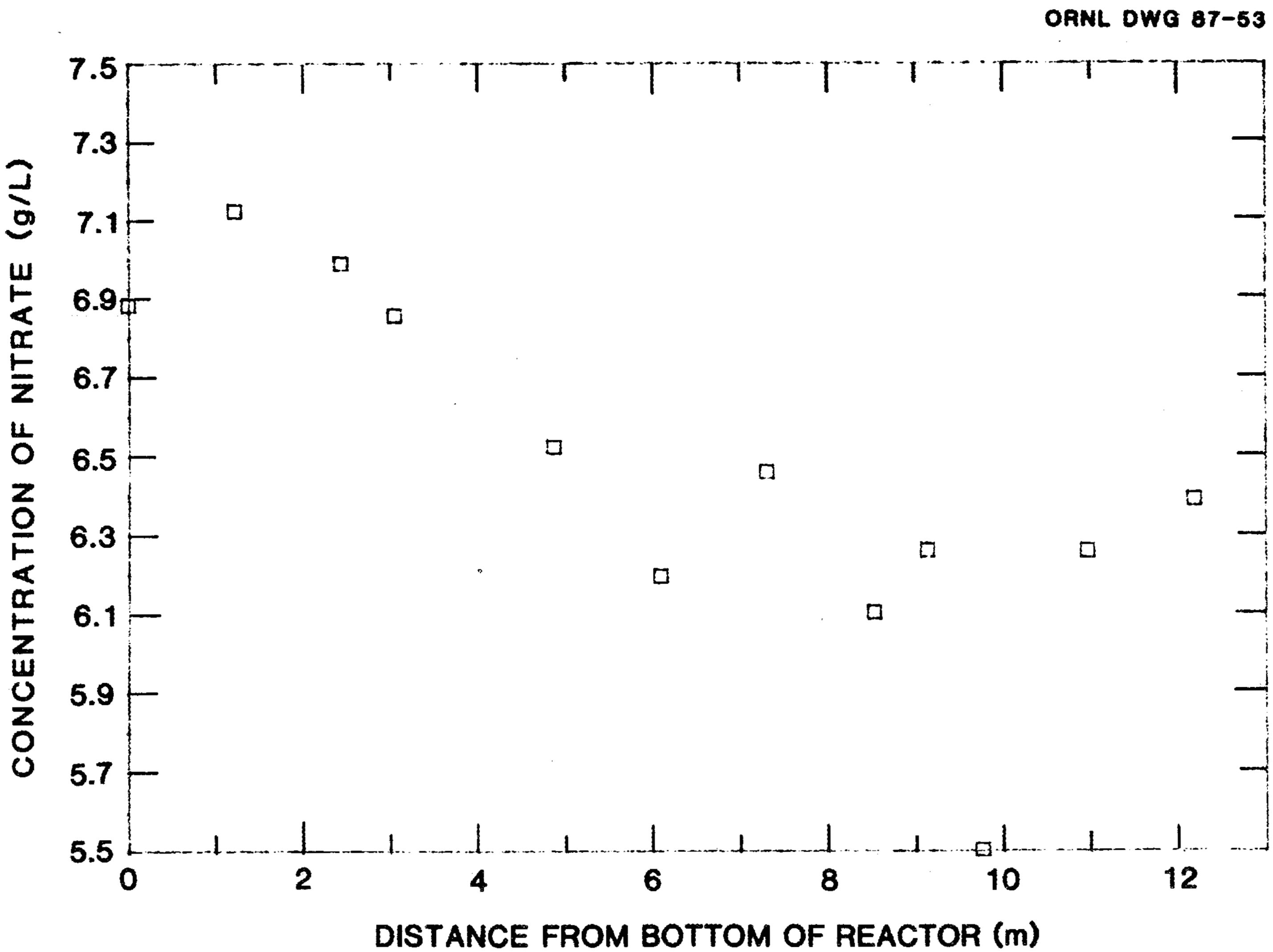


Fig. 15. Typical nitrate profile for the 12-m bioreactor system while operating on softened FMPC wastewater, using ethanol as the carbon source, which is similar to the profiles obtained when the system was operating on softened clearwell water with methanol as a carbon source.

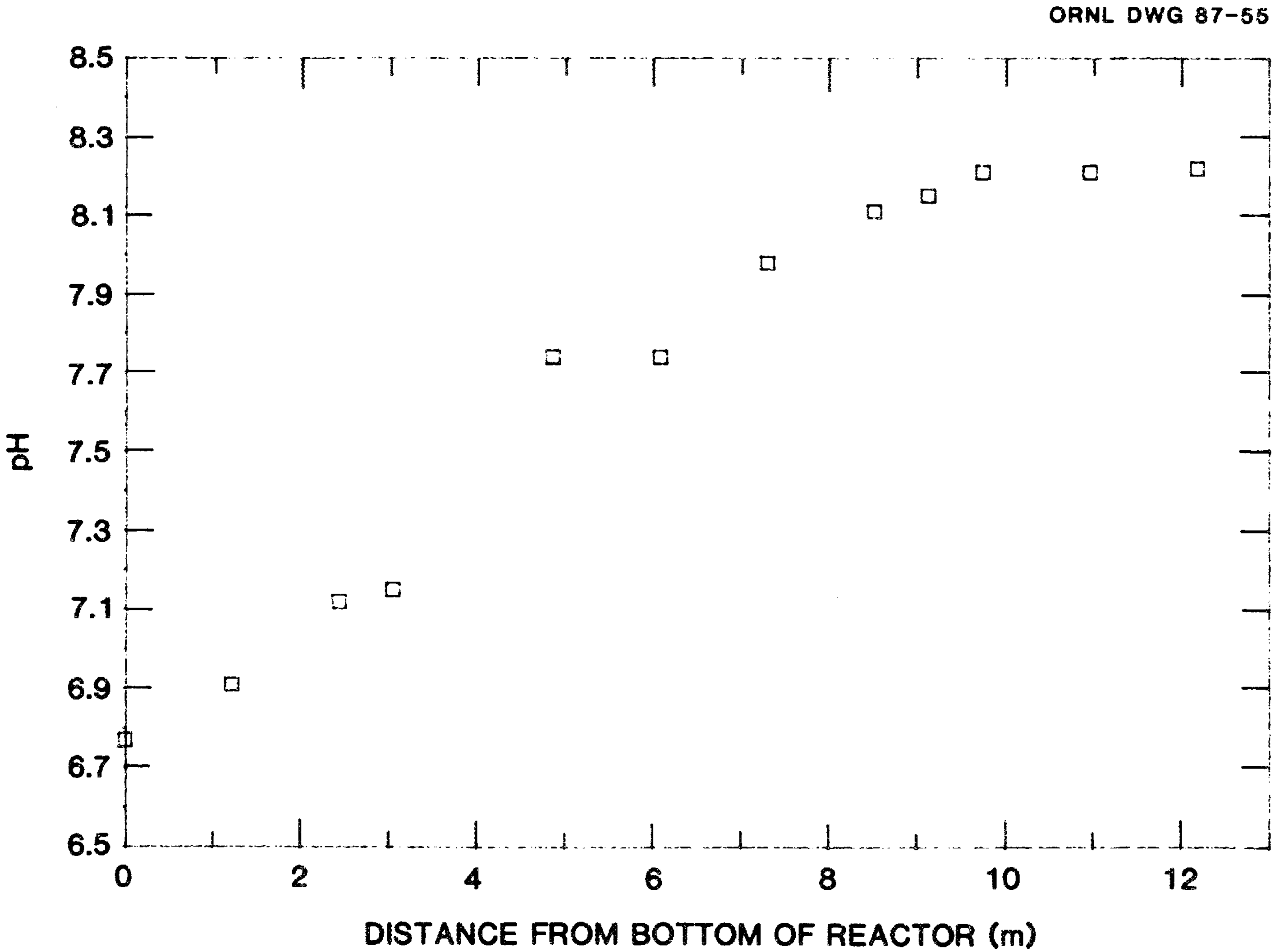


Fig. 16. Typical pH profile for the 12-m bioreactor system while operating on softened FMPC wastewater using ethanol as the carbon source.

entire reactor since switching to the single 12-m-high bioreactor, the focus for Task 3 was changed to improve the denitrification rate. A chronological order of events for Task 3 is presented in Table 5.

The off-gas record for Task 3 of the Biodenitrification Development Program is presented in Fig. 17. As can be seen, from April 20 to April 28, ~30–35 L/h of off-gas was generated. This corresponds to a denitrification rate of ~9 kg $N/d \cdot m^3$, which was substantially below the FMPC design rate of 32 kg $N/d \cdot m^3$. On April 25, in an attempt to increase the biodenitrification rate, the nitrate feed was cut off and process water was pumped through the bioreactor for ~2 h. If there was a contaminant present which was inhibiting the biodenitrification process, this might flush it out. This approach had been successful in smaller fluidized-bed bioreactors at ORNL; however, in this case it did not seem to affect the denitrification rate. After restarting the bioreactor, the off-gas rate returned to its previous level of ~35 L/h and remained there until April 28.

Table 5. Chronological order of events for Task 3 of the Biodenitrification Development Program (April 17-May 22, 1986)

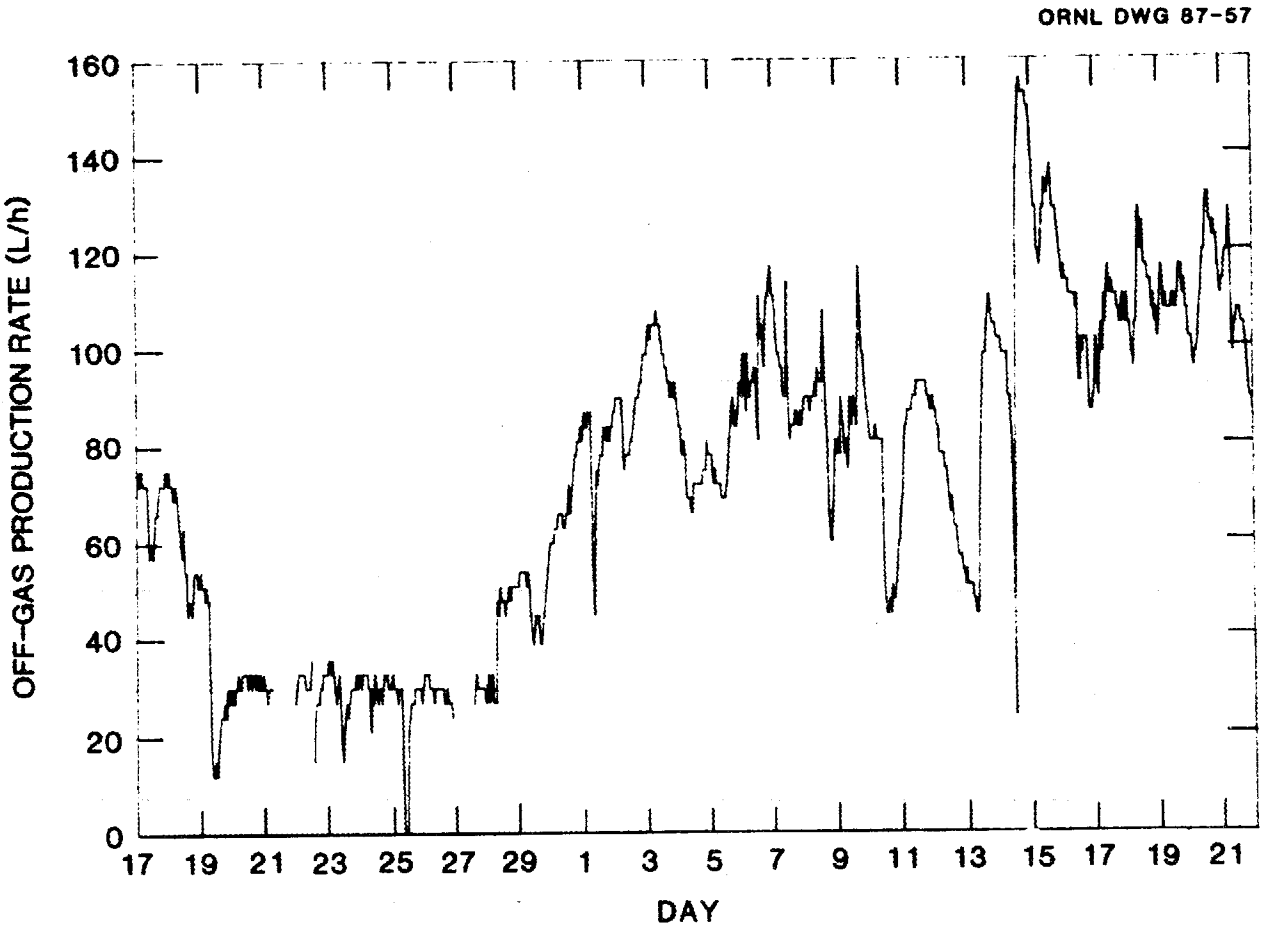
Date	Event
April 17:	The supply of raffinate ran out, the 40-ft bioreactor was fed raw unsoftened clearwell water, and 5% phosphoric acid addition was started at the 20-ft level.
April 19:	The pH addition at the 20-ft level was stopped.
April 22:	A load of clearwell water was received. The bioreactor inlet and effluent assayed at 21 and 6.7 mg/L of calcium, respectively.
April 24:	A load of clearwell was received, and the ethanol flow rate was increased from 7 to 11 mL/min to ensure the adequate quantity of carbon for the bacteria.
April 25:	The bioreactor was flushed with process water for hours to remove any contaminant which might be present.
April 28:	The daily addition of from 2% to 5% of the reactor volume of fresh coal was initiated to force more bioparticles to be recycled from the top of the bioreactor through the vibrating screen filter.

Table 5 (continued)

Date	Event
April 29:	A load of clearwell water was received.
May 1:	The acid used to adjust the pH of the feed was changed from phosphoric to acetic.
May 2:	A partial plug was found in the ethanol line, which had reduced the supply of carbon to the bacteria during the previous night.
May 5:	The concentrated feed pump malfunctioned, which had reduced the supply of carbon to the bacteria the previous night.
May 6:	A load of clearwell water was received.
May 9:	A load of clearwell water was received.
May 12:	The acid used to adjust the pH of the feed was changed from acetic to sulfuric.
May 14:	A load of clearwell water was received, and the pH dropped to 3.4 for several minutes.
May 16:	A 10% sulfuric acid addition was started at the 20-ft level.
May 22:	The biosystem was shut down, marking the end of Task 3.

Prior to April 28, enough fresh coal was added daily to maintain the solid/liquid interface in the top tapered section of the bioreactor. On April 28, a daily addition was initiated of enough coal to force more bioparticles to be recycled from the top of the bioreactor into the vibrating screen filter. As the biofilm thickness increases, the particles become less dense and have a tendency to clump and float to the top of the bioreactor. Forcing more bioparticles into the vibrating screen filter could increase the total particles capacity and the active biofilm surface area, and, therefore, the denitrification rate.

Following this action, the off-gas rate climbed to a level of ~90–110 L/h (23–28 kg N/d·m^3) over an ~48-h period and remained at that level for ~13 d, except for brief upsets. It should be noted, however, that the off-gas rate had climbed from ~35 to ~50 L/h in the 8 h prior to the



OFF-GAS RATE VS TIME
APRIL 17 - MAY 21

Fig. 17. Off-gas record for the 12-m bioreactor system for Task 3 of the Biodenitrification Development Program, which shows an increase in the denitrification rate after the daily addition of coal was initiated on April 28.

forced recycle of the additional bioparticles, and the forced recycle alone may not have caused the increase in the denitrification rate.

On May 14, the pH in the bioreactor feed dropped to ~3.5 for ~10 min. Following this upset, the off-gas rate rapidly fell to ~25 L/h (6 kg $N/d\cdot m^3$) and then rapidly climbed to ~150 L/h (38 kg $N/d\cdot m^3$) before leveling out at the ~120–130 L/h (30–33 kg $N/d\cdot m^3$) range. The denitrification rate remained at this level for the remaining seven operational days of the Biodenitrification Development Program. This indicates that the FMPC design rate of 32 kg $N/d\cdot m^3$ can be met or exceeded for an extended period in the single 12-m bioreactor, as well as in the two 6-m bioreactors in series. In order to maintain the thin active biofilms necessary for these denitrification rates, operational experience with the 12-m pilot biosystem indicates that 2 to 5% of the reactor volume of fresh coal must be added daily.

Presented in Figs. 18, 19, and 20 are axial pH profiles taken on three separate days during Task 3 and the axial nitrate profiles for the same days with the data fit by the least-squares method. The axial pH and nitrate profiles in Fig. 18 indicate that as the pH climbs above ~8, the denitrification rate decreases. However, when comparing the pH profiles in Figs. 19 and 20 with their respective nitrate profiles, it seems the denitrification rate is independent of the pH in the 7.4 to 9 range. This is particularly evident for the pH and nitrate profiles taken on May 19, shown in Fig. 20. As can be seen in Fig. 20, the pH rises from ~7.5 to ~8.5 in the first 2 m of the bioreactor. Acid addition then drops the pH to ~7.6 in the second 5 m of the bioreactor, and the pH climbs to ~8.6 in the top 5 m of the bioreactor. During this entire process, the denitrification rate is essentially constant. In Fig. 19, the pH climbs to ~9 in the first 5 m of the bioreactor and remains there. Again, the denitrification rate is essentially constant throughout the bioreactor.

As indicated earlier, most of the literature indicates the optimum pH to be in the range of 6.5 to 8.0,[1,2,3] with the denitrification rate falling off sharply outside this range. However, the optimum pH for denitrification varies with the organism, and it has been reported that denitrification may occur in wastes up to about pH 11.[4].

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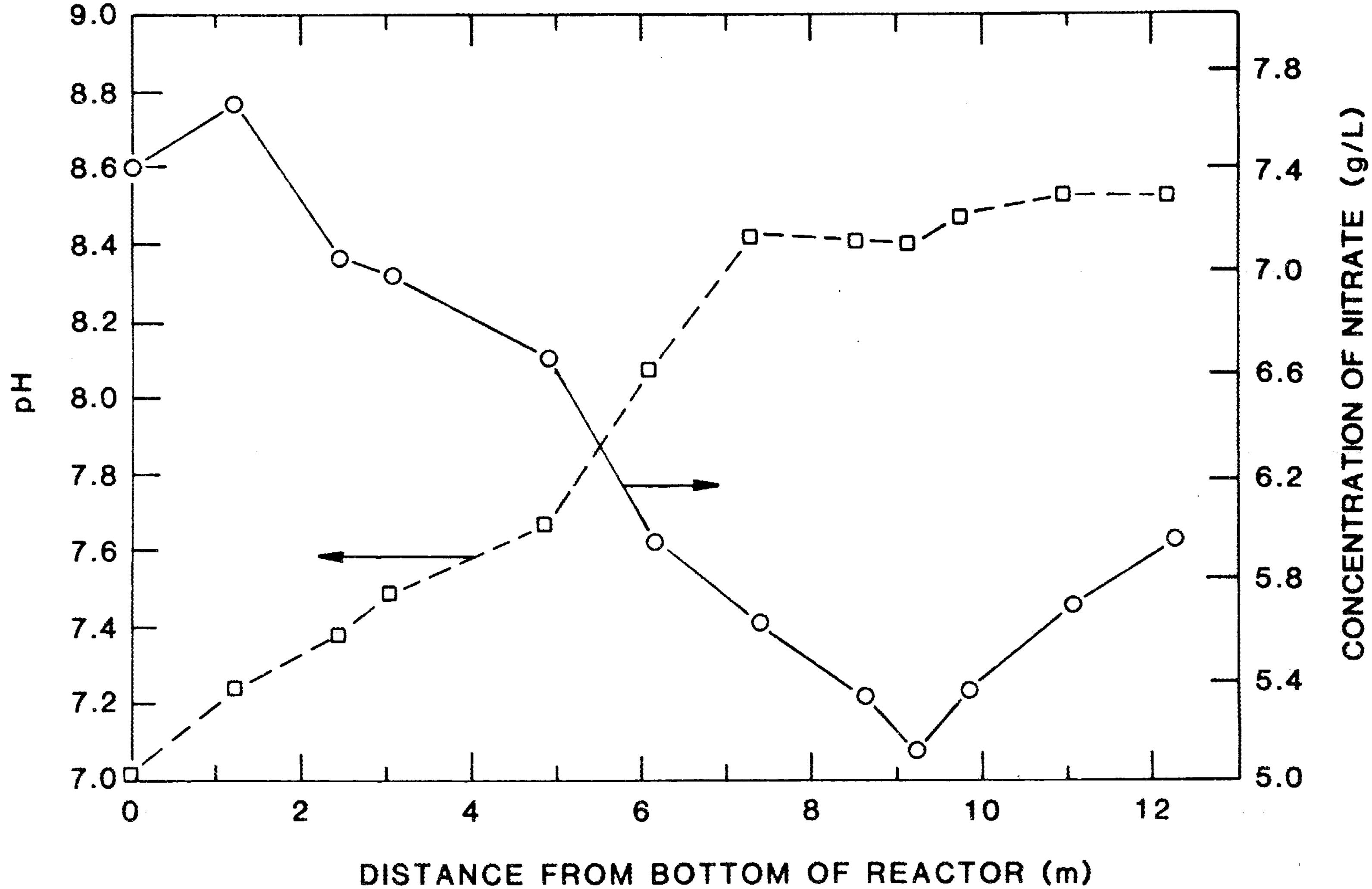

Fig. 18. pH and nitrate profiles taken from the 12-m bioreactor on April 17, 1986, showing the denitrification rate decreasing as the pH rises above ~8.

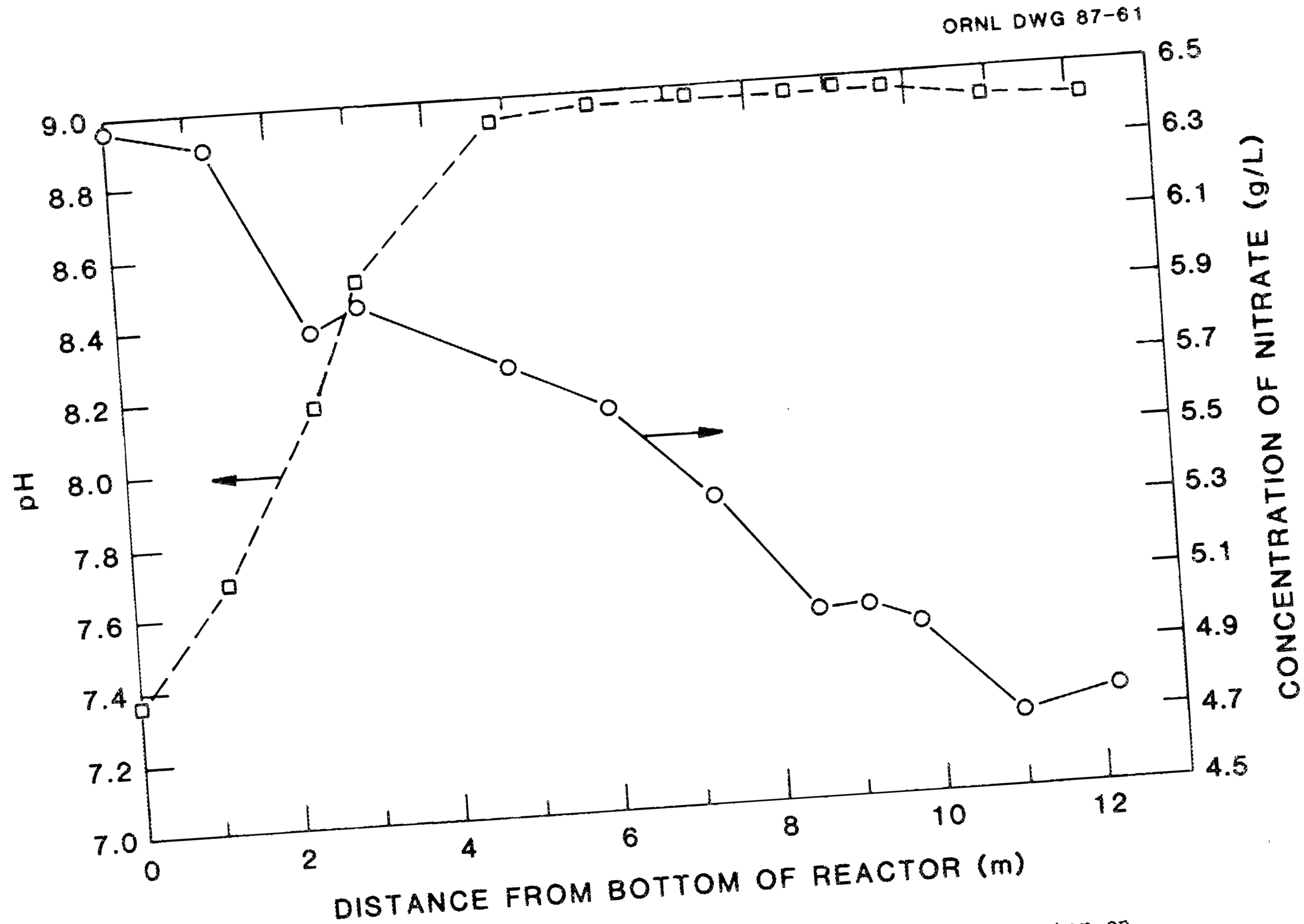

Fig. 19. pH and nitrate profiles taken from the 12-m bioreactor on May 7, 1986, which indicate that the denitrification rate is independent of pH in the ~7.4 to 9.0 range.

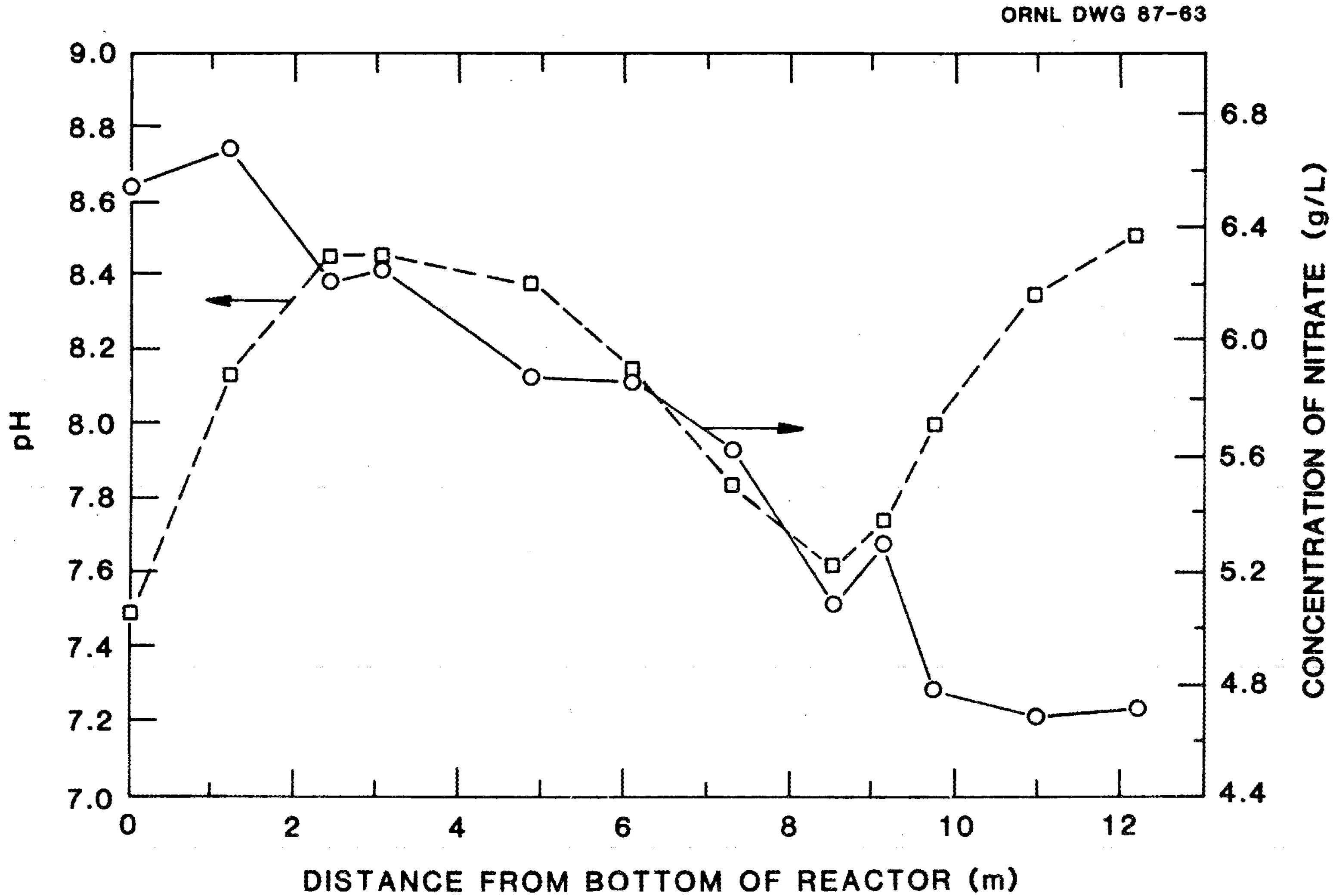

Fig. 20. pH and nitrate profiles taken from the 12-m bioreactor on May 19, 1986, which indicate that the denitrification rate is independent of pH in the 7.5 to 8.5 range.

The change in the effect of the pH on the denitrification rate in the pilot unit may be due to changing microbial populations within the bioreactor. Bioparticles were taken from the same sample port on the bioreactor on several occasions and subjected to a fatty acid analysis to determine if shifts in the microbial population were occurring. These analyses suggest changes in the microbial population on each occasion.[10]

Another possibility is that the pH in the bulk liquid may not be representative of the pH within the denitrifying biofilm. Resistance to the diffusion out of bicarbonate and carbonate (alkalinity), produced from the oxidation of the carbon source by nitrate, may cause the pH to be substantially higher in the microbial film than in the bulk liquid. The literature indicates that a difference of two pH units between the interior and the surface of a denitrifying biofilm may exist.[11]

The effect of the pH on the denitrification rate and the changing microbial population within the bioreactor again highlight the importance of maintaining constant operating conditions. While the bioreactor may operate at high denitrification rates (>32 kg $N/d \cdot m^3$) at a pH up to ~9 for a period of time, a change in the operating conditions (i.e., clear-well composition, pH) may cause a shift to a microbial population where the denitrification rate falls dramatically above a pH of ~8. As a result, it is recommended that the pH within the bioreactor be maintained in the 6.5 to 8.0 range and that intrareactor pH control be installed.

It should also be mentioned that during ~5 weeks of operation of Task 3, the inlet calcium concentration was ~20 mg/L, and most of this was precipitated in the form of calcium carbonate within the bioreactor. During these 5 weeks, there was no visual evidence of an accumulation of calcium carbonate on the bioparticles. At this low inlet calcium concentration, the rate of deposition of the calcium carbonate on the bioparticles was slow enough so that it was sheared off the bioparticles with the excess biomass in the vibrating screen filter.

8. TEMPERATURE RISE WITHIN THE BIOREACTOR

Resistance temperature devices (RTDs) were installed along the length of the 12-m bioreactor to measure the temperature at various locations within the bioreactor. These RTDs were installed at the inlet, and at 3-m increments along the length of the bioreactor. The literature indicates that denitrification is an exothermic reaction with a ΔG of −138.36 kcal per mol of methanol;[5] therefore, at higher denitrification rates more heat would be generated, and one would expect a rise in the temperature of the wastewater within the bioreactor. Presented in Table 6 is a comparison of the theoretical and the average measured temperature rise for various denitrification rates within the 12-m pilot bioreactor.

Table 6. Comparison of the theoretical and measured temperature rise in the 12-m pilot bioreactor at various denitrification rates

Experimental period	Denitrification rate (kg N/d·m³)	Theoretical temperature rise (°C)	Experimental temperature rise ± standard deviation (°C)
4/20 – 4/28	8	1.5	0.93 ± 0.50
5/3 – 5/10	20	3.7	3.59 ± 0.52
5/15 – 5/21	30	5.5	4.46 ± 1.11

The theoretical temperature rises were calculated with the assumption that all the heat generated by the denitrification reaction was transferred to the wastewater and none was lost to the environment. The experimental values were obtained from data during periods when the denitrification rate remained fairly constant for at least 7 d. During these periods, the temperature profiles were taken several times a day, and the average difference between the temperature at the top and bottom of the bioreactor was determined for the entire period. Table 6 includes these operational periods as well as the standard deviations for the measured temperature rises.

As can be seen from the experimental values in Table 6, the higher the denitrification rate the greater the temperature rise. These experimental values also compare well with the calculated theoretical temperature rises at the same denitrification rate. It should be mentioned that the 12-m pilot bioreactor was not insulated, and some of the heat generated in the denitrification reaction may have been lost to the environment. Also, the ambient temperature ranged from ~18 to ~28 °C.

Calculations for the FMPC bioreactors indicate that, with a denitrification rate of 30 kg N/d·m^3, a temperature rise of ~4°C per bioreactor would occur. This again assumes that all the heat generated is transferred to the wastewater and none is lost to the environment. During the summer months, the FMPC bioreactors might pick up additional heat from the surroundings and the temperature rise within each bioreactor might be larger than the calculated 4°C. During the winter months, the wastewater feed to the FMPC bioreactors may have to be heated and the bioreactors may have to be insulated to maintain a temperature above the 24°C minimum inlet design.

9. BIOMASS-TO-COAL-LOADING

The loading of biomass on the coal particles is intuitively expected to be related to the performance of the bioreactor. Efforts were undertaken to measure the biomass loading and to correlate it with bioreactor performance for diagnostic purposes. Several generalizations were established, but no clear quantitative relationship could be determined.

Several sets of axial profile samples of particles were assayed for biomass loading. The biomass loading ranged from 3 to 37% on a dry weight basis. No direct correlation with biodenitrification rate could be determined. Samples taken a few days apart showed large differences in the biomass loadings even though the denitrification rates were similar.

It was generally observed that the biomass loading was the smallest at the bottom of the column and increased with position up the column. However, the opposite relationship was also observed on occasion. At these times, bioparticles were removed from the bottom and fed back to the system through the centrifugal feed pump. This action stripped much of the excess biomass off the particles.

Although quantitative relationships were not established, it was observed visually that the denitrification rates were usually higher when the biomass loadings were relatively small. Thin films were maintained deliberately by adding 2 to 5% new coal daily, which also forced bioparticles to overflow at the top of the column and pass through the vibrating screen to dislodge excess biomass. This procedure is recommended for operation of the FMPC bioreactors for optimal reaction rates to ensure that an overflow of bioparticles is maintained to the vibrating screens in order to flavor thin films.

10. pH ADJUSTMENT

Several different acids, including phosphoric, acetic, and sulfuric, were used for pH adjustment in the bioreactor feed, as well as within the bioreactor. No difference was detected in the denitrification rates with these acids, and the FMPC design rate of 32 kg $N/d \cdot m^3$ was met with each acid. Phosphoric and acetic acids may cause problems with the FMPC discharge limits for phosphate and total organic carbon, respectively; therefore, sulfuric may be the preferred acid for pH adjustment.

It is difficult to determine the amount of acid required for pH adjustment within the bioreactor because of the many variables which affect the pH profile within the bioreactor. Some of these variables include (1) the denitrification rate, (2) the buffering capacity of the clearwell water, and (3) the inlet bioreactor pH. Because of these variables, it would be extremely difficult to maintain the pH within acceptable limits without pH monitoring and adjustment. Presented in Fig. 21 is a titration curve for the effluent from the 12-m bioreactor. This titration curve gives an indication of the amount of acid required for pH adjustment of the effluent from the bioreactor at a single point in time and will not be representative of all periods of operation.

11. SUMMARY AND RECOMMENDATIONS

A development program was undertaken at ORNL to provide answers to questions regarding the operation of the FMPC biodenitrification facility.

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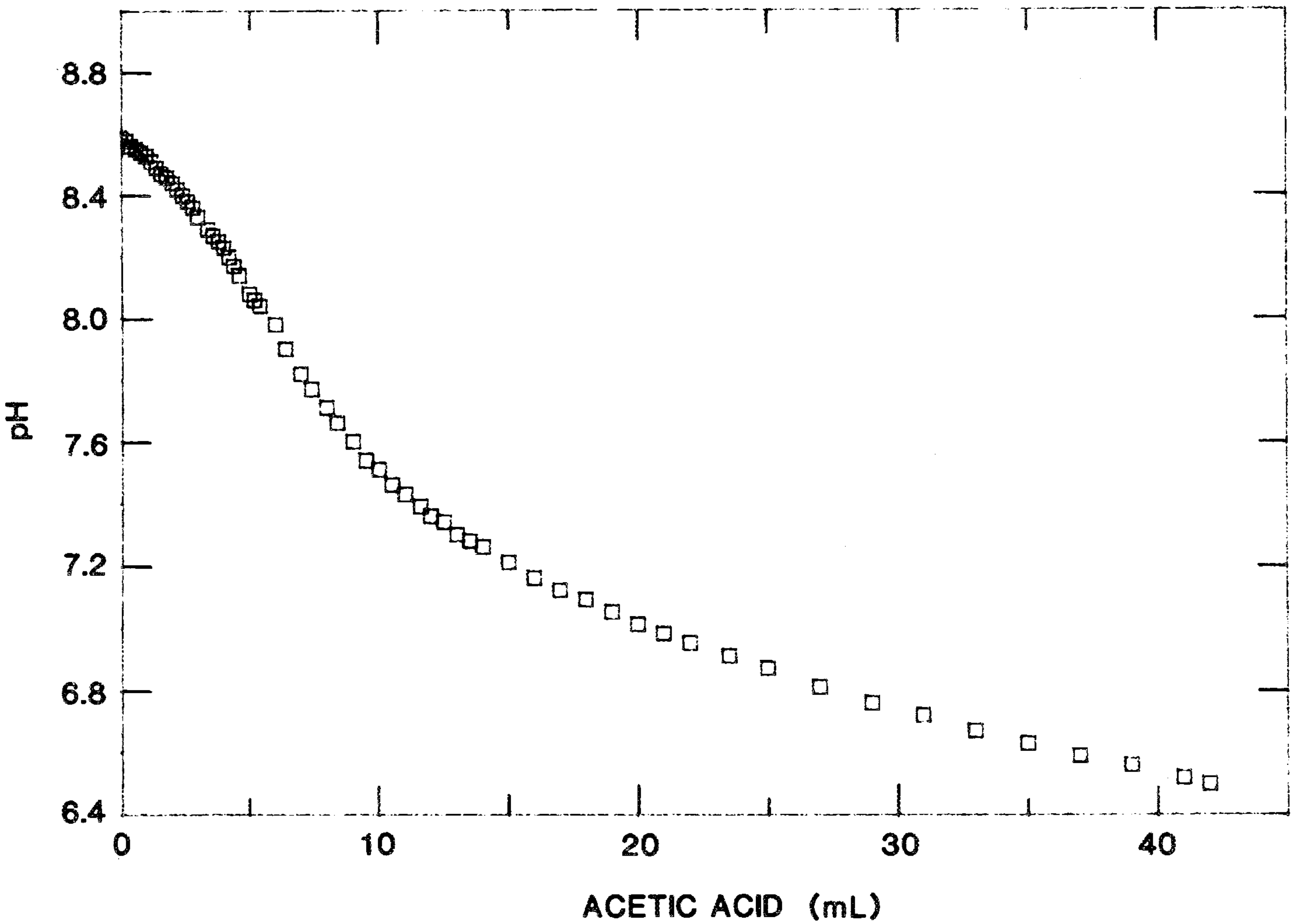

Fig. 21. Titration of the effluent wastewater from the 12-m bioreactor with 0.5 N acetic acid on May 20, 1986.

This Biodenitrification Development Program utilized two separate pilot systems to simulate the operation of a single 12-m-high FMPC bioreactor. The first of these pilot facilities, which consisted of two 10-cm-diam, 6-m-high bioreactors operated in series, already existed at ORNL and was utilized until a single 10-cm-diam, 12-m-high bioreactor could be constructed to more closely simulate an FMPC bioreactor.

The Biodenitrification Development Program was divided into three operational periods. During the first operational period, the two bioreactors in series were operated on a synthetic feed to establish a mature culture of biomass and to determine if the FMPC design denitrification rate of 32 kg N/d·m^3 could be obtained while using a synthetic feed. The results of this operational period, which were published in an earlier report[1], indicated that the FMPC design rate could be achieved while operating on a synthetic feed; however, pH adjustment within the 12-m FMPC bioreactor would be required.

In the second operational period, the biodenitrification pilot facilities were operated on softened clearwell wastewater and a combination of softened FMPC clearwell and raffinate wastewaters. This was done to determine if any components that were present in the FMPC wastewaters were toxic to the bacteria and if the FMPC design denitrification rate could be obtained while treating the actual wastewaters from the FMPC facility.

With the introduction of the softened clearwell water into the two bioreactors in series, there was an immediate 45% increase in the denitrification rate. This increase from ~25 to ~36 kg N/d·m^3 was attributed, at least in part, to the buffering capacity of the softened clearwell water such that the pH rise was less than with synthetic wastewater. However, with the addition of the softened raffinate (88% clearwell and 12% raffinate mixture), the denitrification rate dropped from the ~35 to 43 kg N/d·m^3 range to ~4 kg N/d·m^3 over a 2-d period. As a result, the addition of softened raffinate was discontinued until jar tests indicated that the softened raffinate was not toxic to the bacteria.

When the 12-m bioreactor was completed, the bioparticles were transferred from the two reactors in series to the single bioreactor. The bacteria were then acclimated to the softened raffinate, by increasing from a 0.8% to a 5% raffinate mixture over a period of 7 d and then operating at a 5% raffinate mixture for ~20 d. After acclimation, the bioreactor generally operated with a denitrification rate in the range of 18 to 20 kg N/d•m^3.

The third operational period consisted of the operation of the biodenitrification system utilizing raw, unsoftened FMPC wastewater. Because no raffinate had been processed at the FMPC facility for several months, the calcium concentration in the clearwell wastewater had dropped from ~450 mg/L, at the beginning of the program, to ~20 mg/L, at the initiation of the third operational period. The initial focus of the third operational period had originally been to examine the effect of the calcium carbonate precipitation on the denitrification rate. However, because of the low calcium concentration in the FMPC clearwell water and the concern that the FMPC design denitrification rate had not been achieved since switching to the single bioreactor system, the focus of the third operational period was changed to attempt to improve the denitrification rate. It was found that the daily addition of from 2 to 5% of the reactor volume of fresh coal promoted higher denitrification rates by helping to maintain thin, more active biofilms. With this daily addition of coal, the denitrification rate climbed to the 30 to 33 kg N/d•m^3 range.

Several acids, including phosphoric, acetic, and sulfuric, were used for pH adjustment, and both methanol and ethanol were used as carbon sources. The FMPC design denitrification rate was met while operating on both carbon sources and with each acid listed above. As a result, the carbon source and the acid used for pH adjustment may be chosen to achieve the best combination for economic and environmental concerns.

Resistance temperature devices placed along the length of the 12-m bioreactor showed a correlation between the denitrification rate and the temperature rise within the bioreactor. As the denitrification rate rose, the increase in temperature through the bioreactor also increased. At a denitrification rate of ~30 kg N/d•m^3, an average temperature rise of 4.46 ± 1.11 °C in the bioreactor occurred.

The results of this Biodenitrification Development Program indicate that there is a reasonable expectation that the FMPC bioreactors can operate for extended periods at or above the design denitrification rate if special attention is paid to their operation. To help ensure the successful operation of the FMPC biodenitrification facility, the following recommendations are made.

1. Upon startup, the bioreactors should be operated in a recycle mode for ~5 to 10 d to allow the bacteria to attach to the support particles. During this startup, the pH, nitrate concentration, and carbon concentration should be monitored and adjusted.
2. The wastewater should be softened or otherwise segregated to remove most of the calcium being introduced into the bioreactor. The pilot biosystems successfully operated for ~6 months with inlet calcium concentrations up to 20 mg/L. During this period, there was no visible evidence of calcium carbonate precipitation on the bioparticles. The upper limit of calcium that can be tolerated was not determined. It was demonstrated earlier that the biosystem will not work at 300–400 mg/L of calcium.[1] Satisfactory operating strategies at intermediate calcium concentrations have not been established.
3. The feed conditions to the bioreactor, which include nitrate concentration, carbon source, pH, and trace metals, should be kept relatively constant or changed slowly. This is evident from the changes in the denitrification rate with new loads of clearwell wastewater. With the delivery of most loads of clearwell water, there was a drop in the denitrification rate. The bacteria usually acclimated to the changes in the wastewater within 2 d, and the denitrification rate climbed back to the previous level.
4. The pH within the bioreactor should be kept in the 6.5 to 8.0 range. This would require that a pH control system be installed to monitor and control the pH within the bioreactor.
5. Operational experience has shown that higher denitrification rates can be achieved if thin, active biofilms are maintained on the support particles. With the pilot biodenitrification facility, the daily addition of from 2 to 5% of the reactor volume of

fresh coal was required to maintain these thin biofilms. To ensure these active biofilms in the FMPC facility, the visible carryover of the bioparticles into the vibrating screen should be maintained by the daily addition of fresh coal.

6. The introduction of gas into the pilot bioreactor helped to break the clumps of biomass that formed within the bioreactor. If clumps of bacteria form in the FMPC bioreactors, gas could be injected in an attempt to break them up.

7. The off-gas rate from each bioreactor should be continuously recorded, as it provides a reliable means for monitoring the denitrification system.

8. Operators should clean small lines, pH probes, etc., daily to ensure that biomass does not build up.

9. Calculations indicate, and are confirmed by experimental results from the 12-m pilot bioreactor, that enough heat is generated to raise the temperature by ~4°C in each of the four FMPC bioreactors. Previous studies indicate that the denitrification rate reaches a maximum and levels out in a 24 to 30°C range.[12] No information is provided about the effects of higher temperatures on the dentrification rate. Therefore, this temperature rise may be enough to take the reactor out of the optimum temperature range for biodenitrification. This relationship should be further examined when the FMPC bioreactors are started and operated.

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13. APPENDIXES

APPENDIX A. DENITRIFICATION STOICHIOMETRY

Using Methanol as a Carbon Source[a]

1) Nitrate removal:

$$1/6\ CH_3OH + 1/5\ NO_3^- = 1/10\ N_2 + 1/6\ CO_2 + 1/5\ OH^- + 7/30\ H_2O$$

2) Bacterial synthesis:

$$1/6\ CH_3OH + 1/84\ CO_2 + 1/28\ NO_3^- + H^+ = 1/28\ C_5H_7O_2N + 19/84\ H_2O$$

3) Overall nitrate removal:

$$NO_3^- + 1.08\ CH_3OH + H^+ = 0.065\ C_5H_7O_2N + 0.47\ N_2 + 0.76\ CO_2 + 2.44\ H_2O$$

Using Ethanol as a Carbon Source[a]

4) Nitrate removal:

$$1/12\ CH_3CH_2OH + 1/28\ NO_3^- = 1/6\ CO_2 + 1/10\ N_2 + 3/20\ H_2O + 1/5\ OH^-$$

5) Bacterial synthesis:

$$1/12\ CH_3CH_2OH + 1/28\ NO_3^- + 1/84\ CO_2 + 1/28\ H^+ = 1/28\ C_5H_7O_2N + 1/7\ H_2O$$

6) Overall nitrate removal:

$$NO_3^- + 0.54\ CH_3CH_2OH + H^+ = 0.76\ CO_2 + 0.47\ N_2 + 0.065\ C_5H_7O_2N + 1.89\ H_2O$$

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[a]These equations were developed using the consumptive ratio method as defined by McCarty et al., "Biological Denitrification of Wastewaters by Addition of Organic Materials", in Proceedings of the 24th Industrial Waste Conference, May 1969.

APPENDIX B. GRAPHS OF OFF-GAS RATES AS A FUNCTION OF TIME AND A LIST OF CAUSES OF CHANGES IN OFF-GAS RATES

December 10: Started addition of softened clearwell water at 1 L/min.

December 11: Raised flow of clearwell water to 2 L/min.

December 12: Raised flow of clearwell water to 3 L/min.

December 13: Raised flow of clearwell water to 4 L/min.

December 16: Column shut down for half-hour.

December 18: Equipment problems, resulting in system shutdown for 5 h.

December 19: New load of clearwell water arrived.

December 20: System shut down to replace leaking tubing.

December 21: System shut down for several hours.

December 22: Gas chart ran out of paper.

December 23: Methanol pump leaking; no methanol added to system.

December 25: Methanol line leaking.

December 26: Column 2 plugged, resulting in system shutdown.

December 31: New load of clearwell water arrived.

January 1: Methanol drum empty; no methanol added to system.

January 2: Methanol pump leaking.

January 3: New load of clearwell water arrived.

January 6: Started addition of softened raffinate at 460 mL/min, stopped 20 min later.

January 7: Restarted addition of raffinate to 500 mL/min.

January 8: Ran out of soda ash in softening unit; Ca concentration at 353 mg/L.

January 9: Water softening unit down due to frozen pipes; raffinate addition discontinued.

January 13 Stopped methanol addition.

January 14: Started methanol addition.

January 17: New load of clearwell water arrived.

January 18: pH rise in bioreactor (pH in column 1 at 11.5) for ~12 h.

January 23: Started addition of synthetic feed.

January 27: Emptied contents of columns in 500-gal tank.

February 11: Startup of 12-m bioreactor on synthetic feed.

February 17: SWECO malfunction causing inlet pH to rise to 8.1.

February 18: Shut down system to replace SWECO part.

February 19: pH adjustment started at 6-m level.

February 20: pH adjustment started at 3-m level.

February 25: Reinoculated bioreactor.

March 2: Level in feed tank dropped; inlet pH at 5.6.

March 4: Changed flow rate through bioreactor to 3 L/min from 4 L/min.

March 5: Started clearwell water at 1 L/min.

March 6: Ran out of methanol, replaced drum; increased clearwell water flow rate to 2 L/min.

March 7: Increased clearwell flow rate to 4 L/min; now running on 100% clearwell water.

March 11: Started addition of softened raffinate at 400 mL/min.

March 12: Reduced raffinate flow rate to 200 mL/min.

March 13: New load of clearwell water arrived; stopped addition of raffinate.

March 17: Started raffinate addition at 30 mL/min.

March 18: New load of clearwell water arrived.

March 19: New load of clearwell water arrived.

March 21: Increased raffinate addition to 113 mL/min.

March 24: Increased raffinate addition to 200 mL/min.

March 25: New load of clearwell water arrived.

March 26: Increased raffinate addition to 300 mL/min.

March 27: Shut down system to clean lines.

March 28: Feed tank pH at 12 for 15 h due to malfunction of acid addition pump; reinoculated column.

March 31:	Put system in total recycle mode during day; running clearwell water at 2 L/min at night.
April 1:	Switched to ethanol as a carbon source.
April 3:	Started raffinate addition at 60 mL/min.
April 4:	Raffinate addition increased to 100 mL/min.
April 8:	Two new loads of clearwell water arrived; raised flow rate in bioreactor to 4 L/min.
April 9:	Two new loads of clearwell water arrived; soda ash pump failed during early evening, off all night.
April 11:	New load of clearwell water arrived.
April 15:	Shutdown of system due to ruptured line.
April 16:	Dropped ethanol addition from 11 mL/min to 7 mL/min.
April 17:	Ran out of raffinate, switched back to addition of concentrated feed.
April 18:	New load of clearwell water arrived.
April 19:	Effluent pH at 4.5; stopped acid addition at 6-m level.
April 22:	New load of clearwell water arrived; put bioreactor on total recycle for several hours.
April 23:	Put bioreactor on total recycle for several hours.
April 24:	Put bioreactor on partial recycle for an hour; new load of clearwell water arrived.
April 25:	Shut off feed and ran process water through bioreactor for several hours.
April 28:	Reduced flow through bioreactor 2 L/min.
April 29:	Returned flow through bioreactor to 4 L/min, new load of clearwell water arrived.
May 1:	Plug in ethanol line caused addition of ethanol to drop from 11 to 3 mL/min; started using acetic acid to adjust pH in feed tank.
May 2:	Plug in ethanol line.
May 6:	New load of clearwell water arrived.

May 7: Started addition of acetic acid at 6-m level.

May 8: Stopped intracolumn pH adjustment.

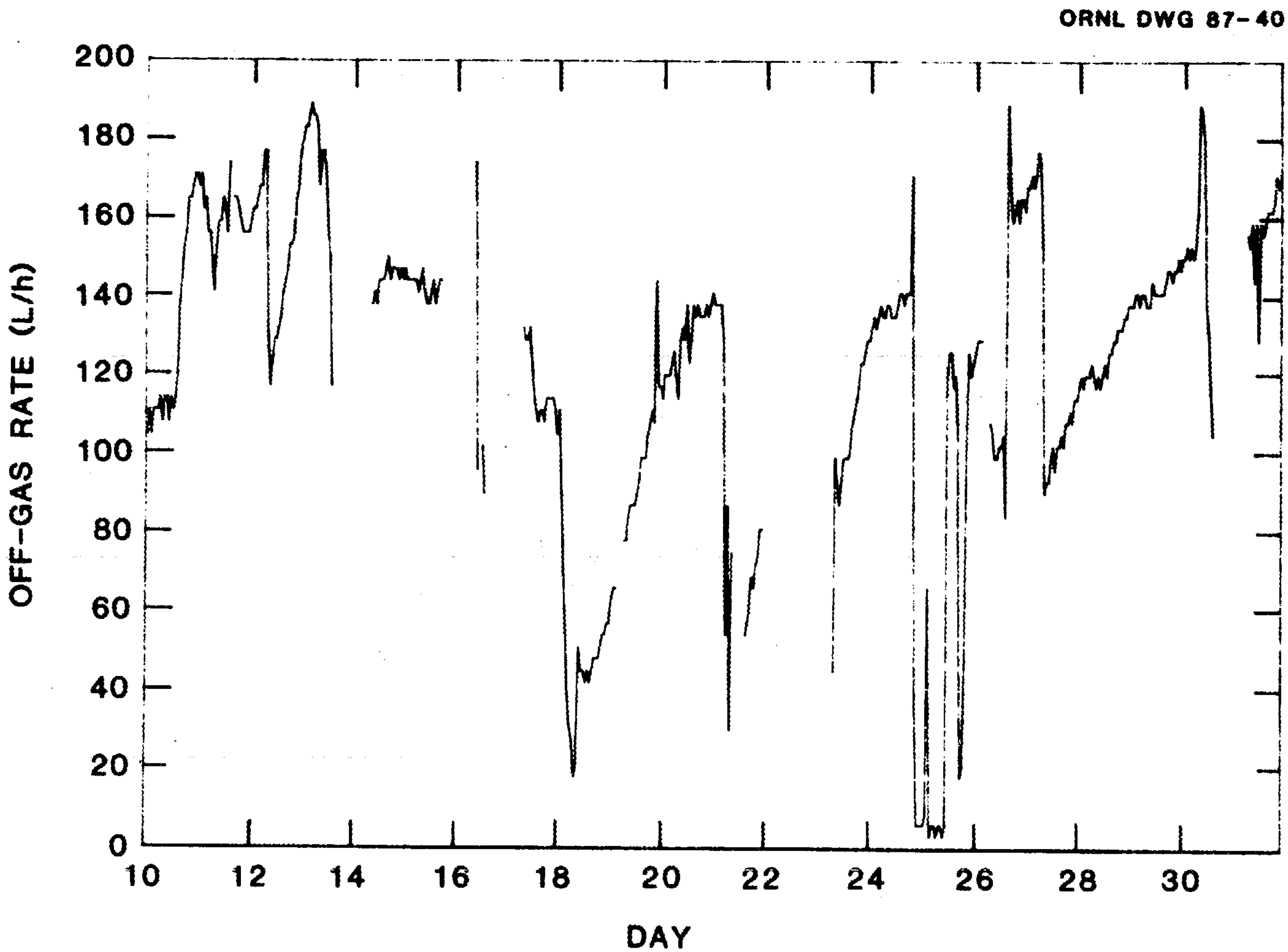
May 9: New load of clearwell water arrived.

May 12: Changed to sulfuric acid for pH adjustment in feed tank.

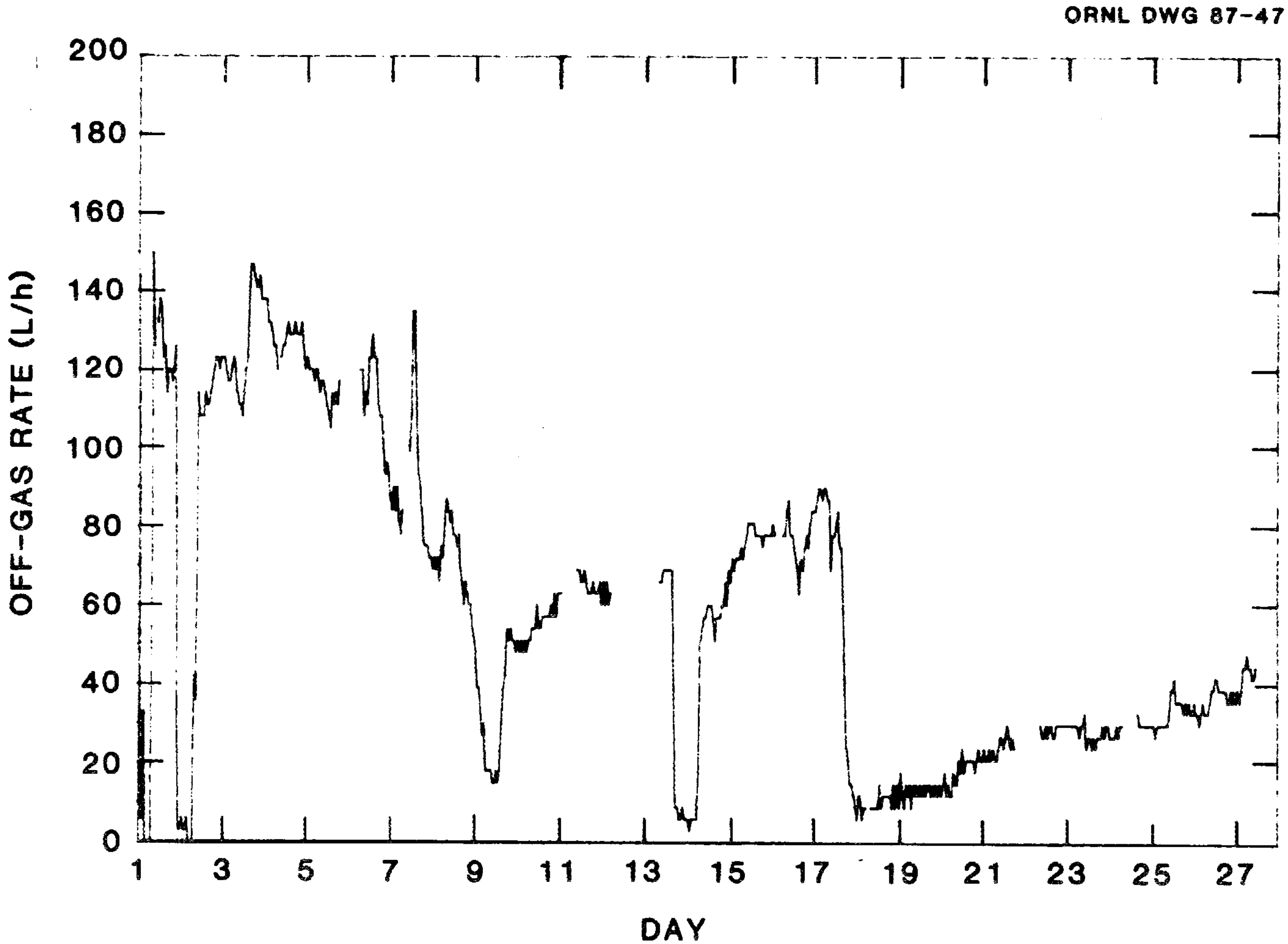
May 14: New load of clearwell water arrived; pH in feed tank dropped to 3.4 for several minutes.

May 16: Began addition of 10% sulfuric acid at 20 mL/min at port S-7; later reduced this to 10 mL/min.

May 22: Shut down bioreactor for end of project.



OFF-GAS RATE VS TIME
DECEMBER 10 - DECEMBER 31, 1985



OFF-GAS RATE VS TIME
JANUARY 1 - JANUARY 27, 1986

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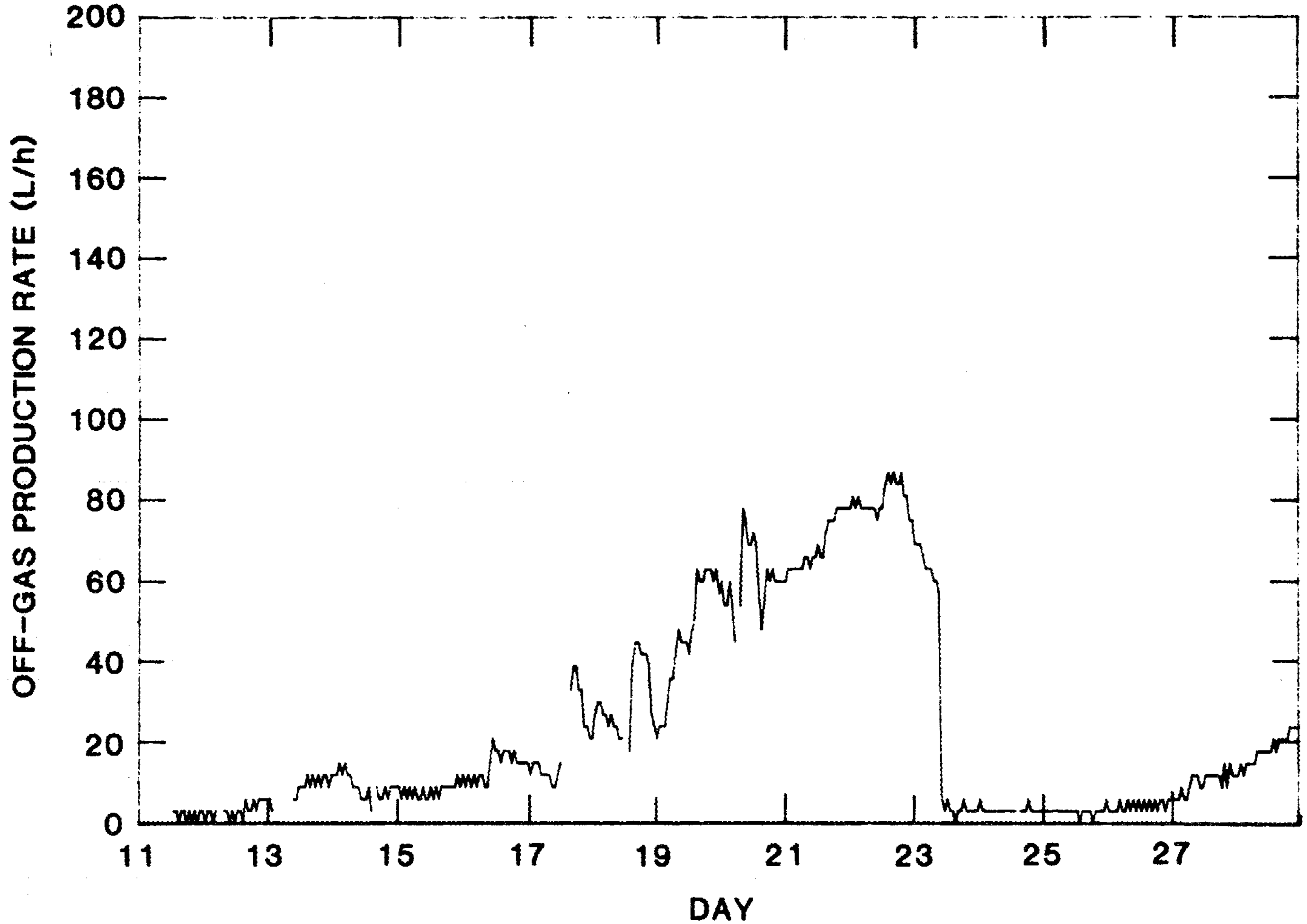
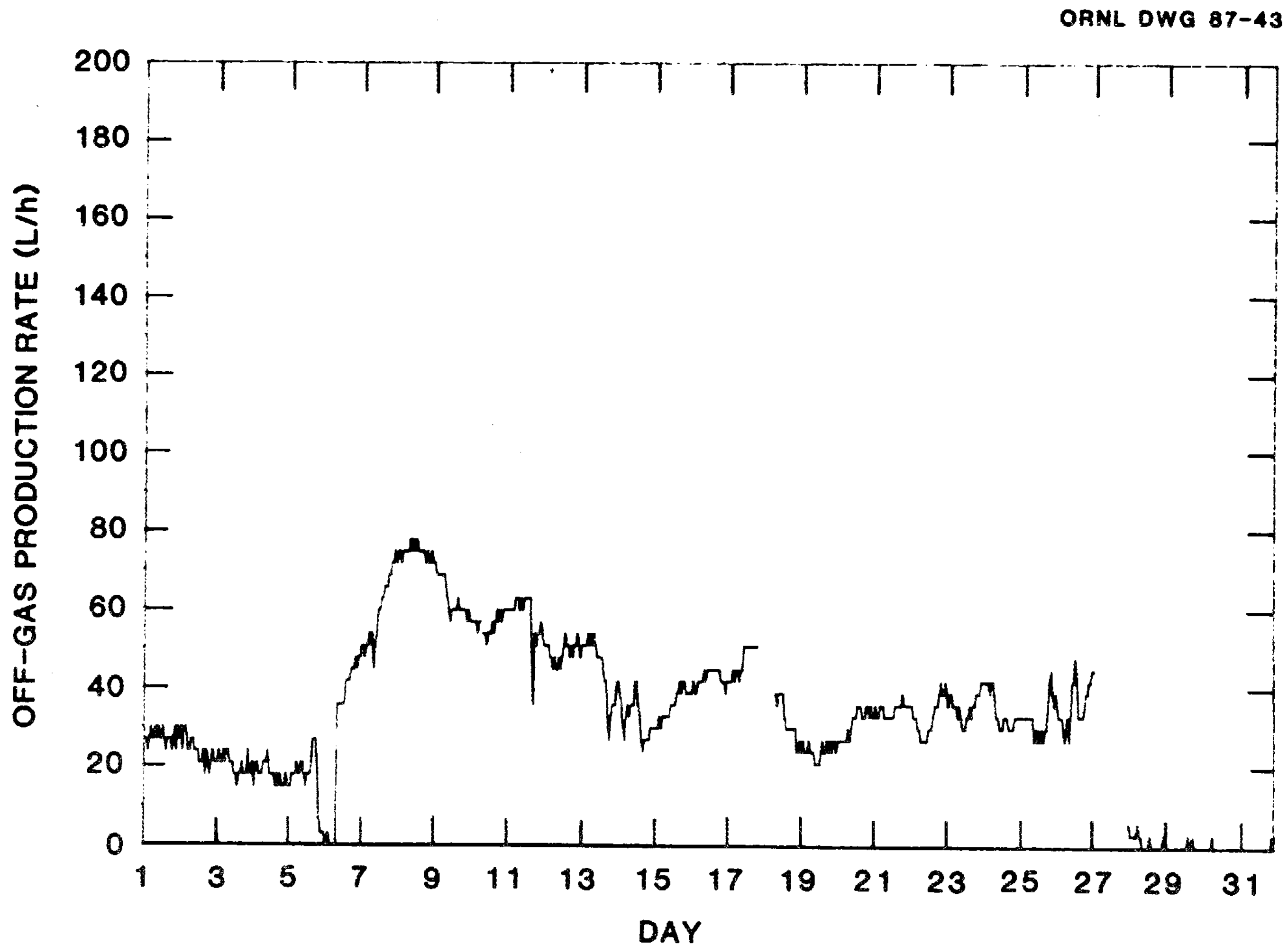
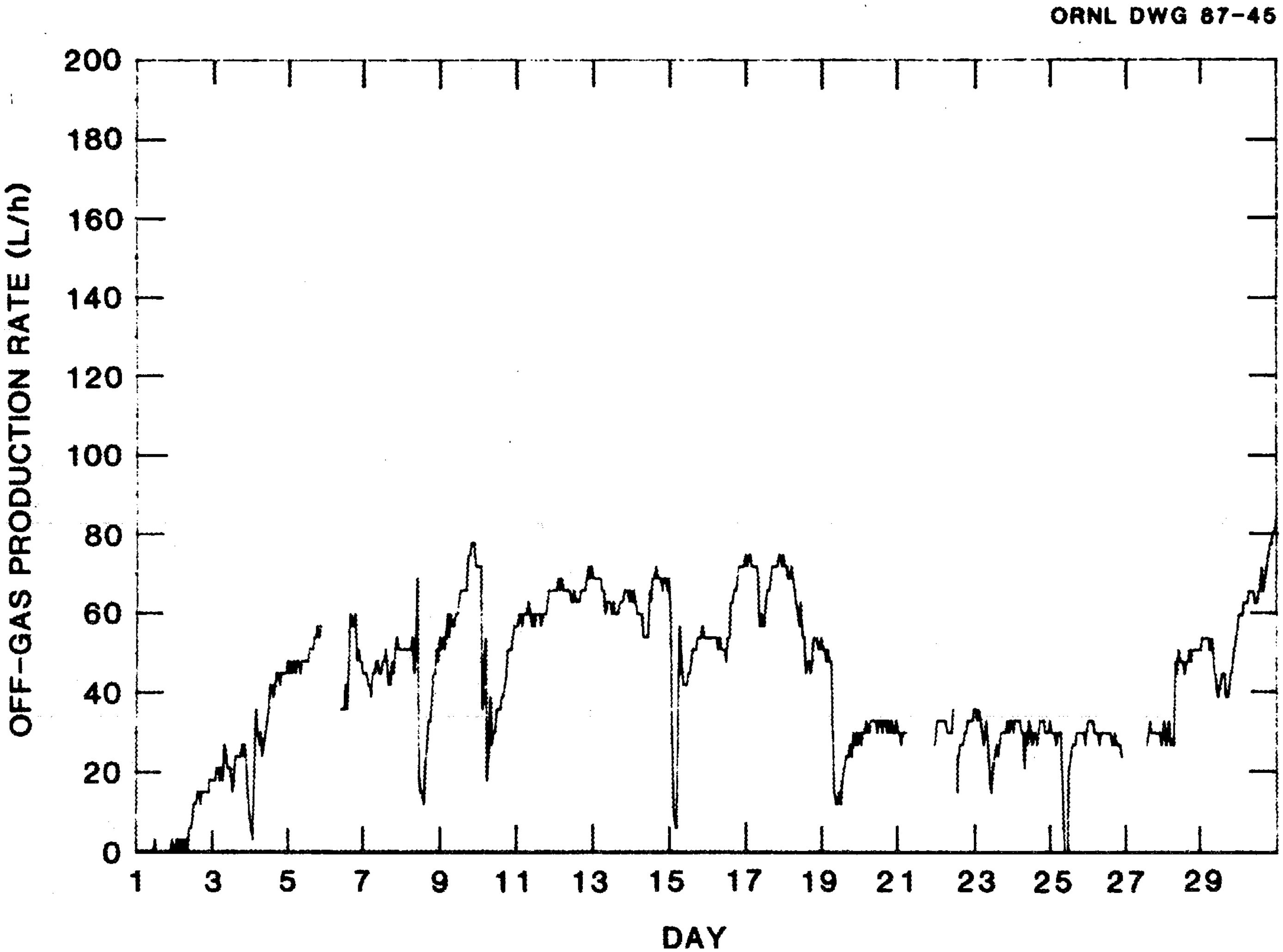


OFF-GAS RATE VS TIME
FEBRUARY 11 - FEBRUARY 28, 1986



OFF-GAS RATE VS TIME
MARCH 1 - MARCH 31, 1986



OFF-GAS RATE VS TIME
APRIL 1 - APRIL 30, 1986

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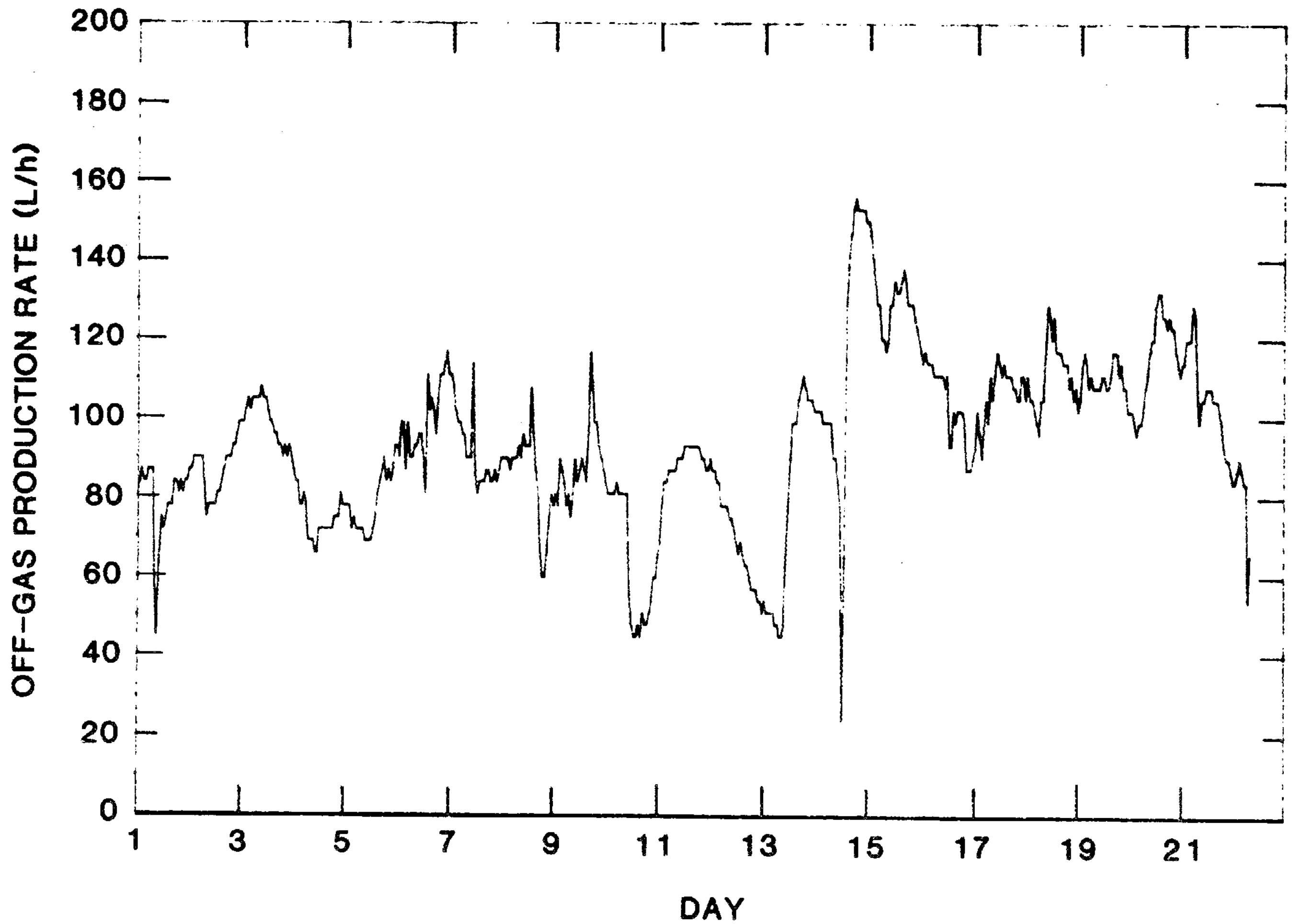

OFF-GAS RATE VS TIME
MAY 1 - MAY 22, 1986

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