BIOLOGICAL DENTRIFICATION OF POLLUTED GROUNDWATER

by

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Colorado Water

Resources Research Institute

Completion Report No. 153

Colorado State University

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September 1989

Grant No. 14-08-0001-1551
Project 03

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INTRODUCTION

Motivation for Denitrification Research: Many groundwaters are contaminated with nitrate from fertilizers, domestic wastewater lechates and municipal waste treatment plant effluents which have entered groundwater aquifers. Nitrate is a mobile and very soluble ion, thus it has become a common groundwater pollutant. For example, a recent report of the Colorado Water/Sewer Needs Committee (Colorado Division of Local Governments) categorized the drinking water supplies of Baxter, Brighton, Chambers Subdivision, Fort Lupton, Gilcrest, Hudson, Kim, LaSalle, Milner, Peyton, Platteville, and Southgate as demonstrated health hazards or producing immediate health effects due to high nitrate concentrations.

Because the nitrate ion is toxic to infants, drinking water supplies that contain greater than the U.S. primary drinking water standard of 10 mg/L as nitrogen require treatment. Unfortunately, conventional water treatment processes do not remove the nitrate ion.

Biological Denitrification: Nitrate is removed from water readily by denitrification, a bacterial respiration process which converts nitrate to harmless dinitrogen gas. Denitrification is carried out by numerous bacterial species found in soil and aquatic environments. Most denitrifying bacteria are facultative hetertrophes, which can respire using either nitrate or oxygen as the terminal electron acceptor. These bacteria require a reduced

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exogenous carbon source for energy production and cell synthesis. We chose acetic acid as the carbon source for our research because it is readily available in bulk quantities, not toxic to humans and is less hazardous to handle and store than alternatives such as methanol.

Biological denitrification of wastewater has been carried out in suspended growth, fluidized bed and biofilm reactors. The fixed biofilm process is a suitible choice for potable water denitrification because it avoids the problems of solids separation and recycle associated with the activated sludge process, and produces less effluent solids than fluidized bed processes. The simplicity of operation associated with fixed biofilm processes is also a significant advantage for small communities which can not employ large staffs of specially trained operators.

Reactor Configurations Investigated: Pilot scale tests of a fixed media denitrification process were conducted at the University of Colorado Environmental Engineering Laboratories from November, 1988 through October 1989. Figure 1 shows the reactor configuration which was investigated. Each reactor was 2.6 meters (8.4 feet) long and 15 cm (6 inches) in diameter. Eighty five percent of each reactor volume was filled with high-porosity plastic media (Jaegar Tripack #1). The remaining volume of each reactor was reserved for bed expansion during the air scour procedures which were carried out periodically to remove excess biomass.

EFFLUENT

BACKWASH

BACKWASH

INFLUENT
FEED

ACETATE
FEED
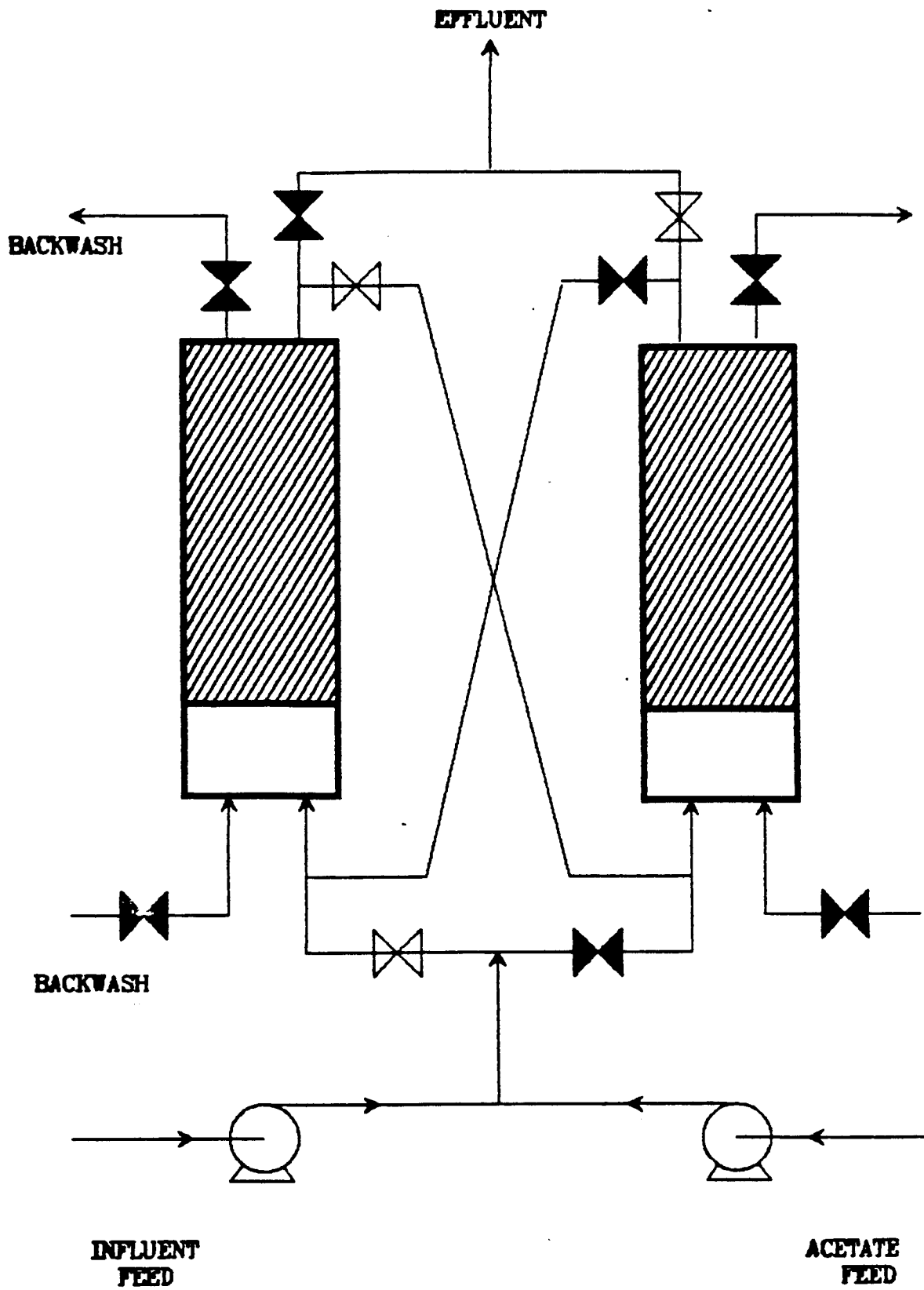
DENITRIFICATION REACTOR CONFIGURATION

FIGURE 1

An influent flow rate of 1.2 L/min (0.32 gpm) was maintained throughout the period of reactor operation. This influent flow rate corresponds to a hydraulic loading of 66 (L/min)/sq.meter (1.6 gpm/sq.ft). During normal operation the reactors were operated in series with each reactor providing a nominal (bare bed) hydraulic detention time of 40 minutes.

The reactor system influent was intended to simulate nitrate polluted groundwater. This simulation was achieved by adding alkalinity (200 mg/L as CaCO3) and Nitrate (20 mg/L as Nitrogen except during nitrate pulse experiments) to Boulder tap water. The tap water was pretreated to achieve dissolved oxygen (DO) concentrations between 2.0 and 3.0 mg/l except for periods when the effects of higher (6-7 mg/L) influent dissolved oxygen concentrations were specifically being investigated. During the course of the investigations influent temperatures varied from 16 C to 22 C (61 F to 72 F). No attempt was made to modify or prevent these naturally occurring temperature variations.

A supplemental carbon source, required for biological denitrification of potable quality water, was provided by mixing acetic acid into the influent upstream of the reactor system.

During three months of operation the denitrification reactor effluent was applied to a pair of slow sand filters. Figure 2 is a schematic diagram of one of these filters. Each filter was 30.5 cm (12 inches) in diameter and contained one meter (3.25 ft.) of filter sand. The two identical filters were cleaned and disinfected prior to each filter run and then operated in

carbon
feed

orifice

constant head
box

coliform
feed

overflow

feed line

sample
line

inlet

sight
tubes
to
measure
head

spill cup

thermocouple

res.

sand
surface

1 cm
5 cm

10 cm

20 cm

40 cm

effluent
line

gravel
underdrain
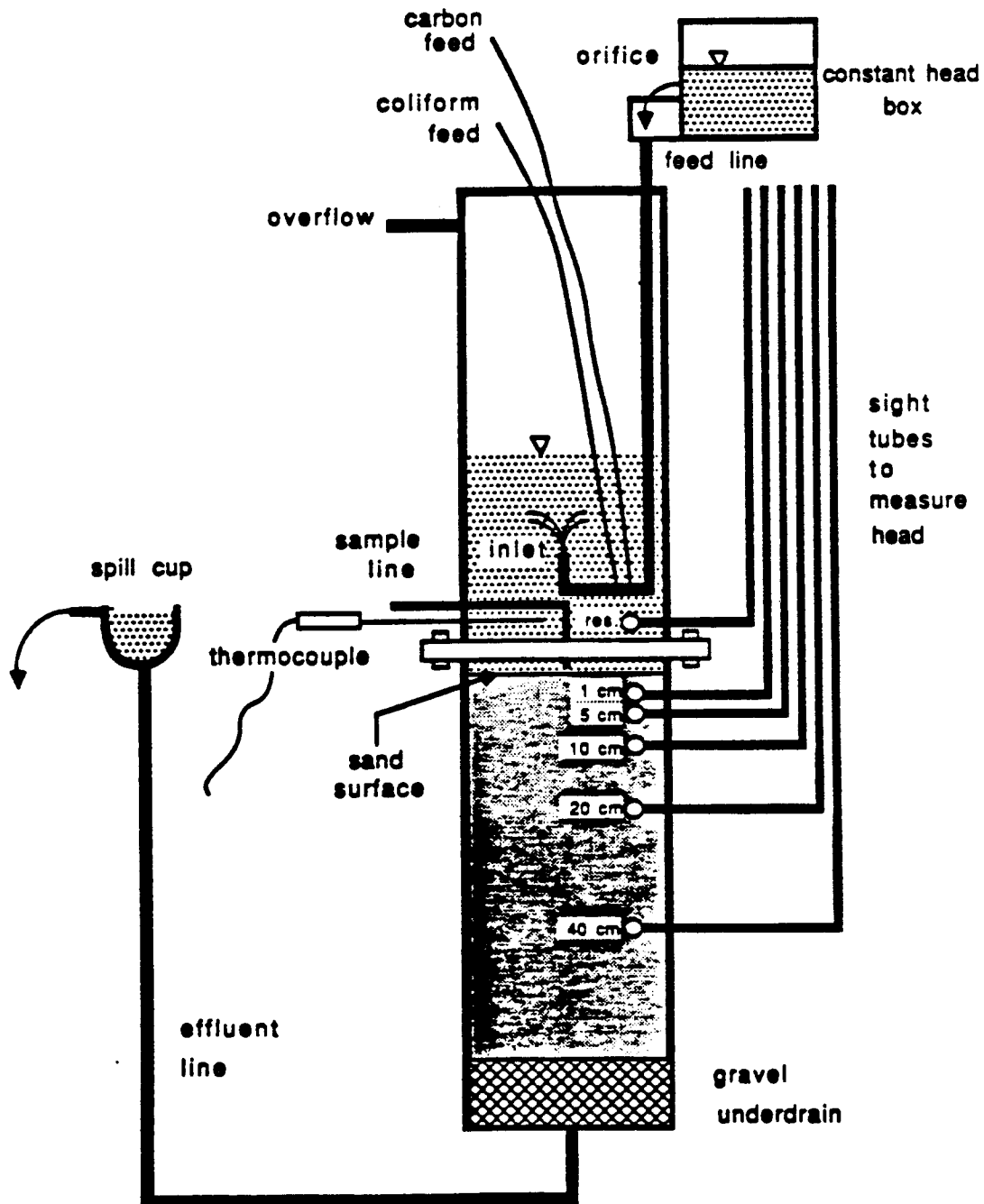
SLOW SAND FILTER SCHEMATIC

FIGURE 2

parallel. Initially experiments were conducted to determine an appropriate filter sand size. Following these experiments the effects of solids settling and effluent reaeration prior to filtration were investigated.

Goals of the Research Program: The Biological Denitrification of Polluted Groundwater project had the following goals (as identified in the original proposal):

1. Determine the appropriate level of acetic acid addition required to maintain acceptable reactor performance with respect to nitrate removal.

2. Develop an excess biomass removal procedure and determine quantity of waste biomass produced.

3. Determine the steady state performance of the reactor system with respect to nitrate concentration reduction over an extended and continuous operating period.

4. Monitor the reactor effluent Turbidity and Suspended Solids over an extended and continuous operating period.

5. Measure the effects of time varying influent nitrate concentrations on reactor effluent nitrate concentration.

6. Evaluate the chlorine demand of the denitrification reactor effluent and evaluate effluent trihalomethane formation potential.

7. Demonstrate a filtration technology, appropriate for small communities, capable of producing water meeting the turbidity standards for potable water (not included in the original proposal).

Some of goals were achieved by modifying our operating methods as we gained experience during continuous reactor operation; others were achieved by performing specific, preplanned experiments as outlined in the original proposal. The remainder of this report presents our operating experiences and the results of the planned experiments.

REACTOR OPERATION

Theoretical Acetic Acid Requirements: It is appropriate to have a rational theoretical framework for determining the quantity of acetic acid required for complete reaction of all influent nitrate and dissolved oxygen. This framework was developed and then verified experimentally.

The stoichiometric equations given below were developed by assuming that 65% of the carbon source (acetate) is used for cell production when molecular oxygen is the terminal electron acceptor, and that 35% of the carbon source (acetate) is converted to cell mass when nitrate is the terminal electron acceptor:

$$1.00\, O_2 + 1.43\, CH_3COO^- + 0.263\, NO_3^- + 0.263\, H^+ \ \text{------>}$$

$$0.265\, C_5H_7NO_2 + 0.0523\, CO_2 + 1.43\, HCO_3^- + 0.63\, H_2O \qquad . \ . \ \text{Equation (1)}$$

$$1.00\, NO_3^- + 0.877\, CH_3COO^- + H^+ \ \text{------>}$$

$$0.0877\, C_5H_7NO_2 + 0.456\, N_2 + 0.422\, CO_2 + 0.877\, HCO_3^- + 1.07\, H_2O \ . \ . \ \text{Equation (2)}$$
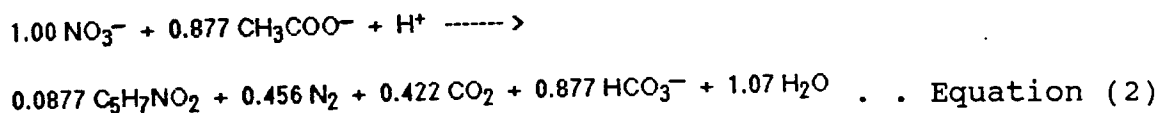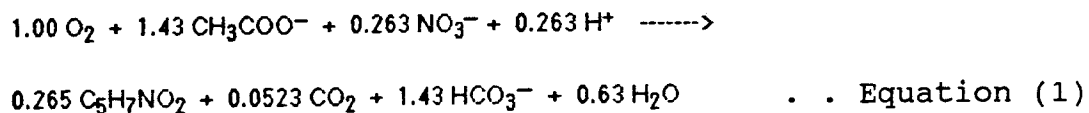
Experimental determinations of acetate consumption in the denitrification reactor were then carried out to verify the proposed stoichiometric equations. Figure 3 presents two sets of measured acetate consumption data obtained when the denitrification reactor was removing 3 mg/l of dissolved oxygen and 18 mg/l of nitrate nitrogen from the reactor influent. The

data plotted with the open squares was taken one week after the data plotted with the solid squares. The solid line in Figure 3 is the theoretical acetate consumption predicted by the stoichiometric equations presented above. We feel that the agreement is good enough to accept the proposed theoretical stoichiometry as accurate enough for engineering design and reactor operating requirements.

It should be emphasized that it may not be desirable to add sufficient acetic acid to remove all the influent nitrate nitrogen nor does addition of sufficient acetic acid assure complete removal if adequate hydraulic detention is not also provided. The first of these points is discussed in the following section. Removal rate results are presented in the section of this report titled 'Steady State Reactor Performance'.

Acetic Acid Addition for 'Standard' Operation: The reactor system was fed the full stoichiometric acetic acid requirement for complete removal of influent dissolved oxygen and nitrates for the first six months of operation. During this period some biomass was observed to grow in the effluent pipes and plastic hoses. During the initial development of the reactor there was insufficient biomass to remove all the influent nitrates so some unused acetic acid was expected in the effluent. Following complete reactor development, however, (about six weeks after innoculation with seed bacteria) some biomass was still observed to accumulate at the outfall of the reactor exit hose where the reactor effluent drained into the labratory sink. The importance

ACETATE CONSUMPTION

FIGURE 3

Nitrates Removed (as nitrogen — mg/l)

Acetate Consumed (as carbon — mg/l)

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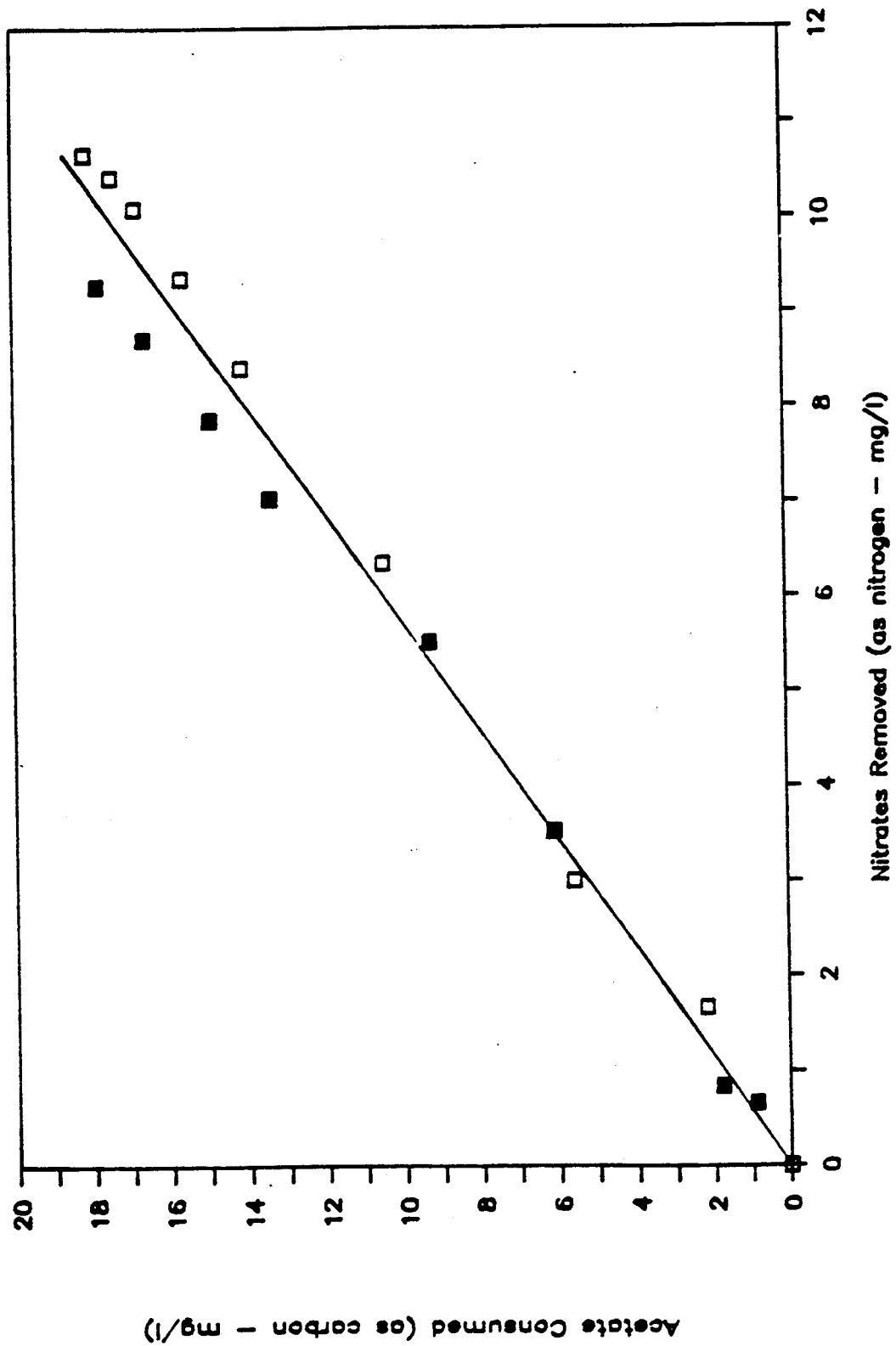
of this regrowth was even more apparent when slow sand filtration was attempted. In the initial implementation of the slow sand filters the denitrification reactor effluent was passed through a small settling basin upstream of the filters. Because the denitrification reactor was at this time producing an effluent with very low (less than 0.1 mg/L) nitrate nitrogen and dissolved oxygen, the settler conditions were anaerobic. It was apparent from the definite (but not overwhelming) odor of rotten eggs which developed that sulfate reducing bacteria were capable of utilizing the carbon (including some acetic acid) in the effluent to produce hydrogen sulfide.

Recognizing that sulfates would not be reduced under oxidizing conditions, we began reaeration of the reactor effluent upstream of the settlers. After ten weeks of operation with reaeration upstream of settling, we abandoned this approach. The reaeration basin was obviously functioning as a well-aerated stirred tank reactor. In this reactor suspended and fixed (to the walls) biomass grew readily; this increased both the suspended solids and turbidity of the reactor effluent. In addition this process arrangement of denitrification reactor, aeration basin, settler and filter was too elaborate.

It is important to note that there is no need for the denitrification system to reduce the nitrate ion concentration to very low levels because the nitrate standard of 10 mg/l is believed to be safe with an adequate margin of safety. We concluded that to achieve an effluent nitrate nitrogen

concentration of consistantly less than 4 mg/L with an influent
nitrate nitrogen concentration of 20 mg/L would be acceptable.
Since the reactor had adequate detention time for complete
nitrate removal the proposed reduced level of treatment was
achieved by limiting the acetic acid feed supply to 90 percent of
the stoichiometric requirement for complete removal of influent
dissolved oxygen and nitrate. This mode of operation has the dual
advantages of minimizing acetic acid and simultaneously avoiding
true anaerobic conditions in the reactor effluent.

Table 1 summarizes the 'standard' operating conditions which
were adopted for the final four months of the experimental
program. Unless otherwise noted the results presented in the
following sections were obtained using the 'standard' operating
condtions summarized in Table 1.

Control of Excess Biomass: One purpose of the proposed research
was to develop a reactor operating scheme which would allow for
continuous operation for an indefinitely extended period. A
critical requirement for continuous operation was the need to
remove excess biomass which accumulates in the reactor due to
growth of the denitrifying bacteria.

The series configuration and valve arrangement of the
reactor was intended to allow one reactor (half the reactor
system) to be isolated from the process stream for removal of
this excess biomass. Either half of the reactor could be placed
in the lead (upstream) or lag (downstream) position with respect
to the process flow. Experience prior to beginning the research

TABLE 1
STANDARD OPERATING
CONDITIONS

PARAMETER	
INFLUENT NITRATE	19.5 mg N /L
INFLUENT DISSOLVED OXYGEN	2.8 mg/L
INFLUENT ACETATE	90% of stoichiometric
INFLUENT ALKALINITY	200 mg/L as CaCO3 added
TEMPERATURE	21C
pH	6.5
FLOW	1110 mL/min
AIR SCOUR CYCLE	5 min air scour 14 days in lead position 14 days in lag position

described in this report indicated that applying an air scour of 0.5 cubic meters per minute per square meter of reactor cross section (1.5 cfm/sq.ft) for five minutes followed by draining the reactor to remove the loose biomass might be appropriate. During the initial six months of reactor operation this 'backwash' procedure was applied alternately to each half of the reactor. The 'lag' half of the reactor was always isolated from the process stream, air scoured, and placed in the 'lead' position of the two reactor system. The time between backwash procedures averaged four weeks, thus each half of the reactor was backwashed on average only once each two months.

On one occasion a reactor was operated for 16 weeks between backwash procedures. The biomass which accumulated during this extended period could not be removed adequately by the 'standard' five minute relatively light air scour procedure. We were forced to apply a longer more intense air scour after this experiment. It was also observed that after six months of operation and six air scour procedures that the biomass was becoming tougher; less was removed by each scour procedure, and headlosses returned to pre-air scour levels in as little as two weeks. Based on these observations the time between backwash operations was decreased to two weeks for the final four months of the research program. The two-week period between air scour procedures (each tube backwashed once a month), coupled with the five minute, 0.5 (M^3/min)/sq. Meter (1.5 cfm/sq.ft) air scour procedure has worked smoothly since it was implemented; hence we have adopted it as our 'standard' operating procedure as noted in Table 1.

Excess Biomass Production: Excess biomass production was monitored during the course of the denitrification research program. After each five minute reactor scour the reactor being backwashed was drained into a holding tank large enough to contain all the reactor effluent (biomass and fluid). The total mass of filterable suspended solids in the holding tank was then determined. This total mass determination, coupled with a knowledge of the mass of nitrates removed by the backwashed reactor during the period since it was last backwashed allowed computation of excess biomass production per unit mass of nitrates removed.

Although any one determination might give misleading results, the accuracy of the procedure just described increases considerably as the results are integrated over several complete reactor cycles. The results presented in Table 2 give the excess solids determinations for a reactor operating period of 10 weeks. During this period the reactor was operating under the 'standard' operating conditions summarized in Table 1.

TABLE 2
AIR SCOUR SOLIDS

DATE	AIR SCOUR VOLUME	SOLIDS CONCENTRATION	MASS REMOVED	NITRATE REMOVED	SOLIDS PRODUCED NITRATE REMOVED
	(L)	(gm/L)	(g)	(g)	(gm/kg N)
10–Jul–89	36.6	2.36	86.4	462	187
28–Jul–89	33.9	1.2	40.7	258	158
14–Aug–89	34.5	1.49	51.4	550	93
04–Sep–89	30.1	1.53	46.1	449	103

NITRATE REMOVAL PERFORMANCE

Steady State Reactor Performance: During the 10 months of continuous denitrification reactor operation, 60 nitrate concentration profiles were determined. The data presented below are representative of all the profiles obtained during 4 months of 'standard' operation (Table 1) of the denitrification reactor system.

Figures 4 and 5 present profiles of nitrate concentration versus detention time for five weeks of reactor operation during July and August of 1989. The data presented in these figures is representative of other periods of operation. Although biomass accumulates steadily with time after each reactor backwash, the rate of removal does not follow any regular pattern with time. For example, Figure 5 shows the removal rate just after backwash to be greater than the rate six days later. Despite this random variation of removal with time, the removal rate was always sufficient to reduce the influent nitrate nitrogen concentration of 20 mg/L to below 4 mg/L in the effluent with one exception. This reduction required between 52 and 77 minutes of the total 80 minutes of detention time available. Thus the denitrification reactors were appropriately sized for our experimental conditions; however, a rate model which predicts the effluent nitrate concentration in terms of the influent nitrate concentration and available (barebed) reactor detention time is needed to extend the results to other influent nitrate

FIGURE 4

NITRATE REMOVAL PROFILE

BARE BED RESIDENCE TIME (min)

□ 5 DAYS + 8 DAYS ◇ 13 DAYS △ 14 DAYS

NITRATE CONCENTRATION (mg N /L)

FIGURE 5

NITRATE REMOVAL PROFILE

BARE BED RESIDENCE TIME (min)

NITRATE CONCENTRATION (mg N / L)

□ 1 DAY   + 6 DAYS   ◇ 10 DAYS   △ 17 DAYS

18
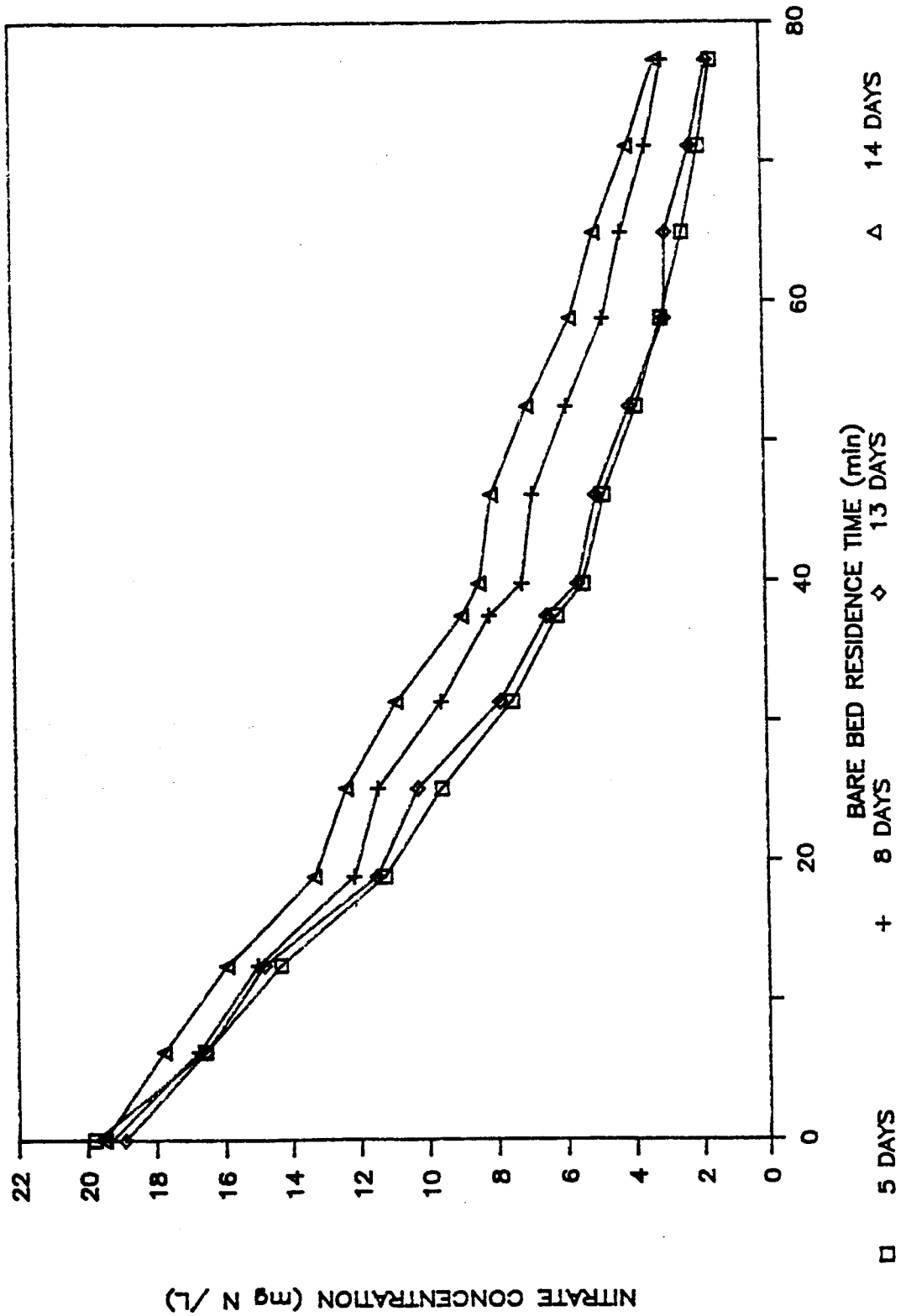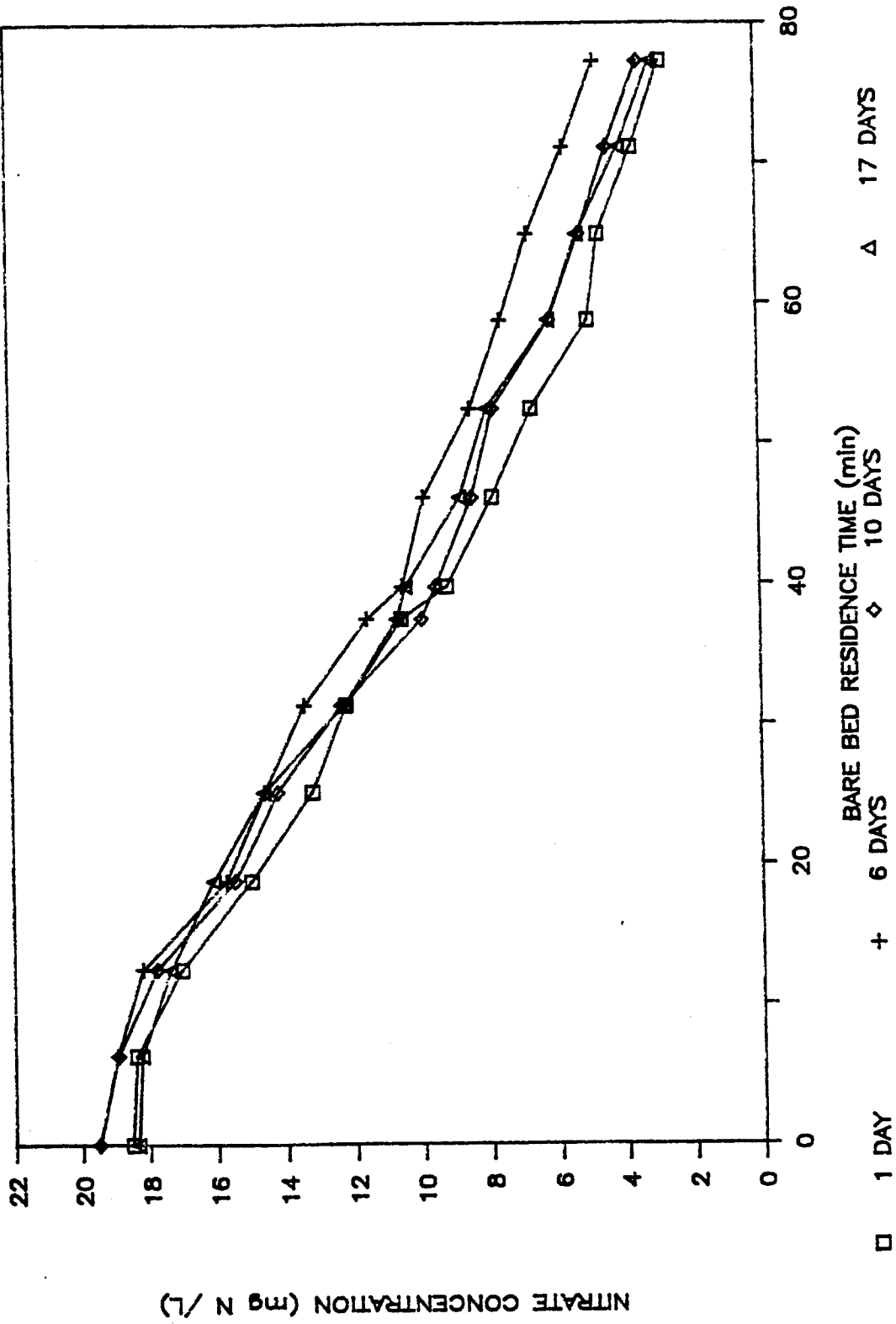
concentrations and effluent nitrate requirements.

A half-order model is often used to model fixed film denitrification kinetics (Harremoes, 1976). The mathematical expression for this model is given by:

$$\sqrt{N} = \sqrt{No} - K * (t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{Equation (3)}$$

Where: N = Nitrate nitrogen concentration after detention time 't' in the reactor system.

No = Initial (reactor influent) nitrate nitrogen concentration.

K = Half-order Rate coefficient, determined from a fit of the data from a nitrate concentration profile.

Half-order rate coefficients were determined for each of the eight nitrate concentration vs. time profiles previously presented in Figures 4 and 5. Data points corresponding to nitrate nitrogen concentrations below 1.5 mg/L were excluded from each data set. Figure 6 presents the data (symbols) and the rate models (solid lines) obtained from the nitrate versus time profiles which produced the highest and lowest half-order rate coefficients.

As shown in Figure 6 the highest rate coefficient value obtained was 0.046 $\sqrt{mg/L}$ /min. and the lowest was 0.028 $\sqrt{mg/L}$ /min. Each of these two rate coefficients was substituted into Equation 3 to produce a theoretical nitrate nitrogen versus time profile. These profiles are plotted as solid lines in Figure 7. Also included in Figure 7 are all of the data obtained during 'standard' operation of the denitrification reactor. The results

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FIGURE 6

SQUARE ROOT NITRATE PROFILE

K = 0.028 SQRT[mg/L]/min

K = 0.046 SQRT[mg/L]/min

SQRT[NITRATE CONCENTRATION (mg N /L)]

BARE BED RESIDENCE TIME (min)

□ 7/15   + 8/3   —— MODEL

20

FIGURE 7

NITRATE PROFILE MODEL

K = 0.028 SQRT[mg/L]/min

K = 0.046 SQRT[mg/L]/min

BARE BED RESIDENCE TIME (min)

X   ACTUAL DATA

———   MODEL

NITRATE CONCENTRATION (mg N /L)
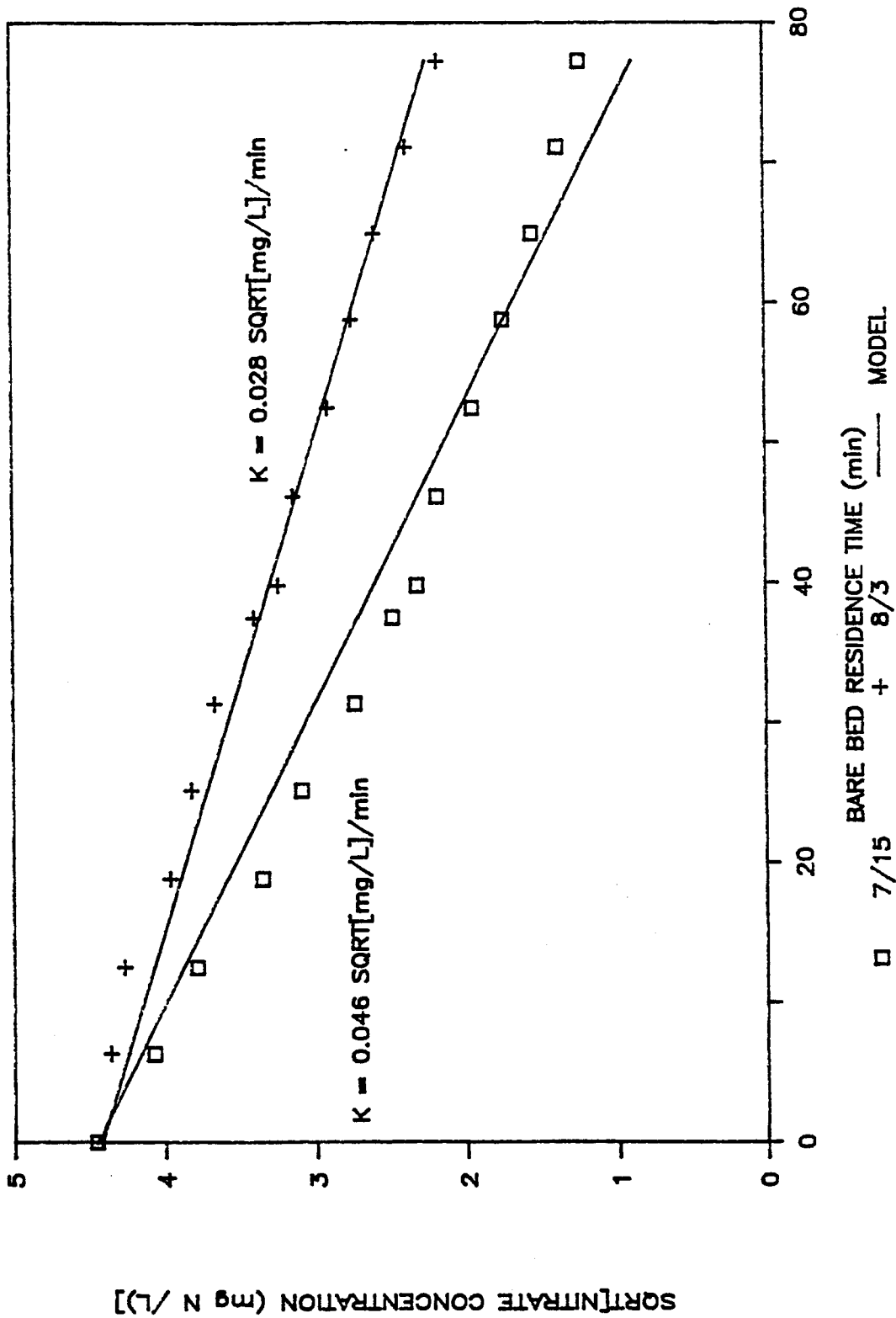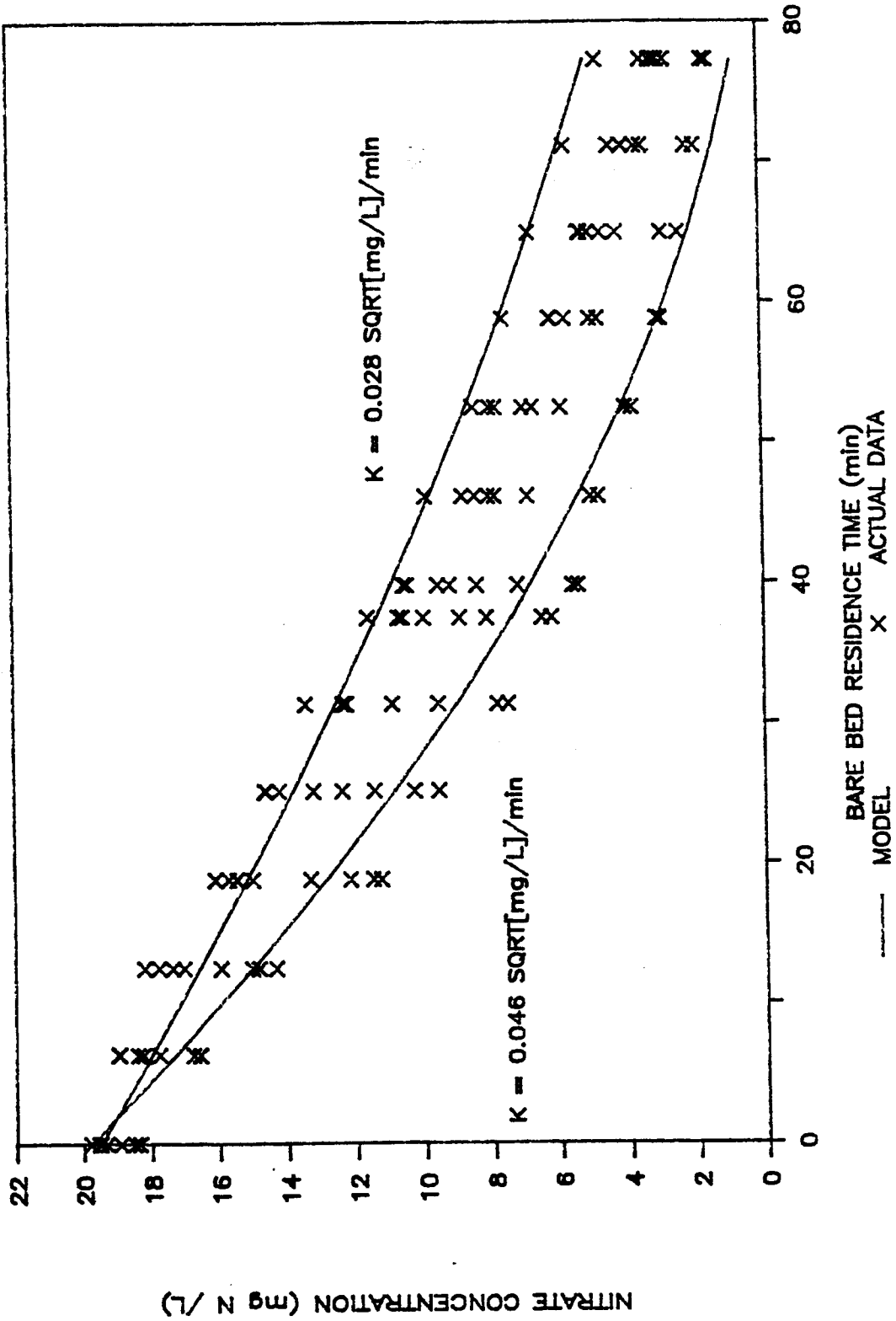
presented in Figure 7 show that the theoretical predictions obtained from maximum and minimum half-order rate coefficients bracket one hundred percent of the effluent data points obtained during 'standard' operation. Furthermore, 88 percent of the data points fall below the theoretical curve obtained with the lower rate coefficient; thus this coefficient is a conservative predictor of reactor performance and is recommended by the authors for denitrification reactor design.

Reactor Effluent Quality Parameters: In addition to the nitrate concentration profiles previously presented many determinations of pH, Temperature, Dissolved Oxygen, Turbidity, Suspended Solids and Nitrate concentration were performed on the reactor influent and effluent. The results of those determinations which were made during a typical 60 day period of 'standard' reactor operation are presented in the current section of this report.

The period of operation reported on in the following paragraphs began July 3 and ended August 3, 1989. During this period the average dissolved oxygen concentrations in the reactor influent and effluent were 2.6 mg/L and 0.1 mg/L respectively. The influent temperature averaged 20.7 C and increased an average of 1.3 C while passing through the reactor system. The average influent pH of 6.1 increased to 6.8 in the reactor effluent.

Figure 8 presents influent and effluent nitrate nitrogen concentrations versus time. The reactor system did not experience any periods of extremely poor or erratic denitrification performance during any other period of our study. The performance

shown in Figure 8 for the month of July was typical of most operating periods. The performance shown in Figure 8 for August, while still acceptable, was the poorest performance observed during normal reactor operation.

Figure 9 presents the results of the Turbidity determinations versus time of operation. The maximum and minimum turbidity values obtained were 4.5 NTU and 1.2 NTU respectively. The average turbidity value for the eight week period of operation was 2.5 NTU. These data do not include values determined during the first 60 minutes after an air scoured reactor was returned to service. Immediately after installation turbidity values were typically as high as 10 NTU but fell rapidly to normal levels in approximately 60 minutes.

Figure 10 presents the results of the Suspended Solids determinations versus time of operation. The maximum and minimum Suspended Solids concentrations obtained were 12.5 mg/L and 1.2 mg/L respectively. The average Suspended Solids concentration for the eight week period of operation was 4.8 mg/L. These data do not include values determined during the 60 minutes after an air scoured reactor was returned to service. Immediately after installation suspended solids concentrations were as high as 42 mg/L but fell rapidly to normal levels in approximately 60 minutes.

In summary, the effluent Turbidity and Suspended Solids concentrations were low for a biological process but not low enough for direct (with disinfection) potable use. This conclusion, which was anticipated from previous work, underscored
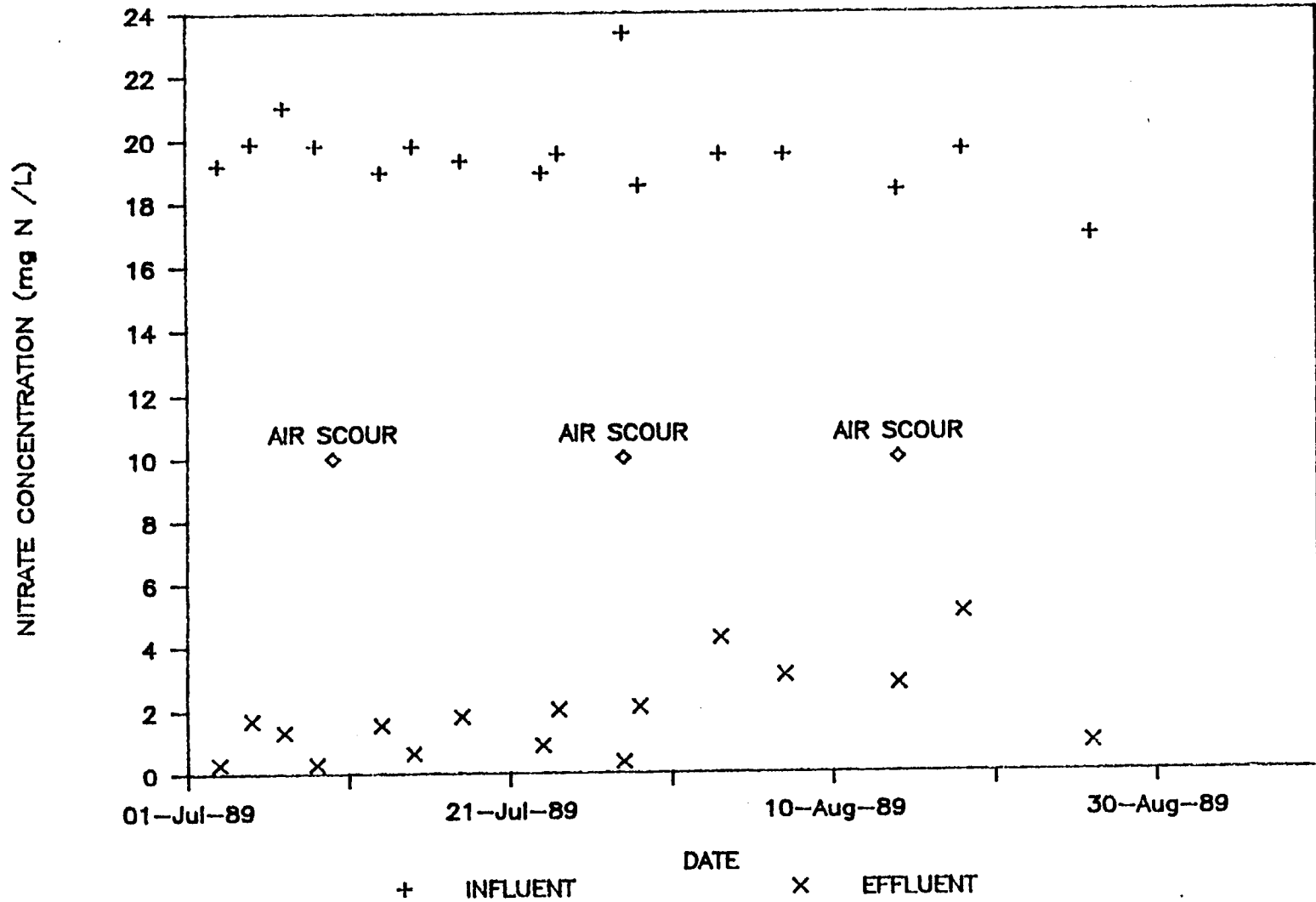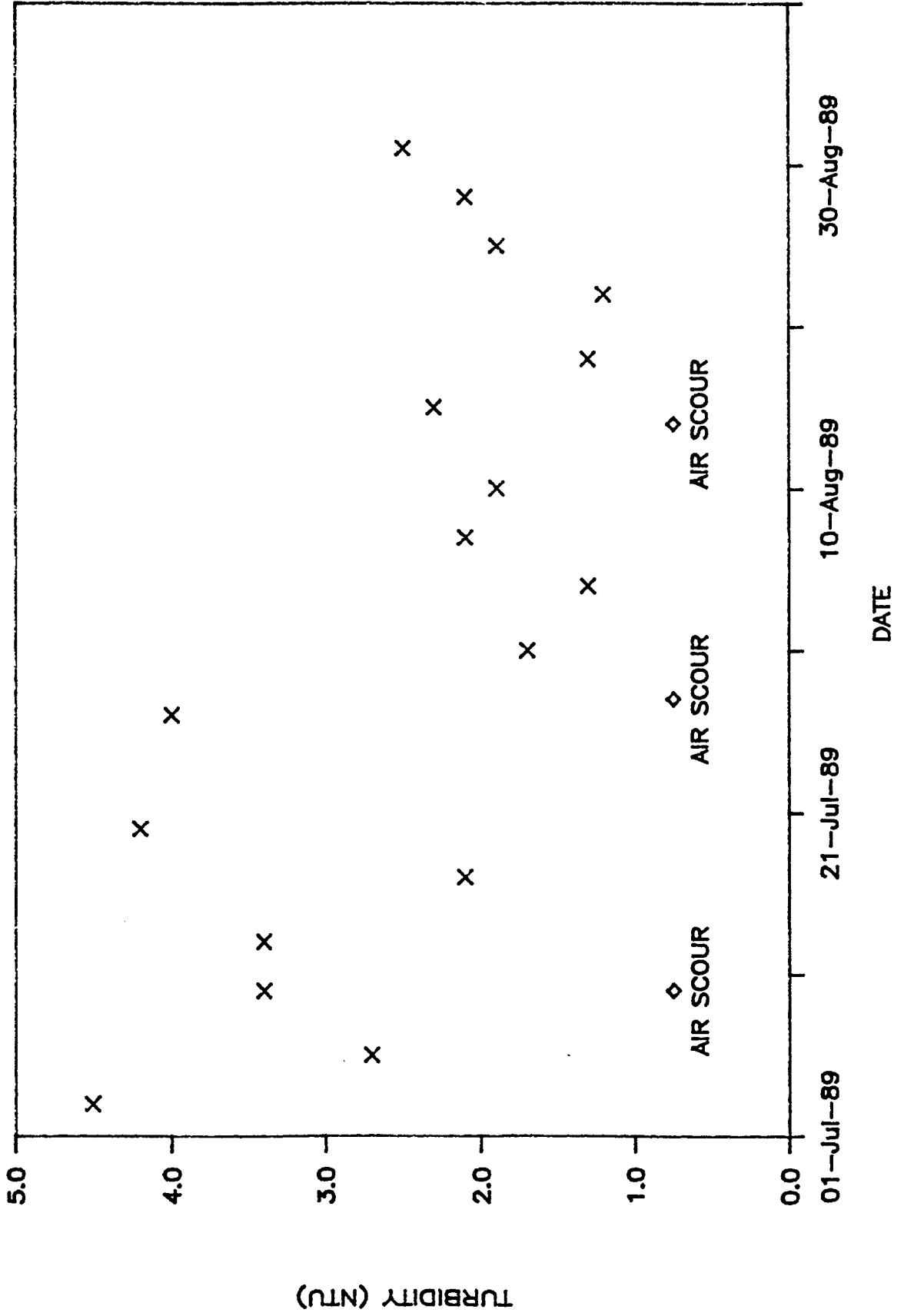
FIGURE 8
INFLUENT & EFFLUENT NITRATE CONC.

AIR SCOUR   AIR SCOUR   AIR SCOUR

NITRATE CONCENTRATION (mg N /L)

DATE

+   INFLUENT   X   EFFLUENT

24

FIGURE 9

EFFLUENT TURBIDITY

25

FIGURE 10

EFFLUENT TOTAL SUSPENDED SOLIDS

26

the need to develop appropriate filtration technologies for the denitrification reactor effluent. We successfully utilized slow sand filtration to eliminate the effluent suspended solids and consistantly reduce the turbidity below 1.0 NTU. Our slow sand filtation research is described in a later section of this report.

Response to Nitrate Concentration Step Increase: This section reports the response of the denitrification reactor system to a sudden step increase in influent nitrate concentration. The purpose of the nitrate 'pulse' experiments was to determine if the reactor system would remove all or some of the additional nitrate ions, through increased biological activity of the existing biomass, or pass the excess nitrates through to the effluent. The results of a representative nitrate pulse experiment are presented below.

After operating the denitrification reactor for more than one hundred days with a constant influent nitrate nitrogen concentration of 20 to 22 mg/L, the concentration of nitrate nitrogen was suddenly increased to 40 mg/L. Prior to applying the nitrate step increase, acetic acid was being added to satisfy the stoichiometric requirement for complete dissolved oxygen and nitrate removal. When the nitrate nitrogen pulse was begun additional acetic acid was simultaneously supplied so that the full stoichiometric acetate requirement was still avialable. Figure 11 presents the results obtained in terms of nitrate nitrogen concentration reduction through the reactor. Before the nitrate concentration increase the reactor system was removing a

FIGURE 11

RESPONSE TO 20 mg/L NO3–N STEP CHANGE

(INITIAL CONCENTRATION 20mg/L)

HOURS AFTER STEP CHANGE

□   1ST REACTOR   +   BOTH REACTORS   ◆   2ND REACTOR

28
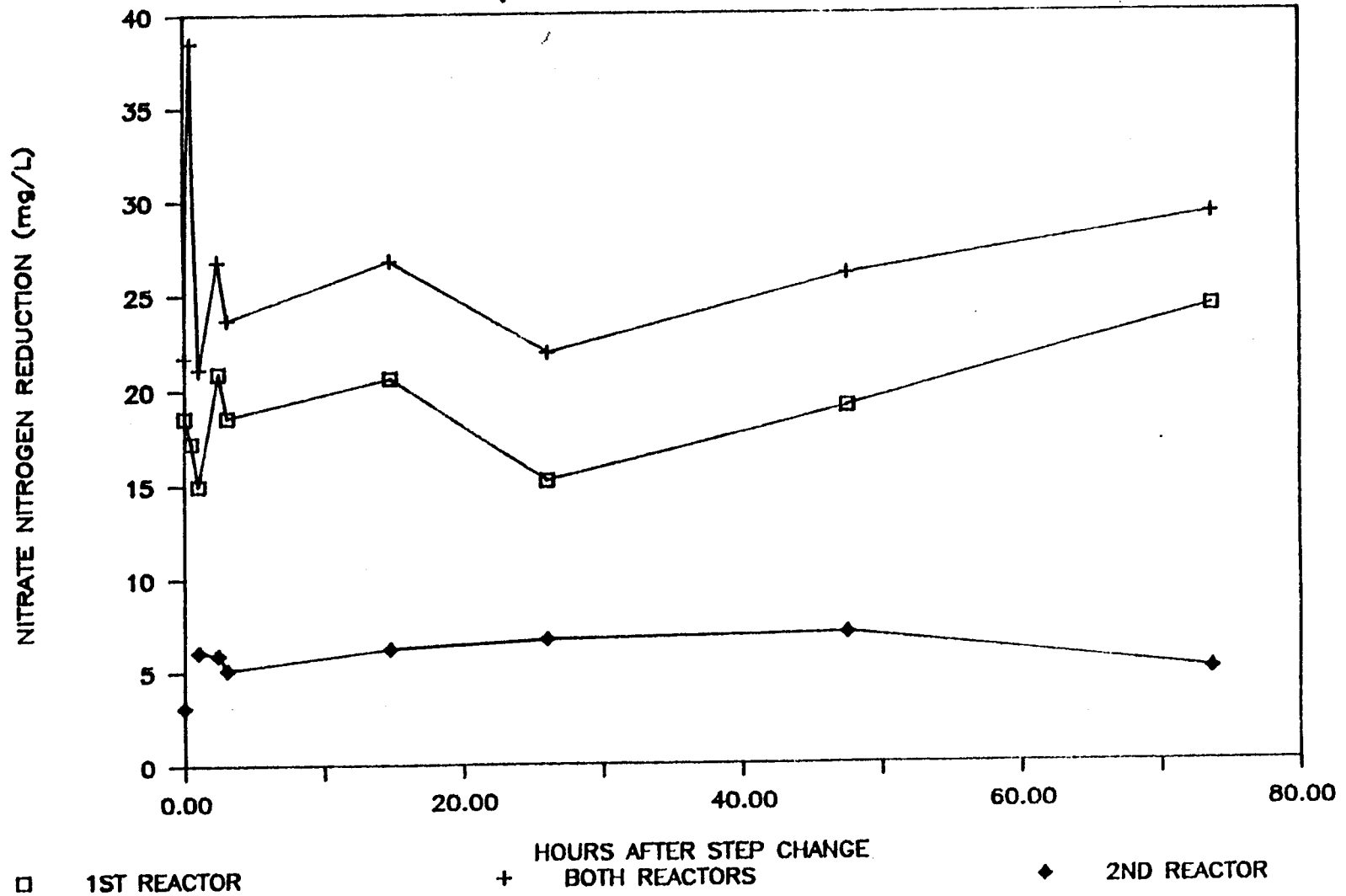
total of 22 mg/L of nitrate nitrogen. The first reactor was removing 18 mg/L and the second was removing 3 to 4 mg/L of nitrate nitrogen. Thus it would appear that the second reactor, which is the same size as the first reactor, was severely nitrate limited and might be capable of removing more nitrate if additional nitrates were suddenly passed through from the first reactor. This was observed not to be true, as illustrated by the data presented in Figure 11. During the first hour after the nitrate concentration increase in the influent no, effects were detected in the reactor effluent. This was as expected for a reactor system which approximates plug flow conditions. For three days following this initial period the first half of the reactor system was observed to remove between 15 and 21 mg/L of nitrate nitrogen. The average for this period was approximately the same as the first reactor was removing before the nitrate concentration increase. More surprising was the lack of additional removal in the under utilized second half of the reactor system during this period. Immediately after the nitrate concentration increase, this reactor was removing 5 to 6 mg/L of nitrate nitrogen. However, three days later the second reactor was still producing this small decrease in nitrate concentration.

In conclusion the reactor system (two reactors in series) did not respond significantly to the increased nitrate nitrogen which suddenly became available. This illustrates the importance of a reasonably constant nitrate nitrogen concentration to maintain low nitrate nitrogen concentration in the reactor effluent.

CHLORINE DEMAND AND TRIHALOMETHANE FORMATION POTENTIAL

Chlorine **Demand** **of** **Denitrification** **Reactor** **Effluent:** Samples of reactor influent, unfiltered effluent and (glass fiber) filtered effluent were breakpoint chlorinated to determine their chlorine demand. These sample sets were collected at times ranging from one day after the previous reactor backwash to thirty days after the previous reactor backwash. In addition to chlorine demand the trihalomethane formation potential (THMFP) of some sample sets was determined.

The chlorine demand results, which were obtained using the amperometric titration procedure, are presented in Table 3. Note that the chlorine demand results are expressed in terms of mg/L of chlorine gas (Cl_2). The reactor influent (generated from tap water) had very little chlorine demand or already contained residual free chlorine. The chlorine demand results for samples containing residual chlorine have been expressed in the Table 3 as having negative chlorine 'demand'. The results for the unfiltered effluent range from a high of 22.3 mg/L to a low of 5 mg/L. The results for the glass fiber filtered effluent range from a high of 16.8 mg/L to a low of 1.6 mg/L. The chlorine demand of the filtered effluent was, as expected, always lower than the demand determined for the unfiltered sample of the pair.

The chlorine demand results showed a trend with respect to the time elapsed since the previous reactor air scour. This trend is clearly illustrated by the data presented in Figure 12. We

TABLE 3

REACTOR EFFLUENT CHLORINE DEMAND

Sample	Influent	Unf.Effluent	Fil.Effluent
Days after Air Scour			
1	-0.76	22.3	15.6
3	-0.69	20.8	16.8
10	-0.36	16.0	13.9
12	-0.78	16.4	15.5
15	-0.80	11.0	10.0.
18	-0.76	5.0	3.8
25	0.36	8.7	8.3
30	nd	6.1	1.6

* All Chlorine Demand values are in mg/l of Cl_2
* Negative values mean residual chlorine

FIGURE 12

REACTOR EFFLUENT CHLORINE DEMAND
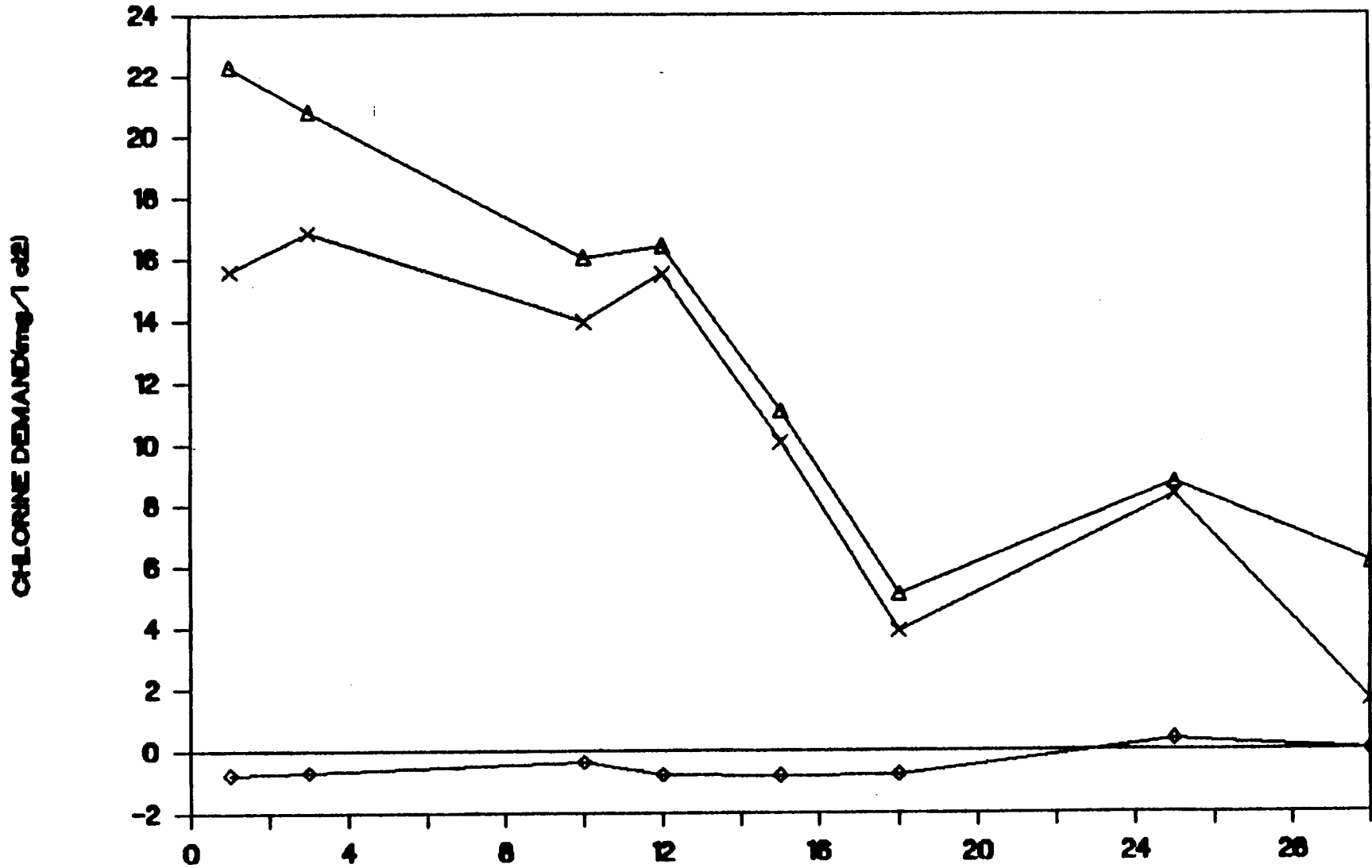
◇ Influent   △ Unfiltered Eff.   ✕ Filtered Effluent

feel that, although the trend is strong, there is still insufficient evidence to establish a quantitative numerical relationship between chlorine demand and time elapsed since previous air scour.

Details of the source of the chlorine demand present in the reactor effluent have not been determined. It has been determined, however, that the demand measured is not due to ammonia nitrogen or hydrogen sulfide.

Reactor Effluent THM Formation Potential: Selected samples of reactor influent, unfiltered effluent, and (glass fiber) filtered effluent were breakpoint chlorinated to produce a free chlorine residual of 1 mg/L (as Cl). Aliquots of these samples were dechlorinated at times of 10, 100, 3000 and 10,000 minutes after initial chorine addition. A flowchart illustrating this sample preparation procedure is given by Figure 13. The dechlorinated samples were subsequently analysed to determine trihalomethane concentrations using chromatography. Of the trihalomethanes only chloroform was detected; the other trihalomethanes appeared to be absent.

For our initial set of trihalomethane determinations, the results of which are presented in Table 4, a purge and trap sampler and flame ionization detector was used. For our subsequent trihalomethane measurements, the results of which are presented in Table 5, direct injection and electron capture detection was employed. Both techniques gave similar results. Figure 14 presents the average concentration data from Table 4
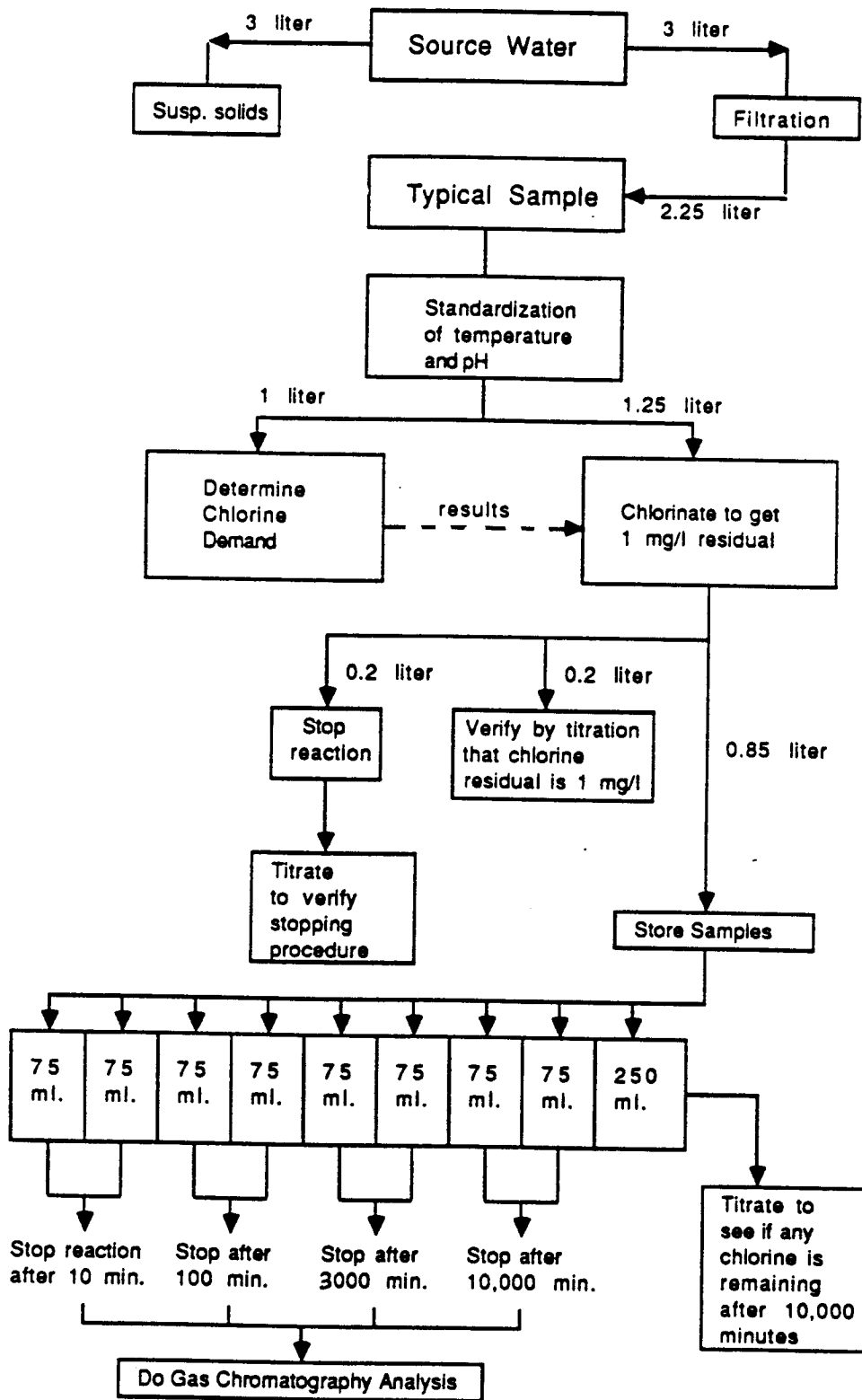
FIGURE 13

SAMPLE PREPARATION FLOW CHART

CHLOROFORM CONCENTRATION
(micrograms per liter)

TIME (min)	10	100	3,000	10,000
Sample				
REACTOR INFLUENT	43	46	78	83
UNFILTERED EFFLUENT	28	33	45	45
FILTERED EFFLUENT	23	30	44	45

(each value is average of two tests)

TABLE 4

CHLOROFORM CONCENTRATIONS
(PURGE and TRAP ANALYSIS)

TABLE 5

CHLOROFORM CONCENTRATIONS
(DIRECT INJECTION with ELECTRON CAPTURE DETECTOR)

Test #	1	2	3	4	5
Days After Air Scour	1	10	12	18	25
Sample	Mintues after air scour				
Influent 0	43	94	60	59	82
10,000	83	107	77	90	127
Fil.Effluent 0	23	46	50	40	50
10,000	45	61	55	70	83
Unf.Effluent 0	28	47	52	43	58
10,000	45	65	62	75	97

Each value is an average of two or more tests

FIGURE 14

CHLOROFORM FORMATION RATE
INFLUENT UNFILTERED FILTERED EFFLUENT

TIME AFTER CHLORINATION (MINUTES)
(Thousands)

CHLORIFORM CONCENTRATION (MICROGRAMS/L)
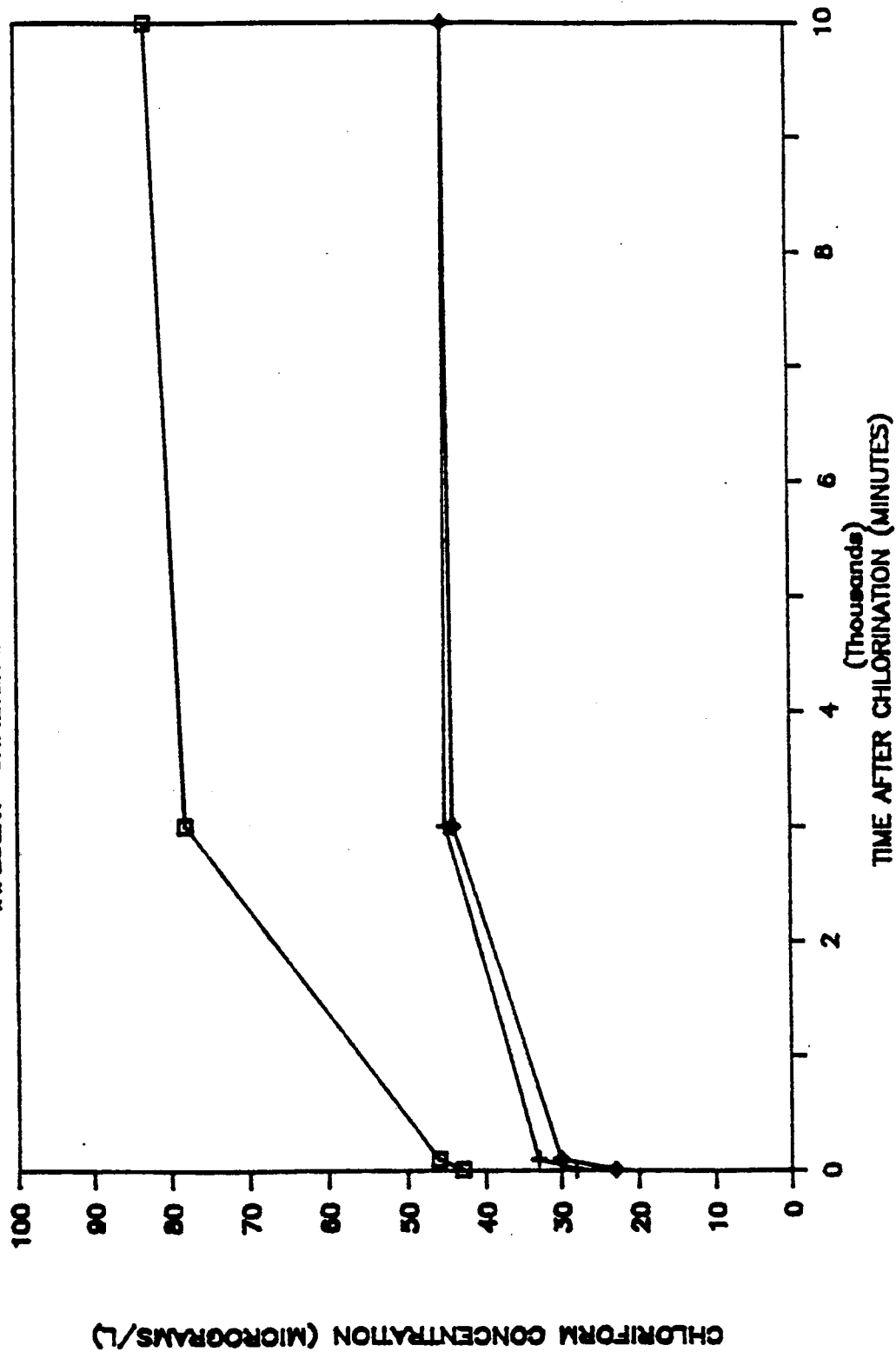
plotted against duration of exposure to free chlorine. These results, which are representative of all six of our sample sets, indicate that the Trihalomethane formation potential of the reactor influent exceeded that of both the filtered and unfiltered effluent. In addition the chloroform concentrations formed in the filtered and unfiltered effluents were very close to the same for every pair of measurements. None of the trihalomethane determinations on reactor effluent detected a concentration exceeding the U.S. primary drinking water standard of 100 micrograms per liter.

Although the results are complicated by the presence of both trihalomethanes (coloform) and trihalomethane formation potential in the influent to the reactor we have concluded that the biological denitrification process does not enhance the potential for trihalomethane problems in a water supply and may in fact reduce this potential.

Slow Sand Filtration of Reactor Effluent: Two pilot scale slow sand filters, operated in parallel, were used to investigate the application of this filtration technology to the denitrification reactor effluent. All the slow sand filtration studies were conducted at a hydraulic loading of 3.3 (L/min)/sq.meter (0.08 gpm/sq.ft) through 1.0 meters (39 inches) of filter sand. Both filters were disinfected with household bleach solution prior to beginning each filter run. Filter runs were terminated when the head loss through the filter sand reached 1.0 meter (39 inches).

Our initial studies employed a rough settler upstream of the filters which removed the larger individual biofilm particles. No reaeration was provided for in these studies so the effluent applied to the slow sand filters was anoxic and possibly anerobic. One filter contained sand with a size analysis considered typical for slow sand filters. The effective size (D_{10}) of this sand was 0.22 mm (.008 inches) with a uniformity coefficient (D_{10}/D_{60}) was 2.50. The other filter contained a larger sand with an effective size (D_{10}) of 0.92 mm (.036 inches) and a uniformity coefficient (D_{10}/D_{60}) of 2.3. This coarse sand had previously proved successful in filtering simulated tropical waters in our laboratory. Under the conditions described above odor problems developed and the filter with the smaller sand reached terminal head loss in less than a week of operation.

For our second slow sand filter experiment we employed the

conditions summarized in Table 6 for both filters. The denitrification reactor effluent was split into two streams and one stream was passed through the previously described rough settler. The denitrification reactor effluent was reaerated within both the slow sand filters by raising the spill cups 60 cm (24 inches) so that the filters filled to this depth before the reactor effluent began to flow through them. An air stone was suspended in filter influent basin above the filter sand surface.

Figures 15a and 15b present the turbidity results obtained under the conditions described in the previous paragraph. Both slow sand filters achieved effluent turbidity values consistantly below 1.0 NTU after the fifth day of operation. The apparent exception to this statement occurred on day 31 when the reactor pump was inadvertently turned off for twenty-four hours (an operational error). It should be noted that in practice slow sand filters are scraped (not disinfected) prior to each filter run, and take less time to begin effective turbidity reduction than the filters in our laboratory. The filters receiving unfiltered and filtered effluent operated for 51 days and 59 days respectively before one meter of head loss had developed across the sand beds. This was considered an acceptable length of filter run for practical application.

Coliform bacteria concentrations were determined, using the membrane filter technique, for the influent and effluent of each slow sand filter several times during the course of the second slow sand filter experiment. Table 7 presents the results obtained. Note that the concentration of coliform bacteria in the

TABLE 6

SLOW SAND FILTER OPERATING COND'ITIONS

SLOW SAND FILTER

SAND DEPTH: 3.25 FEET (1.0 METER)

SAND SIZE: D_{10} = 0.036 INCH (0.92 mm)

UNIFORMITY COEFF: D_{60}/D_{10} = 2.3

OPERATION

HYDRAULIC LOADING: 0.08 gpm/SQ.FT

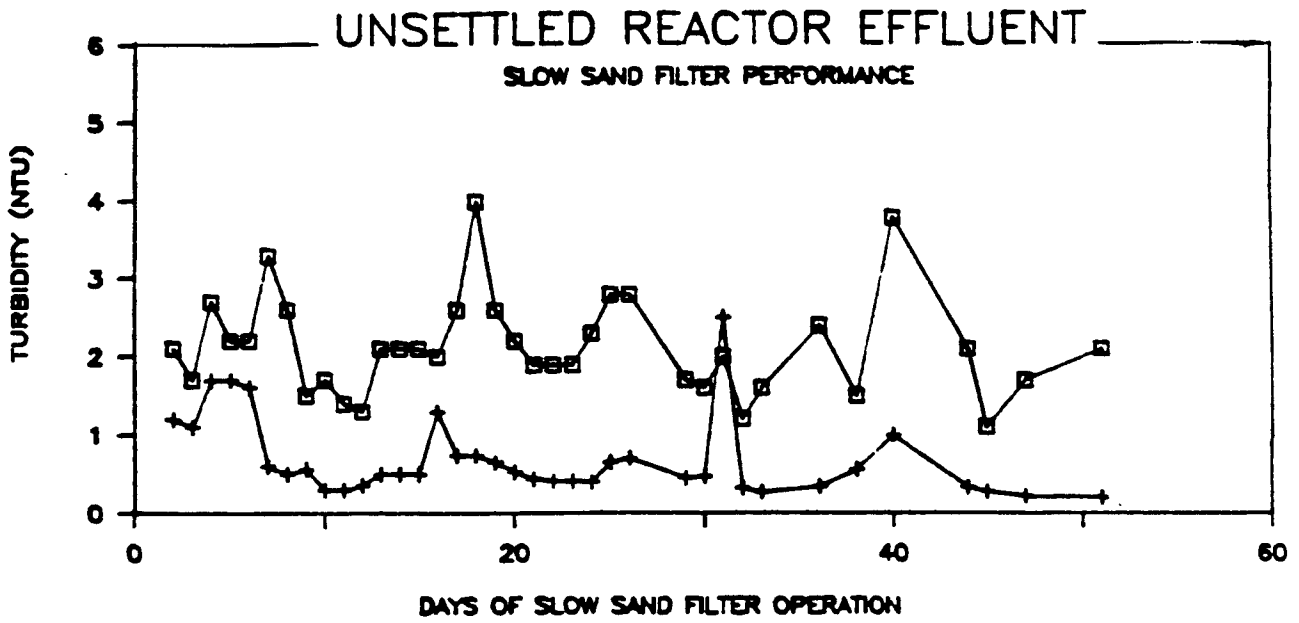DISINFECTED PRIOR TO OPERATION
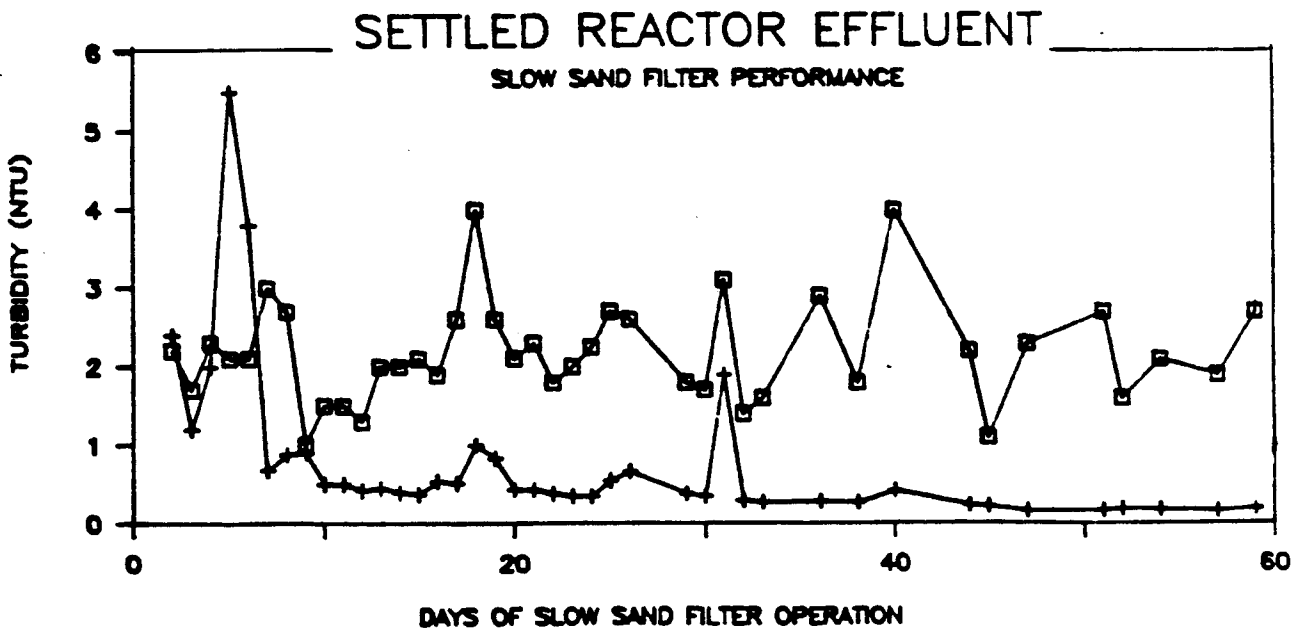
TERMINAL HEAD: 3.25 FT. (1.0 METER)

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FIGURE 15a

UNSETTLED REACTOR EFFLUENT

SLOW SAND FILTER PERFORMANCE

FIGURE 15b

SETTLED REACTOR EFFLUENT

SLOW SAND FILTER PERFORMANCE

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TABLE 7

COLIFORM BACTERIA COUNTS

NUMBER PER 100 MILLILITERS

		UNFILTERED		FILTERED	
DAY	INFL	EFFL	INFL	EFFL
2	223	< 100	472	< 100
9	590	7	963	14
16	1368	17	1031	< 1
23	7833	18	5833	< 1
30	567	19	200	23

influent increased steadly from day 2 through day 23. This occurred because of regrowth in the long (8 meters; 25 feet) plastic hose which carried the denitrification reactor effluent to the slow sand filters. The lower coliform counts obtained for day 30 are explained by the fact that this hose was replaced with a new hose on day 24. The effluent coliform counts ranged from less than 1 per 100 milliliters up to 23 per 100 milliliters. In practice an effective chemical disinfectant (such as chlorine) would be required as the next step in the potable water production process.

CONCLUSIONS

This section summarizes our conclusions with respect to the operation and performance of the biological denitrification process, and slow sand filtration technology, which were investigated in the University of Colorado Environmental Engineering Research Labratory for the purposes of preparing this report.

1. Acetic acid is a suitable choice for the supplemental carbon substrate which is required for biological denitrification of potable quality water. Acetic acid is readily degraded by numerous species of bacteria, is available in bulk and is not toxic to humans.

2. The stoichiometric acetic acid requirement for complete removal of influent dissolved oxygen and nitrates can be computed from the following results: 2.7 grams of acetic acid (as acetic acid) are required per gram of dissolved oxygen present in the reactor influent. 3.8 grams of acetic acid (as acetic acid) are required per gram of nitrate (as N) present in the reactor influent.

3. During normal laboratory operation, feeding only 90 percent of the full theoretical acetic acid requirement reduced the effluent acetic acid concentration to acceptable levels and eliminated the hydrogen sulfide odor problems which occasionally developed when the full stoichiometric acetate was fed.

4. For removal of the excess biomass which accumulates during denitrification reactor operation an air scour should be applied to half the reactor at two week intervals. Applying 0.5 $(M^3/min)/M^2$ (1.5 cfm/sq.ft.) for five minutes proved adequate in the laboratory investigations. Once air scoured, loose biomass was removed by draining the half of the reactor system which had been air scoured.

5. The quantity of excess biomass removed from the reactor system averaged 0.13 kilograms of filterable solids per kilogram of nitrate nitrogen removed (0.13 lbs of filterable solids per pound of nitrate nitrogen).

6. The biological denitrification system described in this report was capable of continuously and reliably removing 80 percent or more of the nitrate nitrogen in the reactor influent. This was achieved with an influent nitrate nitrogen concentration of 20 mg/L (as N) and an acetic acid supply which was 90 percent of the theoretical stoichiometric requirement for complete removal. No denitrification failures, or serious process upsets, occurred during eight months of continuous operation in the laboratory.

7. The fixed biomass denitrification system required a relatively constant influent nitrate concentration to be effective. Sudden nitrate concentration increases in the influent were passed on to the reactor effluent. The reactor system described in this report is not appropriate for denitrification of waters with highly variable nitrate nitrogen concentrations. This conclusion does not apply to nitrate concentrations which are seasonal in nature. Under such conditions, if sufficient reactor detention time is provided, biomass growth can accomodate large nitrate concentration changes.

8. The chlorine demand of the unfiltered reactor effluent (expressed as CL_2) ranged from 5.0 mg/L to 22.3 mg/L. The chlorine demand of the (glass fiber) filtered effluent (as CL_2) ranged from 1.6 mg/L to 16.8 mg/L. The chlorine demand of both the unfiltered and filtered effluents decreased with time after each air scour. The source of the measured chlorine demand was not determined.

9. Following breakpoint chlorination, less trihalomethanes formed in the reactor effluents, both filtered and unfiltered, than formed in the chlorinated reactor influent. This was true for all durations of exposure to free chlorine up to the maximum duration tested which was 10,000 minutes (one week). Of the several trihalomethanes, only chloroform was detected. No sample of reactor effluent developed a trihalomethane concentration greater than the U.S. primary drinking water standard of 100 micrograms per liter.

10. Slow sand filtration proved to be a successful filtration technology for the denitrification reactor effluent. Filter effluent turbidity values below 1.0 NTU were produced consistently for the duration of filter runs longer than seven weeks. A majority of the turbidity measurements were below 0.5 NTU. Filter effluent coliform counts ranged from less than one up to 23 per 100 ml.

11. The following rate model is proposed for denitrification reactor design:

$$\sqrt{N} = \sqrt{No} - K (t)$$

The rate constants, K , which best fit (least squares method) this half-order model varied during the course of reactor operation. The maximum rate constant computed for 'standard' operation was 0.046 $\sqrt{mg/L}$ /min. The minimum rate constant observed was 0.028 $\sqrt{mg/L}$ /min. The smaller rate constant (.028) is recommended for denitrification design.

Biological treatment of water is not new to small communities; many operate biological waste treatment facilities. The processes investigated for this report have been selected because for normal day-to-day operation they are easy to operate and require minimal operator attention. The introduction of bacteria into a potable water source may meet considerable resistance, yet one of the oldest water treatment methods, slow sand filtration, is now recognized to be primarily a biological process. In summary, biological denitrification appears to the authors to be the most reliable and economical solution to the widespread problem of nitrate polluted potable water supplies.