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The Regeneration of Clinoptilolite by Biologically
Restored Brine

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Abstract

Previous studies demonstrated that ammonium saturated clinoptilolite may be regenerated by nitrifying bacteria if a base is added for pH control. The mechanism was identified to be ammonium release by ion exchange followed by nitrification of the liberated ammonium. In this study the ion exchange and nitrification processes were studied separately to identify the best procedure for effective regeneration. The regeneration of clinoptilolite with neutral pH brine was studied and its effectiveness was measured by comparing breakthrough curves for ammonium removal. In addition the column performance was evaluated using recycled regenerant to evaluate the impact of the buildup of Ca^{++} , Mg^{++} and K^+ in the regenerant.

Nitrification studies conducted with recycled regenerant allowed the kinetics of ammonium oxidation to be identified. Both dispersed and attached growth systems were investigated. The observed nitrification kinetics were comparable to those reported by other investigators for domestic wastewater treatment.

The information provided in this report allows for the rational design of ammonium removal by clinoptilolite which is regenerated using biologically restored regenerant.

Acknowledgment

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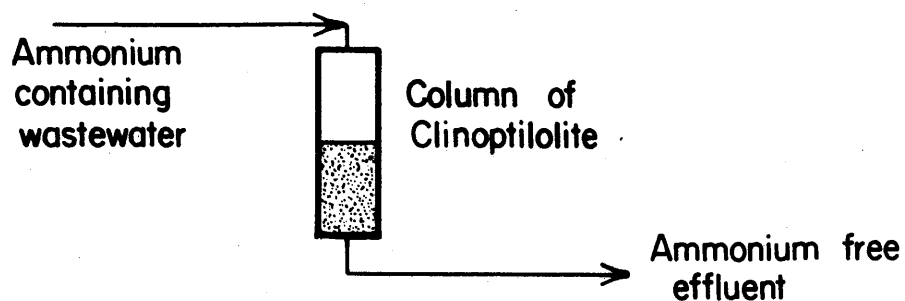
In the absence of nitrifying bacteria exchange would take place according to equation 1-1 until chemical equilibrium was achieved. However, when the bacteria are present, they oxidize the liberated ammonium and shift the equilibrium to the right and in this way contribute to the regeneration of the zeolite.

Regeneration of the zeolite is considered complete when the ammonium concentration in the regenerant leaving the column reaches a low value (say 1 mg/l). Studies conducted on the combined regeneration system were reported by Semmens, et al. (3,4).

The second process and the subject of this study is referred to as "sequential regeneration" and is depicted schematically in Figure 1-2. This process is very similar in nature to that described above except that the ion exchange and nitrification steps are completely separated. The exhausted zeolite is regenerated using a neutral pH brine containing 0.3-0.4M NaNO_3 . The spent regenerant then flows to a feed reservoir from which it is fed to a nitrification unit. The nitrified brine is clarified in a sedimentation tank and stored, ready for reuse.

Both processes have their advantages and disadvantages. The combined regeneration process is attractively simple and requires only an aeration tank, however, the process has several problems: 1) There is an unsteady NH_4^+ concentration in the aeration tank. Since high NH_4^+ concentrations appear in the first few bed volumes of spent regenerant, a slug of ammonium may pass through the aeration tank and back to the exchange column. This problem may be reduced with a larger aeration tank or a multistage nitrification tank. This problem, however, effectively ties the regeneration time to the nitrification rate since any buildup of NH_4^+ in the regenerant will influence the time required to achieve satisfactory regeneration; 2) High flowrates of regenerant are required to fluidize the zeolite in order to ensure that the nitrifying bacteria are flushed through the column and returned to the aeration tank.

1. Service Cycle



2. Regeneration Cycle

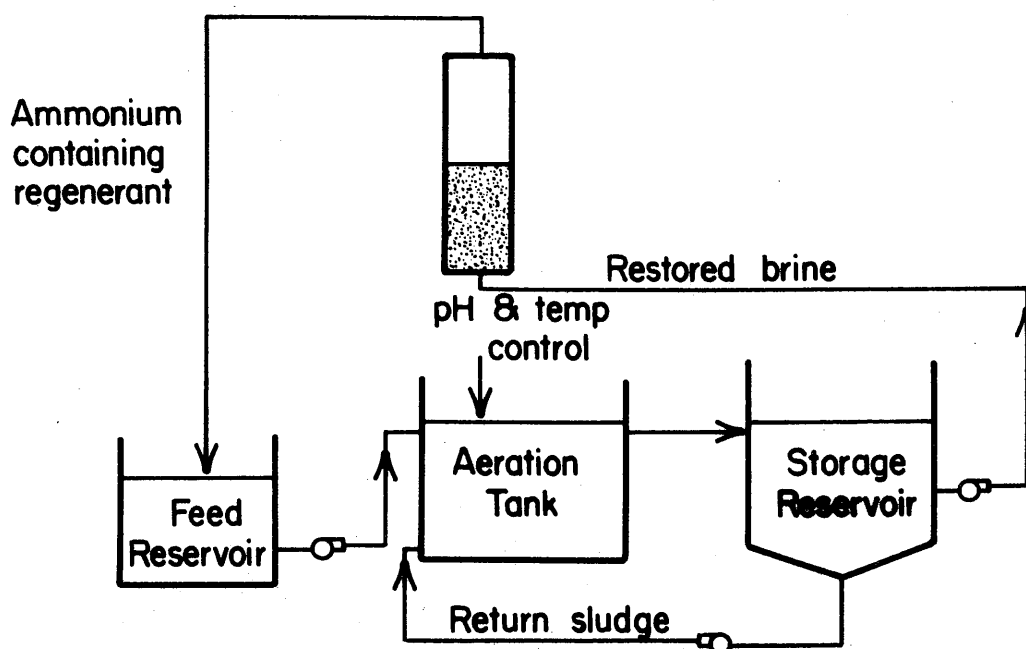


Figure 1-2 A Process Scheme for Sequential Biological Regeneration

Nevertheless, a fraction of the bacteria remain in the column when regeneration is complete and these bacteria may be lost during backwash unless special operating procedures are implemented; 3) Finally, this process is limited to regenerating one column at a time since the ammonium concentration in the regenerant is altered during regeneration.

By comparison, sequential regeneration may have a higher capital cost since two additional storage reservoirs and possibly a sedimentation tank are required. However, separation of nitrification and regeneration presents an opportunity to optimize each process. Lower regenerant flowrates may be employed and higher ammonium concentrations may be achieved in the spent regenerant fed to the nitrification reactor. The time required for column regeneration will be that required for chemical regeneration and it will not be limited by the nitrification rate in the aeration tank. The nitrification system may be designed to treat a constant flow of relatively constant ammonium concentration from the spent brine storage reservoir. The smaller regenerant volumes to be treated in this process will allow a smaller aeration tank to be employed.

The objective of this study was therefore to consider the sequential regeneration process in detail and obtain the data required to optimize the ion exchange and nitrification processes separately.

The report is divided into seven subsections. Sections 2,3, and 4 examine the ion exchange behavior of clinoptilolite in detail. Neutral pH regeneration studies were conducted initially with brine concentrations that were compatible with the nitrification process. These studies were extended with computer modelling studies. The simulation models were designed to predict regeneration efficiency and ammonium removal performance during service operations. The

models were developed for use as a design tool and also to predict the performance of the zeolite under varying conditions of operation. Section 4 examines the choice of zeolite for this process. No reported information was available comparing the ammonium removal ability of different natural zeolites and since earlier studies (30) had indicated that the exchange capacity of the zeolites varied depending upon the conditions of treatment, studies were conducted to evaluate some natural zeolites and pretreatment techniques.

In section 4 the results of studies conducted on the sequential regeneration process are presented. In this study the ion exchange and nitrification processes were operated simultaneously. The conditions of regeneration were determined from the results presented in section 2. The objectives of this study were to identify the operational difficulties that may be anticipated, to evaluate the ammonium removal performance over a large number of operating cycles, to evaluate the chemical requirements and the best regenerant pH, and finally to determine the buildup of calcium and magnesium in recycled regenerant.

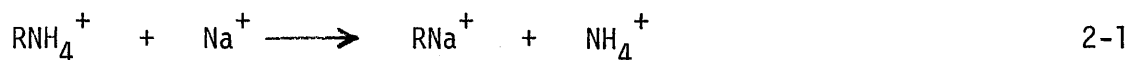
Sections 5 and 6 were devoted to evaluating the kinetics of nitrification in recycled regenerant containing high calcium and magnesium concentrations. Section 5 details experiments conducted to evaluate the kinetic coefficients for dispersed growth systems and section 6 contains information on the use of rotating discs for supporting nitrifying cell mass.

The final section provides an analysis of the overall biological regeneration process and compares the estimated cost of operation with that for chemical/physical regeneration alternatives. Ideas and suggestions for reclaiming the oxygen content of the nitrate for reuse are also discussed.

Section 2

The Regeneration of Clinoptilolite by Neutral pH Brine

The first detailed studies of clinoptilolite regeneration suggested that high pH brine gave the most rapid and complete regeneration⁽⁵⁾. In this process the high pH conditions promote the conversion of liberated ammonium to ammonia gas. In this way ammonium was removed from the right hand side of equation 2-1 and, the reaction moves to



the right and complete regeneration. In this regeneration scheme ammonium must be stripped from the spent regenerant in order that the regenerant may be reused. However, many problems were encountered in this process including attrition of the zeolite under high pH conditions, precipitation on the clinoptilolite and scaling in the stripping tower. These operational difficulties lead investigators to seek alternative neutral pH regeneration methods.

Economics dictate that neutral pH regenerants must also be reused and different approaches have been taken to reclaim the spent regenerant. Electrolytic destruction of the ammonium in the brine was tried, but proved to be uneconomical⁽⁷⁾. Currently air stripping of the brine appears attractive and is to be used in the Upper Occoquan Treatment Plant⁽⁷⁾.

There is relatively little information on the regeneration of clinoptilolite with neutral pH regenerants however. Some of the early studies by Koon and Kaufman suggested that neutral pH regeneration was very poor in displacing NH_4^+ by comparison with the high pH brines. Unpublished studies by CH₂M Hill indicated that neutral pH regeneration was feasible⁽⁷⁾, but there is little detailed information available on the performance of clinoptilolite following neutral pH regeneration under varying conditions.

This section of the report presents the results of some neutral pH regeneration and service performance studies for ammonium removal by clinoptilolite. These studies were also used to test a computer model designed to predict column performance following any conditions of regeneration. The computer model will be discussed in later sections of the report.

MATERIALS

Zeolite

Clinoptilolite from a deposit in Buckhorn, New Mexico, was provided by the Double Eagle Mining Company, Casper, Wyoming. The zeolite was crushed and sieved. The zeolite sample tested in column studies had the same particle size distribution as that used by Koon and Kaufman⁽⁵⁾. The effective size was 0.38 mm and the uniformity coefficient was 1.40. The sieve analysis is provided in Table 2-1.

Table 2-1

Clinoptilolite Sieve Analysis

U.S. Sieve No.	Sieve Opening (mm)	% Passing Sieve
20	0.840	100
30	0.589	72
40	0.42	29
50	0.297	0

Synthetic Secondary Effluent

Champaign-Urbana tap water was spiked with chemicals to obtain a feed solution comparable to a filtered secondary effluent. The final composition of the feed solution is presented in Table 2-2.

Table 2-2
Composition of Solution Employed in Column Studies

Na^+ = 95 mg/l	NH_4^+ = 20 mg/l
Ca^{++} = 21 mg/l	Alkalinity (CaCO_3) = 358 mg/l
Mg^{++} = 18 mg/l	Ionic Strength = 0.0054
K^+ = 6.5 mg/l	pH = 8.0

Regenerant

Rock salt (Diamond Crystal Halite, Diamond Crystal Salt Co.) was added to tap water for use as a regenerant. In studies addressing the impact of calcium in the regenerant anhydrous technical grade calcium chloride was added to the regenerant. The pH of the regenerant ranged between 7.0 and 8.5.

Equipment

A flow diagram of the equipment employed in this study is presented in Figure 2-1. A 1.8 m plexiglass column having an internal diameter of 3.8 cm contained a 61 cm (2 feet) depth of clinoptilolite supported on a 30 cm gravel bed. During service the feed solution was pumped from a 550 liter fiberglass tank downflow through clinoptilolite by means of a

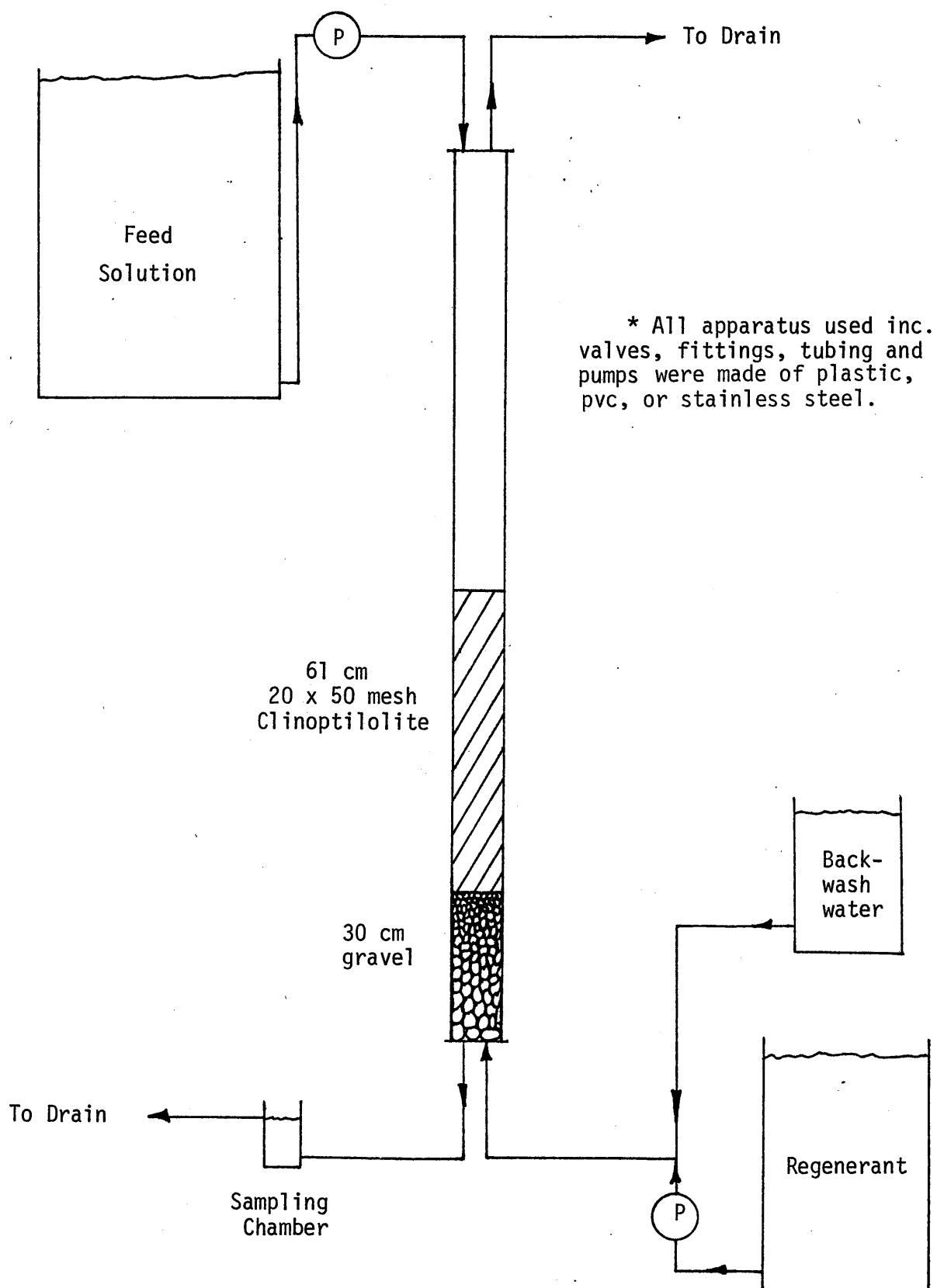


FIG. 2-1 FLOW DIAGRAM OF EQUIPMENT

metering pump (FMI, Model RRP). Column effluent passed through a 0.48 liter sampling chamber to a floor drain. A sequential sampler (N-Con Systems, Sentry 500) connected to the sampling chamber could be programmed to withdraw samples at specified time intervals.

Following service the column was backwashed with tap water stored at room temperature in an elevated 10 gallon storage tank. The column was then regenerated by pumping regenerant stored in a 320 liter nalgene tank upflow through the clinoptilolite using a masterflex variable speed pump.

When regeneration was complete the column was rinsed with water from the backwash water reservoir to displace the regenerant. The salinity of the effluent rinse was monitored by a conductivity meter (Y.S.I. Model 33, SCT meter) and the rinse was terminated when the effluent salinity was equal to that of the influent. The column was then returned to the service mode.

Analytical

Ammonium measurements were made using an Orion Model 95-10 ammonia selective electrode connected to an Orion Model 701 digital pH/mV meter. The electrode tended to drift and standard ammonia samples were analyzed frequently during test periods as a check on the calibration curve.

Calcium and magnesium concentrations were measured with a Perkin Elmer, Model 370, atomic absorption spectrophotometer.

Experimental Methods

Prior to conducting any column studies the clinoptilolite was operated for six service-regeneration cycles to condition the column

and ensure reproducible behavior. In all of the studies the column was operated in the service mode to complete breakthrough in order that the influence of regeneration conditions on the shape of breakthrough curve could be evaluated. The exhausted bed was always backwashed for 5 minutes prior to regeneration.

The influence of flow rate on the rate of regeneration was determined by regenerating the bed with 0.3 M NaCl at flow rates of 4, 12 and 20 bed volumes/hr. The spent regenerant was collected in a well stirred storage tank and the cumulative ammonium concentration was recorded every 15 minutes. Knowing the regenerant flow rate, the amount of ammonium eluted from the column was evaluated as a function of time. At the conclusion of regeneration the rinse water was collected and its ammonium content was also measured.

The effectiveness of lower salt concentrations was evaluated by monitoring the extent of regeneration in the same way as described above, but with a salt concentration of 0.2 M NaCl. The regenerant flow rate was maintained at 12 bed volumes/hr in order that the results could be compared with elution achieved under the same conditions with 0.3 N NaCl.

When regenerant is recycled calcium and magnesium are usually present in significant concentrations and so the influence of these ions on the rate of regeneration was also tested. A regenerant was constituted with 0.25 N NaCl and .05 N Ca Cl_2 and the extent of elution was monitored in tests conducted at a flow rate of 12 bed volumes/hr.

In order to determine the rate and the extent of elution of ions other than ammonium during regeneration, studies were made on the simultaneous rates of displacement of Ca^{++} , Mg^{++} , K^+ and NH_4^+ . In this study a 0.3 N NaCl regenerant was pumped through the column at

a flow rate of 13.22 bed volumes/hr and samples were collected from the top of the column at 15 minute intervals.

Results

Several regeneration runs were made for each set of experimental conditions and the reproducibility is shown in Figure 2-2 for tests conducted at 12 Bv/hrs. The scatter in Figure 2-2 is due mainly to variations in the ammonium concentration in the service feed solution.

The influence of flow rate on the rate of regeneration is shown in Figure 2-3. It is apparent that the rate of displacement of ammonium from the clinoptilolite was independent of flow rate in the range considered. The curves in Figure 2-3 fall within the bounds of reproducibility shown in Figure 2-2. These data support the findings of Prettyman et al. (7) and indicate that the rate of regeneration is limited by equilibrium conditions rather than exchange kinetics in the range of flow rates considered.

Under all flow conditions 75 percent of the ammonium was eluted in approximately 15 bed volumes of regenerant. The actual degree of regeneration would be slightly higher than that depicted in Figure 2-3 since ammonium displaced, but still within the column is not included.

Breakthrough curves obtained following regeneration for 3 hours at different regenerant flow rates are depicted in Figure 2-4. All the service cycles were operated under almost identical conditions. The influent ammonium concentration, and flow rate during service are recorded on the figure. As expected the extent of ammonium leakage decreased and the column capacity increased with increasing volumes of regenerant applied to the column. Mass balances on ammonium dis-

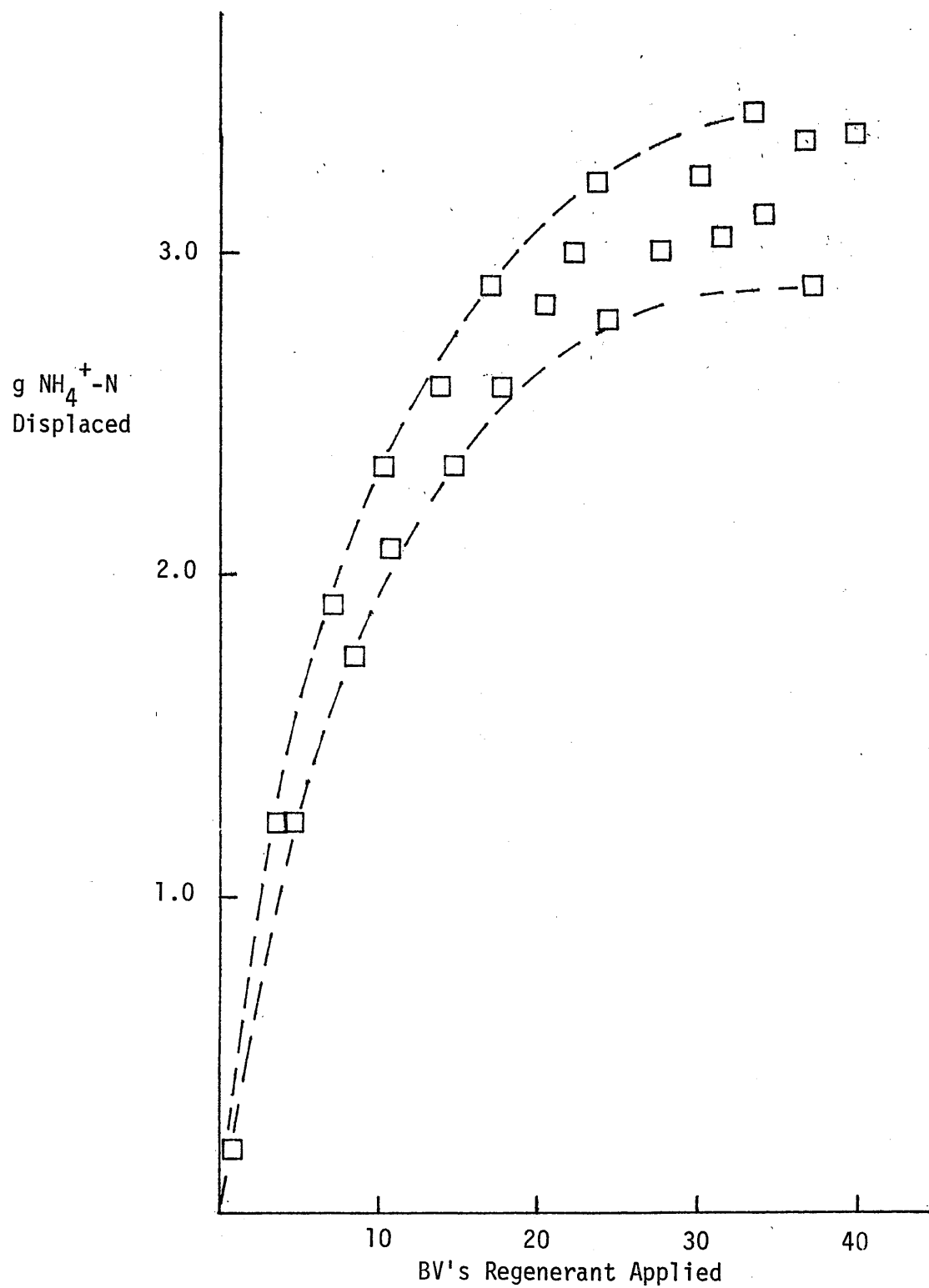


FIG. 2-2 REGENERATION CURVES GENERATED
AT A REGENERATION FLOW RATE OF 12 BV/hr

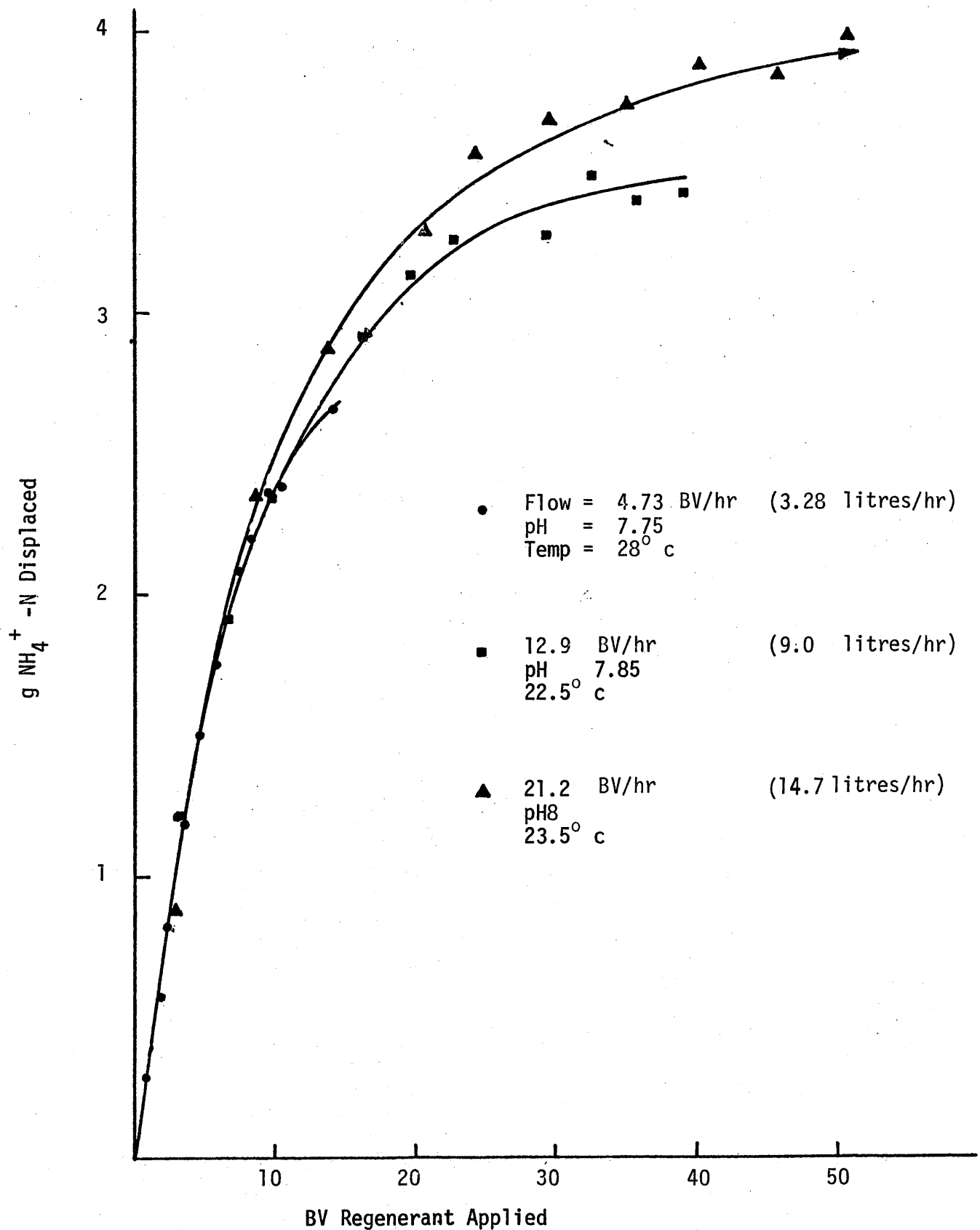


FIG.2-3 THE INFLUENCE OF VARYING REGENERANT FLOWRATE ON THE RATE OF AMMONIUM DISPLACEMENT

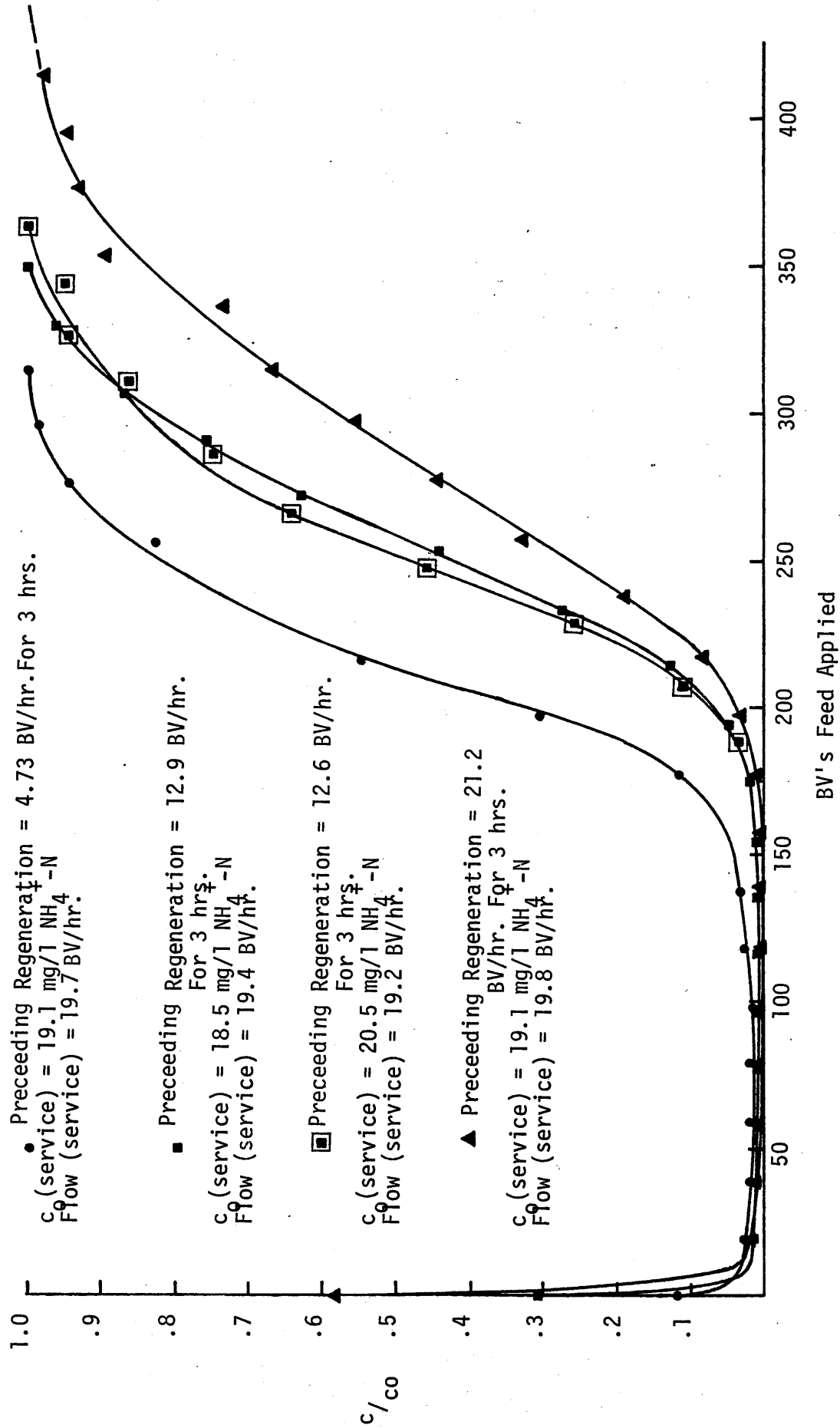


FIG. 2-4 AMMONIA BREAKTHROUGH CURVES FOLLOWING 3 HRS. OF REGENERATION AT 4.73, 12.9, 12.6, AND 21.2 BED VOLUMES/HR.

placed during regeneration and ammonium removed during the previous service cycle showed good agreement. These effects are summarized in Table 2-3. Two breakthrough curves are presented following regeneration at 12.9 bed volumes/hr. for 3 hours to show the reproducibility of the breakthrough data.

Table 2-3

The Effect of Regenerant Volume on Column Capacity and Leakage

Bed Volumes Regenerant Applied	Ammonium-N Removed Grams	Ammonium-N Leakage Following Regeneration, mg/l
14.2	2.66	0.3 - 0.4
38.7	3.42	0.2
63.6	3.92	0.1 - 0.2

In Figure 2-5 the influence of lower salt concentration on the rate and extent of regeneration is depicted. At a salt concentration of 0.2 M the rate of regeneration was slower, as expected. The initial slopes of the curves in Figure 2-5 indicate that at 0.2 M NaCl the slope was approximately 66 percent of that observed at 0.3 M NaCl which is another indication that equilibrium conditions govern the initial rate of ammonium displacement. Comparison of the slopes obtaining from the two curves at the same levels of ammonium displaced indicate that at 0.2 M salt concentrations the slope was 55-56 percent of that observed at 0.3 M salt concentrations.

In order to achieve 75 percent regeneration 28 bed volumes of regenerant were required at 0.2 M NaCl by comparison to only 15 at 0.3 M NaCl.

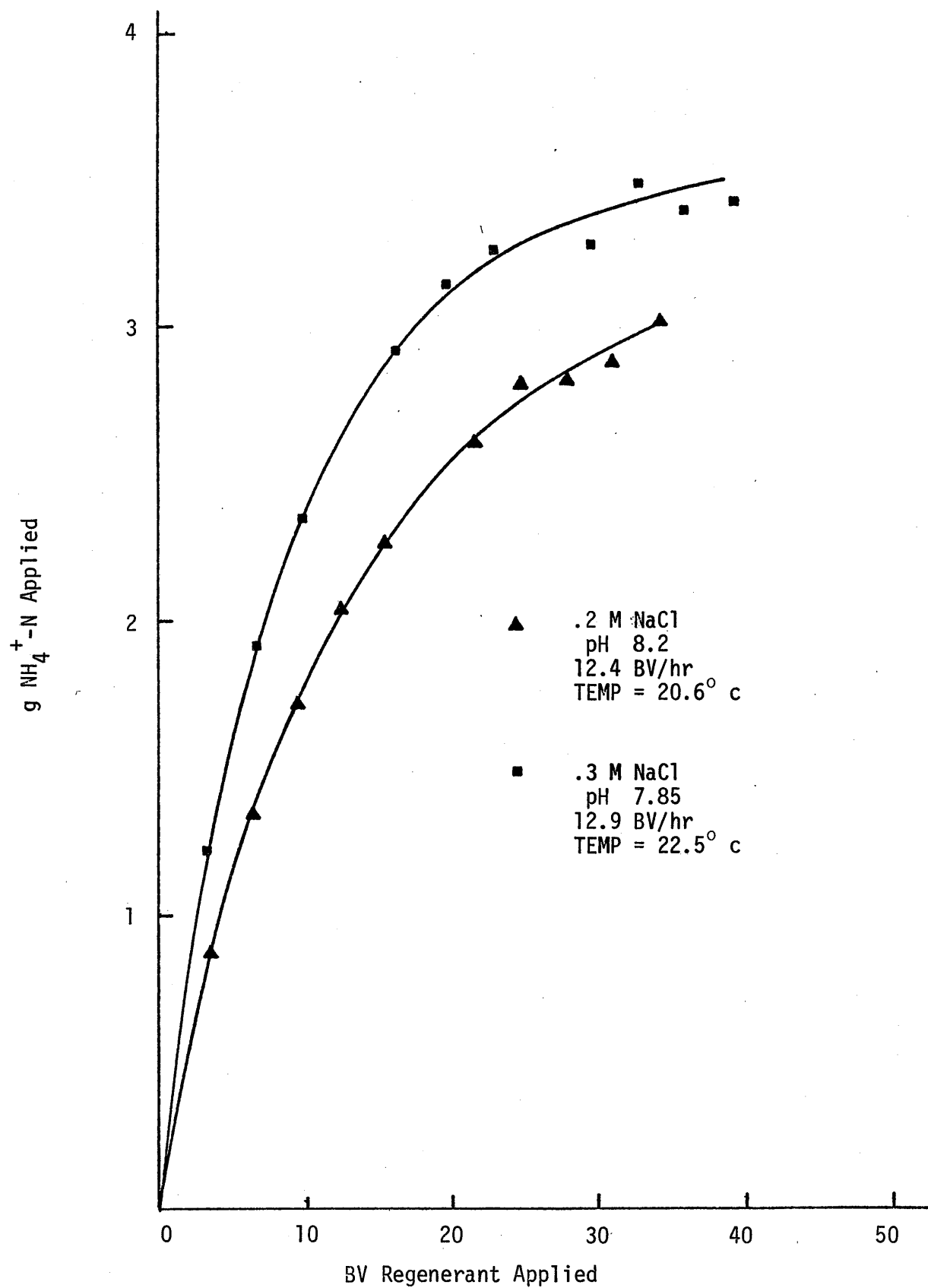


FIG.2-5 REGENERATION VARYING REGENERANT SALT CONCENTRATION

In Figure 2-6 the influence of regenerant concentration on column performance is shown. These breakthrough curves were obtained following the regeneration conditions presented in Figure 2-5. The influence of reduced salt concentration was only to cause a slight decrease in the column exchange capacity. Column leakage was approximately the same in both cases. Regeneration for shorter periods of time than the 3 hours employed in this comparison would undoubtedly cause a more marked difference in operating performance however.

During the course of regeneration significant concentrations of calcium and magnesium ions are displaced in addition to ammonium. If the regenerant is reused, the presence of divalent metal ions may influence the rate of regeneration and column performance. Studies were therefore conducted with regenerant containing 50 meq/l of Ca^{++} .

The presence of calcium in the regenerant had little effect on the rate of ammonium displacement as shown in Figure 2-7. The rate of displacement was very slightly slower, and the total ammonium displacement after 3 hours regeneration was less in the presence of calcium. However, when the scatter in Figure 2-2 for regenerations conducted at approximately 12 bed volumes/hr. is considered the difference between these curves is within experimental error. The impact of calcium on the breakthrough curve is, however, more pronounced. The breakthrough curves obtained following regeneration with calcium presented in Figure 2-8 indicate that higher leakages and earlier ammonium breakthrough were obtained by comparison with regeneration with only sodium in the regenerant.

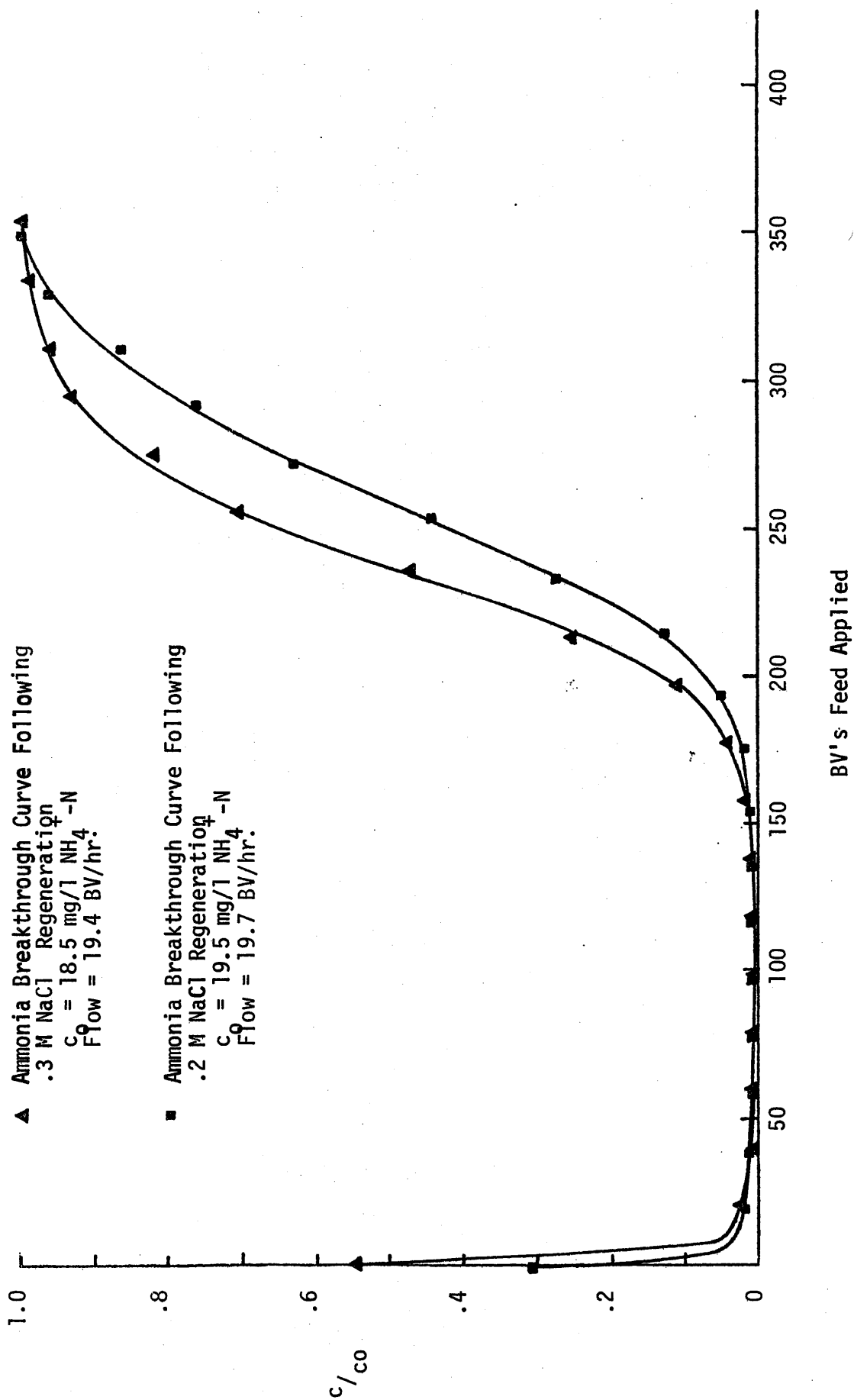


FIG. 2-6 AMMONIA BREAKTHROUGH CURVES FOLLOWING REGENERATION WITH VARIED SALT CONCENTRATION

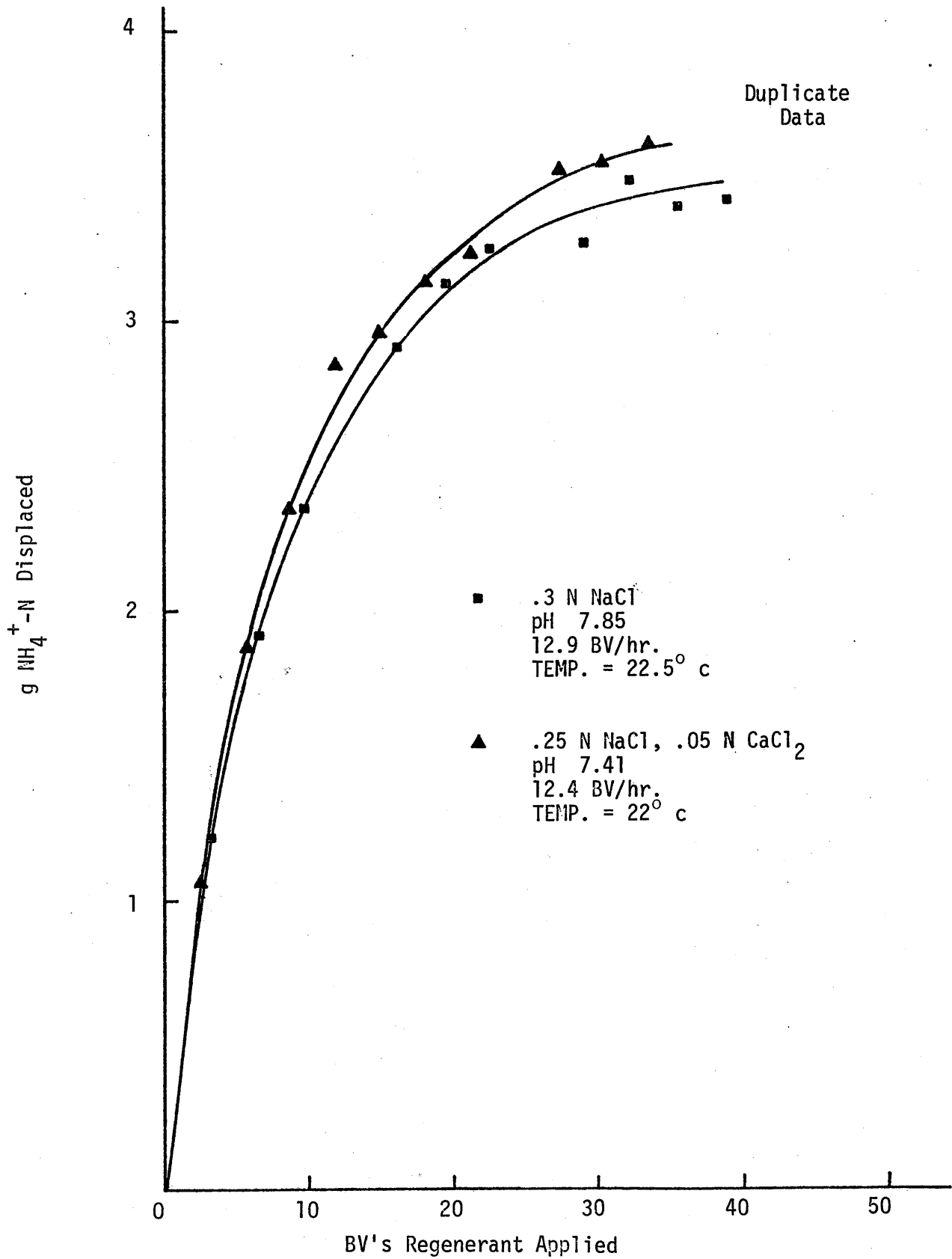


FIG. 2-7 REGENERATION WITH Ca^{++} PRESENT IN THE REGENERANT

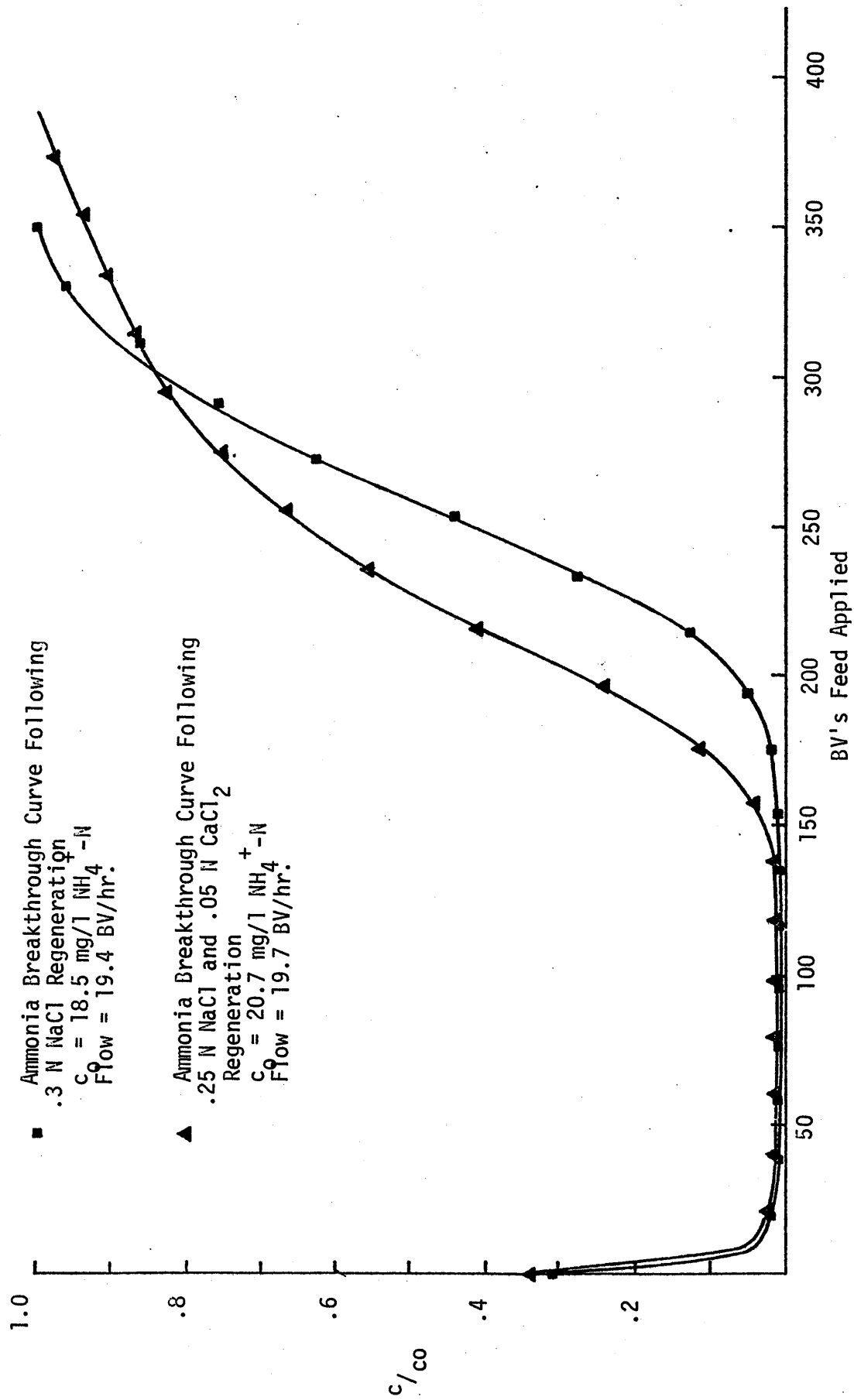


FIG. 2-8 AMMONIA BREAKTHROUGH CURVES FOLLOWING .3N
 REGENERATIONS, WITH AND WITHOUT CALCIUM PRESENT IN THE REGENERANT

Studies on the actual concentrations of ammonium in the column effluent during regeneration with 0.3 M NaCl only, are presented in Figures 2-9, 2-10 and 2-11. The ammonium concentrations that developed in the column effluent are shown in Figure 2-9. The ammonium concentration was observed to reach 470 mg/l after 15 minutes and then fall. However, higher concentrations may have been achieved before the first samples were taken. After fifteen bed volumes of regenerant the ammonium concentration fell to 130 mg/l, but the ammonium concentration in the regenerant after 30 bed volumes had only dropped to 60 mg/l.

By comparison the rates of calcium and magnesium elution depicted in Figures 2-10 and 2-11 respectively were more rapid than ammonium displacement. Calcium and magnesium concentrations as high as 800 mg/l and 240 mg/l respectively were observed after fifteen minutes of regeneration. These concentrations fell rapidly to the background concentrations present in the regenerant. The tap water used in making the regenerant contained 14 mg/l Mg^{++} and 85 mg/l Ca^{++} .

To check whether the extent of calcium displacement during regeneration could be reduced by increasing the regenerant flowrate, calcium measurements were made on the first twelve bed volumes of regenerant collected in regeneration tests conducted at flowrates ranging between 12 to 22 bed volume/hr. The results presented in Figure 2-12 indicate that the extent of calcium elution observed during regeneration was apparently independent of the regenerant flowrate.

DISCUSSION

These studies indicate that clinoptilolite may be regenerated effect-

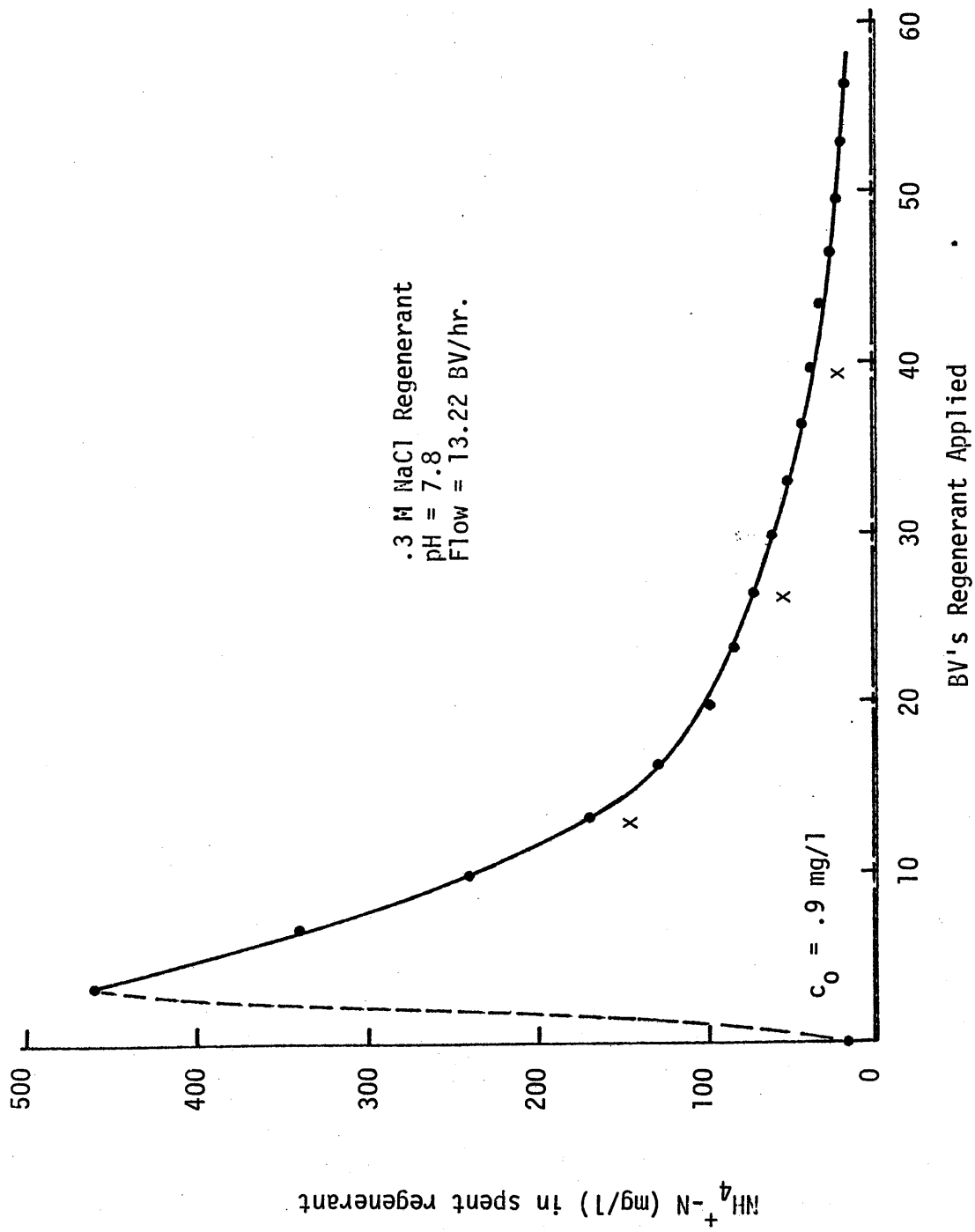
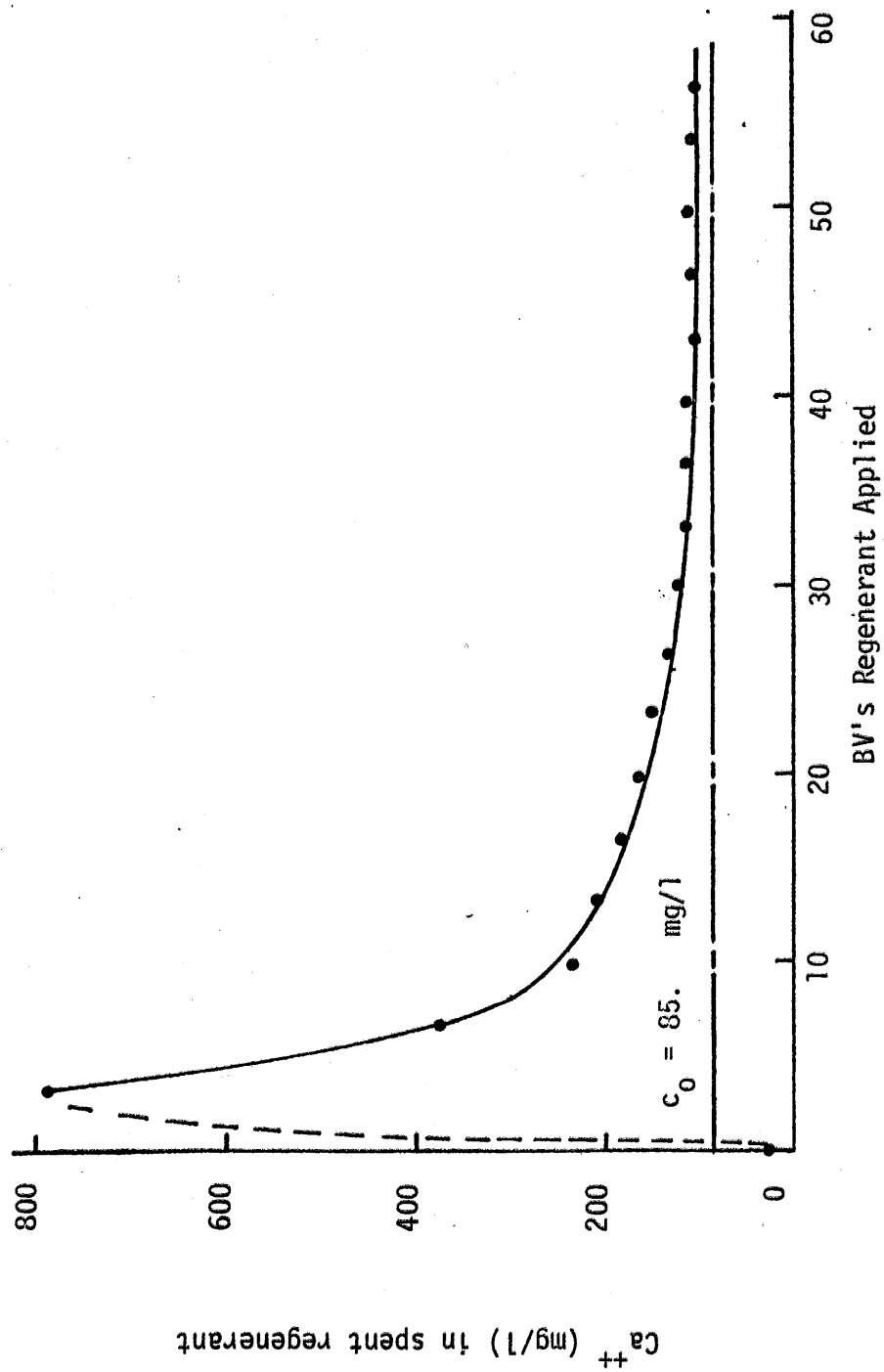


FIG. 2-9 AMMONIUM ELUTION DURING REGENERATION

FIG. 2-10 Ca^{++} ELUTION DURING REGENERATION

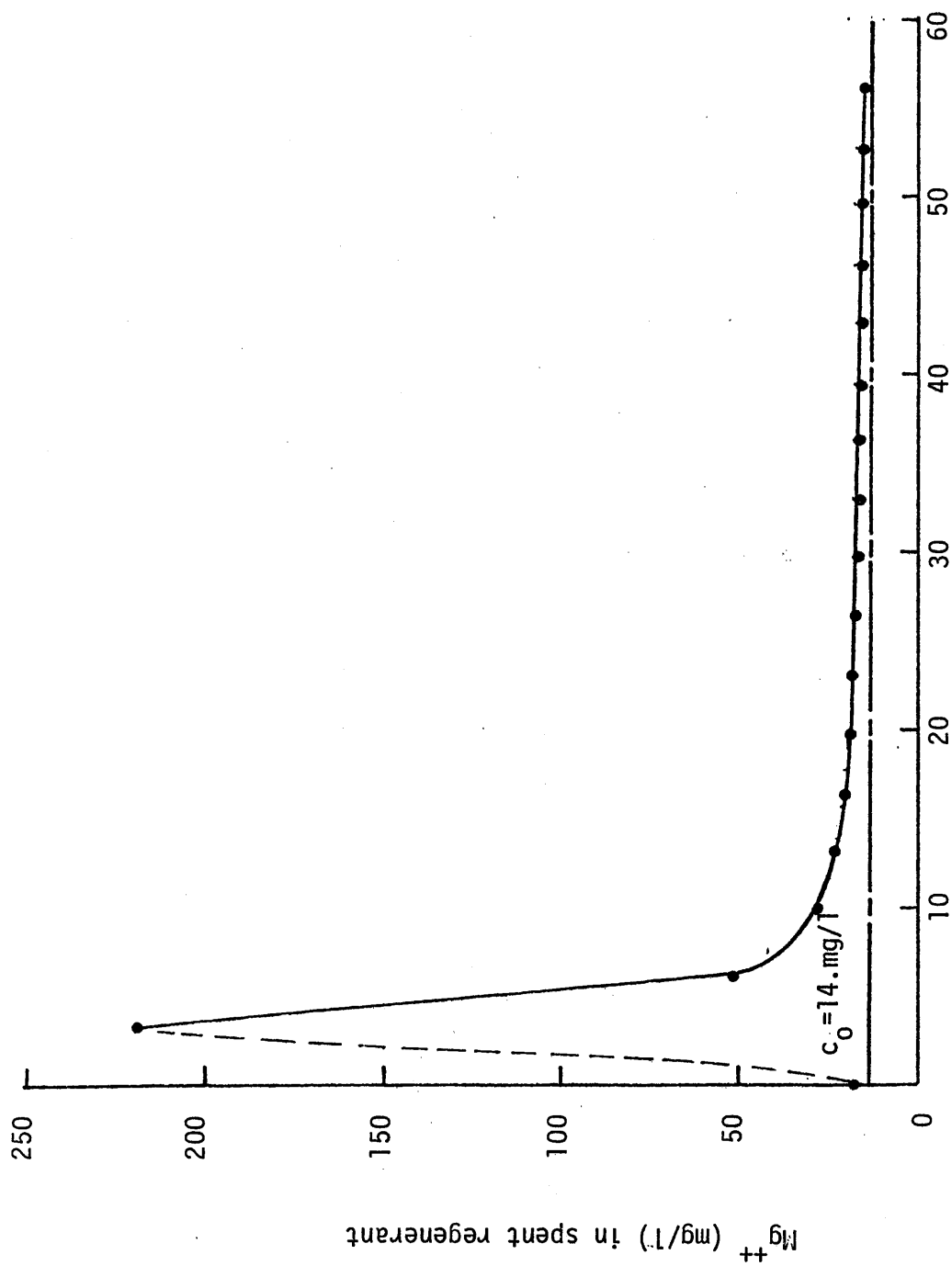


FIG. 2-11 Mg^{++} ELUTION DURING REGENERATION

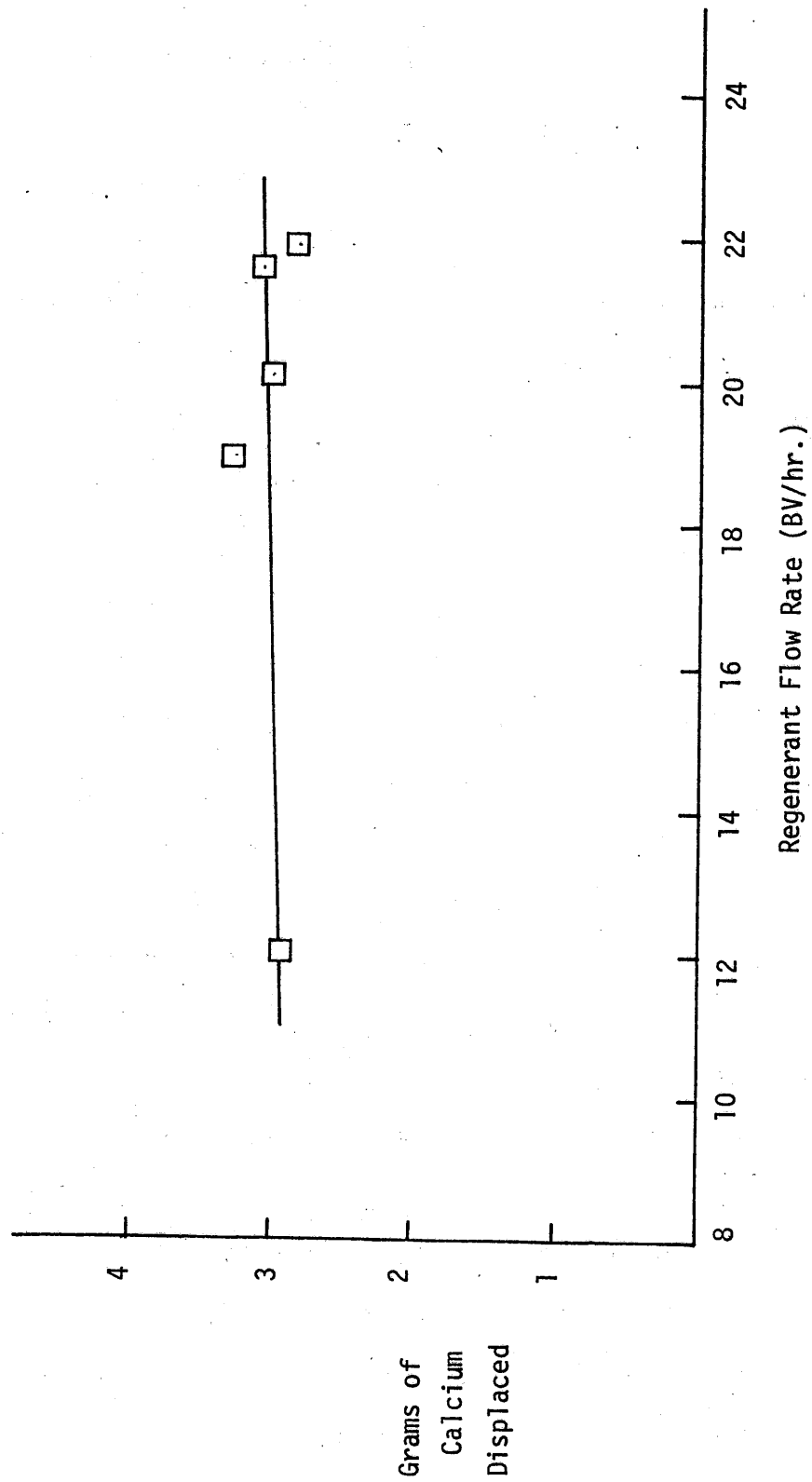


FIG. 2-12 CALCIUM ELUTED IN THE FIRST 12 BED VOLUMES OF REGENERANT AS A FUNCTION OF REGENERANT FLOWRATE

ively and rapidly by a neutral pH regenerant of 0.3 M NaCl. The rate of ammonium displacement is not influenced significantly by flowrates in the range of practical interest and there is no preferred flowrate that would result in less calcium (and magnesium) build up in the regenerant. Calcium and magnesium ions were displaced rapidly during regeneration since the selectivity of clinoptilolite for divalent ions over sodium is reduced in the presence of high salt concentrations. High concentrations of calcium and magnesium will therefore build up in recycled regenerant and the pH of the regenerate must be kept low enough to prevent problems associated with calcium carbonate precipitation in the nitrification reactor.

Koon and Kaufman⁽⁵⁾ conducted some studies on regeneration at neutral pH. Using clinoptilolite columns that were only exhausted to an incipient breakthrough of ammonium they obtained a peak ammonium concentration of only 75 mg/l during regeneration with 0.21 M NaCl at pH 8.2. The higher salt concentration and the complete exhaustion of the clinoptilolite employed in this study would naturally increase the ammonium concentration observed in the regenerant. However, Koon and Kaufman found it necessary to use a 0.35 M NaCl regenerant at pH 12.3 to observe a peak ammonium concentration of 500 mg/l which is close to the peak ammonium concentration observed under neutral pH conditions in this study.

Further studies were made to compare the rate of ammonium elution from a clinoptilolite column following complete exhaustion and following exhaustion to the incipient breakthrough (3.8 mg/l) of ammonium only. Both tests were conducted with a feed solution during service containing

20 mg/l $\text{NH}_4\text{-N}$. Regeneration, achieved by passing 12 bed volumes per hour of 0.3 M NaCl through the clinoptilolite yielded ammonium concentrations after 15 minutes of 380 and 320 mg/l respectively. Studies on the regeneration of clinoptilolite exhausted to incipient breakthrough of ammonium were also conducted using a biologically restored brine, these data reported in the next chapter indicate that a peak ammonium concentration of 350 mg/l was achieved after 15 minutes. These figures suggest that the initial ammonium concentration is affected only slightly by the above variation in the degree of exhaustion, and that neutral pH regeneration is more feasible than Koon and Kaufman's data⁽⁵⁾ would suggest.

Comparison of high pH regeneration with neutral pH regeneration clearly indicates that much more 'tailing' occurs under neutral pH conditions. For example, 60 mg/l and 20 mg/l ammonium concentrations were observed in the regenerant after 30 and 50 bed volumes respectively. Koon and Kaufman observed very little tailing under high pH conditions. In order to achieve an acceptable level of regeneration at neutral pH a greater volume of regenerant is therefore required.

High calcium and magnesium concentrations are certain to build up if a neutral pH regenerant is recycled for reuse. However, these ions should remain in solution and not cause any problems by precipitating if the pH is sufficiently low. These ions will not have a significant effect on the rate or extent of regeneration, but they will certainly influence the column performance during service and may necessitate

lower loading rates to avoid significant leakage of ammonium or an early ammonium breakthrough.

Conclusions

- 1) The rate and extent of ammonium displacement by neutral pH regenerant was observed to be independent of regenerant flowrate in the range of 4-20 bed volumes/hr.
- 2) 75% regeneration of exhausted clinoptilolite may be achieved with as little as 12 bed volumes of 0.3 M sodium chloride.
- 3) Higher operating capacities and lower leakages may be achieved with larger columns of regenerant, but it may not be desirable to operate a column under such conditions.
- 4) If the salt concentration in the regenerant is reduced from 0.3 M to 0.2 M then approximately 26 bed volumes of regenerant are required for 75% regeneration.
- 5) Calcium and magnesium ions are displaced more rapidly than ammonium ions during the course of regeneration and it was shown that the extent of calcium displacement was independent of regenerant flowrate.
- 6) Calcium ions do not influence the rate of ammonium displacement when they are present in the regenerant.
- 7) The presence of calcium ions in the regenerant does affect column performance in the subsequent service cycle, and tends to decrease the operational capacity to any specified ammonium concentration in the effluent.
- 8) Regeneration of exhausted clinoptilolite with a neutral pH, 0.3 M sodium chloride solution yielded ammonium concentrations in the range

of 300 to 500 mg/l after 15 minutes of regeneration. The actual concentration observed in the regenerant depended upon the ammonium concentration in the wastewater fed to the clinoptilolite, and the degree of exhaustion achieved in the previous service cycle. These figures suggest neutral pH regeneration was more rapid and effective than previously thought.



Section 3

Modelling the Ion Exchange Behaviour of Clinoptilolite

Ammonium removal is most desirable in wastewater treatment for several reasons: ammonia exerts an oxygen demand on receiving streams (7) it contributes a source of nitrogen which may foster increased algal growth where nitrogen is a limiting nutrient (8,9,10) free ammonia is extremely toxic to aquatic life (11,12) and finally ammonia has been found to accelerate the corrosion of metals and materials used in construction (11).

Ames and Mercer (13,14) were the first to identify the ability of clinoptilolite to remove ammonium from wastewaters. Clinoptilolite is a naturally occurring zeolite that has been found in abundance in large surface deposits in the Western United States. It has a high selectivity for ammonium ions compared with its selectivity for calcium, magnesium and sodium ions, and as such the zeolite maintains a good working capacity for ammonium ions in the presence of these other ions.

Following the early pilot plant studies of Ames and Mercer (13,14) Koon and Kaufman (5) completed an investigation of the best conditions for the use and regeneration of clinoptilolite. Later McClaren (15) also reported on his studies of the factors influencing the removal of ammonium by clinoptilolite.

These studies provide engineers with guidelines for the design of ammonium removal facilities but they do not obviate the need for pilot plant studies to determine the design criteria for specific wastewaters.

If a model could be developed that would accurately predict the performance of clinoptilolite columns for removing ammonium from wastewaters

with only a small amount of easily obtained experimental data as an input, then the scale of pilot studies would be reduced significantly. Such a model would also be of benefit in describing the exchange behavior of the zeolite under different conditions.

DEVELOPMENT OF A MODEL

In order to provide a simple but useful model of ammonia removal from wastewaters, ammonium removal was modelled as a single solute system. Although wastewaters contain a complement of cations such as calcium, magnesium and sodium, if one is concerned with the removal of a specific ion such as ammonium it may be possible to develop an isotherm for the ammonium ions for a wastewater having a specified composition. An attempt was made therefore to modify a model of the type employed by Keinath (16) to simulate column performance for ammonia removal from a specific wastewater.

The distributed parameter approach employed in Keinath's model (16) requires the segmentation of a packed bed column into a number of discrete elements of equal volume as depicted in Figure 3-1. Both the liquid and the solid phase concentrations of the solute are assumed to be uniform throughout each element and axial dispersion in the column is assumed to be negligible compared with bulk flow. As shown by Keinath, a mass balance conducted on the nth column segment yields the following equations for the liquid and solid phases, respectively:

$$\frac{dC_n}{dt} = \frac{U}{\epsilon \cdot V} (C_{n-1} - C_n) - \frac{\rho}{\epsilon} \cdot R_A \quad (3-1)$$

$$\frac{dq_n}{dt} = R_A \quad (3-2)$$

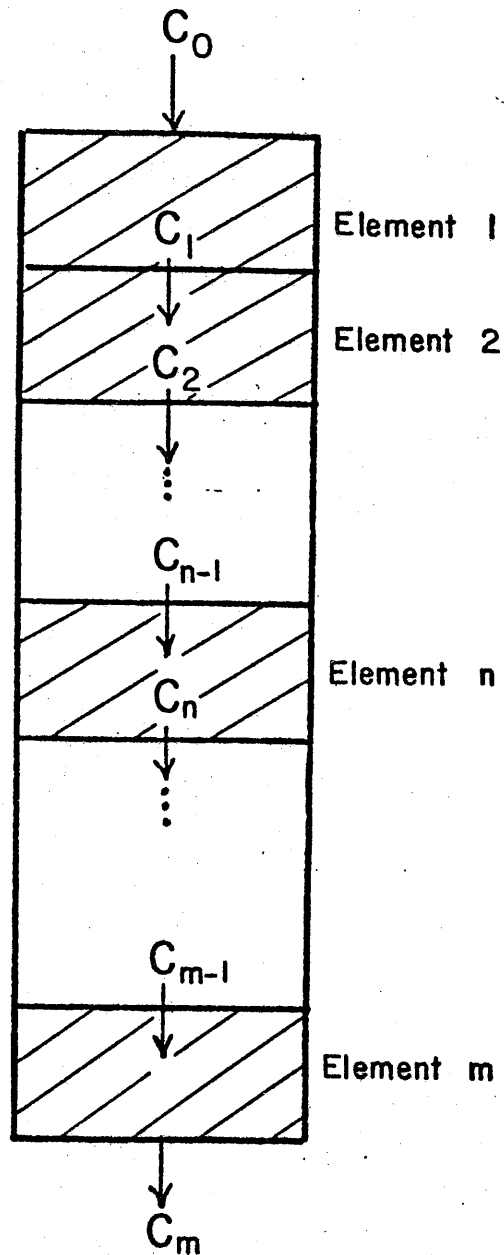


FIGURE 3-1 SEGMENTATION OF COLUMN BED
USED IN THE DISTRIBUTED PARAMETER
METHOD

where

- C_n = ammonium concentration in the liquid phase of the nth segment (mg/l)
 C_{n-1} = ammonium concentration in the liquid phase of the (n-1)th segment (mg/l)
 q_n = ammonium concentration in the solid phase of the nth segment (mg/g)
 u = volumetric flowrate of wastewater (l/hr)
 ρ = packed bed density of clinoptilolite (g/l)
 ϵ = packed bed porosity (dimensionless)
 V = volume of each column segment (l)
 R_A = rate of ammonium exchange (mg/g/hr)

The above differential equations include a rate expression, R_A , which describes the kinetics of ammonium exchange. This rate expression also incorporates the equilibrium relationship between the solid and liquid phase ammonium concentrations.

The Choice of a Rate Expression

The exchange sites in zeolites are contained within a crystal lattice structure often referred to as a cage. In the case of clinoptilolite each cage has two openings through which exchanging ions must pass to approach the exchange sites. Clinoptilolite consists of an aggregate of crystallites cemented together by quartz, feldspar, unaltered glass and other impurities. Ions must therefore migrate through both the pores in the aggregate and the channels of the crystallites during the course of ion exchange. The minimum free diameter of the zeolite channels reported by Barrer (17) ranged from 2.2 to approximately 9 \AA . The small size of crystallite channels is responsible for the selectivity patterns of many

of the zeolites but they also result in poor kinetics of exchange. The rate of exchange is usually controlled by diffusion within the particle (17,18,19).

An empirical but widely employed rate expression for particle diffusion control is the simple linear driving force equation of Glueckauf and Coates (20) which may be written as follows:

$$\frac{dq_n}{dt} = \frac{K_{pf} \cdot a_p}{D_\Sigma \cdot \epsilon} (q_n^* - q_n) \quad (3-3)$$

where

$$K_{pf} \cdot a_p = \frac{60 \cdot D_{pf} \cdot D_\Sigma \cdot \epsilon}{d_p^2} \quad (3-4)$$

and K_{pf} = mass transfer coefficient, a_p = external surface area of the zeolite, D_Σ = distribution ratio, D_{pf} = solid phase diffusivity of the ammonium ions, d_p = equivalent spherical diameter of the resin, and q_n^* is the solid phase ammonium concentration in equilibrium with the liquid phase ammonium concentration, C_n . Combining Equations (3-3) and (3-4) the following rate expression is obtained:

$$\frac{dq_n}{dt} = \frac{60 \cdot D_{pf}}{d_p^2} (q_n^* - q_n) \quad (3-5)$$

Equilibrium Relationships

The capacity of clinoptilolite for ammonium is influenced by the concentration of ammonium ions and the concentration of competing cations such as calcium, magnesium, sodium and potassium. In order to completely describe all the interrelationships between the cations in such a system, it is necessary to develop ten selectivity coefficients and these may only

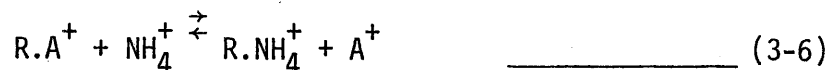
be used to calculate the capacity for ammonium if the binary equilibria are characterized by constant separation factors.

Ames (13,21) studied ammonium removal from agricultural waste using clinoptilolite and observed that the equilibrium for each cation pair was independent of other cation pairs in a multicomponent system. This observation greatly simplifies the calculation of ammonium exchange capacities in multicomponent systems. McClaren (15) detailed how the binary equilibrium data of Ames (13,21) could be employed to calculate the ammonium capacity of clinoptilolite for a wastewater of any composition. In this technique, selectivity coefficients were not assumed to be constant, but were variable depending upon the cation concentration ratios in the wastewater considered. Comparison of measured and calculated ammonium ion exchange capacities were quite close and McClaren concluded that "batch equilibrium data provide a good estimate of the ammonium capacity obtained--over a wide range of ammonium concentrations."

In this study, ammonium ion exchange capacities were calculated using the data of Ames (13,21) and the technique described by McClaren (15) and compared with experimentally determined values.

Batch isotherm studies were also conducted to measure ammonium ion exchange capacities directly, and to determine whether the data collected in batch studies could be employed to predict column performance in a multicomponent system.

In order to simplify the model, the exchange system was treated as a binary system in which the calcium, magnesium, potassium and sodium ions were considered as a single competing cation, A, in exchange with ammonium ions. The exchange could therefore be represented by Equation (3-6) in which R. represents the zeolite phase.



A separation factor, r , may be defined for this system to describe the ion exchange equilibria (22):

$$r = \frac{Y_A}{Y_N} \cdot \frac{X_N}{X_A} \quad (3-7)$$

where Y_A and Y_N represent the equivalent fractions of A and ammonium in the zeolite phase, and X_A and X_N represent the corresponding equivalent fractions in the solution phase. If r is assumed to be constant, then Equation (3-7) may be rearranged to obtain the fractional ammonium capacity, Y_N^* , in equilibrium with X_N :

$$Y_{NH_4}^* = \frac{X_{NH_4}}{r + (1 - r)X_{NH_4}} \quad (3-8)$$

This equation is analogous to the Langmuir Isotherm for a single solute system. If the zeolite phase ammonium concentration at equilibrium, q_n^* , is expressed as mg NH_4 -N/gram of clinoptilolite, and the solution concentration, C_n , is expressed as mg NH_4 -N/l, Equation (3-8) may be rewritten thus:

$$q_n^* = \frac{k' C_n}{1 + k'' C_n} \quad (3-9)$$

where

$$k' = Q^0 / C_T$$

$$k'' = (1 - r) / 14 C_T$$

$$Q^0 = \text{total ion exchange capacity of the clinoptilolite in meq/gram}$$

$$C_T = \text{total equivalent concentration in solution, meq/l}$$

EXPERIMENTAL

Materials

Clinoptilolite from Buckhorn, New Mexico, was provided by the Double Eagle Mining Company, Casper, Wyoming. The crushed zeolite was sieved and 18 x 20 mesh, 30 x 35 mesh, and 20 x 50 mesh samples were retained for study.

The samples of clinoptilolite were conditioned by alternate treatments with 1 M sodium chloride and 0.25 M ammonium sulphate four times. The samples were then converted to the sodium form with excess sodium chloride (0.24 lbs/gal) at pH 11.5 and rinsed with dilute hydrochloric acid and tap water until the pH was reduced to 8.5. This technique was chosen since Koon & Kaufman (5) found these conditions provided complete regeneration of the zeolite reproducibly. The clinoptilolite was then oven dried overnight and stored.

A synthetic wastewater having an ionic composition of an "average" secondary effluent was constituted by adding chemicals to Champaign-Urbana tap water. The composition of the wastewater is presented in Table 3-1.

Batch Isotherm Measurements

Batch isotherm measurements were made by equilibrating weighed quantities of conditioned clinoptilolite with wastewater samples containing 10, 20, 40, and 50 mg $\text{NH}_4\text{-N}/\ell$. For each initial ammonium concentration between 5 and 9, samples were prepared. From 0.03 to 5.80 gram quantities of clinoptilolite were added to 250 mL capped glass bottles containing 150 mL samples of wastewater. The samples were then shaken at room temperature for 24 hours. Control samples, with no added clinoptilolite,

Table 3-1

Composition of the Synthetic Wastewater

Ammonium-N	Variable
Sodium	95 mg/ℓ
Calcium	21 mg/ℓ
Magnesium	18 mg/ℓ
Potassium	6.5 mg/ℓ
Alkalinity (as CaCO ₃)	358 mg/ℓ
pH	8.0-8.5

were also shaken for each ammonium concentration. The final pH and ammonium concentrations were measured.

Column Studies

A schematic of the equipment employed in this study is presented in Figure 3-2. During service the ammonium containing wastewater was pumped from a 550 ℓ feed tank to the top of the test column by a metering pump (FMI Model RRP). The column effluent passed through a 0.48 ℓ plexiglass sampling chamber to a floor drain. Effluent samples were collected automatically from the sampling chambers by a sequential samples (N-con Systems Company, Sentry 500).

Varying depths of clinoptilolite and flow were tested but the length of the service cycle was usually about 20 hours. The ammonium concentration, temperature and pH of the feed were therefore checked before and after a service run. Flow rates were also checked. Details of the test conditions are provided in Table 3-2.

Following service the exhausted clinoptilolite was backwashed for five minutes with tap water. Countercurrent regeneration was accomplished

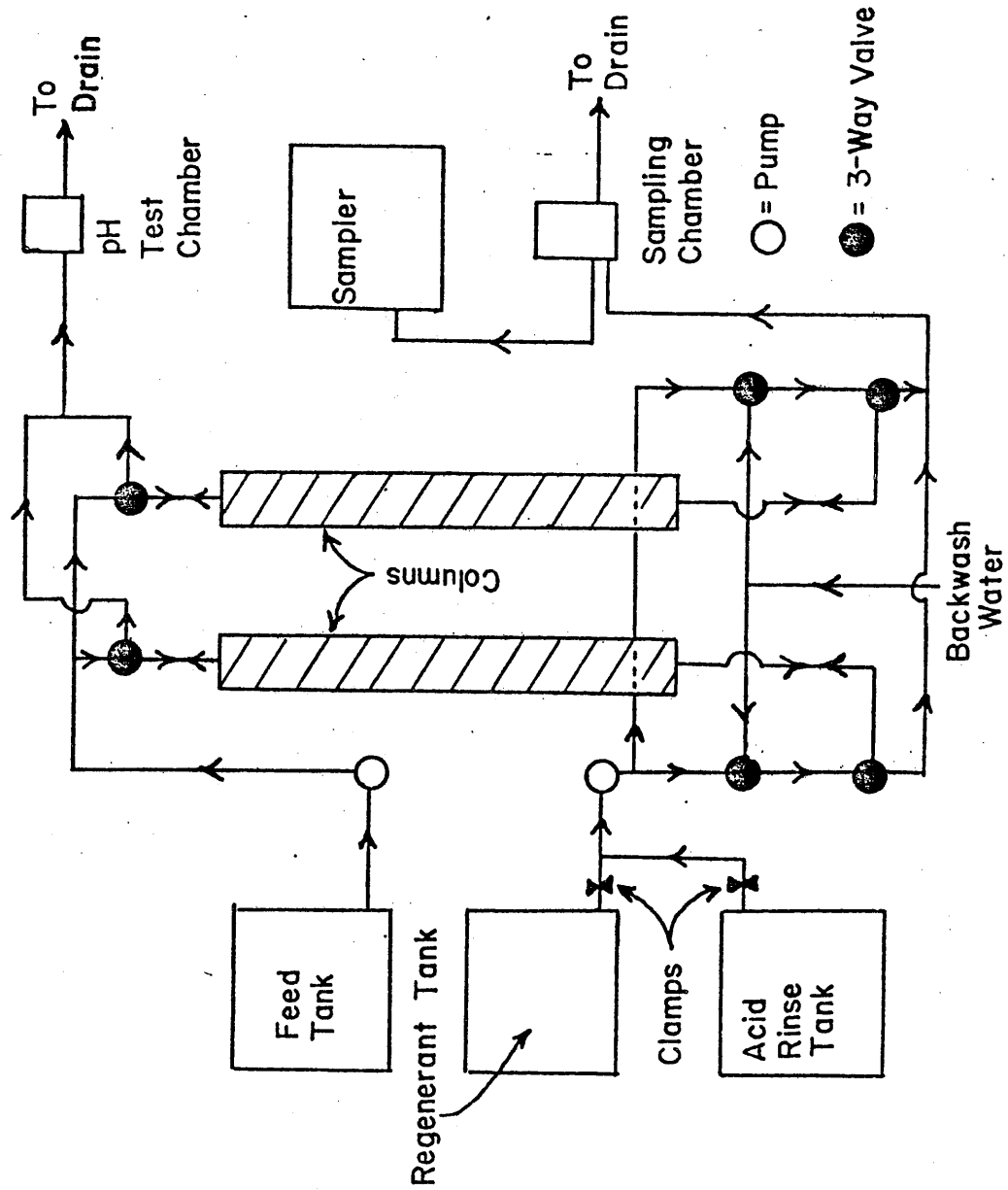


FIGURE 3-2 SCHEMATIC OF APPARATUS USED FOR BREAKTHROUGH STUDIES

by pumping sodium chloride solution (0.24 lbs/gal) having a pH of 11.5 upflow through the column at a flow rate of 15 bed volumes/hr for two hours. An acid rinse was then pumped upflow through the bed at a rate of 15 bed volumes/hr to reduce the pH from 11.5 to 8.3 (approximately 30 minutes) and finally the column was backwashed briefly with tap water.

The regeneration conditions were identical for all the column studies reported in Table 3-2. However additional studies were conducted on a column filled with 20 x 50 mesh clinoptilolite and in these studies countercurrent regeneration was provided by a neutral pH salt solution (0.3 M NaCl) at a flow rate of 20 bed volumes/hr for three hours.

Analytical

Ammonium concentrations were measured by means of an ORION Model 95-10 ammonia selective electrode coupled to an ORION Model 701 digital pH meter. Standard calibration curves were developed each time the ammonium electrode was used and since the electrode was prone to drift, frequent standard checks were made.

RESULTS AND DISCUSSION

Batch Isotherms

In Figure 3-3, the equilibrium capacities of the clinoptilolite, q^* , are plotted versus the equilibrium solution concentration of ammonium, C_N . It is apparent that each initial ammonium concentration yielded a separate curve. This result may be anticipated by inspection of Equation (3-9) since in changing the ammonium content of the wastewater, C_T is altered. When the data were plotted with the dimensionless solution fraction of ammonium, X_N , on the abscissa all the data fell on a single curve. A plot of $1/q_N^*$ versus $1/X_N$, shown in Figure 3-4 yielded a linear

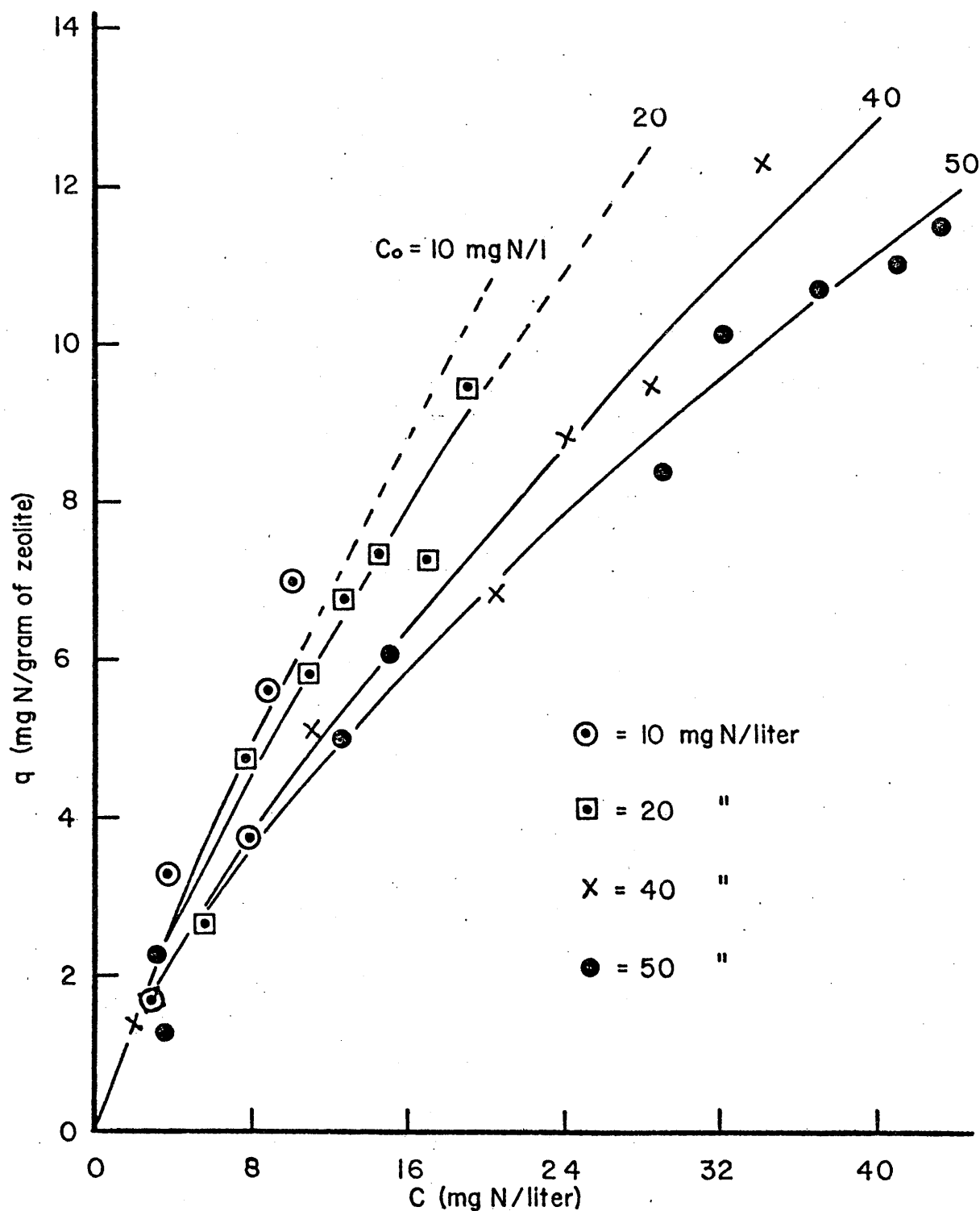


FIGURE 3-3 ISOTHERMS DEVELOPED FROM BATCH ANALYSES FOR FOUR DIFFERENT INITIAL AMMONIA CONCENTRATIONS

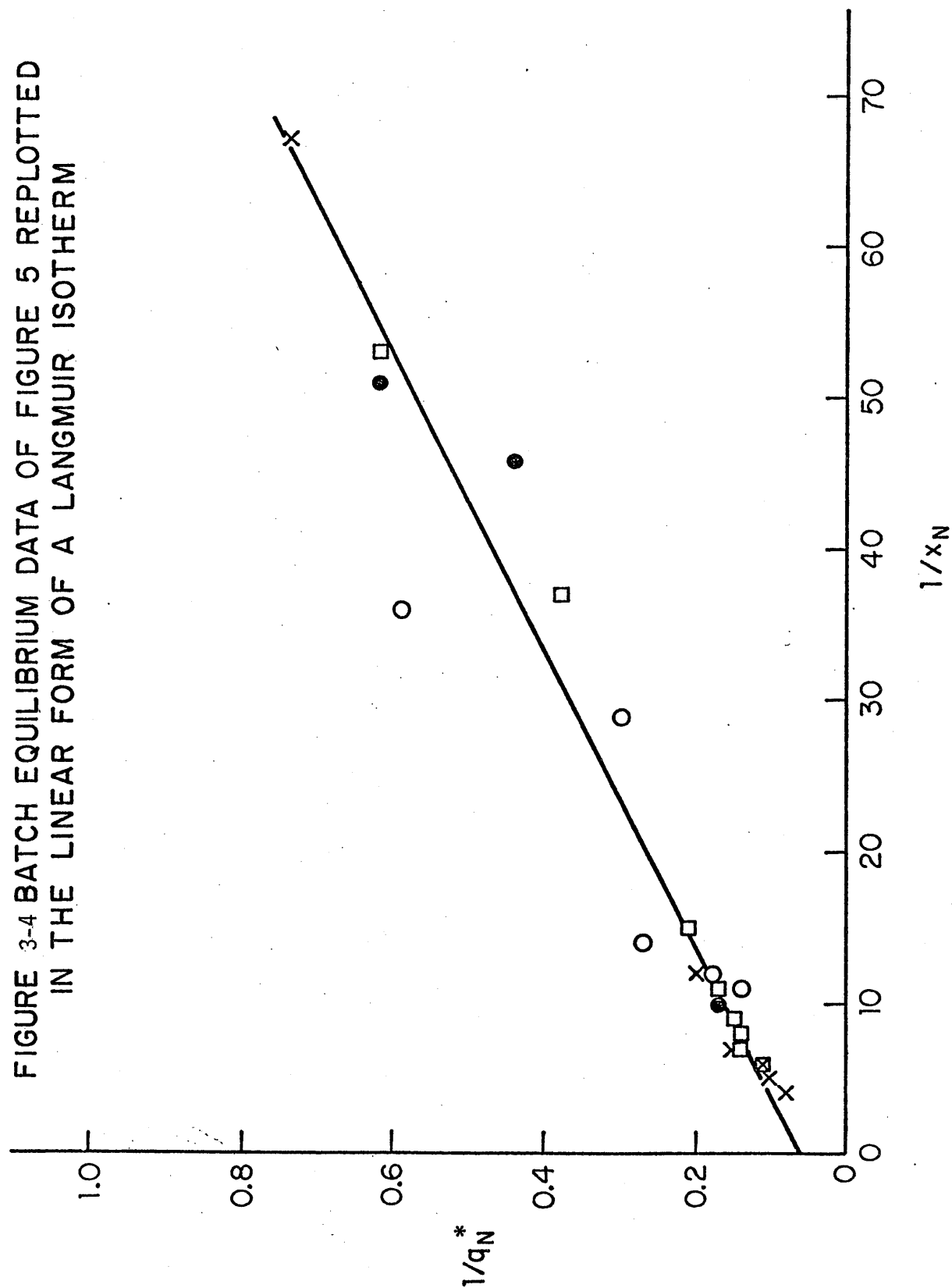
Table 3-2
Summary of Test Conditions for the Column Studies

Case	Column # ^a	No. of Runs	Flowrate (mL/min)	Bed Depth (cm)	Temp. (°C)	Influent pH	C _O (mgN/L)
I	1	3	170-177 (174) ^b	47	22-27 (25.0)	8.0-8.1	18.0-19.7 (19.0)
II	2	2	168-173 (172)	47	23.5-25 (24.5)	8.0-8.2 (8.1)	19.1-20.3 (19.6)
III	2	3	345-348 (346)	45	25-29.5 (27.0)	8.0-8.2 (8.2)	9.2-11.3 (10.3)
IV	2	2	170-174 (172)	45	26-29 (27.0)	8.0-8.1	27.8-29.0 (28.4)
V	1	3	170-175 (172)	63	24-30.5 (27.0)	8.1-8.2	18.0-19.4 (18.4)

^aColumn #1 was filled with 18 x 20 mesh clinoptilolite, and column #2 contained 30 x 35 mesh clinoptilolite.

^bValues in () represent the average value for runs where a range of values occurred.

FIGURE 3-4 BATCH EQUILIBRIUM DATA OF FIGURE 5 REPLOTTED
IN THE LINEAR FORM OF A LANGMUIR ISOTHERM



plot indicating that the Langmuir model describes the equilibrium relationship. The scatter in the data reflects the experimental error involved in the batch studies. When tests were conducted for high solution concentrations of ammonium, the change in concentration, ΔC_N , was rather small and the experimental error associated with the analysis of ammonium became significant.

The capacity of the clinoptilolite could also be evaluated from the breakthrough curves obtained in the column studies. The capacity was determined by integrating the area to the left of the breakthrough curve. Since the service cycles were operated to complete exhaustion the measured capacities yielded q_N^* values which could be plotted on an isotherm versus their corresponding influent ammonium concentration values, C_N . The isotherm so obtained is plotted in Figure 3-5. This plot was, like the batch isotherm, shown to follow the form of a Langmuir isotherm. However, the batch isotherm in Figure 3-4 predicted higher ammonium capacities than those measured during column operation.

This was found to be a result of incomplete regeneration. The conditions employed for regeneration in this study were found to give complete regeneration of Hector clinoptilolite by Koon and Kaufman (5) but were apparently inadequate to completely regenerate the clinoptilolite used in this study.

The selectivity data of Ames (13,21) were used to calculate the ammonium exchange capacity of the clinoptilolite in equilibrium with the feed wastewater employed in the column studies. Following the technique described by McClaren (15) the computed fractional capacities were very much greater than the measured values. For example, it was computed that Y_N^* would be 0.45 in equilibrium with 20 mg/l of ammonia

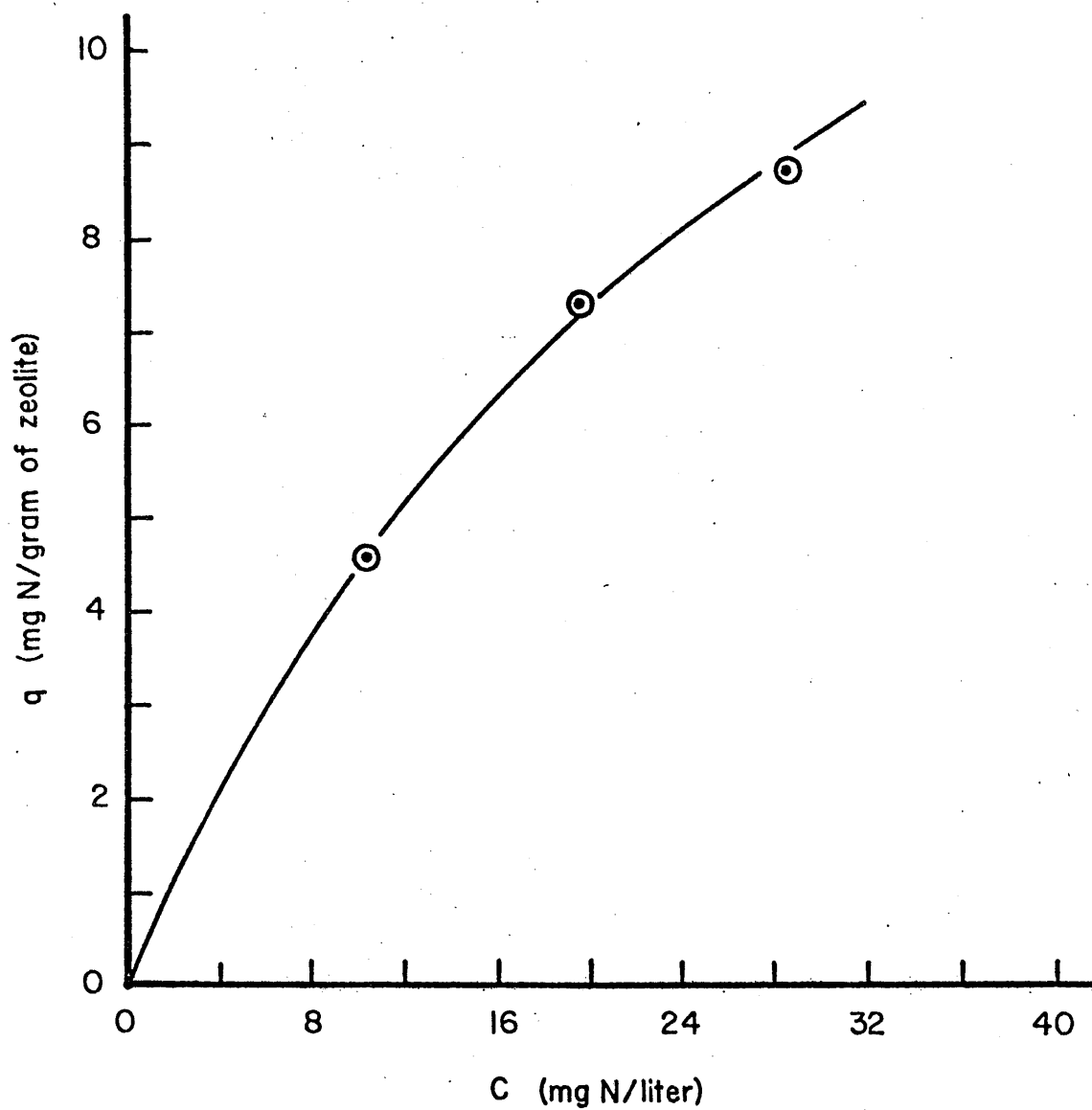


FIGURE 3-5. ISOTHERM DEVELOPED FROM COLUMN
BREAKTHROUGH CURVES FOR CASES II, III, AND IV

nitrogen, while the observed capacity was only 0.26. This may again be explained in part by the difference in the source of clinoptilolite. The selectivity studies of Ames (13,21) were for Hector clinoptilolite. However, Koon and Kaufman (5) conducted column studies with Hector clinoptilolite and found poor agreement between predicted and experimentally determined capacities, also.

Column Breakthrough Studies

Ammonium breakthrough curves were obtained under conditions of varying flow rate, ammonium concentration, bed depth and particle size. The exact test conditions are provided above in Table 3-2. Duplicate or triplicate breakthrough curves were obtained under each set of conditions to ensure reproducible behavior. The average breakthrough curves obtained under each set of test conditions are presented in Figure 3-6. The actual breakthrough data points are presented in Figure 3-8 to 3-12 where they are compared with the model predictions.

The breakthrough curves exhibited the anticipated changes in slope and displacement with changes in slope and displacement with changes in test conditions, and since these have been widely observed and discussed in various ion exchange and adsorption studies no discussion will be presented here on the shape of the breakthrough curves themselves.

Modelling Performance

The first attempt to model the performance of clinoptilolite was made using the same program as that used by Keinath (16). This program used the CSMP/360 program package developed by IBM (23). For the n^{th}

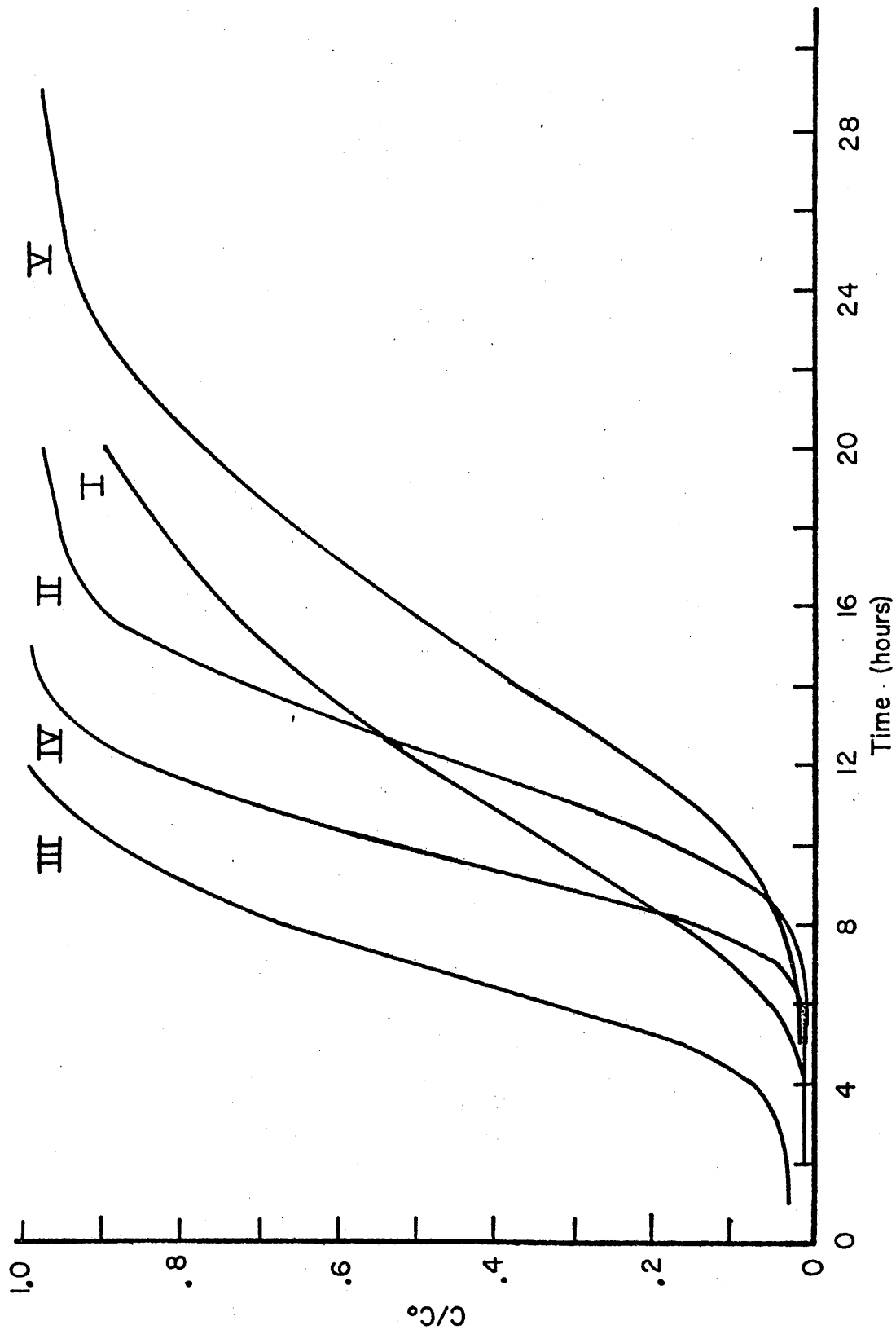


FIGURE 3-6 BREAKTHROUGH CURVES OF COLUMNS FOR ALL FIVE CASES

segment, the program solved the following equations:

$$\frac{dC_n}{dt} = \frac{U}{\epsilon \cdot V} (C_{n-1} - C_n) - \frac{\rho}{\epsilon} \left(\frac{60 D_{pf}}{d_p^2} \right) (q_n^* - q_n)$$

$$C_n = \int_0^{\Delta t} \frac{dC_n}{dt} \cdot dt + C_{ns}$$

$$\frac{dq_n}{dt} = \frac{60 \cdot D_{pf}}{d_p^2} (q_n^* - q_n)$$

$$q_n = \int_0^{\Delta t} \frac{dq_n}{dt} \cdot dt + q_{ns}$$

and $q_n^* = K_F C_n^a$

where C_{ns} and Q_{ns} are the ammonium concentrations in the liquid and solid phases of the n^{th} segment at time zero, respectively.

The equilibrium relationship was described by the Freundlich isotherm. Initial values for the integration step size, Δt , were set below 2×10^{-4} hrs, the number column segments were set to 10 and the diffusivity, $D_L = 10^{-5} \text{ cm}^2/\text{hr}$. Under these conditions the program was extremely unstable and predicted negative solution concentrations in the early stages of exchange. The program as written required a large amount of computer time and was quite costly.

Several changes were made to the program to reduce computer execution time and also to avoid the instability problems experienced in the first attempts. The Freundlich isotherm was replaced by a linear expression of the form

$$q_n^* = k_1 C_n + k_2 \quad \text{_____} \quad (3-10)$$

and approximated by four straight lines, as illustrated in Figure 3-7. Secondly, the Runge-Kutta numerical integration technique was employed instead of Simpson's method. A Runge-Kutta subroutine names RKGS is available from IBM (24). The advantage of RKGS is that should the integration error exceed a certain preset value, the integration step size, Δt , is automatically halved. The subroutine will halve Δt eleven times before program execution is terminated. In the first minutes of service, dc/dt is large but for most of the service period the values of dc/dt are considerably smaller. With RKGS it is possible to set the time interval, Δt , such that it is satisfactory during most of the service cycle and the subroutine will automatically reduce Δt during the initial stages of exchange. In this way, the execution time may be reduced significantly.

The accumulation term, dc_n/dt , was estimated using the finite difference approximation shown in Equation (3-11).

$$\frac{dc_n}{dt} = \frac{C_n^1 - C_n^0}{\Delta t} = \left[\frac{C_{n-1}^0 + C_{n-1}^1}{2} - \frac{C_n^0 + C_n^1}{2} \right] A - B \left[k_1 \frac{(C_n^0 + C_n^1)}{2} + k_2 - q_n \right] \quad (3-11)$$

where C^0_i refers to the concentration in the i^{th} segment at time t^0 and C^1_i is the corresponding concentration at time $t^0 + \Delta t$; $A = U/\epsilon \cdot V$, and $B = \rho 60 D_L / \epsilon d_p$.

This program was tested extensively. In order to reduce the computer cost, tests were conducted to find the minimum number of column segments and the maximum values for the allowable integration error and the

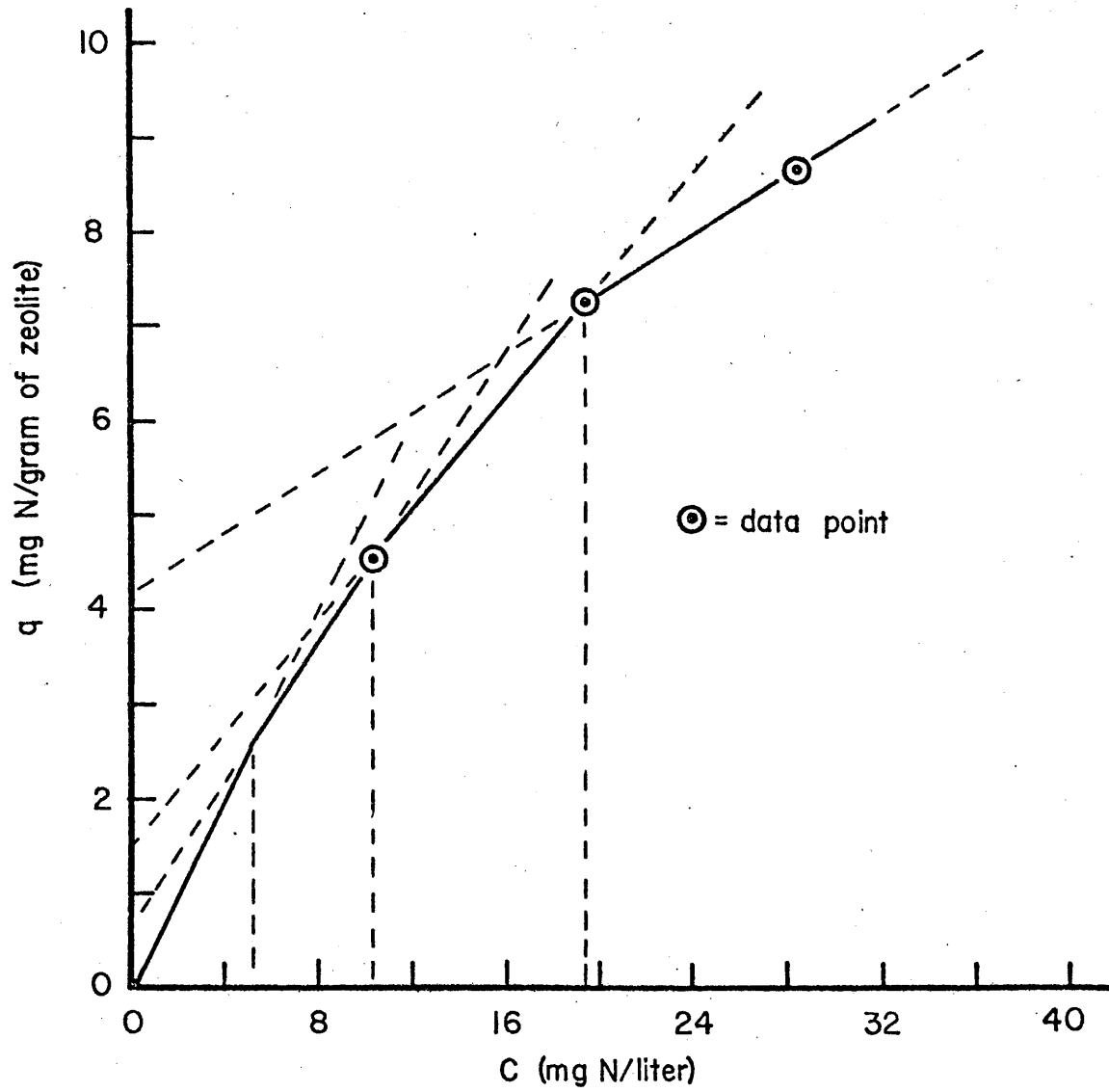


FIGURE 3-7 LINEARIZED VERSION OF BREAKTHROUGH CURVE ISOTHERM USED IN MODEL ANALYSIS

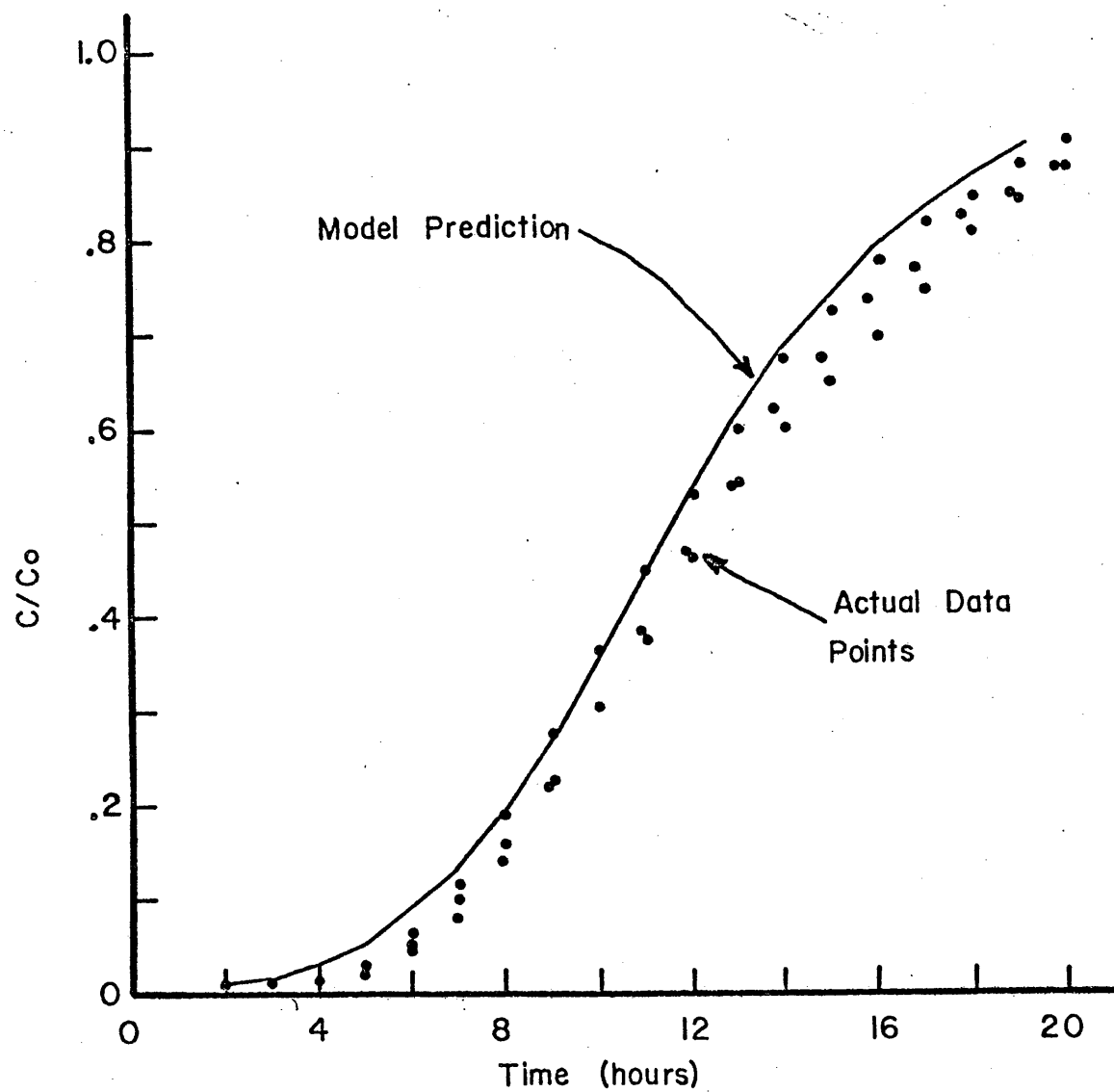


FIGURE 3-8 COMPARISON BETWEEN MODEL PREDICTION AND ACTUAL COLUMN BREAKTHROUGH FOR CASE I COLUMN OPERATION

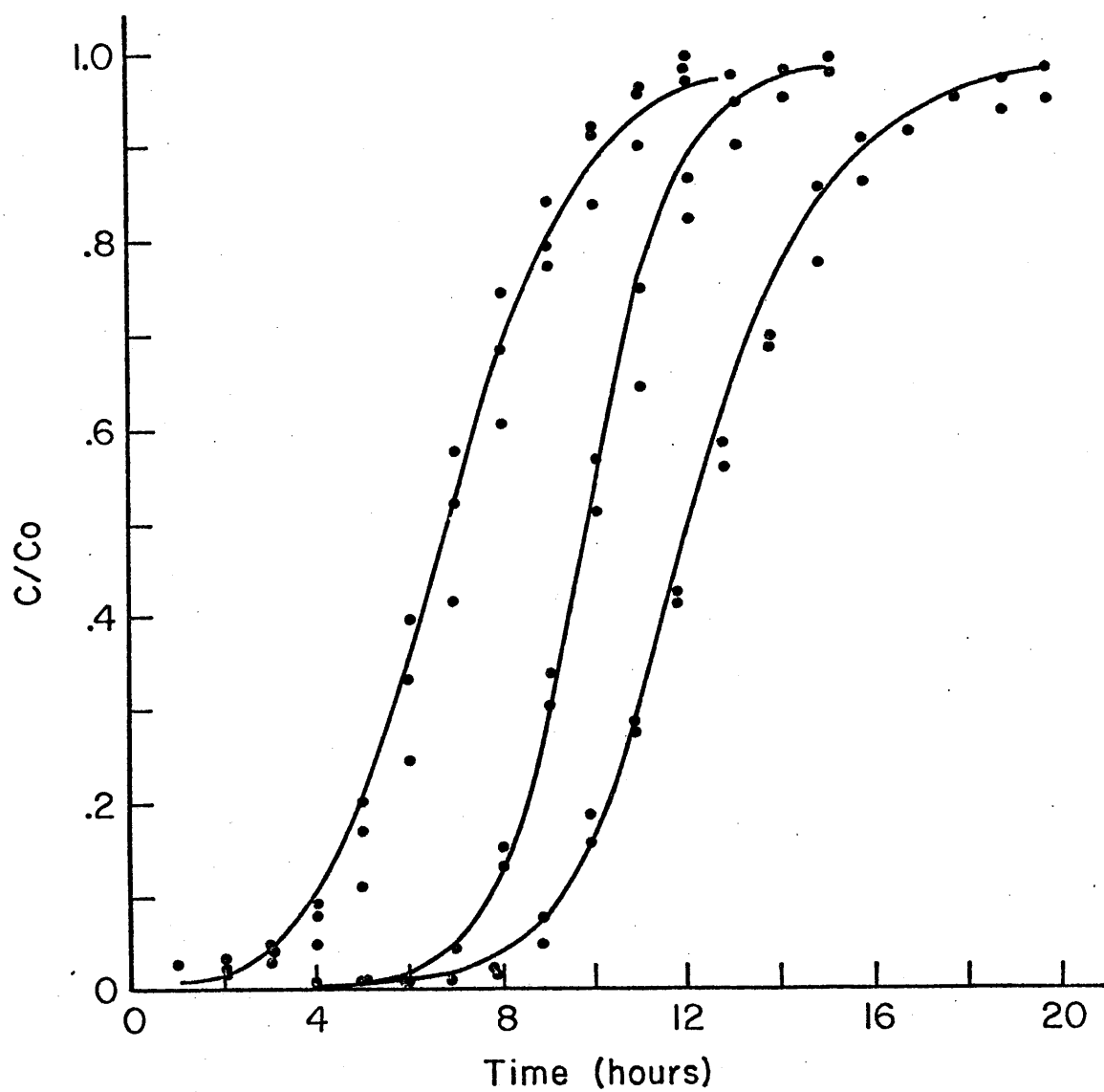


FIGURE 3-9 COMPARISON BETWEEN MODEL PREDICTION AND ACTUAL COLUMN BREAKTHROUGH FOR CASES II, III AND IV

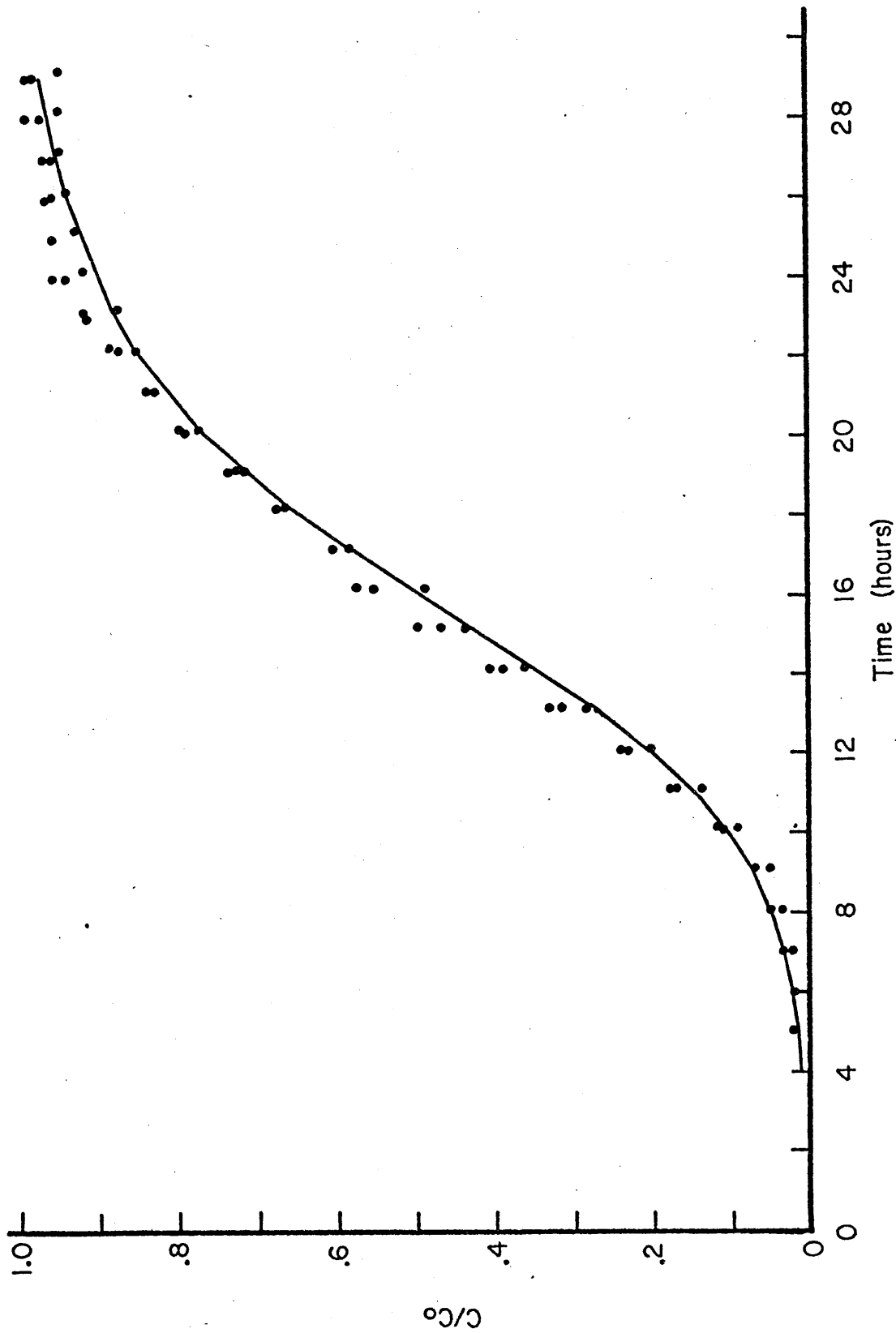


FIGURE 3-10 COMPARISON BETWEEN MODEL PREDICTION AND ACTUAL COLUMN BREAKTHROUGH FOR CASE V COLUMN OPERATION

integration time interval that could be employed without loss in accuracy. It was found that these numbers should be 100, 10^{-4} hrs and 2×10^{-3} hrs, respectively. With these values it was found that the experimentally determined breakthrough curves could be predicted well with the model if the value of the particle phase interdiffusion coefficient had a value of $8 \times 10^{-5} \text{ cm}^2 \text{ hr}^{-1}$. A comparison of the experimental data points and the predicted curves are presented in Figures 3-8 - 3-10.

The value of D_L , $2.2 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ appears to be reasonable when compared with other literature values for exchange on clinoptilolite. Ames (18) found the particle phase diffusion coefficient to be $1.66 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$ for Na-Cs exchange at 25°C on clinoptilolite. Barrer (17) found that diffusion coefficients ranged between 10^{-8} to $10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ for the exchange of various alkylammonium ions in clinoptilolite. The estimated values of D_L in this study should be lower than the values reported by Ames for several reasons. Caesium has a smaller hydrated radius than ammonium; the presence of calcium and magnesium ions in the wastewater used in this study would undoubtedly act to reduce the value of the interdiffusion coefficient (5) and finally, the clinoptilolite employed by Ames (18) was pretreated with acid to remove basic impurities in the aggregate, which would tend to enlarge the pores of the zeolite perhaps allowing higher rates of diffusion within the particle phase.

In summary it was found that the model was able to predict column performance quite well for a particular regeneration condition.

This model had several shortcomings, however. 1) it was unable to predict the ammonium leakages observed experimentally, 2) it was unable to predict the impact of varying regeneration conditions on ammonium removal performance and, 3) it required column studies to accurately

describe the equilibrium isotherm for the wastewater studied and the regeneration conditions desired.

Some effort was made to employ batch isotherm data in the model in the earlier study. However, there was a discrepancy between the batch and column isotherms. The batch studies conducted with zeolite samples under slightly different conditions indicated that higher capacities should be achieved than measured in the column tests. In order to employ the batch isotherm in the model a column of zeolite was regenerated more extensively and ammonium removal performance was monitored under varying conditions. It was found that the model predictions were close to the observed performance in some cases but discrepancies were observed in other predictions. It was later discovered that the extent of regeneration was not nearly as complete as was thought initially. A batch isotherm obtained following complete regeneration (1N NaCl for 24 hours) is presented in Figure 3-11 together with the isotherm obtained from the column studies (Figure 3-5) for reference. It is clear that the high pH conditions recommended by Koon & Kaufman (5) for complete regeneration were inadequate for the zeolite studied. It was found that ammonium is very rapidly displaced when regeneration is initiated but large volumes of regenerant are required to displace the last traces of ammonium from the zeolite. The divergence between predicted and observed results was therefore caused by the use of incorrect forms of the batch isotherm itself and the initial conditions of the columns.

In the following studies the model previously presented was extended to simulate both regeneration and service performance. The interaction of the models is illustrated in Figure 3-12. The regeneration model predicted the ammonium displacement during regeneration and the column

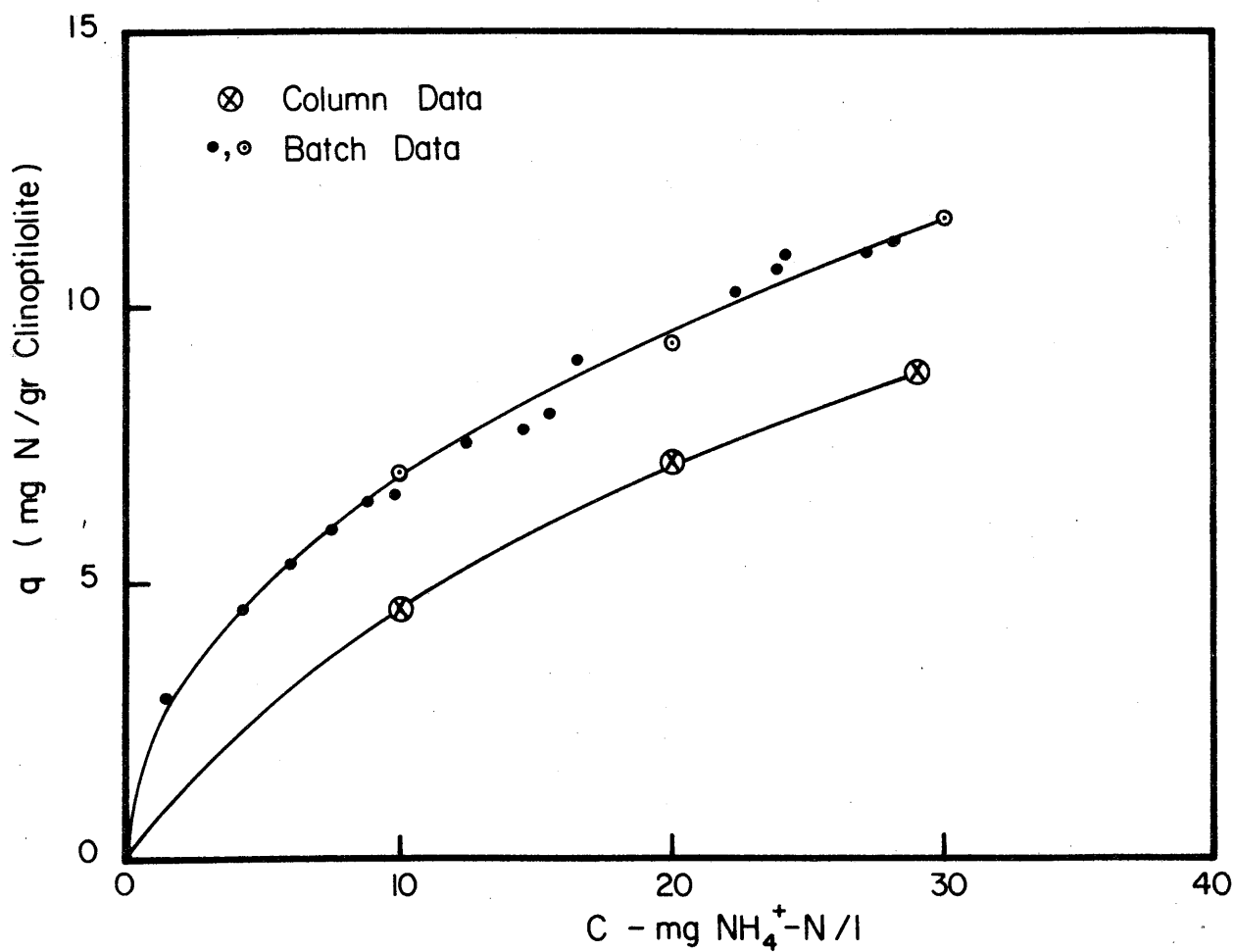
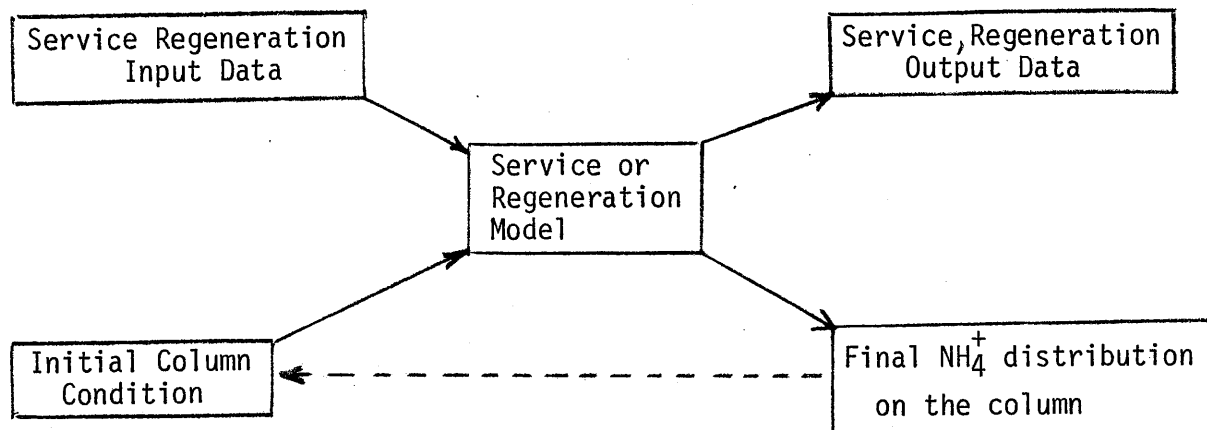


FIGURE 3-11 COMPARISON OF BATCH ISOTHERM DATA FOR COMPLETELY REGENERATION CLINOPTILOLITE WITH THE ISOTHERM OBTAINED FROM COLUMN STUDIES (FIG 3-5)



Service Regeneration Data Input:-

Volume Zeolite
 Particle Size Distribution
 Equilibrium Isotherm
 No. of Column Segments
 Ammonium Diffusivity

Influent Flowrate
 Influent NH₄⁺ Concentration
 Packed Bed Density
 Integration Variables

Initial Column Conditions:-

Ammonium distribution on the column at the beginning of the service cycle.

Service Regeneration Output Data:-

The effluent ammonium concentration is described as a function of time in service, and volume of water treated.

Final Colum Condition:-

Ammonium distribution on the column at the conclusion of the service cycle.

FIGURE 3-12

SCHEMATIC REPRESENTATION OF THE COMPUTER FILE INTERACTION.

distribution of ammonium that may be used as an initial condition for the subsequent service cycle, this information is stored on the computer and is called by the service program when needed. The service model, as before, predicts ammonium removal performance and the column condition at exhaustion. The combination of the models should therefore allow the impact of any regeneration condition on ammonium removal performance to be predicted for a given wastewater quality.

Since the model had previously been tested extensively for predicting ammonium breakthrough during service, this study concentrated on testing the model's prediction for varying regeneration conditions. The model was tested in its ability to predict the regeneration and service performance observed with the neutral pH regeneration studies reported in Section 2.

Program Modifications for Regeneration

Copies of the service model computer program are included in Appendix A. However, several changes were made to the service program in order that it could be used for regeneration. The major modifications are listed below:

- 1.) The column segment sequence was reversed since regeneration was always countercurrent. The segment numbers were changed back to their original sequence when the computation was complete in order that the column ammonium distribution would be correct for the following downflow service cycle model.
- 2.) The program was provided with a mechanism for determining the distance the brine had moved through the column following the initiation of regeneration. This determined the number of segments exposed to regenerant and in which exchange had occurred. No exchange was allowed in segments not yet contacted with regenerant.

- 3.) The equilibrium curve used for the regeneration program was in the form of a Freundlich Isotherm and this required an iterative procedure for the solution of the ammonium concentration in solution at any time.

EXPERIMENTAL

Equilibrium Relationships

1. Service Equilibrium

In order to determine the service isotherm exactly, a number of tests had to be conducted very accurately. The zeolite was completely regenerated by passing an excess (2-5 liters) of 1N NaCl through a burette containing approximately 50 grams of clinoptilolite over a 24 hour period. The zeolite was then rinsed with ammonia free water.

The regenerated zeolite was drained and dewatered by centrifugation at 5000 rpm for about 30 seconds and mixed well to ensure a uniform moisture content. Known weights of the moist zeolite were then added to known volumes of the influent wastewater containing three initial ammonium concentrations. The zeolite-solution mixture was stirred with a slow speed paddle in a covered 1 liter beaker for approximately 12 hours. The final ammonium concentrations of the filtered solutions were measured by using an Orion ion selective electrode. One control test was conducted without added zeolite for each initial ammonium concentration to evaluate ammonia loss attributable to the mixing conditions. At least three samples of moist zeolite were weighed and dried for an evaluation of the zeolites' moisture content. The best procedure included drying for 1-2 hours at 104°C followed by equilibration with a constant humidity environment provided in a desiccator containing saturated sodium chloride at 20°C. In this way moisture contents

were measured accurately to within 1%.

Regeneration Isotherm

Essentially the same procedure was employed for the regeneration isotherm. Samples of completely regenerated clinoptilolite prepared as described above were contacted with an excess of the influent wastewater containing known initial concentrations of ammonium. The amount of ammonium exchanged, mgN/g, was obtained from the service isotherm data.

Known weights of moist ammonium from zeolite were added to known volumes of 0.3M NaCl and ammonium concentrations were measured after approximately 12 hours of mixing. Control beakers containing various ammonium concentrations in 0.3M NaCl with no added zeolite were also tested following the same procedure.

RESULTS AND ANALYSIS

Service Isotherms

The equilibrium curve obtained in this study is shown above in Figure 3-11. The equilibrium curve is influenced by the ammonium concentration in the influent water. This isotherm may be employed to evaluate the equilibrium curve for any desired influent ammonium concentration in the wastewater studied if converted to dimensionless form as shown above. The equilibrium curve shown in Figure 3-13 was obtained in this way from Figure 3-11 for $C_o = 20$ mg/l.

Regeneration Isotherms

The regeneration isotherm obtained following the technique described above was not able to model the displacement of ammonium during regeneration. Even when the value of the diffusivity of ammonium was increased to unrealistically high values, the model predicted much slower ammonium displacement than that observed. The isotherm data was therefore suspect and appeared to

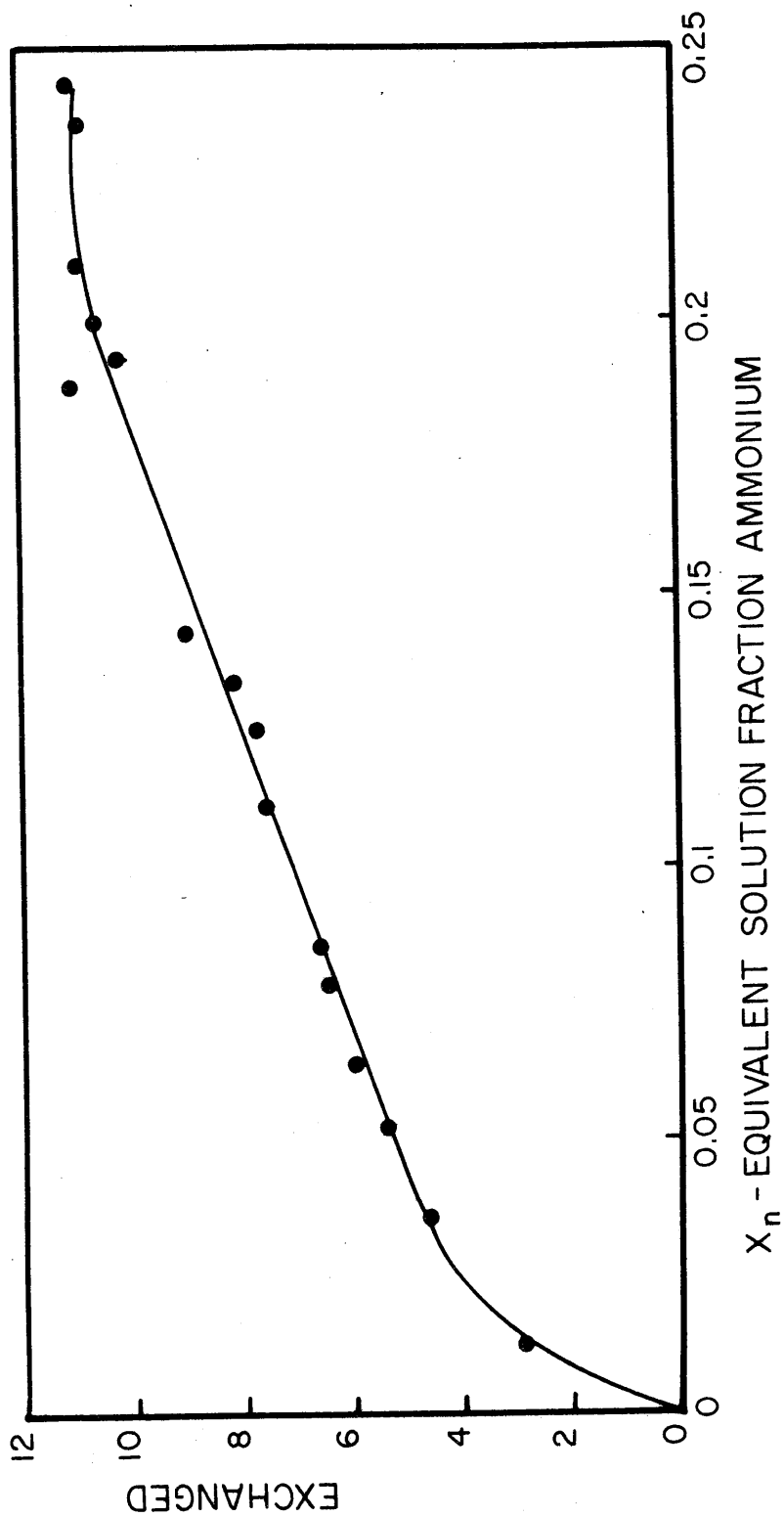


FIGURE 3-13 NON-DIMENSIONAL SERVICE EQUILIBRIUM CURVE

give lower ammonium concentrations than it should. The isotherm was repeated several times but appeared quite reproducible. A reverse equilibration was tested. In this test sodium form clinoptilolite was equilibrated with a 0.3M solution containing varying concentrations of ammonium and sodium ions. Ammonium was exchanged during mixing and the final ammonium concentration was measured. The results of this study proved less accurate (analytical problems with ammonium measurement) and also gave a poorer isotherm.

A kinetic study of ammonium displacement was conducted. The original test procedure was followed but the ammonium concentration in solution was monitored with time. The results of this study are presented in Figure 3-14. The study clearly indicated that when high ammonium concentrations were displaced, the ammonium concentration in solution showed a maximum value after approximately 15 minutes of mixing and then declined slowly. A maximum was not observed for low ammonium concentrations (low zeolite weights added).

The reason for this behavior which was not attributable to ammonia stripping under the conditions tested is thought to be related to Ca and Mg displacement during the batch equilibration.

In order to get high ammonium concentrations in the regeneration isotherm large weights of moist zeolite had to be added to a small volume of regenerant. These conditions also lead to the development of high calcium and magnesium concentrations. Since the ammonium ion diffusivity is greater than that of the divalent ions, it is most rapidly displaced into solution. However, as Ca^{++} and Mg^{++} are displaced with time the equilibria may shift and NH_4^+ may be re-exchanged.

It was decided, therefore, to use the 15 minute maximum ammonium

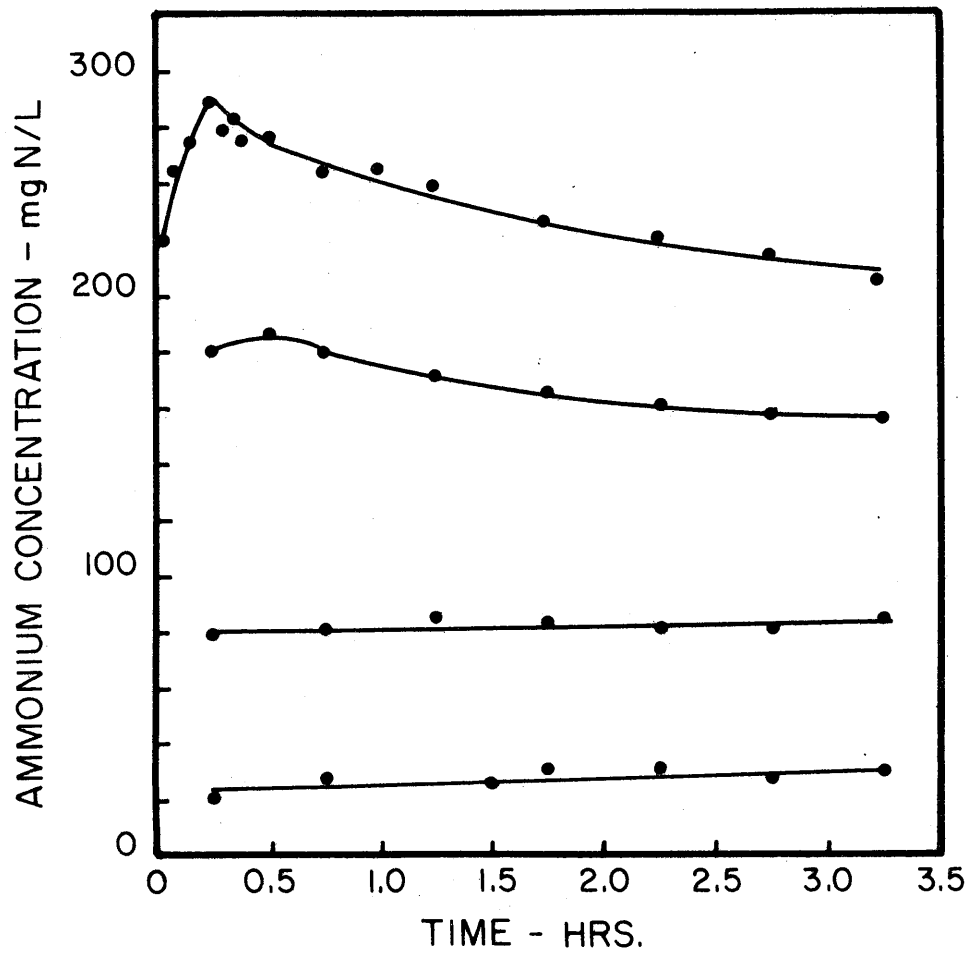


FIGURE 3-14 AMMONIUM RELEASE DURING BATCH
EQUILIBRIUM TESTING FOR REGENERATION
AS A FUNCTION OF TIME

concentration for large zeolite dosages and the 1 hr. ammonium concentration for the smaller dosages. In addition, some column studies were conducted to check on the higher ammonium concentrations values. Burettes (50 ml) were filled with approximately 30 ml of clinoptilolite that had been saturated with wastewater containing known ammonium concentrations (10, 20, 30, 40 mgN/l). The 0.3M NaCl regenerant was applied to the top of the zeolite columns after the water level had been reduced to just below the top of the zeolite. This procedure ensured that the dilution of the regenerant was minimized. The regenerant flowrate was fixed between 8 and 12 bed volumes/hr. Since studies in Section 2 had indicated the ammonium displacement was not influenced by flowrate in this range, the column effluent was captured in 5 ml volumes and the ammonium content was measured. A well-defined maximum ammonium concentration was observed for each column effluent as shown in Figure 3-15 and this was assumed to be the concentration in equilibrium with the initial zeolite phase ammonium concentration.

The regeneration isotherm data collected from these studies is presented in Figure 3-16. The batch and column results show good agreement in the lower concentration. However, the column consistently gave higher ammonium displacement than the batch equilibration study.

The addition of moist zeolite to 0.3M NaCl tended to dilute the salt concentration in solution and the data had to be corrected accordingly. Batch test data is shown in Appendix B and the corrections are illustrated.

The data presented in Figure 3-15 followed the form of a Freundlich Isotherm reasonably well as shown in Figure 3-17. The line of best fit was described by the expression $q = .729C^{.383}$

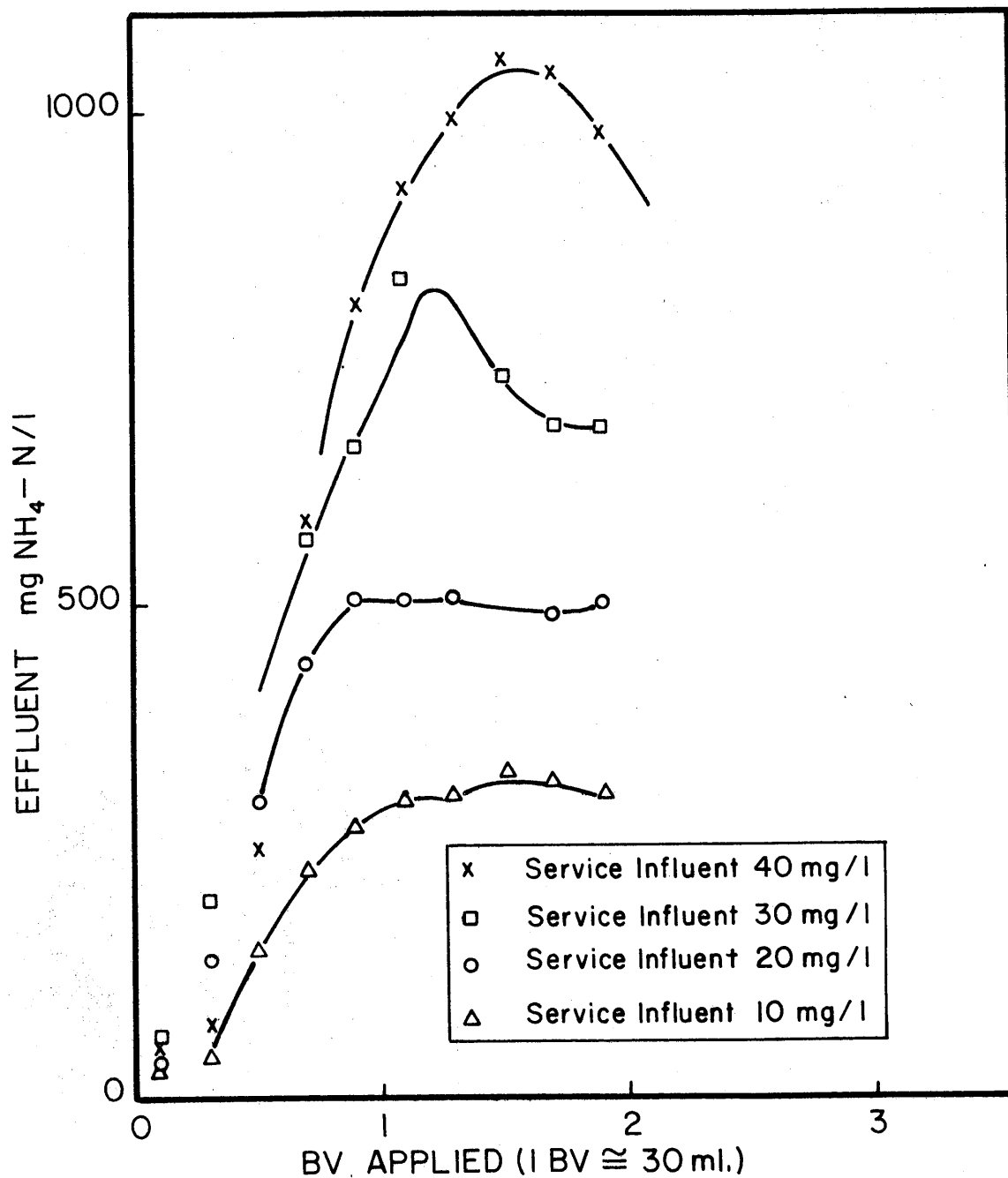


FIGURE 3-15 EFFLUENT AMMONIUM CONCENTRATIONS OBSERVED IN COLUMN DISPLACEMENT STUDIES

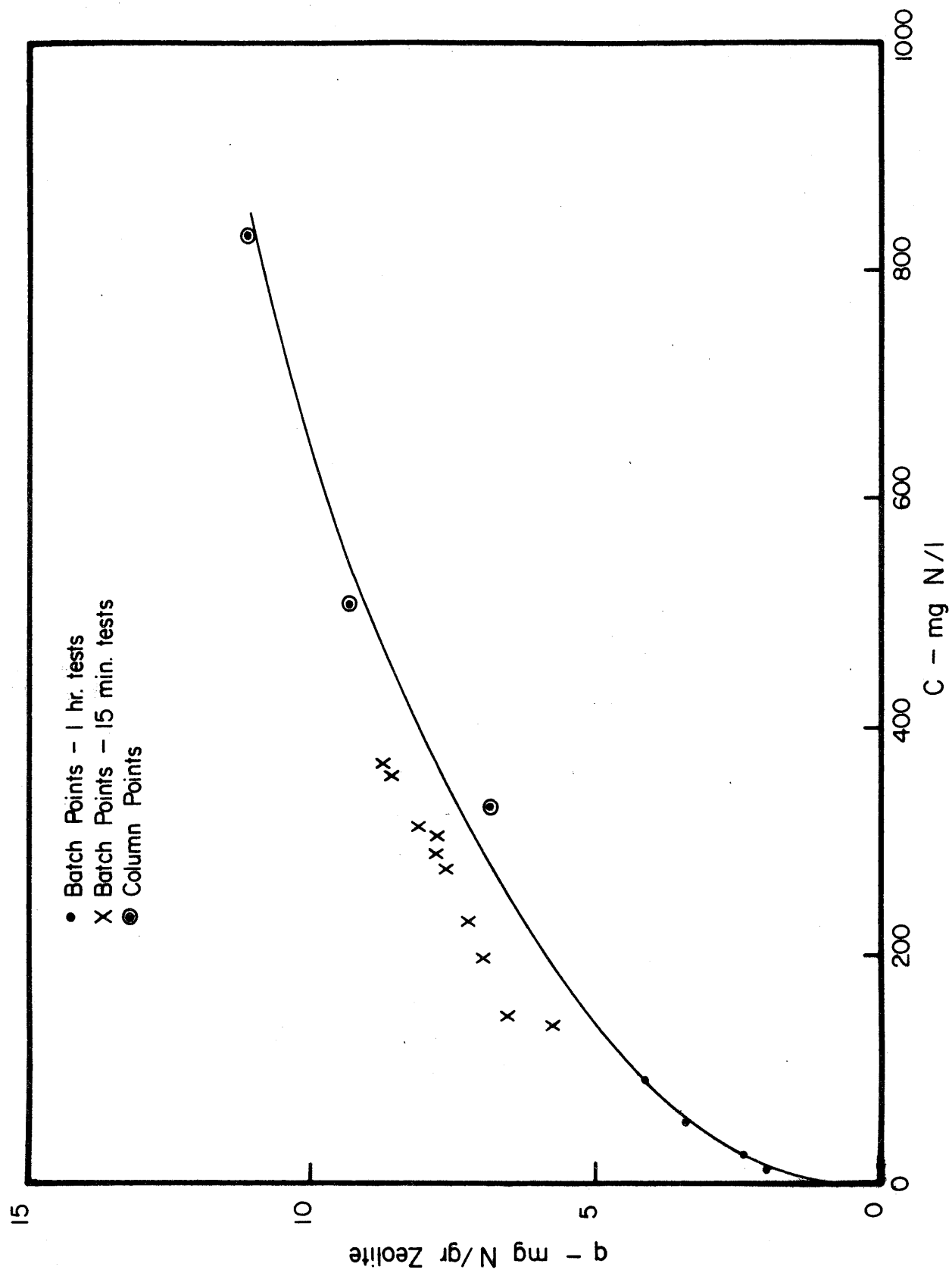


FIGURE 3-16 REGENERATION ISOTHERM

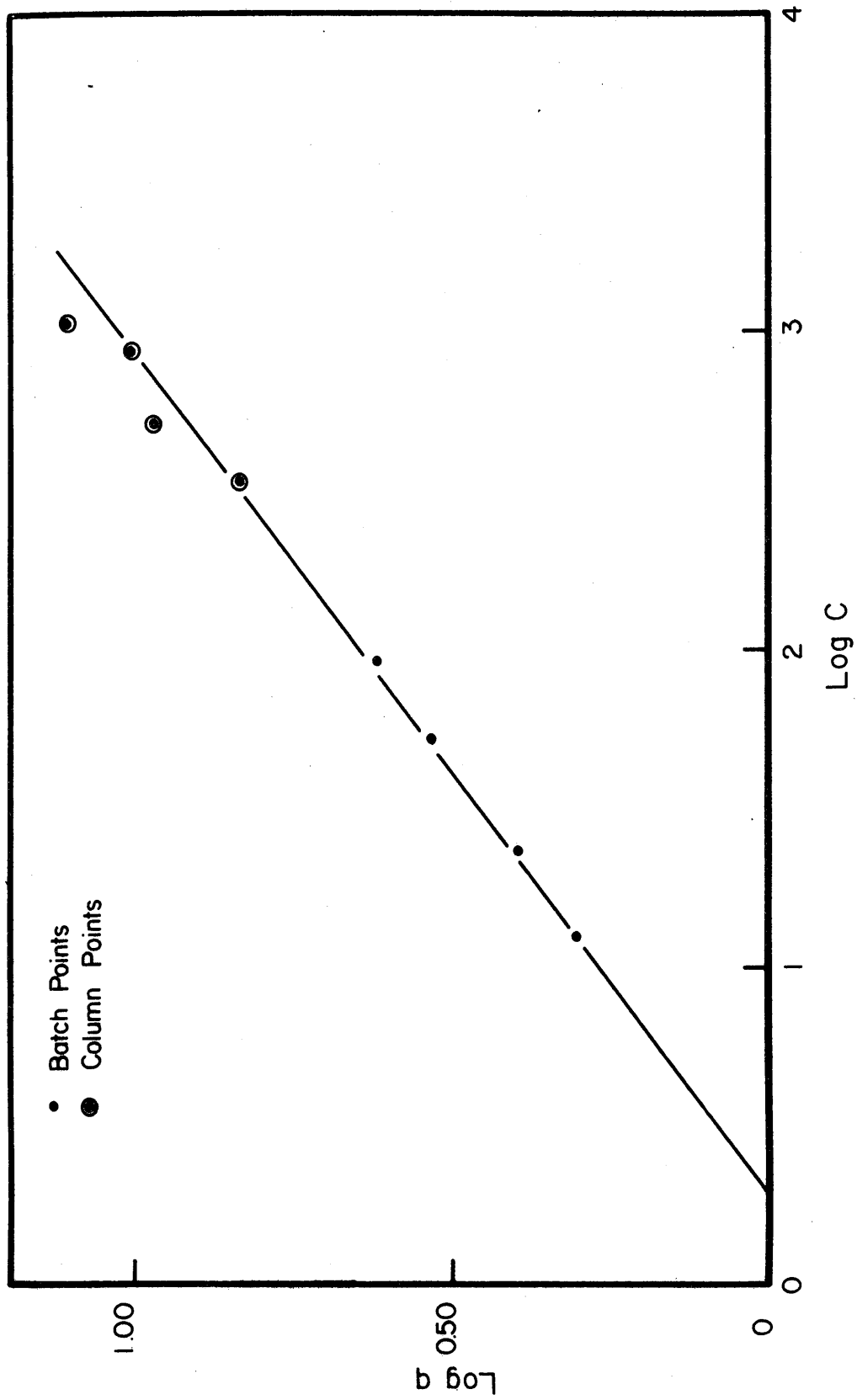


FIGURE 3-17 FREUNDLICH PLOT OF REGENERATION DATA

Regeneration and Service Studies

Studies reported in Section 2 were used to test the model predictions. The test conditions used are summarized in Table 3-3.

Model Predictions and Column Studies

Using the isotherms that were obtained for the service and regeneration cycles, attempts were made to model the performance observed in actual column studies. It was observed that ammonium displacement was extremely rapid during regeneration and the first batch regeneration studies provided an isotherm that was completely inadequate in describing the initial rate of ammonium displacement. However, following the modified techniques to avoid kinetic effects in regeneration, as described above, an isotherm was obtained which was reasonably successful in predicting the observed behavior.

The best value of the interdiffusion coefficient for regeneration was selected by trial and error. The final selection of the value was made by examining its influence on both regeneration itself and also on performance in the succeeding service cycle. The impact of changing the diffusion coefficient is considered in detail in the discussion below. The selected values of the interdiffusion coefficient for service and regeneration were 8×10^{-5} and $3 \times 10^{-4} \text{ cm}^2/\text{hr}$, respectively. With these values the agreement between the observed and predicted results are shown in figures 3-17 to 3-24.

Figures 3-18, 3-19, 3-20 and 3-21 compare the measured ammonium elution as a function of bed volumes of regenerant applied with computer predictions. The solid lines represent the measured data taken from Figures 2-3 and 2-5. The predicted curves depicted in these Figures fall within the bounds of reproducibility shown in Figure 2-2.

Breakthrough curves obtained following 3 hours regeneration at different regenerant flow rates are depicted in Figure 3-22. All the service cycles

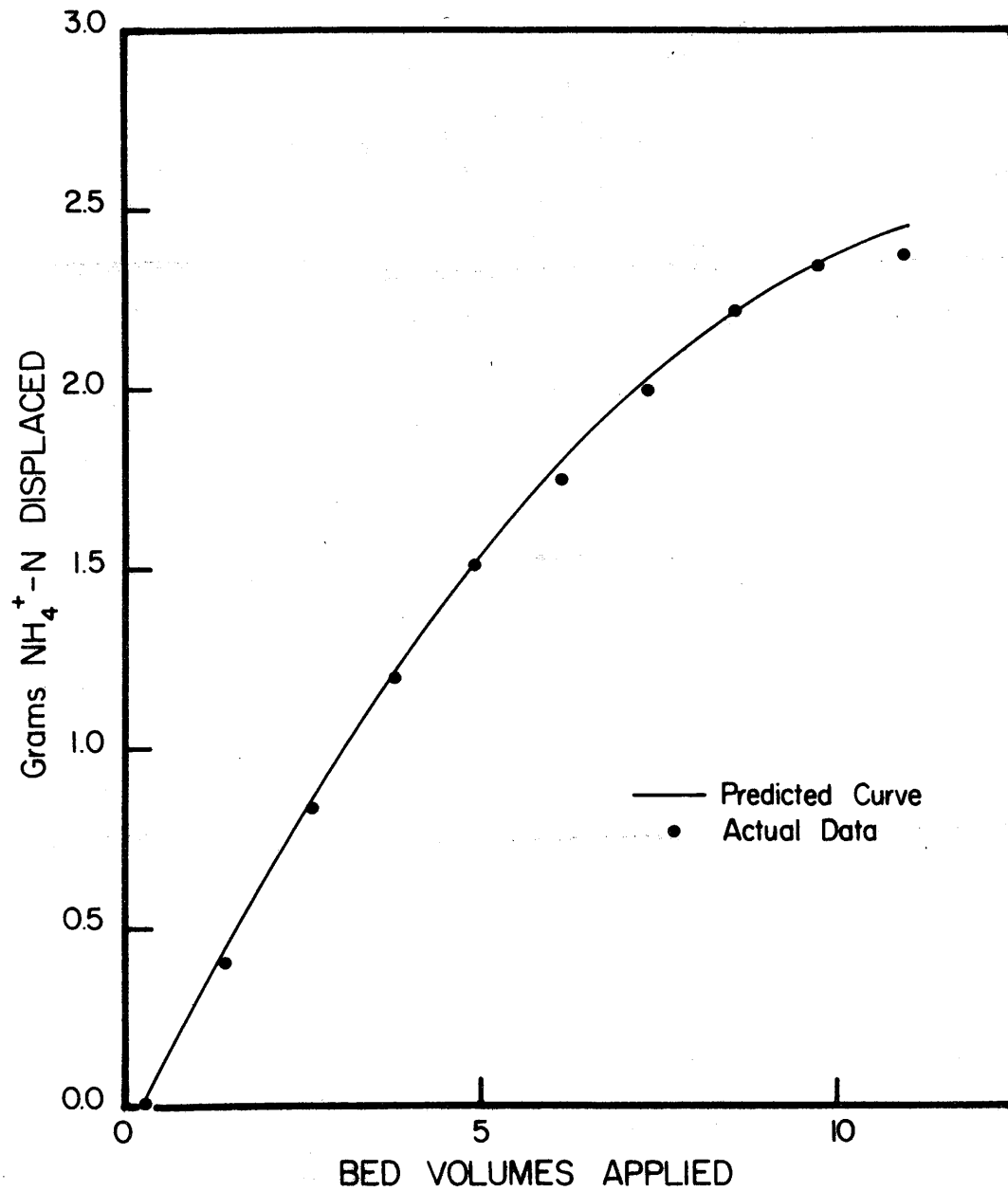


FIGURE 3-18 MODEL PREDICTION OF AMMONIUM DISPLACEMENT
DURING REGENERATION
CASE 4R

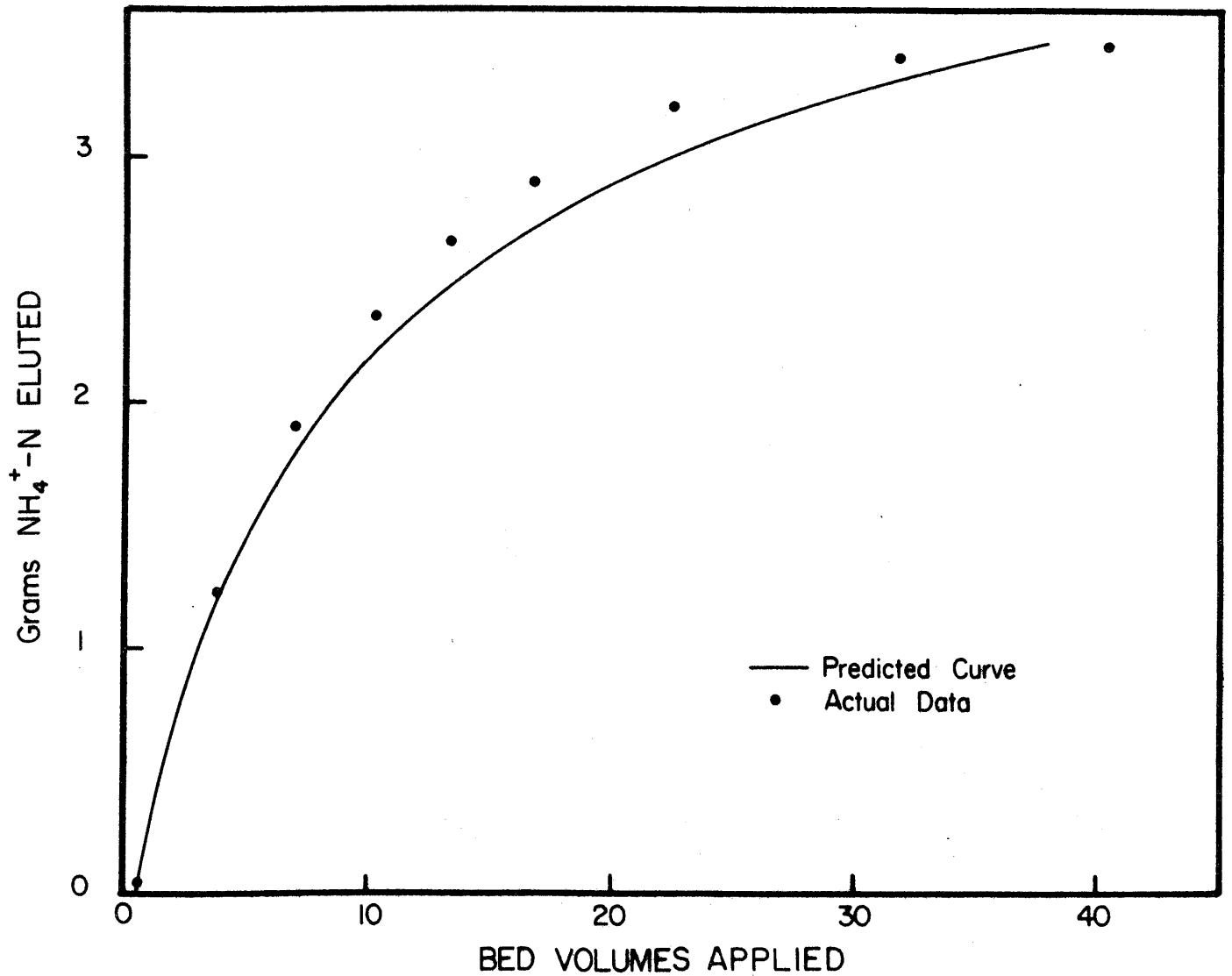


FIGURE 3-19 MODEL PREDICTION OF AMMONIUM DISPLACEMENT DURING REGENERATION
CASE 9R

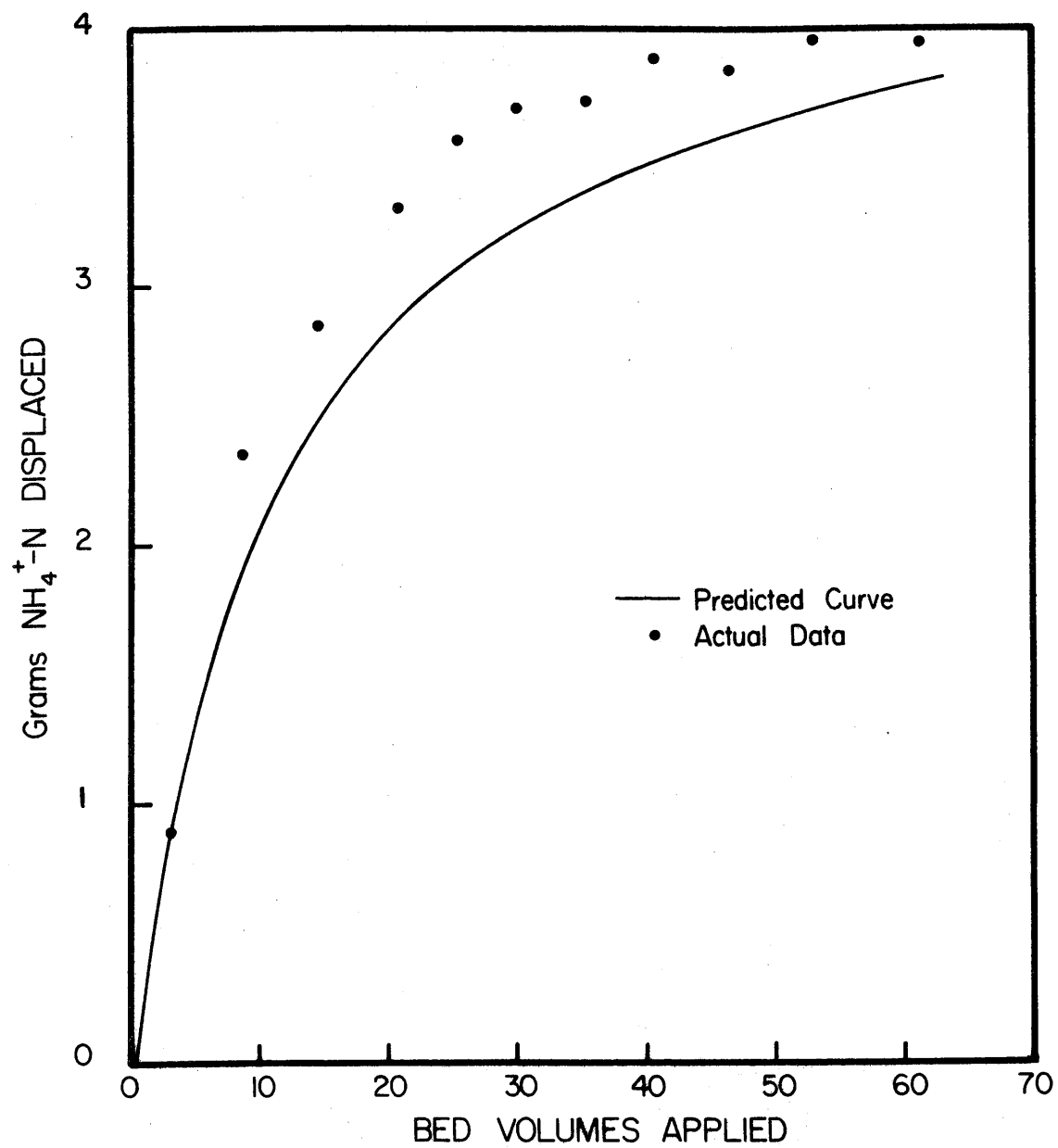


FIGURE 3-20 MODEL PREDICTION OF AMMONIUM DISPLACEMENT
DURING REGENERATION
CASE 8R

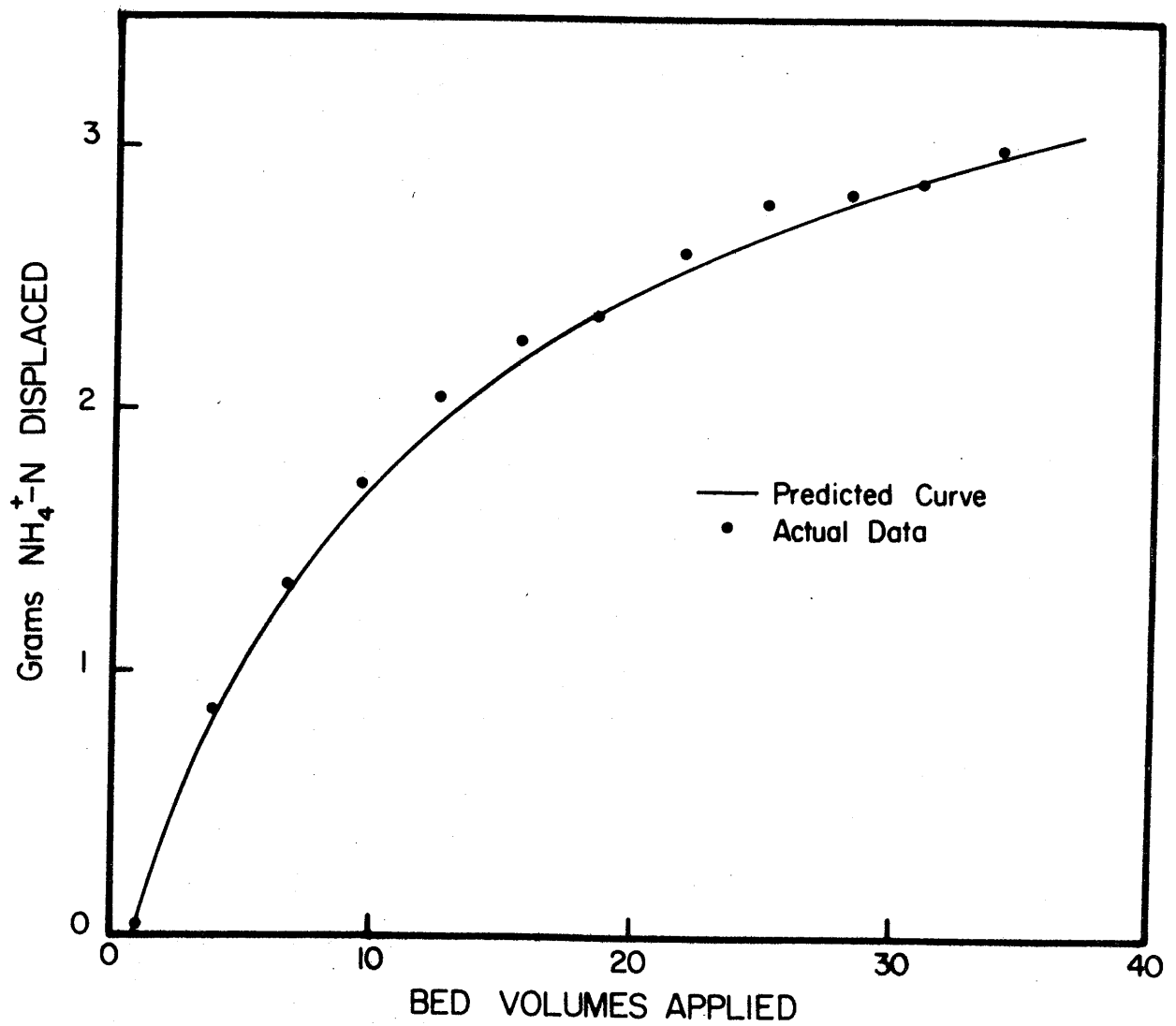


FIGURE 3-21 MODEL PREDICTION OF AMMONIUM DISPLACEMENT DURING REGENERATION CASE 13R.

TABLE 3-3

SERVICE TEST CONDITIONS:

Run #	Flowrate liters/hrs.	BV/hr.	Temp °C	NH ₄ -N Conc. Mg/l	Preceding Regeneration Run #
4s	13.70	19.7	26.0	19.1	4R
8s	13.75	19.8	21.6	19.1	8R
9s	13.50	19.4	21.0	19.0	9R
13s	13.67	19.67	22.5	19.5	13R
20s	20.25	29.2		10.0	20R

REGENERATION TEST CONDITIONS

Run #	Flowrate litres/hrs.	BV/hr.	Temp °C	Brine Conc. M	Preceding Service Run #
4R	3.29	4.73	28.0	0.3	3S
8R	14.7	21.1	23.5	0.3	7S
9R	9.0	12.9	22.5	0.3	8S
13R	8.59	12.36	20.6	0.2	12S
20R	13.97	20.10	20.0	0.3	19S

were operated under almost identical conditions as noted above. The influent ammonium concentration and flow rate during service are recorded in Table 3-3. As observed in Section 2 the extent of ammonium leakage decreased and the column capacity increased with increasing volumes of regenerant applied to the column. Mass balances on ammonium displaced during regeneration and ammonium removed during the previous service cycle showed good agreement.

Table 3-4
The Effect of Regenerant Volume on Column
Capacity and Leakage

Run #	Bed Volumes Regenerant Applied	Ammonium-N Removed Grams		Ammonium-N Leakage Following Regeneration, mg/l	
		Observed	Predicted	Observed	Predicted
4R	14.2	2.66	2.6	0.3-0.4	0.3-0.4
9R	38.7	3.42	3.3	0.2	0.2-0.3
8R	63.6	3.92	4.09	0.1-0.2	0.15-0.25

The computer predicted breakthrough curves are also plotted on Figure 3-22 and the predicted capacities and leakage are summarized in Table 3-4 for comparison with the observed results. It is apparent that the predicted breakthrough occurs before the observed breakthrough for run 4s and after run 8s. In addition, the observed ammonium breakthrough curve always approached the influent ammonium concentration more rapidly than the predicted curve. The actual shape of the predicted breakthrough curve was better in Figures 3-8 - 3-10. However, the combined regeneration-service model was able to predict leakage and breakthrough quite accurately.

To test the models further the regeneration and service programs were used to predict the breakthrough curve for cycle 20s (see Table 3-3). In this cycle the service flowrate was increased to 30 BV/hr and the ammonium concentration was reduced to 10 mg/l. The predicted curve is plotted in Figure 3-23 with the observed data. The correlation between observed and predicted results is only fair. The initial ammonium leakage observed was significantly higher than predicted probably as a result of insufficient rinsing. More importantly however, there was significant deviation between the predicted and observed curves for the initial rise in the breakthrough curve. The computer predicted 11 hours service for an effluent ammonium concentration of 2 mg/l to be reached whereas this concentration was observed in 10 hours. More positively, the actual leakage did fall to predicted levels and the upper portion of the breakthrough was modelled quite accurately.

Changing the influent ammonium concentration during service requires that the service isotherm be modified to take account of the change in the ionic strength. The corrected isotherm is obtained from Figure 3-12. The next test was conducted to determine whether the regeneration isotherm could be extended to other similar but different regenerant concentrations, and still reliably predict regeneration and service performance. In order to determine how Figure 3-15 would change with a change in regenerant concentration one must reconsider equation 3-9.

This equation may be written with a non-dimensional concentration in the form:

$$q^* = \frac{b (C_n/C_T)}{1 + b' (C_n/C_T)} \quad \text{_____} \quad (3-12)$$

where $b = Q^0$

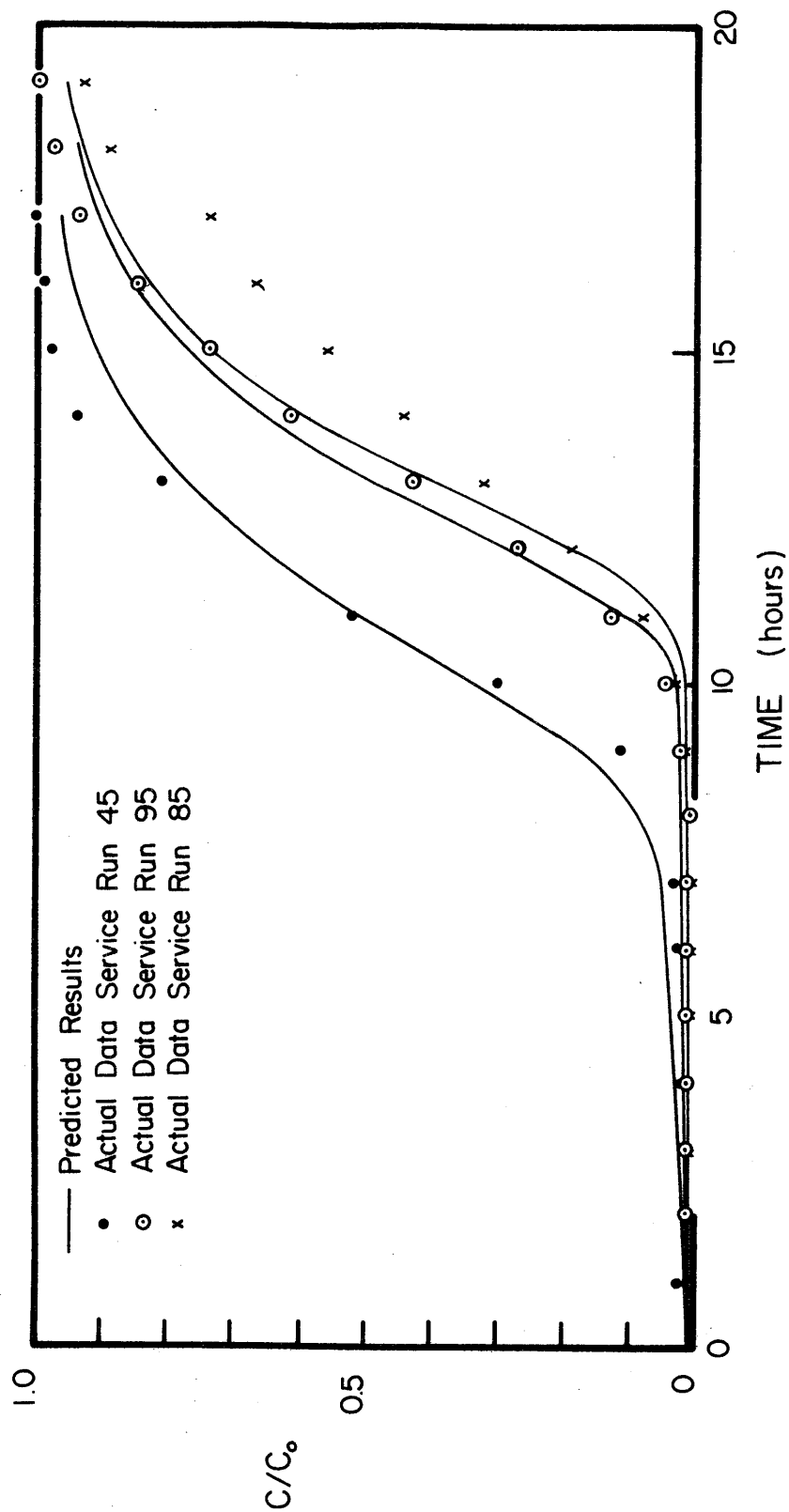
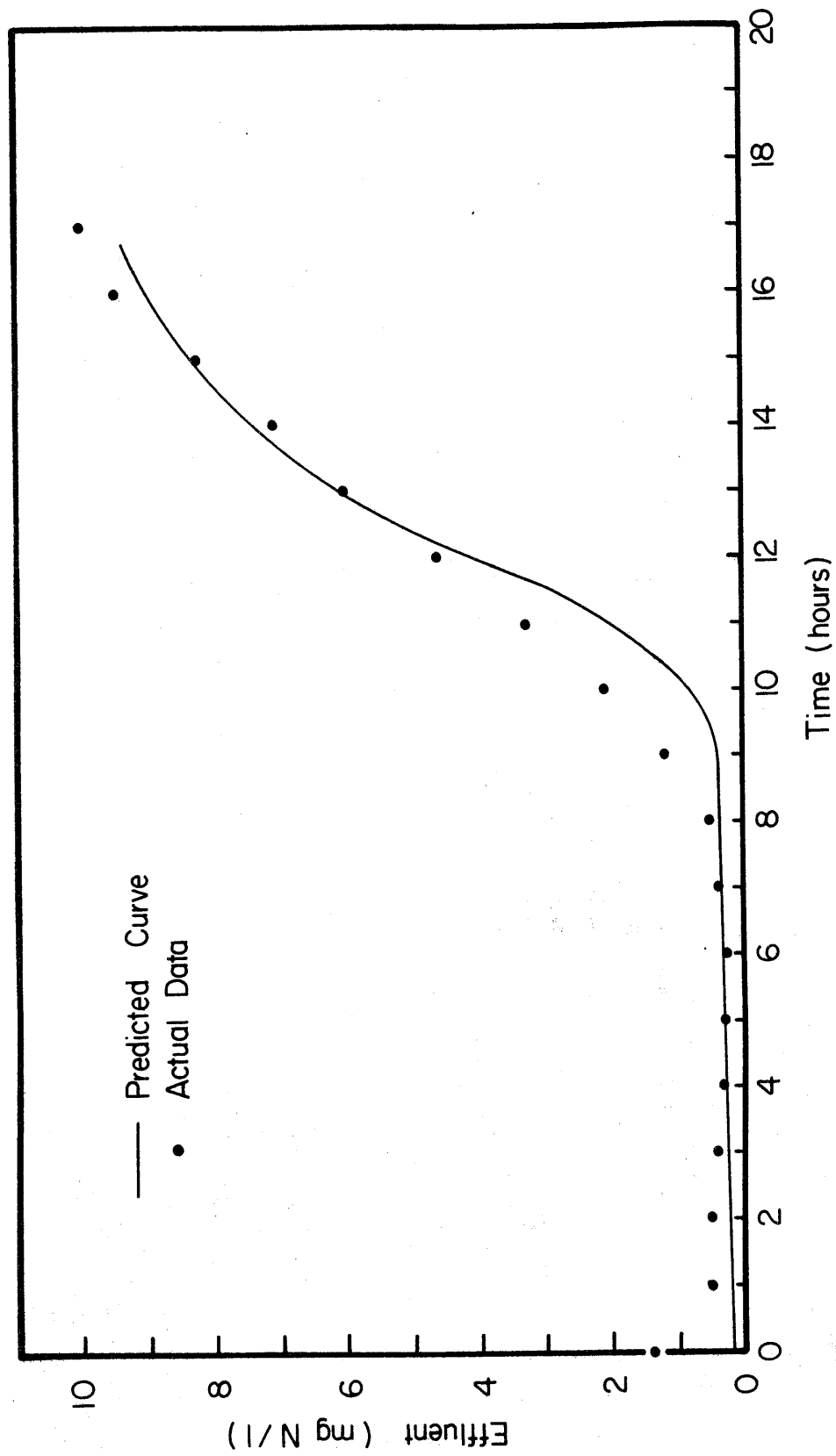


FIGURE 3-22 PREDICTED BREAKTHROUGH CURVES FOR CASES 4S, 8S AND 9S

Figure 3-23. Predicted Breakthrough Curves for Case 20S



and $b' = (1-r)/14$ and all other symbols remain as previously defined. Thus the equation in a nondimensional form should be applicable to different regenerant concentrations as long as the concentrations are not too dissimilar. Since in this study a Freundlich Isotherm was obtained, then the isotherm shown in Figure 3-16 for 0.3M NaCl could be modified as indicated in equation 3-13.

$$q_n = K \left(\frac{C_n}{300} \cdot C_T' \right)^n \quad (3-13)$$

where $C_T' = \text{meq/l}$ of salt in the regenerant used.

A study was conducted using 0.2M NaCl as a regenerant (i.e. $C_T' = 200$). The modified isotherm was employed in the regeneration model to predict the behavior observed in run 13R. The comparison between predicted and observed behavior is plotted in Figure 3-23, and compared with the results of run 9R in which the regenerant concentration was 300 meq/l. The predicted ammonium displacement rate is slightly less than observed consistently for both 9R and 13R. However, predicted performance in the following service cycle, shown in Figure 3-24, compares very well with the observed breakthrough curve.

Discussion:

The computer models for regeneration and service interface well on the computer and predict observed performance quite well for a varying regeneration and service operating conditions. The isotherms obtained in this study are reported in a non-dimensional way and the information provided may be reasonably extended to predict the influence of varying regenerant strengths between approximately 0.2 and 0.4M NaCl and varying ammonium concentrations between 5 and 40 mgN/L in the influent wastewater. Unfortunately the information provided was evaluated for clinoptilolite obtained from Buckhorn, New Mexico and, therefore, it does not necessarily indicate how clinoptilolite obtained

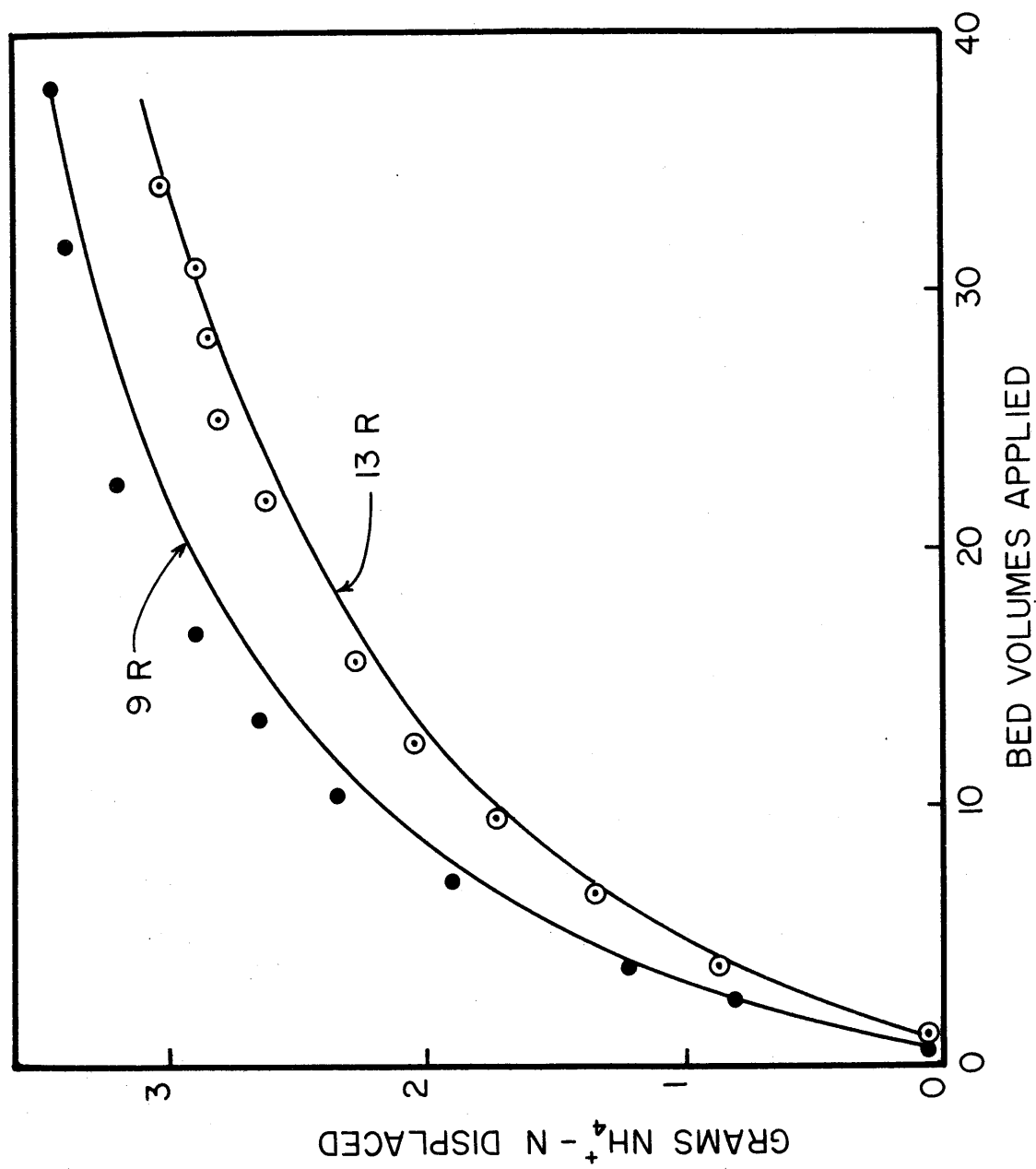


FIGURE 3-23 IMPACT OF BRINE CONCENTRATION ON AMMONIUM DISPLACEMENT

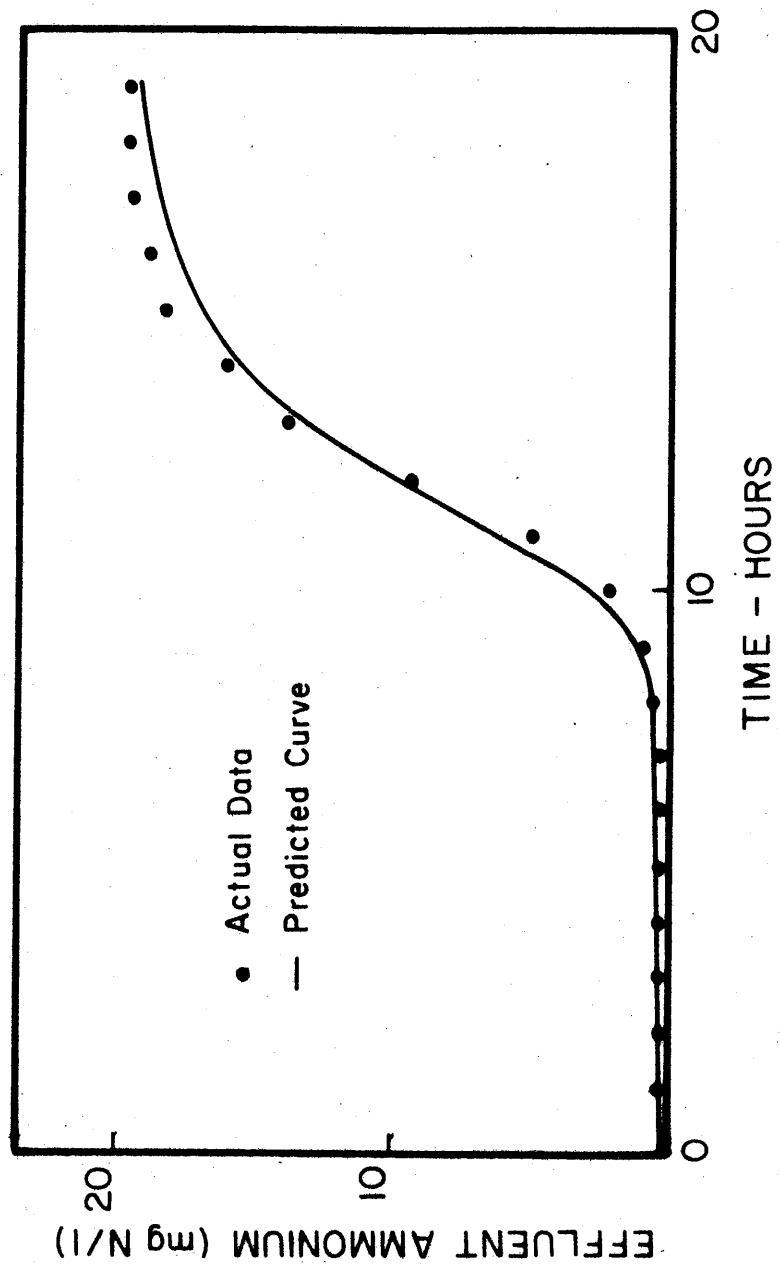


FIGURE 3-24 PREDICTION OF BREAKTHROUGH CURVE FOLLOWING
REGENERATION WITH 0.2M NaCl

from other sources will behave.

The development of interfacing models represents a significant improvement in the tools available to design engineers. The models should for example enable the following questions to be answered:

1. How much ammonium may be tolerated in the regenerant if it is recycled?
 2. What is the impact of using staged regeneration to approach continuous countercurrent regeneration performance?
 3. What benefit would there be to using two columns in series under different loading conditions?
- etc.

The models developed in this study work quite well but could be improved significantly. The areas that appear weakest are the equilibrium isotherms themselves. The equilibrium isotherm for the service cycle, Fig. 3-11, was evaluated in triplicate and is considered reliable except perhaps at low ammonium concentrations (i.e. $< 4\text{mg/L}$) where little data was collected. The regeneration isotherm is probably responsible for most of the deviation of the predicted results from observed performance. The kinetic effects that interfered with the equilibrium measurements leave some questions as to the validity of the isotherm used. Would equilibrium actually be realized in column regeneration tests? Intuitively it seems doubtful. Furthermore, there was a lack of data collected for low ammonium concentrations. The results obtained in this region were for 1 hour batch equilibrium tests which proved obviously inaccurate for higher ammonium concentrations. They are, therefore, also likely to be inaccurate for low ammonium concentrations. Another indication of the inaccuracy of the regeneration is the very high

interdiffusion coefficient obtained by fitting the regeneration data, 3×10^{-4} cm/hr. This value is four times higher than the calculated coefficient obtained for the service cycle, 8×10^{-5} cm/hr. The interdiffusion coefficient values are not expected to be exactly the same but the observed difference is larger than anticipated.

Before the models may be expected to accurately predict performance under varying conditions, an improved technique for collecting the isotherm data will be required.



Section 4

An Evaluation of Alternative Natural Zeolites
and Pretreatments for Improved Ammonium Removal

INTRODUCTION

The clinoptilolite is normally crushed and graded when it is mined before being used as an ion exchange medium. However, the capacity of clinoptilolite is influenced significantly by chemical and physical treatments. In practice facilities using untreated clinoptilolite may observe an improvement in performance following several service-regeneration cycles. Figure 4-1 shows breakthrough curves obtained for ammonium removal by clinoptilolite in which curve I was obtained with freshly graded untreated zeolite and curve II was obtained after several service-regeneration cycles.

The influence of pretreatments on zeolite capacity and selectivity is poorly documented, and where information exists, care must be exercised in comparing the zeolite capacities and pretreatment effects reported. The capacity of a zeolite varies with the source of the zeolite, the location within a particular deposit and the capacity measurement technique employed. Past studies evaluating the capacity of clinoptilolite samples had received slight pretreatment were summarized by Koon and Kaufman (1) as shown in Table 4-1. It can be seen that slight acid pretreatment as employed by Ames (2,3) did nothing to improve the clinoptilolite's capacity. Acid would be expected to dissolve basic impurities which may block pores and/or add weight to the zeolite.

Murphy, et al., (8) compared various pretreated clinoptilolite samples

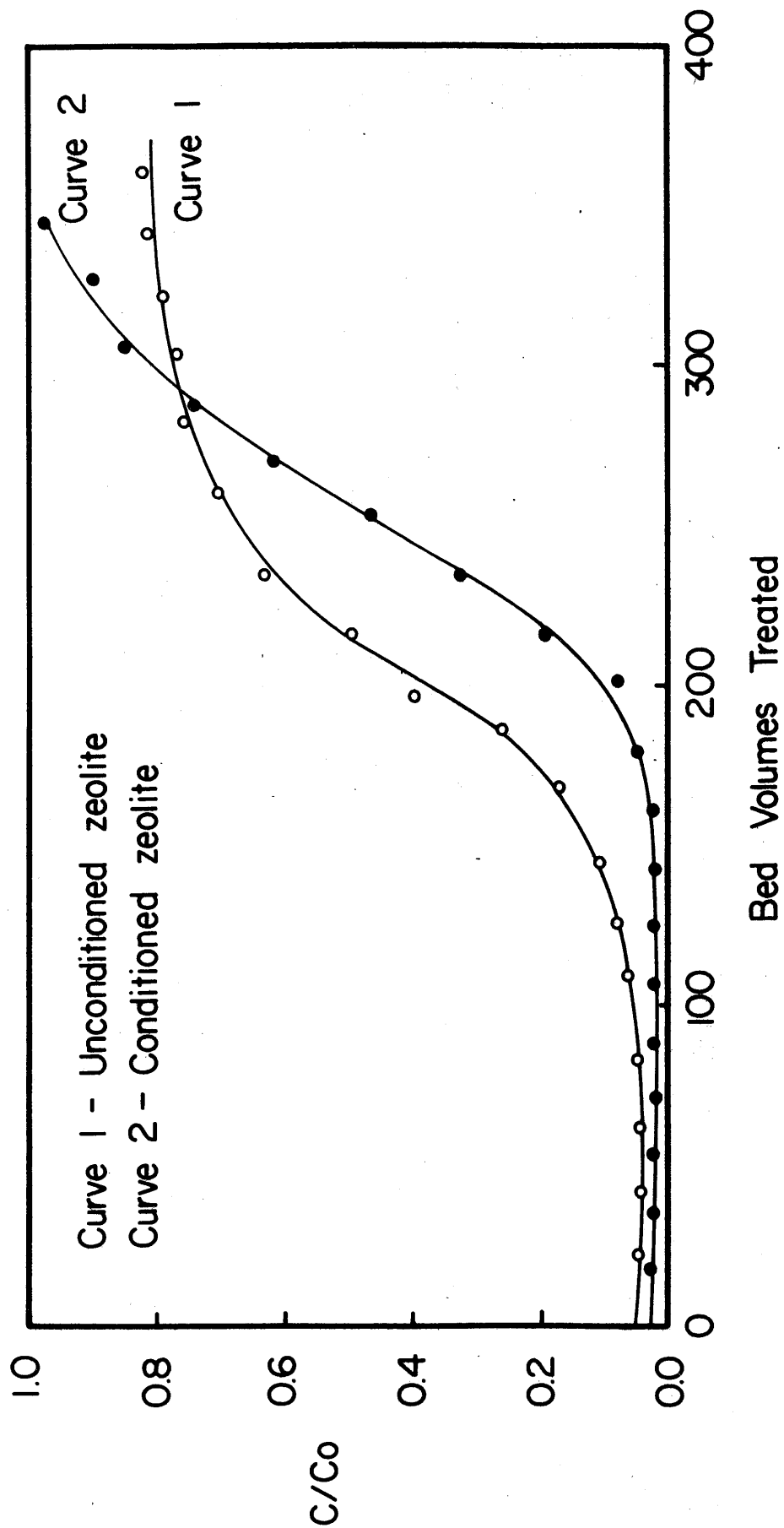


Figure 4-1. The impact of conditioning on ammonium breakthrough curves for clinoptilolite (Influent $\text{NH}_4^+-\text{N} = 20 \text{ mg/l}$, 20 Bv/hr)

TABLE 4-1 ION EXCHANGE CAPACITIES OF CLINOPTILOLITE

Study Number	Reference	Capacity, meq/g	Ion used	Size Material	Method
1	Ames (25)	1.7	Na ⁺ replaced by Cs ⁺ ; Cs ⁺ replaced by Na ⁺	Not specified	Double tracing technique; substantiated by titration of H ⁺ based sample.
2	Ames (26)	1.7	Li ⁺ replaced by Cs ⁺ ; Ba ⁺⁺ replaced	0.25-0.50 mm (35x60 mesh)	Shallow bed method using radioactive tracers.
3	Ames (13)	1.81	NH ₄ ⁺	30x50 mesh	Not specified
4	Howery and Thomas (28)	2.05 2.04 1.97	Na ⁺ Cs ⁺ NH ₄ ⁺	30x80 mesh	Small column method; direct determination of NH ₄ ⁺ by distillation of clinoptilolite in kjeldahl flask. 4-3 Determination of Na ⁺ and Cs ⁺ radiochemically; determination of NH ₄ ⁺ by difference from an Na ⁺ based clinoptilolite
5	Barrer, Papadopoulos, and Rees (17)	1.83	Na ⁺ replaced by NH ₄ ⁺	18x30 mesh	Na ⁺ measured radiochemically by analyses of nitrogen in the NH ₄ exchanged sample.
6	Frysinger (29)	1.61	Cs ⁺	20x40 mesh	Column method using radioactive Cs ⁺ as tracer

^aClinoptilolite from John Day Formation, Oregon. Other samples from Hector, Calif. except that used by Frysinger who did not specify the source.

for ammonium removal from municipal wastewater. Hector clinoptilolite was contacted in a batch pretreatment process with the solutions of 1) acid, 2) alkali, 3) alkali followed by NaCl and 4) acid followed by NaOH and then NaCl. Capacities were measured using a sequential batch equilibration (2 hours) technique. The authors concluded that pretreatment 4 resulted in the greatest increase in exchange capacity; 20% over samples lacking pretreatment. The other pretreatments resulted in an increase in the exchange capacity of 5% or less. Additional studies indicated that the influence of a pretreatment on zeolite capacity varied widely depending on the source of the clinoptilolite.

Seyforth et al (30) investigated the influence of pretreatment on the capacity of clinoptilolite (Buckhorn, New Mexico) for ammonium ions. To ensure meaningful capacity values were measured, a zeolite sample was conditioned by several alternate treatments with 0.4N NH_4Cl and 1N NaCl. Portions of this sample were given additional treatments. One portion was reconditioned repeating the conditioning procedure but an alkaline (pH 10) 1N NaCl regenerant was employed. The other portion was exposed to excess 10% HNO_3 for an hour and then 1N NaCl to convert the zeolite to the Na^+ form. All zeolite samples were dried before use for convenience.

The average capacities of the several different preparations of clinoptilolite were not the same as shown in Table 4-2. The capacity of the conditioned zeolite, 1.69 ± 0.08 meq/g dry zeolite, was smaller than those of the reconditioned and acid-washed zeolite, 1.82 ± 0.23 and 1.86 ± 0.05 meq/g dry zeolite, respectively. Although the latter two preparations gave approximately the same average capacity, the variability in the value of the reconditioned zeolite was much greater than that of the acid-washed zeolite. Reconditioning with a salt solution adjusted to pH 10.0 should have removed acidic impurities

from the zeolite. Similarly, acid-washing should have removed any basic impurities.

Table 4-2
Results of the Capacity Tests Conducted by Seyforth (30)

Type of Clinoptilolite Sample	Number of Samples Tested	Capacity meq/gram	Sample Test Number
Conditioned	5	1.69 ± 0.08	1
Conditioned	3	2.11 ± 0.10	2
Conditioned	2	2.23 ± 0.01	3
Reconditioned	6	1.82 ± 0.23	1
Reconditioned	2	2.25 ± 0.07	2
Acid Washed	4*	1.85 ± 0.05	1

*Capacities measured by both ammonium and sodium elution studies.

When capacity tests on the same zeolite sample were repeated following regeneration with 1N NaCl, the zeolite capacities were observed to increase. After repeating the test three times the capacity appeared to level off at 2.24 meq/g dry zeolite.

Jorgensen, et al. (31) also noted that the capacity of a sample of clinoptilolite increased with the number of regenerations. Their regeneration process consisted of treatment with 4 percent NaOH for 30 minutes, followed by a rinse with one liter of deionized water for 40 minutes. After repeating this procedure four times, the measured capacity was found to be constant. They concluded that the sodium hydroxide "activates" the clinoptilolite. The results of Seyforth's study suggest that it was not necessarily the sodium hydroxide which was responsible for the increased capacity. It may, however, be related

to the number of exchange cycles that the zeolite is exposed to after being oven dried at 103°C. This may be seen by comparing the conditioned and reconditioned zeolite capacities in Table 4-2. Since the reconditioned zeolite was exposed to an additional 2 conditioning cycles, one might expect the first capacity test with this sample to be approximately equal to the third measured capacity of the conditioned zeolite. There is, however, a significant difference in these values and the first capacity measurement of the conditioned and reconditioned samples are closer in value.

In summary, therefore, the capacity of natural zeolite is influenced significantly by the pretreatments the zeolite has received and the influence of various pretreatments is poorly documented. In addition, zeolites other than clinoptilolite have not been evaluated for removing ammonium from wastewater by ion exchange. Hayhurst (32) evaluated mordenite, phillipsite and clinoptilolite for removing NH_3 from gas streams. Phillipsite was demonstrated to be best in removing NH_3 from gas.

This paper presents the results of some laboratory studies to evaluate phillipsite, mordenite, erionite and pretreated clinoptilolites for ammonium removal from wastewater. Ammonium capacities were measured in two ways: 1) using a 100 mg/l solution of NH_4^+ -N as a feed solution in column exhaustion tests and 2) using a synthetic sewage containing 14 mg/l NH_4^+ -N as a feed solution in column exhaustion tests. Packed bed densities were determined to convert observed capacities on a weight of zeolite basis to capacities on a volume of zeolite basis. A crushing test was used to assess physical differences in the zeolites.

II. LABORATORY TECHNIQUES AND EQUIPMENT

A. Grading and Pretreating the Zeolites

Twenty-five pound samples of erionite, mordenite, and phillipsite were

provided by Anaconda Company for use in this study. Clinoptilolite from Buckhorn, New Mexico was provided by Double Eagle Mining Company and graded with U.S. standard mesh sieves. The 20x30 mesh fractions were retained for use in this study.

Zeolite samples were pretreated in different ways. Solutions were pumped from a feed reservoir upflow through a 2.5 cm acrylic column containing approximately 80 g of a zeolite sample. A nylon screen supported the zeolite in the column. Table 4-3 presents the various pretreatment conditions employed to prepare the zeolite samples.

All samples were treated with approximately 4 liters of 1N NaCl over a 2 hour period. Some samples were given 2 treatments. Following NaCl treatment zeolite samples were washed with deionized water. Nitric acid treatment was accomplished by contacting a zeolite sample with 2 liters of 1N HNO₃ over a 1 hour period. Samples 5 and 5B were contacted with 1N NaOH treatments of 2 liters in 70 minutes and 3 liters in 110 minutes, respectively. The heat treated zeolite samples were heated to 600°C for 1 hour, cooled over night and rewetted. Some samples were autoclaved at 30 psig (120°C) for one hour.

B. Testing the Zeolites

Measurements were made of the total ammonium capacities of the pretreated zeolites. In addition, their capacities for ammonium in the presence of competing ions were measured to determine any improvement in selectivity.

i) Total Capacity Measurements

A 50 ml. burette containing 30 ml. of pretreated zeolite supported on a glass wool plug was contacted downflow with a solution of ammonium chloride (100 mg/l NH₄⁺ -N) in deionized water. The apparatus is depicted schematically in Figure 4-2. The feed solution was supplied to the column from an elevated reservoir at a flow rate of 20 bed volumes/hr. (10 ml/min.). One liter samples

Table 4-3

PRETREATMENT SCHEME FOR CLINOPTILOLITE SAMPLES TESTED

Sample	First NaCl	Backwash	HNO ₃ Rinse	NaOH Rinse	Heat Treatment	Autoclaving	Second NaCl + Rinse
Clinoptilolite 1	x	x					
Clinoptilolite 1B	x	x					
Clinoptilolite 2	x	x	x				x
Clinoptilolite 2B	x	x	x				x
Clinoptilolite 3	x	x			x		x
Clinoptilolite 3B	x	x			x	x	x
Clinoptilolite 4	x	x			x	x	x
Clinoptilolite 5	x	x		x			x
Clinoptilolite 5B	x	x		x			x
Phillipsite	x	x					
Mordenite	x	x					
Irionite	x	x					

4-8

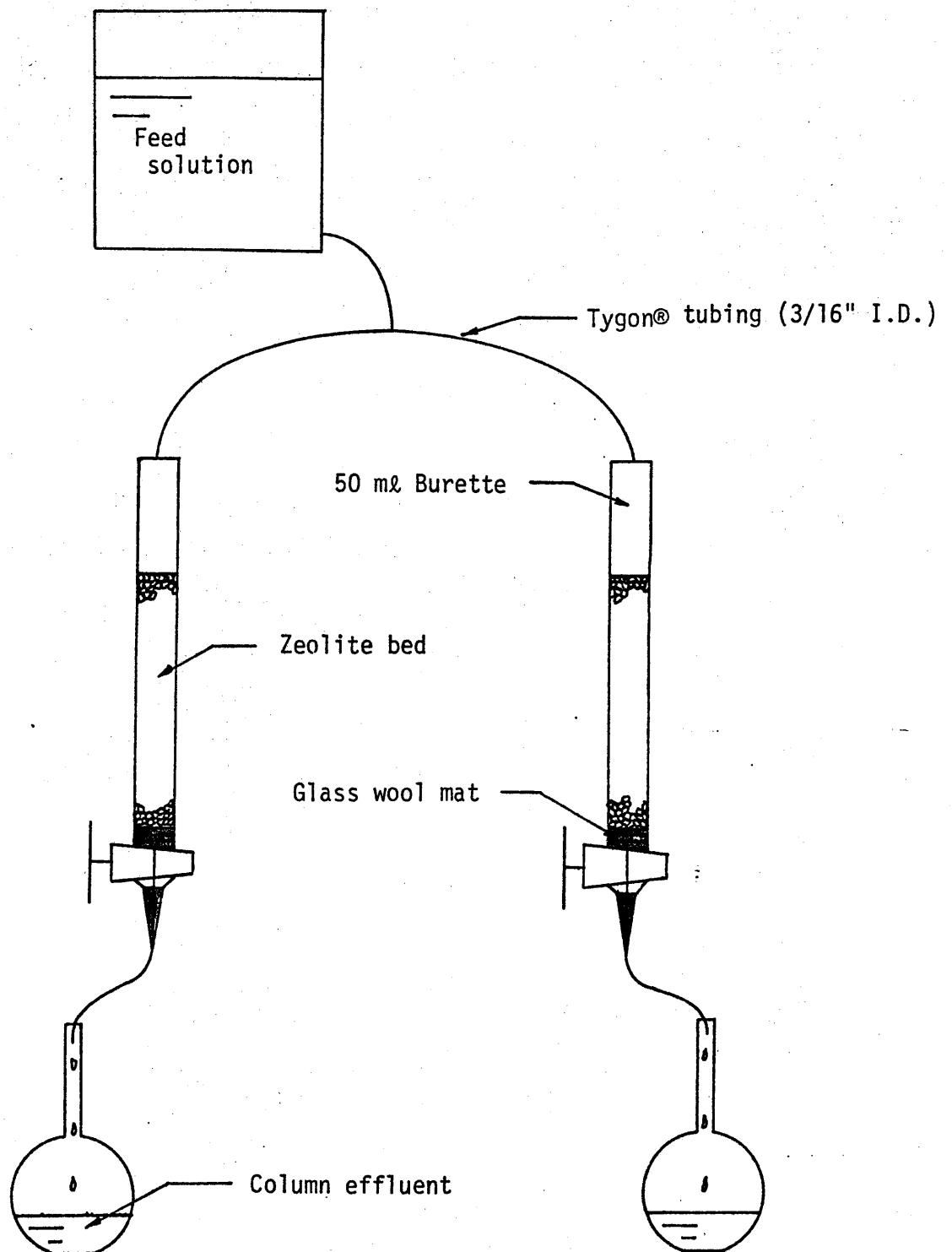


FIGURE 4-2 APPARATUS FOR EXHAUSTING THE ZEOLITES

of the column effluent were collected and analyzed for ammonium concentration. Samples of the feed were analyzed for ammonium concentration each time an effluent sample was collected to ensure there was no change in the feed ammonium concentration during the test period. When the effluent ammonium concentration was the same as that of the feed (within analytical error), the zeolite was flushed with deionized water removed from the column, dried and weighed.

ii) Total Operating Capacity Measurements

These measurements were made using exactly the same procedure employed for total capacity measurements except that the feed solution had the composition presented in Table 4.4. This solution composition was identical to that used by Breck (33).

Table 4-4
COMPOSITION OF THE SYNTHETIC SEWAGE (33)

Element	Concentration	Compound Used
NH_4^+	14 mg/l	$(\text{NH}_4)_2 \text{SO}_4$
Na^+	58 mg/l	NaCl , NaHCO_3
K^+	12 mg/l	KCl
Mg^{++}	8 mg/l	MgSO_4
Ca^{++}	34 mg/l	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
pH	7.45	adjusted with proper ratio of NaHCO_3 to NaCl

C. Analytical Techniques

Ammonium measurements were made using an Orion Model 95-10 ammonia

selective electrode connected to an Orion Model 701 digital pH/mV meter. The electrode tended to drift and standard ammonia samples were analyzed between every analysis of an unknown sample as a check on the calibration curve. Duplicates of the unknown samples and occasionally triplicates of the unknown samples were run when the drift was excessive.

To weigh the zeolites in a reproducible way wet zeolite samples were dried in a 100°C oven overnight and then placed in a desiccator over a saturated solution of NaCl. The desiccator was placed in a constant temperature (37°C) oven to maintain a constant temperature--constant humidity environment (34). The samples were held in the desiccator for 2 to 3 days to assure equilibrium with the humidity in the desiccator.

Zeolite Packed Bed Densities

Since the specific gravity and packing characteristics of the zeolites vary, packed bed densities were measured in order that volumetric capacities could be determined. Volumetric capacities are important for sizing ion exchange equipment.

A 25 ml graduated cylinder filled partially with water was filled to 25 ml with wet zeolite. The cylinder was rapped on the lab counter until the zeolite volume showed no further reduction. Final volume was recorded. The samples were removed from the cylinder, dried and weighed.

E. Zeolite Strength

To compare the physical strength of the zeolite samples a crushing test developed by Hayhurst (32) was used. Zeolites employed in column operations are prone to physical attrition during backwashing and regeneration cycles. It is desirable therefore to compare the physical strength of the zeolites in order to determine their suitability for column operation.

A single zeolite grain was placed on the weighing pan of a top loading-direct reading Mettler Balance. The balance was positioned beneath a drill

press fitted with a 1/4 inch steel rod. The rod was slowly lowered on to zeolite particle and pressure was applied gradually until the grain fractured. The weight required to crush the particle was recorded as a measure of crushing strength. The test was run on 20 grains of each zeolite sample to obtain a significant mean value for comparative purposes.

RESULTS

The results of the capacity tests are presented in Tables 4-5 and 4-6. The test techniques ensured excellent reproducibility as indicated by the standard deviation values. Clinoptilolite samples 1, 2 and 4 all had an average total ammonium capacity of 1.63-1.64 meq/g. Sample 3 treated clinoptilolite had a somewhat lower capacity of 1.57 meq/g and sample 5, the sample that received a treatment of sodium hydroxide had the highest observed capacity of 1.77 meq/g.

Mordenite had a similar capacity to clinoptilolite but erionite had a very much lower total exchange capacity of only 0.3 meq/g. Phillipsite, with a capacity of 2.64 meq/g was clearly superior to clinoptilolite.

Tests on the ammonium capacities measured following exposure to synthetic sewage indicated that the heat treated clinoptilolite (sample 3) was most selective for ammonium. The other clinoptilolite samples showed that the other pretreatment techniques had little impact on ammonium selectivity. Phillipsite was equally selective for ammonium and its higher total capacity resulted in an effective capacity that was about double that of clinoptilolite on a weight basis.

The packed bed densities of the zeolite samples are presented in Table 4-7. The type of pretreatment had no effect on the packed density of clinoptilolite which remained at a value of approximately 0.85 grams dry zeolite/ml. The phillipsite was considerably lighter, having a packed density of only 0.53

Table 4-5

CAPACITY OF ZEOLITES USING 100 mg NH_4^+ -N/g
SOLUTION AS THE FEED SOLUTION

Zeolite	Capacity (meq NH_4^+ -N/g)	
	Individual Tests	Mean
Clinoptilolite 1	1.70, 1.61, 1.60, 1.61, 1.64	1.63 ($\sigma = .04$)
Clinoptilolite 2	1.51, 1.61, 1.76, 1.67, 1.65	1.64 ($\sigma = .09$)
Clinoptilolite 3	1.62, 1.50, 1.57, 1.57	1.57 ($\sigma = .05$)
Clinoptilolite 5	1.85, 1.73, 1.75, 1.75	1.77 ($\sigma = .05$)
Phillipsite	2.73, 2.55	2.64 ($\sigma = .13$)
Mordenite	1.76, 1.83	1.80 ($\sigma = .05$)
Erionite	.30	.30

Table 4-6

CAPACITY OF ZEOLITES USING SYNTHETIC SEWAGE AS THE FEED SOLUTION

Zeolite	Capacity (meq NH_4^+ - N/g)	
	Individual Tests	Mean
Clinoptilolite 1	.499, .502, .498	.500 ($\sigma = .002$)
Clinoptilolite 2	.530, .514, .526	.523 ($\sigma = .008$)
Clinoptilolite 3	.590, .594	.592 ($\sigma = .003$)
Clinoptilolite 5	.500, .514	.507 ($\sigma = .010$)
Phillipsite	.970, 1.031	1.001 ($\sigma = .043$)
Mordenite	.439, .444	.442 ($\sigma = .004$)

TABLE 4-7

PACKED BED DENSITIES OF 20x30 MESH ZEOLITE IN Na⁺ FORM

Zeolite	Packed bed density g dry zeolite/submerged ml
Clinoptilolite 1	.848
Clinoptilolite 2	.844
Clinoptilolite 3	.853
Clinoptilolite 4	.849
Clinoptilolite 5	.857
Mordenite	.699
Phillipsite	.534
Erionite	.503

TABLE 4-8

RESULTS OF CRUSHING TEST

Zeolite	Number of tests	Mean Crushing Strength (g)	σ
Clinoptilolite 1	20	366	114
Clinoptilolite 3	20	329	111
Phillipsite	20	83	63
Mordenite	20	129	100
Erionite	20	105	51

grams of dry zeolite/ml.

The crushing tests indicated that samples 1 and 3 of clinoptilolite had the highest measured crushing strengths. The results are depicted in Table 4-8. The other pretreatments for clinoptilolite reduced the strength of the zeolite. Phillipsite was observed to be extremely friable and yielded a very low crushing strength. The standard deviations were poor for this test and the difference between samples 1 and 3 of clinoptilolite reported in Table 4-8 cannot be considered significant.

DISCUSSION OF RESULTS

The observed capacities of the pretreated clinoptilolite samples tested in this study appear a little lower than those reported by Seyforth (30) for the same batch of clinoptilolite. The reason for this difference in measured capacities may stem from the different techniques employed for measuring the weight of zeolite. Seyforth dried the zeolite at 105°C, cooled it in a desiccator and weighed the dry zeolite. In this study it was observed, however, that this technique could cause significant variation in the measured weight of a zeolite sample. Natural zeolites are extremely effective dessicants themselves and the dried zeolite samples compete with chemical dessicants for the available water. Thus, if the dessicant used is partially exhausted, the zeolite may extract some of the available water and as a result weigh heavier than when fresh dessicant is used. The preferred equilibration with a constant, high humidity atmosphere gives more reproducible results but the absorbed water tends to make the weight capacity appear smaller.

As noted above, differences between the clinoptilolite sample studied and other zeolites preclude direct comparison of these results with those reported by other investigators, but the values obtained (Table 4-5) do appear similar to those reported by others (Table 4-1).

In this study phillipsite was observed to have a weight capacity that was 70% greater than that of similarly treated clinoptilolite. Tests conducted on the selective removal of ammonium from a synthetic sewage containing competing ions indicated that the phillipsite was more selective for ammonium than clinoptilolite and removed twice as much as ammonium on a dry weight basis. However, the low packed bed density of the phillipsite compared to that of clinoptilolite reduced the performance of phillipsite on a volumetric basis. Its volumetric capacity was only 26% better than similarly treated clinoptilolite for ammonium removal from synthetic sewage.

Phillipsite has two disadvantages that must influence its use in water treatment, however. Firstly, this zeolite is structurally very weak and breaks easily. Even in limited laboratory studies physical attrition of the phillipsite was significant and the fines produced created large headlosses in the column studies. Secondly, phillipsite is considerably more expensive than clinoptilolite as shown in Table 4-10.

Table 4-10

APPROXIMATE COST OF ZEOLITES IN BULK QUANTITIES (22) (FOB)

Zeolite	\$/ton
Clinoptilolite	200-210
Phillipsite	400-450
Mordenite	300
Erionite	400

Possibly the attrition problem could be overcome by mixing powdered phillipsite with a porous binder but as can be seen the costs of the zeolite would not be competitive with clinoptilolite. However, if through the use of a binder the packed bed density of the zeolite could be increased without reducing the exchange capacity significantly, then this may prove feasible.

Analysis of the volumetric capacities of the clinoptilolite indicated that the heat treated sample was the best for ammonium removal from synthetic sewage. The heat treated clinoptilolite had approximately 17% more capacity than clinoptilolite that had been exposed only to NaCl. This pretreatment improved the selectivity of the zeolite for NH_4^+ in exchange with competing cations and its measured capacity approached that of phillipsite.

The heat treatment caused the clinoptilolite to turn dark brown, suggesting that iron oxidation had occurred within the zeolite structure. Why this should improve the zeolite's selectivity for NH_4^+ is not clear. Studies conducted by Anaconda have shown that the iron content of clinoptilolite is not exchangeable nor is it leached by applied EDTA (35). X-ray diffraction studies on the variously treated clinoptilolite samples unfortunately provided no evidence of any structural changes. Indeed, all the x-ray diffraction scans on the pretreated samples were identical. Further studies are needed to characterize the influence of heat on the zeolite. In this study a fixed time at a fixed temperature was examined. The time and temperature of pretreatment may be important. In addition, the technique of rehydration may be influential in affecting zeolite performance.

During the course of pretreatment the actual weight of a zeolite sample may change. Thus, capacities reported per unit weight of the pretreated zeolite may be misleading. For example, if pretreatment reduces the weight of a zeolite sample without influencing capacity, then naturally the exchange capacity/unit weight will appear higher. Yet no great advantage may be realized from such a pretreatment. In this study weight changes were recorded for different pretreatments. No significant weight changes were recorded apart from the following:

1. Heat treatment caused a 4% weight loss. Since the total exchange capacity also declined by 4% following heat treatment, it would appear that some exchange sites are lost during heat pretreatment.
2. NaOH pretreatment caused a slight weight gain, 2%. The improved total exchange capacity of the base pretreated zeolite must therefore stem from the exposure of more exchange sites.
3. Acid pretreatment caused a 9% weight loss and no impact on the exchange capacity which suggests that zeolite structure itself may be broken down by the strongly acidic conditions employed in pretreatment.

The ion exchange process is a diffusion controlled process and the kinetics of exchange may be influential in the choice of a zeolite where capacity and selectivity are more or less equal. Some data was collected from the column studies on the pretreated clinoptilolite samples that indicated that the kinetics of exchange were not significantly influenced by pretreatment. Additionally, the kinetics of exchange with phillipsite was comparable with clinoptilolite.

V. CONCLUSIONS

Several pretreated clinoptilolites and other natural zeolites have been evaluated for ammonium removal from wastewater. The following conclusions may be drawn from this study:

1. The weight of a natural zeolite is influenced significantly by the relative humidity. It was therefore necessary to weight zeolites equilibrated with a constant relative humidity in order to obtain accurate and reproducible capacity data.

2. By heat treating clinoptilolite, the zeolites capacity for NH_4^+ was not significantly affected but the zeolite capacity for NH_4^+ -N in the presence of competing cations was observed to increase. The selectivity of the zeolite for ammonium was thus enhanced.

3. By treating the clinoptilolite with NaOH, capacity for NH_4^+ -N using a pure solution of NH_4Cl as feed was slightly improved, but the zeolite's selective capacity for NH_4^+ -N in the presence of competing cations was not affected.

4. Acid and steam treatments did not influence clinoptilolite's capacity for NH_4^+ -N.

5. Erionite, mordenite and phillipsite samples (Anaconda) were also tested although no pretreatments were applied to these other than conversion to the sodium form by 1N NaCl. The phillipsite sample was very effective in ammonium removal but erionite and mordenite behaved poorly.

6. The phillipsite proved to be better than even pretreated clinoptilolite samples in both weight and volumetric capacities. Unfortunately, phillipsite is structurally weak and breaks down easily to produce fines. This will limit application of this zeolite in water treatment. If the strength of the zeolite could be improved through the use of a binder, it may find a wider application.

7. The pretreatments used for clinoptilolite apparently had little influence on the kinetics of ammonium removal.



Section 5

Pilot Studies with Sequential Biological Regeneration

INTRODUCTION

Following the studies on the neutral pH regeneration of clinoptilolite with sodium chloride studies were initiated on sequential biological regeneration. The process scheme is depicted schematically in Figure 1-2.

The objectives of this study were as follows:

- 1.) To identify the impact of continuous recycling of biologically restored regenerant on the ammonium removal performance of the clinoptilolite.
- 2.) To identify any operational difficulties that would be significant in design.
- 3.) To identify the best operating conditions for the regeneration process.

Experimental

The pilot plant used in this study is depicted schematically in Figure 5-1.

A synthetic wastewater was constituted by the addition of chemicals to tap water. The wastewater contained no organic matter; only inorganic salts were added. The wastewater had the following composition:

$\text{NH}_3\text{-N}$ - 20 mg/l, Na^+ 62 mg/l, Ca^{++} 14 mg/l, Mg^{++} 12 mg/l and K^+ 4 mg/l.

The wastewater was drawn from a 500 liter fiberglass storage reservoir and delivered to the top of the clinoptilolite column by a metering pump (Fluid Metering, Inc.)

The clinoptilolite column was 2.5 meters long with an internal diameter of 5.7 cm and contained approximately 1400 grams of clinoptilolite in a bed depth of 77 cm. The zeolite was supported on 25 cm of gravel which in turn was supported by a perforated plexiglass disc.

The zeolite from Buckhorn, New Mexico was provided by Double Eagle Mining Company. 20 x 50 mesh clinoptilolite was conditioned by alternate treatments with 0.25M $(\text{NH}_4)_2\text{SO}_4$ and 1N NaCl. As a further precaution to ensure reproducible behavior 3 service and regeneration cycles also served as a conditioning procedure prior to testing. The particle size distribution of the zeolite is provided in Table 5-1.

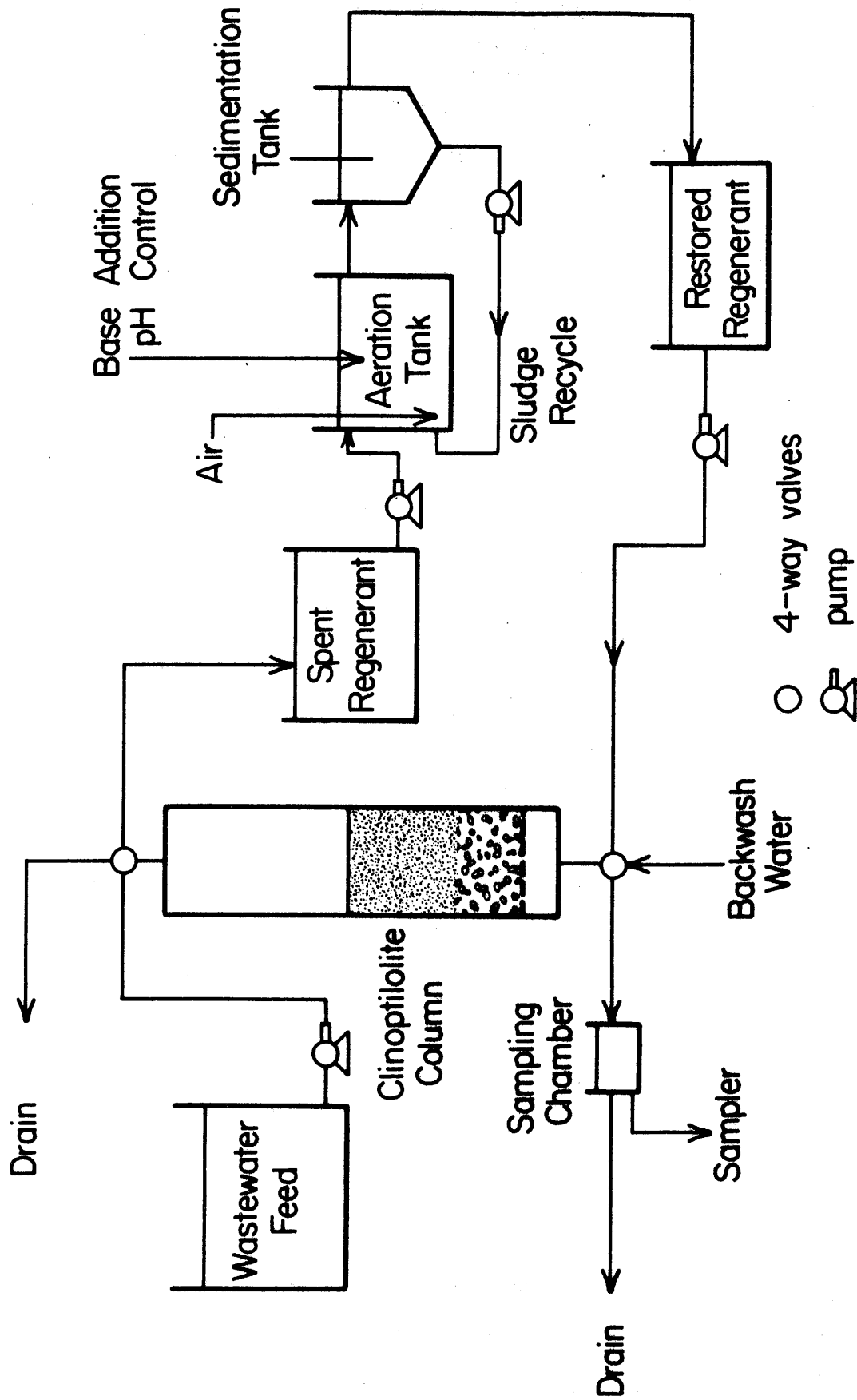


Figure 5-1 A Schematic Representation of the Pilot Plant Employed in this Study

Table 5-1

Particle Size Distribution of Clinoptilolite Studied

U. S. Standard Sieve Number	Sieve Size mm.	% Finer
18	1.00	100
20	0.84	74
30	0.589	31.5
40	0.42	10
50	0.297	0

During service the column effluent flowed through a sampling chamber and then to a drain. The sampling chamber shown in Figure 3 contained 400 ml of column effluent and had a mean hydraulic residence time of about one to two minutes. Once every hour a sequential sampler (N-Con Systems, Sentry 500) would automatically collect a 250 ml acidified sample of the column effluent. The sampler was programmed to purge the sample line before and after sample collection.

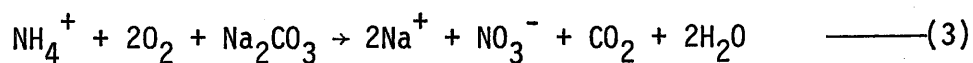
The samples were analyzed for ammonium content using an ammonium specific electrode (Orion). Severe drift problems were overcome by the frequent analysis of standards. The column was operated on a standard 20 hr. service cycle. This simulated operation where the column would be regenerated once a day.

Following service the column was backwashed for 10 minutes at 50% expansion and then regenerated. Initially, a regenerant was constituted by making a 0.3M NaCl solution with secondary effluent from the Urbana Sewage Treatment Plant. This regenerant was used, nitrified and recycled for reuse.

The spent regenerant flowed into a 30 liter acrylic storage reservoir from which it was pumped to a 7.35 liter aeration tank by means of a metering pump (Fluid Metering, Inc.). The aeration tank was equipped with a Leeds and Northrup Model 7018 pH controller. 1N sodium carbonate solution was added to the aeration tank as needed through a two-way stainless steel solenoid valve. An 8.5 liter baffled acrylic sedimentation tank provided secondary clarification before the restored regenerant flowed into a storage tank for reuse. A sludge recycle pump returned the settled sludge to the aeration tank.

The nitrifying bacteria were grown from an activated sludge inoculum by selective enrichment. The bacteria were fed a solution containing nutrients plus 400 mg/l $\text{NH}_4\text{-N}$. The composition of the feed is the same as that previously employed by Semmens et al. (3). Initially, batch feeding was used and then continuous flow was employed when significant nitrification became noticeable. The bacteria were grown in a 0.3M salt medium at pH 8.4 and were therefore acclimated to the conditions used in regeneration.

During the course of nitrification 1M Na_2CO_3 was added for pH control as described by equation (3).



The salt concentration in the regenerant increased accordingly. In order to ensure that roughly the same salt concentration in solution prevailed throughout the study, the conductivity of the brine was monitored. When the conductivity exceeded that of a 0.3M NaNO_3 solution, some brine was wasted and the remaining brine was diluted with make up water. In this study the make up water was secondary effluent from the Urbana Sewage Treatment Plant. The secondary effluent provided the only nutrients for bacterial growth. No other nutrients were added.

studied in detail in later sections.

The pH of the regenerant was expected to have a major influence on nitrification kinetics. The effect of pH on nitrification rate has been investigated extensively and most investigators have observed an optimal pH between 7.4 and 8.4. There is some disagreement in the reported optimum pH, possibly a result of the different experimental conditions employed. Specifically, it was not clear whether bacteria grown and acclimated to pH 7.0 would operate most effectively at this pH. To identify the impact of pH on nitrification kinetics respiration studies were conducted. A sample of nitrifying sludge taken from a reactor that had been maintained at pH 7.0 for 40 days was placed in the 2 liter respirometer cell depicted schematically in Figure 5-10. The cell was equipped with an oxygen supply, pH control, temperature control and a dissolved oxygen probe. The test procedure involved providing a fixed ammonium concentration in solution and elevating the dissolved oxygen to 20 mg/l. Then the oxygen supply was cut off, the contents of the covered reactor were stirred and the oxygen concentration was monitored with time. Each test for a particular set of conditions was run in triplicate to ensure reproducibility.

The oxygen consumption curves so obtained are plotted in Figure 5-11. It is clear from this figure and Figure 5-12 computed from these data that the bacteria nitrify more effectively at pH 8.0 even though they are acclimated to lower pH conditions.

It is evident therefore that operating the regeneration process at pH 7.0 to avoid calcium precipitation will require a larger nitrification reactor than would be necessary if the brine was maintained at pH 8.0.

The average influent and effluent ammonium concentrations from the nitrification reactor, as well as the average nitrifying activity of the

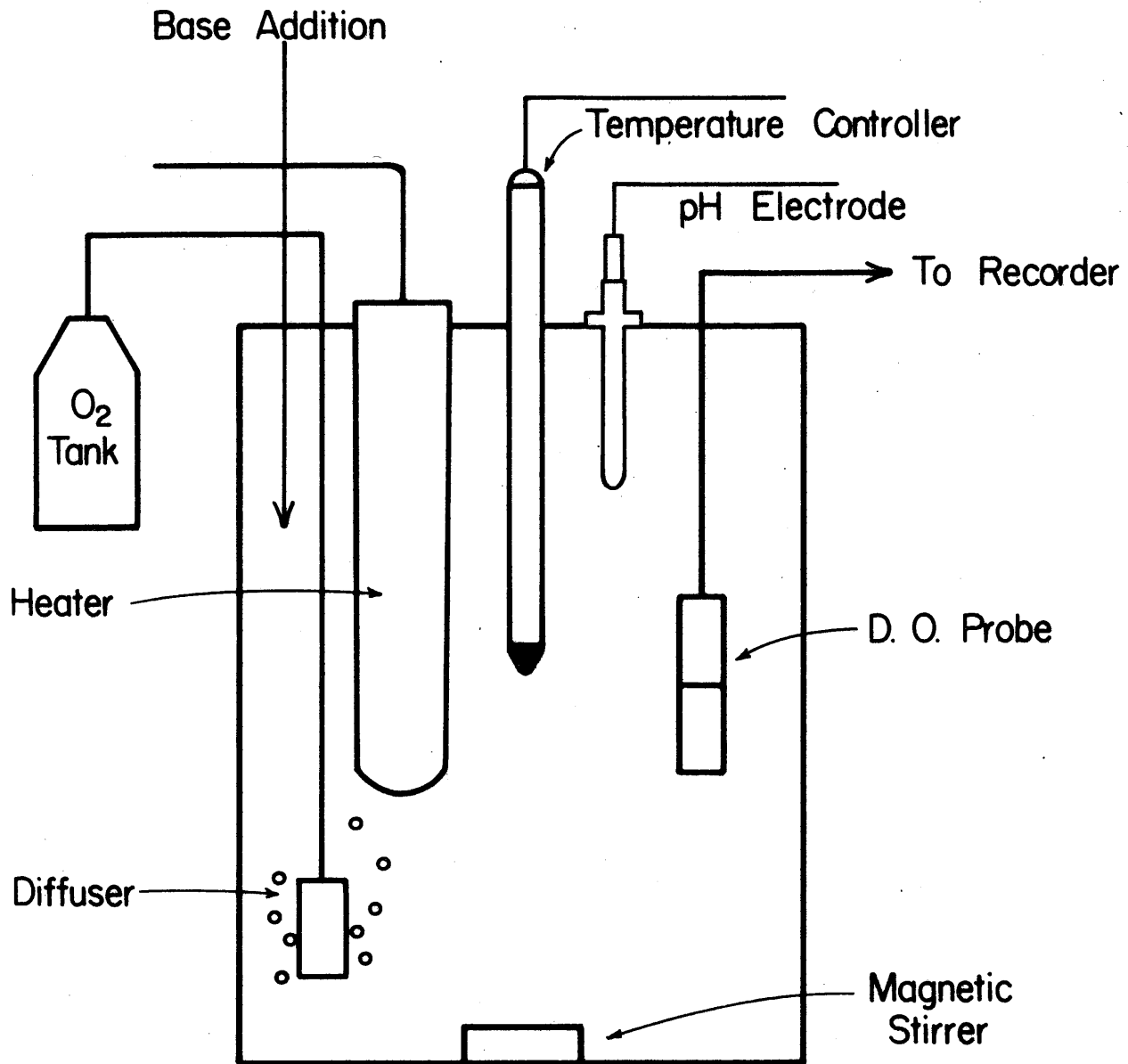


Figure 5-10 Respirometer Cell

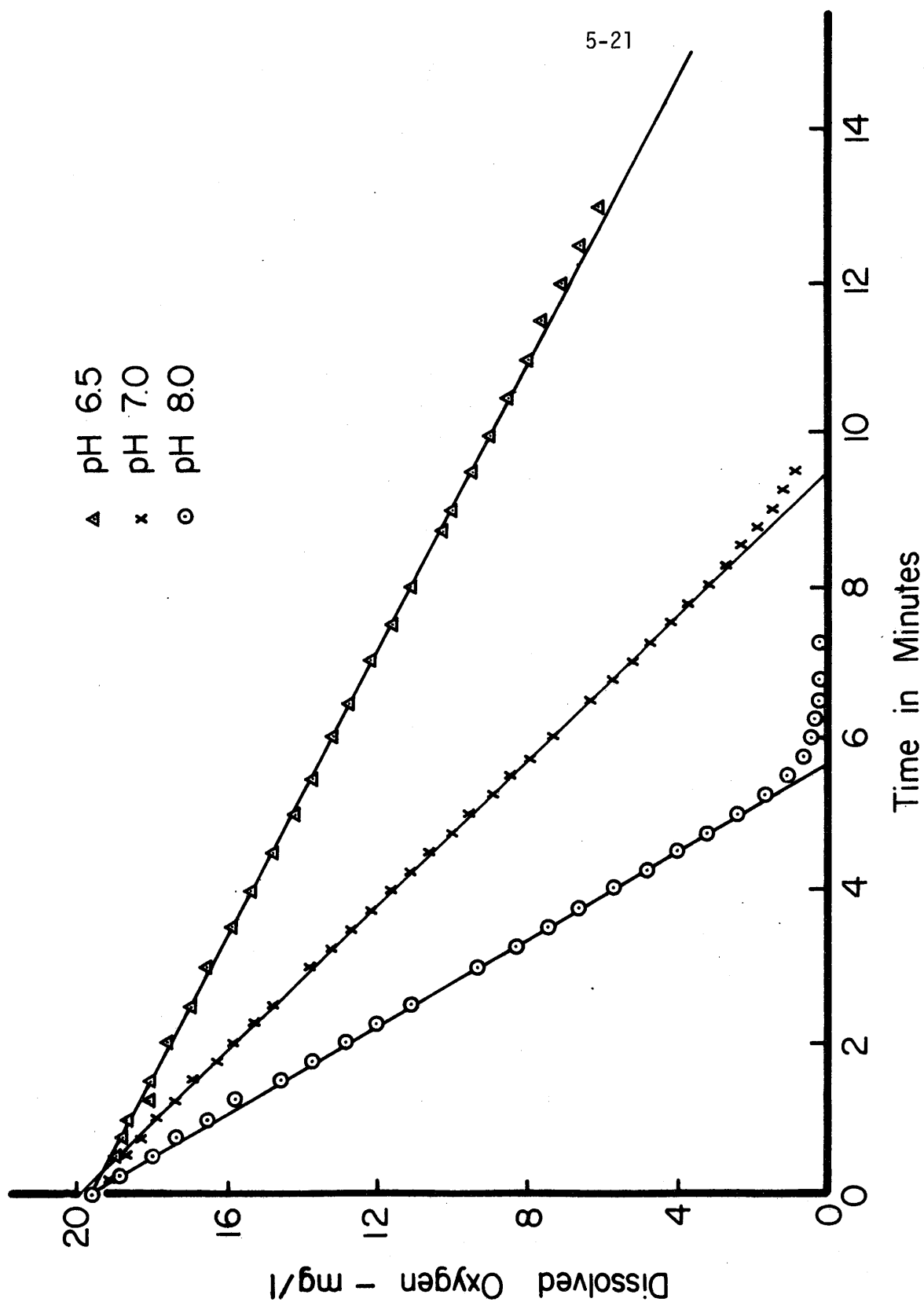


Figure 5-II Oxygen Uptake by Nitrifying Bacteria

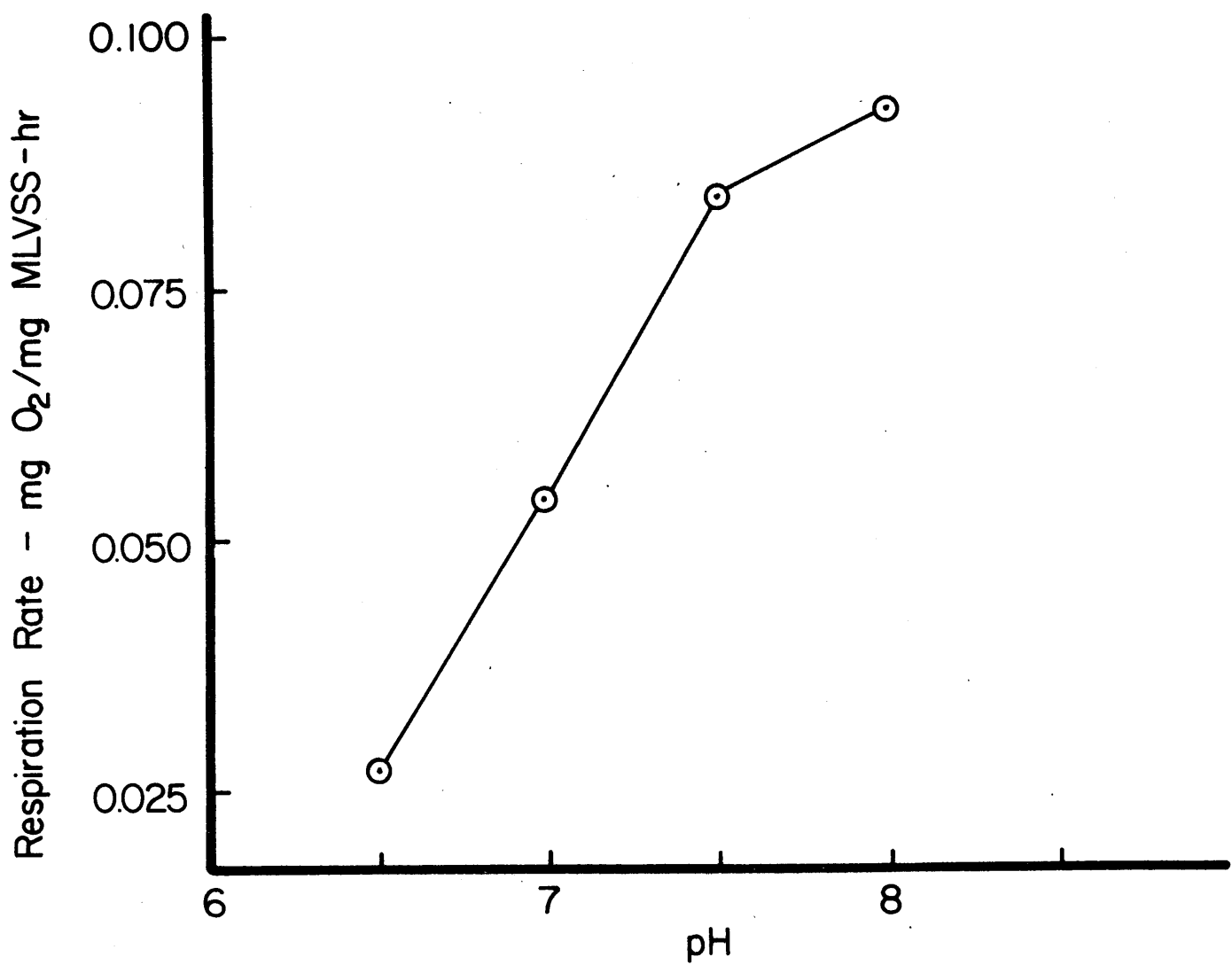


Figure 5-12 Oxygen Utilization as a Function of pH

bacteria are summarized in Table 5-3 for the four test sequences.

Table 5-3

A Summary of Nitrification Reactor Performance

	Test Period			
	1	2	3	4
Average Influent NH_4^+ -N (mg/l)	202	198	112	158
Average Effluent NH_4^+ -N (mg/l)	2.4	8.5	8.0	4.4
Average MLVSS (mg/l)	2290	1860	4700	2360
Average Nitrifying Activity (MgNH_4 -N/mg MLVSS.hr)	.014	.015	.005	.008

No conclusions may be drawn from the nitrifying activity reported in Table 5-3 for the different test sequences since, as mentioned above, the biological system was not operated under steady state conditions. The system was operated to obtain restored regenerant that could be recycled.

Base Requirements

The major cost in biological regeneration is that of base addition for pH control in the nitrification reactor. Reported base requirements vary above and below those calculated from the stoichiometry of ammonium oxidation. Sodium carbonate additions were monitored carefully in this study and the influence of operating pH was examined to identify the conditions that minimized the base requirement for nitrification.

It was evident that base consumption increased when CaCO_3 precipitation occurred. Table 5-4 summarizes the base consumption for the four test sequences.

At pH 8.0 the base requirement averaged 117% of the stoichiometric requirement. However, a steady state was never reached because of excessive CaCO_3 precipitation. Ca^{++} dropped from 32 to 16 meq/l in the last 4 cycles as base consumption steadily rose to 197% of the stoichiometric amount.

The excess CaCO_3 remaining in the reactor during test sequence two was in-

fluent in reducing the base requirement to only 92% of the stoichiometric amount. When the change in CaCO_3 content was accounted for, it was clear that the base addition was in all cases equal to the stoichiometric requirement. No benefit was apparent in reducing the operating pH from 7.0 to 6.5.

Table 5-4

A Summary of Base Consumption During the Study

Test Sequence	Nitrification pH	<u>Average Percent of Stoichiometric Requirement</u>		
		Na_2CO_3 added (1)	CaCO_3 formed (2)	Net (1) - (2)
1	8.0	117	22	95
2	7.0	92	-13*	105
3	6.5	101	- 4*	105
4	7.0	101	0	101

Overall Average % of Stoichiometric 101%

* Negative numbers denote CaCO_3 dissolution.

Salt Concentration

Consideration of equation 1-3 leads one to expect that if a regenerant is used and recycled following nitrification, then the salt concentration in the regenerant must increase by virtue of the base added for pH control. Thus some brine must be wasted and replaced with an equivalent volume of secondary effluent in order to maintain a constant salt concentration. In this study deviations from plug flow in the exchange column often diluted the brine with rinse and backwash water. At the beginning of regeneration, brine collection was initiated when the conductivity of the column effluent was equivalent to approximately 0.15 N NaNO_3 . Because high ammonium concentrations occur very early in regeneration waiting longer to collect the

brine may result in significant ammonium losses to the rinse water. The same criterion was applied to stop regenerant collection during the final backwash.

As a result of this operating technique it was not always necessary to waste brine and add makeup water.

Metals

Clinoptilolite will contain NH_4^+ , Ca^{++} , Mg^{++} , Na^+ and K^+ ions at the completion of a service cycle. Elution of the ammonium with a sodium brine (during regeneration) also displaces the other major cations. In this study the concentrations of these cations were monitored carefully during each cycle since they influence column performance.

Figure 5-3 shows the metal concentrations over the four test sequences. The curves indicate that the metal concentrations in the regenerant increase with increasing reuse. One may anticipate that a particular metal concentration in the regenerant may increase until a steady state condition is achieved or the limit of solubility is reached.

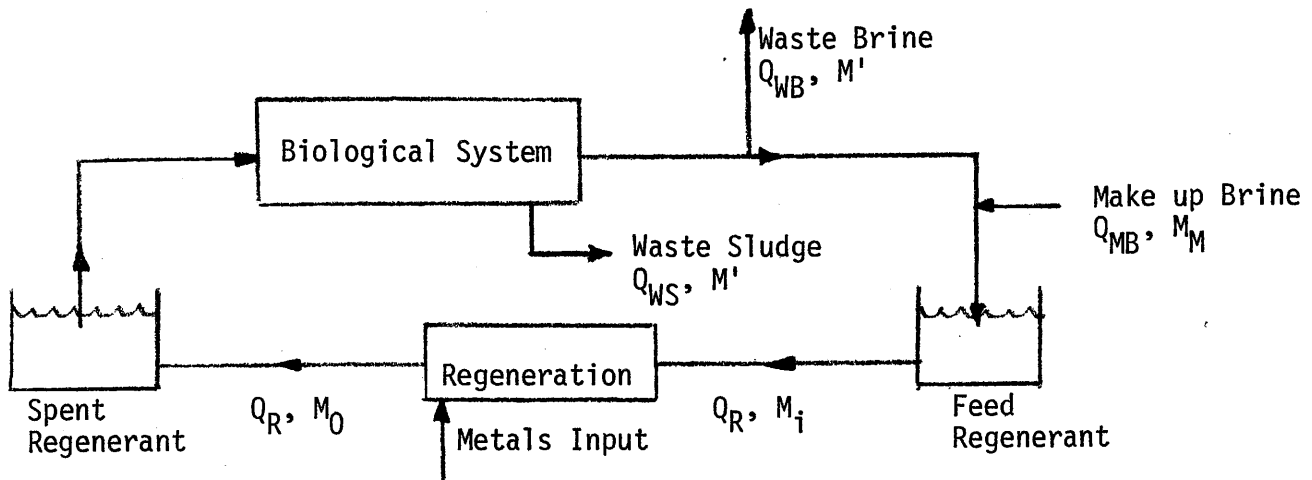
During test period 1, for example, the calcium and magnesium concentrations increased with reuse. However, calcium exceeded its solubility at pH 8.0 and calcium carbonate precipitation ensued. When the solution pH was reduced to 7.0, the solubility of CaCO_3 was increased and the calcium concentration increased accordingly.

Several factors may be expected to influence the metal concentrations in solution: 1) the wastage rate of the brine; 2) the sludge wastage rate (and its included brine content); 3) chemical precipitation; 4) the strength (salinity) of the brine; 5) the metal concentrations in the wastewater; and 6) the clinoptilolite itself.

One may consider a mass balance on the calcium and magnesium in the

regenerant as it is recycled in the system depicted below in Figure 5-13.

Figure 5-13



V_T = Total Volume of Regenerant in System

Q_R = Regenerant Flowrate

Q_{WS} = Sludge Wastage Rate

Q_{WB} = Brine Wastage Rate

Q_{MB} = Make Up Water Flow Rate

M_i = Metal Concentration in the Feed Regenerant

M_0 = Metal Concentration in the Spent Regenerant

M' = Metal Concentration in the Biological System

M_M = Metal Concentration in the Make Up Water

It should be noted that the metal input from the clinoptilolite varies with the metal concentration in the regenerant and the value of M_0 is related to the value of M_i for a particular system and a set of operating conditions.

A mass balance on the system provides the following equation:

$$Q_R (M_0 - M_i) + Q_{MB} \cdot M_M = V_T \frac{dM}{dt} + Q_{WS} \cdot M' + Q_{WB} \cdot M' \quad (4)$$

Assuming steady state conditions prevail and the make up water contains a negligible metals concentration the equation may be simplified:

$$Q_R (M_o - M_i) = (Q_{WS} + Q_{WB}) M' \quad \text{---(5)}$$

In addition at steady state the metals concentration in the biological system, M' , will be very close to the metals concentration in the spent regenerant, i.e., $M' \approx M_o$. Therefore

$$Q_R (M_o - M_i) = (Q_{WS} + Q_{WB}) M_o \quad \text{---(6)}$$

The relationship between M_o and M_i for the tests conducted in this study with 12 bed volumes of regenerant are shown in Figure 5-14. In this figure the elution of calcium and magnesium is documented as a function of the metals content of the initial regenerant. The dashed reference line shown on the figure represents the situation in which no change in metals content occurs during regeneration. It is clear from this figure that the line of best fit drawn through the data points has a slope less than the dashed line. Initially metals are displaced and the curve starts well above the dashed line, but as the metal content of the regenerant increases metal displacement is reduced and the curve moves towards the dashed line.

The curve in Figure 16 is described by equation (7).

$$M_o = 16 + 0.93 M_i \quad \text{---(7)}$$

By substituting equation (7) in equation (6) the steady state concentration of metals in the regenerant M_o may be estimated:

$$M_o = \frac{16 Q_R}{0.93 (Q_{WS} + Q_{WB}) + 0.07 Q_R} \quad \text{---(8)}$$

In this study $Q_{WS} = 0.35$ litres/day, $Q_{WB} \approx 1.5$ litres/day and $Q_R = 24$ litres/day and M_o is calculated to be 113 meq/l. The corresponding value

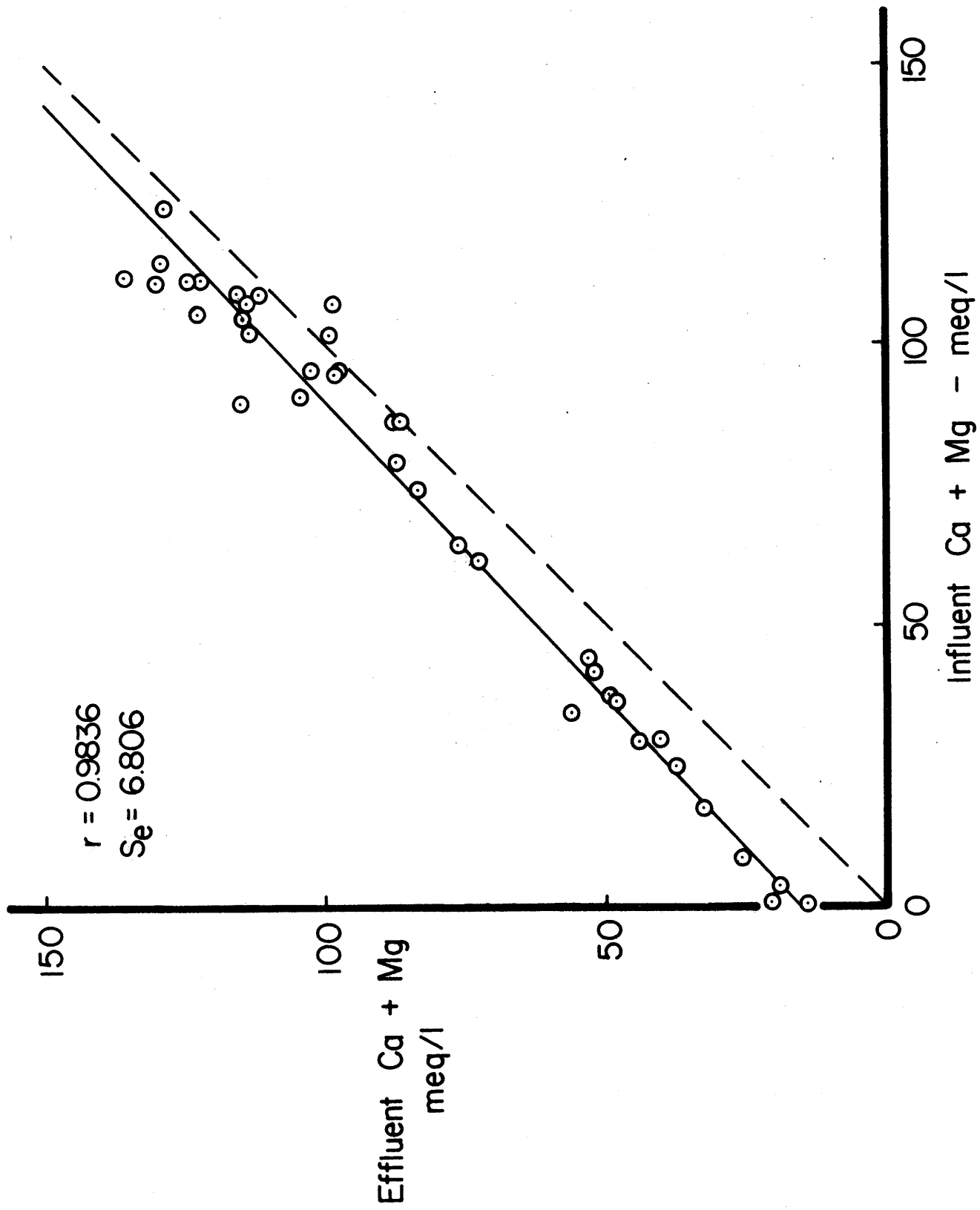


Figure 5-14 Elution of Metals from Clinoptilolite with
12 BV of Regenerant

of M_i is 104 meq/l. The steady state condition is represented on Figure 5-14 by the filled in circle. It is clear that there was a good deal of scatter in the data in this concentration range. However, the observed data points fall around the predicted value.

The scatter in Figure 5-14 may be attributed to a number of factors: slight changes in the salinity of the regenerant, in wastewater composition and in the brine wastage rate. The value of 1.5 litres/day used for Q_{WB} was estimated from stoichiometric considerations. The actual value of Q_{WB} was not known due to the losses of regenerant in column operation as mentioned above. On certain days no brine was wasted at all in this study since the brine was diluted sufficiently with rinse water. It is clear from equation (8) that M_o is very sensitive to the value of Q_{WB} . If Q_{WB} is reduced to 1 litre for example, the predicted value of $M_o = 131$ meq/l which is roughly equal to the highest measured metal concentration in the spent regenerant.

From this analysis one may conclude that the metal (Ca + Mg) concentration in the regenerant will stabilize at a concentration of approximately 110 - 120 meq/l for the system studied. Thus, a steady state condition was achieved in Test Period 4 of this study and the breakthrough curves obtained are indicative of those that would be obtained if a full scale system was operated continuously under these conditions.

Fouling

Some biological fouling evidenced by mudball formation in the upper layers (0.5 cm) of the zeolite was apparent. Examination of the mudballs showed that they resulted from the aggregation of the smallest particles in the column. Surface wash and air scour were required to alleviate this problem.

Section 6

Studies on the Kinetics of Nitrification
in Recycled Regenerant
Part 1. Dispersed Growth

INTRODUCTION:

Detailed nitrification studies were not conducted in Section 5. The intent was to characterize the chemical-physical behavior of the bio-regeneration system in simulated operation. Once the character of the steady state regenerant was evaluated nitrification studies could be conducted in solutions having this composition.

The intent of this study was to evaluate the performance of dispersed growth nitrification for ammonium oxidation. The impact of loading rates and mean cell residence times on performance were evaluated. In addition the coefficients describing the kinetics of nitrification were evaluated from continuous and batch studies. The values of these coefficients may be compared with those measured by other investigators and provide the basis for a rational design of nitrification facilities.

Model for Microbial Growth:

In this study Monod's model for microbial growth was employed. This model has been employed extensively in the environmental engineering field to describe the kinetics of growth and substrate utilization in mixed culture systems. The relatively simple mathematical form of this model makes it attractive.

Growth rate may be expressed as a function of microbial concentration, x , and specific growth rate, μ .

$$\frac{dx}{dt} = \mu x \quad (6-1)$$

where x = bacterial concentration at time t (mg/L)

t = time (hr)

μ = specific growth rate (hr^{-1})

The specific growth rate varies with substrate availability. The influence of substrate concentration may be expressed mathematically in an empirical form:

$$\mu = \mu_m \frac{S}{K_s + S} \quad (6-2)$$

where S = rate limiting substrate concentration at time, t (mg/L)

μ_m = maximum specific growth rate, a constant (hr^{-1})

K_s = saturation constant, (mg/L). The value of K_s is equal to the substrate concentration at which $\mu = 0.5\mu_{\text{max}}$.

As substrate is consumed the mass of micro-organisms increases. The yield coefficient, Y , is defined as the mass of cells produced per unit mass of substrate utilized. For a pure culture system in the exponential growth phase and a single substrate Y may be calculated using the relationship:

$$Y = \frac{X - X_0}{S_0 - S}$$

where S_0 and X_0 are the initial microbial and substrate concentrations (mg/L) respectively.

Batch System:

In certain cases batch systems provide the most accurate means of identifying microbial kinetics since the initial mass of cells, X_0 , may be controlled and the substrate and cell mass concentrations may be monitored with time.

Combining equations 6-1 to 6-3 leads to the following equation:

$$\frac{ds}{dt} = -\frac{1}{Y} \frac{\mu_m S \cdot X}{(K_s + S)} \quad (6-4)$$

which when integrated yields the following relationship:

$$-\frac{K_s}{S_o + (X_o/Y)} \ln \left[\frac{S(-X_o/Y)}{S_o[S - S_o - (X_o/Y)]} \right] + \ln \left[\frac{S - S_o - (X_o/Y)}{-X_o/Y} \right] = \mu_m \cdot t \quad (6-5)$$

when $K_s \ll S_o$, equation 6-5 is reduced to the form:

$$\ln[S_o - S + (X_o/Y)] - \ln(X_o/Y) = \mu_m \cdot t \quad (6-6)$$

Experimentally, this relationship may be used to evaluate μ_m . If the left hand side of equation 6-6 is plotted versus t , the slope of the line will equal the maximum growth rate, μ_m .

In addition K_s may be evaluated by averaging the K_s values calculated from equation 6-5 over the linear portion of the growth curve.

Continuous Flow Studies:

In a continuous flow system mass balances must be applied to the biological reactors to relate the accumulation of micro-organisms and substrate within the reactors to the system inputs and outputs. In addition for systems in which the micro-organisms are recycled, account must be made for the growth phases of the micro-organisms in the system.

A schematic representation of a completely mixed biological reactor with recycle is depicted in Figure 6-1.

In such a system the organisms growth rate is modified to account for the death of some micro-organisms viz:

$$\frac{d\bar{X}}{dt} = Y \cdot \frac{ds}{dt} - k_d \cdot \bar{X} \quad (6-7)$$

where k_d = micro-organisms decay coefficient, time^{-1} .

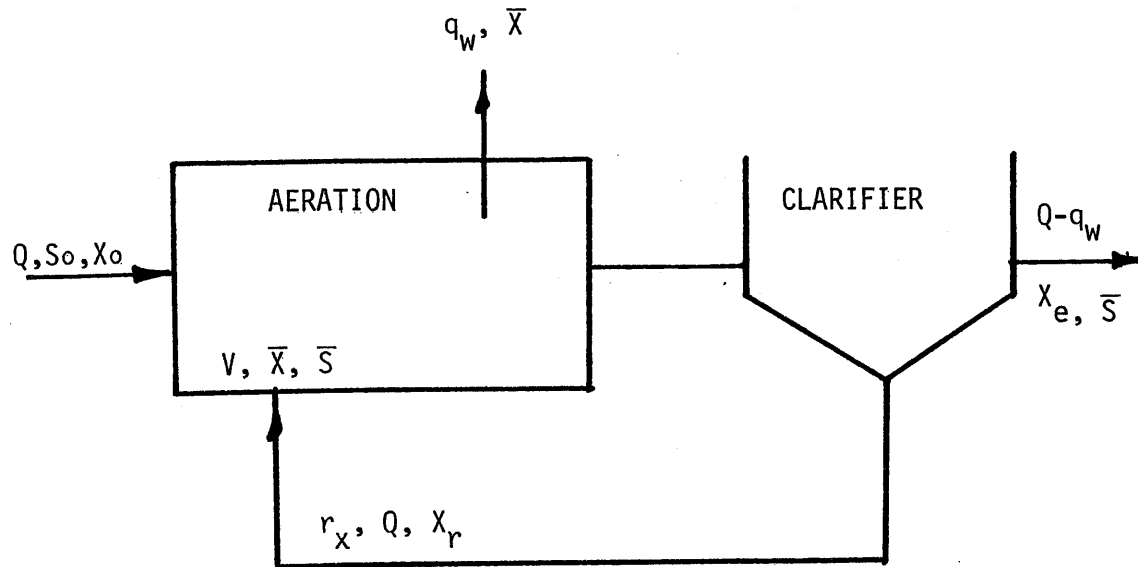


Figure 6-1

A SCHEMATIC REPRESENTATION OF A COMPLETELY MIXED
BIOLOGICAL REACTOR WITH SOLIDS RECYCLE.

Legend

- Q = Influent Flowrate
- \bar{X} = Average micro-organisms concentration in the reactor
(Mixed Liquor Volatile Suspended Solids, mg/L)
- V = Volume of biological reactor
- \bar{S} = Substrate concentration in the reactor
- q_w = Wastage rate from reactor
- X_e = Micro-organisms concentration in the effluent
- X_r = Micro-organisms concentration in the return sludge
- r_x = Fraction of influent flow recycled

Dividing throughout by \bar{X} and rearranging

$$\frac{1}{\bar{X}/(d\bar{X}/dt)} = \frac{Y}{\bar{X}} \cdot \frac{ds}{dt} - k_d \quad (6-8)$$

The term $\bar{X}/(d\bar{X}/dt)$ is often referred to as the sludge age or mean cell residence time, θ_c .

The rate of substrate utilization may be approximated by the following expression:

$$\frac{ds}{dt} = \frac{k \bar{X} S}{K_s + S} \quad (6-9)$$

where k = maximum rate of waste utilization per unit weight of micro-organisms.

Thus equation 6-9 may be rearranged as follows:

$$\frac{1}{\theta_c} = \frac{Y}{\bar{X}} \cdot \frac{k \bar{X} S}{K_s + S} - k_d \quad (6-10)$$

$$\text{but since } \mu_{\max} = Y \cdot k \quad (6-11)$$

$$\text{it follows that } \frac{1}{\theta_c} = \frac{\mu_{\max} \cdot S}{K_s + S} - k_d \quad (6-12)$$

A mass balance on the substrate may be conducted across the biological reactor to yield the following equation:

$$V \cdot \frac{ds}{dt} = Q \cdot S_o - q_w \cdot \bar{S} - (Q - q_w) \bar{S} - \left(\frac{k \cdot \bar{S}}{K_s + S} \right) \cdot \bar{X} \cdot V \quad (6-13)$$

if one considers a steady state condition equation 6-7 reduces to the form:

$$\frac{Q}{V} (S_o - \bar{S}) = \left(\frac{k \cdot \bar{S}}{K_s + S} \right) \bar{X} \quad (6-14)$$

Using equation 6-10 and 6-14 the following expression may be derived:

$$\frac{1}{\theta} (S_o - \bar{S}) = \left(\frac{1}{\theta_c} + k_d \right) \cdot \frac{\bar{X}}{Y} \quad (6-15)$$

where θ = hydraulic residence time = V/Q .

A mass balance may also be conducted across the biological reactor for the micro-organism mass. The following equation is obtained:

$$V \frac{d\bar{X}}{dt} = Q \cdot X_0 - q_w \bar{X} - (Q - q_w) X_e + \left(\frac{\mu_{\max} \cdot \bar{S} - k_d}{K_s + \bar{S}} \right) \cdot \bar{X} \cdot V \quad (6-16)$$

If steady state is assumed and the cell mass concentration in the influent is negligible this equation may be simplified to the following form:

$$\left(\mu_{\max} \cdot \frac{\bar{S}}{K_s + \bar{S}} - k_d \right) \bar{X} \cdot V = q_w \cdot \bar{X} + (Q - q_w) X_e \quad (6-17)$$

substituting equation 6-12 into equation 6-17:

$$\frac{1}{\theta_c} \cdot \bar{X} \cdot V = q_w \bar{X} + (Q - q_w) X_e \quad (6-18)$$

$$\therefore \theta_c = \frac{\bar{X} \cdot V}{q_w \cdot \bar{X} + (Q - q_w) X_e} \quad (6-19)$$

Evaluation of Kinetic Coefficients:

It may be seen from the above equations that for given values of the kinetic coefficients k , K_s , Y and K_d and specified values of Q , S_0 and θ_c , the mass of micro-organisms in the biological reactor, \bar{X} , and the effluent substrate concentration, S , are fixed and may be determined. When these kinetic coefficients are known treatment facilities may be designed and scaled up accurately to meet specified removal efficiencies.

In order to evaluate these coefficients accurately one must conduct batch and continuous flow studies in small scale tests and use the above model equations for interpreting the results.

1. Batch Studies

Batch studies may be employed to estimate the values of μ_{\max} and K_s as described above, using equation 6-6.

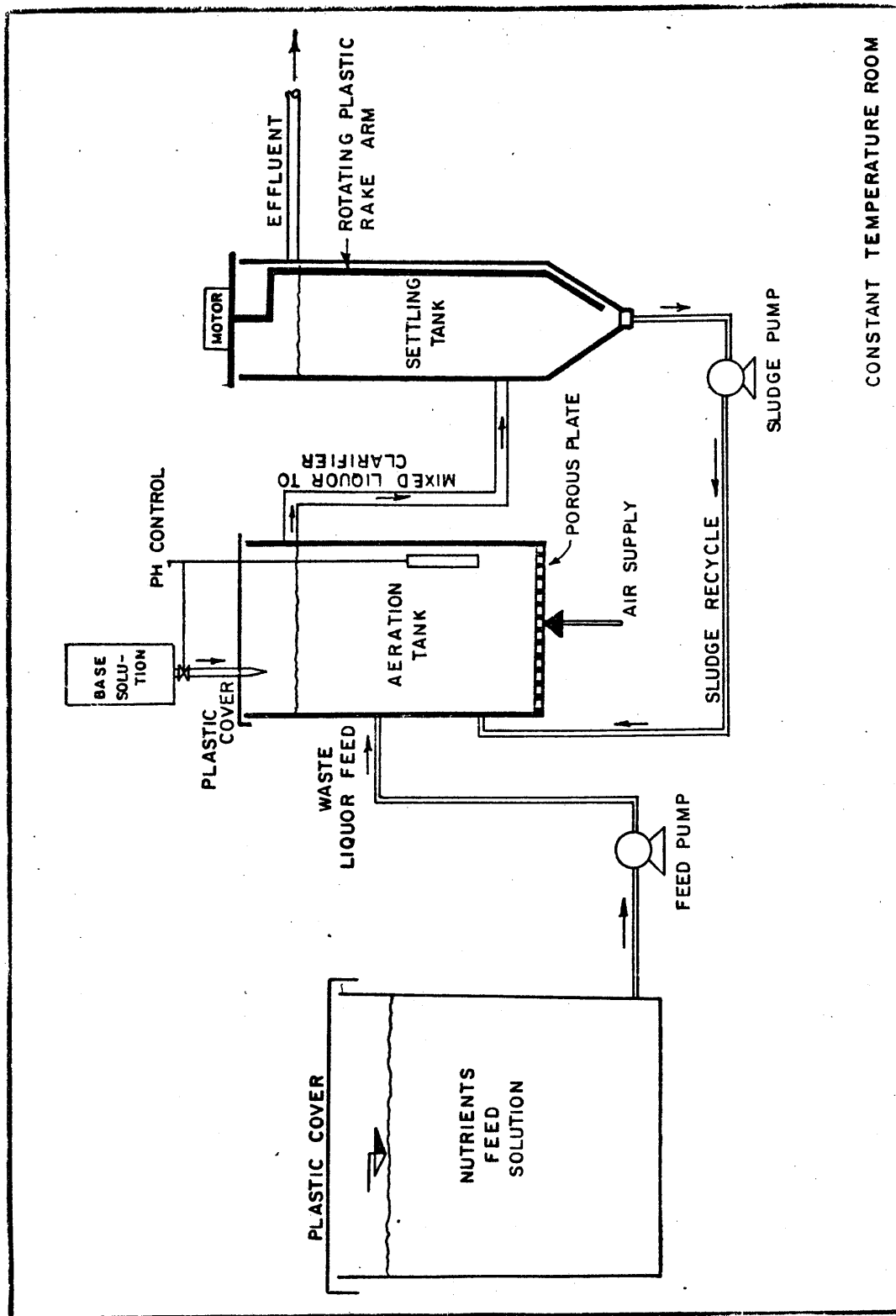


FIGURE 6-2 SCHEMATIC REPRESENTATION OF THE CONTINUOUS FLOW EQUIPMENT

2. Continuous Flow Studies:

The value of k_d and Y may be estimated using equation 6-15. If this equation is rearranged to the linear form:

$$\frac{S_0 - \bar{S}}{\bar{X}} \cdot \frac{1}{\theta} = \frac{1}{\theta c} \cdot \frac{1}{Y} + \frac{k_d}{Y} \quad (6-20)$$

then a plot of $\frac{S_0 - \bar{S}}{\bar{X}} \cdot \frac{1}{\theta}$ versus $\frac{1}{\theta c}$ (which may be calculated by using 6-19) should yield a straight line. The slope of the plot should equal $1/Y$ and the intercept on the ordinate axis will enable k_d to be evaluated.

The values of μ_{\max} and K_s may be evaluated using equation 6-14. Multiply the RHS by Y/Y and rearranging:

$$\frac{Y}{\theta} \frac{(S_0 - \bar{S})}{\bar{X}} = \frac{\mu_{\max} \cdot \bar{S}}{K_s + \bar{S}} \quad (6-21)$$

$$\frac{\theta}{Y} \frac{\bar{X}}{(S_0 - \bar{S})} = \frac{K_s}{\mu_{\max} \cdot \bar{S}} + \frac{1}{\mu_{\max}} \quad (6-22)$$

If $\frac{\theta(\bar{X})}{Y(S_0 - \bar{S})}$ is plotted against $\frac{1}{\bar{S}}$ then the slope should yield the value of K_s/μ_{\max} and the intercept should give the value of $1/\mu_{\max}$.

The values obtained in the continuous flow studies and in the batch studies should be the same.

Experimental

Equipment

1. Continuous Flow Studies

The apparatus employed in the continuous flow studies is depicted schematically in Figure 6-2. A "synthetic" regenerant containing 420 mg/L of ammonium nitrogen was pumped to the aeration tank which is sketched in

detail in Figure 6-3. The flowrate was accurately controlled by an FMI metering pump equipped with a micrometer to adjust the piston displacement.

The volume of the aeration tank could be varied by adjusting the height of the overflow to the sedimentation tank. The sedimentation tank sketched in detail in Figure 6-4 was also of plexiglass construction. The sedimentation tank was equipped with a rotating plastic arm that swept across the inside wall surface to prevent the accumulation of solids on the walls of the tank. A small timed motor turned the arm through 2 revolutions per minute.

Sludge was returned to the aeration tank using a variable speed Masterflex pump connected to an adjustable timer. Continuous sludge recycle resulted in high solids losses to the sedimentation tank effluent so the pump was adjusted to operate intermittently.

The aeration tank was equipped with a pH controller (Leeds and Northrup Model 7018) which operated a solenoid valve to control the addition of 1M Na_2CO_3 solution for pH control.

Water saturated air was introduced into the aeration tank through a porous diffuser plate installed in the base.

Three such pilot plants were operated. Two were operated with a constant temperature room 20°C and the third was tested in the laboratory, with temperature ranging $\pm 3^\circ\text{C}$ about a mean of 22° .

2. Batch Studies

Three well mixed reactors were employed in this study and they are depicted schematically in Figure 6-5.

Each reactor consisted of a 3 litre glass bottle. Each was supplied with prefiltered and water saturated air at a constant rate. Magnetic stirrers

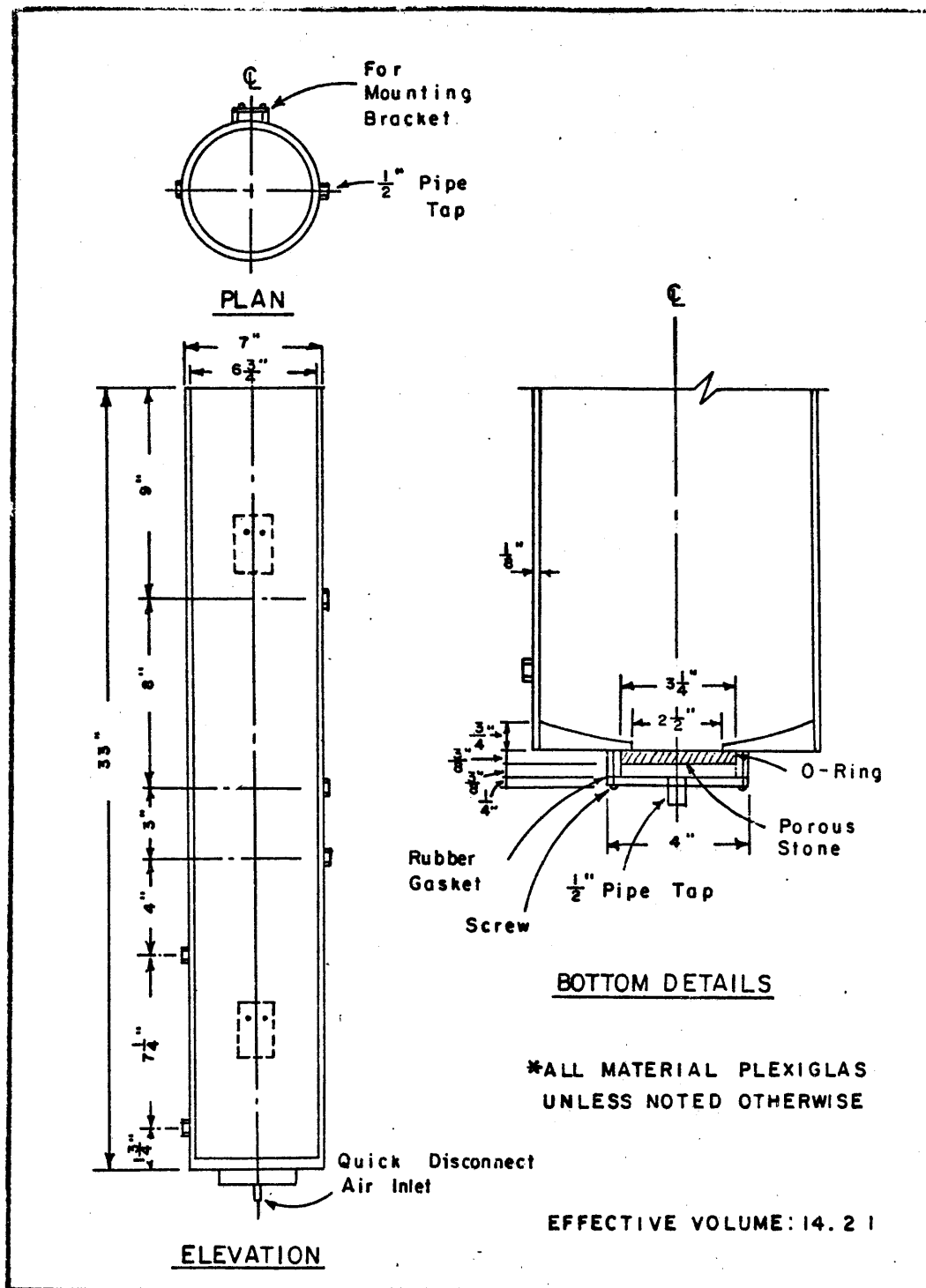


FIGURE 6-3 DETAIL OF AERATION TANK

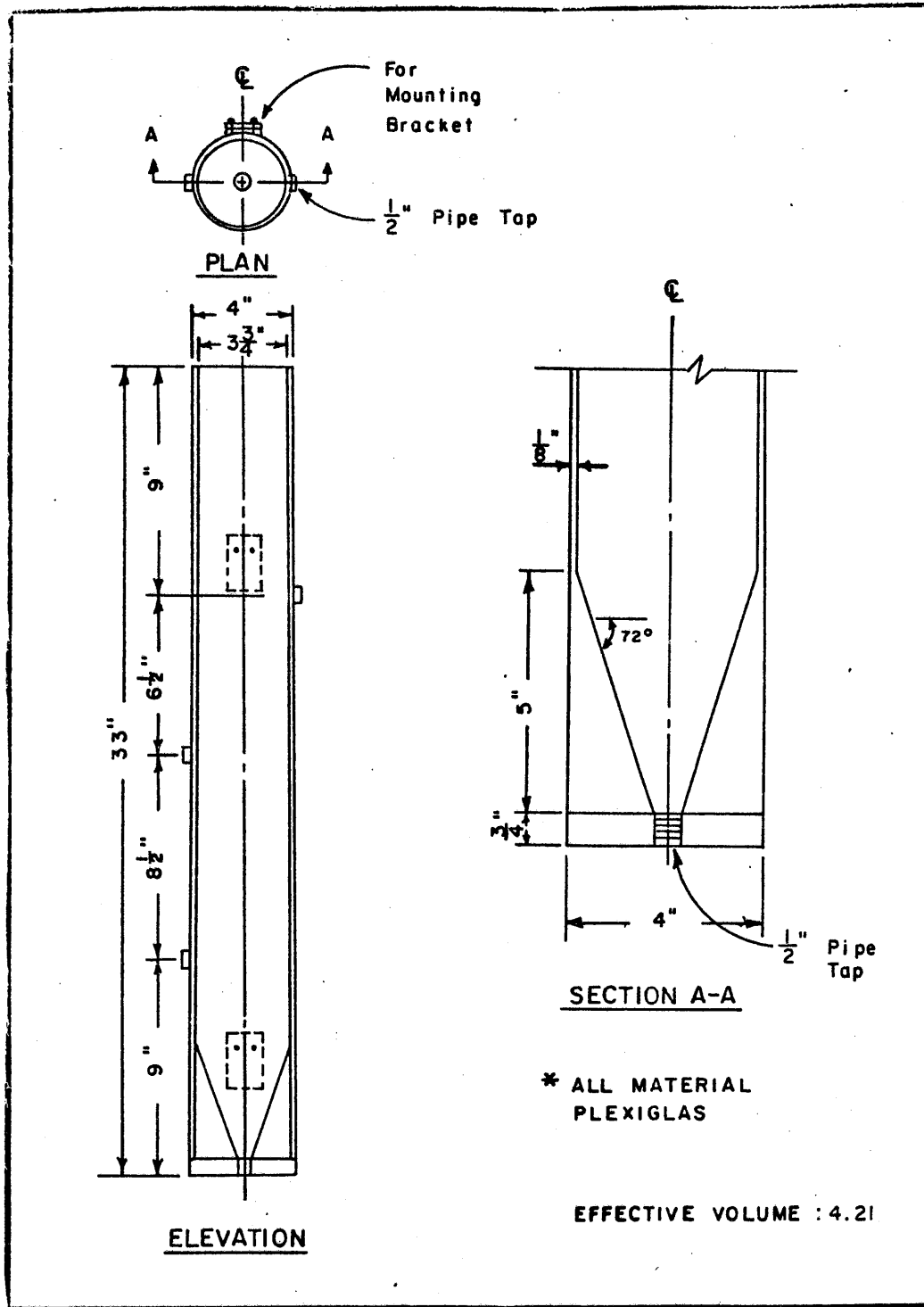


FIGURE 6-4 DETAIL OF SEDIMENTATION TANK

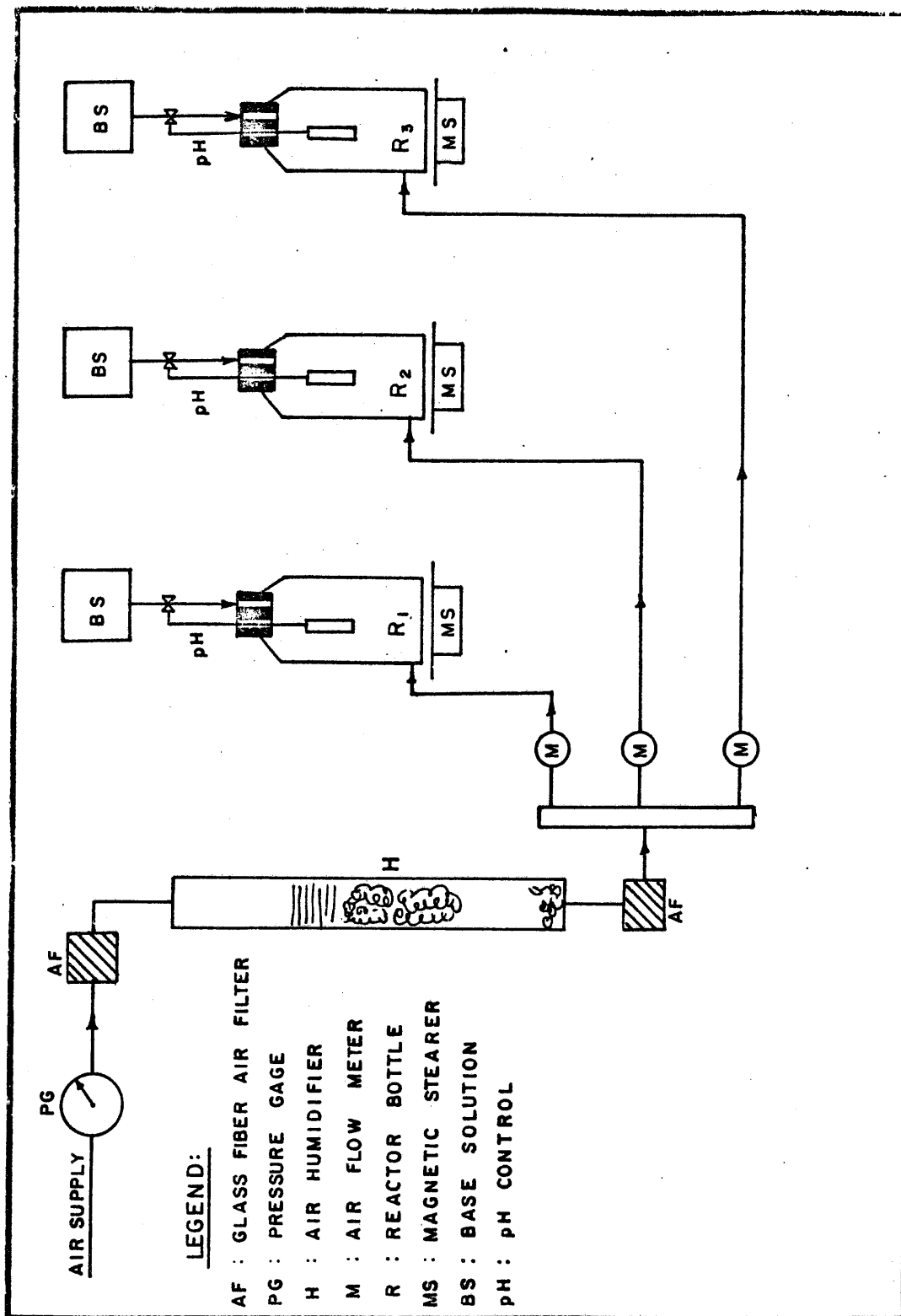


FIGURE 6-5 BATCH SYSTEM SCHEMATIC DIAGRAM

were provided to ensure adequate mixing throughout the reactors and pH controllers regulated the addition of 0.3M NaOH for pH control. The sodium hydroxide solution was added from a burette so that the volume change could be taken into account.

All batch studies were conducted at 20°C.

Feed Solution:

The synthetic regenerant feed solution was constituted by mixing technical grade chemicals into a mixture of 15% secondary effluent and 85% dechlorinated Minneapolis tap water. The secondary effluent was obtained from the St. Paul Metropolitan Waste Water Treatment facility and filtered before use. The composition of the feed solution is specified in Table 6-1 and represents a typical quality of recycled regenerant observed in the studies conducted in Section 5.

Table 6-1

FEED SOLUTION COMPOSITION		
CONSTITUENT	CONCENTRATION	SALTS USED
Ammonium $\text{NH}_3 - \text{N}$	420 mg/l as N	$\text{NH}_4 \text{Cl}$ as source of N
Calcium Ca^{++}	1,804 mg/l as Ca	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ source of Ca
Magnesium Mg^{++}	486 mg/l as Mg	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ source of Mg
Potassium K^+	98 mg/l as K	KNO_3 as source of K
Sodium Na^+	3,632 mg/l as Na	NaCl as source of Na

The feed pH was adjusted to 5.0 to inhibit nitrification in the feed reservoir and supply lines, and also to reduce the loss of NH_3 gas. The feed reservoir was also covered.

The same feed solution was employed in batch and continuous flow studies. No nutrients were added and the only source of nutrients was the secondary effluent. Following nitrification in the continuous flow studies the effluent was collected and reused. To reuse the effluent, salt content had to be reduced by wastage and make up secondary effluent to maintain the composition shown in Table 6-1.

Nitrifying Bacteria:

The nitrifying bacteria studied in this investigation were cultivated by selective enrichment of a seed culture obtained from the aeration tank of a local extended aeration treatment plant. An active nitrifying culture was obtained from the seed after approximately 2 weeks of exposure to an ammonium rich nutrient solution.

Analytical Techniques and Procedures:

1. Continuous Flow Studies:

The following measurements were made on a routine daily basis: Aeration tank ammonium concentration and mixed liquor volatile suspended solids concentrations, dissolved oxygen concentration, feed solution flowrates pH and base consumption. The pH was set at 7.0 always.

Ammonium concentrations were measured directly by raising the sample pH to 12 and analyzing for NH_3 using an ORION Model 95-10 Ammonia Selective Electrode.

Solids concentrations were measured following "Standard Methods" procedures. However samples were only taken when the recycle pump had just turned off and the contents of the reactor had been stirred to ensure solids accumulations on the walls were resuspended.

Dissolved oxygen was monitored using a YSI Model 54 Oxygen Meter. Initially, a Dissolved oxygen content of 6 mg/l was maintained in the

aeration tank.

In order to maintain a desired mean cell residence time, θ_c , sludge was wasted from the aeration tank daily. The volume to be wasted was calculated daily when the MLVSS of the aeration tank and effluent were known using equation 6-19.

Batch Studies:

To obtain a nitrifying culture in the log growth phase 1 ml of effluent from the continuous flow reactor was inoculated into 2 litres of the feed solution in a batch reactor. Following depletion of the ammonium a sample of the turbid solution was taken and diluted. A fraction of the diluted sample provided the inoculum for the batch studies.

Two litre samples of feed solution and an inoculum of bacteria were aerated and maintained at pH 7.0. Samples were taken every 4 hours for ammonium concentration measurements. When the concentration started to decrease rapidly 3 hour sampling periods were used.

The amount of base consumed was also recorded at each sample time. Samples were also collected to estimate the increase in cell mass in the batch study. Two samples (30 ml's) were taken from the batch reactor before and right after addition of inoculum. At the conclusion of the test another 2 samples were taken. One sample in each pair was filtered through a 0.45μ filter; the other sample was sonicated and both samples were tested for their Total Organic Carbon Content using a Beckman TOC Analyzer.

RESULTS

Continuous Flow Studies:

Many operating difficulties were experienced in the continuous flow study and the reactors were operated for 3 months before any reliable data could be collected. Operating difficulties included zinc inhibition caused

by the use of a galvanized steel fitting, problems with the ammonium selective electrode, variations in the solids concentrations measured in the system, and loss of solids in the sedimentation tank effluent caused by excessive shear in the aeration tank, etc. These difficulties were overcome and by reducing the DO to 4-5 mg/l in the aeration tank and applying a standard procedure for solids sampling reliable data were collected. These data are presented in Appendix C.

The data collected from the continuous flow studies was used to calculate the expression $(S_o - \bar{S}/\bar{X}) \frac{1}{\theta}$ for each sludge age, θ_c . The values were then plotted in the form of equation 6-20. The results are shown in Figure 6-6. The values of $1/\theta_c$ on the abscissa were not all calculated simply by equation 6-19. It was found that in some of the studies the influent solids concentrations were significant, (before filtration of the secondary effluent was practised). In these cases θ_c was calculated using the following equation:

$$\theta_c = \frac{\bar{X} V}{q_w \cdot \bar{X} + (Q - q_w) X_e - Q X_o} \quad (6-23)$$

The data shown in Figure 6-6 fall on a reasonable straight line and the line of best fit gives values of $Y = 0.154$ mg of cell mass produced/mg N oxidized. and $k_d = 0.0015 \text{ day}^{-1}$. The vertical bars shown on Figure 6-6 represent the observed scatter for each sludge age. A plot of $\frac{\theta}{Y} \cdot \frac{\bar{X}}{(S_o - \bar{S})}$ versus $\frac{1}{\bar{S}}$ to follow the form of equation 6-22 is shown in Figure 6-7. The results show considerable scatter and the line of best fit has a correlation coefficient of only 0.84. The value of μ_{\max} was calculated to be 0.132 hr^{-1} and $K_s = 1.7 \text{ mg/l}$.

Figures 6-8 and 6-9 show the influence of loading rate and sludge age on the ammonium removal in the continuous flow studies.

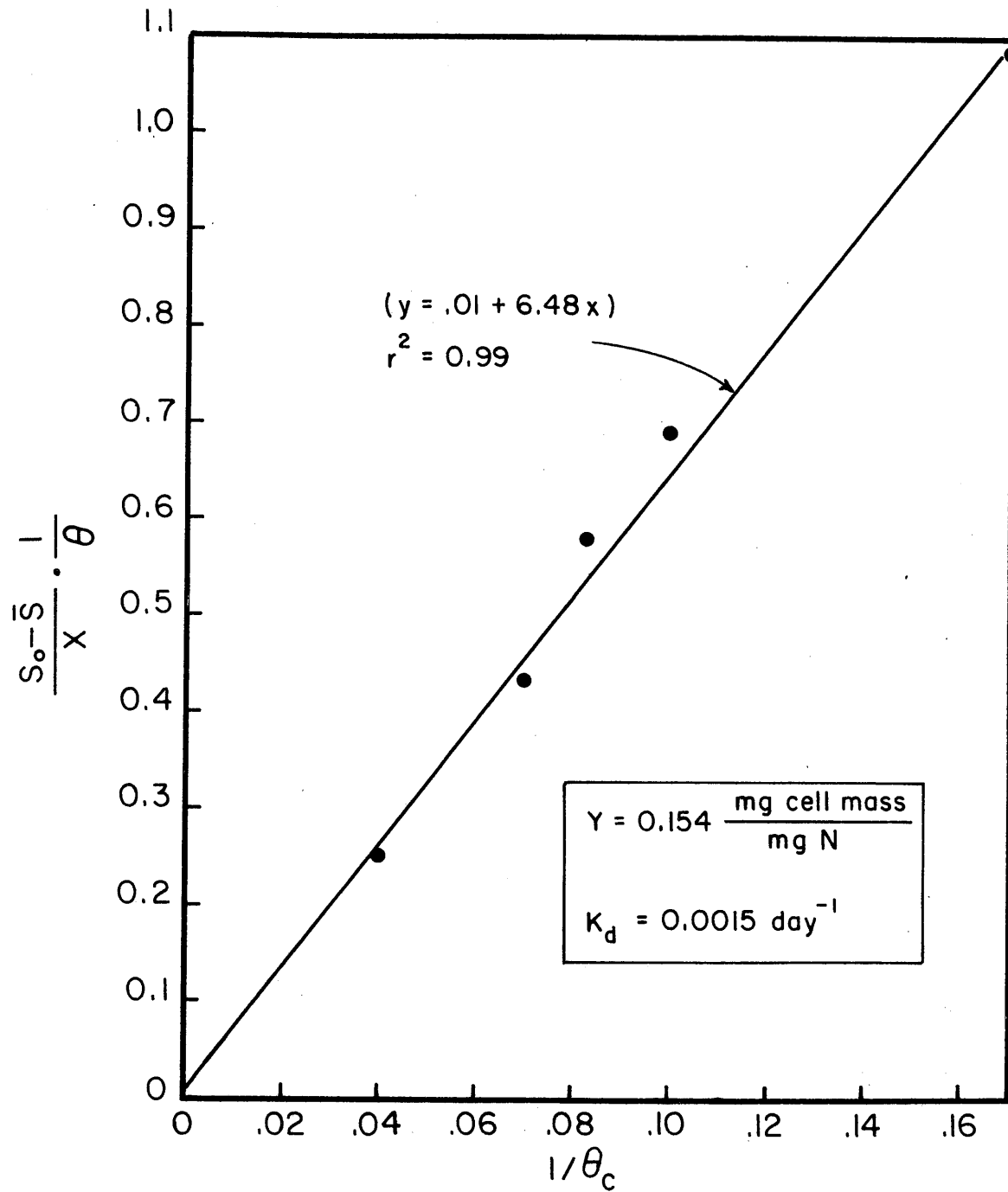


FIGURE 6-6 SUBSTRATE REMOVAL RATE VERSUS NET GROWTH RATE FOR THE EVALUATION OF Y and K_d

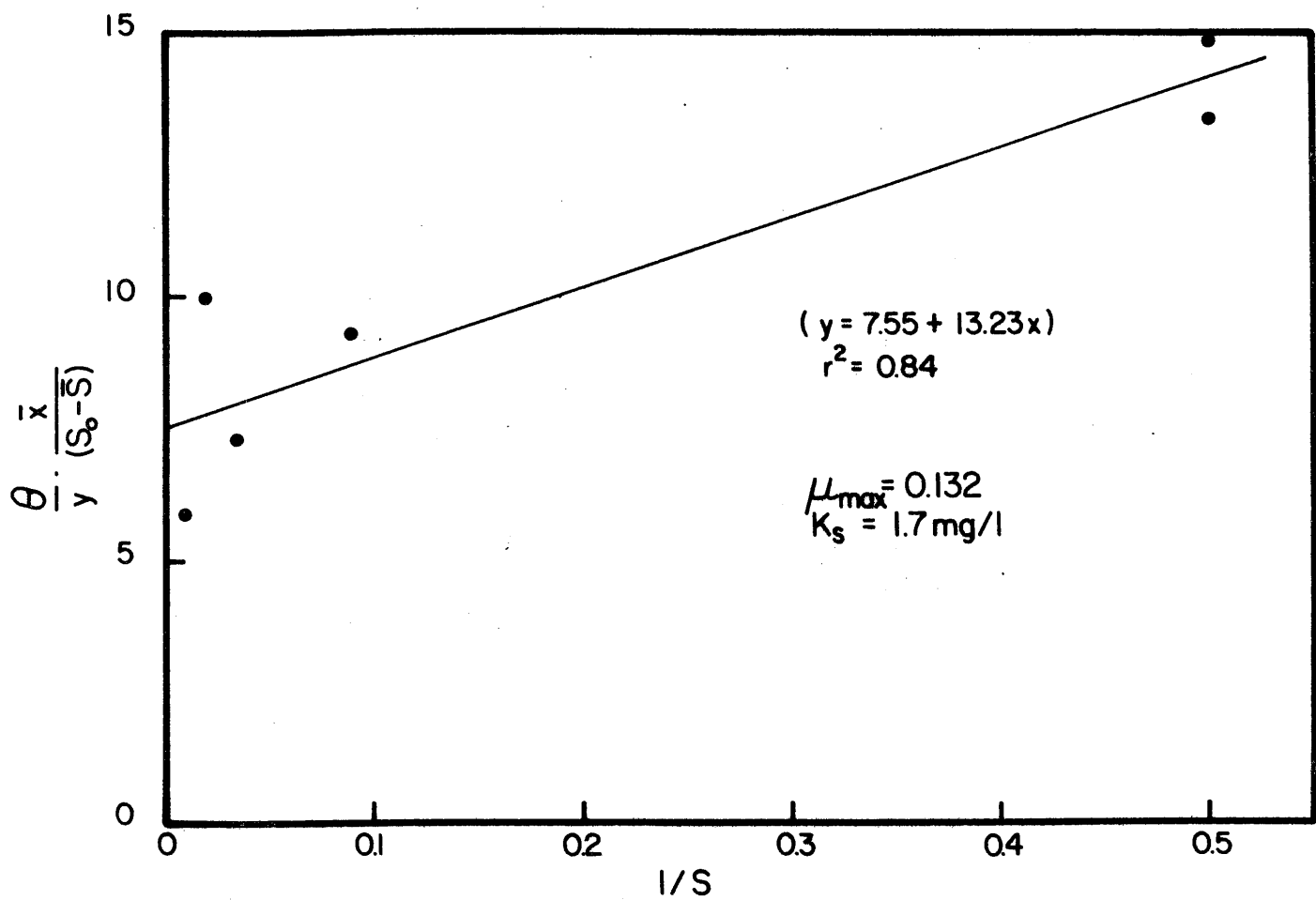


FIGURE 6-7 PLOT OF EQUATION 6-22 FOR THE EVALUATION OF μ_{\max} and K_s

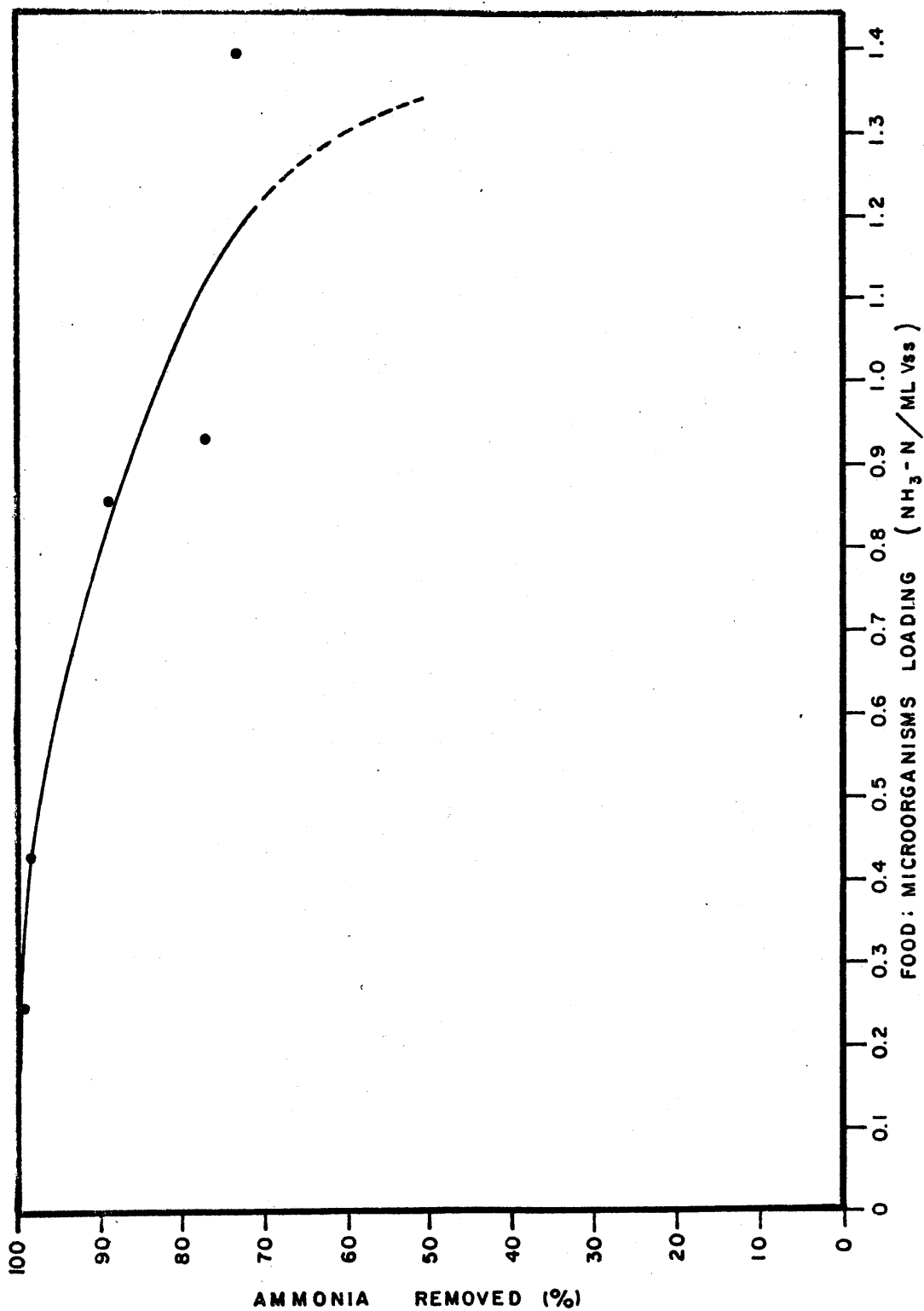


FIGURE 6-8 EFFECT OF LOADING RATE ON NITRIFICATION

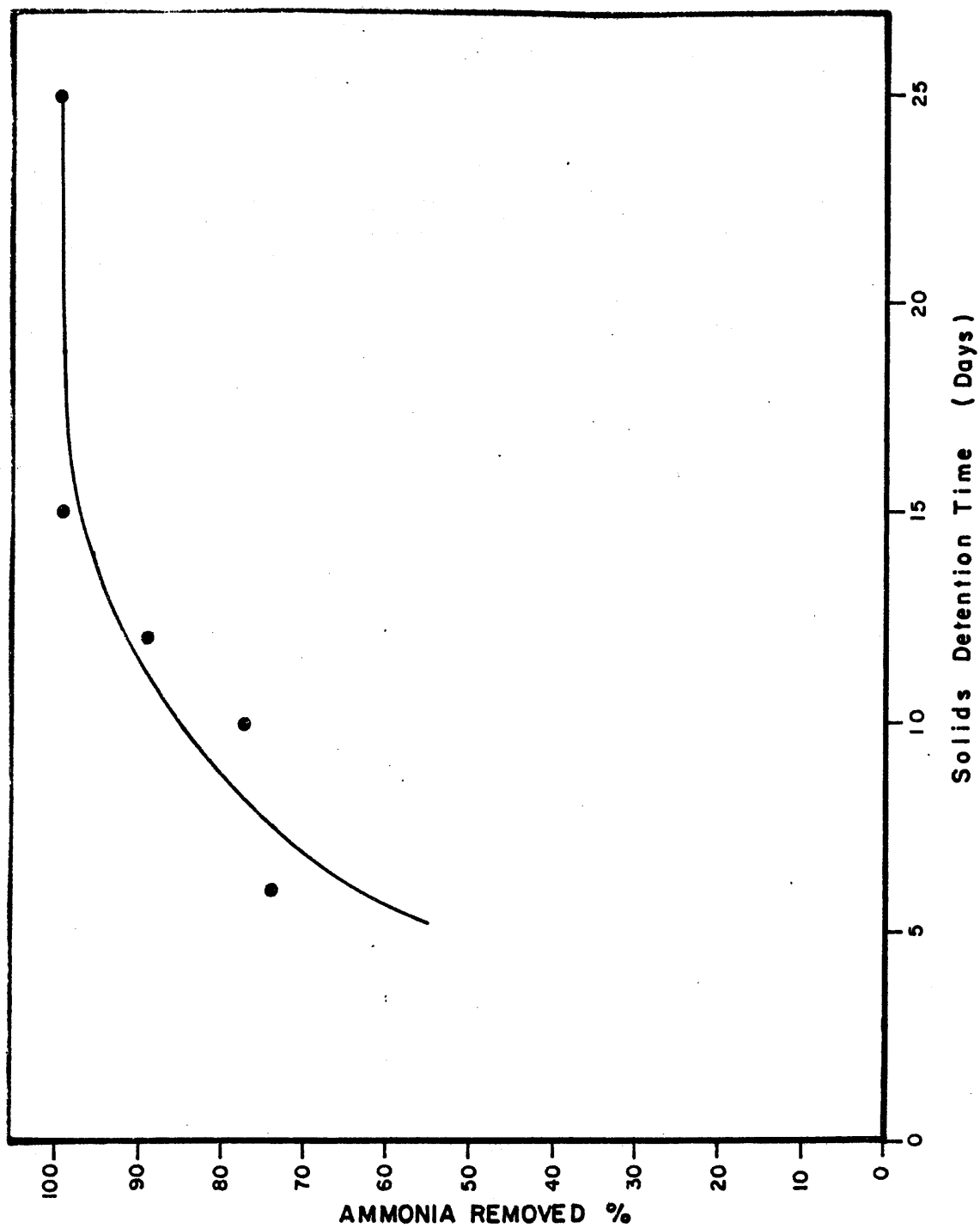


FIGURE 6-9 INFLUENCE OF SLUDGE AGE ON AMMONIUM REMOVAL

Batch Studies

Five batch studies were made, however, the first 3 studies failed since the volume of solution was depleted by sampling before the ammonium concentration was reduced significantly. An additional two studies proved more successful. The results are graphed in the form of equation 6-6 in Figure 6-10.

One of data sets appears to have a definite curvilinear form rather than being linear as expected. The reasons for this behavior are not clear. The best lines drawn through the data yielded values of $\mu_{\max} = 0.76$ and 0.86 day^{-1} .

K_s values could not be reliably predicted from the batch data since in both tests the rate of ammonium oxidation appeared to increase as S approached zero and insufficient data were collected in this concentration range. It would appear $K_s < 5 \text{ mg/l}$.

From the measured total organic carbon content of the batch reactors before and after nitrification the yield coefficient was evaluated in both reactors. Y was found to equal $0.07 \text{ mg of cellmass/mgN oxidized}$.

Discussion

The values of the kinetic coefficients are tabulated in Table 6-2.

Table 6-2
Measured Values of the Kinetic Coefficients

Parameter	Batch Study Value	Continuous Flow Study
Y	$0.07 \text{ mg cells/mg N}$	$0.154 \text{ mg cells/mg N}$
K_s	5 mg/l	1.7 mg N/l
μ_{\max}	$0.76 - 0.86 \text{ day}^{-1}$	0.132 day^{-1}
k_d	--	$.0015 \text{ day}^{-1}$

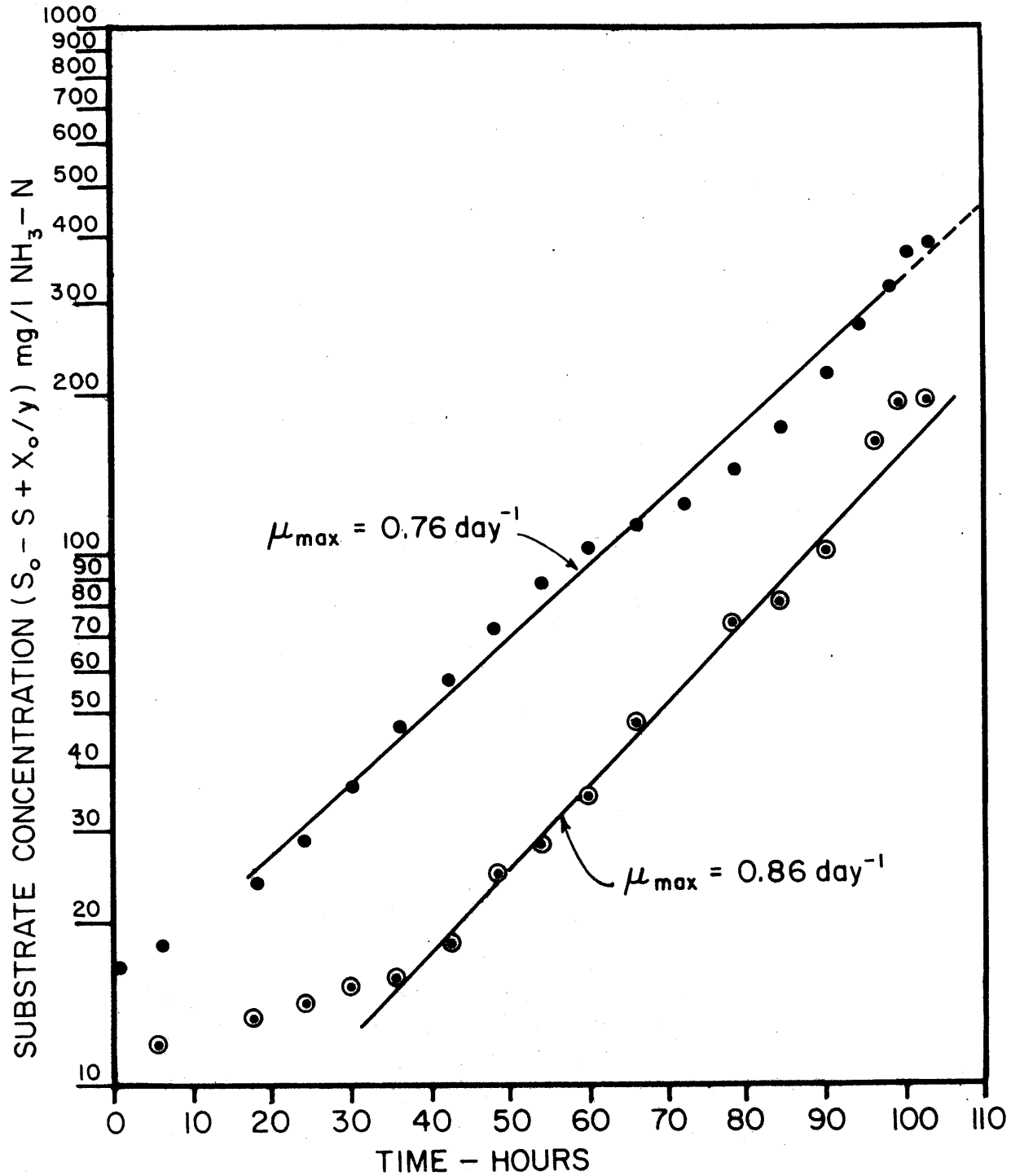


FIGURE 6-10 BATCH REACTORS NITRIFICATION RESULTS FOR THE EVALUATION OF μ_{\max}

The difference in the measured values of Y and μ_{\max} between batch and continuous flow studies is significant. It is possible that different species were selectively enhanced in the two studies. In addition nitrification is a two step oxidation process with nitrite being an intermediate oxidation product. If nitrite had been formed, under the conditions employed in the batch study, and not oxidized further to nitrate immediately this may have influenced the values of μ_{\max} and Y . A nitrite build-up may cause inhibition, and if significant nitrite concentrations remained when the ammonium concentration was reduced to zero, and final TOC samples were collected, the production of cell mass may have been incomplete. The batch data is therefore suspect and the continuous flow data should be considered a more accurate assessment of the coefficient values.

The values obtained in this study compare favorably with values reported in the literature some of which are presented in Table 6-3. Since the measured coefficients fall within the range of reported values it seems probable that design procedures employed in the construction of nitrification facilities for the treatment of low strength ammonium wastewaters may be reasonably extended for the treatment of recycled regenerant.

Table 6-3

REPORTED KINETIC COEFFICIENTS FOR BIOLOGICAL NITRIFICATION

Environment and reaction	Growth yield Coefficient Y	Microorganisms decay coefficient K_d	Maximum growth rate coefficient μ_{max}	Half saturation constant K_s	Temperature	Reference
	(mg/mg)	(day ⁻¹)	(day ⁻¹)	(mg/l)	°C	
1. <u>Synthetic river water:</u>						
a) NH_3 - N oxidation	0.29	0.05	-	3.4	25	36
	0.29	0.05	-	3.6	20	36
	0.29	0.05	-	2.8	15	36
b) NO_2 - N oxidation	0.084	0.05	-	0.3	25	36
	0.084	0.05	-	1.1	20	36
	0.084	0.05	-	0.7	15	36
2. <u>Activated sludge:</u>						
a) NH_3 - N oxidation	0.05	-	0.33	1	20	37
b) NO_2 - N oxidation	0.02	-	0.14	2.1	20	37
3. <u>Thames estuary water:</u>						
a) NH_3 - N oxidation	0.05	-	0.65	0.6	18.8	38
	0.05	-	1.50	1.7	27	38
b) NO_2 - N oxidation	0.02	-	0.83	1.90	18.8	38
	0.02	-	2.00	4.70	29	38

Section 7

Nitrification Studies with an Attached Growth System

INTRODUCTION

The ability of suspended growth systems to effectively nitrify high-strength ammonium solutions and allow for the reuse of regeneration brine solutions was demonstrated in Section 6.

In this section experiments are described that were performed with an attached growth system for comparative purposes. The type of attached growth system selected was a rotating biological contactors (RBC). RBC systems consist, briefly, of a number of adjacent, vertical discs which are partially submerged in the wastewater solution. The structure of these discs provides a large surface area for the attachment of a biological surface film. Having rotated through the wastewater, the microbial layer, and the overlying substrate-rich wastewater film will be exposed to air thus providing oxygen and facilitating the oxidation process. To be effective the biomass must be contacted frequently with the wastewater and also with oxygen.

The rotating discs have a number of functions (39):

- 1.) They provide a large surface area for the development of a fixed biological growth.
- 2.) They provide an effective contact of the slime layer with the wastewater.
- 3.) They provide aeration by rotating the attached growth directly into the air.
- 4.) The structure of the discs also provides an efficient means of mixing the reactors.

The attractiveness of the RBC System stems from its ability to combine, to a certain extent, the favorable aspects of both suspended and attached growth systems. Previous studies have shown them to be advantageous due to their low capital, maintenance, and operating costs, steady performance under variable flow conditions, low detention times, favorable mixing dynamics, and finally the production of a sludge with good settling and dewatering properties.

There are a number of reports in the literature which deal with the use of RBC Systems to nitrify ammonium present in various wastewaters. (40-44) In most cases they deal with low strength ammonium wastewaters and thus are not necessarily indicative of the behavior expected in recycled regenerant. In many of the reported studies, nitrification was studied in conjunction with carbon oxidation, and since no significant BOD is present in the regenerant the available information may not necessarily be extended to estimate nitrification under the conditions of interest in this report.

Finally, in most studies, the chemical constitution of the wastewaters studied, including pH, nutrient abundance, etc., was sufficiently different to limit any correlations which possibly could be drawn. The relatively unique nature of this regeneration process and the regenerant which contains high dissolved solids and ammonium concentrations, as well as low phosphorous and BOD concentrations, necessitated the implementation of actual pilot plant operations to determine the needed design information.

EXPERIMENTAL

A rotating disc pilot plant shown in Figure 7-1 was provided for this study by the Autotrol Corporation. This rotating biological contactor (RBC) consisted of a 32 gallon tank divided into four compartments of equal volume.

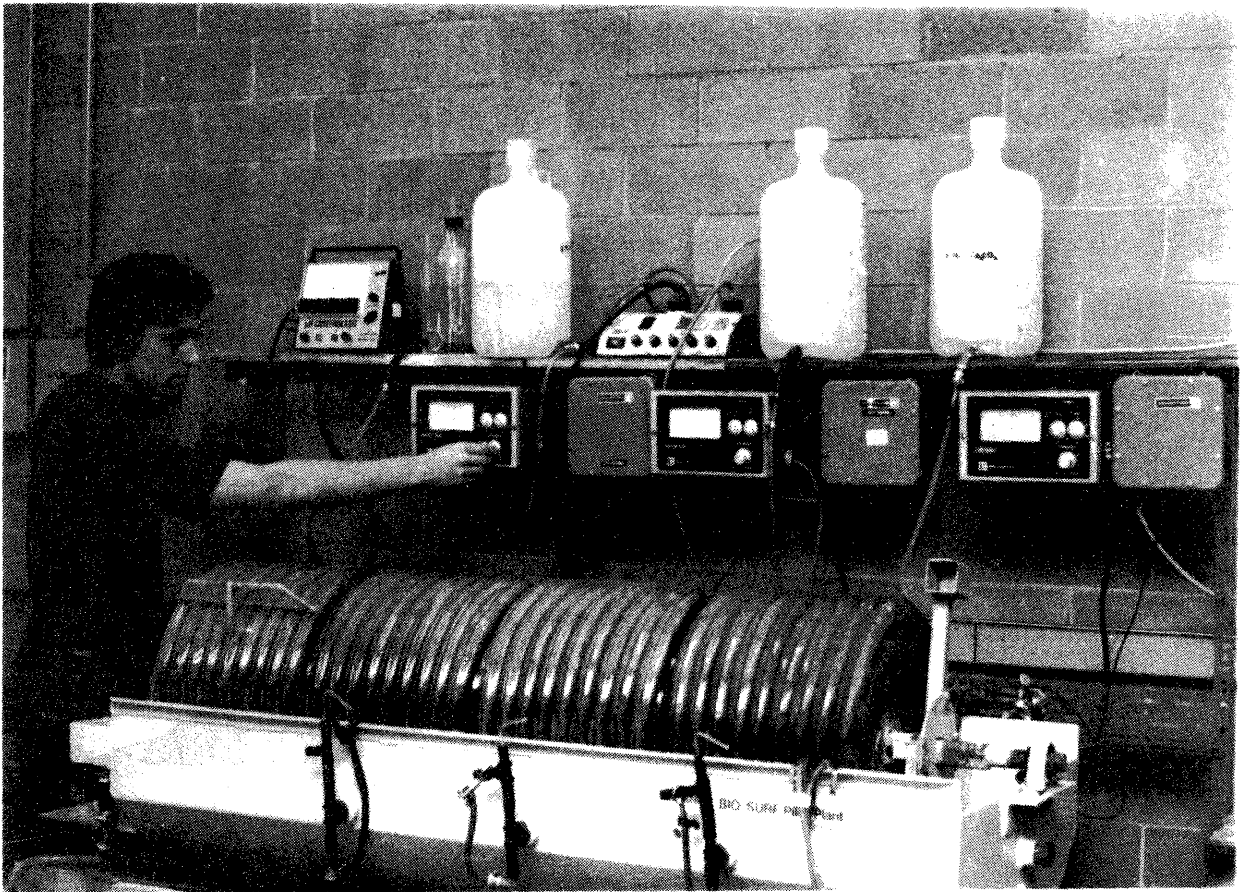


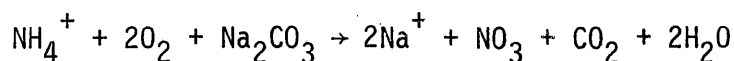
Figure 7.

Experimental Apparatus Used in Attached Growth Studies.

Light weight corrugated polyethylene discs, 0.5 meters in diameter and providing a total surface area of 250 ft², were placed such that 40% of the surface area was submerged. The rotational speed of the discs was controlled by selecting the appropriate gear ratio for the 0.25 HP drive motor. The unit as designed contained appurtenances which allowed several modes of operation. In this study, it was used firstly as four separate completely mixed flow reactors and later as four reactors arranged in series.

Since the feed solution had an inadequate buffering capacity, each reactor was equipped with a pH controller which added 1M Na₂CO₃ as needed. The physical arrangement of the RBC unit and pH adjustment apparatus is shown in Figure 7-1. Three Leeds & Northrup model 7075-3 pH receivers & model 316529 Transmitter modules and one Horizon Type 5997 pH meter/Controller were used to control the pH in the reactors.

Each reactor was equipped with its own base reservoir. The pH probes and base addition tubes were located about an inch apart to provide a steady base addition and prevent large fluctuations in the pH of these reactors. The pH in each reactor was kept in the range of 7.0-7.3 to prevent CaCO₃ precipitation due to high calcium concentrations in the feed solution. The amount of base consumed in the complete oxidation of ammonium to nitrate is described by the relationship;



and theoretically will be about 7.1 units of alkalinity (as CaCO₃) per unit of ammonium oxidized (46).

The original feed solution for these experiments was made up in an 85% dechlorinated tap water solution and 15% unchlorinated secondary effluent obtained from the Seneca Waste Treatment Plant located in Apple Valley,

Minnesota. Secondary effluent was obtained in large volumes and aerated until used. Chemicals were added to give cation concentrations representative of the equilibrium concentrations which will develop in a regeneration solution under steady-state conditions as discussed in Section 5. The cation concentrations are summarized in Table 7-1.

Table 7-1. Cation Concentration in Feed Solution

<u>Cation</u>	<u>Concentration</u>
$\text{NH}_4\text{-N}$	420 mg/l
Na^+	3632 mg/l
Ca^+	1804 mg/l
Mg^+	486 mg/l
K^+	98 mg/l

Sodium and ammonium were added in the chloride form while calcium, magnesium, and potassium were added as nitrates. The feed solution used in these experiments was recycled to simulate practical operating conditions and also to save on chemical costs. Since a significant amount of sodium was added for pH control (2 moles of Na^+ per mole of $\text{NH}_4^+\text{-N}$ completely oxidized), the composition of the recycled brines had to be modified before reuse. The recycle solution was modified by conducting a mass balance on the amount of sodium added, and then diluting the brine with secondary effluent to the Na^+ concentration listed in Table 1. Then Ca^{++} , Mg^{++} , and K^+ salts were added to again give the feed concentrations listed in Table 1. Finally, the $\text{NH}_4^+\text{-N}$ concentration was measured and NH_4Cl was added to give a feed concentration of 420 mg/l $\text{NH}_4\text{-N}$. A portion of the final make-up solution, about equal to the amount of secondary effluent used for dilution was wasted after each make-up in order to maintain a constant regeneration volume.

Sludge which accumulated in the recycle feed resevoirs was allowed to settle after the solution had been modified for reuse. The recycled feed was decanted and reused such that the amount finally wasted contained the settled biomass. The conductivity of the recycle solution was monitored as a check on the procedure, beginning on day 32 of the single staged studies.

The secondary effluent was the sole source of nutrients in these experiments. When the pilot plant was operated as four independent reactors, the effluents from all the reactors were collected, mixed, and reused as described previously. The same feed solution was applied to all the reactors.

Four feed pumps were used initially, two were equipped with Masterflex pumping heads with specially adapted variable speed drives, and two were model 7545 Masterflex Variable speed pumps which were later replaced with Zero-max Variable Speed drives and Sigmameter pumping apparatus due to the unstable performance of the Masterflex pumps at the low flowrates tested.

Operational parameters which were monitored daily included: dissolved oxygen, temperature, influent flow rate, base consumption, pH, and the ammonium concentrations. Dissolved Oxygen concentrations were measured using a YSI 5700 Series Dissolved Oxygen Probe. Ammonium concentrations were analyzed using an Orion ammonia specific ion eletrode. The conductivity of the recycle feed solutions was measured with a Model PM-70 CB Conductivity Bridge. Nitrite and nitrate concentrations were not monitored as the only concern in these experiments was the change from the positively charged ammonium nitrogen species to one of the negatively charged nitrogen species.

Past studies have shown that, under the operating pH range, there are

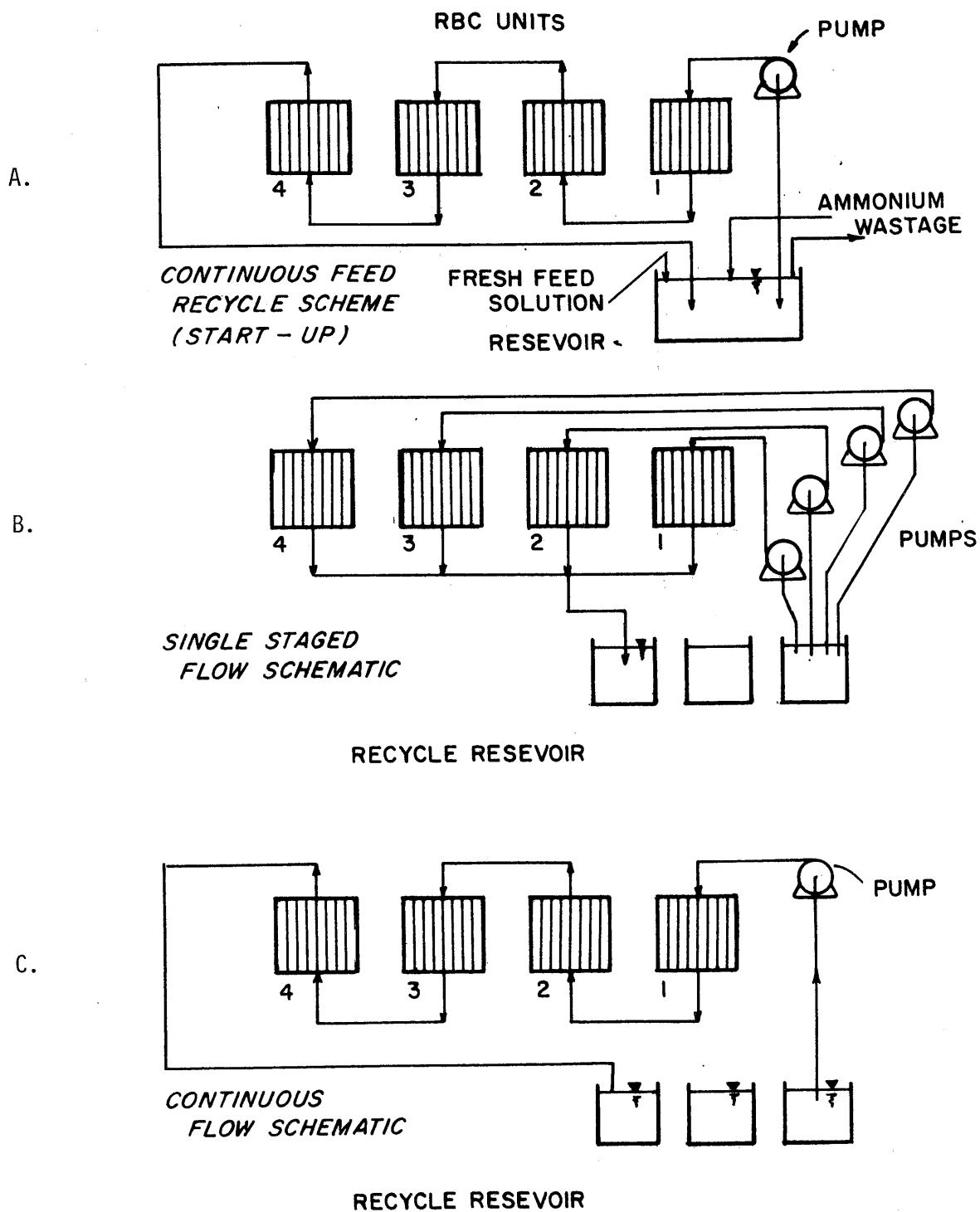
no significant nitrogen losses due to the stripping of ammonia gas from solution. Therefore, monitoring the distribution of nitrogen species, either as a verification of the actual nitrification process or in terms of the eventual operational implications was not considered necessary.

In addition to this, the high initial background nitrate in the recycled regenerant as well as the formation of both nitrite and nitrate in the recycled feed would make analysis difficult in light of the reuse and wastage procedure.

START-UP

Initially, a synthetic wastewater was constituted having approximately half the chemical concentrations listed in Table 7-1. This solution, spiked with a biological culture from a previous dispersed growth nitrification study, was added to each reactor. The rotation of the discs was set at 7 RPM. The ammonium concentrations were monitored daily until the concentrations dropped significantly; about 1 week. At this time a continuous flow system with complete recycle was implemented. This is shown schematically in Figure 7-2. The same feed solution was fed at a rate of about 12 litres/hr with the entire effluent being returned to the influent reservoir. The ammonium concentration of the reservoir was monitored and adjusted several times a day and a fraction of the feed was wasted and replaced with fresh solution on a daily basis. The RBC was operated in this mode for approximately three weeks in order to establish a visible slime layer on the discs prior to experimentation. Slime could be felt

FIGURE 7-2 VARIOUS FLOW SCHEMES EMPLOYED IN STUDY



after about one and a half weeks of operation. However, a thick microbial film, characterized by complete discoloration of the disc, was not formed until the final weeks of operation.

When significant ammonium removals were observed indicating significant nitrifying activity the reactors were drained and refilled with solution having the chemical composition depicted in Table 7-1. The V-notch weirs which connected the four reactors were plugged and the feed was applied.

Single Staged Studies

The operation of the single staged reactors is shown schematically in Figure 7-2B. The pilot plant was operated in this mode for approximately eight weeks to identify the impact of varying loading rates. The performance of the reactors over that period are shown in Figures 7-3 and 7-4. A number of operating difficulties were encountered during the first weeks of experimentation including pumping failures and pH control malfunctions. These are summarized in Table 2 and influenced the variability of the data plotted in Figures 7-3 and 7-4.

The operational conditions and results of these studies are summarized in Table 3. The reactors were operated at a speed of rotation of 7rpm until the effluent concentrations had stabilized for a sufficient period of time that steady state conditions could be assumed. Analysis of the results obtained indicated that the ammonium oxidation rate varied between 0.25 lbs $\text{N}/1000\text{ft}^2/\text{day}$ for the lowest loading rate. A dissolved oxygen limitation was checked by inserting a small air diffuser into the reactor with the smallest loading rate on day 44. As a result the NH_4^+-N effluent concentration dropped from 115 to 79 mg/l NH_4^+-N in two days. It was therefore concluded that the rotational speed was too slow and it was changed to 13 rpm.

Grab samples taken to check the availability of phosphorous. These samples

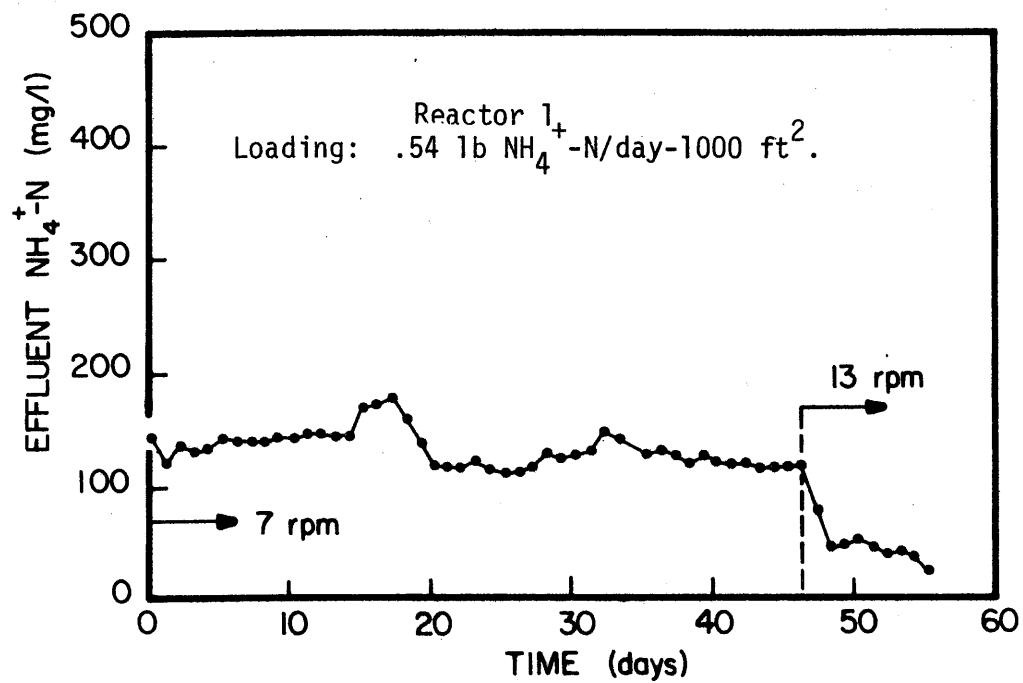
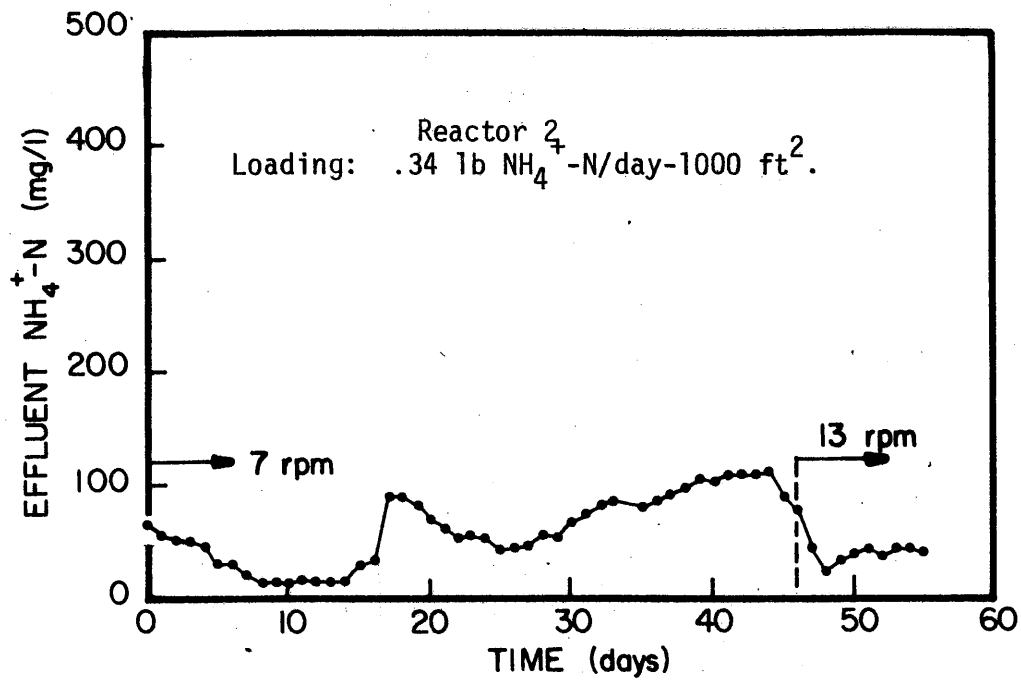


FIGURE 7-3 SINGLE STAGED AMMONIUM REMOVAL PERFORMANCE FOR REACTORS 1 AND 2

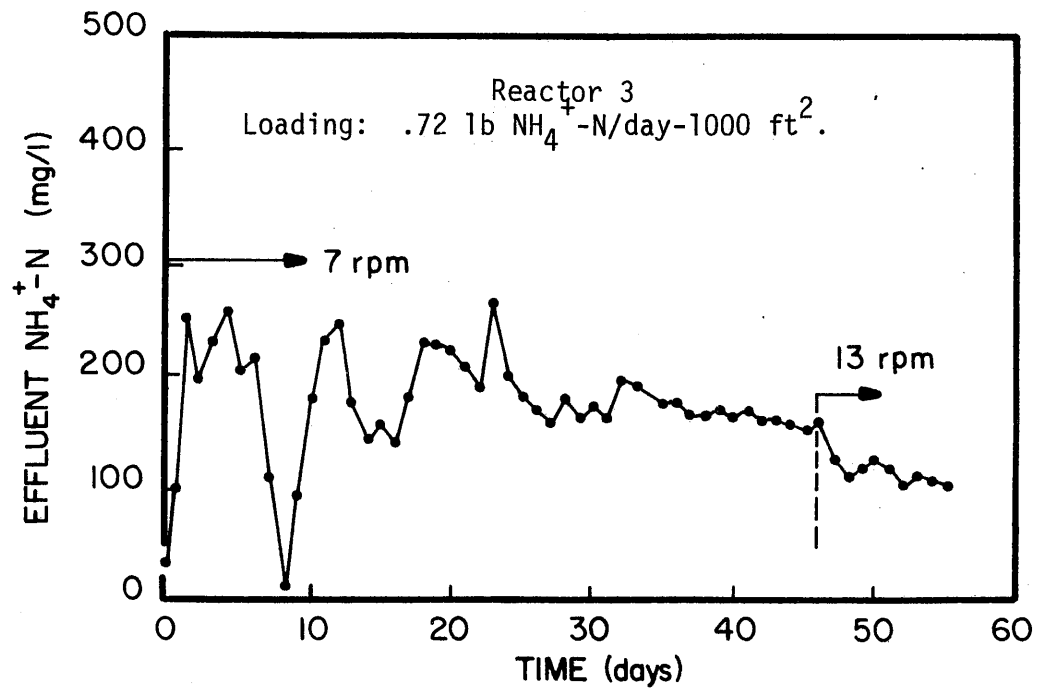
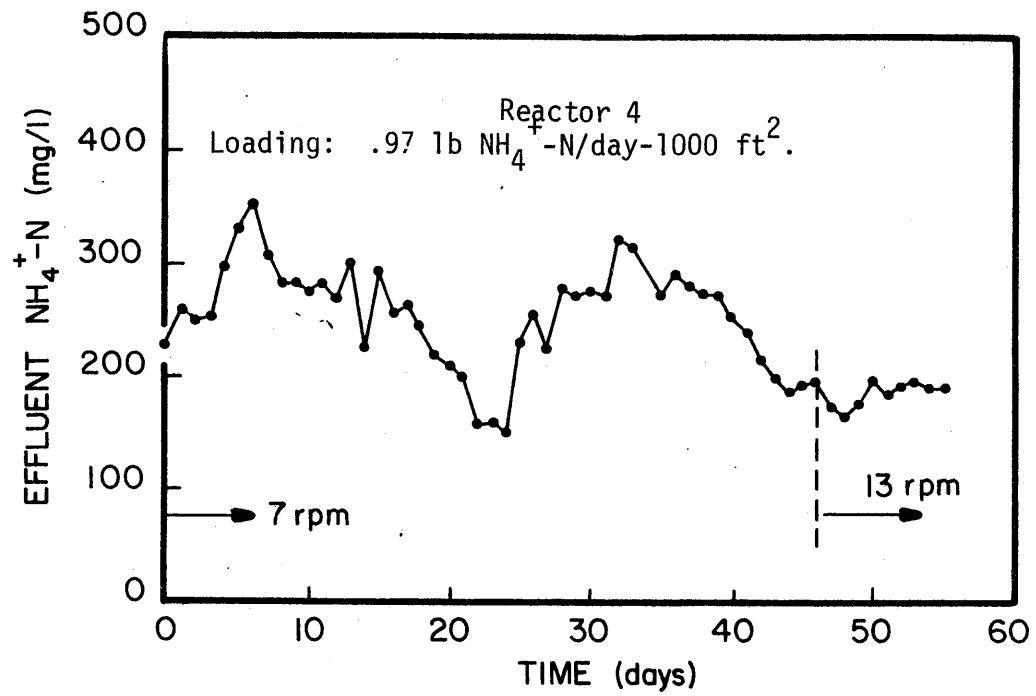


FIGURE 7-4 SINGLE STAGED AMMONIUM REMOVAL PERFORMANCE FOR REACTORS 3 AND 4

Table 7-2
Operating Difficulties - Single Staged Studies

<u>Day</u>	
1	Daily monitoring for all reactors commenced (rotational speed of 7rpm)
1-12	Pumping instability in reactors (3) & (4)
12	Pumping changes in reactors (3) & (4)
14	Ammonium concentration in feed incorrectly adjusted to 440 mg/l NH_4^+-N pH Controller (Horizon) that functions in reactor (4) base influent line plugged in reactor (2)
15	base influent line plugged in reactor (1)
22	base influent line plugged in reactor (3)
24	base influent line plugged in reactor (4)
25-32	Gradual build-up sodium in system due to error in recycle make-up
32	Conductance bridge used to monitor the ionic strength of solution
44	Diffuser inserted in reactor (2) to study effect of an increase in dissolved oxygen
46	Change of rotational speed to 13 rpm
56	Termination of single staged studies

Table 7-3 Operating Conditions and Results for Single Staged Studies

Temperature: 26-30°C, Influent Conc. = 420 mg/l $\text{NH}_4\text{-N}$

Detention Time (days)	Disc Speed (rpm)	Loading $\frac{\text{lb } \text{NH}_4\text{-N}}{\text{day} \cdot 1000\text{ft}^2}$	Loading $\frac{\text{lb } \text{NH}_4\text{-N}}{4}$	Dissolved Oxygen Standard Deviation Average (mg/l)	Alkalinity Added $\frac{\text{lb ac CaCO}_3}{\text{lb } \text{NH}_4\text{-N}}$ Oxidized	Effluent $\text{NH}_4\text{-N}$ Standard Average Deviation (mg/l)	$\text{NH}_4\text{-N}$ Removal Rates $\frac{\text{lb } \text{NH}_4\text{-N}}{1000\text{ft}^2 \cdot \text{day}}$	Percent Removal
1.40	7	.34	18.22	4.40 (6)* .12	6.7	112 (6)* 3.7	.25	73
0.95	7	.51	27.33	3.67 (10) .08	6.8	119 (10) 4.3	.39	72
.67	7	.75	39.86	3.59 (11) .45	6.7	163 (11) 5.4	.44	61
.51	7	.96	51.24	3.52 (4) .20	6.6	192 (4) 6.2	.53	54
1.40	13	.34	18.22	5.48 (6) .17	7.1	35 (9) 5.1	.31	92
.95	13	.51	27.33	4.51 (6) .16	7.1	45 (7) 4.5	.46	89
.67	13	.75	39.86	4.34 (7) .23	6.5	110 (8) 6.9	.53	74
.51	13	.96	51.24	4.36 (5) .25	6.8	190 (6) 5.1	.53	55

7-13

* Numbers in parentheses denote number of days that data was collected at equilibrium.

were found to contain a total phosphorous concentration on the order of 2 mg/l for the reactors indicating that it was probably not limiting. The effluent concentrations reached steady state conditions quickly and within 10 days single stage experiments were terminated.

The increased removal rates are illustrated in Figures 7-5 and 7-6. The rates of removal increased with decreasing loading indicating that enhanced substrate-biomass contact was probably more effective in producing increased removal than higher dissolved oxygen concentrations which generally were increased by about 1 mg/l due to the increased rotational speed.

Continuous Flow Studies

The pilot plant was next operated as a continuous four-staged system (see Figure 3c), to determine if the effluent ammonium concentrations could be reduced to 10-20 mg NH_4^+ -N/l. The unit was loaded at .48 lbs NH_4^+ -N/day-1000 ft² for the entire unit (1.93 lbs NH_4^+ -N/day-1000 ft² for the first reactor along) or an overall detention time of 1.02 days. The concentrations approached equilibrium within several days and the unit was operated until steady-state conditions were established for several days at which point the project was terminated. The operating conditions and results are summarized in Table 7-4, and the removals are depicted in Figure 7-7. An optimum removal rate of .74 lb NH_4^+ -N/day-1000ft² was observed through the first reactor which was greater than the removal rate of about .53 lb NH_4^+ -N/days-1000 ft² which had been observed at these concentrations for the single staged experiments. The removals in the other reactors were generally consistent with those found previously.

FIGURE 7-5 EFFLUENT CONCENTRATIONS AS A FUNCTION OF DETENTION TIME

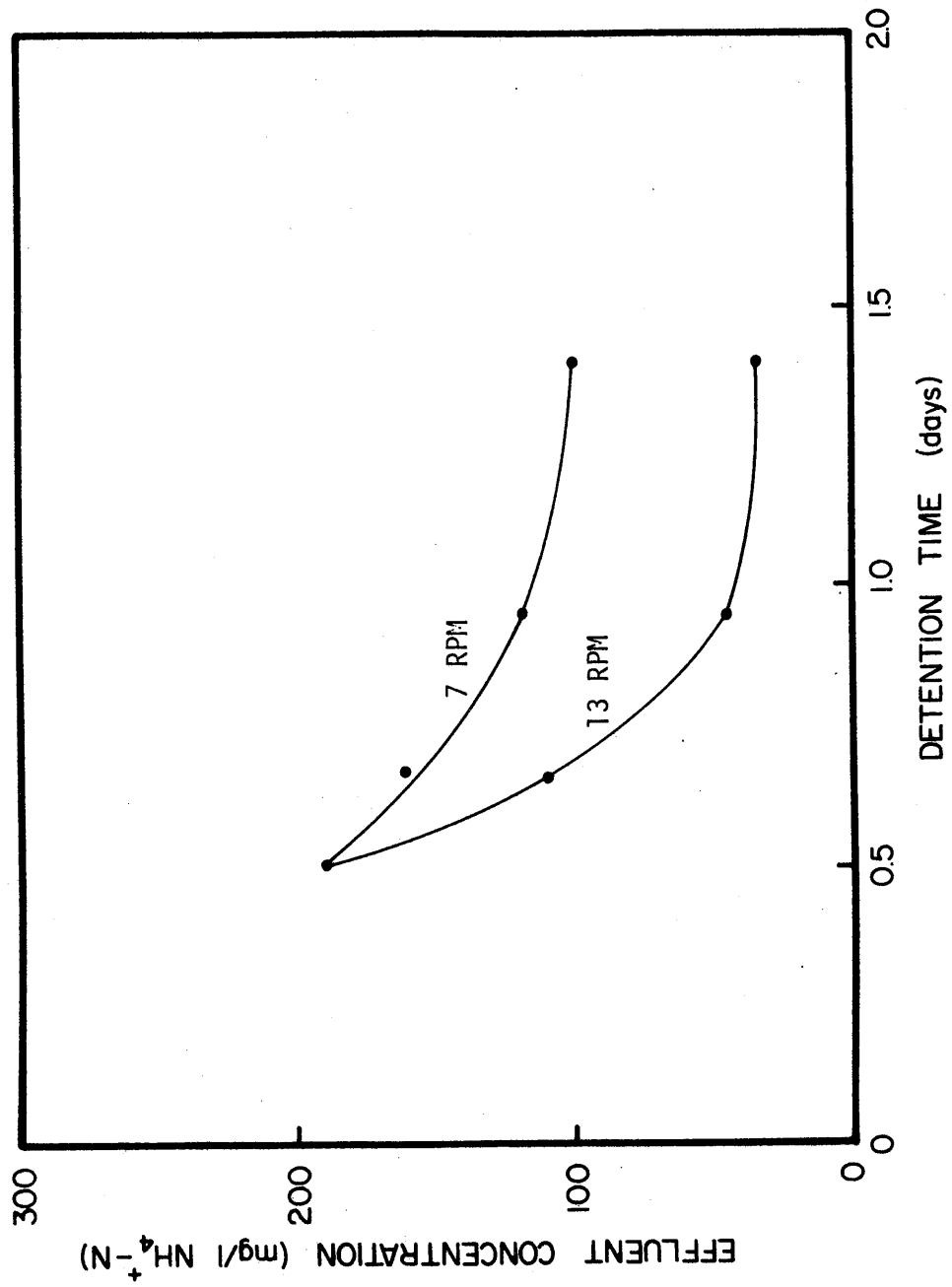
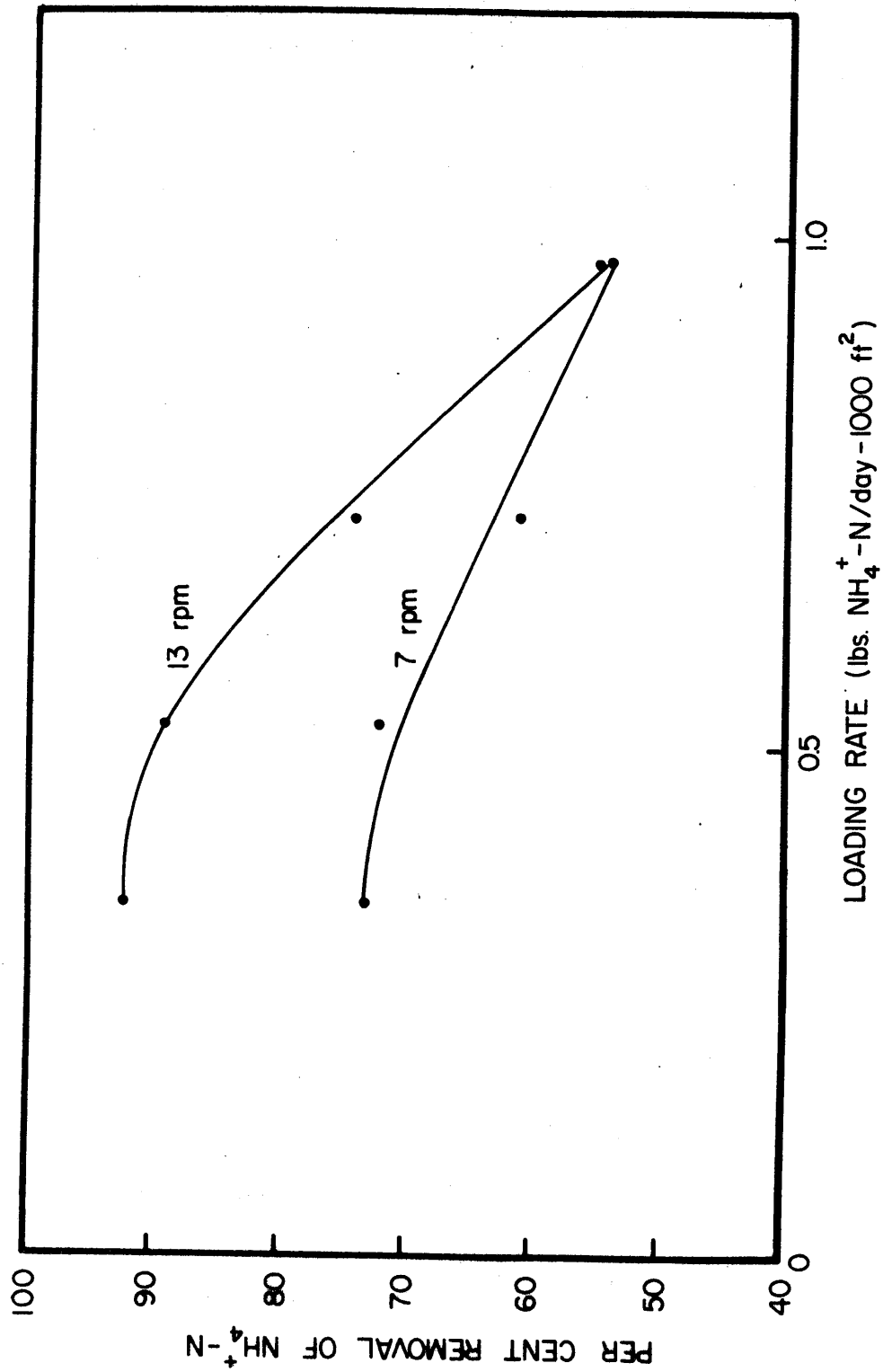


FIGURE 7-6 PERCENTAGE AMMONIUM REMOVAL RATES FOR VARYING LOADING RATES



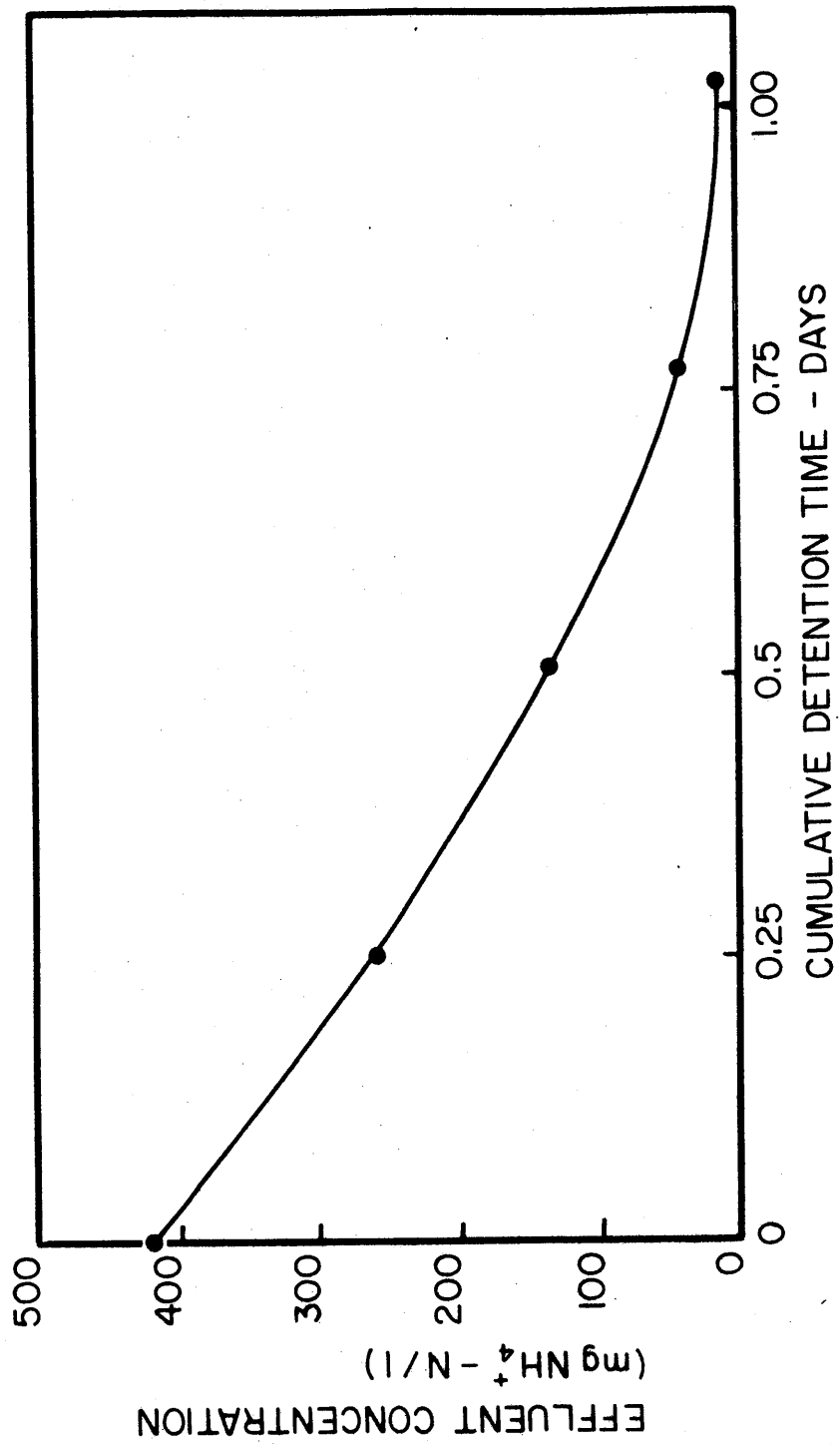


FIGURE 7-7 AMMONIUM REMOVALS THROUGH CONTINUOUS FOUR-STAGED SYSTEM

Table 7-4: Operation and Results of Continuous Flow Experiments
 Temperature = 24-26°C, 13 rpm Speed of rotation

Total detention time: 1.02 days (.255 days per reactor)
 (Equilibrium samples taken for four days)

Reactor	NH ₄ -N Influent (mg/l) (Average)	Loading Per Reactor $\frac{1b \text{ NH}_4^{+}-N}{\text{day} \cdot 1000\text{ft}^2}$	Dissolved Oxygen (mg/l) Average	Effluent mg NH ₄ ⁺ -N/l Average	σ	Removals per reactor $\frac{1b \text{ NH}_4^{+}-N}{\text{day} \cdot 1000\text{ft}^2}$
1	420	1.93	4.0	258	2.5	.74
2	258	1.19	5.0	134	2.1	.57
3	134	0.62	5.25	40	3.3	.45
4	40	0.18	6.45	10	3.3	.14

Discussion

The Kinetic data from the 13 rpm batch and continuous flow studies are shown in Figure 7-8. The results would seem to clearly indicate zero-order removal Kinetics at concentrations approximately above 45 mg $\text{NH}_4\text{-N/l}$. Similar relationships have been made in previous studies with nitrification in attached growth systems, but inherent differences in process variables make reasonable correlations difficult. Antonie (39) reported on nitrification in activated sludge treatment plant effluents with RBC pilot plants and apparently obtained removals in the first-order range of about .8 lb $\text{NH}_3\text{-N/day-1000ft}^2$ in equilibrium with ammonium concentrations of less than 18 mg $\text{NH}_3\text{-N/l}$, a rate which is greater than the highest observed in these experiments. However, the possible differences in operational parameters such as pH and temperature would prohibit any comparison. Murphy et al (42) concluded, that a zero-ordered removal rate of .22 lb TKN/day-1000ft² best described the performance of rotating discs at even very low ammonium concentrations. However, the wastewater contained high organic carbon concentrations and this may not necessarily be compared to the regenerant which was free of BOD.

Lue-Hing et al (43,44) performed experiments on the nitrification of high ammonium concentrations in sludge supernatant. They conducted comprehensive studies, and evaluated the influence of various loading rates, temperature, rotational speeds, and sludge recycle. Their experiments probably represent the most valid comparison to the work performed in this project in that the concentrations of ammonium and other ions are similar in magnitude and the operational parameters are well specified. They observed removals on the order of 2.25 lb $\text{NH}_3\text{-N/day-1000ft}^2$, at 22°C and pH 8.0. This removal rate is nearly three times the highest rate

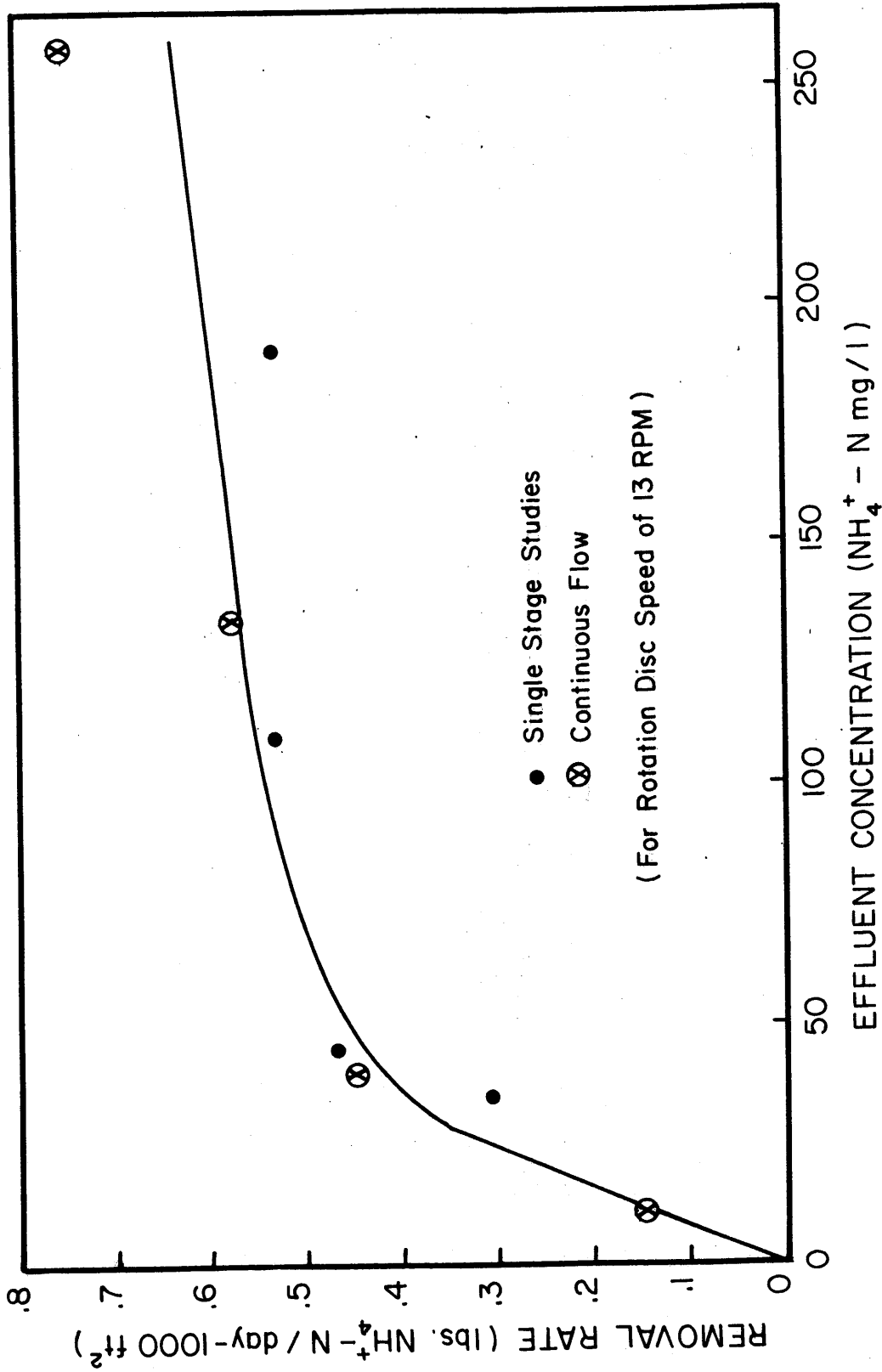


Figure 7-8. Removal Rate as a Function of Effluent Concentration

observed in this study conducted at pH 7.0 and the same temperature. There are a number of possible reasons for this discrepancy.

The difference in solution pH was probably most important. One report on nitrification in attached growth systems (45) indicates that the nitrification rate at a pH of 7 will be approximately half of that observed at pH 8.0. Results obtained in Section 5 with suspended growth cultures originally acclimated at a pH of 7 confirm the magnitude of this pH effect.

The high dissolved solids concentrations present in the regenerant may also cause a slight decrease in the nitrification rate (2).

Finally, the inherent differences in the two different waste solutions are significant. Sludge supernatant is, relatively, nutrient abundant while the recycled regenerant solution may be nutrient deficient. Specifically the phosphorous concentrations observed in the supernatant tested by Lue-Hing et al (43,44) were as much as two orders of magnitude greater than those found in the recycled brine solution tested in this study ($P \approx 2$ mg/l). Kaufman and Boquel (4) found that phosphorous concentration had no effect on the growth of nitrifiers in soil down to very low phosphorous concentrations. There were however, a number of possible errors introduced by their procedures in growing their cultures. Droogenbroeck & Laudelot (47) performed more carefully controlled experiments. Nitrifying cultures were grown in a number of phosphate free solutions to deplete their internal accumulation of the polymetaphosphates. These cultures were then tested to assess the effect of low phosphate concentrations on their growth. These investigators found that the optimum phosphorous concentration for *Nitrobacter* was between 10 and 30 mM and between 10 and 100 mM for *Nitrosomonas*. Unfortunately, the influence of low phosphate concentrations in the range observed in this project and as reported by Lue-Hing (44), was not clarified. It is difficult

therefore, to quantify the change in the nitrification rates which might be observed in these two studies as a function of phosphorous concentration. In similar experiments, Aleem & Alexander (48) found that the optimum concentration for cultures of Nitrobacter was 5 mg P/l and it appeared that growth was limited slightly at concentrations of approximately 0.5 mg P/l. The report did not specify the influence of intermediate phosphorous concentrations.

In summary the results obtained here compare favorably with other nitrification studies on rotating biological contactors. The oxidation rates achieved in this study were slightly slower than those observed by other investigators. However, when the influence of the quality of the recycled regenerant, and the operating conditions are considered the observed performance is comparable to that obtained with lower strength wastes.

Section 8

Economic Considerations

The studies reported above and published previously provide the information required for the tentative design of a biological regeneration process. Since the sequential regeneration process is more flexible in operation it was chosen for comparison with alternative physico-chemical regeneration processes.

In order to assess the economical feasibility of such a process, a brine nitrification plant was sized for the wastewater treatment facility at Alexandria, Virginia. In 1977 the Alexandria Sanitation District published information on proposed advanced wastewater treatment processing costs including ammonia removal by chemically regenerated clinoptilolite. Greeley and Hansen Engineers in Chicago, Illinois, were responsible for the design of the ammonium removal facilities and were kind enough to provide cost and design information which may be compared with the costs of biological regeneration.

The basis for design was the average flow and the maximum flow conditions predicted for 1992, 54 and 81 MGD, respectively. The ammonium concentration in the influent to the ion exchange units was 25 mg N/l and the effluent had to be less than 1 mg/l as N. The average design ammonium loading to the nitrification unit was therefore 10,808 lbs N/day.

The design by Greeley and Hansen Engineers provided 12 ion exchange beds each containing 7300 cu ft of zeolite. Under average flow conditions, 7 of the beds would be in service and with a cycle time of 24 hours, 7 beds would be regenerated per day. The time interval between regenerations would therefore be a little over 3 hours.

In order to regenerate the ion exchangers using the biological regeneration process, 15 volumes of neutral pH regenerant are required. The average ammonium concentration in the regenerant will be approximately 240 mg/l as N. The regenerant flow is therefore 5.7 MGD or approximately 10 percent of the raw wastewater flow.

As our laboratory analyses have shown the time required for regeneration could be as little as 1 hour without any loss in efficiency, regeneration may be completed readily within the available time period. Each regeneration cycle will produce about 820,000 gallons of spent brine which would be contained in a 1.5 MG storage tank and continuously fed to a nitrifying "activated sludge" treatment plant. The aeration tank would contain 3 million gallons of mixed liquor and provide a hydraulic detention time of just over 12 hours under average flow conditions. At a mixed liquor volatile suspended solids concentration of 1200 mg/l the loading would be approximately 0.015 mg N/mg MLVSS/hr, and comparable to that achieved under laboratory conditions. Loading rates higher than this have been reported in Manassa, Virginia, where they operated with a BOD/TKN ratio of 1:2. In addition it is anticipated that the very high oxygen demand would be better met by the use of pure oxygen, since when vigorous aeration is provided to maintain adequate DO values, the high shear gives rise to a poor settling sludge. The sludge settling characteristics should improve significantly with the use of pure oxygen.

The effluent of the aeration tank would be clarified in a sedimentation tank and directed to another 1.5 MG brine storage tank. The clarified brine may be reused to regenerate another zeolite column.

The brine must be maintained at approximately 300 meq/l of nitrate salts. During regeneration of the zeolite, an average of 240 mg/l of ammonium are released to solution. This is equivalent to 17 meq/l of ammonium and during nitrification 34 meq/l of sodium carbonate must be added to the brine for pH control. The concentration of the brine therefore increases to 317 meq/l ; some of the brine must be wasted and replaced with salt-free makeup water. Since 820,000 gallons of brine are used per regeneration cycle, 44,000 gallons of brine would have to be wasted per cycle. This amount of wastage would occur

naturally through losses with waste sludge and brine hold up in the zeolite beds following regeneration. Secondary effluent would be used for makeup.

The most critical aspect of the design of the nitrification system is providing sufficient oxygen. At an ammonium concentration of 240 mg N/l, the nitrogenous oxygen demand is 1080 mg O₂/l. The oxygen transfer facilities have to be capable of providing up to 150 mg/l/hr of oxygen, while simultaneously maintaining high dissolved oxygen concentrations. For these reasons it was felt necessary to use pure oxygen. The cost estimates were provided by Union Carbide (November 1976).

The estimated costs (all computed for November 1976) in Tables 8-1 to 8-3 provides the estimated capital costs of the facilities required for biological regeneration. Table 8-2 presents a summary of the total annual costs for biological regeneration, and Table 8-3 presents similar costs for a chemical regeneration process in which ammonia is recovered using a steam stripping process.

The biological regeneration process clearly requires a very much larger investment in capital costs but the total annual costs of the biological regeneration process are still competitive with chemical regeneration. This difference is even more pronounced if one considers only the operating costs. Certain costs are not included in the analysis of the biological regeneration process as noted in Table 8-2. These include land costs, zeolite replacement costs and sludge disposal costs. These costs cannot be estimated but are expected to be low. For example no significant attrition was observed in the zeolite samples tested over a one year period under laboratory conditions.

Advantages of the Biological Regeneration Process Compared with Alternative Chemical Regeneration Processes

1. The major difference is that the product of the regeneration process is a concentrated solution of nitrate salts rather than a solution of ammonium.
2. No brine has to be wasted since the regenerant loss during each regeneration cycle approximately equals the amount that must be wasted.

Table 8-1. CAPITAL COSTS (1) FOR THE BIOLOGICAL REGENERATION PROCESS
DEPICTED IN FIGURE 1-2

2 Brine Storage Tanks, 1.5 MG each	=	\$ 680,000
1 Aeration Tank, 3.0 MG	=	646,000
Brine Pumps, 8 MGD Capacity	=	140,000
Sludge Recycle Pump, 1.5 MGD Capacity	=	64,000
40 ton/day Cryogenic Plant Plus Aeration Equipment (UNOX)	=	2,200,000*
Subtotal		\$ 3,730,000
Engineering Costs:	=	150,000
Legal and Admin. Costs	=	35,000
Interest During Construction 8%	=	300,000
Subtotal		\$ 4,215,000
Capital Recovery, 20 years, 7.5%	=	\$ 413,070

(1) Patterson, W.L., et al. "Estimating Costs and Manpower Requirements for Conventional Waste Treatment Facilities," EPA Report, 17090 Dan, 10/71.

* Includes instrumentation, installation, etc.

Table 8-2 SUMMARY OF COSTS FOR BIOLOGICAL REGENERATION

Capital Cost Recovery, 20 years at 7.5%	=	\$ 413,070
Utility Costs/year @ 3 cents/Kwh		
Aeration	=	183,220
Brine pumping	=	3,350
Chemical Costs/year	=	1,120,141
Maintenance/Materials	=	60,000
		<hr/>
Total	=	\$ 1,779,781
At a Design Flow of 54 MGD Cost	=	8.3¢/1000 gals.

NOTES:

- 1) Clinoptilolite Replacement costs not included.
- 2) Sludge Disposal not included.
- 3) Manpower Costs Judged equivalent to Chemical Regeneration.
- 4) If Denitrification is Achieved the Capital and Operating Costs of Aeration will be offset to some Degree. Possible savings ~ 1.0¢/1000 gallon.
- 5) Land costs are not included.

Table 8-3 SUMMARY OF COSTS FOR CHEMICAL REGENERATION

(STEAM STRIPPING)	
Capital Costs Recovery/20 years at 7.5%	\$ 24,500
Utility Costs/years at \$3/1000 lbs steam	394,200
Chemical Costs/year	*1,222,885
Zeolite Replacement Costs/year @ \$300/ton	102,000
Sludge Disposal Costs @ \$5/cu yd	327,385
	<hr/>
TOTAL	\$ 2,070,970
At a design flow of 54 MGD Cost	= 10.5¢/1000 gals.

NOTES:

- 1) Based on conversations (5/5/77) with operating personnel at Rosemont, Minnesota, the chemical requirements would be somewhat greater than those estimated by Greeley and Hansen Engineers, Chicago for the Alexandria plant. The operating costs at Rosemont, scaled up on the basis of the pounds of ammonium removed would yield an annual cost of \$1,597,500.
- 2) The manpower requirements were judged to be comparable for both biological and chemical regeneration.
- 3) No cost benefit has been given for the 30% aqueous NH_3 that is obtained as a byproduct.

The small amount of regenerant lost during each cycle will be flushed out of the ion exchanger with the rinse water.

3. The regenerant will contain a high nitrate concentration (approximately 4200 mg/ $\text{NO}_3\text{-N}$) and therefore will contain a high concentration of oxygen (14,400 mg/l). Thus regenerant lost in the rinse water is available for denitrification and may be used to reduce the BOD of untreated sewage or wastewater, or to stabilize the organic content of waste sludge.

4. Though sizeable aeration facilities are required for oxidizing the concentrated ammonium containing regenerant, the oxygen employed in the nitrification of the ammonium may be reused if denitrification facilities are provided. Thus, the size of the aeration facilities required for BOD removal will be reduced. For example, consider the Alexandria STP, the BOD removed = 200 mg/l (say) and $\text{NH}_4^+\text{-N}$ removed = 25 mg/l . If the ammonium is oxidized to nitrate and then recycled and mixed with the plant influent in a denitrification process, the 114 mg/l of the influent BOD will be reduced by denitrification alone.

5. If the nitrate brine is denitrified as described then the products of the process are harmless nitrogen gas and an increase in sodium bicarbonate concentration in solution.

6. The nitrate brine product of this regeneration process has a certain monetary value which is comparable with the marketable ammonium products produced from certain chemical regeneration processes. However, the nitrate brine is much more valuable to the treatment facility because of its high oxygen content and the value of the product is not dependent upon fluctuations in local market demands.

7. Since the ammonium is removed from the wastewater and concentrated by ion exchange the nitrifying bacteria are protected from the toxic

organic concentrations that may upset a conventional nitrification facility.

8. The absence of BOD, the high concentration of ammonium, and a salt medium rich in the essential metals encourages more rapid nitrification rates than are commonly achieved in conventional nitrification facilities.

9. Chemical regeneration processes conducted at high pH produce a calcium carbonate sludge that must be disposed of. Sodium carbonate is added to the regenerant to precipitate calcium as calcium carbonate since the calcium can build up in the regenerant and cause undesirable scale formation in either the clinoptilolite column or in the ammonium stripping equipment. No significant chemical sludge by-products result from the use of the neutral pH biological regeneration process.

10. The nitrate containing rinse waters may also be used to reduce odors if the influent wastewater at the treatment plant is anaerobic. Adding part or all of the nitrate at the headworks of the treatment facility will prevent the development of anaerobic conditions in the grit chambers and primary sedimentation tanks.

Disadvantages of the Biological Regeneration Process

1. The stability of the nitrifying sludge has not yet been demonstrated in field tests, but only in simulated laboratory studies.

2. The nitrifying activity will be reduced in cold weather operation unless waste heat from the anaerobic digesters may be employed to maintain higher temperatures.

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APPENDIX A

Service Program

```

PROGRAM SER(SERDAT,QRTOS,QSTOR,SEROUT,TAPE5=SERDAT,TAPE4=QRTOS,
1TAPE4=SEROUT,TAPE8=QSTOR)
COMMON/Z1/NDIM,PRMT(5),Q(100),DERY(100),AUX(8,100),C(100)
COMMON/Z2/AA(100),AB(100),AC(100),TA(100),TB(100),TC(100)
1,TD(100)
EXTERNAL FCT,OUTP
COMMON A(3),CO,COUNT,D(100),E(100),LDIM,PRCON,SL(4),
1YCEPT(4),XCEPT(4),NL
C
C INPUT OF PARAMETERS *****
C
READ(5,7)NDIM,NL,(PRMT(I),I=1,4),RHO,EPSI,CO,DL,U,VOL,
1(SL(I),I=1,NL),(YCEPT(I),I=1,NL),(XCEPT(I),I=1,NL),PRCON
2,DPDIST,DPINT,CIN
7 FORMAT(2I10/(F10.0))
C COUNT IS A PRINT CONTROLLER VARIABLE
COUNT=0.
C CALCULATION OF DO-LOOP CONTROLLERS
LDIM=NDIM
C CALCULATION OF EQUATION PARAMETERS
V=VOL/FLOAT(LDIM)
DL60 = DL* 60.
T1 = 2.302585*DPDIST/FLOAT(NDIM)
T2 = 2.302585*DPINT
READ(4,141) (Q(I),I=1,LDIM)
141 FORMAT(8F10.0)
A(1)=U/(EPSI*V)
TEMP=1./FLOAT(LDIM)
DO 140 IKJK=1,LDIM
DP = EXP(-(T1*FLOAT(IKJK) + T2))
DP2 = DP*DP
AA(IKJK)=DP
AB(IKJK) = RHO*DL60/(EPSI*DP2)
AC(IKJK) = DL60/DP2
TA(IKJK) = PRMT(3)*A(1)*.5
TB(IKJK) = PRMT(3)*AB(IKJK)*.5
TC(IKJK) = PRMT(3)*AB(IKJK)
TD(IKJK) = 1.0 + PRMT(3)*A(1)*.5
D(IKJK)=SL(NL)
E(IKJK)=YCEPT(NL)
DERY(IKJK)=TEMP
140 CONTINUE
C DECLARATION OF ERROR WEIGHTS AND INITIAL CONDITIONS *****
IL=NL
ASL=SL(NL)
AYCEPT=YCEPT(NL)
TEST=XCEPT(NL)*ASL+AYCEPT
DO 142 I = 1,LDIM
QNO=Q(I)
143 IF(QNO.GT. TEST) GO TO 144
IL = IL - 1
ASL = SL(IL)
AYCEPT = YCEPT(IL)
TEST = XCEPT(IL)*ASL+AYCEPT
GO TO 143
144 CONTINUE
C(I) = (Q(I) -AYCEPT)/ASL
142 CONTINUE
C PRINTING OF INPUT VALUES*****

```



```

      WRITE(6,8)
8  FORMAT("1",10X,"PROGRAM TO SIMULATE THE RESPONSE OF A CLINOPTILOLI
1  ITE COLUMN "/" " ,10X,"TO A CONSTANT INPUT OF AMMONIA SOLUTION."
2/" " ,10X,"DEVELOPED BY ALAN C. BOOTH, UNIVERSITY OF ILLINOIS, URBANA,
3NA, "/" " ,10X,"ILLINOIS, 1976.")
      WRITE(6,9)NDIM,(PRMT(I),I=1,4),PRCON
9  FORMAT("0",10X,"THE VALUES OF THE INPUT PARAMETERS"/
1  " " ,10X,"NDIM=",I3/" " ,10X,"PRMT(1)=",F4.1/" " ,10X,"PRMT(2)=",
2F5.1/" " ,10X,"PRMT(3)=",E11.3/" " ,10X,"PRMT(4)=",E11.3/" " ,10X,
3"PRCON=",F6.3)
      WRITE(6,10)DP,RHO,EPSI,CO,DL,U,VOL,DPDIST,DPINT
10 FORMAT(" " ,10X,"DP=",F7.4/" " ,10X,"RHO=",F5.0/" " ,10X,"EPSI=",F5.2
1/" " ,10X,"CO=",F5.1/" " ,10X,"DL=",E11.3/" " ,10X,"U=",F6.2/" " ,10X,
2"VOL=",F6.3/" " ,10X,"DPDIST=",F9.5/" " ,10X,"DPINT=",F10.4)
      WRITE(6,11)NL,(SL(I),I=1,NL)
11 FORMAT(" " ,10X,"NL=",I2/" " ,10X,"SL(I)=",4(5X,F6.3))
      WRITE(6,12)(YCEPT(I),I=1,NL)
12 FORMAT(" " ,10X,"YCEPT(I)=",4(5X,F6.2))
      WRITE(6,13)(XCEPT(I),I=1,NL)
13 FORMAT(" " ,10X,"XCEPT(I)=",4(5X,F6.2))
C  PRINTING OF COLUMN HEADINGS*****
      WRITE(6,147)(I,C(I) ,Q(I),AA(I),I=1,NDIM,10)
147 FORMAT("1INITIAL CONDITIONS FOR C AND Q /(1X,I5,
11P3E15.6))
      WRITE(6,5)
5  FORMAT("- ",13X,"TIME",8X,"C/CO",17X,"C",17X,"Q")
      WRITE(6,6)
6  FORMAT(" " ,12X,"HOURS",20X,"MG N/LITER",9X,"MG N/GRAM")
C  CALLING SUB. RKGS FOR INTEGRATION *****
      CALL RKGS(IHLF,FCT,OUTP)
      WRITE(6,2) IHLF,PRMT(5)
2  FORMAT(" " ,20X,"IHLF=",I2," PRMT(5)=",F6.2)
      WRITE(8,145)(Q(I),I=1,NDIM)
145 FORMAT(8F10.6)
      STOP
      END
C
      SUBROUTINE RKGS(IHLF,FCT,OUTP)
      COMMON/Z1/NDIM,PRMT(5),Y(100),DERY(100),AUX(8,100),CIKJK(100)
C
      DIMENSION A(4),B(4),C(4)
      DO 1 I=1,NDIM
1  AUX(8,I)=.06666667*DERY(I)
      X=PRMT(1)
      XEND=PRMT(2)
      H=PRMT(3)
      PRMT(5)=0.
      CALL FCT(X)
C
C  ERROR TEST
      IF(H*(XEND-X))38,37,2
C
C  PREPARATIONS FOR RUNGE-KUTTA METHOD
2  A(1)=.5
      A(2)=.2928932
      A(3)=1.707107
      A(4)=.1666667
      B(1)=2.
      B(2)=1.
      B(3)=1.
      B(4)=2.
      C(1)=.5
      C(2)=.2928932
      C(3)=1.707107
      C(4)=.5
C

```

```

C     PREPARATIONS OF FIRST RUNGE-KUTTA STEP
      DO 3 I=1,NDIM
      AUX(1,I)=Y(I)
      AUX(2,I)=DERY(I)
      AUX(3,I)=0.
3     AUX(6,I)=0.
      IREC=0
      H=H+H
      IHLF=-1
      ISTEP=0
      IEND=0

C
C
C     START OF A RUNGE-KUTTA STEP
4     IF((X+H-XEND)*H)7,6,5
5     H=XEND-X
6     IEND=1

C
C     RECORDING OF INITIAL VALUES OF THIS STEP
7     CALL OUTP(X,IREC)
      IF(PRMT(5))40,8,40
8     ITEST=0
9     ISTEP=ISTEP+1

C
C
C     START OF INNERMOST RUNGE-KUTTA LOOP
      J=1
10    AJ=A(J)
      BJ=B(J)
      CJ=C(J)
      DO 11 I=1,NDIM
      R1=H*DERY(I)
      R2=AJ*(R1-BJ*AUX(6,I))
      Y(I)=Y(I)+R2
      R2=R2+R2+R2
      AUX(6,I)=AUX(6,I)+R2-CJ*R1
11    CONTINUE
      IF(J-4)12,15,15
12    J=J+1
      IF(J-3)13,14,13
13    X=X+.5*H
14    CALL FCT(X)
      GOTO 10
C     END OF INNERMOST RUNGE-KUTTA LOOP
C
C
C     TEST OF ACCURACY
15    IF(ITEST)16,16,20

C
C     IN CASE ITEST=0 THERE IS NO POSSIBILITY FOR TESTING OF ACCURACY
16    DO 17 I=1,NDIM
17    AUX(4,I)=Y(I)
      ITEST=1
      ISTEP=ISTEP+ISTEP-2
18    IHLF=IHLF+1
      X=X-H
      H=.5*H
      DO 19 I=1,NDIM
      Y(I)=AUX(1,I)
      DERY(I)=AUX(2,I)
19    AUX(6,I)=AUX(3,I)
      GOTO 9

C
C     IN CASE ITEST=1 TESTING OF ACCURACY IS POSSIBLE
20    IMOD=ISTEP/2
      IF(ISTEP-IMOD-IMOD)21,23,21

```

```

21 CALL FCT(X)
   DO 22 I=1,NDIM
     AUX(5,I)=Y(I)
22  AUX(7,I)=DERY(I)
   GOTO 9

C
C   COMPUTATION OF TEST VALUE DELT
23  DELT=0.
   DO 24 I=1,NDIM
24  DELT=DELT+AUX(9,I)*ABS(AUX(4,I)-Y(I))
     IF(DELT-PRMT(4))28,29,25

C
C   ERROR IS TOO GREAT
25  IF(IHLF-10)26,36,36
26  DO 27 I=1,NDIM
27  AUX(4,I)=AUX(5,I)
     ISTEP=ISTEP+ISTEP-4
     X=X-H
     IEND=0
     GOTO 18

C
C   RESULT VALUES ARE GOOD
28  CALL FCT(X)
   DO 29 I=1,NDIM
     AUX(1,I)=Y(I)
     AUX(2,I)=DERY(I)
     AUX(3,I)=AUX(6,I)
     Y(I)=AUX(5,I)
29  DERY(I)=AUX(7,I)
     CALL OUTP(X-H,IHLF)
     IF(PRMT(5))40,30,40
30  DO 31 I=1,NDIM
     Y(I)=AUX(1,I)
31  DERY(I)=AUX(2,I)
     IREC=IHLF
     IF(IEND)32,32,39

C
C   INCREMENT GETS DOUBLED
32  IHLF=IHLF-1
     ISTEP=ISTEP/2
     H=H+H
     IF(IHLF)4,33,33
33  IMOD=ISTEP/2
     IF(ISTEP-IMOD-IMOD)4,34,4
34  IF(DELT-.02*PRMT(4))35,35,4
35  IHLF=IHLF-1
     ISTEP=ISTEP/2
     H=H+H
     GOTO 4

C
C   RETURNS TO CALLING PROGRAM
36  IHLF=11
     CALL FCT(X)
     GOTO 39
37  IHLF=12
     GOTO 39
38  IHLF=13
39  CALL OUTP(X,IHLF)
40  RETURN
   END

C
C   *****
C
C
C
C

```

```

SUBROUTINE FCT(X)
COMMON/Z1/NDIM,PRMT(5),Q(100),DERY(100),AUX(8,100),C(100)
COMMON A(3),CO,COUNT,D(100),E(100),LDIM,PRCON,SL(4),
1YCEPT(4),XCEPT(4),NL
COMMON/Z2/AA(100),AB(100),AC(100),TA(100),TB(100),TC(100)
1,TD(100)
DO 1 I=1,LDIM
DERY(I)=AC(I)*(D(I)*C(I)+E(I)-Q(I))
1 CONTINUE
RETURN
END
SUBROUTINE OUTP(X,IHLF)
COMMON/Z1/NDIM,PRMT(5),Q(100),DERY(100),AUX(8,100),C(100)
COMMON A(3),CO,COUNT,D(100),E(100),LDIM,PRCON,SL(4),
1YCEPT(4),XCEPT(4),NL
COMMON/Z2/AA(100),AB(100),AC(100),TA(100),TB(100),TC(100)
1,TD(100)
6 ANY=C(LDIM)/CO
IF(COUNT.GT.X)GO TO 10
COUNT=COUNT+PRCON
WRITE(6,2)X,ANY,C(LDIM),Q(LDIM)
2 FORMAT('0',10X,F7.4,6X,F6.4,6X,E12.4,6X,E12.4)
10 CNM10=CO
CNM1N=CO
IL=NL
ASL=SL(NL)
AYCEPT=YCEPT(NL)
TEST=XCEPT(NL)
DO 3 I=1,LDIM
CNO=C(I)
8 IF(C(I).GT.TEST)GO TO 7
IL=IL-1
ASL=SL(IL)
AYCEPT=YCEPT(IL)
TEST=XCEPT(IL)
GO TO 8
7 D(I)=ASL
E(I)=AYCEPT
5 C(I)=(CNO+TA(I)*(CNM10+CNM1N-CNO)-TB(I)*ASL*CNO-TC(I)*
1 (AYCEPT-Q(I)))/(TD(I)+TB(I)*ASL)
CNM10=CNO
3 CNM1N=C(I)
RETURN
END

```

READY.

bye

3KZMYWV LOG OFF 16.29.24.
 3KZMYWV SRU 65.011 UNTS.



Appendix B

Illustration of the Corrections Made for Dilution Water in the Regeneration Isotherm

When the large weights of moist zeolite were added to a volume of regenerant, the moisture content provided a significant amount of water which acted to dilute the regenerant. Following ammonium release it was necessary to correct the measured solution concentration of ammonium to compensate for the lower salt content of the diluted water. This calculation is shown below:

Wt. of dry zeolite added = 14.39 grams

Moisture content of zeolite when added = 22.5%

Wt. of water added to the regenerant = 4.14 grams

Volume of regenerant used = 30.1 ml

Total solution volume = 4.14 + 30.1 = 34.24 mls

Measured ammonium concentration = 194 mg N/L

Corrected ammonium concentration = $194 \times \frac{34.24}{30.1}$

Ammonium on the zeolite initially = 6.07 mg/g

Final ammonium content of the zeolite = $\frac{(14.39) \times 6.07 - .0301 \times 221}{14.39}$

Amount of ammonium remaining adsorbed = 5.607 mg N/g



CONTINUOUS FLOW NITRIFICATION STUDY

[illegible]

TABLE C-2

CONTINUOUS FLOW NITRIFICATION STUDY

A. Steady state period no.3, April 10-24 1978. Mean cell residence time θ_c : 15 days. Pilot plant no.3.

AERATION TANK NO.	NH ₄ CONCEN- TRATION	pH	MIXED LIQUOR VOLATILE SUSPEND SOLIDS MLVSS								VOLUME SLUDGE WASTED	DISSOLVED OXYGEN DO	TEMPERATURE	FEED FLOW- RATE Q
			AERATION		EFFLUENT		WASTAGE							
			VS	TS	VS	TS	VS	TS						
	(MG/L)													
FEED SOLUTION	420													
3	1.92	7	724	928	88	121	724		75	5.45	25 ^o	144		
3	2.40	7	750	917	86	164	750		102	5.50	24.5 ^o	144		
3	1.87	7	732	932	72	125	732		151	5.30	25.5 ^o	144		
3	1.98	7	728	916	72	152	728		142	6.15	25 ^o	144		
3	1.30	7	640	840	75	164	640		112	6.05	26.5 ^o	144		
3	2.15	7	720	848	76	136	720		120	6.00	24.5 ^o	144		
3	1.85	7	664	836	78	106	664		95	6.10	26 ^o	144		
3	2.05	7	725	843	80	148	725		100	6.30	24 ^o	144		
3	1.85	7	724	826	76	160	724		120	6.50	24 ^o	144		

TABLE C-2 (cont')

AERATION TANK NO.	NH ₄ CONCEN- TRATION	pH	MIXED LIQUOR VOLATILE SUSPEND SOLIDS MLVSS								VOLUME SLUDGE WASTED (ML/DAY)	DISSOLVED OXYGEN DO (MG/L)	TEMPERATURE (°C)	FEED FLOW- RATE Q (ML/HOUR)
			AERATION		EFFLUENT		WASTAGE							
	VS		TS	VS	TS	VS	TS	VS	TS					
	(MG/L)													
3	1.80	7	769	942	76	140	769		143	6.05	26°	144		
3	2.30	7	717	907	80	108	717		95	6.20	24.5°	144		
3	1.95	7	695	950	72	96	695		125	6.15	26°	144		
3	2.15	7	757	911	76	176	757		137	5.80	25°	144		
3	2.39	7	675	850	68	108	675			5.80	23.5°	144		
3	1.90	7	684	916	68	132	684			6.00	24.5°	144		

TABLE C-3

CONTINUOUS FLOW NITRIFICATION STUDY

A. Steady state period no.4, March 25, April 24, 1978. Mean cell residence time θ_c : 25 days. Pilot plant no.2.

AERATION TANK NO.	NH ₄ CONCEN- TRATION	pH	MIXED LIQUOR VOLATILE SUSPEND SOLIDS MLVSS								VOLUME SLUDGE WASTED (ML/DAY)	DISSOLVED OXYGEN DO (MG/L)	TEMPERATURE (°C)	FEED FLOW- RATE Q (ML/HOUR)
			AERATION		EFFLUENT		WASTAGE							
	VS		TS	VS	TS	VS	TS							
	(MG/L)													
FEED SOLUTION	420													
1	2.95	7	848	1068	72	72	848		180	7.8	20°	132		
1	3.05	7	896	1037	80	116	896		156	8.0	20°	132		
1	3.10	7	853	1017	84	132	853		134	7.9	20°	132		
1	3.20	7	867	906	88	105	767		122	7.5	20°	132		
1	2.20	7	804	928	83	125	804		129	6.3	20°	132		
1	1.18	7	792	981	76	92	792		154	7.4	20°	132		
1	1.22	7	747	890	84	96	747		112	6.05	20°	132		
1	2.85	7	764	902	68	100	764		182	6.15	20°	132		
1	1.30	7	744	956	70	100	744		180	7.15	20°	132		

TABLE C-3 (cont')

AERATION TANK NO.	NH ₄ CONCEN- TRATION	pH	MIXED LIQUOR VOLATILE SUSPEND SOLIDS MLVSS								VOLUME SLUDGE WASTED (ML/DAY)	DISSOLVED OXYGEN DO (MG/L)	TEMPERATURE (°C)	FEED FLOW- RATE Q (ML/HOUR)
			AERATION		EFFLUENT		WASTAGE							
	VS		TS	VS	TS	VS	TS							
								(MG/L)						
1	1.95	7	776	976	86	100	776		110	6.40	20°	132		
1	1.40	7	724	804	72	72	724		159	7.40	20°	132		
1	1.90	7	688	748	86	86	688		78	7.40	20°	132		
1	1.52	7	729	849	86	86	729		90	6.95	20°	132		
1	1.72	7	686	776	72	104	686		156	7.50	20°	132		
1	1.37	7	672	780	70	88	672		159	7.00	20°	132		
1	1.90	7	693	813	80	92	693		117	7.50	20°	132		
1	1.45	7	688	769	88	88	688		78	6.95	20°	132		
1	1.90	7	700	804	80	120	700		119	7.90	20°	132		
1	1.70	7	704	848	80	120	704		120	6.95	20°	132		

TABLE C-3 (cont')

AERATION TANK NO.	NH ₄ CONCEN- TRATION	pH	MIXED LIQUOR VOLATILE SUSPEND SOLIDS MLVSS								VOLUME SLUDGE WASTED (ML/DAY)	DISSOLVED OXYGEN DO (MG/L)	TEMPERATURE (°C)	FEED FLOW- RATE Q (ML/HOUR)
			AERATION		EFFLUENT		WASTAGE							
	VS		TS		VS		TS							
	(MG/L)													
1	1.55	7	687	804	80	80	80	687		116	7.20	20°	132	
1	2.00	7	715	833	82	84	84	715		113	7.00	20°	132	
1	1.95	7	686	764	80	100	80	686		115	7.10	20°	132	
1	2.25	7	761	900	88	88	88	761		98	8.40	20°	132	
1	2.52	7	708	808	76	108	76	708		139	7.15	20°	132	
1	1.55	7	728	808	80	116	80	728		125	7.20	20°	132	

TABLE C-4

BATCH REACTOR NITRIFICATION STUDYA. TYPICAL DATA FROM REACTOR 3:

<u>SAMPLE IDEN- TIFICATION</u>	<u>SAMPLING TIME (hour)</u>	<u>pH</u>	<u>AMMONIUM CONCENTRATION (MG/L)</u>	<u>AMMONIUM REMOVED (MG/L)</u>
S _m	-	-	-	-
S _n	-	-	-	-
S ₀	0	7.0	373.0	-
S ₁	6	7.0	371.2	1.8
S ₂	12	7.1	*	-
S ₃	18	7.0	365.6	7.4
S ₄	24	7.0	360.2	12.8
S ₅	30	7.2	352.6	20.4
S ₆	36	7.0	348.8	30.2
S ₇	42	7.1	330.5	42.5
S ₈	48	7.0	318.0	55.0
S ₉	54	7.1	303.3	69.7
S ₁₀	60	7.2	288.4	84.6
S ₁₁	66	7.0	275.1	97.9
S ₁₂	72	7.0	260.2	112.8
S ₁₃	78	7.0	246.1	126.9
S ₁₄	84	7.0	215.8	157.2

TABLE C-4 (cont')

A. TYPICAL DATA FROM REACTOR 3: (cont')

<u>SAMPLE IDEN- TIFICATION</u>	<u>SAMPLING TIME (hour)</u>	<u>pH</u>	<u>AMMONIUM CONCENTRATION (MG/L)</u>	<u>AMMONIUM REMOVED (MG/L)</u>
S ₁₅	90	7.1	164.0	209.0
S ₁₆	93	7.0	115.2	257.8
S ₁₇	96	7.0	64.8	308.2
S ₁₈	99	7.1	5.8	367.2
S ₁₉	102	7.0	0.0	373.0
S ₂₀	-	-	-	-

B. YIELD DETERMINATION DATA:

<u>SAMPLE</u>	<u>TOTAL CARBON (MG/L)</u>	<u>INORGANIC CARBON (MG/L)</u>	<u>ORGANIC CARBON (MG/L)</u>
S _m	19.9	15.1	4.8
S _n	16.5	12.3	4.2
R ₂ M ₂	23.5	10.1	13.50
R ₂ M ₁	26.0	13.6	12.40
S ₂₀ U	23.6	6.0	17.60
S ₂₀ F	17.2	8.5	8.7

TABLE C-4 (cont')SAMPLE IDENTIFICATION

S_m	:	Sonicated sample, taken at time 0, before adding microorganisms
S_n	:	Filtered sample, taken at time 0, before adding microorganisms
$R_2 M_2$:	Unfiltered sample, taken at time 0, after adding microorganisms
$R_2 M_1$:	Filtered sample, taken at time 0, after adding microorganisms
$S_{20} U$:	Unfiltered final sample
$S_{20} F$:	Filtered final sample

TABLE C-4 (cont')C. CALCULATION OF THE YIELD COEFFICIENT:1. Final solids:

$$17.6 - 8.7 : 8.9 \text{ mg/l carbon}$$

2. Original solids before adding microorganisms:

$$4.8 - 4.2 : 0.6 \text{ mg/l}$$

3. Added microorganisms:

$$13.5 - 12.4 - 0.6 : 0.5 \text{ mg/l}$$

4. Net increase in microbial mass:

$$8.9 - 0.6 - 0.5 : 7.8 \text{ mg/l}$$

5. Yield:

$$7.8/373 : 0.03 \text{ mg/l carbon/mg/l NH}_3 \text{ assuming 40\% of the cell mass is nitrogen the yield becomes:}$$

$$\frac{7.8}{0.4} / 373 : 0.07 \frac{(\text{mg/l cells})}{(\text{mg/l NH}_3)}$$

6. Calculation of X_o/Y, needed to determine M_{max}:

$$X_o/Y : 0.5/0.03 : 16.6 \text{ mg/l NH}_3$$

NOTE: Three reactors were run simultaneously at each batch system study. The information given in table 5-1 is typical data from one reactor.