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OPTIMATION OF AMMONIA REMOVAL BY ION EXCHANGE USING CLINOPTILOLITE

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OPTIMIZATION OF AMMONIA REMOVAL BY ION EXCHANGE USING CLINOPTILOLITE

by

Sanitary Engineering Research Laboratory
College of Engineering
and
School of Public Health
University of California
Berkeley, California 94720

for the

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ABSTRACT

The zeolite ion exchanger clinoptilolite was investigated with the objective of optimizing its application to ammonia removal from wastewaters. The study included multiple cycle pilot plant operations at three municipal sewage treatment plants. Particular attention was given to cation interference with exhaustion performance and with minimum cost regeneration.

The ammonia capacity of clinoptilolite was found to be nearly constant over the pH range of 4 to 8, but diminished rapidly outside this range. In regeneration the pH was critical in determining the NaCl requirements, a higher pH favoring lesser amounts of salt. However, at a pH over 12.5 zeolite attrition became excessive and exchanger makeup contributed significantly to operating costs.

An average ammonia removal of 95.7% was obtained in demonstration studies on three municipal wastes having an NH_3-N content of about 20 mg/ℓ. The cost of ammonia removal using clinoptilolite for a 10-mgd plant operating under these conditions was estimated to be $0.082/1000 gal. Ammonia removal down to less than 0.5 mg/ℓ NH_3-N is technically feasible, but only with shorter exhaustion runs and greater regenerant requirements.

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FIGURES

FIGURES (Continued)

TABLES

TABLES (Continued)

I. CONCLUSIONS

The principal objectives of this investigation were: 1) to determine the effect of water composition, ionic form of the zeolite, and pH on the exhaustion performance of clinoptilolite; 2) to optimize the regeneration cycle of clinoptilolite; 3) to conduct studies to determine the performance of clinoptilolite in removing ammonia from chemically different sewages; and 4) to develop design criteria and estimate treatment costs associated with the removal of ammonia using clinoptilolite Experimental studies were conducted using clinoptilolite beds 4 in. in diameter by 3 ft in length. Tests in chemically defined systems using fortified tap water were made to determine ion exchange properties of clinoptilolite in column operation. Subsequent tests with sewage were made to optimize column operation and to evaluate the performance of clinoptilolite in wastewater systems. A cost analysis of the process was made based on the experimental results of the study. Conclusions are presented with respect to the various parts of the study with specific implications regarding the operation and design of clinoptilolite ion exchange units listed where appropriate.

EXHAUSTION PERFORMANCE OF CLINOPTILOLITE

The exhaustion performance of clinoptilolite was examined using tap water containing cation concentrations typical of domestic sewages. Clinoptilolite was exhausted in the Na and Ca forms to compare their operational characteristics. Results indicated that column kinetics were considerably more favorable for exhaustion and regeneration using the Na form.

The effect of water composition on the ammonia exchange capacity was analyzed by exhausting clinoptilolite with waters having different chemical compositions. For a relatively constant influent ammonia concentration, the ammonia exchange capacity decreased sharply with increasing competing cation concentrations representative of "average" sewages. At higher concentrations the ammonia exchange capacity decreased to a much lesser degree as the cation concentration of the feed was increased. The results of these tests may be used to estimate the ammonia exchange capacity of clinoptilolite for wastewaters containing cation concentrations which are not unusually different from concentrations used in tests made during this study.

A model was formulated to describe the effect of pH on ammonia exchange in a ternary NH_4-Na-H system. This model described the solid phase ammonium ion concentration as a function of pH for specific values of

the NH_4-H and NH_4-Na selectivity coefficients and the ammonia dissociation constant. Experimental tests were made using both 2-hr batch equilibrations and column runs to demonstrate the validity of this model. The results of these tests make it possible to understand the effect of pH on column performance during exhaustion and to combine the ammonia exchange process with other unit processes required to meet specific treatment objectives.

The following specific conclusions were made regarding the exhaustion of clinoptilolite in columnar systems:

1. The ammonia exchange capacity of domestic wastewaters can be estimated from the cationic strength (similar to total ionic strength) of the column influent. The ammonia exchange capacity was observed to decrease sharply with increasing competing cation concentrations to a cationic strength of about 0.01 mole/ℓ. Increases of cationic strength above this value continued to decrease the exchange capacity, but to a much lesser degree.

2. While the total ammonia exchange capacity was identical for Na- and Ca-based clinoptilolite, the breakthrough exchange capacity was more than twice as great for Na-clinoptilolite. This observation was accounted for on the basis of the greater mobility of the smaller sodium ion in the zeolite pore spaces.

3. While this phase of the study was principally concerned with the exhaustion performance of clinoptilolite, it became apparent that regeneration using calcium salts was much less efficient than using sodium salts. Approximately three times as much regenerant, expressed on an equivalent basis, was required for complete ammonia elution using $CaCl_2$ and $Ca(OH)_2$ compared to NaCl and NaOH. Operation of clinoptilolite using sodium salts for regeneration resulted in a greater throughput per cycle to ammonia breakthrough and led to economies of regeneration.

4. Optimum conditions for ammonia exchange exist between pH 4.0 and pH 8.0 with little variation in ammonia exchange capacities between these values. However, the ammonia exchange capacity decreased rapidly outside this range. Results of these tests were predicted by a model of the exchange reaction and independently determined selectivity coefficients.

5. The ineffectiveness of ammonia sorption at high pH corroborated observations that regeneration of an ammonium-based clinoptilolite is best accomplished at high pH. The exchange model predicted an ammonia exchange capacity of 0.53 meq/g at pH 10, 0.08 meq/g at pH 11, and 0.008 meq/g at pH 12 for clinoptilolite in equilibrium with a solution containing 60 mg/ℓ Na and 20 mg/ℓ NH_3-N. While regeneration is not an equilibrium process, these values indicate that elution of ammonia becomes much more favorable as the pH of the regenerant is increased.

REGENERATION

Regeneration of clinoptilolite was examined to determine the effects of flow rate, regenerant pH, and regenerant NaCl concentration on the regeneration efficiency and on the volume of regenerant required. (Here regeneration efficiency was defined as the equivalents of NH_3-N removed during exhaustion divided by the equivalents of Na used for regeneration expressed as a percentage.) Results indicated that the regenerant pH was the controlling factor in determining the amount of regenerant required to remove ammonia from clinoptilolite. It was hypothesized that the unionized ammonia formed at the high pH was able to diffuse through the zeolite pores more readily than the ammonium ion. This coupled with the maintenance of a maximum differential between solid and solution phase ammonium ion concentrations at high pH resulted in an increased rate of ammonia elution.

Attrition studies were made to determine the stability of clinoptilolite in the presence of caustic solutions. In small column tests designed to simulate exhaustion and regeneration cycles, attrition rates of 0.25, 0.35, and 0.55%/cycle were measured for exposure to pH 11.5, 12.0, and 12.5 solutions, respectively. Although the attrition rate appeared to decrease after exposure to approximately 100 simulated regeneration cycles, it could not be concluded from these tests that this would lead to a decrease in the required replacement rate of clinoptilolite.

The following specific conclusions were made with respect to the regeneration of clinoptilolite:

6. Regeneration of clinoptilolite with caustic solutions is necessary if the process is to be feasible for ammonia removal. However, the strength of caustic used for regeneration will be limited by the attrition of clinoptilolite in caustic solutions.

7. The pH at which clinoptilolite was regenerated affected both the volume of regenerant required and regeneration efficiency. Regeneration at pH 12.5 was more effective and more efficient than regeneration at pH 11.5 or 12.0.

8. Increasing the regenerant NaCl concentration beyond a certain value at a particular pH had no effect on the volume of regenerant required. For regeneration at pH 12.0 and 12.5, no benefit was realized by using a salt concentration greater than 0.10 lb NaCl/gal. Likewise, increasing the salt concentration beyond 0.17 lb NaCl/gal at pH 11.5 produced no improvement in regeneration performance.

9. Flow rate had no effect on regeneration efficiency over the range of 4 to 20 BV/hr. Flow rates of 25 BV/hr produced minor impairment of regeneration performance, but regeneration at a flow of 30 BV/hr resulted in unacceptable performance judged by the amount of ammonia eluted per unit volume of regenerant.

10. The rinse requirement varied with the buffering capacity of the rinse water. Eleven bed volumes of product water was sufficient to reduce the pH to 10.0, while 35 BV of tap water having a lower buffer capacity was required for equivalent rinsing. The application of small amounts of acid to the bed prior to rinsing reduced the rinse requirement. However, this reduction was insufficient to justify the added expense of purchasing and storing acid.

PROCESS PERFORMANCE

Process demonstration studies were conducted at three locations to provide measures of column performance. Observations made during these tests may be summarized as follows:

11. The performance of clinoptilolite was related to various operating variables. Flow rates in the range of 7.5 to 15 BV/hr had no effect on ammonia effluent values. Ammonia leakage was observed to decrease with increasing levels of regeneration.

12. An overall ammonia removal of 95.7% was achieved in these tests with an average effluent ammonia concentration of 0.75 mg/ℓ NH_3-N. Removals at the SERL treatment facility averaged 97.8% with an average effluent concentration of 0.39 mg/ℓ NH_3-N for one test series and 91.5% with an effluent concentration of 1.7 mg/ℓ NH_3-N for a second series. However, in the second series of runs an effluent average of 0.94 mg/ℓ NH_3-N could have been achieved if runs had been stopped after a throughput of 135 BV instead of the 180 BV run length which was used. Average effluent concentrations of 0.20–0.30 mg/ℓ NH_3-N could have been achieved in the first series of runs for run lengths of 90 BV. Removals in tests at the East Bay Municipal Utility District pilot plant averaged 94.0% with an effluent value of 0.71 mg/ℓ NH_3-N. In tests at the Central Contra Costa Sanitary District an average removal of 97.5% with an average effluent concentration of 0.50 mg/ℓ NH_3-N was achieved.

COST OF AMMONIA REMOVAL

Results obtained in the experimental phases of the study were utilized in the conceptual design and cost analysis of a 10-mgd clinoptilolite ion exchange facility. The design included the use of gravity flow reinforced concrete vessels as ion exchange reactors. Estimates were based on costs of rapid sand filters. Treatment costs were calculated for a system where regenerant would be wasted after one use and for a system in which regenerant would be stripped of ammonia and reused. The following conclusions were reached:

13. The cost of regeneration where regenerant would be used only once was strongly dependent on the concentration of salt used in the regenerant. Costs were least for regeneration at pH 12.5 because of the higher regeneration efficiency at this pH. The minimum cost of regeneration was $0.092/1000 gal for a waste having 20 mg/ℓ NH_3-N using a regenerant containing 0.049 lb NaCl/gal at pH 12.5. This corresponded to a regeneration level of 5.2 lb NaCl/cu ft. Costs using a regenerant containing only NaOH with the pH raised to 12.5 were slightly higher. Because chemical prices and transportation costs will vary according to the treatment plant location, the choice of regenerant composition in this case will depend on the specific location being considered.

14. When reuse of regenerant was considered, regeneration costs were relatively insensitive to the NaCl concentration of the regenerant but were significantly influenced by zeolite replacement costs. The minimum cost of regeneration was $0.042/1000 gal for a waste containing 20 mg/ℓ NH_3-N and was achieved using a regenerant composed of either 0.10 or 0.17 lb NaCl/1000 gal with sufficient lime to raise the pH to 11.5. This corresponded to regeneration levels of 18.5 and 24.6 lb NaCl/cu ft, respectively; however, the amount of salt required for regenerant makeup corresponded to 1.2 and 1.5 lb NaCl/cu ft, respectively.

15. Because the cost of salt is heavily dependent on transportation charges, the cost of regeneration will vary for areas where the transport distance is significantly different from the 300 miles for NaCl and NaOH and 200 miles for CaO assumed in this analysis.

16. The cost of replacement clinoptilolite was estimated including 400 miles transportation of clinoptilolite. If the zeolite must be shipped farther, clinoptilolite replacement costs will increase and regeneration at a lower pH might result in lower treatment costs.

17. The total cost of ammonia removal using clinoptilolite was estimated to be $0.134/1000 gal where regenerant is used only once and $0.082/1000 gal where regenerant is reused. Costs for disposal of spent regenerant solutions were not included in the cost estimate for the case where regenerant would be wasted after one use. These costs indicate that the reuse of regenerant by air stripping ammonia from the spent regenerant solution will be the most feasible method of operation. However, in areas where transportation charges for chemicals are minimal and where regenerant solutions can easily be disposed of, wasting of regenerant solutions after one use might be competitive with treatment costs where regenerant is reused.

II. RECOMMENDATIONS

Results of this study showed that the ammonia exchange capacity of clinoptilolite was significantly influenced by the concentration of competing cations in the wastewater and by the ammonium concentration. However, it was not possible to develop a multicomponent model suitable for the prediction of both effective capacity and leakage. For example, it is expected that increased cation concentrations will not only result in a decreased ammonia exchange capacity, but that higher ammonia leakage prior to breakthrough will also result. In addition, the effect of varying ammonia concentrations on column performance have not been identified. Ammonia concentrations ranging from less than 10 to more than 25 mg/ℓ NH_3-N might be expected in municipal wastewaters, depending on the nature of the wastewater and on the types of treatment processes which precede ammonia removal. Diurnal concentration fluctuations and the time of their arrival with respect to the ion exchange exhaustion cycle will also affect column performance. It is recommended that a systematic study of the relationship between cation composition and performance be carried out.

Additional factors relating to the effective ammonia exchange capacity of clinoptilolite concern the influence of process design on the exchange capacity. The effective ammonia exchange capacity per unit weight of zeolite will increase with the depth of the bed; however, the extent to which an increase in bed depth will increase the useful run length is not precisely known. In addition, little information exists concerning the change of effective capacity in increasing the diameter/height ratio of the exchanger bed from experimental to prototype units. Both of these considerations will be important in the design of clinoptilolite ion exchange units and are worthy of further investigation.

In portions of this investigation chemically precipitated wastewaters were applied to clinoptilolite columns without prior filtration. In these systems the clinoptilolite served as both exchanger and filter. No impairment of the ion exchange function of the zeolite was observed due to plugging of the bed or fouling of exchange sites. While some removal of suspended solids and turbidity were achieved, it is believed that the addition of another filter medium, perhaps plastic chips, above the clinoptilolite and the injection of a small amount of alum or polyelectrolyte ahead of the column would greatly improve the filtration performance of this unit. By combining two unit processes, a considerable savings in overall treatment costs would be realized. This matter also merits further investigation.

While data obtained from laboratory studies in this investigation demonstrated that a significant loss of clinoptilolite will occur from exposure to caustic regenerant solutions, longer-term attrition data

from operating systems are needed. This information should be obtained from cyclically operated units using actual wastewaters as the column influent.

Estimated costs for ammonia removal using clinoptilolite made in this study showed that the reuse of regenerant will result in significant reductions of process operating costs. While previous work has indicated that regenerant reuse is possible, many factors relating to this aspect of the process remain to be demonstrated. The exact amounts of caustic and NaCl which must be added to the regenerant after each cycle of use, the effect of the accumulation of potassium and calcium in regenerant solutions on regeneration performance, and the loss of regenerant volume during each cycle are factors which must be investigated before a more thorough evaluation of regenerant reuse can be made. In addition more information is needed concerning the design and operation of towers to be used for the stripping of solutions containing high concentrations of ammonia. It is recommended that a study of problems relating to the reuse of regenerant solutions be made to determine the most effective methods of minimizing regeneration costs.

III. INTRODUCTION

THE CONCERN FOR AMMONIA IN WASTEWATERS

Traditionally, emphasis in wastewater treatment has been placed on the removal of biologically degradable organic material, suspended solids, and floating substances. The water quality objectives requiring such treatment were to produce a clear effluent, which, when mixed in the receiving water, would produce no more than acceptable oxygen depletions and no gross signs of pollution or objectionable odors. As a means of meeting these objectives, physical and biological treatment developed in the 1930's generally proved to be a satisfactory solution to pollution problems. Properly operated, these processes removed sufficient organic matter to prevent oxygen depletion in the receiving water, provided adequate removal of suspended matter, and generally made it possible to achieve some degree of control of oil, grease, and other floating materials. Any removal of nitrogen achieved in these processes was incidental to the fulfillment of the treatment objectives. More recently, increased use of water brought about by a rise in the standard of living and the pressure of population growth has had the effect of requiring a reevaluation of waste treatment objectives. Recent interest in the removal of nitrogen from wastewaters is consistent with current waste treatment objectives of producing a water which is not detrimental to the environment and of treating to a level of quality suitable for direct reuse.

Need for Nitrogen Removal

Investigation into the causes of eutrophication have led many workers to conclude that a nutrient such as nitrogen or phosphorus is likely to be the growth-limiting factor in many cases. While phosphorus has most often been implicated as being the major sewage constituent contributing to eutrophication, the factor which limits algal growth in a particular water can be correctly defined only in the context of the local aquatic environment. In studies of eutrophication in Lake Tahoe [1], data from chemostat assays indicated that nitrogen was the limiting nutrient. However, it was pointed out that nitrogen concentrations might only be indicative of other substances which do control algal growth rates.

In developing water quality standards for the Potomac River, the Department of the Interior has recommended that nitrogen removal be required at the 240-mgd Blue Plains plant and at the 30-mgd Piscataway treatment plant in Washington, D. C. [2]. In studies of water quality in the San Francisco Bay and Delta, questions have been raised

concerning the role of nitrogen in maintaining suitable water quality. In one study it was concluded from batch assays that nitrogen was the limiting algal nutrient [3]. However, in other work [4] a nitrogen mass balance indicated that nitrogen concentrations did not limit algal growth. Disputes concerning the exact causes of eutrophication and the role of sewage effluents in stimulating algal growths probaby will not be resolved for some time. However, it seems unlikely that all eutrophication problems will be explained by attributing stimulation to a single factor — either nitrogen or phosphorus.

In some locations demands on available water resources have increased to the extent that water reuse for both industrial and domestic purposes has become economically attractive. If water is to be reused for municipal supplies, ammonia will adversely affect the efficiency of chlorination of the water as well as increase chlorine consumption. While ammonia in concentrations found in sewage is apparently not toxic to man, the PHS Drinking Water Standards [5] limit nitrate nitrogen to 10 mg/ℓ because of its role in infant methemoglobinemia. Thus, nitrogen removal will be necessary wherever wastewaters are to be reused for drinking purposes. For cases where water is reused for fishing and recreation, ammonia may be toxic to game fish. An ammonia concentration of 0.7 mg/ℓ has been reported as toxic to trout by McKee and Wolf [6]. However, ammonia toxicity is a function of pH, fish species and size, and other factors in addition to the ammonia concentration. Ammonia can also cause oxygen depletion in the receiving water as it is oxidized to nitrate.

Methods of Nitrogen Removal

Methods of removing nitrogen from wastewaters can be grouped as either biological or chemical-physical processes. General reviews of these methods have been written by Stern [7], Rohlich [8], McCarty [9], and Samples [10]. Nitrogen removal achieved in conventional waste treatment processes is primarily due to microbial denitrification. Removals reported tend to be erratic and are usually not sufficient to meet water quality criteria where nitrogen removal is required.

Biological processes specifically designed for nitrogen removal include microbial nitrification-denitrification and algal harvesting. Nitrification-denitrification using the standard activated sludge process requires a sufficient mean cell residence time to allow nitrifying bacteria to become established in the system. This usually requires long aeration periods, thus negating the economic advantages of high-rate biological systems. Even in a compartmentalized system such as the one proposed by Barth et al. [11], treatment periods are long and problems develop in maintaining individual systems having uniquely different biological functions. Algal stripping of nitrogen requires considerable land area compared to other processes. Removals are dependent on weather conditions, and cell separation is still a costly and uncertain process [9].

Chemical and physical processes for nitrogen removal have the advantages of being more amenable to control than biological processes and more adaptable to the fluctuating flows and concentrations inherent to municipal wastewater systems. While air stripping has the potential of being the least expensive method of removing nitrogen, the process becomes less efficient in cold weather and is impractical to use at all when the temperature drops below freezing. This precludes serious consideration of air stripping in most northern parts of the country until improved designs are available. An additional problem with the stripping process is that scale deposition occurs in the tower as a result of the high pH required for ammonia removal.

Nitrogen removal using conventional ion exchange resins is unattractive because of the preference of these exchangers for ions other than the ammonium and nitrate ions. In addition, disposal of the regenerant brine poses a problem in some locations. However, work by Ames and Mercer [12-14] demonstrated that the ammonium selective zeolite, clinoptilolite, is effective in removing ammonia from wastewaters. By regenerating the zeolite with a high pH brine solution, it is possible to strip the ammonia from the regenerant and reuse the regenerant solution, thus reducing regenerant costs and minimizing the problem of brine disposal. The work by Mercer showed that ammonia removals of greater than 95% can be achieved using clinoptilolite.

As a unit process, ion exchange is easily controlled to achieve almost any desired product quality. The efficiency of the process is not significantly impaired at temperatures usually encountered in the United States. Ion exchange equipment can be automatically controlled and requires only occasional inspection and maintenance.

While a number of processes have been proposed to accomplish nitrogen removal, full-scale treatment units are still in the planning and testing stages. Perhaps the most obvious reasons for this is that the presence of nitrogen in wastewaters has become objectionable only in the last few years. At the present time plans for nitrogen removal facilities are underway in several locations where existing or anticipated uses of a waterway have dictated the need for this type of treatment. However, an equally compelling reason for the absence of nitrogen removal in wastewater treatment has been a combination of high costs and a lack of adequate technology applicable to process design and operation. Studies of nitrogen removal methods have generally been more concerned with proving that a particular process works than with defining operational problems and treatment costs. Although very recent work has begun to answer some of these questions, a definite need exists for more information applicable to process operation and design.

This investigation will concentrate on defining various operational parameters necessary to efficiently remove ammonia by ion exchange using clinoptilolite. By studying different aspects of column operation,

it will be possible to evaluate more clearly the applicability of this process to operating conditions and to more accurately predict column performance and costs.

OBJECTIVES

This study was concerned with the optimization of ammonia removal from wastewaters by ion exchange using clinoptilolite. The general objective of the investigation was to establish the conditions under which clinoptilolite can be used most effectively and economically for ammonia removal. The fulfillment of this objective involved the experimental determination of certain ion exchange properties of clinoptilolite which are important in its use for ammonia removal. These results were used to define optimum operating conditions for clinoptilolite exchangers and to estimate the cost of ammonia removal using clinoptilolite. The necessary assumptions made in arriving at valid cost estimates are listed where appropriate. However, the reader is reminded that the cost of a single process is not independent of the system in which it is placed.

The study had the following specific objectives:

1. Determination of factors influencing the exhaustion performance of clinoptilolite including the effect of pH on ammonium exchange.

2. Optimization of the regeneration cycle of clinoptilolite to establish the least-cost method of operation.

3. Determination of the performance of clinoptilolite under normal conditions by operating test facilities at several wastewater treatment plants.

4. Development of a basis for the design of clinoptilolite exchange systems.

5. Establishment of the costs associated with the construction and operation of processes for the removal of ammonia using clinoptilolite.

A brief review of the contents of this report will serve to acquaint the reader with its organization. In Chapter IV the general definitions and fundamentals of ion exchange theory, past work concerned with the removal of ammonia by ion exchange, and the properties of clinoptilolite are reviewed. While this material provides a general background for the rest of the report, it is not essential for an understanding of the conclusions of the study. However, the material reviewed in this chapter was chosen to complement observations made later in the report.

Chapter V considers the potential for the use of clinoptilolite for ammonia removal and sets forth the rationale for the specific phases of the experimental work. In Chapter VI the equipment used in the study is described and the analytical methods and operating procedures are outlined. The findings of experimental investigations are presented and discussed in Chapters VII, VIII, and IX. Work presented in Chapter VII concerns the effect of pH, ionic form of the zeolite, and water composition on the exhaustion performance of clinoptilolite. Regeneration of clinoptilolite, considered in Chapter VIII, includes individual regeneration runs, studies of clinoptilolite attrition in the presence of caustic solutions, and column rinsing tests. In Chapter IX the performance of clinoptilolite using three different wastewaters is presented. Results of the study are used in discussing the design of ion exchange units and the cost of ammonia removal by this process in Chapter X.

IV. ION EXCHANGE CHARACTERISTICS OF THE ZEOLITES

ION EXCHANGE THEORY

Equilibrium Relationships

Ion exchange may be defined as the stoichiometric, reversible exchange of ions between a liquid and solid which produces no significant changes in the structure of the solid. The mass action equilibria expression provides a useful model for ion exchange behavior. In a binary system, the reaction,

$$bA^{+a} + aBZ_b \rightleftarrows bAZ_a + aB^{+b} \tag{1}$$

expresses the reversible equilibrium where a and b are the valences of ions A and B, respectively, and Z is the exchange site in the solid. Helfferich [15] has referred to ions having charge signs opposite that of the exchange sites as "counter ions" and ions having the same charge sign as the exchange site "co-ions." This reaction may be expressed as the equilibrium constant,

$$K = \frac{(a)^b_{AZ_a} \cdot (a)^a_B}{(a)^b_A \cdot (a)^a_{BZ_b}} \tag{2}$$

in which $(a)_A$, $(a)_{AZ_a}$, etc. are the activities of the various species. Because of the difficulty in measuring activities, especially in the solid phase, it is convenient to use concentrations uncorrected for activity. In doing so, the equilibrium constant in Equation 2 varies with concentration and has been termed the "selectivity coefficient" by Helfferich [15],

$$K^A_B = \left(\frac{q}{c}\right)^b_A \left(\frac{c}{q}\right)^a_B \tag{3}$$

where q is the solid phase ionic concentration in meq/g and c is the solution phase concentration in meq/ℓ. Alternatively, the selectivity coefficient can be expressed in terms of dimensionless concentrations,

$$K_B^A \left(\frac{Q}{C_o}\right)^{a-b} = \left(\frac{y}{x}\right)_A^b \left(\frac{x}{y}\right)_B^a \qquad (4)$$

These variables are expressed in terms of the total solution concentration, C_o, in meq/ℓ and the total exchange capacity, Q, in meq/g. Thus, $x = c/C_o$ and $y = q/Q$.

In performing calculations with equilibrium data it is frequently desirable to make corrections for solution and solid phase activities. In dilute solutions, when ions A and B have the same valence, the solution phase activity coefficients may be taken as unity in most cases. However, for ions of unequal valence, the distribution of these ions depends on the relative dilution of the two species. Activity corrections for the solution phase in dilute solutions is usually made using the Debye-Huckel equation [16]. However, activity corrections in the solid phase are more difficult. If the exchanger could be considered as an independent solid phase, activity in the particle could be taken as constant and equal to unity. However, it is more correct to view the components of the solid phase as forming miscible solid solutions with one another [17]. In addition, heterogeneity of the particle matrix makes a single description of exchange sites tenuous. Corrections which have been proposed include considering solid phase activity as a function of the number of ions per unit weight of exchanger or as a function of the mole fraction of an ion in the solid phase [18]. Baetsle [19] reviewed several more complex methods of correcting for solid phase activity which consider the exchanger to be an orderly system of identical sites. While the problem of solid phase activities might be overcome in binary systems by determining values of the selectivity coefficient over a range of solid phase compositions, the problem is more complex in multicomponent systems in which the solid composition is difficult to define. Because of the complex manner in which activities vary, no method of making solid phase corrections has gained wide acceptance.

The preference of an ion exchanger for one ion relative to another in binary systems is often expressed as the "separation factor,"

$$\alpha_B^A = \left(\frac{q}{c}\right)_A \left(\frac{c}{q}\right)_B = \left(\frac{y}{x}\right)_A \left(\frac{x}{y}\right)_B \quad . \qquad (5)$$

Because the numerical value of the separation factor is not affected by the choice of concentration units, equilibrium data are often expressed in this way. If the equivalent fraction of ion A in the solid phase, y_A, is plotted against the equivalent fraction of A in the solution, x_A,

three cases can be identified corresponding to $\alpha < 1$, $\alpha = 1$, and $\alpha > 1$ as shown in Figure 1. Isotherms which are concave upward, $\alpha < 1$, are designated as being "unfavorable" to the uptake of ion A; those which fall along the rising diagonal, $\alpha = 1$, are termed "linear" and exhibit no preference for ion A or B; and curves which are concave downward, $\alpha > 1$, are referred to as "favorable" isotherms since the solid prefers ion A to ion B [20]. Ion exchange operations almost always are concerned

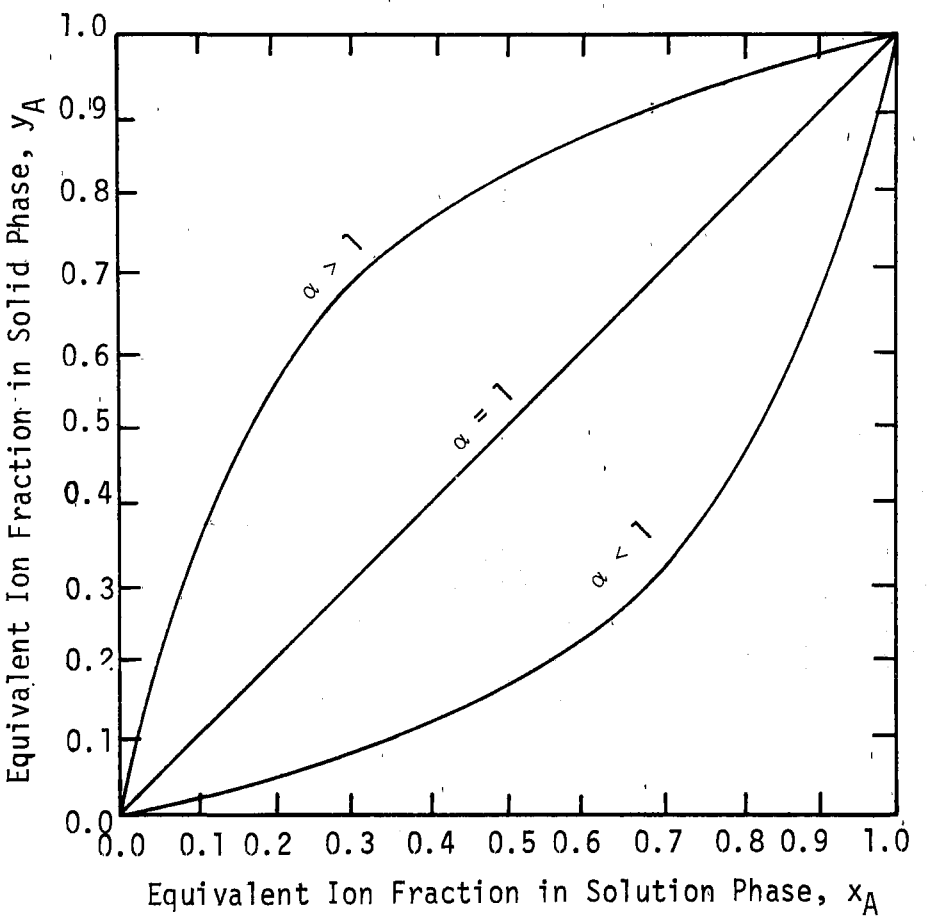


FIGURE 1. GENERALIZED ION EXCHANGE ISOTHERMS

with systems in which the ion of concern has a separation factor greater than unity during exhaustion.

COLUMN THEORY AND RATE PHENOMENA

Most ion exchange operations are carried out in columns as a much larger percentage of the capacity of the ion exchanger can be utilized

than with batch methods. The performance of column processes will depend on the properties of the particular ion exchanger, the composition of the column influent, and the operating conditions and process arrangement. Over the past 20 years, a considerable body of theory has been developed to describe column performance. While these theories are frequently not directly applicable to ion exchange applications, they can be used to provide a better understanding of column behavior and to predict the response of ion exchange processes to changes in design and operating procedures.

In the previous section it was mentioned that in most applications of ion exchange, equilibrium is necessarily favorable with respect to the ion being removed. In this case the exchange zone will establish itself and move at a constant speed through the column provided that flow through the column and the composition of the feed remain constant. This type of behavior is referred to as "constant pattern" because the sharpening effect of equilibrium and the dispersive effects of the rate of exchange tend to balance each other. This results in the exchange front maintaining a constant shape as it moves through the column. The boundary is said to be "self-sharpening" because it becomes steeper relative to the length of the column as the exchange front passes through a progressively deeper section of the bed. For this type of column behavior, increasing the length of the column will have the effect of increasing the breakthrough capacity of the column. If the separation factor is less than one, a "proportionate pattern" is attained because the exchanging ion is attracted to the exchange sites in proportion to the solution phase concentration of that ion. It can be imagined that the exchanging ions in this case have to "push" themselves onto the exchanger, and the less the solution phase ion concentration, the less they are forced onto the exchanger. This type of boundary is "nonsharpening" as the exchange front becomes more diffuse as the column length is increased [21]. For the case where $\alpha = 1$, the boundary becomes neither steeper nor more diffuse relative to column length as the front passes through the column.

Rate Processes

Models describing the variation of effluent concentration as a function of throughput are concerned with three factors: equilibrium, stoichiometry, and rate. The rate of exchange is governed by one or more diffusional steps which have been listed as: 1) external fluid phase or film diffusion, 2) fluid phase pore diffusion, 3) reaction at the liquid-solid interface, 4) solid phase internal diffusion, and 5) mixing by molecular diffusion or axial dispersion [20,22]. These mechanisms will affect column behavior, either individually or in combination with one another. The reaction rate at the phase interface is usually very rapid and does not limit the rate of exchange [23]. While molecular diffusion probably influences column performance, the effects are usually small except at very low flows. Axial dispersion increases with the linear velocity through the column.

Film Diffusion. The transport rate of ions between the bulk fluid phase and the exchanger particles can be estimated from the relationship,

$$\frac{dy}{dt} = \frac{2.62\ (D_f\ F/S)^{0.5}}{d_p^{1.5}}\ \frac{C_o}{Q\rho_b}\ (x-x^*) \qquad (6)$$

where D_f is the fluid phase diffusivity in sq cm/sec, F is the volumetric flow rate in mℓ/sec, S is the column cross-sectional area in sq cm, d_p is the particle diameter in cm, ρ_b is the bulk density in g/cu cm, t is time in sec, and x* is the equilibrium value of x [20]. All abbreviations and nomenclature used in this report including appropriate units are summarized in the Glossary, Chapter XIII. From this relationship it is apparent that film diffusion will tend to be limiting when exchanger particles are small, when the solution phase concentration is low, and when the superficial velocity, F/S, through the column is small.

Pore Diffusion. Pore diffusion in the fluid phase has been represented by the following relationship [20]:

$$\frac{dy}{dt} = \frac{\Psi_{pore}\ 60\ D_{pore}}{d_p^2}\ (1-\varepsilon)\ \frac{C_o}{Q\rho_b}\ \frac{y^*-y}{[1 + (\alpha-1)y]^{1/2}}\ . \qquad (7)$$

Here, Ψ_{pore} is a correction factor, D_{pore} is the pore diffusion coefficient in sq cm/sec, ε is the voids ratio, y* is the equilibrium value of y, and other variables are as previosuly defined. Although pore diffusion occurs in the fluid phase, this equation indicates that its rate is primarily a function of solid phase concentrations. As the equation indicates, pore diffusion is likely to control mass transfer rates where particles are large and solid phase concentrations are near the equilibrium values.

Solid Diffusion. Solid phase diffusion includes diffusion through a homogeneous, permeable solid which results from a concentration gradient within the particle. Several models have been proposed for solid diffusion, but the closest approximation is given by the quadratic driving force model of Vermeulen [24]:

$$\frac{dy}{dt} = \frac{\Psi_q\ 60\ D_p}{d_p^2}\ \frac{y^{*2}-y^2}{2y} \qquad (8)$$

where ψ_q is a correction factor, D_p is the solid phase diffusivity in sq cm/sec, and the other variables are as defined previously. Solid diffusion controlled reactions are the same function of particle diameter as those for pore diffusion, but the rate of solid diffusion is seen to be a different function of the solid phase concentrations. However, as in the case of pore diffusion, solid diffusion tends to be limiting when particle phase concentrations are near equilibrium values. The solid phase diffusivity is affected by the nature of the exchanging ions as well as by the varying ionic composition of the particles [15,22].

Rate Controlling Mechanisms. The rate which limits ion exchange in column operations may be a result of more than one of the above mentioned diffusional steps and, in addition, the rate controlling mechanism may change as the column becomes more saturated. For example, near the rising limb of a breakthrough curve the solid phase concentration gradient will be high while the solution phase gradient will be low near the bottom of a column. Thus, film diffusion tends to control the initial portions of the breakthrough. On the other hand, near the upper end of the breakthrough curve, the solid phase gradient will be low and the solution phase gradient high; thus, the tendency is toward a shift in the rate-controlling mechanism to either pore or solid diffusion. It should be noted that these tendencies are relative to the particular exchanger being used and that it is entirely possible that pore or solid diffusion could predominate throughout the breakthrough. In this case film diffusion would contribute more to the diffusion resistance at the beginning of the breakthrough than at the end, but would, at neither time, control the rate of exchange.

Because the diffusional mechanisms which affect column behavior act together, either in series or parallel, methods have been developed to account for this in predicting column behavior [25]. For combined fluid phase or particle phase resistances, the effective rates are obtained by adding individual resistances if they act in parallel or by adding the reciprocal resistances to obtain the reciprocal combined resistance for series combination. In the case of inorganic zeolites having a bimodal internal structure consisting of individual crystallites bound together into larger particles, the exchange rate will be governed by a series combination of pore diffusion and particle diffusion, with the crystallite diameter replacing the particle diameter, d_p, in Equation 8 [20].

While the rate mechanisms discussed above are valid for ion exchange reactions, the equations which relate these rates to column and particle variables are limited to cases which can be described mathematically without undue complexity. These equations apply to: 1) the average concentration in the neighborhood of a single particle, 2) two-component exchange, and 3) spherical particles of uniform size.

Column Theory

Reaction Kinetic Model. Numerous theories have been proposed to describe column performance under various conditions. These methods make it possible to predict the column effluent concentration profile from properties of the exchanger which can be measured by laboratory batch-type tests. One approach is that taken by Glueckauf [21] in which column performance was described in terms of either fluid or particle diffusion. Thomas [26] developed a solution for systems in which the rate is described by a second-order rate equation. These equations have been used infrequently because, as discussed in a previous section, exchange rate is seldom controlled by the reaction rate at phase boundaries and because Thomas' solution involved the use of functions which are difficult to evaluate. Hiester and Vermeulen [27] utilized this method to obtain solutions in the form of families of concentration-history curves. Solutions were obtained in terms of two dimensionless parameters: N, the number of transfer units analogous to the number of theoretical plates in distillation column, and T, the throughput parameter. N can be defined generally as,

$$N \propto \frac{D(F/S)^c}{d_p^d} \left(\frac{hS}{F}\right) \tag{9}$$

where c and d are functions of the rate mechanism involved as defined in Equations 6, 7, and 8 and h is the column height. T is the ratio of meq of ions passed through the column to the capacity of the column. In the ideal case, complete saturation of the column corresponds to T = 1. This solution was made more workable by allowing rates of fluid or particle phase diffusion to be expressed as an effective reaction rate.

Assumptions made in the Hiester-Vermeulen solution include: 1) a symmetric system (although a correction procedure was outlined for ions of unequal valence), 2) binary exchange, 3) homogenous particle structure including uniform distribution and nature of exchange sites, 4) uniform feed concentration, 5) uniform flow rate, 6) uniform initial sorbent concentration within the particles, 7) constant temperature, and 8) constant separation factor.

From this discussion several qualitative observations may be made concerning column behavior. In the Hiester-Vermeulen model, the effluent concentration is a function of three parameters: the separation factor, α; the number of transfer units, N; and the throughput parameter, T. A sharp breakthrough curve, and therefore a greater utilization of column exchange capacity, is favored by large values of α and N. The separation factor will be determined by the exchanger being used. In this respect, the preference of the exchanger for the

counter ion in the feed should be large, but not so large as to make regeneration difficult. From Equation 9 it is apparent that a large N is favored by a small velocity of fluid through the bed, a large bed depth, and a small particle diameter. The diffusivity, D, is fixed, and little can be done to vary it once the exchange material is chosen. In considering the rate mechanisms given in Equations 6, 7, and 8, it is seen that increasing the linear velocity through the bed increases the exchange rate only in the case of film diffusion. In this case, increased flow rates act to reduce the thickness of the film surrounding the particles. Increasing the particle size is seen to adversely affect the rate of pore and solid diffusion more than film diffusion. The curves shown by Hiester and Vermeulen reveal that sharp breakthrough cannot be achieved even for very large values of α if N is less than about 5.

Pore- and Solid-Diffusion Limited Systems. For particle phase diffusivities, the reaction-kinetic solution of Hiester and Vermeulen assumes a rate governed by a linear driving force. The quadratic driving force model of Vermeulen given in Equation 8 provides a better fit to observed diffusion rates. A solution utilizing this model, as well as a solution for pore diffusion limited systems, was developed by Hall et al. [28]. It applies specifically to constant pattern conditions and to cases where the equilibrium conforms to a Langmuir isotherm. The solution lacks flexibility in that cases in which the rate of exchange is governed by combined mechanisms cannot be treated by this model. However, it is thought that fluid phase resistance is of little significance in ion exchangers having uniform internal pore structures such as the zeolites.

Multicomponent Systems

The foregoing discussion of ion exchange theory can be applied quantitatively only to binary systems. Unfortunately, any application of ion exchange in wastewater treatment will involve multicomponent equilibria. The complexities introduced in dealing with multicomponent systems include having to cope with a different separation factor for each pair of exchanging species and, in the case of solid diffusion, a different diffusion rate for each pair of ions.

For equilibrium relationships, it is possible to solve for the multicomponent equilibria knowing the selectivity coefficients for each ion pair. However, as pointed out above, in systems involving species of unequal valence, activity corrections would be necessary. Dranoff and Lapidus [29] have found that ternary equilibria can be predicted from binary equilibria when the data are treated as adsorption isotherms and when multivalent cations are treated as an equivalent concentration of univalent ions. However, for mass-action equilibria, the lack of suitable solid-phase activity correction methods prohibits accurate prediction of multicomponent equilibria from binary data.

For the general case of multicomponent systems having nonlinear equilibria, no method has yet been developed for determining the rate dependent, breakthrough behavior. Until recently very little theoretical consideration of multicomponent behavior in fixed beds had appeared in the literature. Klein et al. [30,31] discussed the considerations involved in equilibrium calculations and presented a method of determining concentration profiles in constant selectivity coefficient systems. This method is based on equilibrium operation and thus predicts ideal process performance.

Despite the fact that established theory cannot yet deal explicitly with the complex problems of ion exchange encountered in wastewater treatment, it is useful as a qualitative guide for understanding and interpreting column phenomena. The very fact that exchange column behavior is so complex is a compelling reason for having a basic theoretical background to aid in the interpretation of ion exchange performance and to guide the design and operation of ion exchange systems.

AMMONIA REMOVAL BY ION EXCHANGE

Use of Conventional Resins

Perhaps the first use of ion exchange to remove ammonia from wastewater was the zeolite filter in the Guggenheim process [32,33]. Using a "preferred type of zeolite," between 66 and 93% removal of ammonia was achieved at a loading rate of about 20 BV/hr (BV/hr x 0.125 = gal/cu ft-min). The amount of regenerant used corresponded to approximately 64 eq NaCl/eq NH_3-N removed. Ammonia from the spent regenerant was removed by air stripping in a packed tower and the regenerant reused. The zeolite also acted as a filter for the chemically precipitated waste, but the resulting headloss occasionally made it necessary to backwash the bed before ammonia breakthrough was reached. No mention was made of a loss of capacity of the zeolite due to clogging or organic fouling.

Nesselson [34] investigated the use of Amberlite IR-120 and Nalcite HCR strong acid exchange resins for ammonia removal from an activated sludge effluent. Nalcite HCR, which showed the better performance, required 8.8 lb NaCl/lb cations removed for regeneration. Regeneration was accomplished using 25 to 35 lb NaCl/cu ft resin with the regenerant volume amounting to a minimum of 5.8% of the product water volume. Flow rates in exhaustion ranged from 48 to 67 BV/hr. Because of unfavorable selectivity with respect to the ammonium ion, the ammonia exchange capacity of the resin was only about 0.11 meq/mℓ (corresponding to approximately 0.27 meq/g or 2.4 kgr $CaCO_3$/cu ft) out of a total operating exchange capacity of 0.78 meq/mℓ (1.95 meq/g or 17.1 kgr/cu ft as $CaCO_3$) with a water having a hardness of 380 mg/ℓ as $CaCO_3$. The regenerant requirement was approximately 20 eq NaCl/eq NH_3-N removed.

With a hardness of 142 mg/ℓ as $CaCO_3$, a 32% increase in ammonium exchange capacity was realized.

Tests made to determine the effect of prefiltration of the activated sludge effluent on column performance showed that unfiltered effluent could be applied to the columns without adversely affecting ammonia removal efficiency. While no problems of excessive headloss through the bed were reported, the throughput to a breakthrough of 1 mg/ℓ NH_3-N averaged only 100 BV/run. For the design of an ammonia removal unit, Nesselson recommended removal of temporary hardness using lime and regeneration using NaCl with recovery of ammonia by air stripping at a high pH and subsequent reuse of the regenerant. It was estimated that salt costs alone would be $0.26/1000 gal.

The removal of ammonia using Duolite C-25 resin was investigated at the South Tahoe Public Utility District [35,36]. Because the hardness of Lake Tahoe sewage was much less than in the sewage used by Nesselson — 55 as opposed to 380 mg/ℓ as $CaCO_3$ — ion exchange seemed more feasible at Lake Tahoe. The resin column was exhausted downflow at 24 BV/hr until an ammonia breakthrough of 1 mg/ℓ NH_3-N was reached. The column was regenerated with 10 lb NaCl/cu ft in a 10% solution at a rate of 1.6 BV/hr. This corresponded to the use of 5 eq NaCl/eq NH_3-N removed. Exhaustion studies showed that an average of 365 BV could be treated prior to breakthrough which represented an increase of 350% over previous investigations. It was estimated that salt costs would be $0.04/1000 gal based on regeneration with 10 lb NaCl/cu ft. For this reason and because of anticipated problems of brine disposal, further investigation of the ion exchange process was not attempted.

In these studies it is significant to note the strong dependence of the ammonia exchange capacity of the resin on water hardness. In Nesselson's experiments only about 15% of the exchange sites were used for ammonia exchange. Nesselson observed a significant increase in ammonia exchange capacity as the NH_3-N/total cation ratio increased. In the studies at Lake Tahoe using a very low hardness sewage, the throughput to a breakthrough of 1 mg/ℓ NH_3-N was more than three times as great as that achieved in Nesselson's experiments.

Although specific data regarding regeneration efficiency, i.e., equivalents of NH_3-N removed during exhaustion divided by the equivalents of NaCl used for regeneration, were not given in these reports, values calculated from other data indicate that regeneration efficiency was only 1.5 to 5% for the Guggenheim process and in Nesselson's studies, while data reported in the Tahoe report indicated a value of about 20%. Because of the small fraction of exchange sites occupied by ammonium ions, lower regeneration efficiencies would be expected for ammonia removal than for softening. Reuse of regenerant was investigated only by Gleason and Loonam. Regenerant reuse was not considered in cost estimates made by Nesselson or in the Tahoe report.

Use of Clinoptilolite

The first suggested use of clinoptilolite for ammonia removal was contained in a paper by Ames [12] who determined the selectivity series for various zeolites and found that clinoptilolite and a synthetic zeolite, AW 400, produced by the Linde Company were the most promising for ammonia removal from wastewaters. Subsequent reports [13,37] done under the direction of Mercer concentration on column studies using clinoptilolite for ammonia removal because of its favorable ammonium ion selectivity and potential low cost. Tests were made using 20 x 50 mesh material. In order to evaluate column performance using secondary effluent without pretreatment, tests were made in 2-in. columns with upflow loadings of 16.6 BV/hr. High leakage of approximately 1 mg/ℓ NH_3-N and shallow breakthroughs observed in these runs were attributed to channeling of the flow through the bed. Organic fouling resulted in a 25% loss of capacity during the two upflow runs.

In preliminary studies, the columns were regenerated upflow using a lime slurry; however, saturated lime solutions containing added sodium and calcium salts as counter ions were used in later studies. The saturated solution performed as well as the slurry and eliminated deposition of lime particles in the bed. During most of these studies, the regenerant flow rate was 10 BV/hr upflow, although flows of 30 BV/hr were used in two instances. The required regenerant volume was reduced significantly by adding NaCl to the saturated lime solution. In comparing elution curves using various regenerants, approximately 50 BV regenerant was required for complete ammonia elution using a 0.05 M $CaCl_2$ solution (0.046 lb $CaCl_2$/gal) saturated with lime while only 27 BV and 20 BV were required for saturated lime solutions containing 0.035 M $CaCl_2$ plus 0.03 M NaCl and 0.1 M NaCl (0.049 lb NaCl/gal), respectively. Exhaustion concentration histories were compared for columns previously regenerated with 4.5 g/ℓ lime slurries (0.038 lb lime/gal) containing no NaCl and 0.1 M NaCl (0.049 lb NaCl/gal). Leakage was approximately the same for both cases, but the breakthrough capacity to 1 mg/ℓ NH_3-N leakage was 20% greater for the column regenerated with added NaCl. Ammonia exchange capacities were 0.20 meq/g (0.15 meq/mℓ or 3.3 kgr/cu ft as $CaCO_3$) and 0.23 meq/g (0.17 meq/mℓ or 3.7 kgr/cu ft as $CaCO_3$) for the columns regenerated with the lime slurry and with the lime-salt combination, respectively. No attempt was made to determine whether the increased capacity was due to more complete regeneration using the lime-salt solution or to more favorable NH_4-Na exchange kinetics during exhaustion. Regeneration using 0.015 M NaOH was demonstrated to require 35 BV for complete removal of ammonia. Studies were conducted to elucidate the effectiveness of recycled regenerant. Ammonia was removed from the regenerant solution by air stripping in a laboratory column. Regenerant used for three cycles was as effective as fresh regenerant.

Additional tests were performed in three locations using a mobile demonstration plant [14]. The breakthrough capacity to 1 mg/ℓ NH_3-N

for flow rates between 6.5 and 9.7 BV/hr with influent ammonia concentrations of 15 to 17 mg/ℓ NH_3-N ranged from 100 to 120 BV. The ammonia leakage prior to breakthrough averaged 0.7 mg/ℓ NH_3-N. Operation of two columns in series resulted in a 60% increase in the utilized ammonia exchange capacity per column. However, no data were presented to demonstrate the relative regenerant requirements for single columns and those exhausted in series operation.

A batch regeneration technique was studied in which 2 to 4 BV of regenerant were recycled through the column until saturated with ammonia. Subsequently, the spent regenerant was stripped of ammonia and reused.

The results of these studies indicate that clinoptilolite has much potential for removing ammonia from wastewater. Because of its greater ammonia selectivity, clinoptilolite has an advantage over conventional resins for ammonia removal. Tests in the Battelle demonstration unit showed that ammonia removals greater than 95% can be achieved using clinoptilolite. Regeneration was accomplished using lime-salt solutions which were effectively reused after ammonia was removed from the solution by air stripping.

ION EXCHANGE PROPERTIES OF THE ZEOLITES

In order to be used in large-scale process applications, an ion exchange material must meet certain basic requirements related to both its physical and chemical properties. Specifically, the material must be available in abundant supply and at a reasonable price; it must possess good physical stability toward abrasion and be chemically stable toward the fluids with which it will come in contact; it must have a high exchange capacity and exhibit favorable selectivity for the intended use; and the exchange kinetics should allow a large part of the equilibrium capacity to be utilized in column operations. In this section the properties of zeolites will be discussed and compared to conventional ion exchange resins.

Structural Properties

Stoichiometrically the zeolites are derived from the formula $(SiO_2)_n$ by the periodic substitution of Al for Si atoms with sufficient alkali metal and alkaline earth cations to maintain electroneutrality. The zeolite framework consists of tetrahedral SiO_4^{-4} and AlO_4^{-5} combined into crystal structures. Oxygen atoms are shared among groups in such a way that cavities are formed within the zeolite structure which accommodate cations needed to maintain electroneutrality within the crystal lattice. Passageways and restrictions between exchange sites in zeolites are referred to as channels, while the enlargements containing the exchange sites are called ion cages or cavities. Openings between zeolite

crystals but within the same aggregate particle are referred to as pores. These terms are illustrated in Figure 2. Although zeolites may exist as fibrous, lamellar, or rigid three-dimensional structures, the members of the latter group have been studied most extensively for their ion exchange properties [38].

The exchange capacity of zeolites is a function both of the Al/Si ratio of the zeolite framework and the access of the interstitial fluid to the ion cages. Exchange capacities of selected zeolites calculated from hydrated formula weights reported by Amphlett [38] ranged from 2.30 to 5.30 meq/g. Capacities reported by Sherry [39] for similar zeolites were based on the anhydrous weight and were correspondingly higher. Ames measured the exchange capacity of chabazite and obtained a capacity of 2.59 meq/g for sodium and potassium ions, while the cesium capacity was 2.20 meq/g. This compared to calculated capacities of 4.95 and 4.00 meq/g given by Sherry and Amphlett, respectively.

Ion Sieve Properties

The extent to which the cations within the zeolite may be exchanged depends on the nature of the zeolite cages — specifically, the size of the opening and the degree to which the channels are interconnected. Because the rigid, three-dimensional crystal lattice contains definite sized openings into the ion cages, zeolites exhibit ion sieve properties to a much greater extent than conventional ion exchange resins. The extent of ion sieving exhibited by a zeolite depends primarily on the size of the channel opening. In the more dense zeolites some ions are completely excluded from the channels. However, in the "open" zeolites, all alkali metal and alkaline earth cations have access to the passageways, although partial sieving action is observed due to the stripping of hydrated water from the ion as it enters the zeolite cavity [39]. In this case the preference of the zeolite for an ion is a function of the energy with which the water of hydration is bound to both the cation and to the zeolite, the size of the ion, and its valence. If lattice forces are strong enough to overcome the energy of solvation, the ion may have access to the zeolite channels on the basis of the crystal radius of the ion [15].

In addition, steric considerations of internal pore geometry affect the capacity as well as the selectivity of the zeolite. The extent of exchange between ion pairs may depend on whether an ion may enter one end of a channel while the exchanged ion leaves by the other end, or whether the two ions must pass at one point within the channel. These questions were considered in Hey's theory of ion exchange mechanism discussed by Marshall [40]. Channel constrictions between zeolite cavities also influence the preference of a zeolite for univalent ions. Bivalent ions cannot easily occupy positions at channel restrictions for steric reasons; however, failure to completely satisfy the

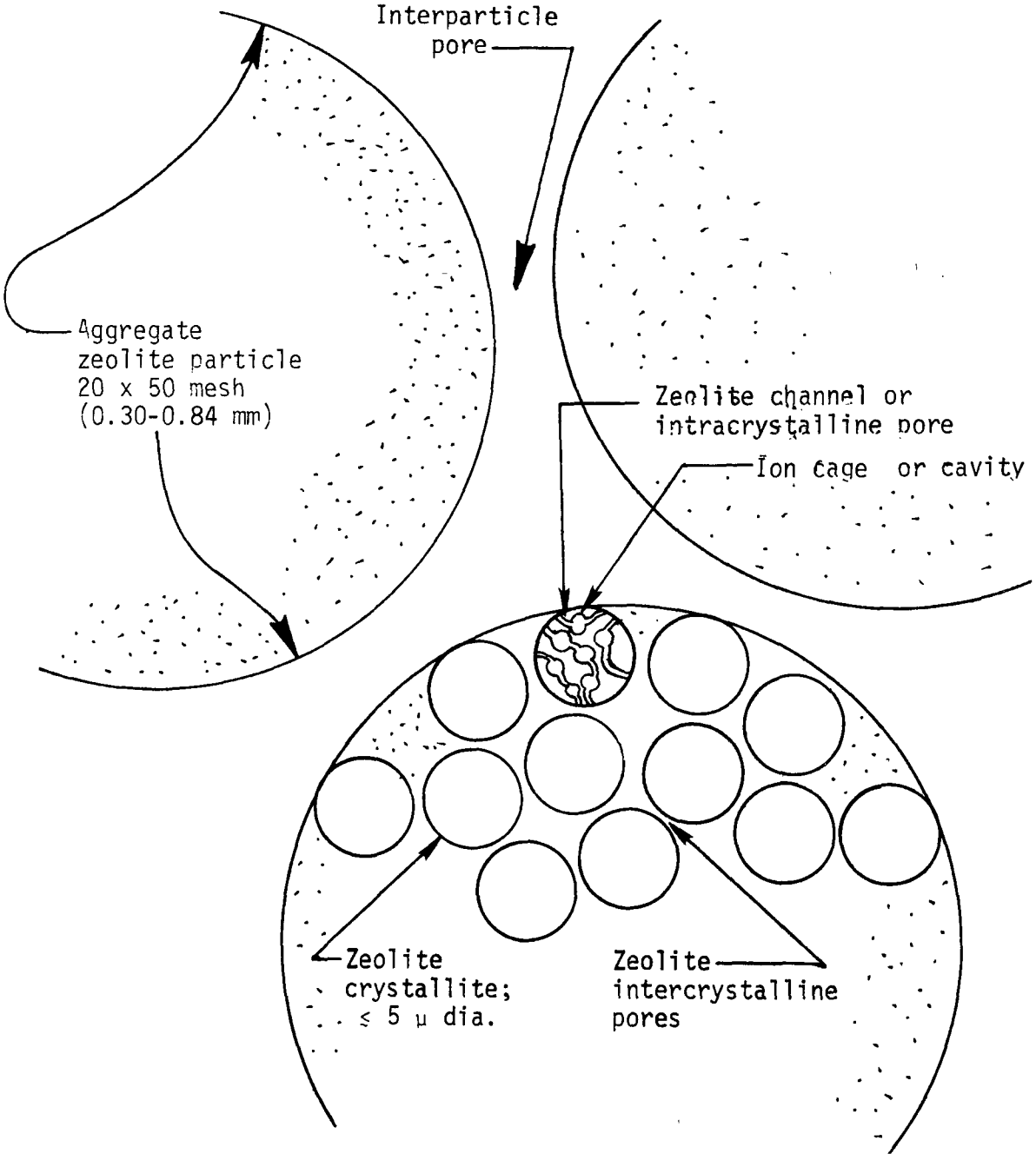


FIGURE 2. IDEALIZED ZEOLITE PARTICLES

electroneutrality requirements of exchange sites adjacent to the restriction leads to instability resulting in the preference of the exchanger for univalent ions [41]. Similarly the volume of the ion cage may be insufficient to accommodate the required number of ions needed to satisfy the charges within the cage. In this case only partial exchange of the particular ion would be possible [38]. Both the degree of channel restriction between cavities and the anion site separation will influence ionic equilibria in these cases. In channels restricted only slightly, it may be possible for multivalent ions to situate themselves in such a way to satisfy exchange sites on either side of the restriction. The anion site separation is partially a function of the exchange capacity of the zeolite and is determined by the number of AlO_2^- groups per unit volume of exchanger.

Another factor which complicates the explanation of zeolite selectivity is the existence of more than one type of cavity in a zeolite. When this occurs, each size cavity may exhibit different ion sieving properties resulting in only partial exchange of some ions. While all functional groups in zeolites originate from the substitution of AlO_2^- groups within the crystal structure, the functionality of these groups varies according to the structure of the particular zeolite and, more specifically, according to the particular cage composition [39].

The structural properties of zeolites which affect selectivity also influence the rate of diffusion of ions through the zeolite. Exchanging ions proceed to exchange sites by diffusion through the liquid in the pores and through the channels of the zeolite framework. The rate of exchange in zeolites is usually controlled by diffusion within the particle which can be 10^6 times slower in zeolites than in organic resins [38]. However, Ames states that diffusion through zeolites composed of crystallites cemented together into aggregate particles is much faster than diffusion through the coarsely crystalline zeolites [42]. These crystallites are usually less than 5 microns in diameter. In such zeolites the rate of exchange would tend to be limited more by diffusion through the pores surrounding the crystallites than by diffusion through the zeolite channels. That particle phase diffusion would be favored in zeolites can be seen from a comparison of average pore diameters for zeolites and organic resins. The minimum free diameter of zeolite channels reported by Barrer [43] ranged from 2.2 to approximately 9 A. The average pore diameter of strong acid resins reported by Kunin [44] averaged 12 A for 8% crosslinking. Thus, zeolite channels are not only smaller than the pores in strong acid exchangers, they are also not able to swell to accommodate larger ions. From the structural properties of zeolites considered above, the relationship between zeolite selectivity and the rate of exchange becomes more evident. The definite sized channels and cavities in the zeolite framework which are largely responsible for the unusual selectivity of zeolites result in poor kinetics of exchange compared to conventional resins. In applications where the selectivity of a particular zeolite is desirable, a sacrifice must be made in terms of exchange kinetics.

In summary, the exchange capacity of a zeolite is a function of the Al/Si ratio of the zeolite framework and the access of ions to the exchange sites. The unusual selectivity exhibited by some zeolites is primarily a result of specific channel geometry as related to cation size and charge, and the binding energy of the structural water in the zeolite lattice. The rate of exchange in zeolites is usually controlled by particle phase diffusivities and is less than the rate in synthetic resins. However, when selectivity for a particular ion is desired, the rate of exchange may be large enough to make feasible the use of a particular zeolite.

Properties of Clinoptilolite

Classification. Mineralogically, the zeolites are classified as a family in the silicate group. Specifically, they are defined as hydrated alumino-silicates of uni- and bivalent bases which can be reversibly dehydrated to varying degrees without undergoing a change in crystal structure and which are capable of undergoing cation exchange [38]. The general composition of zeolites is given by the formula $(M,N_2)O \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O$ where M and N are, respectively, the alkali metal and alkaline earth counter ions present in the zeolite cavities [38].

Clinoptilolite was first identified by Schaller [45] and has been the subject of several mineralogical inquiries since that time. Kostov [46] recognized clinoptilolite as a heulandite rich in silica. However, Berman [47] and Pabst [48] both classed clinoptilolite as a distinct mineral in the heulandite group. More recently, Mumpton [49] found that while the properties of clinoptilolite approximated those of heulandite, clinoptilolite exhibited increased thermal stability due to its higher content of silica. On this basis, it was recommended that clinoptilolite be retained as a valid mineral species. Mumpton defined clinoptilolite as a "mineral of the zeolite group having a molecular composition close to

$$(Na_2O)_{0.70}(CaO)_{0.10}(K_2O)_{0.15}(MgO)_{0.05} \cdot Al_2O_3 \cdot 8.5\text{–}10.5\ SiO_2 \cdot 6\text{–}7\ H_2O$$

and a structure similar to heulandite, but which can clearly be distinguished from heulandite by optical, x-ray, thermal, and chemical means." This composition is essentially the same as ones given by Berman [47], Pabst [48], and Barrer et al. [50].

The largest known deposite of clinoptilolite in the United States is found in southern California within a deposit of bentonite called hectorite because of its proximity to Hector, California [51]. Although Ames stated that clinoptilolite is a common material found in bentonite deposits in the western United States, no information was given concerning the quantities of clinoptilolite present in any deposit.

Clinoptilolite from the Hector deposit has been found to contain from 5 to 15% impurities consisting of quartz, feldspar, and unaltered glass with traces of calcite and montmorillonitic clays [42,50]. Ames [52] also used clinoptilolite from the John Day formation in Oregon which he reported to have a purity of 95% or greater. Sheppard [53] reported the occurrence of clinoptilolite in sedimentary deposits in 66 locations in the United States. However, no information was given concerning the purity or abundance of clinoptilolite in these deposits. The presence of clinoptilolite in Japan has been reported by Iijima [54] and by Minato and Utada [55]. Minato and Utada reached many of the same conclusions concerning the similarities between clinoptilolite and heulandite as did Mumpton [49]. The primary difference between these deposits of clinoptilolite and those found in the United States was that the clinoptilolite of Japan was reported to be found in potassium, calcium, and sodium forms, whereas that found in the United States has been reported to be predominantly in the sodium form.

Capacity. Although the total ion exchange capacity of a material is by no means a complete description of its ion exchange properties, it is an indication of the applicability of the substance for process use. For example, the mineral glauconite (New Jersey greensand), which was widely used in water softening before the development of organic exchangers, has a total exchange capacity of 0.17 meq/g [56]. In comparison, the exchange capacities of strong acid cation exchangers are usually 4 to 5 meq/g. In such a case it is doubtful that any differences in selectivity between these exchangers could be great enough to warrant use of the greensand.

Values of the exchange capacity of clinoptilolite as determined by various investigators are listed in Table 1. Because the exchange capacity is dependent on the method used as well as the ions involved, the conditions under which these capacities were determined are also given. The total exchange capacity of clinoptilolite measured by these investigators ranges from 1.6 to 2.0 meq/g and is slightly lower than the average for zeolites. Several observations may be made concerning these values. For the ions used, there is no apparent difference in the accessibility of the ions to the exchange sites. In comparing the experimentally determined exchange capacity to the composition of clinoptilolite, Barrer et al. [50] found that their exchange capacity corresponded to 98% of the possible capacity. Thus, it appears that practically all of the exchange sites in clinoptilolite are accessible to alkali metal ions. It also appears that the acid wash employed by Ames does not affect the exchange capacity. In fact, the acid wash would be expected to increase the exchange capacity both by opening pores blinded by acid soluble impurities and by removing impurities which contribute to the weight of the exchanger but not to the exchange capacity. However, the values reported by Ames are generally lower than other reported values.

TABLE 1

ION EXCHANGE CAPACITIES OF CLINOPTILOLITE

Reference	Capacity meq/g	Ion Used	Size Material	Preparation of Material	Method
Ames [52]	1.7 2.0[a]	Na^+ replaced by Cs^+; Cs^+ replaced by Na^+	Not specified	Washed in 10% HNO_3; put in proper form by contact with saturated solution of the appropriate chloride salt for two days	Double tracing technique; substantiated by titration of H^+ based sample
Ames [57]	1.7 1.7	Li^+ replaced by Cs^+ Ba^{++} replaced by Cs^+	0.25-0.50 mm (35x60 mesh)	Washed in 10% HCl; put in proper form by contact with saturated solution of the appropriate chloride salt for 21 hours; washed in distilled water	Shallow bed method using radioactive tracers
Ames [12]	1.81	NH_4^+	30x50 mesh	Not specified	Small column method; direct determination of NH_4^+ by distillation of clinoptilolite in kjeldahl flask
Howery and Thomas [58]	2.05 2.04 1.97	Na^+ Cs^+ NH_4^+	30x80 mesh	Contacted with NaCl; rinsed with distilled water	Determination of Na^+ and Cs^+ radiochemically; determination of NH_4^+ by difference from an Na^+ based clinoptilolite
Barrer, Papadopoulos, and Rees [50]	1.83	Na^+ replaced by NH_4^+	18x30 mesh	Contacted with NaCl; rinsed with distilled water	Na^+ measured radiochemically; NH_4^+ determined by analyses of nitrogen in the NH_4^+ exchanged sample
Frysinger [59]	1.61	Cs^+	20x40 mesh	Not specified	Column method using radioactive Cs^+ as tracer

[a]Clinoptilolite from John Day Formation, Oregon. Other samples from Hector, Calif. except for that used by Frysinger who did not specify the source.

Selectivity. In order to identify the preference of clinoptilolite for various ions, Ames [60] determined the cesium capacity of clinoptilolite using 0.01 N cesium solutions in the presence of 1 N concentrations of the competing cations. Capacities were calculated from the point $(c/C_o)_{Cs} = 0.5$ using breakthrough curves obtained from laboratory columns. The results showed that cesium was most preferred by the zeolite and that the more closely a competing cation approached cesium in size, the more selective clinoptilolite became for that ion. Three replacement series were identified for univalent, bivalent, and trivalent metal ions. The cesium capacity in the presence of the ammonium ion was intermediate between the series for univalent and bivalent ions, indicating the influence of the electronic structure of the ion in determining selectivity. The order of preference for the various ions decreased in the order,
$Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{++} > Sr^{++} > Na^+ > Ca^{++} > Fe^{+3} > Al^{+3} > Mg > Li$.
In later work Ames [12] determined the equilibrium isotherms for ammonia and other cations which are present as macrocomponents in wastewaters. These isotherms, which are reproduced in Figure 3, illustrate that clinoptilolite is selective for ammonia relative to all of these ions except potassium. Throughout this report solid phase concentrations, q, selectivity coefficients, K, etc. for ammonia are designated NH_4-N because the ammonium ion is the species exchanged. However, solutions phase ammonia concentrations are more correctly designated as $c_{NH_3\text{-}N}$ as both unionized ammonia and the ammonium ion are measured in ammonia determinations. At low pH there is no significant difference in total NH_3-N and the ammonium ion concentration. Additional nomenclature for high pH solutions is given in Chapter V. In all cases these species are designated as nitrogen in accordance with conventional water and wastewater treatment practice. The separation factors, defined by Equation (5), were calculated from these isotherms and are shown in Table 2. Because they were not constant over the entire concentration range, the values shown in Table 2 were calculated for the point $x_{NH_3\text{-}N} = 0.5$ for comparative purposes.

TABLE 2

SEPARATION FACTORS FOR AMMONIA EXCHANGE ON CLINOPTILOLITE AT $x_{NH_3\text{-}N} = 0.5$[a]

System	Separation Factor, $\alpha_{M,N}^{NH_4\text{-}N}$ at $x_{NH_3\text{-}N} = 0.5$
NH_4-Mg	17.2
NH_4-Ca	6.7
NH_4-Na	4.6
NH_4-K	0.39

[a]Data from Ames [12]

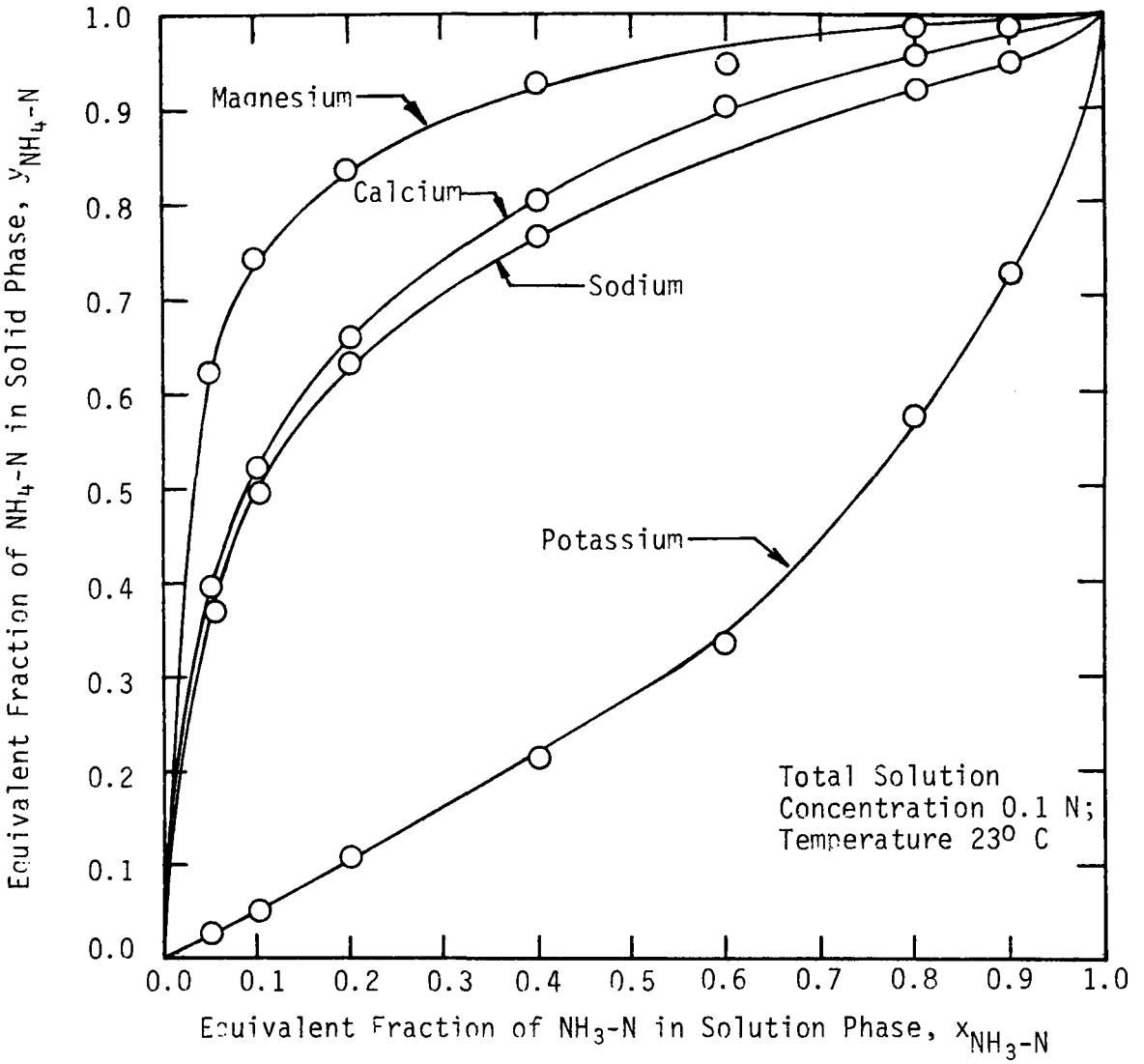


FIGURE 3. ISOTHERMS FOR EXCHANGE OF NH_4^+ FOR K^+, Na^+, Ca^{++}, AND Mg^{++} ON CLINOPTILOLITE [12]

In strong acid organic resins, the effects of electroselectivity [15] and swelling pressure are the primary factors influencing resin selectivity. In dilute solutions under normal operating conditions this results in ions of higher valence and smaller hydrated radius being preferentially exchanged into the resin [44]. The selectivity sequence for organic resins generally follows the lyotropic or Hofmeister series and for sulfonated divinyl benzene resins has the order, $Ba^{++} > Sr^{++} > Ca^{++} > Cs^{+} > Rb^{+} > Mg^{++} \simeq K^{+} > NH_4^{+} > Na^{+} > H^{+} > Li^{+}$ [61]. Although selectivity for ions of equal charge follows the lyotropic series in both clinoptilolite and strong acid exchangers, the selectivity among ions of different valence is quite different.

On the basis of the cation replacement series established for clinoptilolite, Ames [60] concluded that the preference for a given cation by clinoptilolite was dependent on the relationships between cation size, cation charge, and electronic structure of the cation. Temperature in the range 20°–60°C affected selectivity significantly only for Na-Cs exchange. Because clinoptilolite is one of the open zeolites, the effect of cation size is that of partial ion sieving and not complete ion exclusion. In order to determine the effect of hydrated water on clinoptilolite selectivity, Ames [62] conducted exchange studies with clinoptilolite and other open zeolites in molten salt solutions of lithium and potassium nitrates. These studies showed that the structural water of clinoptilolite was not as firmly bound to the zeolite framework as it is to other, less selective, open zeolites. Thus, the structural water of clinoptilolite is free to exert a more intense sieve effect on cations entering the zeolite cavities. In the case of a high field strength cation such as lithium, structural water is attracted to the cation, preventing it from approaching the exchange site as closely as in open zeolites having more tightly bound water. Low field strength cations such as ammonium do not attract as much water of hydration and, therefore, are freer to migrate through the lattice and closely approach exchange sites.

Steric and ion sieve effects in clinoptilolite have been discussed by Barrer *et al.* [50]. The degree of exchange of various alkylammonium ions in clinoptilolite was explained in terms of the free dimensions of channel entrances. Because dimensions of the clinoptilolite framework have not been determined, Barrer assumed that the crystal structure of clinoptilolite was identical to that of heulandite. While the similarities in composition between heulandite and clinoptilolite support this assumption, differences in exchange properties of the two zeolites raise doubts as to the completely iso-structural nature of the two materials [60]. Nevertheless, the correlation between the degree of exchange of organic ions and the size of the heulandite windows seems to indicate a reasonable similarity between the two structures. Barrer used crystallographic data of Merkle and Slaughter [63] showing elliptical windows of two different sizes. Free dimensions of the larger window were approximately 3.5 by 7.9 A and of the smaller window, 3.0 by 4.4 A. The existence of windows of two sizes in the clinoptilolite

framework could explain the sigmoid isotherms for Na-Sr, Na-Ca, and Ca-Sr exchange reported by Ames [64] and the variation of separation factors calculated from isotherms shown in Figure 3.

The partial sieve action in clinoptilolite may be illustrated by comparing ionic diameters in Table 3 to the free diameters of the crystal windows. It can be seen that there is ample room for all of

TABLE 3

SIZE OF SELECTED CATIONS

Ion	Crystal Diameter[a] A	Hydrated Diameter[b] A
Li	1.20	20.0
Na	1.90	15.8
K	2.66	10.6
NH_4	2.80	10.7
Rb	2.96	10.2
Cs	3.38	10.1
Mg	1.30	21.6
Ca	1.98	19.2
Sr	2.26	19.2
Ba	2.70	17.6

[a]Crystal diameters from Pauling [65].

[b]Hydrated diameters from Jenny [66] as found in Grim [67].

these ions to enter the cavities based on the crystal diameter of the ions, but that none of the ions can enter without some of the water of hydration being stripped. Based on crystal diameters, sufficient room exists for any two ions to pass in the larger channel. However, several ion pairs could not pass in the smaller window.

In an effort to explain the general preference of clinoptilolite for univalent ions, Ames [64,68] examined the selectivity of zeolites having different Al/Si ratios. Using the Al/Si ratio as a general predictor of the distance between exchange sites in the zeolites, Ames found that bivalent ion selectivity decreased with decreasing Al/Si ratios. This is explained by the fact that bivalent ions cannot remain stable and occupy two exchange sites which are relatively far apart. However, the inadequacy of this phenomena to completely explain selectivity between ions of different valence was shown by the fact that clinoptilolite is somewhat more strontium selective than other zeolites having higher Al/Si ratios [68]. Howery and Thomas [58] attempted to account for

nonideality of exchange on clinoptilolite by a thermodynamic treatment of the exchange sites. Two suppositions were made concerning the nature of the exchange sites: 1) that the sites were identical and differences in binding energies were influenced only by the population of neighboring sites, or 2) that binding energies varied from site to site but that sites were so widely separated that neighboring ions exerted no influence on each other. However, from results obtained it was impossible to attribute exchange behavior to one of the models.

Diffusivity. Ames [42] has reported that diffusion in clinoptilolite, which is composed of crystallites imbedded in a binder, is much more rapid than in the coarsely crystalline zeolites. Using an expression proposed by Boyd, Ames [62] found the particle phase diffusion coefficient to be 1.66×10^{-7} cm^2/sec for Na-Cs exchange at 25°C in 0.134-mm diameter particles. In another study the particle phase diffusivity was found to be 3.88×10^{-7} cm^2/sec at 29°C for 0.25 to 0.50-mm diameter particles [69]. These values are an order of magnitude smaller than those measured by Boyd et al. [23] of 2.0×10^{-6} and 2.9×10^{-6} cm^2/sec for Cs-K and Na-NH_4 exchange, respectively, in 0.23-mm particles of Amberlite IR-1. In investigating film diffusion, it was not possible to compute the film diffusion coefficient. However, values obtained by Ames [69] for a parameter containing the film diffusity were very close to values obtained by Boyd for Amberlite IR-1 when corrected to similar conditions. Boyd estimated film diffusion coefficients to be about 1.8×10^{-5} cm^2/sec. Thus, while film diffusion coefficients are approximately the same for clinoptilolite and organic resins, particle phase diffusivities are an order of magnitude less for clinoptilolite. Barrer [50] measured diffusion coefficients for various alkylammonium ions in clinoptilolite and concluded that intraparticle diffusion in pore spaces between crystallites was the rate controlling step. Values of the diffusion coefficient ranged from 10^{-8} to 10^{-9} cm^2/sec. While some pore diffusion is not usually affected by the nature of the exchanging ions, differences in hydration characteristics of organic and inorganic cations might be expected to account for differences in these values and those measured by Ames.

In relating diffusion in clinoptilolite to selectivity, Ames [62] concluded that the different selectivities of erionite and clinoptilolite were not caused by differences in diffusion rates, but rather that cation selectivity differences influence exchange kinetics. From studies of the exchange rate of ions under conditions where film diffusion limited the rate of exchange, Ames found that exchange rates did not correlate to liquid diffusion coefficients, but that interaction of the ions with the exchange sites also had to be taken into account. In another study Ames [70] showed that self-diffusion of ions, i.e., diffusion of one ion in an exchanger in the absence of a concentration gradient, decreased as the ion valence increased.

Stability. The instability of natural clays and zeolites toward acids and alkalis has been known since these materials were widely used in

water softening [71]. Studies of the effect of pH on the clinoptilolite structure have been limited, but Ames [60] found that the material was considerably more acid resistant than other zeolites. However, Barrer and Makki [72] found that treatment of clinoptilolite with acid in 1 N and higher concentrations resulted in progressive displacement of aluminum from the crystal framework leaving only the hydroxylated silica after treatment with 5 N acid.

The stability of clinoptilolite in the presence of alkali has been investigated by Barrer et al. [50]. Samples of clinoptilolite were shaken with varying concentrations of NaOH for two days at room temperature. Weight loss during this period was taken as a measure of the degree of chemical attack by the alkali. The relation between weight loss and concentration of NaOH was reported to be nearly linear with a 70% loss of weight occurring from exposure to 20% NaOH. These results indicate that regeneration of clinoptilolite with caustic solutions might result in loss of the zeolite from chemical attack.

V. NATURE AND SCOPE OF THE INVESTIGATION

Based on the previous work concerned with ammonia removal and the ion exchange properties of clinoptilolite reviewed in Chapter IV, the specific nature and scope of this study may be outlined. It is the purpose of this chapter to assess the potential utility of clinoptilolite for ammonia removal, to outline the rationale of the study, and to define the specific scope of the investigation

POTENTIAL ADVANTAGES OF CLINOPTILOLITE

As an ion exchange process, the use of clinoptilolite has several advantages over other methods of ammonia removal. The widespread application of ion exchange processes has led to the development of equipment which functions almost automatically and requires relatively little maintenance. Ion exchange processes are by nature stable and predictable with respect to product quality. While the total exchange capacity of clinoptilolite is somewhat less than that of synthetic organic resins, its selectivity for the ammonium ion compensates for this fact, giving it an advantage over conventional ion exchange resins. Exchange kinetics in clinoptilolite, though poorer than in organic resins, are rapid enough to permit favorable column utilization during exhaustion. In areas where disposal of regenerant brine is a problem, the high pH solution used to regenerate the zeolite can be stripped of ammonia and reused.

In the final analysis the applicability of clinoptilolite for ammonia removal is heavily dependent on process costs. While cost estimates prepared for nitrogen removal processes are based on preliminary operating and design information, they do provide a guide for assessing the potential for the use of clinoptilolite for ammonia removal. The biological nitrification-denitrification process was discussed by McCarty [9] who estimated that costs would be approximately $0.08/1000 gal. Denitrification in this process was accomplished using anaerobic filters with methanol added as a carbon source. Costs for the three-stage biological process investigated by Barth *et al.* [11] were not estimated, but it seems likely that nitrogen removal costs for this process would not differ significantly from the cost of the system proposed by McCarty.

The cost of ammonia removal by chlorination is highly dependent on transportation costs unless on-site production of chlorine is feasible. Given a chlorine cost of $0.04/lb and the assumption that 10 parts of chlorine will completely oxidize 1 part of ammonia, chemical costs for ammonia removal by chlorination will be $0.075/1000 gal for an initial ammonia concentration of 20 mg/ℓ NH_3-N. This cost considers only the

cost of chlorine and does not include capital costs, maintenance costs, or the cost of dechlorination if required. Ammonia removal by superchlorination might be undesirable for water reuse applications where toxicity to aquatic life and tastes and odors are objectionable. Culp [73] has estimated that ammonia removal by air stripping using a low headloss, cross-flow tower costs $0.017/1000 gal. Costs estimated by Smith and McMichael [74] for the same type of tower range from $0.036/1000 gal for a 10-mgd plant to $0.026/1000 gal for a 300-mgd plant. Farrell [75] has quoted a cost of $0.029/1000 gal based on experience at the South Tahoe Public Utility District. These estimates do not include the cost of raising the pH of the waste prior to ammonia stripping. The estimated cost of ammonia removal using clinoptilolite was $0.16/1000 gal for a proposed installation at the South Tahoe Public Utility District [76]. However, Dean [77] reported a cost of between $0.03/1000 gal and $0.06/1000 gal based on operating experience of the Battelle demonstration plant and suggested that a cost of about $0.10/1000 gal sounded most reasonable. Cost estimates for the construction of advanced waste treatment facilities at the Blue Plains wastewater treatment plant in Washington, D. C. prepared by the Bechtel Corp. [78] revealed that ammonia removal by ion exchange would cost $0.103/1000 gal for a 240-mgd plant and $0.097/1000 gal if the plant were expanded to 300 mgd. Estimates for nitrification-denitrification ranged from $0.118/1000 gal to $0.124/1000 gal for a 240-mgd plant and $0.112/1000 gal to $0.117/1000 gal for expansion to 300 mgd, the range of costs for each size design depending on whether or not alum was added to the nitrification stage.

This comparison shows that air stripping is the least costly method with present technology. However, cost estimates for air stripping might not accurately reflect cost of tower replacement due to delignification and maintenance costs required to remove scale from the tower packing. If these problems do not prove to be serious air stripping will probably be the preferred method in areas where low temperatures are not a problem and where ammonia discharge to the atmosphere is not prohibited. Although costs of other methods listed range from $0.075 to $0.10/1000 gal, the preliminary nature of these estimates suggests that the cost of any of these processes is approximately $0.10/1000 gal. On this basis the use of clinoptilolite for ammonia removal is, with the exception of air stripping, competitive with other methods.

SPECIFIC AREAS OF STUDY

Effect of Water Composition on Ammonia Exchange Capacity

The ammonia exchange capacity will vary in proportion to the NH_3-N/total cation ratio of the column influent. Although the equilibrium column loading may be ideally predicted knowing the influent composition and selectivity coefficients as described by Vermeulen, Klein, and Hiester

[20] and as shown by Mercer [14] for small columns, solid phase activity corrections must be made for accurate application of this method to waters of widely varied composition. However, the equilibrium properties of clinoptilolite indicate that the ammonia exchange capacity is a function of cationic strength. The term cationic strength refers to the ionic strength of the water considering only the cation species present. Cationic strength will be designated I_+ and is calculated using the expression for ionic strength [16]:

$$I_+ = \frac{1}{2}\sum (m_i\ z_i^2) \qquad (10)$$

where m_i is the cation concentration of the i^{th} species and z_i is the valence of the particular cation. Ammonia selectivity coefficients determined by Ames [12] show that zeolite selectivity for ammonia increases as the competing cation/ammonia ratio increases. In addition, Equation 4 shows that the selectivity of the exchanger for multivalent cations decreases as the total solution concentration increases. While the ammonia exchange capacity will decrease with increasing cationic strength, these considerations indicate that the decrease will become less with increasing cationic strengths. To determine the nature of the variation of ammonia exchange capacity with water composition, runs were made saturating clinoptilolite with waters having cation compositions representative of chemically different sewages.

Effect of pH on Ammonia Exchange

In removing ammonia by ion exchange, the pH of the waste is of primary importance. The pH of the waste prior to ion exchange may range from 5 to 11, or higher, depending on the chemical used in precipitation processes preceding the ion exchange unit. The pH will also play an important role in regenerating and rinsing of ion exchange beds. The effect on the exchange of ammonia will be twofold. At high pH, ammonia will be predominantly in the unionized form, unavailable for exchange. At lower pH levels, hydrogen ions in the water compete with ammonium ions for exchange sites.

The influence of pH may be examined using equilibrium ion exchange relationships. Although this is done most correctly using a binary NH_4-H system, the result does not correctly predict behavior in a multicomponent system. In the binary case, concentrations of both ammonium and hydrogen ions decrease as the pH increases. However, the equilibrium relationships are such that the clinoptilolite remains predominantly in the NH_4 form even at high pH values. For the case of the multicomponent wastewater system, other ions, unaffected by changes in pH, will replace ammonia in the exchanger at high pH. To represent the multicomponent wastewater system, a ternary NH_4-Na-H system will be considered. Although this can correctly be described only by a ternary diagram or by appropriate activity corrections, the approximate solution

is sufficient to describe a system having a relatively constant equilibrium sodium concentration.

Three equilibria are involved:

$$NH_4^+ + NaZ \rightleftarrows NH_4Z + Na^+$$

$$NH_4^+ + HZ \rightleftarrows NH_4Z + H^+$$

$$NH_3 + H^+ \rightleftarrows NH_4^+ \quad .$$

These equilibria may be described by the NH_4-Na and NH_4-H selectivity coefficients and the ammonia equilibrium constant:

$$K_{Na}^{NH_4\text{-}N} = \left(\frac{q}{c}\right)_{NH_4\text{-}N} \left(\frac{c}{q}\right)_{Na} \tag{11}$$

$$K_{H}^{NH_4\text{-}N} = \left(\frac{q}{c}\right)_{NH_4\text{-}N} \left(\frac{c}{q}\right)_{H} \tag{12}$$

$$K_{eq} = \frac{\left[c_{NH_3^\circ\text{-}N}\right]\left[c_H\right]}{\left[c_{NH_4\text{-}N}\right]} \quad . \tag{13}$$

Because it is necessary to distinguish between ionized and unionized ammonia, $c_{NH_4\text{-}N}$ designates the ammonium ion concentration as nitrogen, while $c_{NH_3^\circ\text{-}N}$ refers only to the unionized ammonia concentration, again as nitrogen. The total ammonia nitrogen concentration, analogous to the concentration measured in a kjeldahl distillation, is designated $c_{NH_3\text{-}N}$ such that,

$$\left[c_{NH_3\text{-}N}\right] = \left[c_{NH_4\text{-}N}\right] + \left[c_{NH_3^\circ\text{-}N}\right] \quad . \tag{14}$$

In order for equilibrium concentrations to be compatible with the units of K_{eq}, they are expressed in moles/ℓ as indicated by the brackets. For the symmetric univalent system, selectivity coefficients, normally expressed using concentrations in milliequivalents per liter, may be used without correction for the difference in units. Solid phase concentrations may still be expressed as meq/g.

In the solid phase the sum of individual concentrations will equal the total exchange capacity, Q.

$$Q = q_{NH_4\text{-}N} + q_{Na} + q_H \quad . \tag{15}$$

Equations 11 and 12 may be solved for $q_{NH_4\text{-}N}$ and substituted into Equation 15.

$$Q = q_{NH_4\text{-}N} + \frac{q_{NH_4\text{-}N}\left[c_{Na}\right]}{\left[c_{NH_4\text{-}N}\right] K_{Na}^{NH_4\text{-}N}} + \frac{q_{NH_4\text{-}N}\left[c_H\right]}{\left[c_{NH_4\text{-}N}\right] K_H^{NH_4\text{-}N}} \quad . \qquad (16)$$

The concentration of $c_{NH_4\text{-}N}$ is a function of pH, and may be expressed in terms of Equations 13 and 14,

$$\left[c_{NH_4\text{-}N}\right] = \frac{\left[c_{NH_3\text{-}N}\right]\left[c_H\right]}{\left[c_H\right] + K_{eq}} \quad . \qquad (17)$$

Substituting Equation 17 into Equation 16, the result is

$$q_{NH_4\text{-}N} = \frac{Q}{1 + \frac{\left[c_{Na}\right]\left(\left[c_H\right] + K_{eq}\right)}{\left[c_{NH_3\text{-}N}\right]\left[c_H\right] K_{Na}^{NH_4\text{-}N}} + \frac{\left[c_H\right] + K_{eq}}{\left[c_N\right] K_H^{NH_4\text{-}N}}} \qquad (18)$$

which expresses the solid phase concentration of ammonia as a function of the total equilibrium ammonia concentration in the solution, the equilibrium pH, and the equilibrium sodium concentration.

The constants necessary for the use of this relationship are K_{eq}, $K_{Na}^{NH_4\text{-}N}$, $K_H^{NH_4\text{-}N}$, and Q. The ammonia equilibrium constant is 5.55×10^{-10} at 25°C [16]. The value of $K_{Na}^{NH_4\text{-}N}$ is 4.6 from Table 2. The value of $K_H^{NH_4\text{-}N}$ has not been determined directly, but may be calculated from other data. From the Cs-NH_4 isotherm given by Mercer and Ames [79], $K_{NH_4\text{-}N}^{Cs} = 5$. From data given by Ames [42], $K_H^{Cs} = 10$. Because of the variation of equilibrium data for clinoptilolite with concentration, average values were chosen for these coefficients. The ammonium-hydrogen selectivity coefficient may be estimated from these data:

$$K_H^{NH_4\text{-}N} = \frac{K_H^{Cs}}{K_{NH_4\text{-}N}^{Cs}} \simeq \frac{10}{5} \simeq 2$$

Equation 18 then becomes,

$$q_{NH_4\text{-}N} = \frac{Q}{1 + \frac{[c_{Na}]\ [c_H] + 5.55 \times 10^{-10}}{4.6\ [c_{NH_3\text{-}N}]\ [c_H]} + \frac{[c_H] + 5.55 \times 10^{-10}}{2\ [c_{NH_3\text{-}N}]}} \quad (18)$$

Although values of Q have been measured by other investigators, a separate measurement was made in this study to confirm values reported elsewhere and to compare the clinoptilolite used in this study with that used by other investigators. In the experimental phase of the study, both batch and column tests were made to establish the validity of this model.

Regeneration

In previous investigations clinoptilolite has been regenerated using a saturated lime solution with $CaCl_2$ or NaCl added to increase the strength of the regenerant. To determine the relative effectiveness of regenerating with sodium and calcium salts, column runs were made with clinoptilolite in sodium and calcium forms.

The cost of chemicals needed for regeneration constitutes a significant fraction of the cost of ion exchange processing. Therefore, the concentration of the regenerant which results in least-cost operation of the process was determined. It was expected that a high pH regenerant would increase the efficiency of regeneration by maintaining a high driving potential between the ammonium ion concentrations in the solid and fluid phases. Because of limiting particle phase diffusion, it was expected that high salt concentrations would not result in increased regeneration efficiency. Depending on the rate of exchange, it was believed that lower flow rates during regeneration might lead to higher regenerant utilization. The effect of regenerant pH, salt concentration, and flow rate was determined to arrive at the least-cost method of regeneration.

Work by Barrer *et al.* [50] indicated that clinoptilolite was attacked by caustic solutions. In order to determine the stability of clinoptilolite in the presence of caustic solutions used for regeneration, tests were run in small columns to simulate regeneration and exhaustion cycles. Results were used to arrive at optimum conditions for regeneration.

Demonstrations of Column Performance

To define the performance of clinoptilolite under normal operating conditions, column studies were made in three locations. Questions of interest in these studies were the amount of ammonia removal which could

be expected in cyclic operation, the dependence of column performance on flow rate and the nature of the previous regeneration, and the capacity of clinoptilolite using different sewages for the column influent. Questions related to fouling and the sustained capacity were also of interest.

Process Costs

To establish the economic feasibility of the clinoptilolite ion exchange process, a detailed cost estimate was prepared for the optimum operating conditions determined during the experimental phase of the study.

VI. EXPERIMENTAL EQUIPMENT AND PROCEDURES

EXPERIMENTAL COLUMN UNITS

The experimental phases of the study involved runs using both synthetic waters and treated sewage from the SERL pilot plant, the East Bay Municipal Utility District (EBMUD), and the Central Contra Costa Sanitary District (CCCSD). Two exchange column units were used in these tests. The SERL unit was designed primarily to be used for runs in which only single column operation was required. The column unit used in studies at EBMUD and CCCSD was designed for easy transport and for flexibility of operation when several columns were employed in series. Both units were constructed so that modifications could easily be made for upflow or downflow operation, backwashing, and regeneration.

SERL Column Unit

Columns. The column unit used in runs made at SERL is pictured in Figure 4. Basically the unit consists of two 4-in. ID plexiglass columns 6 ft in length. Construction details of the columns are shown in Figure 1, Appendix A. The exchange medium was supported on a plexiglass plate containing 5/16-in. holes for flow distribution and a 210 μ mesh nylon screen. Piping to the column consisted of 1/2-in. PVC pipe and fittings and was constructed so that each column could be removed from the unit by uncoupling unions located near the ends of the columns. Valves which came into contact with regenerant solutions were PVC ball type while other valves were gate type of brass. A schematic diagram of the column system is shown in Figure 6. Columns were supported on a welded frame made from 1-1/2 in. x 1-1/2 in. x 1/4 in. steel angle.

Influent to the columns was pumped to a constant head tank located on top of the frame. Flow was regulated by a rate controller consisting of float valve which discharged into a small reservoir. Changes in flow rate were made by adjusting a 1/2-in. gate valve located on the float chamber. This simple and inexpensive arrangement provided excellent control over flow rates and made it possible to maintain flows with less than five percent deviation from the desired value. Flow could be checked by rotometers located in the piping between the constant head tank and the column inlet.

Regeneration was accomplished by pumping regenerant through a Vanton Flexi-Liner pump (Vanton Pump Co., Hillside, N.J.) to a constant head tank from which it flowed to the columns. Regenerant was prepared in a 200-gal Nalgene tank. Following the addition of caustic and mixing,

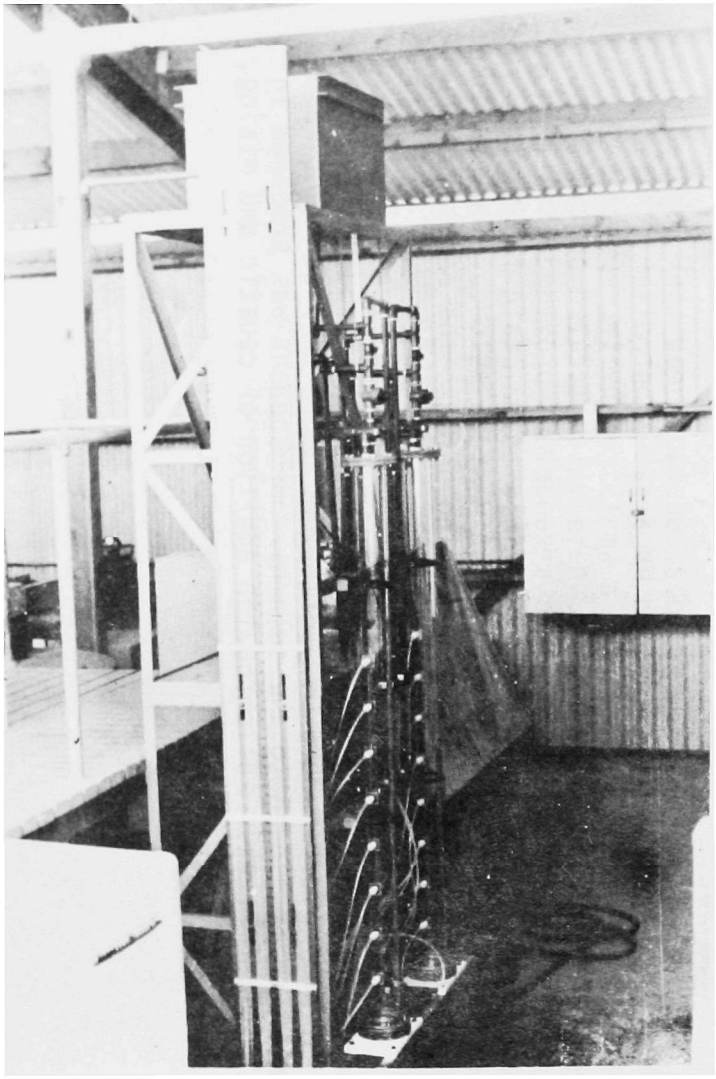


FIGURE 4. COLUMN UNIT LOCATED AT THE SERL TREATMENT FACILITY

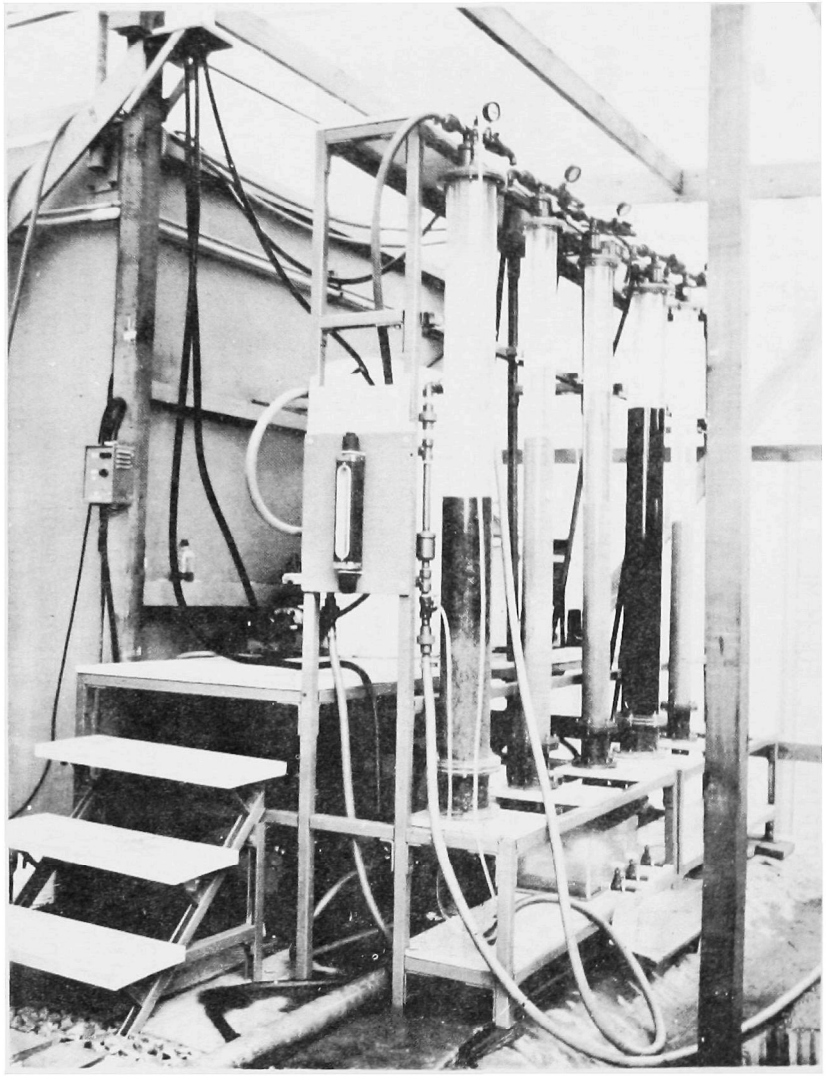


FIGURE 5. COLUMN UNIT USED IN STUDIES AT EBMUD AND CCCSD

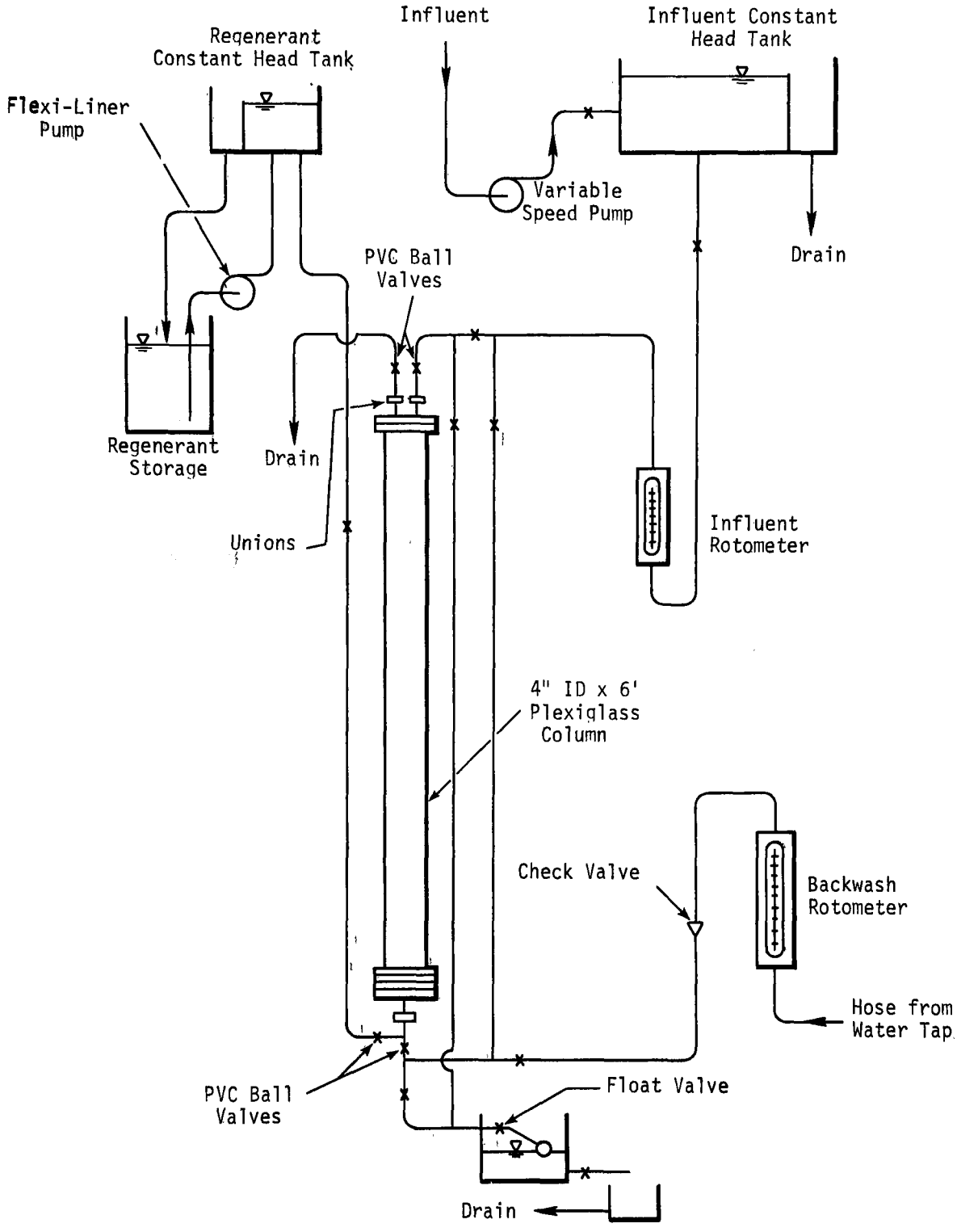


FIGURE 6. SCHEMATIC ILLUSTRATION OF COLUMN UNIT

the solution was allowed to settle overnight. Subsequently, supernatant was siphoned from the tank to a 200-ℓ plastic container using a floating intake.

Headloss measurements were made by means of piezometer taps located at 6-in. intervals in the side of the columns. Plastic tubing from the taps ran to a board attached to the side of the column frame which was marked at 0.02 ft intervals.

Sampling. Composite effluent samples were collected over 2- to 6-hr periods, depending on the nature of the test being run using a Misco fraction collector, Model 6510, (Microchemical Specialties Company, Berkeley, California). The sample was pumped through plastic tubing using a Sigmamotor Model T-6 pump (Sigmamotor, Inc., Middleport, N. Y.) to a glass tube fastened to the edge of the rotating collector. Funnels placed on the table directly beneath the collector caught the sample and transmitted it to bottles placed beneath the table. Composite influent samples were taken from the head tank over longer time intervals using the same Sigma pump.

Column Units Used in EBMUD and CCCSD Studies

The columns used in studies at EBMUD and CCCSD are shown in Figure 5. This unit included four 4-in. ID by 6-ft columns used for ion exchange and two 6-in. ID by 6-ft columns used as filters. Details of the 4-in. columns, which were essentially the same as the 6-in. columns, are shown in Figure 2, Appendix A. A bed of river gravel was included at the bottom of these columns to obtain better flow distribution during backwashing. However, some channeling was still evident when columns were backwashed.

Influent was pumped through the columns using a three-stage Moyno pump (Robbins and Myers, Inc., Springfield, Ohio) run by a 1/2-hp DC motor. A pressure relief valve on the outlet side of the pump protected the columns from excessive pressure. Connections between columns were made using neoprene hose and tubing with PVC unions to facilitate changes from one operating mode to another. A rotometer mounted on the column frame was used to measure both influent and backwash flow rates.

To achieve more effective backwashing, a multiple jet surface wash device was incorporated into the column design. This feature, illustrated in Figure 3 in Appendix A, proved to be very effective in breaking up the cake which frequently formed at the surface of the first column.

The column framework was constructed from Super Strut channel (Imperial Strut and Hanger Co., Oakland, California) and was designed for disassembly and transport. A walkway located behind the columns provided easy access to the top of the columns as well as stability for

the column supports. Regeneration was accomplished in a manner similar to that for the SERL unit. Regeneration flow rates were regulated using a float valve controller. Sampling procedures were identical to those used with the SERL unit.

The filter used ahead of the ion exchange unit consisted of 2 ft of sand having an effective size of 0.27 mm and a uniformity coefficient of 1.63 and 1 ft of anthracite reported by the distributor to have a size range of 0.85–0.95 mm. While this filter performed well during the study, more mixing between layers occurred than was desirable. Better headloss distribution would have resulted had a larger sand been used.

ANALYTICAL PROCEDURES

Sampling Procedure

Wastewater samples taken to monitor performance of treatment processes upstream from column units were collected continuously over 24-hr periods and were refrigerated prior to analysis. While it was not possible to refrigerate column effluent samples as they were taken, samples were refrigerated after they had been collected prior to analysis. Composite samples were collected in the morning and were usually analyzed the same day except on weekends. Priority was given to ammonia, COD, and BOD determinations.

Analytical Methods

Chemical and physical analyses were generally performed in accordance with Standard Methods [80] or the FWPCA Methods for Chemical Analysis [81]. However, in several instances the detailed procedure followed was that given in SERL Analytical Methods [82].

Ammonia Nitrogen. Samples were made alkaline to the phenolphthalein endpoint and distilled in a kjeldahl apparatus. Samples containing more than 3 mg/ℓ NH_3-N were titrated with 0.01 N H_2SO_4 using an alpha-zurine-methyl red indicator [82]; those containing less than 3 mg/ℓ NH_3-N were nesslerized using a Bausch and Lomb Spectronic 20.

Total Hardness, Calcium, Magnesium. The EDTA titrimetric method was employed using Calmagite indicator for total hardness determinations and hydroxy napthol blue indicator (both products of Mallinckrodt Chemical Works) for calcium determination [82]. Magnesium was determined by difference from total hardness and calcium values.

Sodium, Potassium. Sodium was determined by flame spectrophotometry using a Beckman DU spectrophotometer [82]. Potassium was originally determined by flame spectrophotometry. However, most determinations

were made by atomic absorption spectrophotometry using a Perkins-Elmer model 290 B atomic absorption unit because of the increased stability of this method.

Alkalinity, pH. The pH was read using a Beckman model 76 pH meter equipped with a Corning Triple-Purpose electrode designed to measure pH in the range 0 to 14. Alkalinity was determined by potentiometric titration to pH 4.3.

Organic Nitrogen. Organic nitrogen was determined according to FWPCA Methods.

Chemical Oxygen Demand. A modification of the normal COD procedure was used which permitted more accurate determination of samples having low COD values. The only difference in this procedure and the normal method was that a smaller refluxing unit and less concentrated potassium dichromate and ferrous ammonium sulfate were used [82].

Biochemical Oxygen Demand. BOD values were determined according to Standard Methods except that sample dilutions were made directly in the BOD bottle.

Suspended Solids. Suspended solids were determined by filtration of samples through Whatman GF/C glass fiber filters. Filters were pre-washed and baked in a 560°C furnace prior to use. Samples were dried at 105°C to constant weight, then stored in individual desiccator jars prior to weighing.

Total Solids. Total solids were determined according to FWPCA Methods.

Turbidity. A Rossum model 600 turbidimeter (Rossum Instrument Co., Cupertino, California), previously calibrated with a standard silica solution, was used for measurement of turbidity.

Total and Total Soluble Phosphorus. Phosphorus determinations were made by digesting samples to convert all forms of phosphorus to ortho-phosphate followed by measurement of orthophosphate using the ANS reduction method [80,82].

PREPARATION OF THE CLINOPTILOLITE

Clinoptilolite was obtained from the Baroid Division, National Lead Company, Houston, Texas, which mines clinoptilolite from the Hector, California deposit. Originally, only mine run material consisting of 1- to 2-in. chunks was available. A later shipment consisted of minus 4 mesh material. The only guide in crushing the zeolite came from crushing tests reported by Berry [83] who used a Hazemag impact crusher. A recovery of 52% was reported for 16 x 70 mesh material (U. S. Standard Sieve).

Because of limited facilities, crushing was accomplished in batches. Clinoptilolite received in chunk form was run through a jaw crusher set to crush the material into 1/2- to 1-in. pieces. Subsequently, all material was fed through a cone crusher set to deliver the desired 20 x 50 mesh size. Following a rough separation, +20 mesh material was again passed through the cone crusher set with a slightly smaller opening. Finally, all material was screened through 20 x 50 mesh screens to obtain the proper gradation. A recovery of approximately 50% of the original shipment was realized. As the material was used, it was put into columns, soaked to remove air bubbles from the pores, and backwashed to remove dust from the bed.

A comparison between the grain size distributions for this material and clinoptilolite obtained from the Battelle Northwest demonstration plant [14] is shown in Figure 7. Although no effort was made to mix different size fractions to obtain a specific product, the size distributions are very similar. The sample from Battelle had an effective size of 0.38 mm and a uniformity coefficient of 1.63, while the sample crushed in this study had an effective size of 0.34 mm and a uniformity coefficient of 1.59.

CONDUCT OF THE STUDY

Selection of Column Operating Conditions

Wherever possible, data reported by other investigators were used in determining column operating conditions to be used in this study. Ames [60] reported the effect of different particle sizes on cesium exchange. The breakthrough volume to $c/C_0 = 0.05$ for 18 x 60 mesh particles was 70% of that for 60 x 100 mesh particles, while leakage occurred immediately using 10 x 18 mesh particles. As a balance between exchange kinetics and headloss, 20 x 50 mesh particles were used in this investigation. This was also the size material selected by Mercer [13,14,37] in the Battelle demonstration plant.

The optimum flow rate for ion exchange processing is usually the greatest flow which does not result in a sacrifice of kinetics. In studies to determine the effect of flow rate on exchange kinetics of 20 x 50 mesh clinoptilolite, Mercer [13,14,37] found that the breakthrough curve became much shallower when the flow was increased from 20 to 30 BV/hr. In this investigation a flow of 15 BV/hr was most often used both because it resulted in convenient run times to the ammonia breakthrough and because headloss was not excessive. The bed depth used in all studies was 3 ft.

Columns were regenerated upflow. This was desirable both to remove suspended solids from the bed collected during exhaustion and to minimize the entrapment of precipitated $Mg(OH)_2$ and $Ca(OH)_2$ suspended

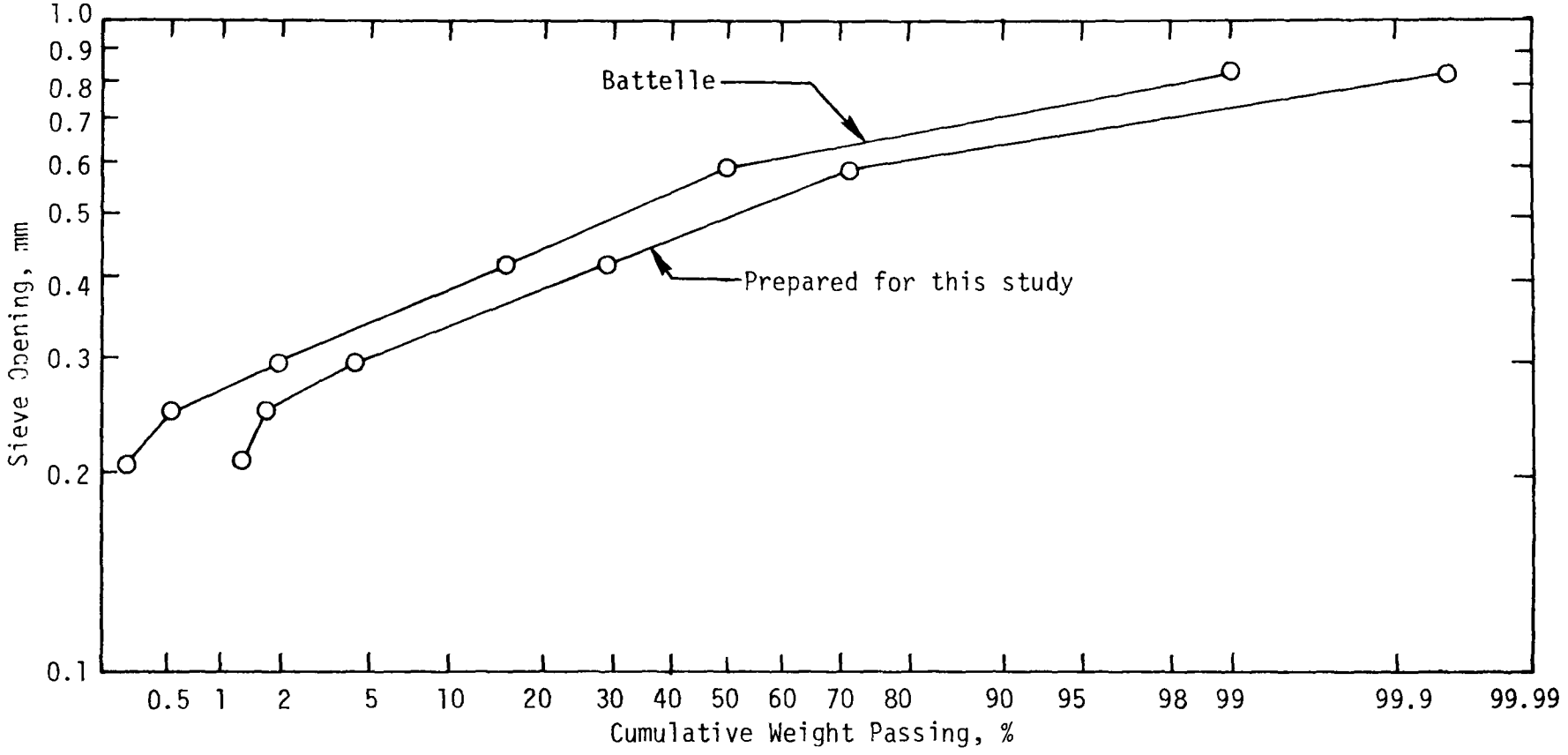


FIGURE 7. GRAIN SIZE DISTRIBUTION OF CLINOPTILOLITE

in the regenerant solution. In addition, countercurrent regeneration should be more efficient than cocurrent regeneration because of the position of ammonia in the upper part of the bed. In cocurrent regeneration ammonia must be pushed through the entire column length and this requires a larger regenerant volume.

The bulk density and specific gravity of clinoptilolite have been measured and reported by Barrer et al. [50]. The specific gravity for 18 x 30 mesh material was 2.19 and the specific gravity of wet particles was 1.61. Ames [60] measured a bulk density of 0.79 g/cu cm. The clinoptilolite used in this study was found to have a specific gravity of 2.38, a wet particle specific gravity of 1.59, and a bulk density of 0.74 g/cu cm.

Runs Using Synthetic Systems

During the course of the study several runs were made using chemically modified tap water for the column influent. The average composition of tap water used for makeup and for column rinsing is shown in Table 4.

TABLE 4

AVERAGE COMPOSITION OF SERL TAP WATER

Ion	Concentration
Na	10 mg/ℓ
K	0.9 mg/ℓ
Ca	26 mg/ℓ
Mg	4 mg/ℓ
pH	8.2

Technical grade chemicals were used to prepare solutions of the desired concentration. Chloride salts were used except for a few runs in which $MgSO_4$ was used. Tests were run to determine the concentration of Na, K, Ca, Mg, and NH_3-N present as impurities in the chemicals. The maximum concentration of a single impurity amounted to 0.2% by weight.

Initially feed water was prepared in 500-gal batches, then pumped to an influent storage tank. In later runs feed water was prepared continuously in a mixing tank from which the solution was pumped directly to the column head tank. Tap water was fed to the mixing tank from a constant head tank in order to eliminate flow fluctuations caused by

water pressure. A stock chemical feed solution was prepared in a separate container and pumped to the influent mixing tank through a Sigmamotor pump. Overflow from the influent head tank was returned to the mixing tank while overflow from the mixing tank was wasted. For runs requiring adjustment of the pH of the column influent, HCl or NaOH was added to maintain a constant pH using the pH analyzer described in the next section. For influent pH less than 9.5, the pH probe was immersed in the mixing tank. When a pH equal to or greater than 9.5 was used, the column influent was mixed in the flocculator described in the next section, then passed through a clarifier to allow precipitated solids to settle from the solution.

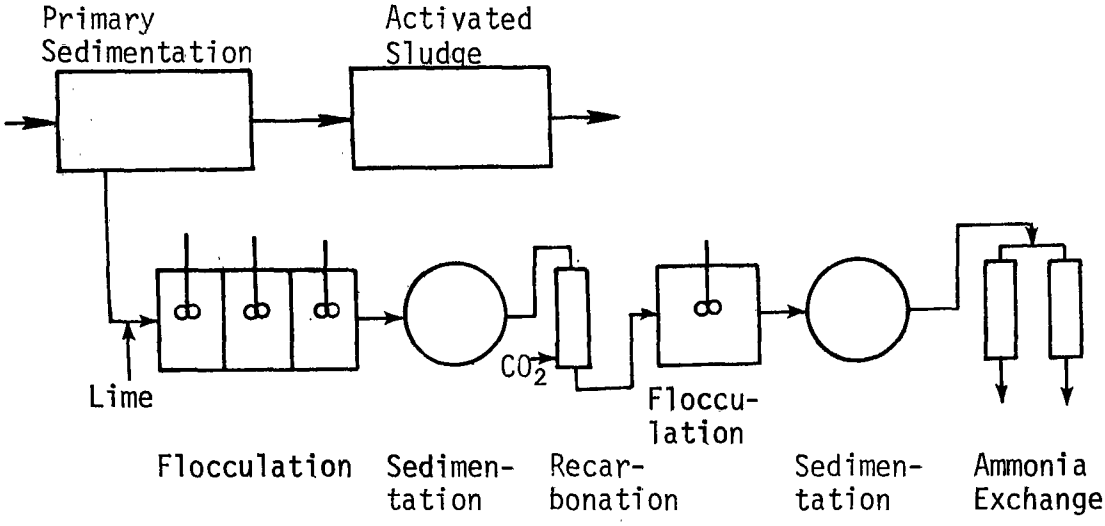
SERL Operations

Wastewater experiments were conducted using both chemical and chemical-biological process trains as shown in Figure 8. Wastewater from primary or secondary sedimentation basins of the SERL waste treatment plant was pumped to the chemical precipitation unit at a flow of 1 gpm by a variable-speed pump powered by a 1/3-hp Bodine DC motor and Minarik speed controller (Minarik Electric Co., Los Angeles, Calif.). Lime addition to pH 9.5 or 11.0 was controlled by a pH analyzer preset to the desired pH value. This control unit consisted of a Beckman model 900 C pH analyzer (Beckman Instruments, Inc., Fullerton, Calif.), a Foxboro model 62H controller (Foxboro Instruments, Foxboro, Mass.), and a Minarik model W-53AM speed controller coupled to a 1/8-hp Bodine DC motor (Minarik Electric Co., Los Angeles, Calif.). The motor drove a Sigmamotor model T-6 pump (Sigmamotor, Inc., Middleport, N. Y.) which pumped the lime slurry to the influent waste stream. The coagulated wastewater was flocculated in a 3-compartment reactor having an average detention time (defined as reactor volume divided by flow rate) of 15 min/compartment and settled in a 30-in. diameter conical-bottom clarifier at a loading of 300 gal/sq ft-day. Because of nitrification during activated sludge treatment, NH_4Cl was added to the secondary effluent when the treatment scheme in Figure 8b was being used to maintain an ammonia concentration of 15 mg/ℓ NH_3-N.

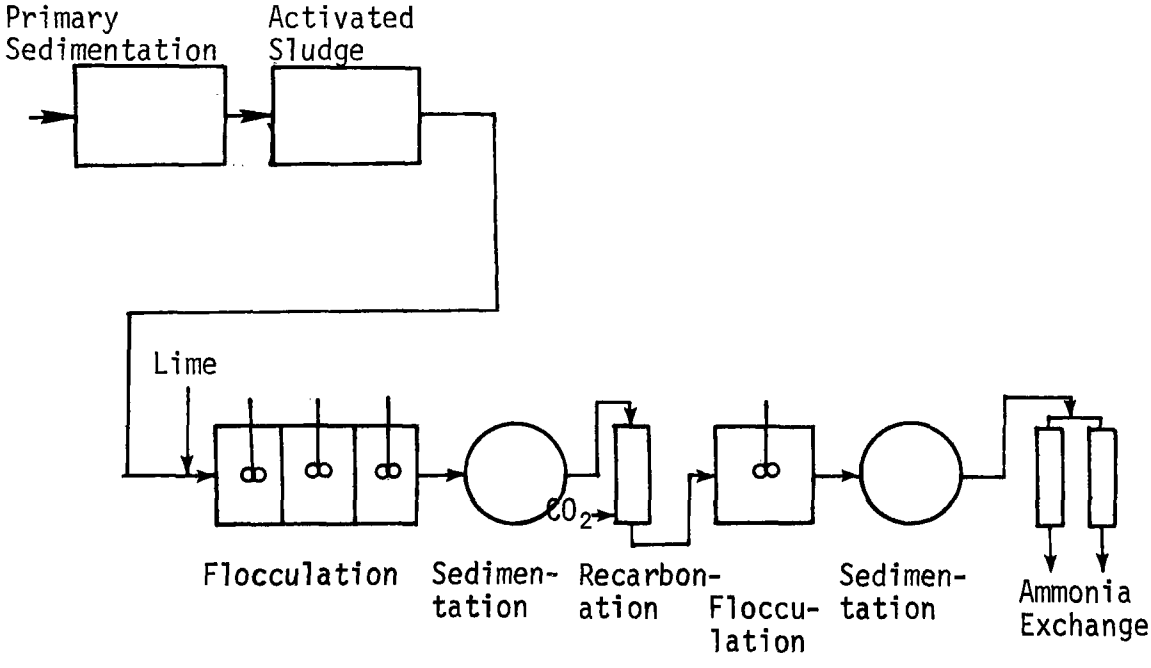
Recarbonation to a pH between 7 and 8 was accomplished in a 6-in. diameter, 4-ft deep plexiglass cylinder through which CO_2 passed countercurrent to the liquid. Following recarbonation the wastewater was stirred in a single reactor having a detention period of ten minutes, then settled in a clarifier identical to the one described above. From a 15-gal holding tank the waste was pumped to the column head tank.

EBMUD Operations

Studies at the East Bay Municipal Utility District were conducted using the chemical treatment system illustrated in Figure 9. Primary effluent was pumped to the treatment unit from a channel of the main treatment



a. Primary Sedimentation Followed by Chemical Coagulation



b. Activated Sludge Followed by Chemical Precipitation

FIGURE 8. TREATMENT SYSTEMS USED IN WASTEWATER STUDIES AT SERL

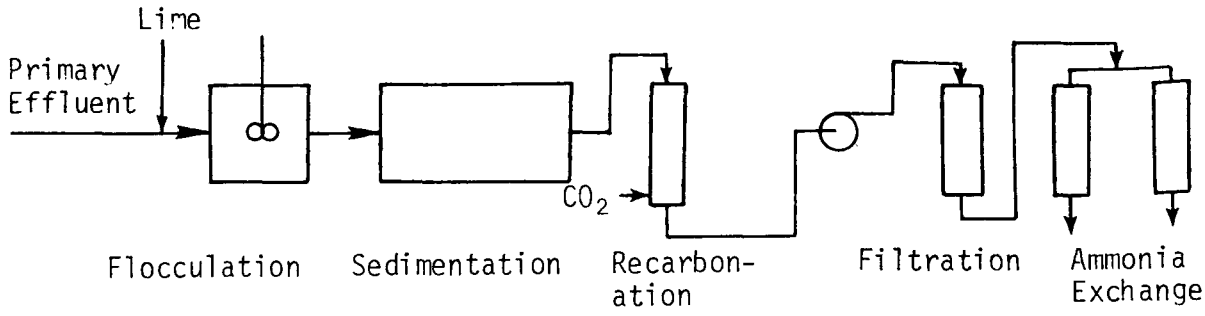


FIGURE 9. TREATMENT SYSTEM USED IN STUDIES AT EBMUD

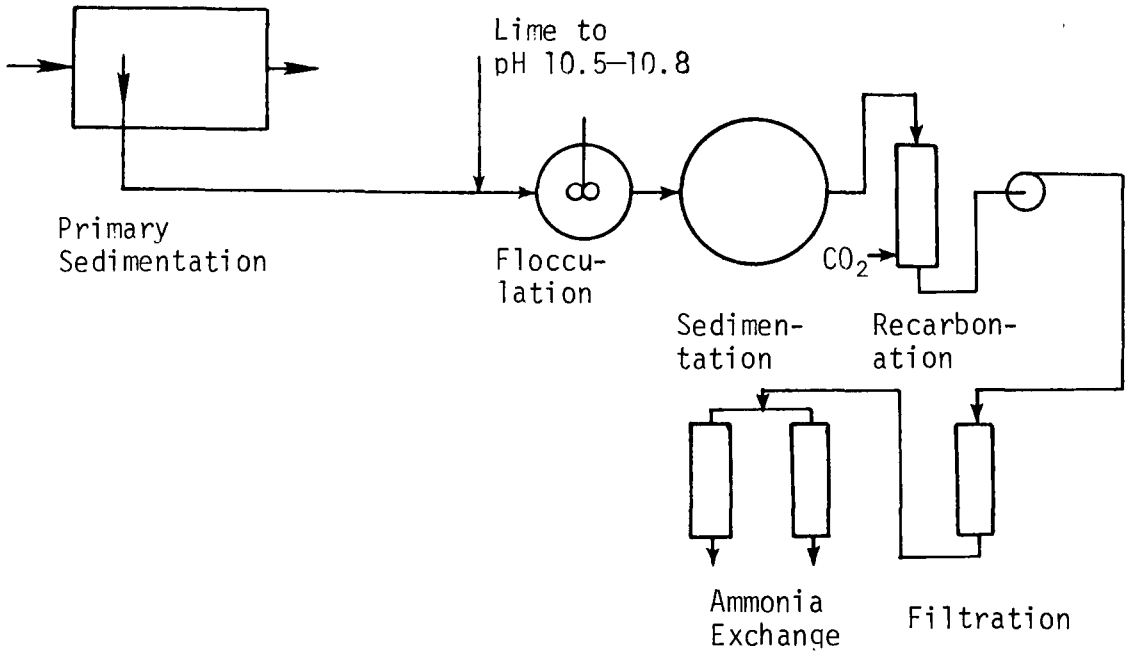


FIGURE 10. TREATMENT SYSTEM USED IN STUDIES AT CCCSD

plant at a flow of 20 gpm. Lime was added in a concentration determined periodically from jar tests. Monitoring of pH during part of the test period showed that the pH of the flocculated waste ranged from 9.5 to 12. The flocculated waste was settled in a rectangular clarifier having a detention time of 80 min and a surface loading of 800 gal/sq ft-day. The chemical effluent was recarbonated by bubbling CO_2 through a 5-in. diameter, 4-ft plexiglass cylinder immersed in the effluent trough of the sedimentation tank. Following recarbonation to a pH between 7 and 8 the waste was pumped to the column unit. During part of the testing period the precipitated effluent was treated by sorption of organics through 4.5 ft of activated carbon (Filtrasorb 300, Calgon Corp., Pittsburgh, Pa.) or 3.3 ft of a macroporous resin (Duolite ES-33, Diamond Shamrock Chemical Co., Redwood City, Calif.) prior to ammonia removal. This modification had no effect on clinoptilolite performance, but the runs made using this treatment scheme are identified in Appendix E, Table 3.

CCCSD Operations

The treatment system illustrated in Figure 10 was used in studies at the Central Contra Costa Sanitary District. Partially settled sewage was pumped to the treatment unit at a flow of 4 gpm from a point near the influent end of the primary clarifier. The influent sewage received approximately 15 min of settling prior to being pumped to the chemical treatment unit. Lime addition to a pH of 10.5–10.8 was controlled by a pH analyzer. The coagulated waste was flocculated in a single-compartment flocculator having a detention time of 25 min. The waste was settled in a clarifier having an overflow rate of 240 gal/sq ft-day and a detention time of 4 hr. The effluent was recarbonated directly in the effluent wet well as described in the previous section and pumped to the column unit.

VII. SATURATION PERFORMANCE OF CLINOPTILOLITE

A necessary precondition for the integration of ammonia exchange on clinoptilolite into advanced wastewater treatment systems is the existence of data defining the optimum exhaustion and regeneration cycle. The purpose of this chapter is to consider the effect of water composition on the effective ammonia exchange capacity, to describe the effect of pH on the performance of clinoptilolite, and to establish general guidelines for the use of clinoptilolite under various operating conditions. Because the characteristics of ion exchange processes are most readily observed in systems in which no concentration fluctuations occur, the work presented in this chapter consists of tests using synthetic systems composed of tap water supplemented with inorganic salts. The composition of these systems was representative of inorganic ions found in domestic wastewaters. In examining column performance, the fundamentals of ion exchange theory and the properties of zeolites discussed in Chapter IV must be used to interpret data in a way which will be meaningful to the more general application of this process. In these respects this work is of a more fundamental nature than other sections of this report. However, the primary objective of this work was to provide answers to specific questions regarding the application of clinoptilolite in real systems. The engineering implications of the work are specifically discussed in a concluding section.

ION EXCHANGE CAPACITY

The ion exchange capacity of clinoptilolite was measured using a small-column method. Fresh clinoptilolite was prepared by washing several times in an erlenmeyer flask to remove fines, equilibrating with 1 M NaCl for two days, and washing with distilled water until the water showed no chlorides when tested with $AgNO_3$. Subsequently, the material was air dried, then dried overnight in a 105°C oven. Clinoptilolite samples weighing 10 or 20 g were placed in 50-mℓ burettes and saturated with 1 M NH_4Cl at a flow of approximately 50 mℓ/hr for two days. Excess ammonia was washed from the column by rinsing with distilled water for two days.

Three methods were used to determine the ammonia exchanged into the zeolite:

1. Direct distillation of ammonia by placing the NH_4-form clinoptilolite in a kjeldahl flask.

2. Elution of ammonia from the clinoptilolite by passing 0.5 M NaCl through the column at 50 mℓ/hr for two days and determining the ammonia content of the eluant.

3. Elution of ammonia using 0.25 M $CaCl_2$ at a flow of 50 mℓ/hr for two days and determining the ammonia content of the eluant.

Ammonia was most easily distilled from zeolite particles passing a 100 mesh sieve. Thus, all samples were crushed and sieved prior to ammonia analyses. Ammonia from -100 mesh particles could be removed in a distillation volume of about 200 mℓ. The contents of each column were thoroughly mixed before taking a sample for crushing.

Experimentally determined exchange capacities are shown in Table 5. These values lie in the same range as values reported by other investigators (cf. Table 1). The exchange capacity of 1.95 meq/g determined from the direct disillation method is identical, within the limits of experimental error, to the value of 1.97 meq/g determined by Howery and Thomas [58]. The value of 1.88 meq/g determined by elution of ammonia with NaCl is very close to the value of 1.85 meq/g reported by Barrer [50] who used the same method.

TABLE 5

CLINOPTILOLITE EXCHANGE CAPACITY

Method Used for Ammonia Recovery	Exchange Capacity[a] meq/g
Distillation of clinoptilolite particles	1.95 (1.93–1.98)
Elution using NaCl	1.88 (1.86–1.91)
Elution using $CaCl_2$	1.77 (1.75–1.79)

[a]Range of experimental values indicated in parenthesis.

The results show that the exchange capacity is affected by the method used to recover ammonia from the zeolite. Values measured by the direct distillation method and by elution with NaCl are nearly identical. A small loss of ammonia from the NaCl eluant could account for the lower value obtained by NaCl elution. It is also possible that a small amount of ammonia remained in the zeolite and could have been eluted had more NaCl been run through the column. Both of these values correspond closely to the exchange capacity of 1.87 meq/g calculated by Barrer [50] from the composition of clinoptilolite. It is reasonable to assume that ammonium and sodium ions have access to practically all exchange sites within the clinoptilolite framework. Elution with calcium resulted in a smaller exchange capacity than did elution with sodium. From these results it is not possible to determine whether the lower capacity was due to a slower rate of exchange of calcium for ammonium ions or to the inaccessibility of calcium to some of the exchange sites.

EFFECT OF WATER COMPOSITION ON AMMONIA EXCHANGE CAPACITY

The objectives of these exhaustion studies were 1) to examine the characteristics of breakthrough curves for clinoptilolite columns exhausted with waters containing different concentrations of competing cations, 2) to determine the equilibrium characteristics of the various ions in the zeolite, and 3) to determine the effect of water composition on the ammonia capacity of clinoptilolite.

In order to compute the total ammonia capacity of the zeolite and to determine the selectivity coefficients, runs were continued until the ammonia concentration in the column effluent equaled the concentration in the influent. The studies were conducted using 3 ft of clinoptilolite exhausted at a rate of approximately 15 BV/hr. The actual flow rates and weights of material used for each test are indicated on the concentration history curves. The compositions of the column influents for these tests are shown in Table 6. Columns for all runs, except run 1, were prepared by complete regeneration with 30 BV of regenerant containing 0.35 M NaCl (0.17 lb NaCl/gal) and a pH of 12.5 adjusted using NaOH. Clinoptilolite for run 1 was regenerated with 40 BV of 0.35 M NaCl (0.17 lb NaCl/gal) adjusted with NaOH to a pH of 12. Columns were exhausted using water having cation compositions typical of domestic wastewater.

TABLE 6

INFLUENT CHEMICAL COMPOSITION FOR SATURATION RUNS

Run	Constituent					
	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ	pH
1	18.8	13.3	1.0	26	5	7.9
2	19.0	62.1	11.7	63	8	7.9
3	19.0	60.5	12.5	66	16	7.9
4	19.4	55.0	14.0	67	3	6.0
5	19.0	84.1	14.8	138	53	8.0
6	16.4	175	35.4	140	48	7.9

Equilibrium Characteristics

Selectivity coefficients were determined from concentration histories measured for each ion during these runs using Equations 3 and 4. Solid phase concentrations were determined by graphical integration of the area between the breakthrough curve and the influent ion concentration.

The concentration history for run 1 is shown in Figure 11 as an example of the results of these tests. Results of runs 2 through 6 are shown in Appendix B. Calcium and magnesium data appear somewhat scattered in these figures. In most instances magnesium concentrations are lower and calcium values are higher than expected. This was probably due to measurement of some magnesium as calcium because of a buffered pH in the calcium determination too low to precipitate all magnesium in the sample solution. In these cases the actual data points are plotted in the figures, but smooth curves have been drawn to match the results expected from adjustment of these points. Adjustments to curves were made only where an increase in the magnesium and an equivalent reduction of calcium, or vice versa, resulted in more regular curves.

Examples of selectivity coefficients are shown in Table 7. Values for these runs illustrate differences in selectivities for a water typical

TABLE 7

EQUILIBRIUM VALUES FOR SATURATION RUNS

Item	Run 2		Run 6	
	Experimental Values	Values from Binary System Ames [12]	Experimental Values	Values from Binary System Ames [12]
$K_{Na}^{NH_4\text{-}N}$	1.12	7.4	1.44	11.6
$K_{K}^{NH_4\text{-}N}$	0.60	0.39	0.45	0.41
$K_{Ca}^{NH_4\text{-}N}$, ℓ/g	1.32	1.24	1.12	1.80
$K_{Mg}^{NH_4\text{-}N}$, ℓ/g	1.84	2.07	a	6.85

[a]Value of q_{Mg} too small to be determined from experimental data.

of an "average" sewage (run 2) and for a highly mineralized water characteristic of a sewage having a high hardness and subject to infiltration of saline water (run 6). Because the zeolite was initially in the Na form, it was not possible to directly measure q_{Na} or the total exchange capacity, Q. Solid phase sodium concentrations were obtained by subtracting the sum of other solid phase concentrations from the total exchange capacity, 1.9 meq/g. This method has the disadvantage of accumulating errors in other solid phase concentrations into the value of q_{Na}. Failure to reach equilibrium or the inability of ions to be exchanged into all sites measured in laboratory exchange capacity measurements are reflected in artificially high values of q_{Na}.

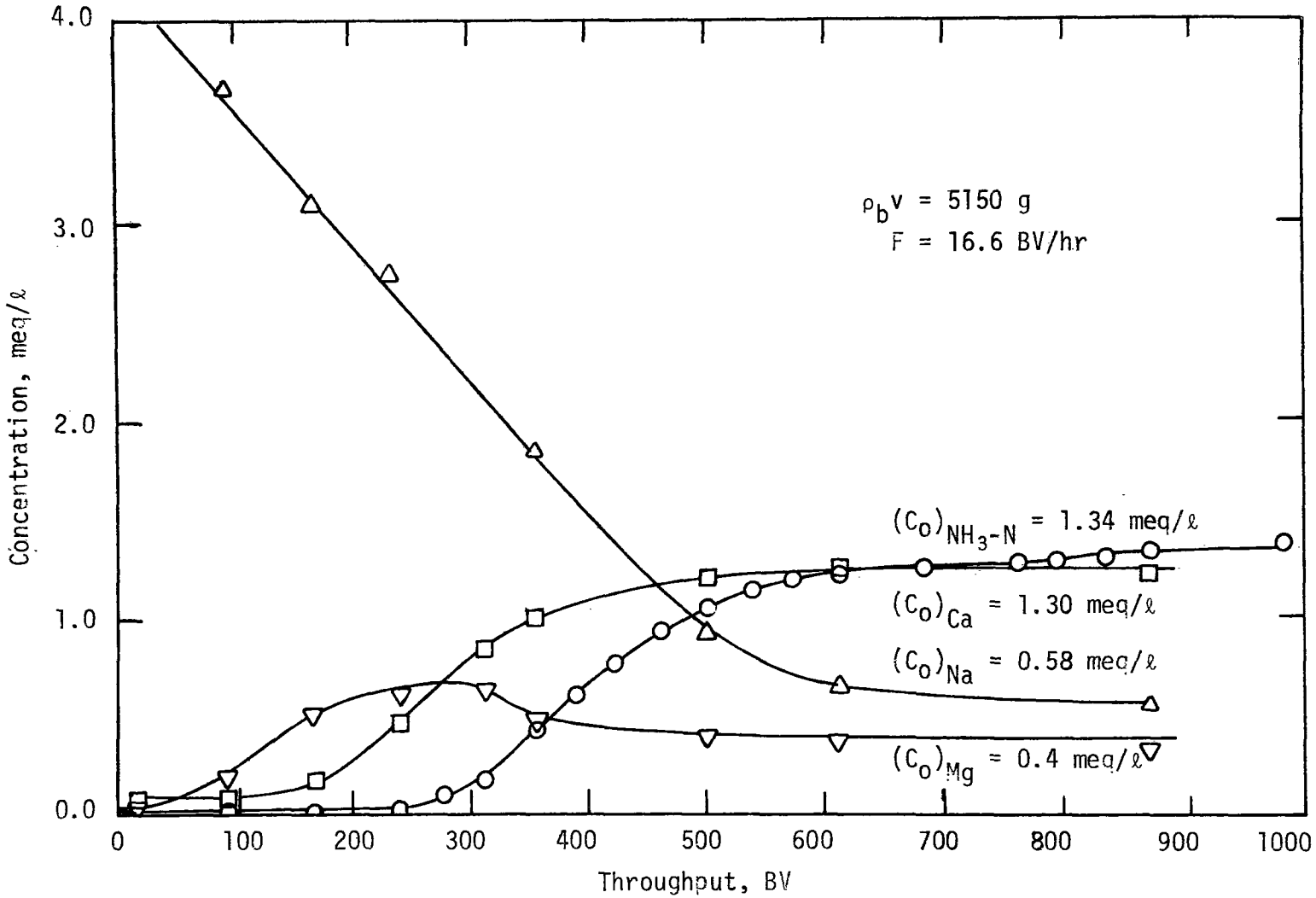


FIGURE 11. EXHAUSTION OF CLINOPTILOLITE IN Na FORM

Selectivity coefficients determined by Ames [12] in batch binary systems are also shown in Table 7 and may be compared to values obtained from multicomponent systems in this study. In both runs the values of $K_{Na}^{NH_4\text{-}N}$ measured from column data were less than corresponding values obtained by Ames in batch systems. Values for the other selectivity coefficients calculated from column data varied somewhat from values determined by Ames. Three explanations of these differences may be offered: 1) that equilibrium was not achieved throughout the column during the length of the test, 2) that the column was not completely regenerated prior to the beginning of the run, or 3) that binary equilibrium data do not adequately describe multicomponent relationships. The first postulate seems unlikely unless equilibrium is approached very slowly near the upper end of the breakthrough curve. Data obtained in these tests indicated that equilibrium was attained in each case. However, it is possible that diffusion in the particle phase becomes extremely slow as equilibrium is approached (cf. Equations 7 and 8). While care was taken to completely regenerate columns to the Na form prior to each run, it is possible that some ions located near the center of zeolite particles were incompletely eluted.

Effective Ammonia Exchange Capacity

The correlation of the ammonia exchange capacity of clinoptilolite to the characteristics of the waste to be treated will aid in determining the applicability of zeolitic ion exchange for ammonia removal. Conditions for which the breakthrough ammonia exchange capacity is very small will result in short run times and higher capital and operating expenses.

Ammonia exchange capacities both to 1 mg/ℓ NH_3-N breakthrough and to complete column saturation for the runs shown in Figure 11 and in Appendix B were calculated by integrating the area above the breakthrough curves. The results, illustrated in Figure 12, show the variation of ammonia exchange capacity with the cationic strength of the column influent. While this relationship is definitely empirical and represents a simplification of the complex effect of competing cation concentration on ammonia exchange capacity, it does illustrate the effect of increased mineral strength on the exchange capacity of a relatively fixed ammonia concentration. The reader is referred to Chapter V for a discussion of the rationale of this approach. The influent ammonia concentration for these tests varied between 16.4 and 19.0 mg/ℓ NH_3-N and was representative of concentrations found in domestic wastewater. The influent compositions of runs 2, 3, and 4 were most indicative of a chemically treated domestic sewage. Exchange capacities in this range of cationic strength illustrate the sensitivity of $q_{NH_4\text{-}N}$ to changes in water composition. The cationic strength for run 6 was higher than that usually encountered in domestic wastewaters. However, values of $q_{NH_4\text{-}N}$ for runs 5 and 6 indicated that $q_{NH_4\text{-}N}$ decreases slowly at a cationic strength greater than about 0.01. While these relationships will not be valid for any conceivable combination of cations, they do provide an estimate of ammonia exchange capacities which can be expected when clinoptilolite is used with many domestic wastewaters.

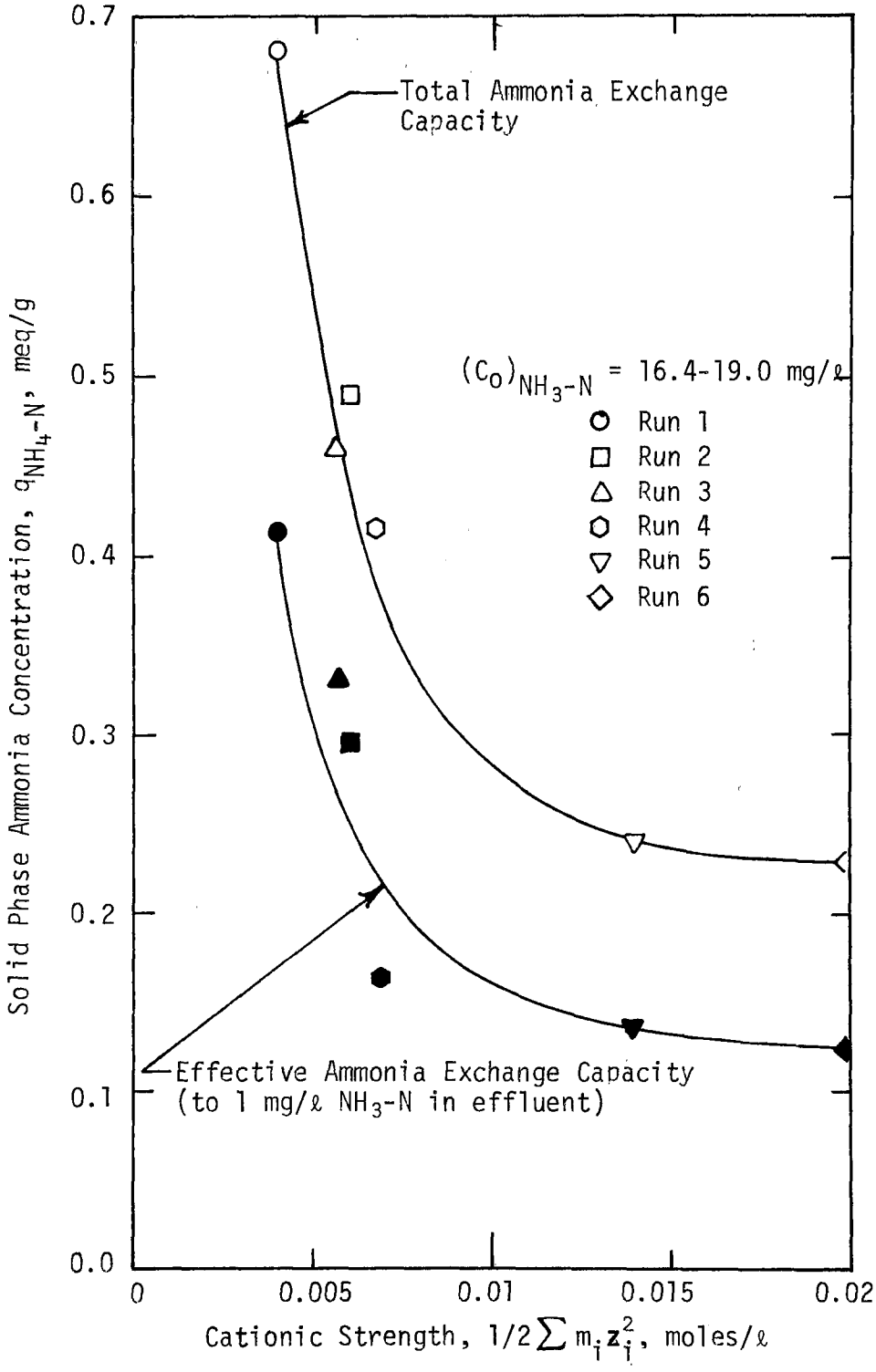


FIGURE 12. VARIATION OF AMMONIA EXCHANGE CAPACITY WITH COMPETING CATION CONCENTRATION

Breakthrough ammonia capacities calculated to 1 mg/ℓ NH_3-N leakage, also shown in Figure 12, bear a similar relationship to cationic strength. (Capacities were calculated to a breakthrough of 1 mg/ℓ NH_3-N because water quality requirements for ammonia removal are likely to stipulate a product water containing no more than 1 mg/ℓ NH_3-N.) Ammonia breakthrough capacities averaged about 60% of the total ammonia capacity in these runs.

COMPARISON OF PERFORMANCE OF Na- AND Ca-CLINOPTILOLITE

To determine the effect of the counter ion initially in the zeolite on exhaustion performance, clinoptilolite columns in Na and Ca forms were exhausted using tap water containing 20 mg/ℓ NH_3-N and the chemical composition shown in Table 8. Clinoptilolite used for these tests had previously been exhausted to saturation using waters having similar cation concentrations such that the solid phase concentration of ions contained in each sample of clinoptilolite was approximately the same. In this way it was possible to make a comparison between the effectiveness of sodium and calcium as regenerants. Clinoptilolite was placed

TABLE 8

INFLUENT CHEMICAL COMPOSITION FOR EXHAUSTION OF Na- AND Ca-CLINOPTILOLITE

Ion	Concentration	
	Na Form	Ca Form
NH_3-N, mg/ℓ	18.8	18.5
Na, mg/ℓ	13.3	9.2
K, mg/ℓ	0.9	0.8
Ca, mg/ℓ	26	27
Mg, mg/ℓ	5	4
pH	7.9	8.1

in the Na form by regeneration using 40 BV of a solution composed of 0.35 M NaCl (0.17 lb NaCl/gal) with the pH raised to 12 using NaOH. This corresponded to the use of 45 lb NaCl/cu ft and was sufficient to reduce the effluent ammonia concentration in the regenerant to less than 3 mg/ℓ NH_3-N. Detailed regeneration studies described in Chapter VIII indicate that a comparable degree of regeneration could be achieved using a somewhat smaller amount of regenerant if regenerant optimization is of major concern. Clinoptilolite in the Ca form was prepared by

regeneration with 0.17 M $CaCl_2$ (0.16 lb $CaCl_2$/gal) in a saturated lime solution having a pH of 12.2. However, the conversion of clinoptilolite to the Ca form proved difficult. Only about 60% of the ammonia in the zeolite was removed in 30 BV of regenerant. An additional 20 BV was needed to complete regeneration of the column, bringing the total amount of $CaCl_2$ required to 147 lb/cu ft.

Concentration histories for these two runs are shown in Figures 11 and 13. Effluent concentrations of sodium, potassium, and magnesium in Figure 13 indicate that these ions were not eluted from the column by calcium regenerant. On the contrary, sodium and, to some extent, potassium were displaced from the column by ammonia during exhaustion. This occurred because these ions occupied larger fractions of the zeolite exchange sites during a previous run and, therefore, were present in greater than equilibrium quantities at the beginning of this particular run. Effluent concentrations of calcium and magnesium for Na-clinoptilolite in Figure 11 show a definite breakthrough indicating that these ions were removed from the zeolite by the sodium regenerant. While the elution of these ions does not directly affect the ammonia capacity of the zeolite during exhaustion, this does illustrate the restricted mobility of calcium in the zeolite. These results also indicate the importance of pH in the elution of ammonia from clinoptilolite. Because ammonia was the only ion significantly removed from the zeolite by the calcium regenerant, this implies that the conversion of the ammonium ion to unionized ammonia by the high pH regenerant leads to more rapid elution of ammonia from the zeolite pores.

The relatively greater difficulty of regenerating clinoptilolite with calcium than sodium ions can be explained from the clinoptilolite selectivity series. Because the zeolite is more selective for sodium than calcium, it can be argued that regeneration should be more easily accomplished using sodium salts. However, it follows that during exhaustion the kinetics of NH_4-Na exchange would be less favorable than for NH_4-Ca exchange. Slopes of the normalized ammonia breakthrough curves for these two cases shown in Figure 14 reveal that the kinetics of NH_4-Na exchange was superior to NH_4-Ca exchange. This demonstrates the influence of particle phase diffusion on exchange kinetics. Although clinoptilolite selectivity results in the preference Na > Ca, steric factors which affect both selectivity and diffusion of ions through the zeolite restrict the mobility of calcium ions more than sodium ions. This results in superior exchange kinetics for sodium relative to calcium regardless of whether these ions are entering the zeolite or are being displaced from it.

These observations are explainable in terms of the size of the hydrated cations (cf. Table 3). Due to its large size (19.2 A diameter), calcium ions cannot approach exchange sites as closely as other ions and, therefore, are less preferred by the zeolite. However, once in the zeolite, the mobility of the ions into the fluid is restricted because of their affinity for the structural water contained in the zeolite

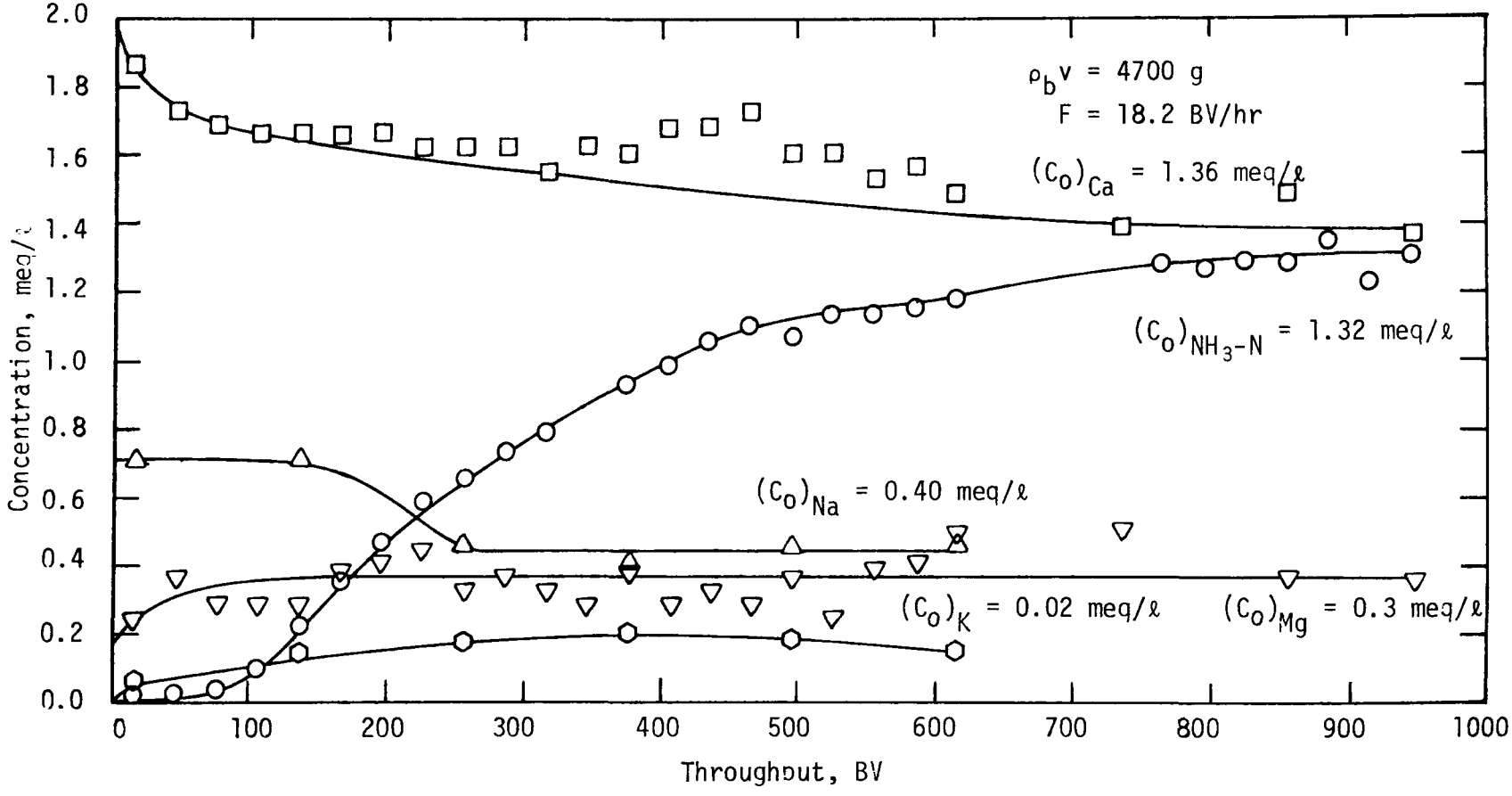


FIGURE 13. EXHAUSTION OF CLINOPTILOLITE IN Ca FORM

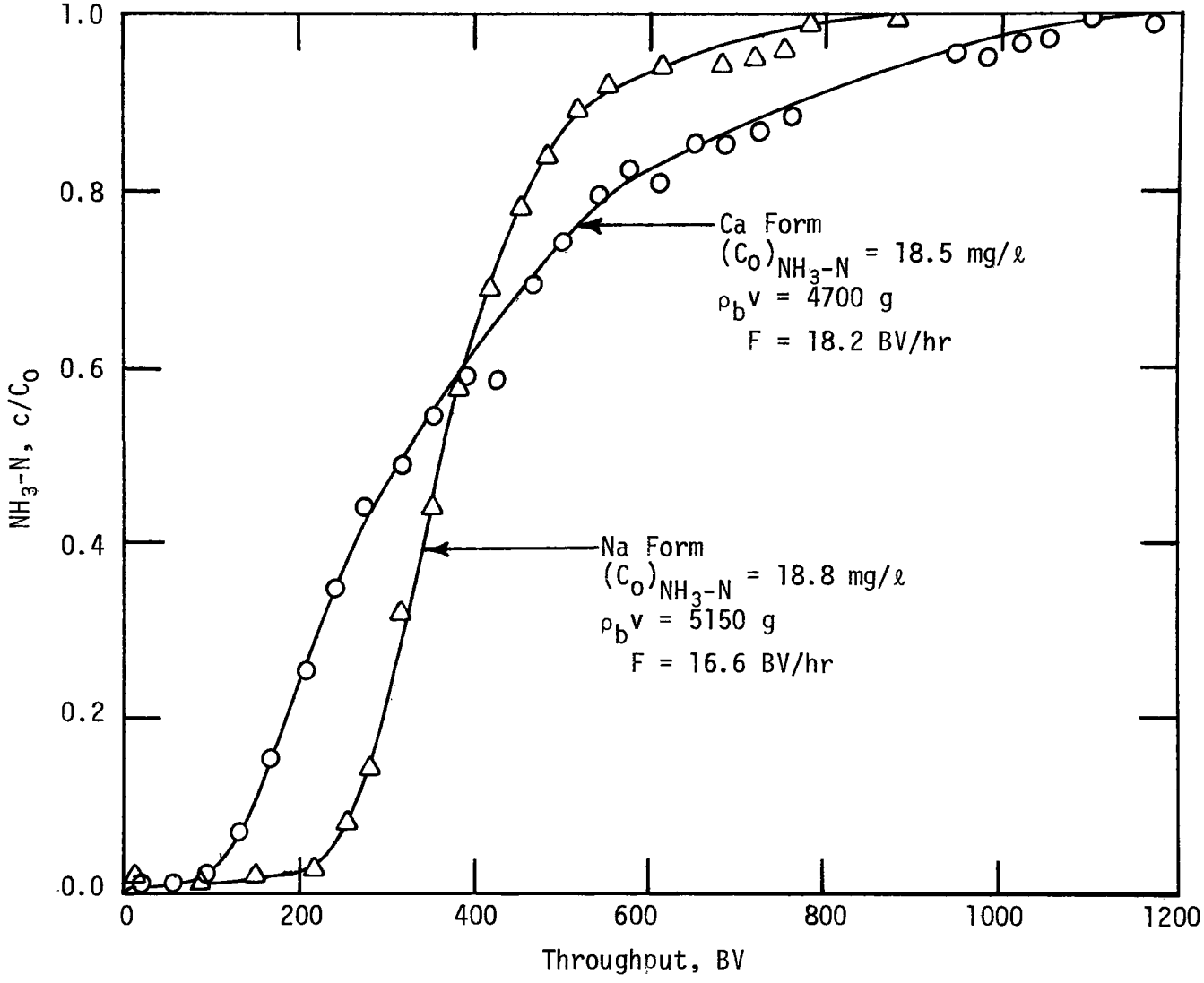


FIGURE 14. AMMONIA CONCENTRATION HISTORIES FOR Ca- AND Na-CLINOPTILOLITE

framework. On the other hand, the sodium ion, having a hydrated diameter of only 15.8 A, is freer to migrate through the zeolite channels and to approach more closely the exchange sites.

The total exchange capacity of the Na-clinoptilolite calculated by integration of the area above the breakthrough curve was 0.68 meq/g, and that of the Ca-clinoptilolite was 0.69 meq/g. However, the capacity to 1 mg/ℓ NH_3-N breakthrough was reached in 220 BV for the Na form, but in only 100 BV for the Ca form. Thus, while the total exchange capacities for the two counter ions were approximately the same, superior column kinetics for Na-NH_4 exchange resulted in a breakthrough capacity for Na-clinoptilolite which was more than twice as great as that for the Ca form.

Breakthrough Curve Characteristics

Several observations concerning the kinetic performance of clinoptilolite columns may be made from the concentration histories presented in this section and in other parts of the chapter. From Figure 11, and Figures 1 through 5 in Appendix B, the selectivity series of clinoptilolite may be determined by the order in which the ions appear in the effluent. As sodium was the ion initially in the zeolite, the sodium curves must be looked upon as "reverse" breakthrough curves. The order in which ions appear in the effluent identifies the order of selectivity as $K > NH_4 > Na > Ca > Mg$ which agrees with the results of Ames.

Although breakthrough curves for ammonia on Na-clinoptilolite are shown in Figure 11 and in Appendix B, the shape of the curve is best illustrated in Figure 14. All curves demonstrate a relatively sharp breakthrough at the lower end of the curve followed by a decrease in slope as the breakthrough progresses. The upper end of the curves tapers off and approaches equilibrium relatively slowly. This type of curve is characteristic of exchangers in which either solid or pore diffusion limits the rate of exchange. While the sharp breakthrough in the lower portion of the curve tends to increase the breakthrough capacity of the zeolite, the shallowness of the rest of the curve shows that a significant portion of the zeolite remains unsaturated when the breakthrough occurs.

EFFECT OF pH ON AMMONIA EXCHANGE

As discussed in Chapter V, the uptake of ammonium ions in clinoptilolite will be significantly affected by pH. An optimum range for ammonium exchange will exist which will be determined by competition of exchange sites for ammonium and hydrogen ions at low pH and by NH_3-NH_4^+ equilibria at high pH. Be determining the optimum pH range it will be possible in column operation to adjust the influent pH to achieve the maximum removal

of ammonia. In Chapter V a model of this exchange reaction was developed which is verified with experimental data in this section. Preliminary batch tests were made in a ternary NH_4-Na-H system using ion concentrations similar to those found in domestic wastewaters. Subsequent column tests were made using an influent solution containing all cations present as macrocomponents in domestic wastewaters.

Batch Tests

Preliminary batch tests were performed to determine the influence of pH on the uptake of ammonia from a sample NH_4-Na-H solution not unlike that encountered in wastewaters. Equilibration solutions consisted of 20 mg/ℓ NH_4-N and 60 mg/ℓ Na in the form of chloride salts which were adjusted to pH values ranging from 2 to 12 using HCl and NaOH. One hundred milliliters of this solution were contacted with 0.5 g of clinoptilolite for 2 hr. Clinoptilolite was prepared by contact with 1 M NaCl, washing to remove excess sodium, and drying at 105°C as described above in the determination of clinoptilolite ion exchange capacity. Control samples containing no clinoptilolite were run to determine the amount of ammonia lost to the atmosphere. Samples were shaken in 125-mℓ erlenmeyer flasks using a Burrell Wrist-Action Shaker (Burrell Corp., Pittsburgh, Pa.). Flasks were capped with rubber stoppers to limit escape of ammonia to the atmosphere. For these tests ammonia was determined by direct nesslerization [80] since no interferences were present.

Results of the 2-hr equilibration are shown in Figure 15. The optimum pH range for ammonia exchange was between 6 and 8. At pH values above 8 the solid phase ammonia concentration decreased rapidly to a pH of 10.7 where no detectable ammonia exchange took place in the 2-hr period. The data taken at final pH values below 6.0 were influenced by acid soluble impurities in the clinoptilolite which acted as a buffer, increasing the final pH of the solution and distorting the observed effect of pH on ammonia exchange below pH 6.

Sodium added to adjust the pH to higher levels depressed the solid phase ammonia concentration, $q_{NH_4\text{-}N}$, resulting in less exchange than would be expected by hydroxyl ion effects alone. However, the amount of sodium added in raising the pH to 10 was only about 2 mg/ℓ, while the amount added in raising the pH to 11 was about 20 mg/ℓ. Thus significant sodium interference would not be expected below a pH of about 11. This may have affected samples having final pH values of 10.7 and 11.8 in Figure 15, but little ammonia exchange would be expected at this pH on the basis of ammonia equilibria. The effect of pH on the ammonia capacity may also be expressed as the ammonia capacity at a given pH relative to the capacity at a pH unaffected by NH_4-H exchange or by the presence of unionized ammonia. Ammonia exchange is least affected by these factors between pH 6 and 8. For the batch results in Figure 15 the ammonia capacity unaffected by pH is about 0.25 meq/g. Data normalized with respect to this value appear in Figure 16. Also shown in Figure 16

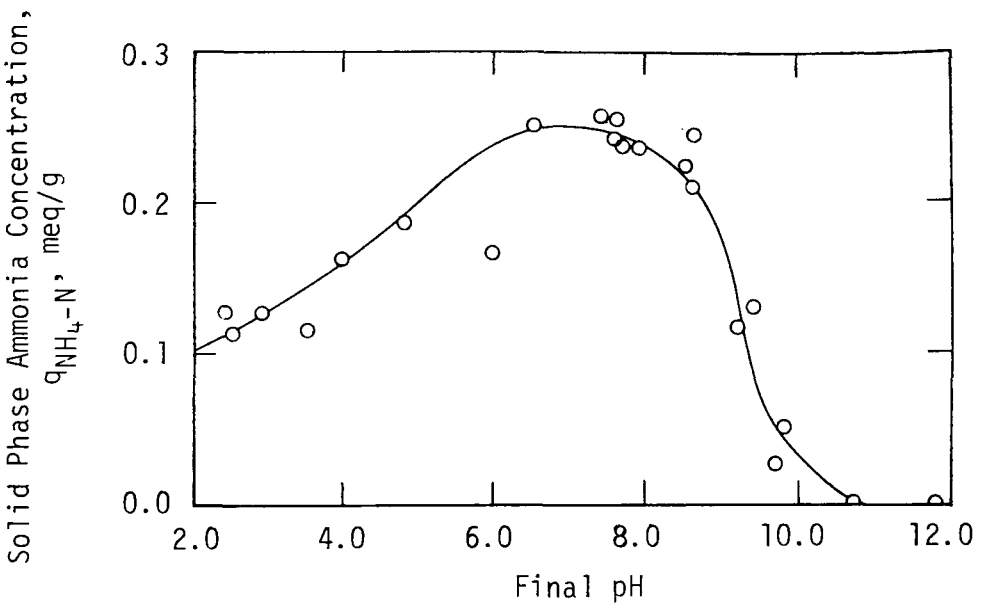


FIGURE 15. BATCH RESULTS – EFFECT OF pH ON AMMONIA EXCHANGE

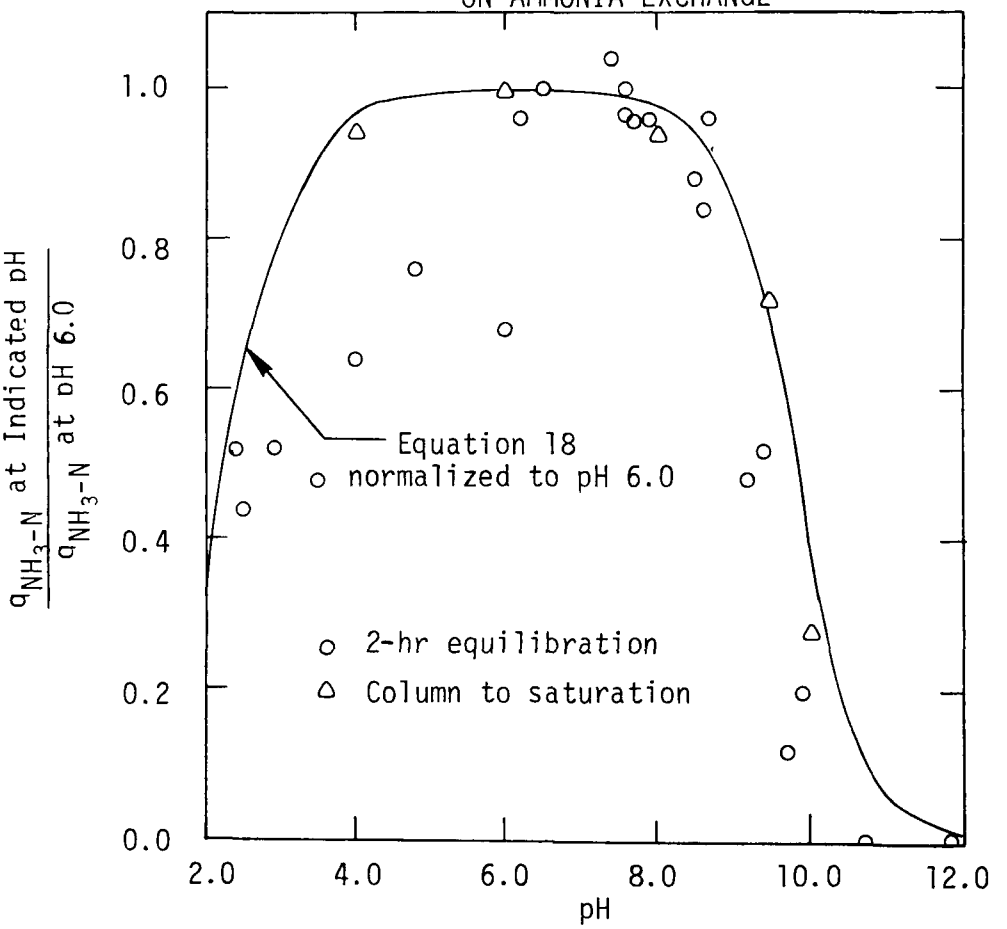


FIGURE 16. RELATIVE EFFECT OF pH ON AMMONIA EXCHANGE CAPACITY

is the curve predicted from Equation 18 normalized with respect to the value predicted by Equation 18 at pH 6. Values for this line were obtained using Q = 1.9 meq/g as determined in the section dealing with the ion exchange capacity of clinoptilolite. While these data do not permit a complete and rigorous description of the batch system, they do demonstrate the validity of the NH_3-NH_4^+-Na^+-H^+ interrelationships described in Equation 18.

Column Tests

Column tests were run to confirm the results obtained in batch studies. Runs were made using 3-ft bed depths and exhaustion rates of approximately 18 BV/hr. Prior to each run, columns were regenerated to the Na form using 30 BV regenerant containing 0.35 M NaCl (0.17 lb NaCl/gal) and sufficient NaOH to raise the pH to 12.5. Column influents were adjusted to pH 4.0, 6.0, 8.0, 9.5, and 10.0 and exhaustion was continued until the concentration of ions in the effluent equaled those of the influent. Ammonia breakthrough curves for these runs are compared in Figure 17. Ammonia data and effluent pH values are shown in Appendix C.

Influent chemical compositions shown in Table 9, were chosen to be reasonably representative of a domestic sewage chemically treated with lime. Since runs were continued until columns were in equilibrium with the feed, these values are also the equilibrium concentrations. The

TABLE 9

CHEMICAL COMPOSITION FOR COLUMN pH RUNS

pH	Concentration, mg/ℓ				
	NH_3-N	Na	K	Ca	Mg
4.0	21.2	65.5	14.6	82	3
6.0	19.5	55.0	14.0	67	3
8.0	18.4	45.3	12.4	62	2
9.5	18.5	68.0	12.7	59	3
10.0	18.4	97.5	12.6	38	4

effluent pH, shown in the figures in Appendix C, varied somewhat from the influent values during some runs, although the equilibrium pH was that shown in Table 9. High effluent pH at the beginning of the pH 4 run was probably a result of acid soluble impurities in the clinoptilolite and lime particles not removed after the previous regeneration. The pH for the pH 10 run was adjusted initially to pH 10.5; however, the influent pH measured in the head tank and the effluent pH averaged 10.0 This decrease was probably due to precipitation of $CaCO_3$ following pH

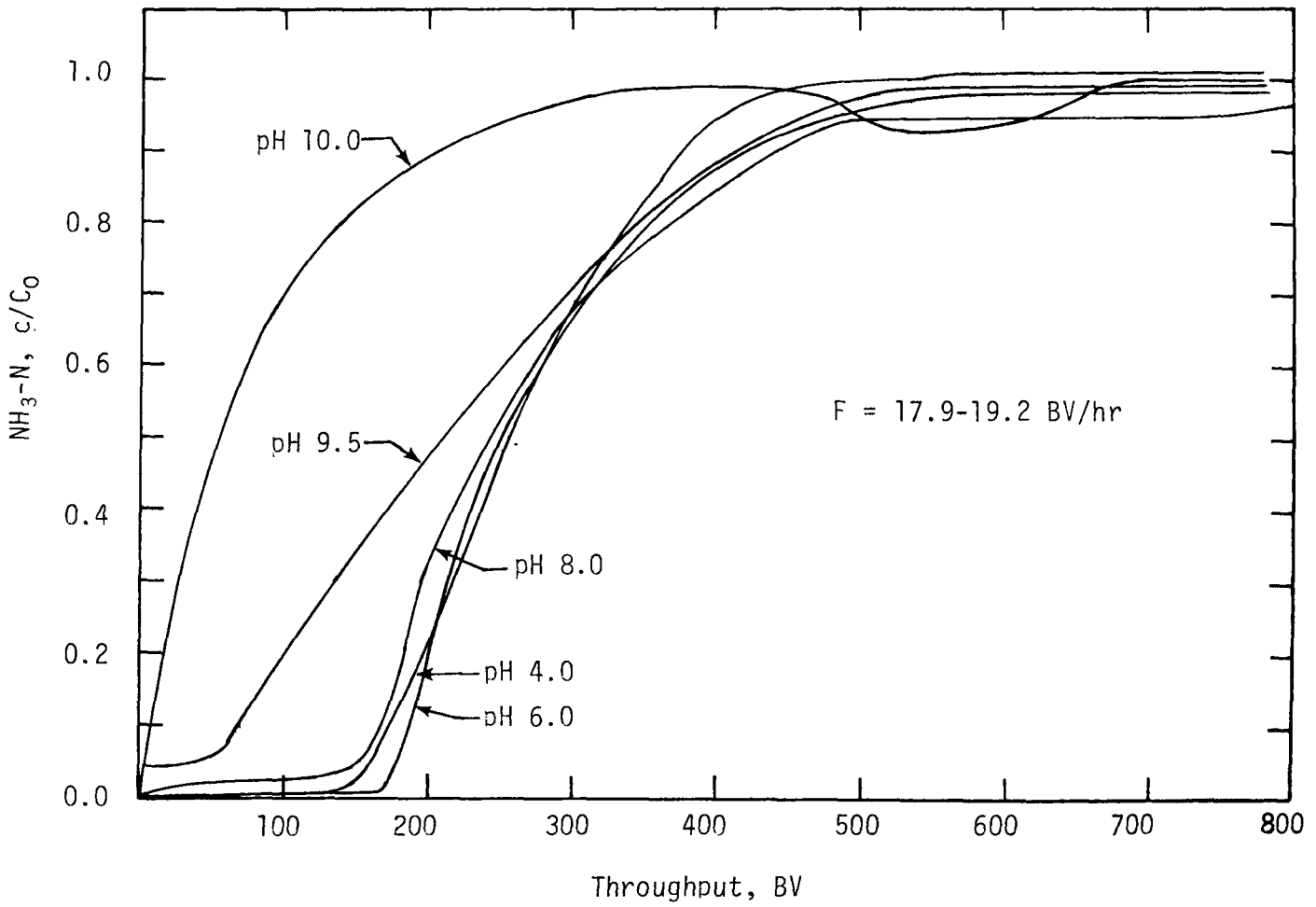


FIGURE 17. EFFECT OF pH ON AMMONIA BREAKTHROUGH

adjustment and was reflected in the lower influent calcium concentration for this run. Periodic determination of calcium in filtered and unfiltered samples showed that a minimum of 98% of the calcium was soluble.

The greatest ammonia capacity was observed at pH 6. Slightly lower capacities at pH 4 and 8 reflect increased competition from hydrogen ions for exchange sites at pH 4 and a shift in the NH_3-NH_4 equilibria at pH 8. Column ammonia capacities for these runs determined from the ammonia breakthrough curves are shown in Table 10. Capacities were calculated both for full column saturation and to 1 mg/ℓ NH_3-N breakthrough. Values for complete saturation, normalized to the capacity at

TABLE 10

COLUMN AMMONIA CAPACITY FOR pH RUNS

Influent pH	$q_{NH_4\text{-}N}$ to Saturation meq/g	$q_{NH_4\text{-}N}$ to 1 mg/ℓ NH_3-N Breakthrough meq/g
4.0	0.48	0.27
6.0	0.51	0.33
8.0	0.48	0.24
9.5	0.37	0.06
10.0	0.14	0.01

pH 6 (0.51 meq/g), are shown in Figure 16. These values closely follow the capacities predicted by Equation 18. While the ternary system described in Equation 18 is less complex than the 6-component system used for column runs, the effect of pH in the two systems was essentially the same. Sodium, potassium, calcium, and magnesium ions in the column system performed the same function as the Na present in the batch system — namely, to replace ammonium ions in the zeolite as the NH_4/total cation ratio decreased at high pH. At low pH, increases in the hydrogen ion concentration acted to decrease the fraction of each ion which would be exchanged into the zeolite at a more neutral pH. As an indication of relative changes in the ammonia exchange capacity, Equation 18 provides a valid description of the more complex multicomponent system.

Several observations may be made concerning the data in Figure 16 and Table 10. Optimum conditions for exhaustion occur between pH 4 and pH 8. Column operation outside this range resulted in a rapid decrease of ammonia exchange capacity and increased ammonia leakage prior to the onset of breakthrough. On the other hand, the ineffectiveness of ammonia exchange at high pH can be utilized advantageously during regeneration.

Equation 18 predicts equilibrium ammonia capacities of 0.53 meq/g at pH 10, 0.08 meq/g at pH 11, and 0.008 meq/g at pH 12 for a solution concentration of 20 mg/ℓ NH_3-N. While regeneration is not an equilibrium process, regenerants having sufficient buffer capacity to keep the pH above 11 throughout the column would result in an increased rate of ammonia desorption.

SUMMARY

The exhaustion performance of clinoptilolite has been examined using chemically defined systems containing cation concentrations typical of domestic sewages. Column tests were continued until the zeolite was in equilibrium with the influent water. It was demonstrated that the ammonia exchange capacity of clinoptilolite can be estimated in terms of the cationic strength of the column influent. From data presented in Figure 12, it is possible to estimate the ammonia exchange capacity of clinoptilolite for a particular wastewater having a composition which is not substantially different from those shown in Table 6. This method provides a practical means of estimating exchange capacities for design purposes.

Exhaustion of clinoptilolite in Na and Ca forms revealed that, while the total ammonia exchange capacity was identical for each form, more favorable column kinetics resulted in more than twice as much breakthrough capacity (to 1 mg/ℓ NH_3-N effluent concentration) for Na-clinoptilolite. In addition, regeneration was much less efficient using calcium salts. These results show that the operation of clinoptilolite on the Na cycle is the preferred mode of operation.

Results of batch and column tests made to elucidate the effect of pH on ammonia exchange showed that optimum conditions for ammonia exchange exist between pH 4 and 8 with the ammonia exchange capacity decreasing rapidly outside this range. A model of the exchange reaction which included effects of increased hydrogen ion competition at low pH and NH_3-NH_4^+ equilibria at high pH (cf. Equation 18) closely predicted changes in the ammonia exchange capacity with pH. These results will help in combining this process with upstream treatment processes in a way to attain maximum ammonia removals. In addition, the results will aid in determining column rinsing procedures following high pH regeneration which will not impair column performance at the beginning of the subsequent exhaustion cycle.

VIII. REGENERATION STUDIES

GENERAL CONSIDERATIONS

Objectives

Considerations in determining the least cost method of regeneration are the efficiency with which regenerant is utilized, the volume of regenerant required, and the time necessary to complete regeneration. Experiments reported in this chapter were designed to furnish information necessary for making decisions regarding the choice of regenerant composition. Objectives of the regeneration study were: 1) to determine the effect of flow rate on regeneration efficiency, 2) to determine the most suitable concentration of salt and pH for regeneration, 3) to determine the effect of attrition caused by exposure of clinoptilolite to high pH regenerant solutions, and 4) to ascertain the rinse requirements of regenerated columns.

In the preceding chapter it was shown that improved performance during exhaustion resulted from regeneration of clinoptilolite to the Na form. Therefore, efforts to optimize column regeneration concentrated on the use of NaCl and NaOH. Sodium hydroxide was used for pH adjustment. However, because of its lower cost, lime would probably be the most desirable source of caustic for pH adjustment in full-scale plants. This substitution will result in little or no change in performance even with the introduction of some calcium into the exchanger during regeneration.

Column Operation

All regeneration studies were performed using chemically treated sewage for the column influent. This work was carried out concurrently with the process demonstration studies at SERL described in Chapter IX. The average cation concentrations in the column influent and the range of values during the test period are shown in Table 11.

Each run commenced with zeolite regenerated to the Na form and continued until incipient breakthrough of ammonia. Data collected using tap water containing cation concentrations similar to those in Table 11 (cf. Figures 1 and 2 in Appendix B) indicated that a throughput of approximately 180 BV could be processed prior to ammonia breakthrough. Therefore, columns were exhausted at a rate of 15 BV/hr for 12 hr and immediately regenerated. In this way columns were loaded with approximately the same amount of ammonia prior to each regeneration. Because of variations in

the influent wastewater composition, it was not possible to maintain precisely the same ammonia loading for each run. Therefore, corrections were made for the amount of ammonia removed during each cycle in all calculations concerning regeneration performance.

TABLE 11

COMPOSITION OF COLUMN INFLUENT
FOR REGENERATION STUDIES

Ion	Average Concentration mg/ℓ	Range mg/ℓ
NH_3-N	19.0	13.0 - 22.9
Na	54.0	48.3 - 62.1
K	9.3	7.8 - 11.3
Ca	71	48 - 94
Mg	5	1 - 13

Column performance and other data pertinent to the regeneration study are shown in Table 12. In each regeneration test 30 BV regenerant was applied to the column. Run designations are those used in the process demonstration studies at SERL so that the supplementary pilot-plant data in Appendix E may be referred to using these run numbers. Table 12 includes data describing the exhaustion of columns prior to each regeneration, the conditions under which each regeneration was made, and the performance of columns during regeneration. A partial substantiation of the reliability of these tests is afforded by comparing the ammonia removed during exhaustion to the quantity of ammonia eluted during the following regeneration. Rarely was less than 80% of the ammonia removed during exhaustion recovered during regeneration. This is satisfactory considering the circumstances under which the tests were conducted and the volatility of ammonia in the high pH regenerant. While care was taken in collecting regenerant samples, some loss of ammonia was inevitable. The low recovery of ammonia in runs 63, 64, and 67 was a result of the composition of the regenerant used in these runs. Appropriate corrections were made and these are described below. For these runs, in which ammonia elution was obviously poor, a stronger regenerant was applied to the column following the 30 BV used for these tests in order to have a column free of ammonia at the beginning of the next exhaustion cycle.

TABLE 12

COLUMN PERFORMANCE DURING REGENERATION STUDIES

Run	Exhaustion			Regenerant[a]				Ammonia Recovery %	Regeneration Efficiency		
	Inf. NH_3-N mg/ℓ	Eff. NH_3-N mg/ℓ	NH_3-N Removed During Run equivalents	Flow (Upflow) BV/hr	NaCl Conc. lb/gal	pH	NH_3-N Eluted equivalents		Regen. to 95% Elution BV	Na Used equivalents[b]	Efficiency[c] %
SERL-12	15.7	0.56	1.44	4	0.049	11.5	1.65	114	27.0	20.9	6.9
10	15.2	0.72	1.39	7	0.049	11.5	1.36	98.0	23.5	18.3	7.6
3	15.2	1.10	1.34	10	0.049	11.3	1.48	108	27.0	20.9	6.4
18	18.6	1.09	1.67	20	0.049	11.6	1.63	97.5	25.4	19.7	8.5
67	20.0	2.95	1.63	30	0.049	11.5	1.02	62.8	-	-	-
27	17.5	0.20	1.65	10	0.24	11.5	1.50	91.0	14.7	55.0	3.0
49	19.3	1.97	1.65	25	0.10	12.5	1.49	90.4	11.0	18.9	8.8
64	22.0	0.53	2.06	15	none	11.5	1.26	61.5	-	-	-
16	13.0	0.02	1.24	15	0.049	11.5	1.04	84.5	26.6	20.7	6.0
22	18.0	0.29	1.78	15	0.10	11.5	1.50	84.3	26.0	39.5	4.5
24	16.9	0.27	1.59	15	0.17	11.5	1.56	98.0	18.2	47.5	3.3
26	21.0	0.43	1.97	15	0.24	11.5	1.69	87.7	17.0	63.2	3.1
53	20.2	0.98	1.84	15	0.73	11.5	1.82	99.1	16.0	178	1.0
66	22.0	4.06	1.71	15	none	12.0	1.62	94.1	28.0	3.1	55.0
51	20.0	3.30	1.60	15	0.049	12.0	1.84	115	21.0	17.9	8.9
38	16.6	0.28	1.56	15	0.10	12.0	1.26	79.0	16.6	26.5	5.9
40	19.0	0.47	1.77	15	0.10	12.0	1.86	105	16.8	26.7	6.6
46	20.0	0.30	1.89	15	0.17	12.0	1.54	81.5	16.0	43.4	4.4
52	16.3	0.47	1.51	15	0.24	12.0	1.57	104	17.0	64.9	2.3
58	22.3	2.03	1.94	15	none	12.5	2.05	105	15.3	3.7	52.0
33	20.0	0.49	1.86	15	0.049	12.4	1.72	92.4	15.0	14.8	12.6
31	17.9	0.11	1.70	15	0.10	12.4	1.37	80.5	10.0	17.3	9.8
29	18.8	0.25	1.77	15	0.17	12.3	1.35	76.2	9.2	26.2	6.8
44	18.1	0.68	1.71	15	0.17	12.5	1.64	95.8	9.0	25.6	6.7
35	19.5	0.31	1.83	15	0.24	12.4	1.46	80.1	9.4	37.3	4.9
48	18.4	1.31	1.63	15	0.73	12.5	1.61	99.4	9.0	101	1.6
56	20.8	1.07	1.89	15	0.73	12.5	1.80	95.5	10.0	112	1.7
63	19.9	1.82	1.73	15	0.10	8.2	0.96	55.2	51.6[d]	76.6[d]	2.3[d]
60	22.0	1.46	1.95	15	0.10[e]	12.2	1.84	106	14.5	22.6	8.6
65	22.9	4.62	1.75	15	0.10[f]	11.8	1.69	96.8	20.0	31.2	5.6

[a] Volume of regenerant used was 30 BV. [b] Includes total Na in regenerant.

[c] $\text{Efficiency} = \frac{\text{Eq } NH_3\text{-N removed during previous exhaustion}}{\text{Eq Na used for regeneration}} \times 100$. [d] Values obtained by extrapolating available data.

[e] Regenerant also contained 0.046 lb $CaCl_2$/gal.

[f] Regenerant also contained 0.32 lb $CaCl_2$/gal.

EFFECT OF REGENERATION FLOW RATE

Because exchange rates in clinoptilolite tend to be limited by particle phase diffusion, it was initially expected that exchange efficiency might vary considerably with flow rate. Therefore, tests were made to establish regeneration flow rates which could be used in later experiments. Regenerant was prepared with tap water containing 0.049 lb NaCl/gal (0.1 M) and with the pH adjusted to 11.5 with NaOH. Runs were made using flow rates ranging from 4 to 30 BV/hr. Ammonia concentration histories for these runs, shown in Figure 18 reveal little difference in rates ranging from 4 to 20 BV/hr. Points for the 15 BV/hr run were lower than points for other runs in this range because the influent ammonia concentration in the previous exhaustion was lower than average (cf. Table 12). Points for regeneration at 30 BV/hr are much below the average of the other runs. Only 63% of the ammonia in the zeolite was eluted in this regeneration indicating that exchange kinetics become limiting between 20 and 30 BV/hr.

As a further means of elucidating the effect of flow rate on regeneration, the amounts of ammonia eluted in various volumes of regenerant were compared. By assuming that essentially all ammonia was eluted from the clinoptilolite in 30 BV of regenerant, it was possible to normalize the amount of ammonia eluted in 5, 10, and 20 BV with respect to the amount removed in 30 BV. This was a good assumption for flows between 4 and 20 BV/hr, but was not valid for regeneration at 30 BV/hr as only 63% of the ammonia was eluted in 30 BV regenerant. Values for this flow were corrected using the quantity of ammonia removed during exhaustion. The percent ammonia eluted in the various regenerant fractions is shown in Figure 19a. If there was no effect of increasing the flow rate, the fraction of ammonia eluted in a particular volume of regenerant should be the same for all flows. These results show that the amount of ammonia removed per volume of regenerant is approximately constant up to a rate of 15 BV/hr. A slight reduction was evident at the 20 BV/hr rate after 5 and 10 BV had passed through the column. However, by the time 20 BV had been passed through the column, no difference was observed between this flow rate and lesser ones. Performance at 30 BV/hr was definitely inferior compared to the lower flow rates, resulting in decreased regenerant utilization.

To determine if a similar relationship existed for different regenerants, regeneration characteristics were compared at 10 and 15 BV/hr using 0.24 lb NaCl/gal (0.5 M NaCl) at pH 11.5 and at 15 and 25 BV/hr using 0.10 lb NaCl/gal (0.2 M NaCl) at pH 12.5. The percentages of ammonia eluted for these conditions, illustreated in Figure 19b, show little difference in performance for comparative regeneration conditions. Ammonia removal at 25 BV/hr using the 0.10 lb NaCl/gal, pH 12.5 regenerant lagged only slightly behind the removal rate at 15 BV/hr. On the basis of these results it can be concluded that variation in flow rates in the range of 4 to 20 BV/hr has no significant effect on ammonia

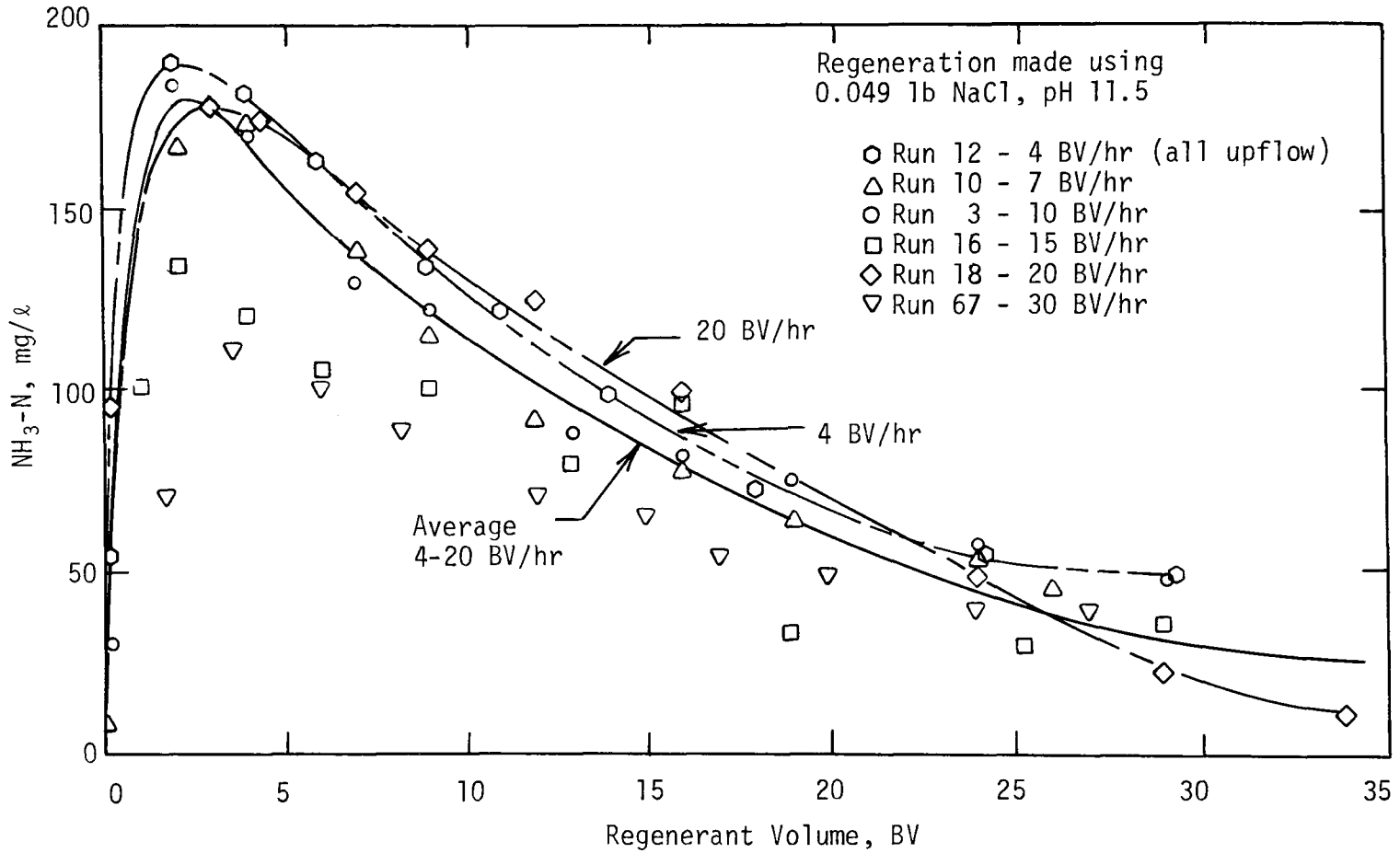
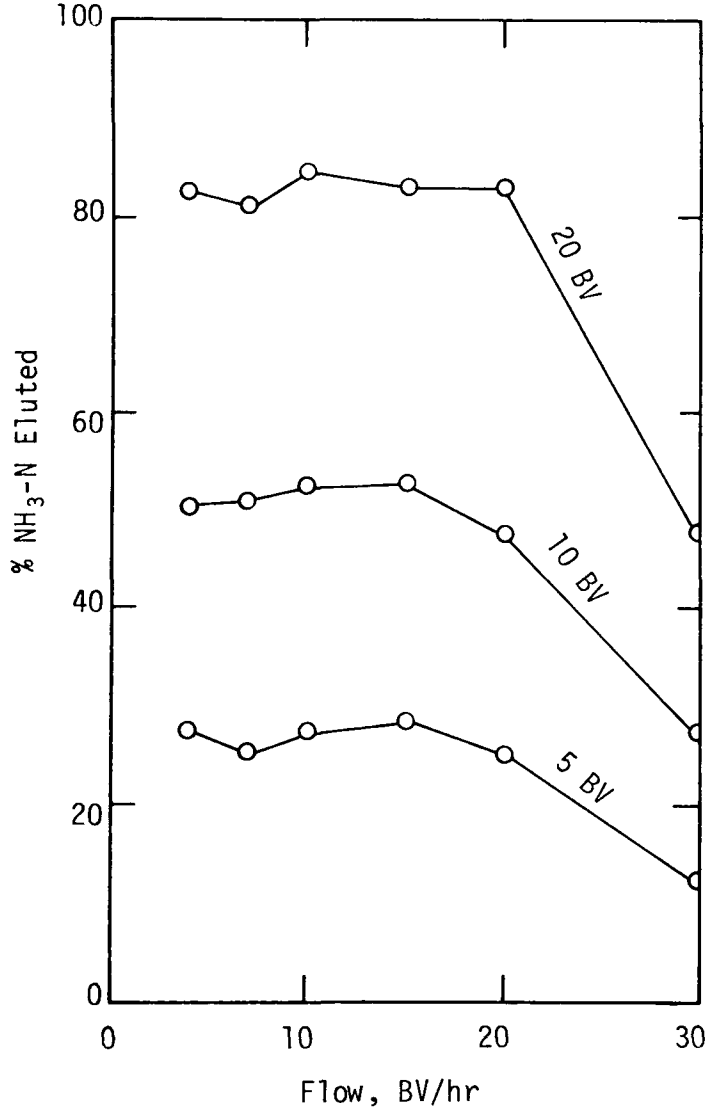
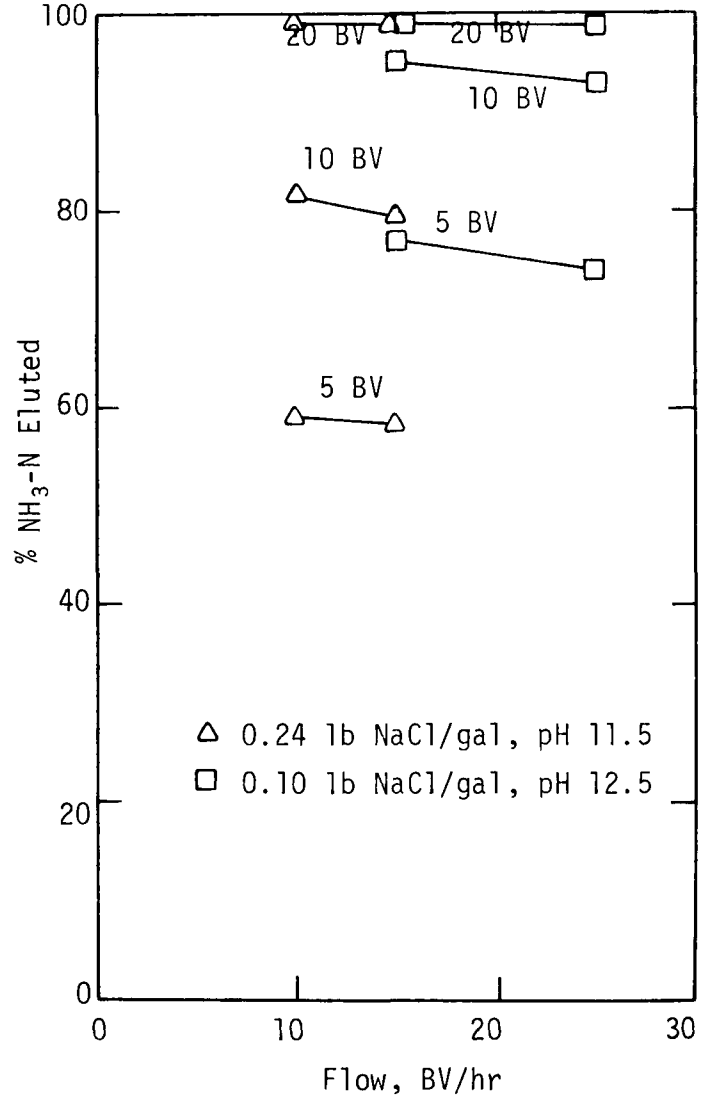


FIGURE 18. EFFECT OF FLOW RATE ON REGENERATION



a. REGENERATION USING 0.049 lb NaCl/gal, pH 11.5



b. REGENERATION USING 0.24 lb NaCl/gal pH 11.5 AND 0.10 lb NaCl/gal, pH 12.5

FIGURE 19. VARIATION OF AMMONIA ELUTION WITH FLOW RATE

elution. Flow rates as high as 25 BV/hr might be used with only minor impairment of exchange efficiency, but rates of 30 BV/hr or higher result in a significant loss of efficiency.

OPTIMIZATION OF REGENERANT COMPOSITION

Effect of Salt Strength and pH

Because of the combined effects of pH and salt concentration on the regeneration of clinoptilolite, tests were made to determine the dependence of regeneration efficiency on these factors. In Chapter VII it was shown that ammonia sorption was limited at high pH, with only 0.008 meq/g NH_3-N held on the zeolite in equilibrium with a 20 mg/ℓ NH_3-N solution at pH 12. This indicates that regenerant utilization might be improved using high pH regenerant solutions.

Salt concentrations used in these tests were 0.049, 0.10, 0.17, 0.24, and 0.73 lb NaCl/gal corresponding to 0.1, 0.2, 0.35, 0.5, and 1.5 M NaCl. Tests were also made using high pH solutions containing no NaCl. Solutions were adjusted to pH 11.5, 12.0, and 12.5 using NaOH. In raising the pH the NaOH added equaled 0.0015 lb NaOH/gal for pH 11.5, 0.005 lb NaOH/gal for pH 12.0, and 0.011 lb NaOH/gal for pH 12.5. The regeneration rate was constant at 15 BV/hr. Data for these tests are shown in Table 12. Elution curves drawn for each test are shown in Figures 20 through 25. The completeness of ammonia elution for 5, 10, and 20 BV of regenerant is shown in Figure 26. As before, the ammonia eluted in 30 BV was taken as the total amount of ammonia in the clinoptilolite and used as the base in calculating the percent ammonia eluted. Because of the low ammonia recovery for run 64, values for this test were corrected using the quantity of ammonia removed during exhaustion.

From these results it is evident that a given quantity of ammonia is eluted in a progressively less regenerant volume as the pH is increased from 11.5 to 12.5. At a pH of 12.5 practically all ammonia was eluted from the clinoptilolite in 10 BV of regenerant, whereas at pH 11.5 and 12.0 elution was not nearly as complete in 10 BV. At pH 11.5 elution approached 100% using 20 BV of regenerant only when the salt concentration was 0.17 lb NaCl/gal or greater. At pH 12.0 nearly complete elution of ammonia was achieved in 20 BV using 0.10 lb NaCl/gal or greater concentrations. Approximately the same degree of elution at pH 12.5 was achieved in 10 BV using a salt concentration of 0.10 lb NaCl/gal or greater. The effect of pH on regenerant performance is illustrated by run 63 shown in Figure 22. This run was made using a regenerant solution containing 0.10 lb NaCl/gal and no caustic (pH 8.2). At this pH ammonia was eluted from the column at a more or less constant rate. As the pH of the regenerant was increased, elution curves became sharper, resulting in the removal of ammonia in much less regenerant volume.

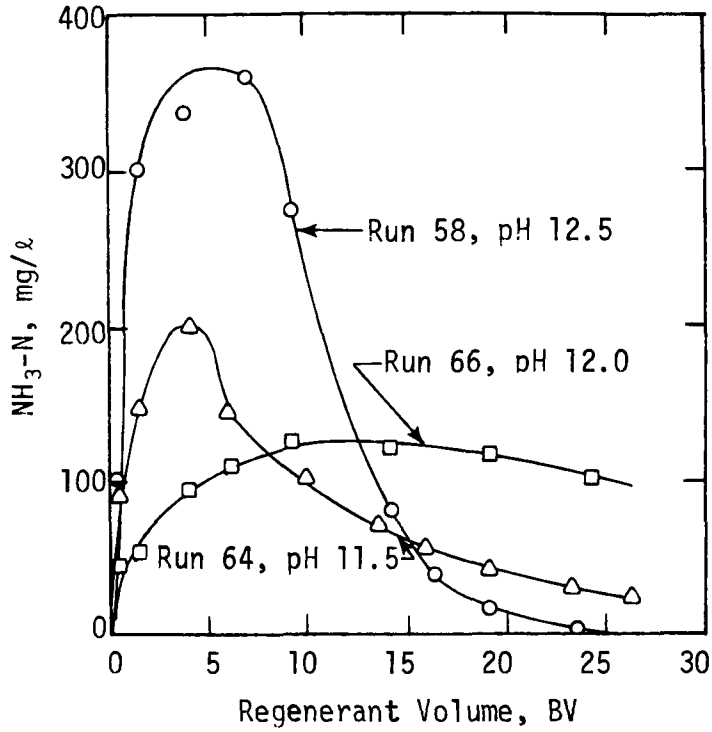


FIGURE 20. AMMONIA ELUTION — NO NaCl

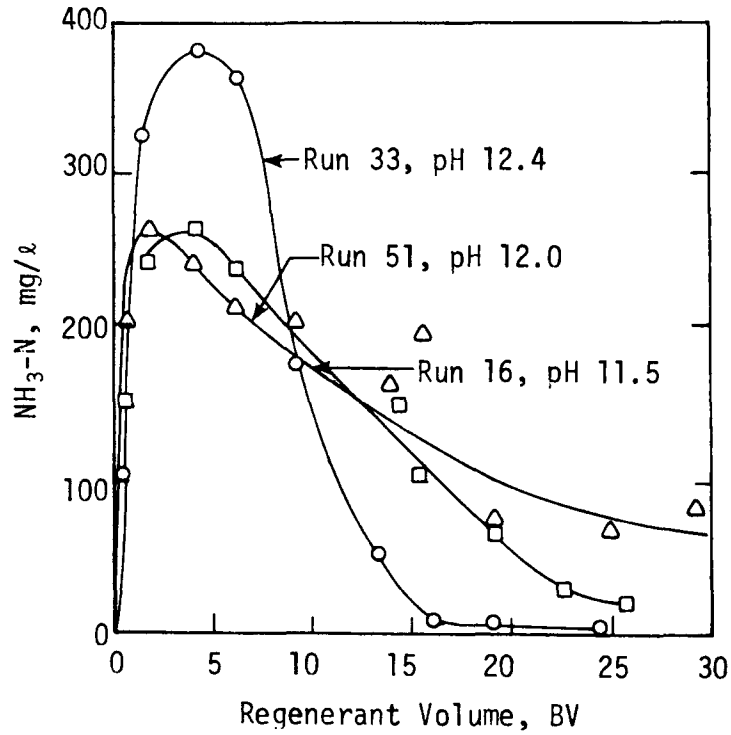


FIGURE 21. AMMONIA ELUTION — 0.049 lb NaCl/gal

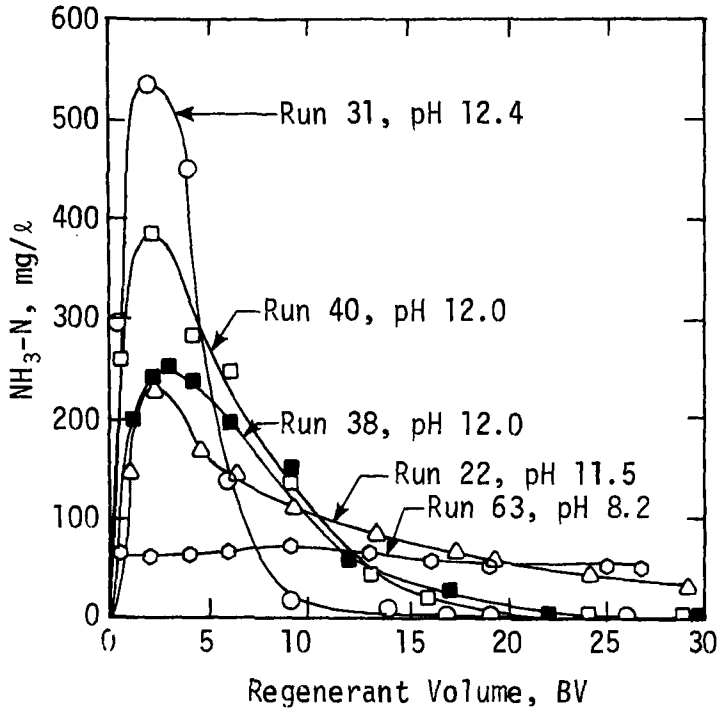


FIGURE 22. AMMONIA ELUTION — 0.10 lb NaCl/gal

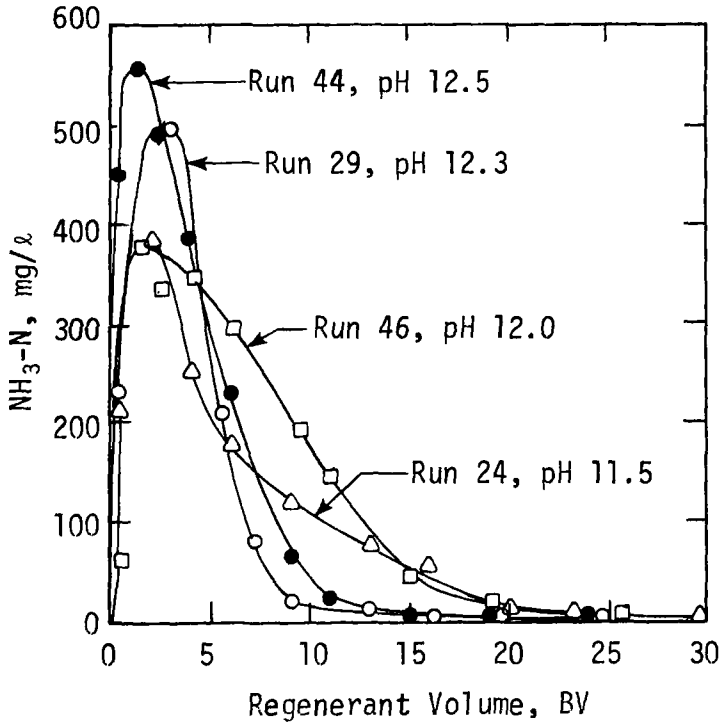


FIGURE 23. AMMONIA ELUTION — 0.17 lb NaCl/gal

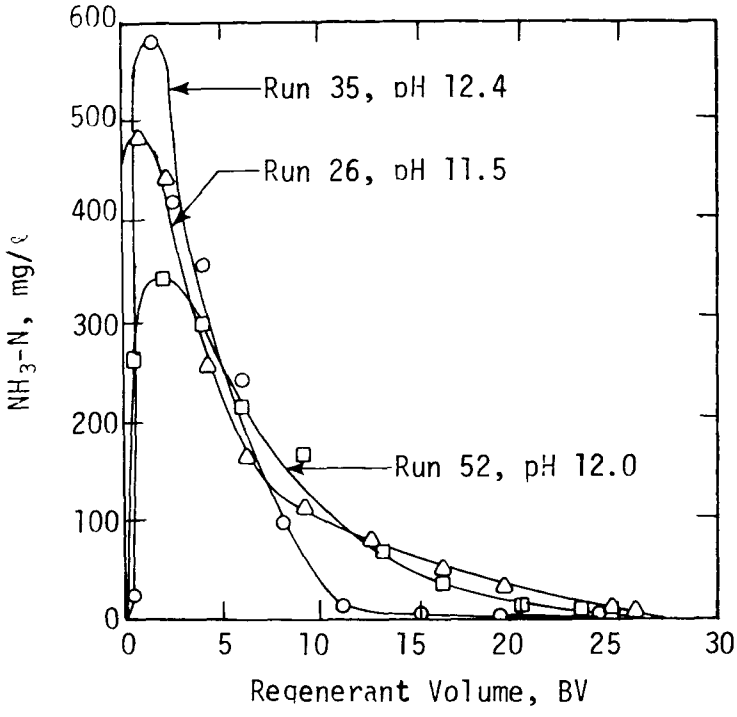


FIGURE 24. AMMONIA ELUTION – 0.24 lb NaCl/gal

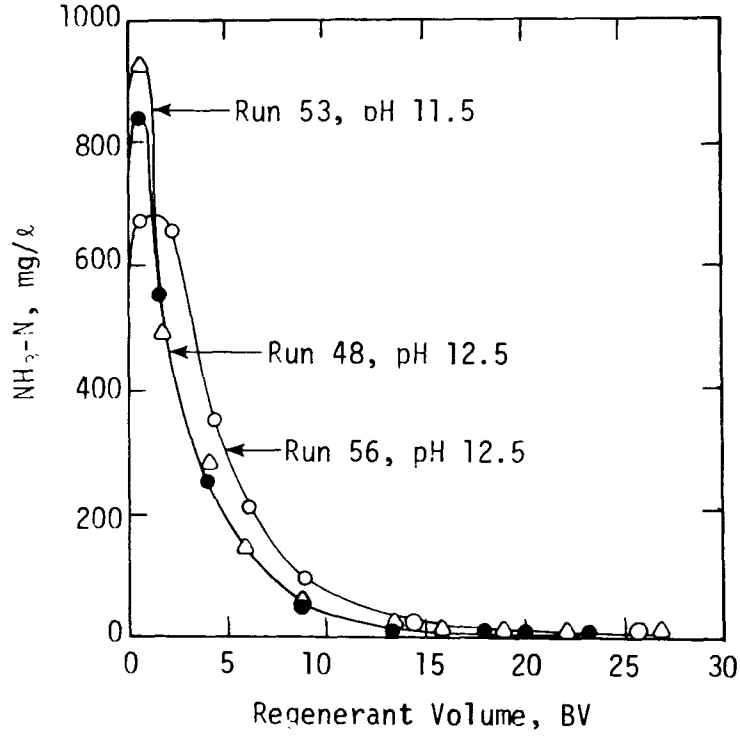
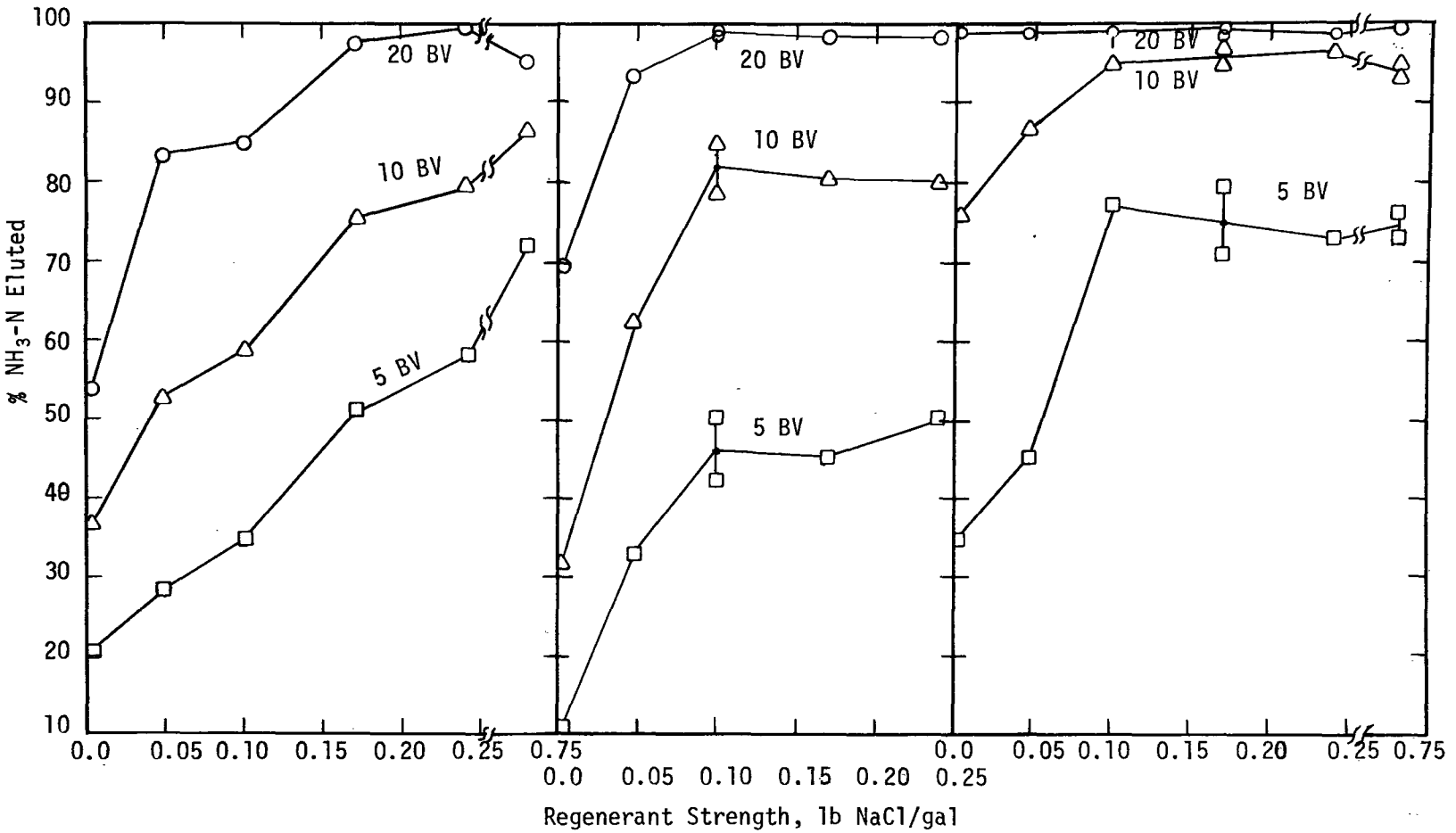


FIGURE 25. AMMONIA ELUTION – 0.73 lb NaCl/gal



a. REGENERATION AT pH 11.5 b. REGENERATION AT pH 12.0 c. REGENERATION AT pH 12.5

FIGURE 26. VARIATION OF AMMONIA ELUTION WITH REGENERANT STRENGTH

Several observations may also be made concerning the effect of NaCl concentration on regeneration. At pH 11.5 ammonia elution was enhanced with increasing salt concentration up to 0.17 lb NaCl/gal. Increasing the salt concentration beyond this value had little effect on elution, especially with the 20 BV required to remove greater than 95% of the ammonia from the zeolite. Likewise, increasing the salt concentration beyond 0.10 lb NaCl/gal at pH 12.0 and 12.5 had no effect on regeneration performance. For this range of caustic concentrations, increasing the NaCl concentration of the regenerant beyond a certain value at a particular pH had no effect on the rate of ammonia elution. In regenerating at pH 12.5, no benefit was realized by using a salt concentration greater than about 0.10 lb NaCl/gal. This result is surprising because of the relatively low concentration at which salt addition ceased to improve ammonia elution. Using conventional ion exchange resins, regeneration is usually accomplished with a 5 to 10% solution. In this case it was not beneficial to use a salt concentration greater than about 1%.

The nature of the ammonia elution characteristics observed by varying regenerant composition suggests that the regenerant pH is the controlling factor in determining the volume of regenerant required to remove ammonia from clinoptilolite. This implies that raising the pH plays a significant role in increasing the diffusion rate of ammonia from the solid phase. Based on observations made in these experiments, the following mechanism of ammonia removal from the solid phase is proposed. (The reader is referred to Figure 2 for an illustration of the various parts of the zeolite particle.) Because anions are, to a great extent, excluded from the intercrystalline channels of the zeolite, no effect of increasing the solution pH is felt inside the crystallites. However, hydroxyl ions probably are free to diffuse into the intercrystalline pores, as these passageways do not contain negatively charged exchange sites. At this point ammonium and hydroxyl ions are free to react producing unionized ammonia and water. Due to its smaller size and reduced affinity for water of hydration, the ammonia molecule thus produced is capable of diffusing more rapidly to the bulk solution phase outside the particle. The basic requirement necessary for ion exchange to occur still exists; namely, that an adequate concentration of a counter ion (sodium in this case) must be present to replace the ammonium ion on the exchange site. Once exchange has taken place, hydroxyl ions act to increase the diffusion rate of ammonia, both by reducing physical constraints and by keeping the concentration differential between solid and solution phase ammonium ion concentrations at a maximum.

Amount of Regenerant Required

The implication of these results to design and operation of ion exchange plants becomes more apparent when the weight of chemicals and the volume of regenerant required for regeneration are considered. In conventional ion exchange practice the amount of regenerant used is frequently

expressed as the weight of salt applied per cubic foot of resin. Because of the importance of pH in addition to salt strength in the elution of ammonia from clinoptilolite, the amount of caustic used must also be considered. The cost of chemicals for regeneration will be proportional to these values. The volume of regenerant required will also be related to process costs as an indication of the amount of storage space needed, of the amount of product water that must be used for regenerant makeup where regenerant is wasted after one use, and of the volume of regenerant to be processed through a stripping tower if regenerant is reused.

The volume of regenerant required for 95% elution of ammonia per equivalent of ammonia in the zeolite bed was calculated for different regenerant compositions from the data given in Table 12. These values are shown in Figure 27. The weight of chemicals required for the same regenerant compositions is shown in Table 13. In all but two instances lime was used as the caustic for regenerant composition listed in Table 13 as lime would be the least expensive source of caustic. The amount of lime required was calculated from the amount of NaOH used in the regeneration tests reported in Table 12 assuming that equivalent amounts of NaOH and lime would be required for pH adjustment.

Regeneration of clinoptilolite using no NaCl at pH 12.0 or 12.5 must be made using NaOH for pH adjustment as indicated in Table 13. The comparisons of Na- and Ca-clinoptilolite in Chapter VII showed that regeneration and exhaustion are much more favorable using regenerants containing sodium. Therefore, regeneration using lime by itself was not considered. It is also observed from Table 13 that nearly identical amounts of NaOH are required for regeneration at pH 12.0 and 12.5 using no NaCl — 1.06 lb NaOH/cu ft for regeneration at pH 12.0, and 1.11 lb NaOH/cu ft at pH 12.5. However, in Figure 27 the volumes of regenerant required using these regenerant compositions are approximately 32 gal/eq NH_3-N removed at pH 12.0 and 15 gal/eq NH_3-N removed at pH 12.5. Regeneration at pH 12.5 would probably be more favorable because of the smaller regenerant volume required.

These data were obtained from regenerating 3-ft deep clinoptilolite beds previously exhausted to a breakthrough NH_3-N concentration of approximately 1 mg/ℓ. Volumes for deeper beds and beds containing a higher solid phase concentration of ammonia may vary somewhat from these values. However, a fully exhausted column containing 9.5 eq NH_3-N/cu ft regenerated using 0.17 lb NaCl/gal at pH 12.5 required 11.8 gal regenerant/eq NH_3-N in the zeolite. The volume indicated in Figure 27 is 11.1 gal/eq NH_3-N. Corresponding chemical requirements were 2.0 lb NaCl/eq NH_3-N removed and 0.12 lb $Ca(OH)_2$/eq NH_3-N for the saturated column compared to 1.87 lb NaCl/eq NH_3-N and 0.11 lb $Ca(OH)_2$/eq NH_3-N calculated from values in Table 13.

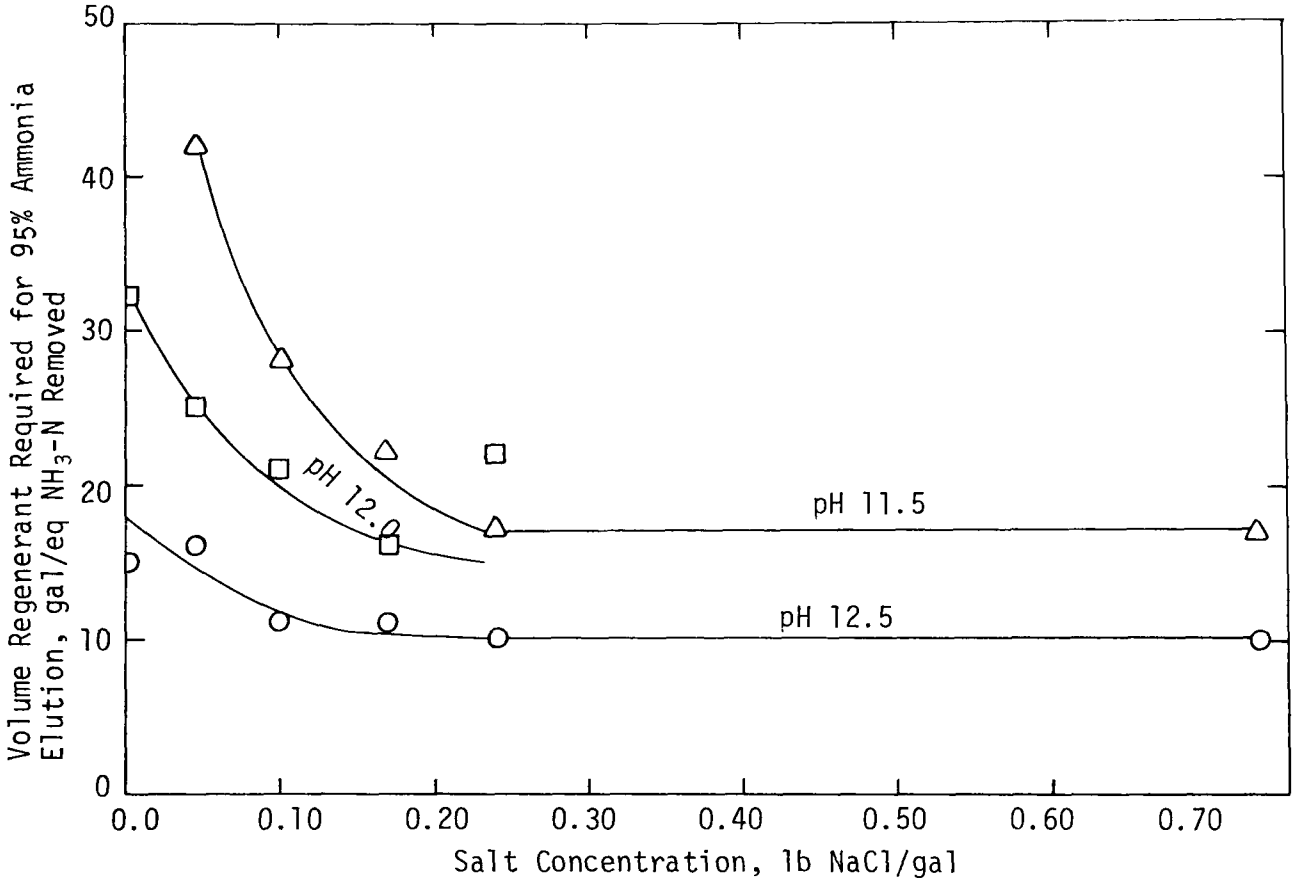


FIGURE 27. VOLUME OF REGENERANT REQUIRED FOR 95 PERCENT AMMONIA ELUTION

TABLE 13

AMOUNT OF CHEMICALS REQUIRED FOR REGENERATION

Regenerant Composition		Regenerant Required for 95% NH_3-N Elution	
pH	lb NaCl / gal	lb NaCl[a] / cu ft	lb $Ca(OH)_2$[a,b] / cu ft
11.5	0.049	13.6	0.38
	0.10	18.5	0.26
	0.17	24.6	0.20
	0.24	26.9	0.16
	0.73	81.9	0.16
12.0	none	0	c
	0.049	8.1	0.77
	0.10	13.9	0.63
	0.17	18.6	0.50
	0.24	34.8	0.66
12.5	none	0	d
	0.049	5.1	1.06
	0.10	7.2	0.72
	0.17	12.3	0.72
	0.24	15.8	0.66
	0.73	48.0	0.66

[a]Calculations shown are for 6.6 eq NH_3-N/cu ft.

[b]Calculated using the amount of caustic required to raise the pH of tap water used in this study. These amounts were 0.0014, 0.046, and 0.010 lb $Ca(OH)_2$/gal for pH 11.5, 12.0, and 12.5 regenerants, respectively.

[c]Regeneration for these conditions must be made using NaOH to provide Na in the regenerant. NaOH required was 1.06 lb/cu ft.

[d]Regeneration must be made using NaOH. NaOH required was 1.11 lb/cu ft.

Efficiency

Although the percent of ammonia eluted with a particular volume of regenerant is a good indication of the volume of regenerant needed and the time required for regeneration, it does not directly indicate the efficiency with which the regenerant is utilized. In this report regeneration efficiency has been defined as follows:

$$\text{Efficiency, \%} = \frac{\text{Equivalents } NH_3\text{-N Removed During Previous Exhaustion}}{\text{Equivalents Na Used for Regeneration}} \times 100.$$

This has also been aptly termed the "regenerant utilization factor" by Klein [85]. Efficiencies were calculated using the volume of regenerant required for 95% elution of ammonia from the zeolite. Data used in making these calculations are shown in Table 12. The efficiency for run 63 could not be calculated, as mentioned previously, because of incomplete elution of ammonia from the zeolite. In this case the volume of regenerant required for 95% ammonia elution was obtained by extrapolating data for this run shown in Figure 22. This was done on the basis of the relatively constant ammonia concentration of the spent regenerant. Efficiencies for runs 64 and 67 also could not be calculated because of incomplete elution of ammonia. However, for these runs, no assumption could be made concerning the volume of regenerant required to complete regeneration.

Efficiencies are shown as a function of regenerant composition in Figure 28. Efficiencies for pH 12.5 were approximately twice as high as for pH 11.5. Points for regeneration at pH 12.0 generally lay between those for pH 11.5 and pH 12.5. The efficiency for run 63 using 0.10 lb NaCl/gal and an unaltered pH of 8.2 is also shown in Figure 28 for comparison with runs made at higher pH values. Efficiencies achieved in these experiments were considerably lower than those usually experienced in water softening. This was expected, based on the poorer exchange kinetics characteristic of clinoptilolite; however, the efficiency calculated here does not reflect the elution of ions other than ammonia during regeneration. Efficiencies would be correspondingly higher had these ions been taken into account. In cases where regenerant is stripped of ammonia and reused, the effective efficiency will approach 100%, as the only sodium ions consumptively used in any cycle will be the stoichiometric amount needed to replace ions eluted from the zeolite and the quantity in the regenerant solution lost in transfer between storage tanks and the ion exchange beds.

An additional consideration when regenerant is reused is the change of composition of the regenerant solution. In addition to salts added to make up the regenerant, ions eluted from the clinoptilolite will accumulate in the regenerant solution. In this respect the composition of the regenerant will differ from that used in these tests. For domestic

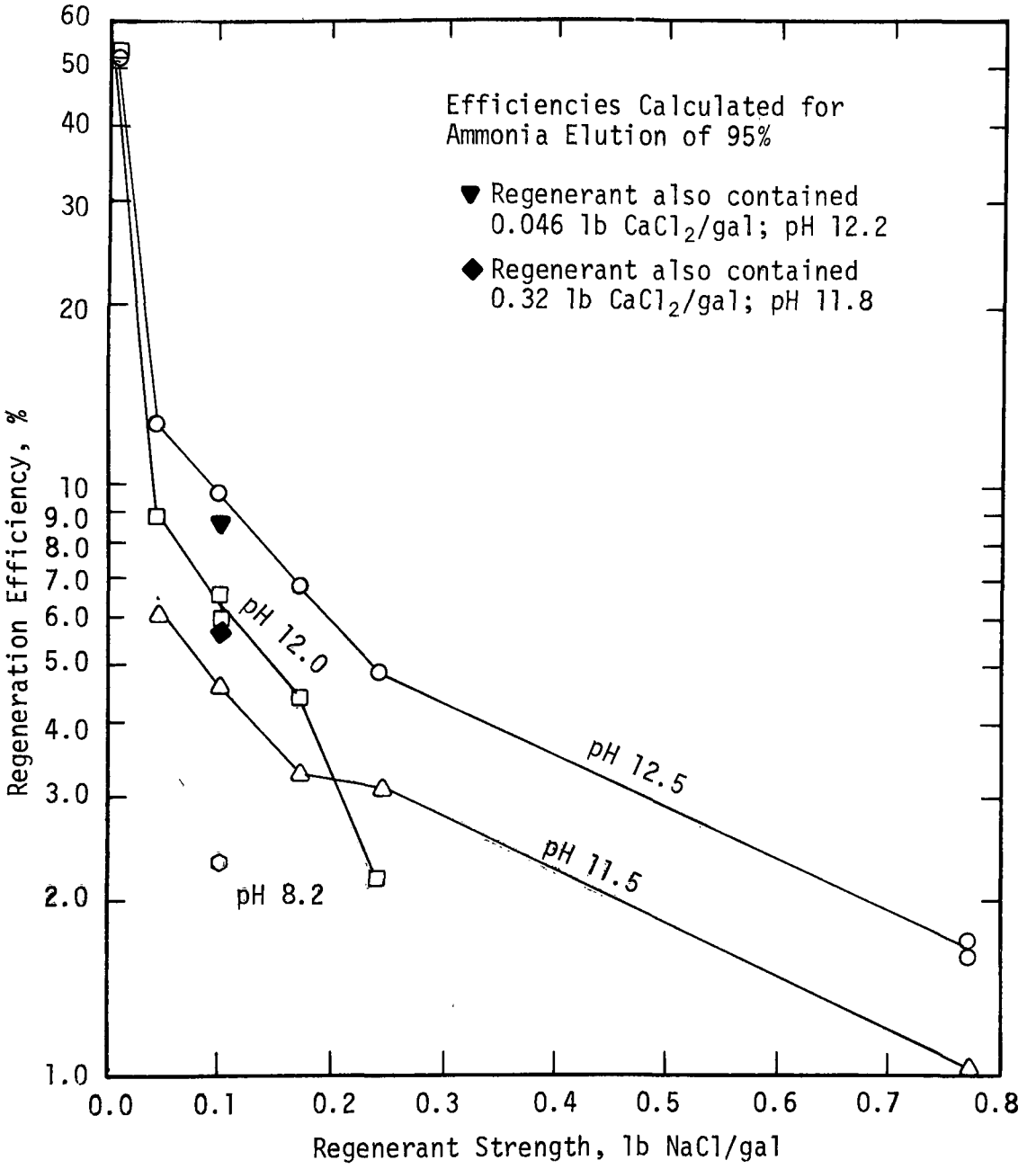


FIGURE 28. EFFECT OF REGENERANT COMPOSITION ON EFFICIENCY

wastewaters calcium will be the most significant ion to accumulate in the regenerant. To determine the effect of added calcium in the regenerant solution, regeneration was carried out in two runs using 0.10 lb NaCl/gal saturated with lime to which $CaCl_2$ was added. For run 60, 0.046 lb $CaCl_2$/gal (0.05 M $CaCl_2$) was added to the regenerant and for run 65, 0.32 lb $CaCl_2$/gal (0.35 M $CaCl_2$) was added. The resulting pH of these solutions was 12.2 for run 60 and 11.8 for run 65. Regeneration efficiencies for these runs were 8.6 and 5.6%, respectively. These values, shown in Figure 28, are close to the efficiencies for runs 38 and 40 in which the regenerant contained 0.10 lb NaCl/gal at pH 12.0. Thus the results of these tests were not significantly affected by the presence of added calcium in the regenerant solution. Regeneration costs based on the results presented in this chapter are considered in Chapter X.

ATTRITION OF CLINOPTILOLITE IN CAUSTIC SOLUTIONS

Results of the regenerant optimization study showed that clinoptilolite can be regenerated more effectively at a pH of 12.5 than at 11.5, indicating that the feasibility of using more concentrated caustic solutions for regeneration should be examined. However, previous work by Barrer *et al.* [50] demonstrated that the zeolite framework was not stable in caustic solutions. Therefore, tests were undertaken to determine the stability of the clinoptilolite used in this study in caustic solutions.

Initial tests were made in a batch system. In order to simulate operating conditions in which the clinoptilolite is exposed to caustic regeneration and exhaustion with a solution of near neutral pH, clinoptilolite samples were alternately exposed to NaOH and distilled water. One-gram samples of previously unused 20 x 50 mesh clinoptilolite were added to 12 flasks. Four flasks were used as controls and exposed only to distilled water. The remaining eight flasks were cyclically exposed to 100 mℓ of 2% NaOH (pH of about 13.3) and distilled water. Samples were shaken in 125-mℓ erlenmeyer flasks using a Burrell Wrist-Action Shaker (Burrell Corp., Pittsburgh, Pa.). During each cycle the clinoptilolite was exposed to NaOH for 2 hr and rinsed with distilled water for 2 hr. When changing solutions, water was also changed in the control flasks, so the decanting error would be the same for all flasks. After 5, 7, 25, and 50 cycles, one control and two test flasks were removed for analysis. Clinoptilolite samples were dried overnight at 105°C and sieved through 20 and 50 mesh sieves. The amount of 20 x 50 mesh material lost is shown in Table 14. These results show that clinoptilolite was significantly attacked by the caustic solution. After exposure to 50 simulated regeneration cycles, the attrition rate of clinoptilolite was 1.6%/cycle considering the total weight loss of 20 x 50 mesh material and 0.8%/cycle when the amount lost in control flasks was subtracted. The latter value is the loss attributable to the high pH alone assuming that mechanical attrition in caustic and control samples was equal. However, the total loss of 20 x 50 mesh material is a better indication of losses which would occur in actual column operation.

TABLE 14

WEIGHT LOSS OF CLINOPTILOLITE EXPOSED TO 2% NaOH (pH 13.3)

Cycles	Caustic		Control		Weight Loss %/Cycle	
	Wt. Loss[a,b] 20x50 Mesh Material,g	Wt. Loss 20x50 Mesh Material,%	Wt. Loss[a] 20x50 Mesh Material,g	Wt. Loss 20x50 Mesh Material,%	Caustic-Control	Caustic
5	0.304	30.4	0.305	30.5	0	6.1
7	0.327	32.7	0.312	31.2	0.21	4.7
25	0.506	50.6	0.350	35.0	0.62	2.0
50	0.789	78.9	0.370	37.0	0.84	1.6

[a]Initial weight for all samples was 1.000 g.

[b]Weights reported are average of two samples; maximum variation between two samples of any set was 5%.

Because of the high rate of attrition of clinoptilolite in the presence of 2% NaOH, further attrition studies were made using small laboratory columns containing 8.000 or 10.000 g of clinoptilolite. These columns consisted of 1-cm ID by 21-cm long glass tubes connected to caustic and rinse solutions using 1/16-in. rubber tubing. Three columns were connected in parallel to permit testing of three samples for each test condition. Three columns were connected only to the distilled water rinse for use as controls. Caustic was fed to the columns from 20-ℓ glass bottles which were refilled daily. Distilled water for rinsing was siphoned from a 20-ℓ bottle which was kept full by continuously dripping distilled water into the bottle from a distilled water line. Feed to the columns was alternated between caustic and rinse solutions at 2-hr intervals using an Intermatic Model T1905 24-hr timer connected to two 1/8-in. solenoid valves (Hoke model S90A180C, Hoke, Inc., Cresskill, N. J.). Both valves were the normally closed type and were connected to be open in alternate 2-hr periods. An illustration of these columns appears in Figure 29. Flow through the columns was set at approximately 4 mℓ/min (17 BV/hr) using screw clamps located at the influent end of the columns. Columns were operated upflow to minimize plugging. Effluent from the columns was collected in 8-ℓ bottles and weighed each day to determine the volume of liquid passed through each column. The pH of the effluent from each column was also measured to insure that approximately equal volumes of caustic passed through each column. These bottles also served to catch any clinoptilolite which might be washed from the columns if an increase of flow through the column occurred.

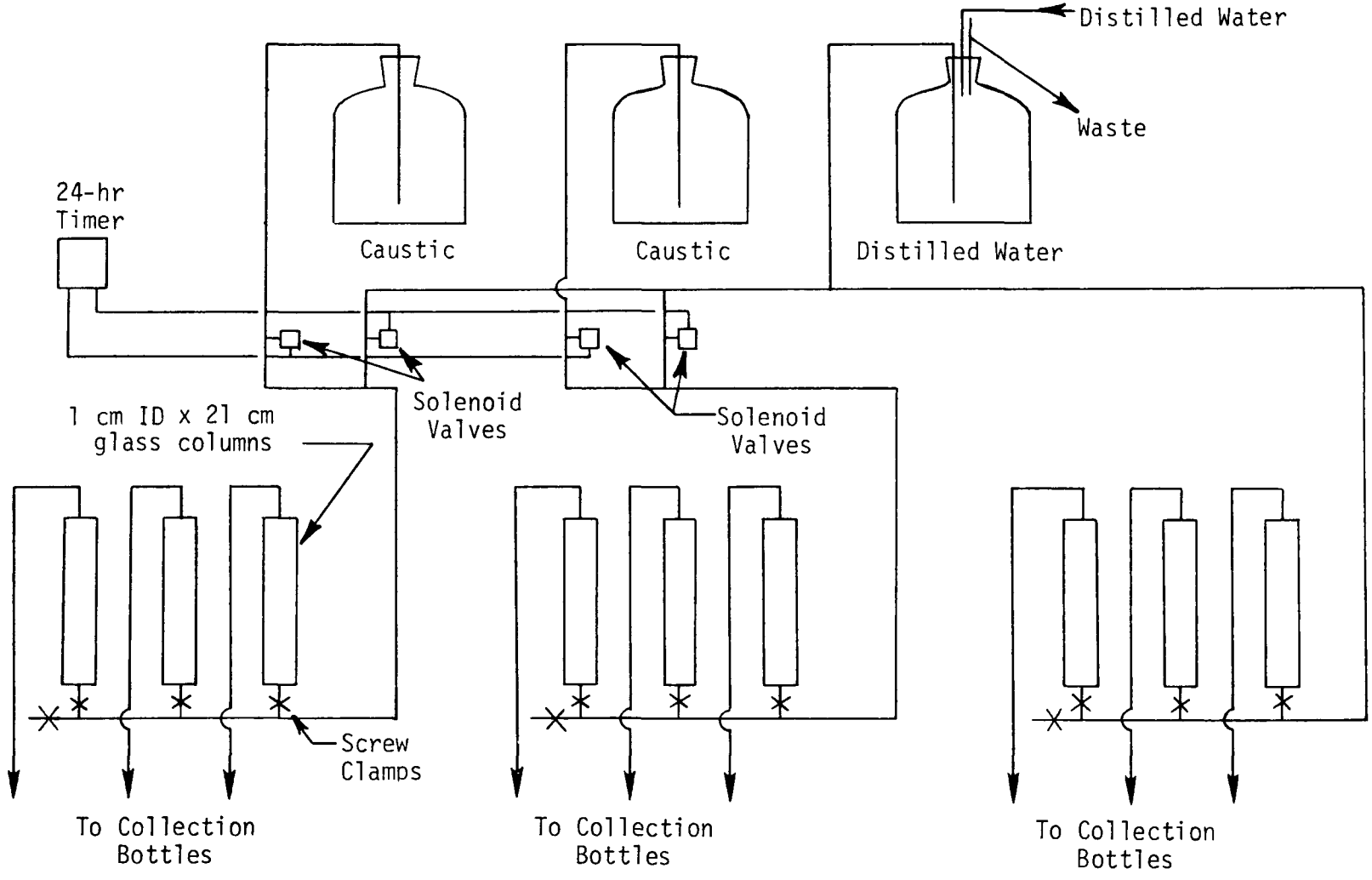


FIGURE 29. LABORATORY COLUMNS USED IN ATTRITION STUDY

Columns were inverted every two or three days to prevent the zeolite from becoming packed and to minimize channeling of flow through the bed. Results of clinoptilolite exposed to 100 simulated regeneration cycles at pH 11.5, 12.0, and 12.5 are given in Table 15. The effect of caustic increased significantly from pH 11.5 to 12.5 as judged by the loss of zeolite weight/regeneration cycle. Over 100 cycles the total attrition rate at pH 12.5 was 0.57%/cycle compared to 0.34 and 0.24%/cycle for exposure to pH 12.0 and 11.5 solutions, respectively. These are significantly less than the 1.6%/cycle measured in batch tests reported in Table 14. However, the rate of mechanical attrition was also significantly higher in the batch tests. Attrition rates were 0.15, 0.25, and 0.48%/cycle for exposure to pH 11.5, 12.0, and 12.5 solutions, respectively, when the amount lost in control flasks was subtracted.

Results of tests made to determine the variation of attrition rate with increasing exposure to caustic are also shown in Table 15. Tests were 50, 100, and 150 cycles in duration. Total attrition rates were 0.56, 0.57, and 0.51%/cycle, respectively, for 50, 100, and 150 cycles of exposure. These results indicate that the attrition rate might become less after exposure to 100 cycles of caustic. This observation is supported by weight losses of 28.3% from 0 to 50 cycles, 29.1% from 50 to 100 cycles, but only 18.6% from 100 to 150 cycles. Part of the observed decrease in weight loss from 100 to 150 cycles could be due to the presence of impurities in the clinoptilolite which constitute an increasingly larger fraction of the weight left in the column as clinoptilolite is broken into smaller pieces (or dissolved) and washed from the column. Barrer [50] reported that a sample of clinoptilolite contained 10 to 15% impurities. However, no attempt was made to measure impurities present in the zeolite used in this study. It is also possible that any harder and more resistant clinoptilolite that might accumulate in the zeolite bed will be less desirable as an ion exchanger because of a lower exchange capacity or poorer exchange kinetics. On the basis of these results, it cannot be assumed that a lower attrition rate after 100 cycles of exposure to caustic will result in a reduced replacement rate of clinoptilolite.

These results indicate that zeolite replacement costs will constitute a significant factor in the cost of ammonia removal using clinoptilolite. Attrition rates will be approximately 0.25, 0.35, and 0.55%/operating cycle using regenerants having a pH of 11.5, 12.0, and 12.5, respectively. The attrition rate for exposure to 2% NaOH (pH about 13.3) was 1.6%/cycle measured in a batch system in which samples were constantly shaken. These values are probably generous estimates of the attrition rate which would be experienced in full-scale operations because the exposure times/cycle used in these experiments were longer than the time required for an actual regeneration cycle. As such, these values constitute liberal estimates of zeolite attrition for use in the determination of the least cost regeneration procedure considered in Chapter IX.

TABLE 15

WEIGHT LOSS OF CLINOPTILOLITE IN COLUMN ATTRITION STUDIES

pH	Cycles	Caustic		Control		Weight Loss %/Cycle	
		Wt. Loss[a] 20x50 Mesh Material,g	Wt. Loss 20x50 Mesh Material,%	Wt. Loss[a] 20x50 Mesh Material,g	Wt. Loss 20x50 Mesh Material,%	Caustic-Control	Caustic
11.5	100	2.436[b]	24.4	0.904[b]	9.0	0.15	0.24
12.0	100	2.698[c]	33.8	0.904[b]	9.0	0.25	0.34
12.5	50	2.261[c]	28.3	0.938[c]	11.7	0.34	0.56
12.5	100	5.738[b]	57.4	0.904[b]	9.0	0.48	0.57
12.5	150	6.071[c,d]	76.0	0.716[c]	9.0	0.45	0.51

[a]Weights reported are average of three samples; maximum variation among samples of any set was 11%, excent as noted.

[b]Initial sample weight was 10.000 g.

[c]Initial sample weight was 8.000 g.

[d]Weight of samples in this set varied by 26%.

RINSE REQUIREMENTS

Removal of salt and caustic from a freshly regenerated zeolite bed is necessary before placing the bed back into operation. In this case the pH of the bed must be reduced before efficient ammonia removal may be achieved. The effects of pH on ammonia exchange described in Chapter VII indicated that the pH of a zeolite bed must be reduced to about 8 in order to permit ammonia removal during exhaustion. However, a reduction in the waste rinse water volume might be achieved by rinsing to a pH of 9.5 or 10.0 with some sacrifice of performance during the first part of the exhaustion cycle. Alternatively, rinsing could be divided into two steps, with water used for the first step being recycled to upstream processes and that used for final rinsing being mixed with product water as long as rinsing is accomplished using ammonia-free water. The high pH of the first fraction might be beneficial in upstream coagulation processes, while the second fraction should not impair the overall quality of the product water.

In evaluating rinse requirements it was assumed that only the volume of water necessary to reduce the pH to 10 would need to be wasted or recycled for additional treatment. Comparisons of SERL tap water and product water used for rinsing are shown in Figure 30. It is evident that the product water, which had a higher buffer capacity, was much more effective in reducing the column pH. The tap water had an initial pH of 8.5 and required 5.0 meq/ℓ of NaOH to raise the pH to 11.5, while product water had an initial pH of 7.8 and required 10.0 meq/ℓ NaOH to raise the pH to 11.5. While it is unlikely that tap water will be used for rinsing, these results do indicate that rinse requirements will vary considerably depending on the quality of the rinse water.

Product water was used both alone and in combination with a small volume of acid applied to the column prior to rinsing. Rinse volumes required for reduction of pH to 10.0 are shown in Table 16. The application of

TABLE 16

COMPARISON OF COLUMN RINSING PROCEDURES

Rinse	Rinse Volume to pH 10.0 BV
Tap water[a]	35
Product water	11
Product water preceded by 1 BV 0.01 M HCl	8
Product water preceded by 2.5 BV 0.01 M HCl	4

[a]For analysis of tap water, see Chapter VI.

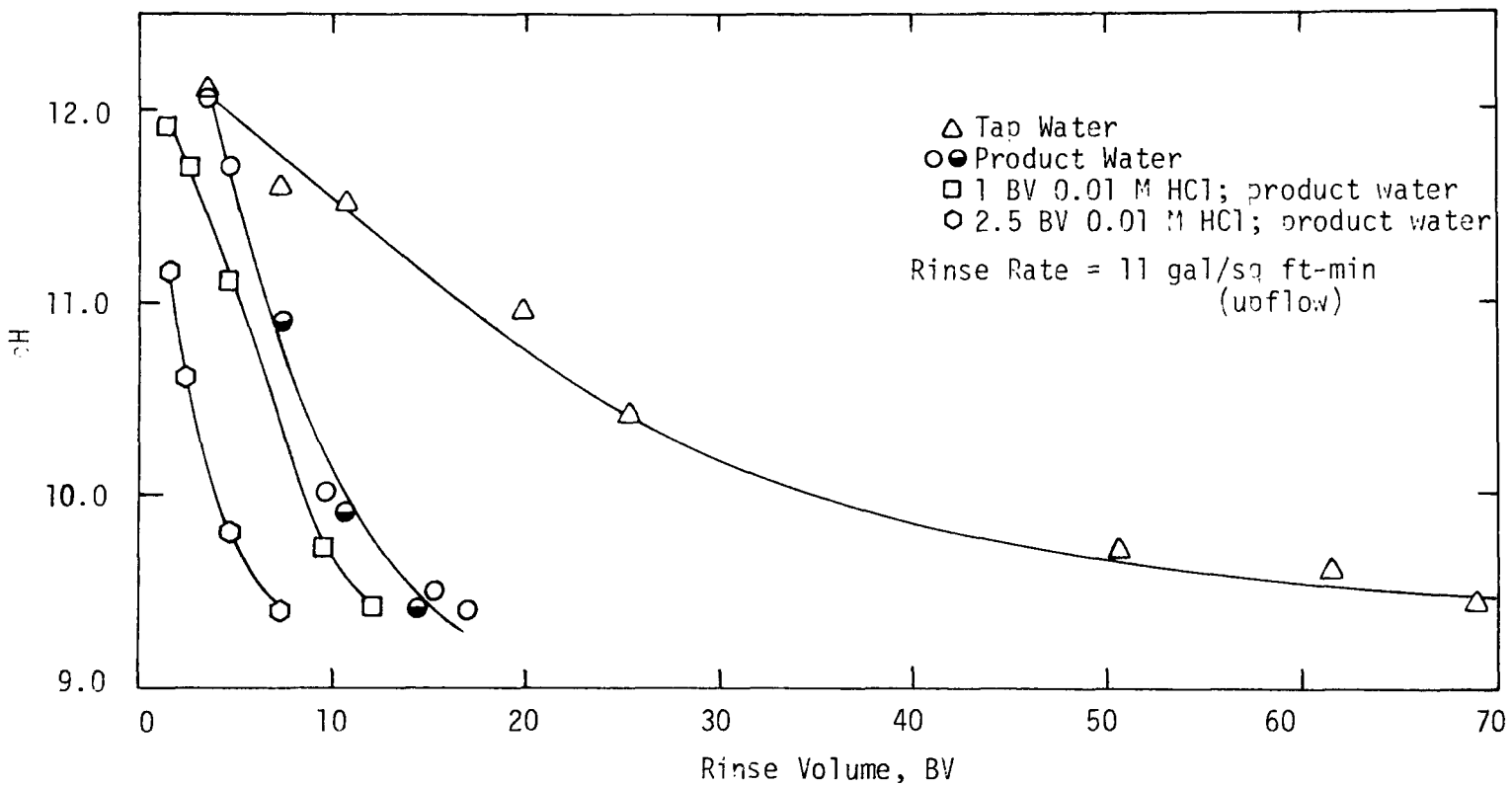


FIGURE 30. COMPARISON OF COLUMN RINSE REQUIREMENTS

acid to the column prior to the product water rinse further reduced the rinse requirement. However, the use of acid would probably not be economically desirable in view of the small rinse volume required using product water by itself.

SUMMARY

In this chapter factors relating to the regeneration of clinoptilolite have been investigated. Columns used in the regeneration study were exhausted to an ammonia breakthrough of approximately 1 mg/ℓ NH_3-N using a chemically treated wastewater as the column influent. In this way all columns were loaded with approximately the same amount of ammonia prior to each regeneration. Regenerant solutions were composed of various concentrations of NaCl and NaOH. Regenerations made using a variety of flow rates showed that regeneration performance was not affected significantly by a variation of flow rates from 4 to 20 BV/hr. However, a significant loss of efficiency was observed using flow rates of 30 BV/hr or higher.

Tests made to determine the effect of regenerant composition on regeneration performance showed that regeneration efficiency increased with increasing regenerant pH. It was hypothesized that a higher diffusion rate of ammonia was possible at higher pH values because of the presence of unionized ammonia. Efficiencies were calculated for the different regenerant compositions and showed that the highest efficiencies were obtained using no NaCl and a pH adjusted to either 12.0 or 12.5. Efficiencies for these conditions were 55% at pH 12.0 and 52% at pH 12.5. Based on the results of these tests, the amounts of regenerant required for 95% elution of ammonia in the zeolite was calculated. Chemical weights expressed as lb/cu ft, are shown in Table 13; the volume of regenerant required, expressed as gal/eq NH_3-N removed, is shown in Figure 27.

Studies made to determine the attrition of clinoptilolite in the presence of caustic solutions demonstrated that zeolite replacement must be considered in estimating the cost of ammonia removal. Attrition rates of 0.25, 0.35, and 0.55%/cycle were measured for exposure to pH 11.5, 12.0, and 12.5 solutions, respectively, in small columns. A loss of 1.6%/cycle was measured for exposure to a pH 13.3 solution using a batch method in which samples were shaken constantly.

The rinse requirement was investigated using a tap water, product water, and product water preceded by various amounts of 0.01 M HCl. While the use of acid reduced the rinse requirement, this reduction was insufficient to justify the added expense which would be incurred in purchasing and storing acid. It was recommended that ammonia-free product water be used for rinsing with the volume being required to reduce the column pH to 10.0 returned to upstream treatment processes and the volume required to further reduce the pH to 8.0 be returned to product water storage.

IX. PROCESS PERFORMANCE

GENERAL CONSIDERATIONS

In order to provide data on column performance under operating conditions, clinoptilolite columns were operated using sewage at SERL, the East Bay Municipal Utility District (EBMUD), and the Central Contra Costa Sanitary District (CCCSD). The objectives of these studies were: 1) to determine ammonia removals which could be expected in cyclic operation of clinoptilolite, 2) to ascertain the dependence of column performance upon various operational variables, and 3) to compare the performance of clinoptilolite using chemically different sewages. To meet these objectives, runs were made under a variety of conditions. Consequently, the conduct of the runs at each location and data particular to each test series are discussed with respect to the test location. Individual tests were designed so that runs continued to the approximate time of ammonia breakthrough. Flow rates were usually adjusted so that ammonia breakthrough would occur in 12 or 24 hours in order that columns could be attended to on a regular basis. Because of the necessity of providing a water which was relatively free of suspended solids for ion exchange processing, clinoptilolite columns were preceded by various upstream treatment processes which, in all cases, included chemical precipitation using lime. Details of the treatment system employed at each test location are discussed in Chapter VI. In addition, treatment schemes are mentioned briefly in the description of each test location in this chapter.

STUDIES AT THE SERL PILOT PLANT FACILITY

Process Operation

Tests made at the SERL pilot plant were more numerous than those at other locations because of the proximity of the facility to the laboratory. Consequently, these tests covered a longer period of time and were designed to furnish information concerning more aspects of column operation than were studies at other locations. For purposes of discussing these data, runs made have been divided into two parts: Series I runs made during the summer and early fall which included tests related to the dependence of column performance on operating variables such as previous regeneration and flow rate; and Series II runs made under slightly different conditions during the winter. Various combinations of upstream treatment processes were used in these studies. In Series I runs, previous treatment of the column influent included primary sedimentation,

activated sludge treatment, and chemical precipitation at pH 11.0; primary sedimentation, activated sludge treatment, and chemical precipitation at pH 9.5; primary sedimentation followed by chemical precipitation at pH 11.0; or primary sedimentation followed by chemical precipitation at pH 9.5. In all cases lime was used as the precipitant in the chemical treatment step. Chemically precipitated effluents were neutralized by recarbonation, then pumped to the column unit. In Series II runs previous treatment of the column influent included primary sedimentation, chemical precipitation at pH 11.0 using lime, and recarbonation. Supplementary data concerning pilot-plant operation appears in Appendix E. Cation compositions of the primary effluent for Series I and II operation are summarized in Table 17.

TABLE 17

CATION COMPOSITION OF PRIMARY EFFLUENT DURING SERL PILOT-PLANT RUNS[a]

Series	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ	pH
I	20.9	54.3[b]	9.3[b]	47	7	7.4
II	21.3	56.3	8.5[c]	44	8	7.3

[a]Values are average of daily composite samples taken during test period.

[b]Values from analysis of chemically precipitated effluents.

[c]Sample filtered prior to analysis.

Corresponding average values for column influent and effluent are shown in Table 18. Values in these tables are averages of daily composite samples taken during the test periods.

Wastewater Characterization. In addition to daily analyses made to monitor overall plant performance, tests were run to determine the nature of the primary effluent of the SERL treatment facility. Raw sewage was pumped to the pilot plant from a City of Richmond sewer and consisted primarily of sewage from a residential area. Hourly grab samples were taken from the effluent launder of the primary sedimentation basin for a 33-hr period. The results of these analyses are shown in Figure 1 and Table 1 of Appendix D.

Column Operation. All runs began with the columns regenerated with NaCl and NaOH or NaCl and $Ca(OH)_2$. The exhaustion phase continued for 12 hr/

TABLE 18

CATION COMPOSITION OF COLUMN INFLUENT AND EFFLUENT DURING SERL PILOT PLANT RUNS[a]

Runs[b]	Series	Prior Treatment	Sample	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ	pH[c]
1- 8	I	Activated sludge; Pptn. at pH 11.0	Influent	14.9	57.5	9.6	86	6	7.8
			Effluent	0.67	102	2.2	67	6	8.0
9-18	I	Activated sludge; Pptn. at pH 9.5	Influent	15.6	58.6	9.4	57	13	8.2
			Effluent	0.25	108	1.6	52	14	8.4
19-36	I	Primary effluent; Pptn. at pH 11.0	Influent	18.8	52.3	9.6	75	2	7.7
			Effluent	0.30	112	1.9	56	4	7.8
38-46	I	Primary effluent; Pptn. at pH 9.5	Influent	19.4	52.7	8.5	51	5	7.4
			Effluent	0.34	106	0.9	42	6	7.6
47-66	II	Primary effluent; Pptn. at pH 11.0	Influent	20.2	54.0	9.3	74	4	7.3
			Effluent	1.86	105	1.8	57	5	7.5

[a]Values are average of daily composite samples taken during each test period.

[b]Individual run data given in Table 19.

[c]Column influent pH adjusted by recarbonation.

run unless otherwise stated. With but one or two exceptions, flow rates of 7.5, 10, or 15 BV/hr were used. The bed depth in all cases was 3 ft. Results of runs made using a synthetic sewage similar to chemically treated SERL primary effluent reported in Chapter VII indicated that columns could be operated for 12 hr at 15 BV/hr without exceeding the ammonia breakthrough capacity. An influent sample for ammonia analysis was composited over the duration of each run. Four 3-hr composites of column effluents were taken during each run.

Column Performance — Series I

Ammonia removal data and other information relating to individual column operation are presented in Table 19. The average ammonia removal for these runs was 97.8% with an average influent NH_3-N concentration of 17.6 mg/ℓ and an average effluent concentration of 0.39 mg/ℓ. The influent varied from 13.0 to 22.2 mg/ℓ NH_3-N and the effluent varied from 0.02 to 1.90 mg/ℓ NH_3-N, the latter value being measured during the second run and was probably more the result of inexperience in column operation than of poor column performance. Effluent concentration averages were greater than 1 mg/ℓ NH_3-N for only three runs out of the 46 made in this part of the study. All of these occurred following regeneration using a salt concentration of 0.049 lb NaCl/gal at pH 11.5 (11.0 lb NaCl/cu ft, 0.34 lb NaOH/cu ft).

Because the column influent had not been previously filtered or treated for removal of soluble organics except for partial removals achieved when upstream treatment included the activated sludge process, attention was given to evidence of fouling. Here fouling is defined as a loss of ammonia capacity per unit of zeolite as opposed to physical losses in weight of material from the ion exchange bed. If fouling occurs it would result in increasing ammonia concentrations in the column effluent. Figure 31 shows the effluent ammonia concentrations for these runs plotted with respect to run number. Increasing run numbers correspond to increasing use of a particular column. Figure 31 indicates that if there is any noticeable trend, it is toward a decreasing ammonia leakage, and thus toward improved column performance. This is partially explained by the fact that columns were regenerated at a pH of 11.5 during the first runs and at a higher pH during later runs. It is also possible that through cyclic use additional pores in the zeolite were opened and became available for ion exchange.

Statistical analysis of these data using Student's t-test revealed that the effluent ammonia concentration can be expected to be equal to or less than 0.97 mg/ℓ NH_3-N 95% of the time. This value is indicative of ammonia removals which can be achieved when operating columns to incipient ammonia breakthrough. For full-scale operation where an excess of regenerant is not applied to the zeolite, higher values might result if adequate process control is not maintained. In order to closely control the ammonia concentration of the product water, it would be desirable to

TABLE 19

SERIES I OPERATIONAL DATA FOR STUDIES AT SERL PILOT PLANT

SERL Run	Flow[a] BV/hr	Col. No.	NH_3-N, mg/ℓ		NH_3-N Removed %	Previous Regeneration[c]				Prior Treatment
			Inf.	Eff.		pH	NaCl lb/gal	lb NaOH / cu ft	lb NaCl / cu ft	
1	15	2	15.1	0.77	94.9	11.2	0.049	0.34	11.0	Activated sludge;pptn. at pH 11.0
2	15	3	15.2	1.90	87.2	11.5	0.049	0.34	11.0	
3	15	2	15.2	1.10	92.7	11.3	0.049	0.34	11.0	
4	10	1	15.2	0.12	99.3	11.5	0.049	0.34	11.0	
5	15	2	15.2	0.82	94.6	11.5	0.049	0.34	11.0	
6	10	3	13.6	0.87	93.4	11.5	0.049	0.34	11.0	
7	15	2	13.6	0.45	97.0	11.5	0.049	0.34	11.0	
8	7.5[b]	1	15.6	0.06	99.4	11.5	0.049	0.34	11.0	
9	7.5	3	15.2	0.02	99.9	11.6	0.049	0.34	11.0	Activated sludge; precipitation at pH 9.5
10	10	2	15.2	0.72	95.4	11.5	0.049	0.34	11.0	
11	10	1	15.7	0.02	99.9	11.5	0.049	0.34	11.0	
12	15	2	15.7	0.56	96.2	11.5	0.049	0.34	11.0	
13	10	3	15.4	0.12	99.4	11.5	0.049	0.34	11.0	
14	15	2	15.4	0.42	97.4	11.5	0.049	0.34	11.0	
15	12	1	13.0	0.23	98.5	11.5	0.049	0.34	11.0	
16	15	2	13.0	0.02	99.8	11.5	0.049	0.34	11.0	
17	9	3	18.6	0.28	98.4	11.5	0.049	0.34	11.0	
18	15	2	18.6	1.09	94.1	11.5	0.049	0.34	11.0	
19	10	2	18.6	0.28	98.4	11.5	0.10	0.34	22.5	Primary; precipitation at pH 11.0
21	15	1	18.9	0.67	96.3	11.5	0.10	0.34	22.5	
22	15	2	18.9	0.29	98.4	11.5	0.10	0.34	22.5	
23	10	3	16.9	0.11	99.4	11.5	0.10	0.34	22.5	
24	15	2	16.9	0.27	98.2	11.5	0.10	0.34	22.5	
25	10	1	21.0	0.22	99.0	11.5	0.10	0.34	22.5	
26	15	2	21.0	0.43	98.1	11.5	0.17	0.34	38.2	
27	15	2	17.5	0.20	98.9	11.5	0.24	0.34	54.0	
28	10	3	18.8	0.13	99.5	11.5	0.17	0.34	38.2	
29	15	2	18.8	0.25	98.9	11.5	0.24	0.34	54.0	
30	10	1	17.9	0.19	98.9	11.5	0.24	0.34	54.0	
31	15	2	17.9	0.11	99.4	12.3	0.17	2.48	38.2	
32	10	3	20.0	0.23	99.0	12.3	0.17	2.48	38.2	
33	15	2	20.0	0.49	97.5	12.4	0.10	2.48	22.5	
34	10	1	19.5	0.18	99.0	12.3	0.10	2.48	22.5	
35	15	2	19.5	0.31	98.5	12.4	0.049	2.48	11.0	
36	7.5[b]	3	19.4	0.62	96.9	12.4	0.049	2.48	11.0	
38	15	2	16.6	0.28	98.2	12.4	0.24	2.48	54.0	Primary; precipitation at pH 9.5
39	10	1	20.0	0.17	99.0	12.5	0.24	2.48	54.0	
40	15	2	20.0	0.30	98.5	12.0	0.10	1.02	22.5	
41	10	3	22.0	0.44	98.2	12.0	0.10	1.02	22.5	
42	15	2	19.5	0.31	98.5	12.0	0.17	1.02	22.5	
43	15	1	22.2	0.15	99.5	12.0	0.17	2.48	38.2	
44	15	2	18.1	0.18	98.9	11.5	0.049	1.02	11.0	
45	15	1	18.0	0.27	98.3	11.4	0.17	1.02	38.2	
46	15	2	19.0	0.47	97.4	12.5	0.17	2.48	38.2	

[a]All runs were 12 hr in length except as noted; [b]Runs 24 hr long; [c]Regenerant volume was 30 BV for all runs.

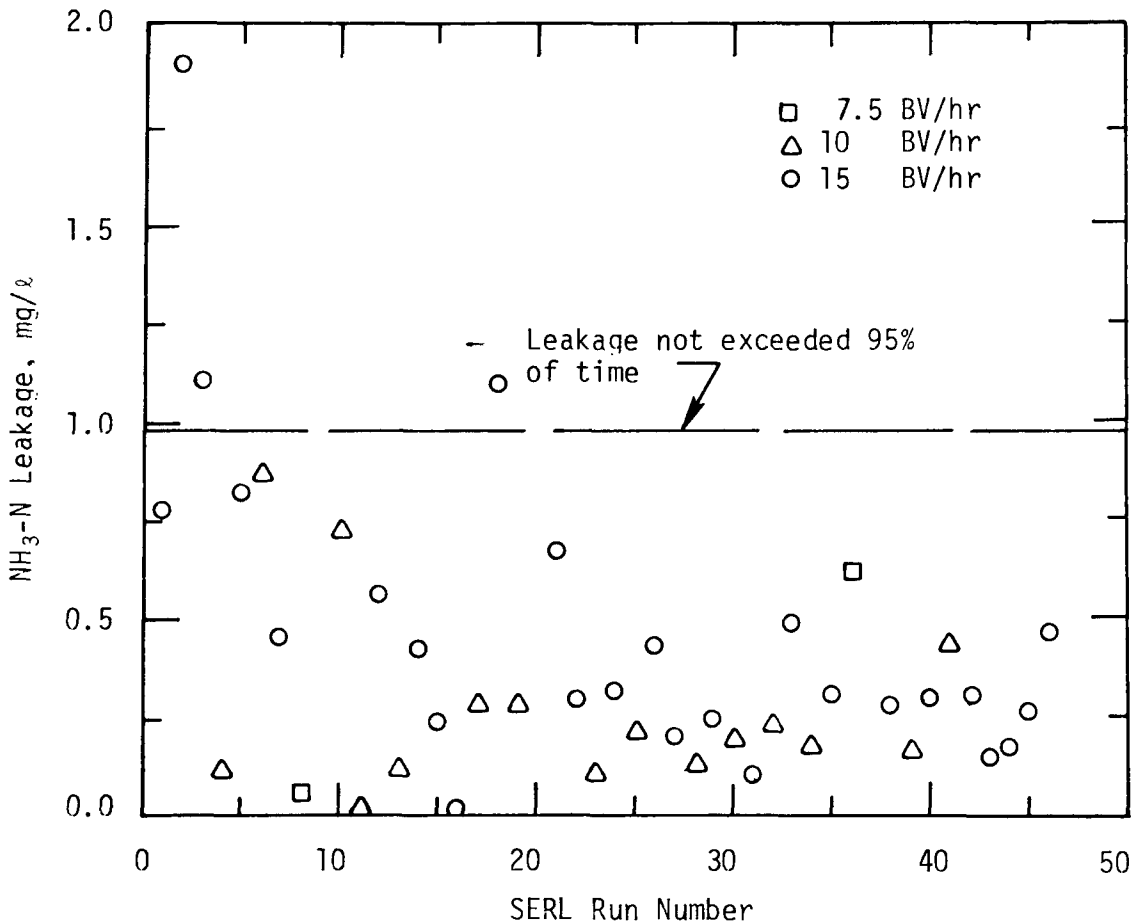


FIGURE 31. ENVELOPE OF AMMONIA LEAKAGE IN TESTS AT SERL PILOT PLANT

have automatic controls capable of rotating zeolite beds from the exhaustion to regeneration modes whenever a preset ammonia concentration in the product water is exceeded. It is believed control could be achieved using a residual chlorine analyzer. Increasing ammonia concentrations in the column effluent would result in an increased chlorine demand which, when sensed by the chlorine analyzer, would initiate rotation of ion exchange beds from the service to regeneration mode and place freshly regenerated beds into the service mode. Inasmuch as chlorination is likely to be required as a final treatment step for water to be reused, this feature could be incorporated into plant design with little additional expense.

Correlation of Column Performance to Operating Variables. Because several operating variables were changed during the course of the study, it is difficult to isolate the precise effect of flow rate and conditions of the previous regeneration on column performance. However, the runs in Series I were made under relatively uniform conditions judged by the column influent and effluent compositions. From the wide range of operating parameters used in these runs, it was evident that some had a more pronounced effect on column performance than others.

Ion exchange theory predicts that leakage through a column will become greater as the flow rate is increased. To determine the effect of flow rate on ammonia leakage, effluent ammonia concentration for the first 90 BV throughput were averaged for each flow rate. It was necessary to use a throughput of 90 BV because this was the volume processed at the lowest column flow (7.5 BV/hr) during the standard 12-hr runs. These results, presented in Table 20, show that effluent ammonia concentrations were nearly identical for each flow. These results also show that effluent ammonia concentrations as low as 0.22 to 0.26 mg/ℓ NH_3-N can be consistently produced at these flow rates for a throughput of 90 BV. These values compare to an average effluent concentration of 0.39 mg/ℓ NH_3-N for the entire length of these runs shown in Table 19. The 90 BV throughput for which these values were averaged was well short of the

TABLE 20

EFFECT OF COLUMN FLOW RATE ON AMMONIA LEAKAGE

Column Flow Rate BV/hr	Runs Made at This Flow	Average Leakage to 90 BV, mg/ℓ NH_3-N
7.5	3	0.22
9	1	0.26
10	13	0.20
12	1	0.06
15	26	0.22

ammonia breakthrough in each case, and indicates that exchange kinetics did not change significantly for this range of flow rates. However, the leakage would increase at higher flow rates as the exchange kinetics must become less favorable and the resulting breakthrough curves flatter.

Another factor which affects column performance is the nature of the previous regeneration. Figure 32 shows the variation of ammonia leakage with regeneration level. Values are shown only for runs made at a flow rate of 15 BV/hr and are effluent averages for the entire length of run (180 BV throughput). Regeneration levels were calculated for 30 BV of regenerant used in each run. Thus, for these runs a regenerant salt concentration of 0.10 lb NaCl/gal corresponded to a regeneration level of 22.5 lb NaCl/cu ft of zeolite. Salt concentrations for other regenerant levels may be calculated proportionally from this value. Figure 33 illustrates the effect of regenerant pH on ammonia leakage. Again, all points are effluent averages for 180 BV throughput at a flow of 15 BV/hr. The relatively high leakage for 11.0 lb NaCl/cu ft in Figure 32 and for pH 11.5 in Figure 33 reflect high effluent values for runs 2, 3, and 4 (cf. Table 19). The high effluent ammonia value for regeneration using 22.5 lb NaCl/cu ft at pH 12.5 appears to be inconsistent with other values in Figures 32 and 33. Because only one regeneration was made under these conditions (run 33), it is quite likely that this value is not entirely representative of the performance which can be expected for operation under these conditions.

Both Figures 32 and 33 illustrate that a small improvement in performance may be achieved by using higher regeneration levels. However, this improvement is small and probably would not be an important consideration in process design. These data indicate that while stable column performance is possible at any of these regeneration levels, the clinoptilolite is more thoroughly regenerated using higher regeneration levels.

Column Performance — Series II

Series I and II runs at SERL were made under approximately the same conditions except that Series II runs were made in the winter, while Series I runs were made during the summer and early fall. Prior treatment of the column influent for Series II runs included primary sedimentation, chemical precipitation at pH 11.0 using lime, and recarbonation.

Data summarizing Series II operation at SERL are shown in Table 21. Ammonia removal during these runs averaged 91.5% which was noticeably less than removals achieved in Series I runs. Effluent ammonia concentrations averaged 1.7 mg/ℓ NH_3-N for 180 BV throughput with an average influent concentration of 20.2 mg/ℓ NH_3-N. Effluent values ranged from 0.35 to 5.48 mg/ℓ NH_3-N, while influent concentrations ranged from 16.1 to 23.9 mg/ℓ NH_3-N. The high effluent concentration for run 66 was a result of incomplete ammonia elution during the previous regeneration.

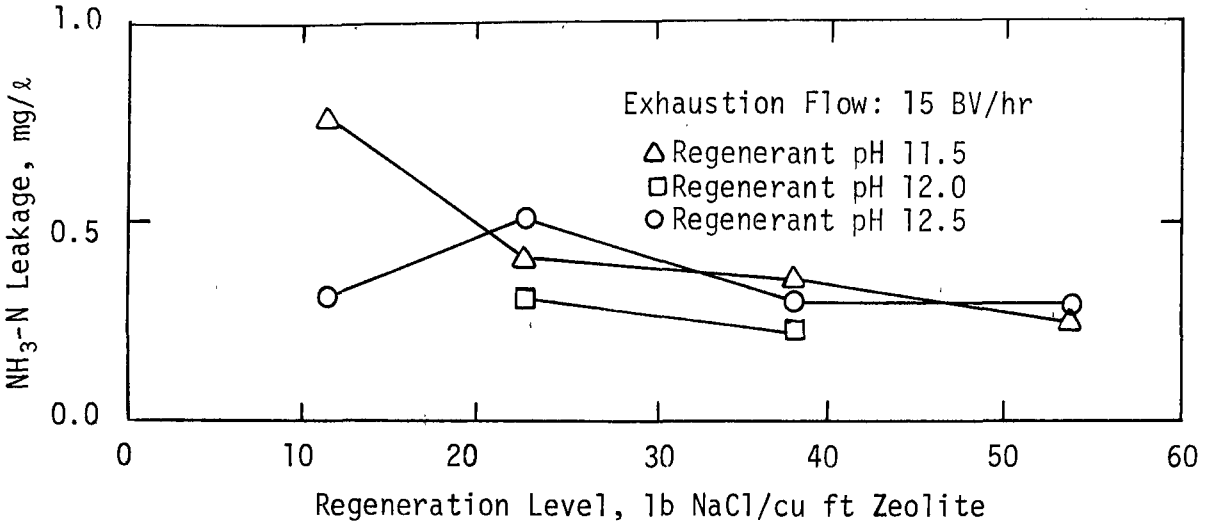


FIGURE 32. VARIATION OF AMMONIA LEAKAGE WITH AMOUNT OF SALT USED IN PREVIOUS REGENERATION

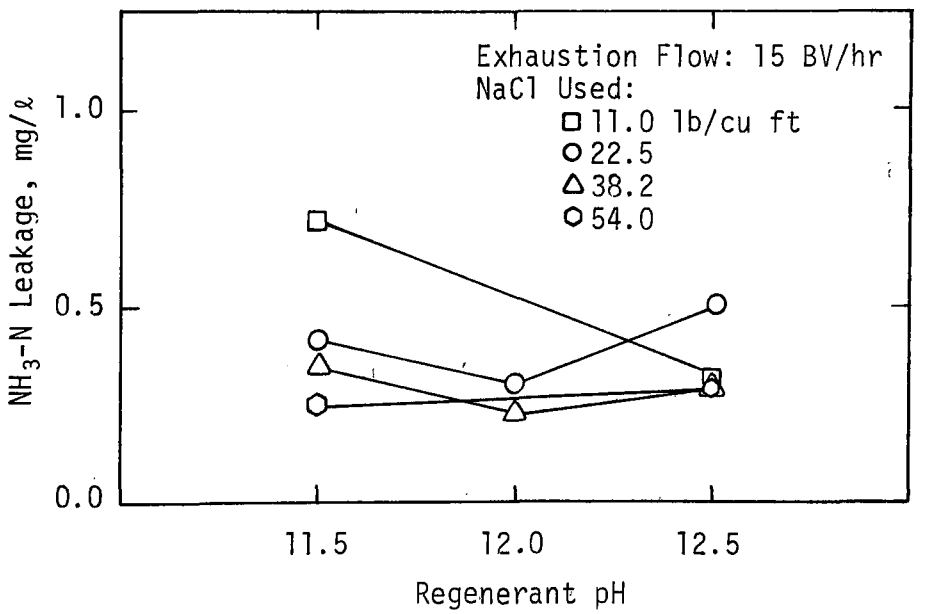


FIGURE 33. VARIATION OF AMMONIA LEAKAGE WITH pH OF PREVIOUS REGENERATION

TABLE 21

SERIES II OPERATIONAL DATA FOR STUDIES AT SERL PILOT PLANT

SERL Run	Flow[a] BV/hr	Col. No.	NH_3-N, mg/ℓ				Previous Regeneration				
			Inf.	Eff. 90 BV Avg.	Eff. 135 BV Avg.	Eff. 180 BV Avg.	pH	NaCl lb/gal	Volume Regen. Used, BV	lb NaCl / cu ft	lb NaOH or $Ca(OH)_2$ / cu ft
47	15	1	21.3	1.25	3.52	5.48	12.5	0.10	30	22.5	2.48
48	15	2	13.4	0.45	0.56	1.31	12.5	0.10	30	22.5	2.48
49	15	1	19.3	0.12	0.26	1.97	12.5	0.10	30	22.5	2.48
50	15	2	16.1	0.07	0.09	0.35	12.2	0.73	30	164	2.48
51	15	1	20.0	0.29	1.37	3.30	12.5	0.10	30	22.5	2.48
52	15	2	16.3	0.33	0.31	0.47	12.5	0.73	30	164	2.48
53	7.5	1	20.2	0.31	0.46	0.98	12.0	0.049	30	11.0	1.02
54	7.5	2	20.8	0.27	0.28	0.40	12.0	0.24	30	54.0	1.02
55	15	2	18.6	-	0.67	0.67	12.5[b]	0.10	13	9.75	1.08
56	15	1	20.8	0.45	0.47	1.07	11.5	0.73	30	164	0.34
57	15	2	17.8	0.39	0.78	1.46	12.5[b]	0.10	13	9.75	1.08
58	15	1	22.3	0.43	0.77	2.03	12.4	0.73	30	164	2.48
59	15	2	18.8	1.15	1.91	-	12.5[b]	0.10	13	9.75	1.08
60	15	1	22.0	0.36	0.54	1.46	12.5	0.00	30	0	2.48
61	15	2	22.0	0.36	1.01	-	12.5[b]	0.10	13	9.75	1.08
62	15	2	23.9	0.53	1.02	-	12.5[b]	0.10	13	9.75	1.08
63	15	1	19.9	0.24	0.51	1.82	12.5	0.10[c]	30	22.5	2.48
64	15	2	22.0	0.25	0.23	0.53	12.5[b]	0.10	13	9.75	1.08
66	20	1	22.9	2.42	3.03	4.06	8.2	0.10	30	22.5	0

[a]Throughput for all runs was 180 BV.

[b]Regenerant pH raised using lime.

[c]Regenerant also contained 0.046 lb $CaCl_2$/gal.

In order to obtain a better estimate of ammonia leakage for Series II runs, the average effluent ammonia concentration for the first 90 and 135 BV throughput was calculated. The effluent average over 90 BV was 0.40 mg/ℓ NH_3-N and for 135 BV was 0.94 mg/ℓ NH_3-N. Effluent values for the first 90 BV throughput were identical to the overall effluent average for Series I runs. However, ammonia leakage for Series II runs increased significantly for throughputs of 135 BV or more. Ammonia analyses for Series I runs, including results of grab samples taken at the end of some runs, showed that the effective ammonia capacity to 1 mg/ℓ NH_3-N breakthrough was equaled or exceeded in many runs. Higher leakages for Series II runs, made at the same flow and for the same length of time as Series I runs, indicated that some difference existed between Series I and II runs which resulted in the effective ammonia exchange capacity of the zeolite being exceeded to a significantly greater degree during Series II runs. While the influent ammonia concentration was somewhat higher for Series II runs (20.2 mg/ℓ NH_3-N for Series II compared to values of 14.9, 15.6, 18.8, and 19.4 mg/ℓ NH_3-N for the four phases of Series I operation), higher effluent ammonia values were not consistently observed for runs having the highest influent ammonia concentrations. Examination of Table 18 shows that competing cation concentrations were very similar for all groups of runs made at SERL. Although these two groups of runs were made at different times of the year, seasonal temperature fluctuations are not great in the San Francisco area, and so these differences would not be expected on the basis of temperature changes. Thus, no explanation for the poor performance of Series II runs may be offered at this time. However, these results do indicate the need to identify more completely the factors which influence ammonia leakage and the ammonia exchange capacity of clinoptilolite.

EAST BAY MUNICIPAL UTILITY DISTRICT STUDY

Process Operation

Studies at the East Bay Municipal Utility District were made utilizing a 20-gpm pilot plant operated by EBMUD personnel for the preparation of column influent. This treatment system included primary sedimentation, chemical coagulation using lime, recarbonation, and filtration prior to ammonia removal.

Wastewater Characterization. The EBMUD plant treats an average wastewater flow of 80 mgd (average for period July 1, 1969 to June 30, 1970) collected from Oakland and surrounding communities. A significant amount of storm runoff enters the system during wet weather. In addition, the system receives some infiltration of brackish water because of the proximity of the service district to San Francisco Bay. The results of analyses run on 2-hr composites of EBMUD primary effluent are shown in Figure 2 and Table 2 in Appendix D.

Column Operation. Columns used in these studies were regenerated using 10 BV of regenerant having a pH of approximately 12.5 and a salt concentration of 0.17 lb NaCl/gal. This corresponded to a regeneration level of 12.7 lb NaCl/cu ft of zeolite and approximately 0.8 lb NaOH or $Ca(OH)_2$/cu ft. As in previous studies, a bed depth of 3 ft was used for all runs. Initially runs were 18 hr long at a flow of 10 BV/hr. However, most runs were made for 24-hr periods using flow rates ranging from 5 to 7.5 BV/hr. Supplementary data concerning pilot-plant operation and column performance appear in Appendix E. Cation analyses of the primary effluent and the column influent appear in Table 22. It is evident that the cation concentration of this sewage was significantly higher than that at SERL described in Tables 17 and 18. Rain which

TABLE 22

CATION COMPOSITION OF EBMUD WASTEWATER

Sample	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ	pH
Primary effluent[a]	19.2	183	33.4	39	11	7.1
Primary effluent[b,c]	11.6	96[d]	16.9[d]	39	9	7.2
Lime precipitated effluent[b,c]	11.5	96	16.9	104	7	7.4
Column effluent[c]	0.71	153	2.7	88	4	7.5

[a]Analyses made during a period of no rain. Values are average of 2-hr samples taken over a 24-hr period.

[b]Analyses made during a period of some rain.

[c]Values are average of daily composite samples taken during test period.

[d]Values from analysis of precipitated effluent.

occurred throughout the testing period was responsible for many fluctuations in sewage strength. Evidence of this is apparent in comparing ammonia concentrations of the two primary effluent values — one which was taken over a 24-hr period during dry weather prior to the beginning of column operation and the other averaged from daily composite samples taken during the testing period when much rain occurred. The large increase in calcium concentration through the chemical treatment step was partially due to floc carried over from the clarification basin and partially redissolved after recarbonation.

Column Performance

Column performance data for the EBMUD tests are presented in Table 23. The average ammonia removal for these runs was 94.0% with an influent average of 11.5 mg/ℓ NH_3-N and an effluent average of 0.71 mg/ℓ NH_3-N. Poor performance in runs 1 and 2 was probably a result of high competing cation concentrations in the column influent, since heavy rains had not yet begun when these runs were made. The cation concentration of a water will influence column performance in several ways. First, the effective ammonia capacity of the zeolite will decrease with increasing concentrations of competing cations as discussed in Chapter VII. Second, the leakage of ammonia preceding the actual breakthrough will be greater for waters having higher competing cation concentrations. In addition an increase in ammonia concentration will result in a decreased throughput to ammonia breakthrough. While the increased ammonia concentration will increase the effective ammonia exchange capacity of the zeolite, this increase will not be sufficient to remove the added ammonia.

Regeneration in these tests was planned to be representative of the procedure which might be used in full-scale operation. From regeneration tests reported in Chapter VIII, it was found that 10 BV of regenerant having a salt strength of 0.17 lb NaCl/gal and a pH of 12.5 would be required to regenerate these columns. This corresponded to the use of 12.7 lb NaCl/cu ft and approximately 0.8 lb NaOH or $Ca(OH)_2$/cu ft. This level of regeneration generally resulted in satisfactory column performance during these runs. However, beginning with run 7, the effluent ammonia concentration increased in runs made in Column 1 until the average effluent concentration was 2.19 mg/ℓ NH_3-N for run 11. In this case successive runs made at 7.5 BV/hr combined with a low regenerant pH resulted in a buildup of ammonia in the zeolite. Higher regenerant pH in subsequent runs resulted in more complete ammonia elution from the column. Lower effluent ammonia concentrations in later runs were a result of improved regeneration as well as a reduced throughput in runs 15 and 17.

CENTRAL CONTRA COSTA COUNTY SANITARY DISTRICT STUDY

Process Operation

Column influent for these tests was pretreated by partial primary sedimentation (15 min detention time), chemical coagulation at pH 10.5–10.8 using lime, and recarbonation.

Wastewater Characterization. The Central Contra Costa Sanitary District plant treats an average flow of 20 mgd consisting primarily of sewage from domestic and commercial origin. Tests at CCCSD were run during dry weather, so no stormwater flow was present in the sewage during the period of study. Results of analyses made on 2-hr composites of CCCSD primary effluent are shown in Figure 3 and Table 3 in Appendix D.

TABLE 23

OPERATIONAL DATA FOR STUDIES AT EBMUD PILOT PLANT

Run	Flow BV/hr	Column	NH_3-N, mg/ℓ		NH_3-N Removed %	Length of Run hr	Previous Regeneration[a]	
			Inf.	Eff.			pH	Caustic[b]
EBMUD-1	10.0	1	10.7	1.33	87.8	18	12.5	Lime
2	10.0	2	14.3	3.2	77.6	18	12.5	Lime
3	4.7	1	5.3	0.41	92.4	24	12.2	NaOH
4	5.7	2	8.5	0.32	96.5	24	12.2	NaOH
5	6.1	1	8.5	0.26	96.5	24	12.2	NaOH
6	6.1	2	8.8	0.31	96.6	24	12.2	NaOH
7	7.3	1	8.1	0.51	93.8	24	12.2	NaOH
8	7.5	2	14.4	0.29	97.9	24	12.4	NaOH
9	7.5	1	12.6	0.83	93.6	24	12.4	NaOH
10	5.1	2	16.5	0.62	96.4	24	12.2	NaOH
11	7.5	1	15.8	2.19	86.1	23	12.2	NaOH
12	7.5	2	16.1	0.19	98.8	23	12.4	NaOH
13	7.8	1	15.1	0.56	96.0	23	12.4	NaOH
14	7.7	2	13.3	0.31	97.7	24	12.4	NaOH
15	5.0	1	11.2	0.35	96.4	22	12.5	NaOH
16	5.1	2	9.7	0.76	91.8	24	12.8	NaOH
17	5.1	1	12.0	0.25	98.3	24	12.8	NaOH
18	10.0	2	8.3	0.35	95.2	24	12.8	NaOH
19	10.0	1	9.7	0.55	93.8	22	12.6	Lime

[a]Regeneration with 10 BV regenerant containing 0.17 lb NaCl/gal which corresponded to the use of 12.7 lb NaCl/cu ft.

[b]Caustic added for pH adjustment was approximately 0.8 lb NaOH or $Ca(OH)_2$/cu ft.

Column Operation. All runs made in this study were 24 hr in duration at a flow of approximately 5 BV/hr. The clinoptilolite depth was 3 ft. Regeneration was made using 20 BV of regenerant containing 0.17 lb NaCl/gal at a pH of 12.0. This corresponded to a regeneration level of 25.4 lb NaCl/cu ft of zeolite and of approximately 0.6 lb $Ca(OH)_2$/cu ft. This amount of regenerant was calculated based on the results of regeneration tests reported in Chapter VIII. In all runs regenerant solutions were made using lime as the source of caustic. Data concerning overall pilot-plant performance appear in Appendix E. The average cation concentrations of the waste at various stages of treatment based on daily composite samples are shown in Table 24.

TABLE 24

CATION COMPOSITION OF CCCSD WASTEWATER[a]

Sample	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ	pH
Partially settled sewage	21.4	108	11.6	58	9	7.2
Lime precipitated effluent	19.5	107	11.5	70	6	7.1
Column effluent	0.50	135	3.0	60	6	7.3

[a]Values are average of daily composite samples taken during test period.

Column Performance

Column performance during the CCCSD study is summarized in Table 25. Poor performance in run 6 was a result of an increase in pH of the column influent due to an inadequate reserve of CO_2. The 24-hr composite sample of column influent for this period had a pH of 9.1 (cf. Appendix E). The four-column effluent samples taken over the period of the run contained ammonia concentrations of 0.64, 1.23, 13.0, 22.1, and 24.2 mg/ℓ NH_3-N compared to an influent concentration of 22.9 mg/ℓ NH_3-N. This indicates that the pH increased throughout the run resulting in a progressive deterioration of effluent quality. The concentration of the last effluent sample exceeded the influent concentration average indicating that desorption of ammonia may have occurred during part of the run. This incident illustrates the importance of column influent pH control in achieving high levels of ammonia removal. In all runs at SERL this was readily achieved by the feedback control of the lime feeding equipment and careful surveillance over recarbonation.

TABLE 25

COLUMN PERFORMANCE FOR STUDIES AT CCCSD[a]

CCCSD Run	Flow[b] BV/hr	Column	NH_3-N, mg/ℓ		NH_3-N Removed %
			Inf.	Eff.	
1	6.7	2	18.5	1.18	93.5
2	5.7	1	19.1	0.52	97.5
3	5.0	2	20.2	0.26	98.5
4	5.0	1	20.1	0.25	99.0
5	5.0	2	19.3	0.27	98.5
6	5.0	1	22.9	9.25[c]	59.9

[a]Regeneration in all runs was with 20 BV regenerant having a salt concentration of 0.17 lb NaCl/gal and a pH of 12.0. This corresponded to the use of 25.4 lb NaCl/cu ft and approximately 0.6 lb $Ca(OH)_2$/cu ft.

[b]All runs were 24 hr long.

[c]Effluent pH averaged over length of run was 9.1.

Disregarding run 6, ammonia removal in this study averaged 97.5% with an average effluent concentration of 0.50 mg/ℓ NH_3-N and an average influent concentration of 19.5 mg/ℓ NH_3-N. Effluent concentrations ranged from 0.25 to 1.18 mg/ℓ NH_3-N, and influent concentrations ranged from 18.5 to 20.2 mg/ℓ NH_3-N. The high effluent concentration observed in run 1 follows the pattern of the tests made at other locations. For the initial runs made at SERL, high concentrations in the first few runs were originally attributed to inexperience in column operation. However, the recurrence of high values in initial tests at other locations implies that other factors were involved. Since all clinoptilolite used was dry prior to the beginning of tests in each location, there is a possibility that several days are required for water to completely displace air initially present in the zeolite pores. Air present in the pore spaces would effectively block the entrance of cations to exchange sites and reduce the exchange capacity accordingly.

OVERALL COLUMN PERFORMANCE

Clinoptilolite columns were operated in three different locations using chemically treated wastewaters. The overall level of performance achieved in these tests was an ammonia removal of 95.7%. The effluent ammonia concentration average for all runs except run 6 at CCCSD was

0.75 mg/ℓ NH_3-N. This average is for the total throughput for all runs which ranged from 120 to 180 BV except for one run which was 90 BV in length. Effluent averages for individual locations were 0.39 mg/ℓ NH_3-N for Series I runs at SERL, 0.71 mg/ℓ NH_3-N for runs at EBMUD, and 0.50 mg/ℓ NH_3-N for runs at CCCSD excluding CCCSD run 6. An average column influent pH of 9.1 for run 6 at CCCSD resulted in an ammonia removal of only 60%, illustrating the importance of pH control in achieving high removals of ammonia. Runs made in these studies were designed to end short of ammonia breakthrough. However, high effluent concentrations were experienced in Series II runs at SERL. In these runs the effluent ammonia concentration averaged 1.7 mg/ℓ NH_3-N for 180 BV throughput, but only 0.40 mg/ℓ NH_3-N for the first 90 BV and 0.94 mg/ℓ NH_3-N for the first 135 BV indicating that higher ammonia removals could have been achieved had these runs been stopped sooner. Removals achieved in these tests are indicative of performance which could be expected from full-scale plants.

Changes in the cation composition of water treated using clinoptilolite should be considered because of the effect these changes might have on potential reuse of the product water. Cation compositions for wastes at the various test locations are included in Tables 18, 22, and 24. Inspection of these values shows that, on an overall average, sodium increased from 78 to 125 mg/ℓ because regeneration was made using sodium as the counter ion. Potassium decreased from an average of 11.7 mg/ℓ in the column influent to 2.3 mg/ℓ in the effluent. The calcium concentration of the influent averaged 80 mg/ℓ and decreased to 67 mg/ℓ through the column. However, practically no decrease was observed in runs at CCCSD due to the use of lime for regenerant preparation. In tests where NaOH was used for regenerant preparation, the total hardness was reduced from 232 to 190 mg/ℓ as $CaCO_3$. This reduction might be beneficial depending on the particular waste treatment objectives. However, no softening would be realized if lime were used as a regenerant.

Overall influent and effluent magnesium concentrations did not differ over the period of these tests. While some removal was noticed in runs at EBMUD, small increases in magnesium through the column at SERL offset this in the overall average. This was probably due to entrapment of precipitated $Mg(OH)_2$ particles in the column during regeneration which subsequently redissolved during exhaustion. This precipitate was probably a result of fine particles in the regenerant solution which did not settle before the regenerant was used. This is corroborated by the small rise in pH observed in all test locations. The rise in pH, which averaged 0.2 pH units, was probably also due to exchange of hydrogen into the zeolite and to a shift in the NH_3-NH_4 equilibrium caused by the removal of ammonium ions from solution.

X. DESIGN CONSIDERATIONS AND COST ANALYSIS

Because the primary objective of engineering design is to find the most economically feasible solution to a particular problem, it is imperative that design and economic considerations be discussed together. It is the purpose of this chapter to apply the results obtained in the experimental phases of the study to the design of a clinoptilolite ammonia exchange plant and to estimate treatment costs associated with the construction and operation of such a plant.

A necessary precondition for the estimation of process costs is the existence of reasonably accurate data describing process performance for all conditions to be considered in the cost analysis. Even when such data are available, much time would be required to analyze all possible alternative methods of process operation to determine the least cost method of operation. An additional consideration which may significantly affect the estimated cost of a unit process is the possibility of complementary operation of several processes in the treatment system. However, in order to take advantage of savings which might result from such operation, it is necessary to know the specific processes to be included in the total design. In order to keep this analysis generally applicable to as many design situations as possible, a minimum of assumptions have been made concerning other treatment processes which might be present in the treatment system. On the other hand, it should be kept in mind that the ammonia exchange process is most likely to operate in conjunction with processes which efficiently remove organic carbon and phosphorus and that these are most likely to include a chemical precipitation step and probably, but not necessarily, a biological one. As a further point, the removal of nitrogen by a zeolite exchanger provides the additional benefit of a high degree of clarification by filtration. It is likely that objectives of effluent clarity would be desired in any system where high performance removal of carbon, phosphorus, and nitrogen was required.

PROCESS DESIGN AND OPERATING PROCEDURE

The design of a clinoptilolite ion exchange unit will be illustrated by considering a 10-mgd waste flow containing an influent ammonia concentration of 20 mg/ℓ NH_3-N. The general properties and operating conditions for clinoptilolite are summarized in Table 26. These values were the optimum operating conditions determined during the experimental phases of the study. Desirable particle sizes and exhaustion flow rates were determined in previous studies by Mercer [13,14,37]. Suggested bed depths were based on breakthrough curve characteristics and headloss

measurements. The gross and net particle specific gravities shown in Table 26 reflect the internal porosity of the individual clinoptilolite particles.

TABLE 26

PROPERTIES AND OPERATING CONDITIONS FOR CLINOPTILOLITE

Item	Value
Total exchange capacity[a]	
Milliequivalents/gram	1.9[b]
Equivalents/liter	1.4
kilograins/cu ft	30.6
Physical properties	
Gross particle specific gravity	1.6
Net particle specific gravity	2.4
Bulk density, lb/cu ft	47[a]
Proposed operating conditions	
Exhaustion flow rate, BV/hr	15
Bed depth, in.	36–72[c]
Regenerant strength, lb NaCl/gal	d
Regenerant flow rate, BV/hr	15
Rinse volume, gal/cu ft	80
Backwash rinse rate, 50% bed expansion, gal/sq ft-min	11
Headloss, ft/ft at 5.6 gal/sq ft-min	0.7

[a]Ammonia exchange capacity will usually be less than this value depending on water composition.

[b]Dry weight.

[c]Greater depths might be used, but allowance must be made for greater headloss.

[d]See Figures 27, 34, and 35, and Table 13.

Most literature concerning the design of ion exchance installations has been based on the use of cylindrical, steel exchange vessels. While this type of unit is feasible for softening and demineralization of industrial process and boiler feed water, gravity flow units constructed from reinforced concrete would be less costly for treating a flow of 10 mgd. Concrete is suitable for use as ion exchange vessels for this process as it is resistant to both NaCl and lime [86]. The use of this

type unit in municipal water softening plants has been reported by Hughes and Crane [87]. An example of this type of construction is the 200-mgd F.E. Weymouth Filtration and Softening Plant located at LaVerne, Calif. [88,89]. Although gravity ion exchange units are mentioned in water treatment texts, little information is given concerning specific design criteria [90,91]. However, basic construction details of this type of structure should be much the same as for rapid sand filters.

Because the cost of ion exchange processing bears a direct relation to the level of performance required, the effluent water quality is an important consideration in estimating process costs. While the treatment objectives concerning nitrogen removal will vary with each specific case, it is reasonable to assume that at least 90% removal of nitrogen will be required where the presence of nitrogen impairs water quality. As the basis of this estimate, the performance objective will be 95% removal of ammonia assuming the influent concentration to be 20 mg/ℓ NH_3-N. According to the process performance data in Chapter IX, this is a realistic objective which can be consistently met in cyclic operation. However, for design purposes complete ammonia removal by the exchanger will be assumed. This will simplify calculations somewhat and will result in a more conservative design. For a situation in which less treatment is required, split treatment could be used to produce a desired effluent concentration. In this case treatment costs would be proportionately less.

In order to calculate the size of the ion exchange unit needed, the ammonia capacity of the clinoptilolite must be determined from the characteristics of the influent water. While this is most accurately determined in pilot studies, the ammonia capacity of clinoptilolite can be estimated from Figure 12 if the cationic strength of the wastewater is known. Assuming that the influent water has a cationic strength of 0.006 moles/ℓ, the breakthrough ammonia capacity of the clinoptilolite will be approximately 0.25 meq/g for a 3-ft bed; the capacity to saturation will be approximately 0.44 meq/g. A greater effective ammonia capacity can be realized by increasing the depth of the zeolite bed. However, increased bed depths result in greater headloss and require that units be built to accommodate the greater head requirement. The use of a 6-ft bed would result in greater ammonia capacity per unit of exchanger and while requiring a deeper structure, the additional cost would be nominal. Assuming that 3 ft of the zeolite bed will have an ammonia exchange capacity equal to 0.25 meq/g and that the remaining 3 ft will have a capacity equal to 90% of the saturation capacity or 0.40 meq/g, the 6-ft bed will have an effective capacity of 0.32 meq/g (equivalent to 6.6 eq/cu ft and 5.1 kgr/cu ft).

The zeolite volume required to treat a 10-mgd waste flow at 15 BV/hr (1.9 gpm/cu ft) is 3650 cu ft. Assuming complete removal of ammonia, the throughput to ammonia breakthrough is 165 BV and a run length of 11 hr. Allowing 2 hr down time per cycle for regeneration and rinsing (one to one and one quarter hours should actually be sufficient), the

zeolite volume must be increased proportionately to 4300 cu ft to accommodate the total design flow. Using four units, each having the dimensions 12 ft x 15 ft x 6 ft deep, the total zeolite volume is 4320 cu ft.

Regeneration procedure and the choice of regenerant composition will be discussed later in this chapter. However, for purposes of determining the volume of reusable water produced by the process, it is assumed that no more than 15 BV of regenerant will be required if regenerant is not reused and that only 0.5 BV of regenerant will be consumed per cycle if regenerant is reused. Column rinsing requirements are summarized in Table 16. To reduce the pH to 10, 11 BV of product water are required which would be returned to upstream treatment processes. Further rinse water required would be returned to product water storage as the slightly higher pH and NaCl concentration of this water should not be detrimental to product water quality. Because both regeneration and rinsing are accomplished upflow, no provision was made for a separate backwashing step prior to regeneration. The effective throughput is 150 BV/cycle when regenerant is wasted and 165 BV/cycle when regenerant is reused. The liberal estimate of down time per cycle includes sufficient time for reprocessing of rinse water returned to upstream treatment. The volume of product water produced is 9.1 mgd when regenerant is wasted and slightly less than 10.0 mgd when regenerant is reused. Operating characteristics of this plant are described in Table 27.

TABLE 27

OPERATING CHARACTERISTICS FOR A 10-mgd CLINOPTILOLITE ION EXCHANGE FACILITY

Operational Feature	Value
Design Flow Rate	15 BV/hr
Ammonia Exchange Capacity	6.6 eq/cu ft (0.32 meq/g, 5.1 kgr/cu ft)
Zeolite Volume	4300 cu ft
Ion Exchange Vessels	4-12 ft x 15 ft x 6 ft deep, reinforced concrete gravity flow units
Cycle Time	13 hr including an 11 hr exhaustion cycle and 2 hr for regeneration, rinsing and reprocessing of rinse water
Throughput	165 BV/cycle; effective throughput of 150 BV/cycle when regenerant wasted, 165 BV/cycle when regenerant reused

Several economies of operation might be realized depending on other processes included in the total waste treatment system. If lime were used as the precipitant in an upstream precipitation-clarification process, lime costs would be appreciably less than those used in this analysis. On-site recalcination of lime usually is feasible where more than 100 tons of lime are used per week. An additional advantage of having a high pH upstream precipitation process would be the use of the high pH effluent for regenerant makeup, thus reducing lime requirements for the ion exchange process. For climates where heating in the regenerant stripping process would be required in winter, waste heat from lime recalcining or carbon regeneration furnaces or the gas from sludge digesters might be used for that purpose.

COST OF AMMONIA REMOVAL

Cost of Ion Exchange Processes

Although the literature concerning specific applications of ion exchange is extensive, little has been written concerning the cost of ion exchange processes. In addition, practically all information available has dealt with small-scale ion exchange softening and demineralization plants. Ion exchange vessels for these installations are characteristically steel and rubber-lined steel pressure vessels as opposed to the reinforced concrete gravity units considered in this analysis. An extensive discussion of the cost of ion exchange processes in pressurized containers has been prepared by Sanks [92] and Sanks and Kaufman [93,94]. Other discussions concerning the design and economic considerations of ion exchange units have been published by Kunin [44], Peak and David [95], and Monet [96,97]. Cost estimating guidelines have been published by Nelson [98] and the Office of Saline Water [99] and were used where applicable in this analysis. Costs of treatment processes analyzed by Smith [100], Smith and McMichael [74], and Koenig [101] were also utilized for cost information.

Cost of Regeneration

In addition to information found in Chapter VIII, costs of salt and lime, zeolite replacement, and stripping of regenerant solutions are needed to estimate the cost of regeneration. Included in the cost of regeneration are chemical costs, all zeolite replacement costs, and all costs associated with regenerant stripping. Costs of chemical and regenerant storage facilities are included in capital costs which are considered separately.

Chemical prices were obtained from manufacturers in the San Francisco area. Because chemical prices vary appreciably, depending on the location and quantity used, it was necessary to make several assumptions regarding the availability of chemicals. Transportation charges

considerably increase the cost of chemicals. Furthermore, it is difficult to accurately estimate transportation charges without knowing the origin and destination of the haul and other factors specific to each locality. However, in order to obtain prices for the purposes of cost estimation, transport distances were assumed and an attempt was made to apply average transport charges for these distances. Transportation charges for 300 miles were used for NaCl shipment. Because lime is manufactured in a greater number of locations across the country, only 200 miles transport of lime was assumed. Commercial grades of chemicals are satisfactory for regeneration and prices were based on this grade of chemicals. The base price of "stack run" NaCl was quoted as $12.90/ton (Leslie Salt Co., San Francisco, California). When freight charges of $15/ton were added, the total price of salt was $27.90/ton or $1.30/cwt. The price of lime was $21/ton and the cost of shipping was estimated to be $12/ton. Assuming the delivered product to be 90% pure, the effective lime cost was $36.70/ton of CaO or $1.83/cwt. The price of NaOH was $81/ton of NaOH as 50% liquid and the price of 300 miles shipping was estimated to be $15/ton of liquid, bringing the total cost of NaOH to $111/ton of NaOH or $5.50/cwt.

Estimation of clinoptilolite replacement costs was complicated by the fact that no large market currently exists for this material. The Baroid Division of National Lead Company, Houston, Texas currently markets clinoptilolite only in a -4 mesh size for $75/ton (equivalent to $1.75/cu ft) f.o.b. Newberry, California [102]. While it is possible that clinoptilolite might be made available in a 20 x 50 mesh size if a firm commitment for purchase of a large quantity of the zeolite were made, no price projections for the 20 x 50 mesh material are available at this time. Therefore, it was assumed that -4 mesh clinoptilolite would be crushed to the desired 20 x 50 mesh size at the treatment plant. A crushing and screening unit consisting of a twin loader impactor crusher, a vibrating screen, conveyor, and 2000 cu ft storage was estimated to cost $40,000 including installation. This was amortized for 10 yr at 5% and added to labor costs (4 man-hr/day) for a total crushing cost of $0.62/cu ft of product zeolite for a 10-mgd plant. This is based on a replacement rate of 50 cu ft of zeolite/day and represents perhaps twice the expected rate of replacement.

Shipping charges for transporting clinoptilolite to the treatment site are highly speculative, both because of uncertainty concerning the treatment plant location and because of the possibility of commercial development of zeolite deposits other than the one at Hector, California. For this analysis transportation of 400 miles from Hector, California was assumed. This resulted in a shipping cost of $0.29/cu ft of -4 mesh zeolite. Costs of zeolite replacement at other locations will vary from this figure if transport over a significantly greater distance is involved. Based on a 50% recovery of clinoptilolite as 20 x 50 mesh material, replacement clinoptilolite would cost $4.70/cu ft of product. Costs of chemicals and clinoptilolite replacement are summarized in Table 28.

TABLE 28

COST OF CHEMICALS AND CLINOPTILOLITE

Material	Units	Cost
Sodium Chloride		
Base price	$/ton	12.90
300 miles transportation	$/ton	15.00
Total cost	$/ton	27.90
Lime (CaO)		
Base price	$/ton	21.00
200 miles transportation	$/ton	12.00
Total cost, 90% pure	$/ton	33.00
Total cost per unit of usable material	$/ton	36.70
Sodium Hydroxide (50% liquid)		
Base price	$/ton	81.00
300 miles transportation	$/ton	30.00
Total cost	$/ton	111.00
Clinoptilolite[a]		
Base price	$/cu ft	3.50
400 miles transportation	$/cu ft	0.58
Crushing and storage	$/cu ft	0.62
Total cost per unit of product	$/cu ft	4.70

[a]Based on 50% recovery of zeolite as 20 x 50 mesh material.

Estimates for stripping of regenerant solutions were based on stripping costs given by Smith and McMichael [74, 100]. Because little work has been published concerning air stripping of concentrated ammonia solutions, it was assumed that the cost of stripping ammonia from sewage could be applied to regenerant stripping without serious error. A cost of $0.10/1000 gal of regenerant was estimated to cover the total cost of regenerant stripping.

Regeneration costs were calculated using the regenerant requirements shown in Figure 27 and Table 13. Zeolite replacement rates were

calculated on the basis of attrition rates measured in Chapter VIII — 0.25%/cycle for regeneration at pH 11.5, 0.35%/cycle at pH 12.0, and 0.55%/cycle at pH 12.5. Two cases were considered: 1) wasting of regenerant after one use, and 2) reuse of regenerant by stripping ammonia from the regenerant solution. For no regenerant reuse, lime requirements were calculated for a regenerant makeup water having an alkalinity of 80 mg/ℓ as $CaCO_3$. When regenerant is reused, the pH of the regenerant will drop both as ammonia from the zeolite is absorbed by the regenerant solution and as the regenerant is passed through the stripping tower. While the level to which the pH will drop is dependent on several factors and cannot be accurately estimated, for this analysis it was assumed that the regenerant pH would have to be raised from 7 or 8 to the desired value. Salt requirements for regenerant reuse were assumed to be equal to the stoichiometric amount of ammonia eluted from the zeolite plus a loss of 0.5 BV of regenerant/cycle.

The cost of regeneration is shown in Figures 34 and 35 for regenerant wasting and regenerant reuse, respectively. Costs are shown both as \$/eq NH_3-N removed and as \$/1000 gal of treated water for a waste containing 20 mg/ℓ NH_3-N. The costs in Figure 34 are heavily dependent on the salt concentration because a high proportion of regeneration costs are due to salt used for regenerant makeup. The prices estimated for regeneration using no NaCl at pH 12.0 and 12.5 were made on the basis of using NaOH for pH adjustment. As shown in Chapter VII, the use of lime alone for regeneration would require an excessive volume of regenerant. In addition the effective ammonia capacity of clinoptilolite is more than twice as great when the zeolite is regeneranted using a regenerant containing sodium. The cost of regeneration when regenerant is used only once was nearly the same for regeneration at pH 12.5 using NaOH and for regeneration at pH 12.0 or 12.5 using lime for pH adjustment and 0.049 lb NaCl/gal. While the use of slightly less salt might result in lower treatment costs, some NaCl must be added to prevent the volume of regenerant required from becoming excessively large as would be the case if calcium were the only cation in the regenerant. The least cost method of regeneration when regenerant is not reused was achieved using 0.049 lb NaCl/gal at pH 12.5 with lime as the source of caustic. However, the cost of regeneration using this regenerant composition (\$0.092/1000 gal) was only slightly less than regeneration using only NaOH at pH 12.0 or 12.5 (\$0.097/1000 gal). Because of the uncertainties in making a cost estimate of this sort, these costs may change when chemical prices and transportation costs in a specific location are considered.

Regeneration costs when regenerant reuse is considered (cf. Figure 35) are relatively insensitive to changes in the salt strength of the regenerant because of the large fraction of salt which is saved for reuse. While no one factor dominated the total cost of regeneration in this case, zeolite replacement costs constituted a much larger proportion of the total regeneration cost and resulted in lower regeneration costs as the regenerant pH was reduced. The least cost of regeneration

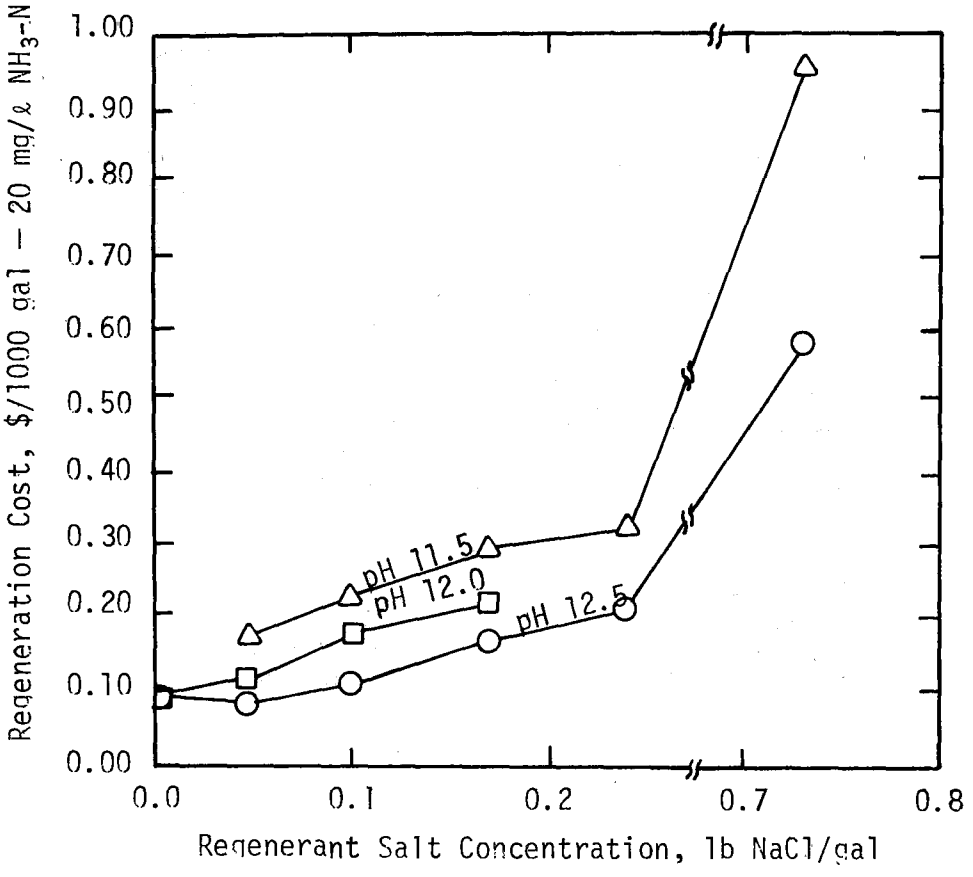


FIGURE 34. COST OF REGENERATION – NO REGENERANT REUSE

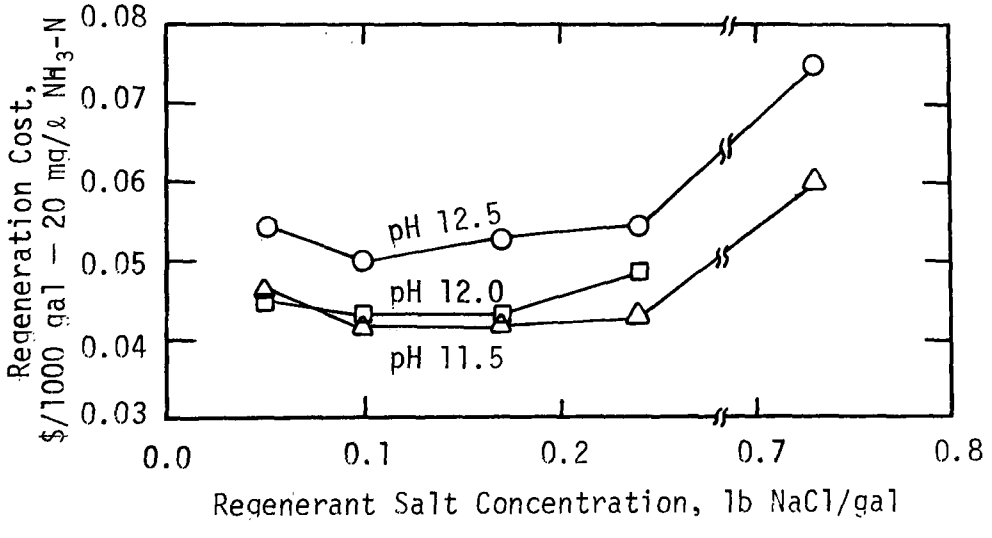


FIGURE 35. COST OF REGENERATION – REUSE OF REGENERANT

when regenerant is reused was achieved using either 0.10 or 0.17 lb NaCl/gal at pH 11.5 and was estimated to cost $0.042/1000 gal for a wastewater ammonia concentration of 20 mg/ℓ NH_3-N. The greater volume of the less concentrated regenerant resulted in somewhat greater costs for lime addition and regenerant stripping which balanced the greater cost of NaCl addition associated with the use of the more concentrated solution. While regeneration at pH values less than 11.5 was not studied, it is doubtful that the use of a lower pH regenerant would lead to reduced regeneration costs, as the increased regenerant volumes required would result in greater costs for regenerant stripping. In addition, zeolite replacement will constitute a less significant fraction of regeneration costs as attrition rates become less at reduced pH levels. These observations are corroborated by the very small differences estimated for minimum regeneration costs at pH 11.5 and 12.0. The minimum cost of regeneration at pH 12.0 was $0.043/1000 gal achieved using either 0.10 or 0.17 lb NaCl/gal. This cost is only slightly more than the minimum regeneration cost at pH 11.5 of $0.042/1000 gal.

The small differences in these costs suggest that the determination of the least cost of regeneration in any particular case will be significantly influenced by assumptions made in this analysis which will not be valid in all cases. Costs of regenerant stripping and zeolite replacement will be affected by geographic and climatic considerations as well as by specific agreements which can be made regarding the purchase of clinoptilolite. (Crushing of clinoptilolite at the mine, if it could be arranged, would result in considerable savings in transportation and operating costs.) Other factors including the volume of regenerant which will have to be replaced after each use and the exact amount of lime required to raise the regenerant pH to the desired level can accurately be determined only from further studies in which problems of regenerant reuse are considered. However, as the basis of this analysis it is believed that regeneration costs of $0.042/1000 gal using a regenerant containing either 0.10 or 0.17 lb NaCl/gal at pH 11.5 constitutes a realistic estimate of regeneration costs for the conditions outlined above.

Capital Costs

The basic cost of gravity flow ion exchange units was estimated from costs of sand filters given by Smith [100], Smith and McMichael [74], and Koenig [101]. It was assumed that the greater depth requirements for an ion exchange unit would be compensated for by the higher rate of flow per unit of surface area compared to that used in sand filters. While the bed depth in this case is 6 ft compared to about 2 or 3 ft for filtration, less headloss would be expected in an ion exchange unit even if the ion exchange medium were also used as a filter due to run lengths of only 11 hr. A cost of $580,000 was estimated for the ion exchange units including influent pumps and piping for influent, effluent, and rinsing waters. This cost was current as of July 1971, having been updated using the Engineering News-Record Construction Cost Index [103].

Piping for regeneration was estimated to cost $26,000. Two 2100-gpm pumps for regeneration were estimated to cost a total of $30,000, including installation.

Regenerant handling facilities were estimated for storage of one day's regenerant volume for the case of regenerant wasting and one-half day's requirement for regenerant reuse. Facilities for chemical storage were provided for a 10-day supply of chemicals. The total cost of these facilities was estimated to be $192,000 where regenerant is wasted and $143,000 where regenerant is reused.

Because ion exchange equipment is amenable to automation, fully automatic instrumentation and control is desirable as this will substantially reduce the amount of labor required. Limon and Calise [104] stated that complete automation and instrumentation of a plant adds less than 5 to 10% to the installed cost of the facility. Because the percentage cost of instrumentation is nearly independent of the plant size, 5% was added to the installation cost to cover automation of the plant. A contengency allowance of 10% was added to the total investment, and an engineering fee of 10% was added to the sum of the investment cost plus contingency allowance.

The magnitude of amortization charges depends on the useful life of the ion exchange equipment and the interest rate. Sanks [92] concluded that the life of ion exchange equipment is probably not less than 15 years, while the Office of Saline Water [99] specified a life of 20 years with shorter lives assumed for some equipment. Because of the innovative nature of this process, a life of 15 years was assumed in this analysis.

Interest rates for municipal bonds have risen sharply in the last few years from a relatively stable interest of about 4% for the preceding 15 years. Bonds listed in the Bond Buyer's Index averaged 6.0% in July 1971. While it seems likely that interest rates will not remain at this high level over a long period, it is the opinion of analysts that the return to a long term rate of 4% is equally unlikely because of techniques which are being used to manage the nation's economy [105]. For this analysis a rate of 5% was assumed. A summary of the cost analysis for the two plant designs is presented in Table 29.

Operating Costs

The amount of labor needed to maintain and operate the plant was estimated to be 2-1/2 persons per 8-hr day. Distribution of this labor included 1-1/2 persons during the day shift and 1/2 person for each of two night shifts. Labor required for operation and maintenance of the stripping tower where regenerant is reused and for crushing of replacement clinoptilolite was included in regeneration costs. Labor charges were based on a cost of $10,000/man-yr. Maintenance was calculated on the basis of the OSW recommendation of 0.0015% of the total plant investment [99]. Power costs were based on a rate of $0.01/kw-hr and a

TABLE 29

COST SUMMARY — 10-mgd CLINOPTILOLITE ION EXCHANGE PLANT

Item	Units	Costs	
		No Regenerant Reuse	Regenerant Reuse
Capital Costs			
Ion Exchange Units	$	580,000	580,000
Piping exclusive of influent, effluent, and rinsing	$	26,000	26,000
Pumping exclusive of influent	$	30,000	30,000
Regenerant handling	$	192,000	143,000
		$828,000	$779,000
Instrumentation	$	41,500	39,000
		$869,500	$818,000
Contingencies	$	87,000	82,000
		$956,500	$900,000
Engineering	$	95,500	90,000
Total capital investment exclusive of regenerant stripping where regenerant is reused		$1,052,000	$990,000
Capital Cost (15 yr life, 5% interest)	$/1000 gal	0.028	0.026
Operating Costs			
Labor	$/day	70	70
Maintenance	$/day	15	15
Power	$/day	55	55
Regeneration	$/day	920	420
Total Operating Cost	$/day	$1,060	560
Operating Cost	$/1000 gal	0.106	0.056
Total Cost	$/1000 gal	$0.134	$0.082

continuous power requirement of 310 hp. Regenerant costs were calculated for the use of 0.049 lb NaCl/gal at pH 12.5 where regenerant is wasted and 0.10 lb NaCl/gal at pH 12.5 where regenerant is reused.

Cost Summary

A summary of the cost analysis presented in Table 29 reveals that ammonia removal using clinoptilolite will cost $0.134/1000 gal when regenerant is used once and wasted, and $0.082/1000 gal when regenerant is reused. Where regenerant is wasted after one use, appropriate disposal costs must be added to this figure. In cold climates where regenerant is reused, heating costs for the air stripping process must be considered. However, as pointed out previously, it is felt that waste heat from other processes could be utilized for this purpose with little additional expense being incurred.

The results of this cost analysis may be compared to analyses made for similar installations at the South Tahoe Public Utility District [76] and Blue Plains [78] treatment plants. Design for a proposed clinoptilolite ion exchange facility at the STPUD was based on the use of twelve 900-cu ft reactors operating at a flow of 6 BV/hr. Regeneration was accomplished using a two-stage process with provision for regenerant reuse. The total cost of this process was estimated to be $0.158/1000 gal. The major difference in this cost and the one obtained in the present analysis was due to the higher capital costs associated with lower flow rates and the increased expenditure for regeneration facilities. Costs estimated for proposed clinoptilolite ion exchange facilities at the Blue Plains plant in Washington, D. C. were $0.097/1000 gal for a 300-mgd plant and $0.103/1000 gal for a 240-mgd plant [78]. The design in this case was based on a flow of 18 BV/hr and the use of two columns in series during the exhaustion cycle. Provisions were made for regenerant reuse and recovery of ammonia by absorption in sulfuric acid. Although costs for this estimate were very similar to those obtained herein, capital costs were somewhat higher and chemical costs somewhat lower than ones obtained in this analysis. The higher capital costs were probably due to the use of two beds in series and costs incurred in providing ammonia recovery equipment. The higher chemical costs obtained in the present analysis were probably due in part to the more detailed regeneration performance data obtained in this study.

Costs for ammonia removal using clinoptilolite have greater meaning when compared to costs of other nitrogen removal methods. Costs for ammonia removal by chlorination discussed in Chapter V were estimated to be $0.075/1000 gal for chlorine costs alone. However, increasing concern for the toxicity of wastewater effluents might make this method undesirable, even if total treatment costs for chlorination were favorable compared to other methods. Costs for nitrification-denitrification processes were estimated to be $0.08/1000 gal by McCarty [9] and $0.12/1000 gal for the Blue Plains treatment plant in Washington, D. C.

[78]. Thus ammonia removal using clinoptilolite is at least comparable to these methods on the basis of cost alone. In addition it is believed that there are advantages to the ion exchange process which make it desirable compared to other processes. It is believed that process stability and its insensitivity to toxicants constitute a significant advantage over biological processes. The relatively insignificant volume of liquid and solid wastes generated by the process will be an advantage when disposal of these wastes is considered. Finally, chemical changes in the product water accompanying the removal of ammonia are much less likely to be objectionable than those introduced by chlorination.

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XIII. GLOSSARY

Symbol	Definition
A, B	Cations.
a	Valence of ion A; activity.
b	Valence of ion B.
BV	Bed volume; equal to the gross volume occupied by the exchange material.
c	Solution phase concentration, meq/ℓ.
C_o	Total solution concentration of cations, meq/ℓ.
CCCSD	Central Contra Costa Sanitary District.
d_p	Particle diameter.
D_f	Film diffusion coefficient, sq cm/sec.
D_p	Solid diffusion coefficient, sq cm/sec.
D_{pore}	Pore diffusion coefficient, sq cm/sec.
EBMUD	East Bay Municipal Utility District.
F	Volumetric flow rate, mℓ/sec or BV/hr.
h	Height of bed, cm or ft.
I_+	Cationic strength, moles/ℓ.
K_B^A	Selectivity coefficient, Equation 3. Ion A in solution phase displacing ion B in solid phase.
K_{eq}	Equilibrium constant.
m_i	Concentration of cation i, moles/ℓ.
N	Number of transfer units, dimensionless; Equation 9.
NH_3-N	Total ammonia nitrogen concentration, mg/ℓ or meq/ℓ.
NH_3^o-N	Unionized ammonia nitrogen concentration, mg/ℓ or meq/ℓ.

Symbol	Definition
NH_4-N	Ammonium ion concentration expressed as N, mg/ℓ or meq/ℓ.
q	Solid phase concentration, meq/g.
Q	Total exchange capacity, meq/g.
S	Column cross-sectional area, sq cm or sq ft.
SERL	Sanitary Engineering Research Laboratory.
t	Time, sec.
T	Throughput parameter, equal to ratio of meq fed to column to meq total column capacity.
v	Volume of zeolite bed, cu cm or cu ft.
x	Dimensionless fluid phase concentration ($x = c/C_o$).
y	Dimensionless solid phase concentration ($y = q/Q$).
z_i	Valence of cation i.
Z	Zeolite exchange site.
α_B^A	Separation factor, Equation 5. Ion A in solution phase replacing ion B in solid phase.
ε	Voids ratio
ρ_b	Bulk density of zeolite bed, g/cu cm.
Ψ_{pore}	Correction factor for pore diffusion, Equation 7.
Ψ_q	Correction factor for solid diffusion, Equation 8.
*	Equilibrium value.

XIV. APPENDICES

APPENDIX A

COLUMN CONSTRUCTION DETAILS

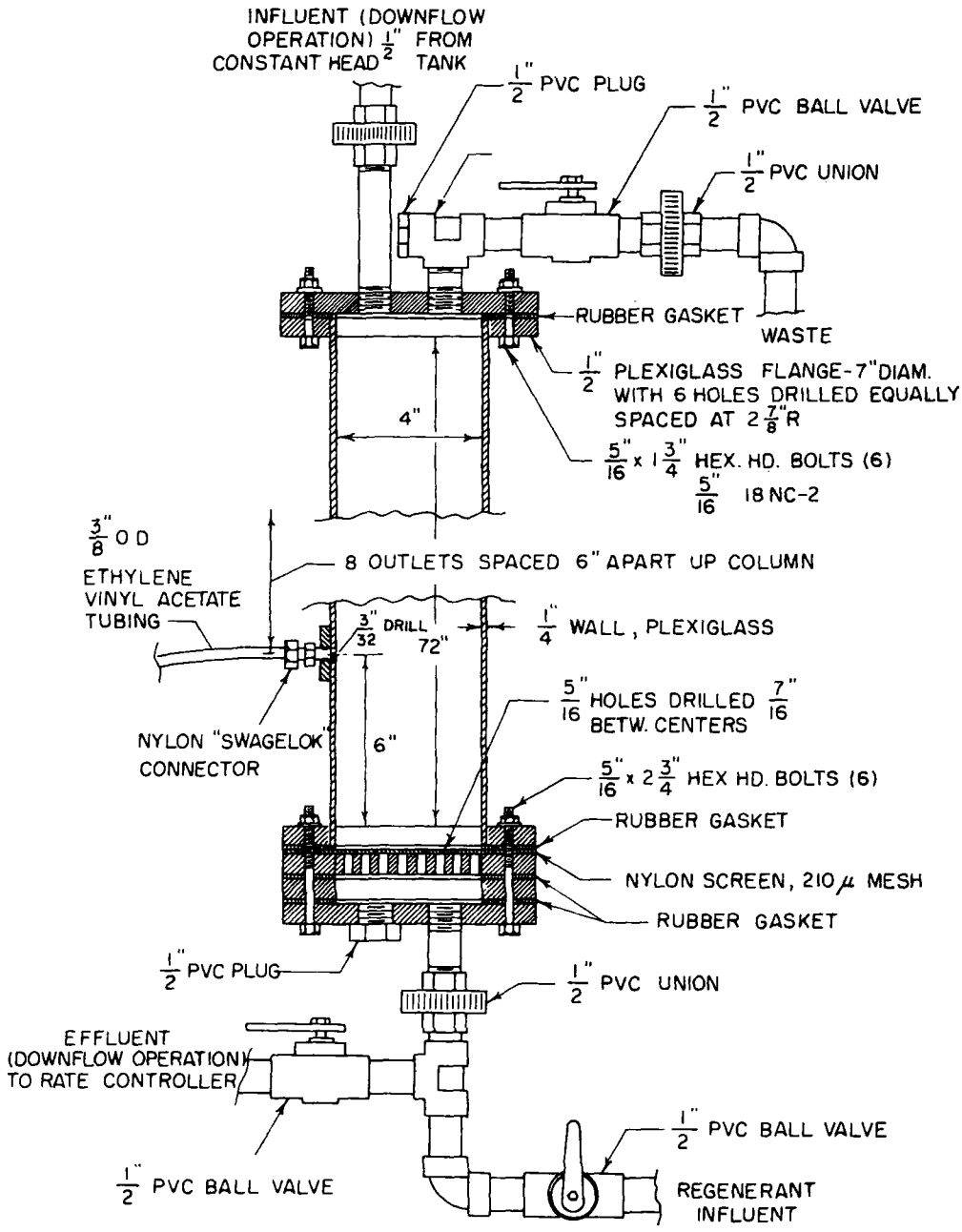


FIGURE I. DETAILS OF COLUMNS IN SERL COLUMN UNIT

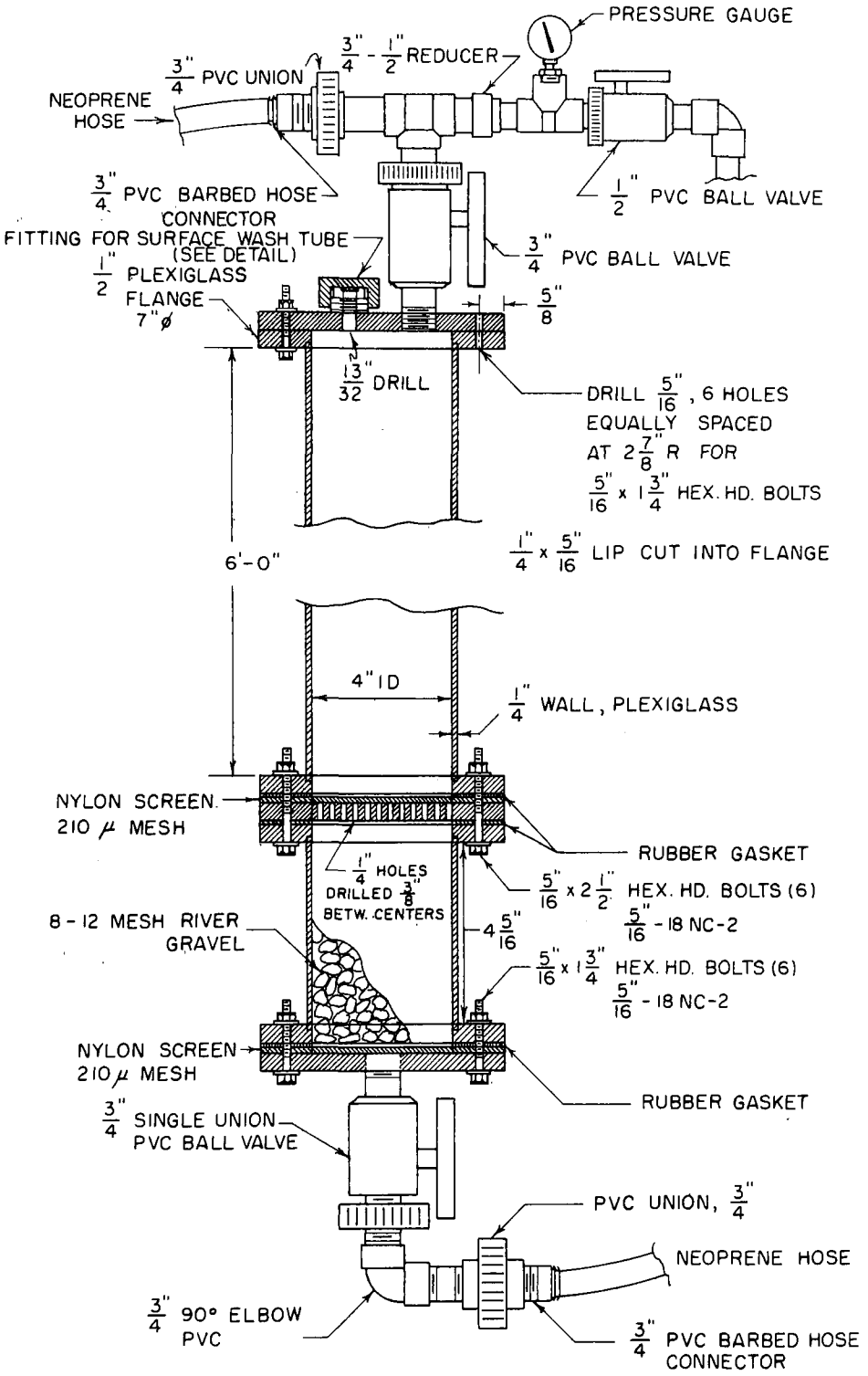


FIGURE 2. DETAILS OF COLUMN UNIT USED IN EBMUD AND CCCSD STUDIES

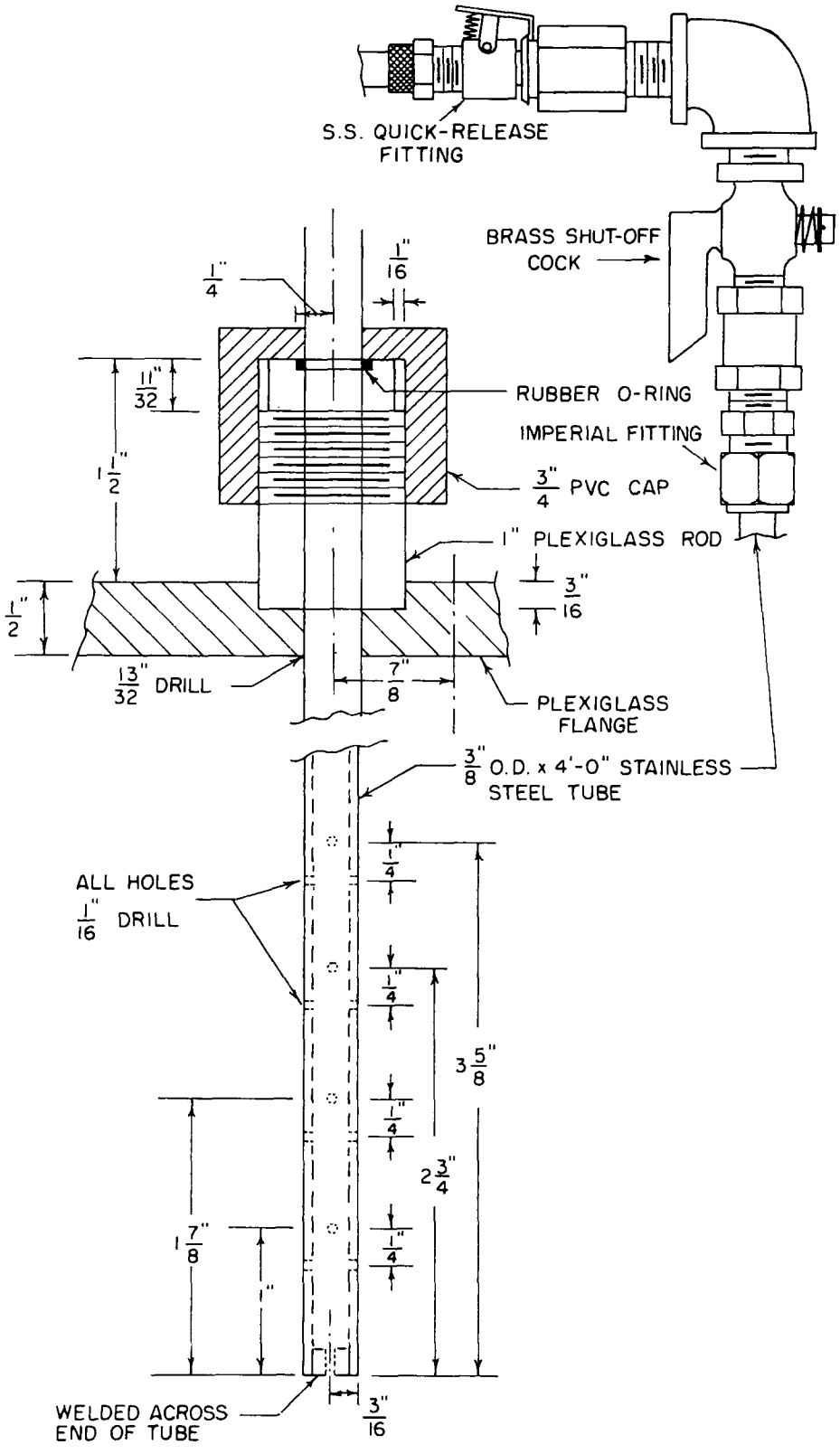


FIGURE 3. DETAIL OF SURFACE WASH APPARATUS

APPENDIX B

CONCENTRATION HISTORIES — EFFECT OF WATER COMPOSITION ON AMMONIA EXCHANGE CAPACITY

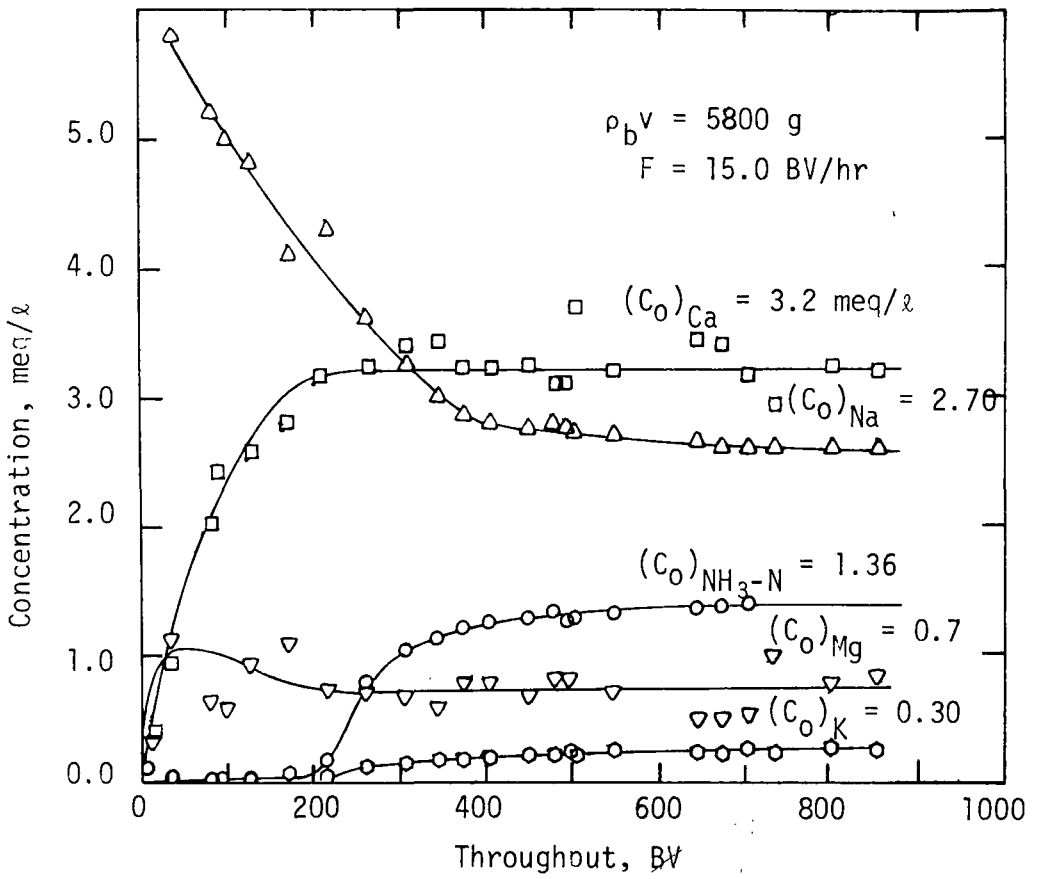


FIGURE 1. EFFECT OF WATER COMPOSITION ON AMMONIA EXCHANGE CAPACITY — RUN 2

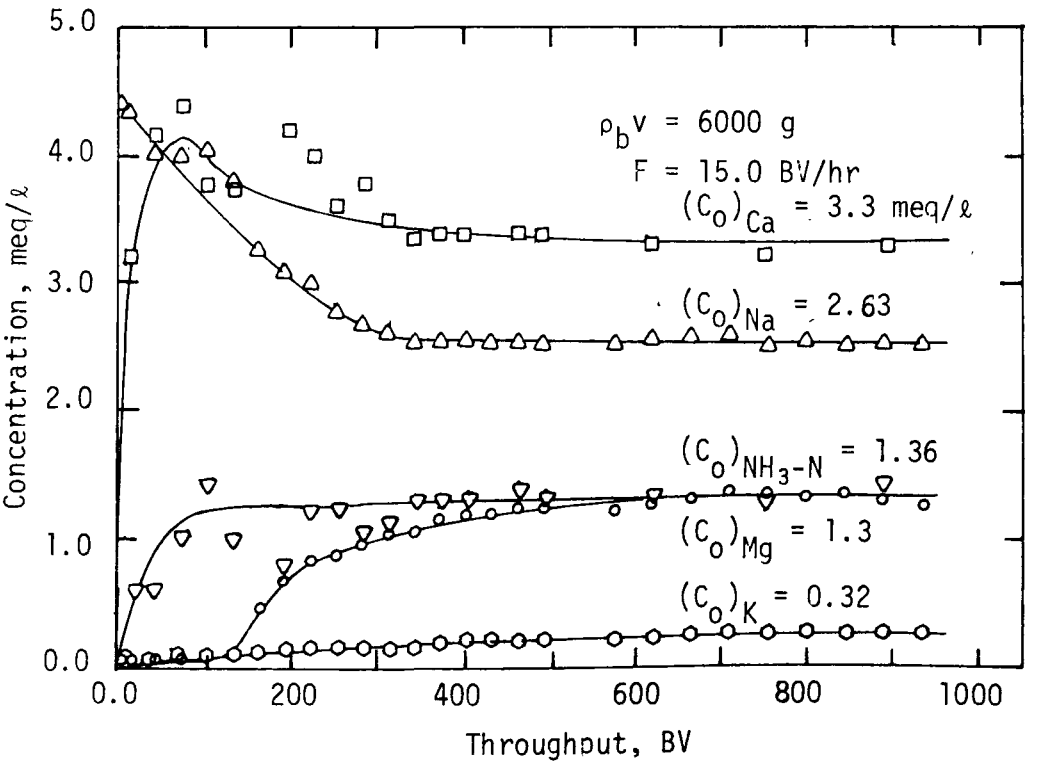


FIGURE 2. EFFECT OF WATER COMPOSITION ON AMMONIA EXCHANGE CAPACITY — RUN 3

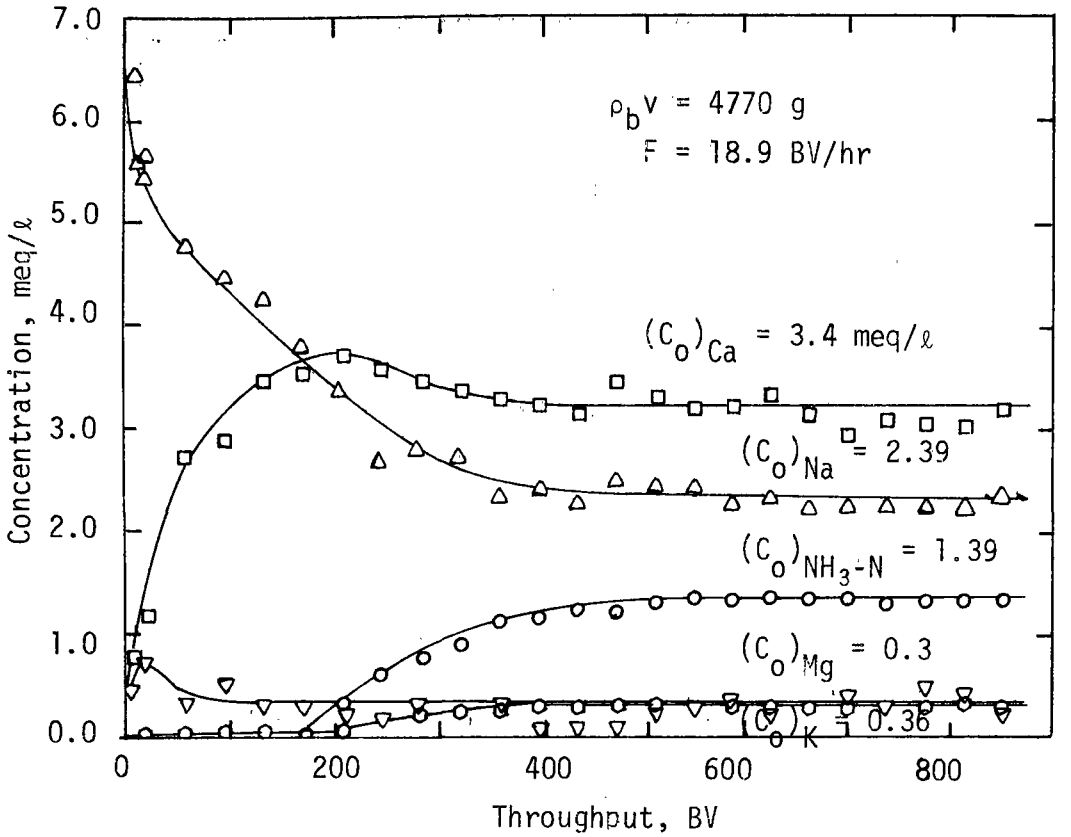


FIGURE 3. EFFECT OF WATER COMPOSITION ON AMMONIA EXCHANGE CAPACITY — RUN 4

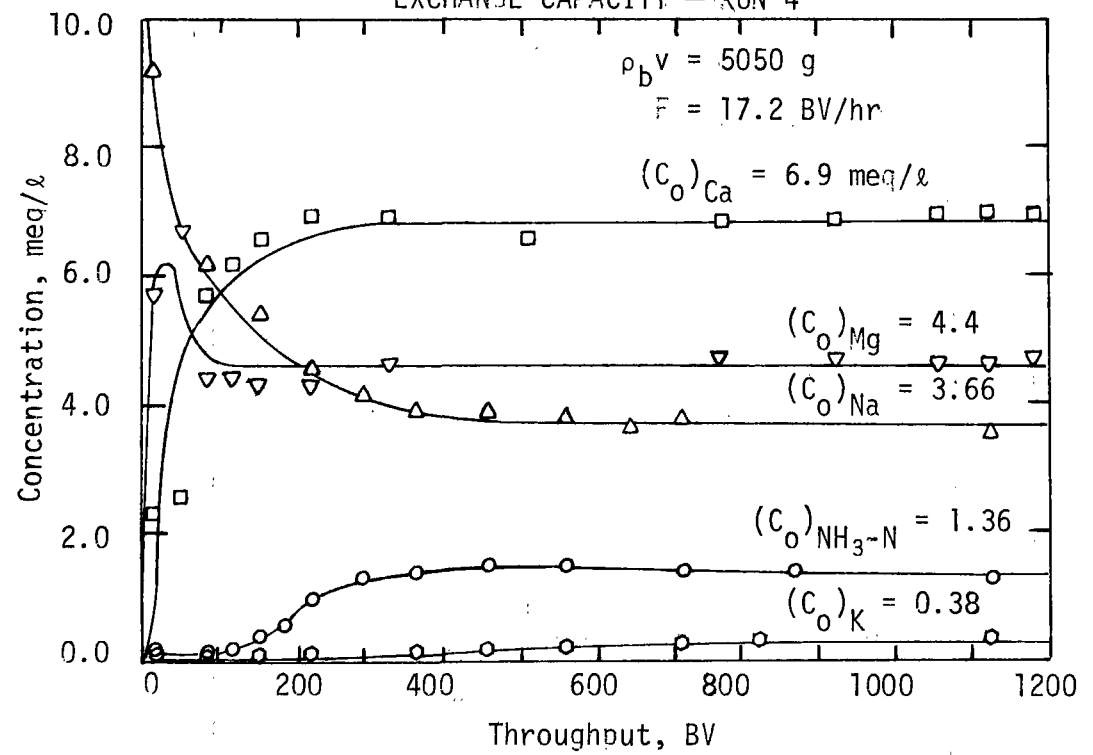


FIGURE 4. EFFECT OF WATER COMPOSITION ON AMMONIA EXCHANGE CAPACITY — RUN 5

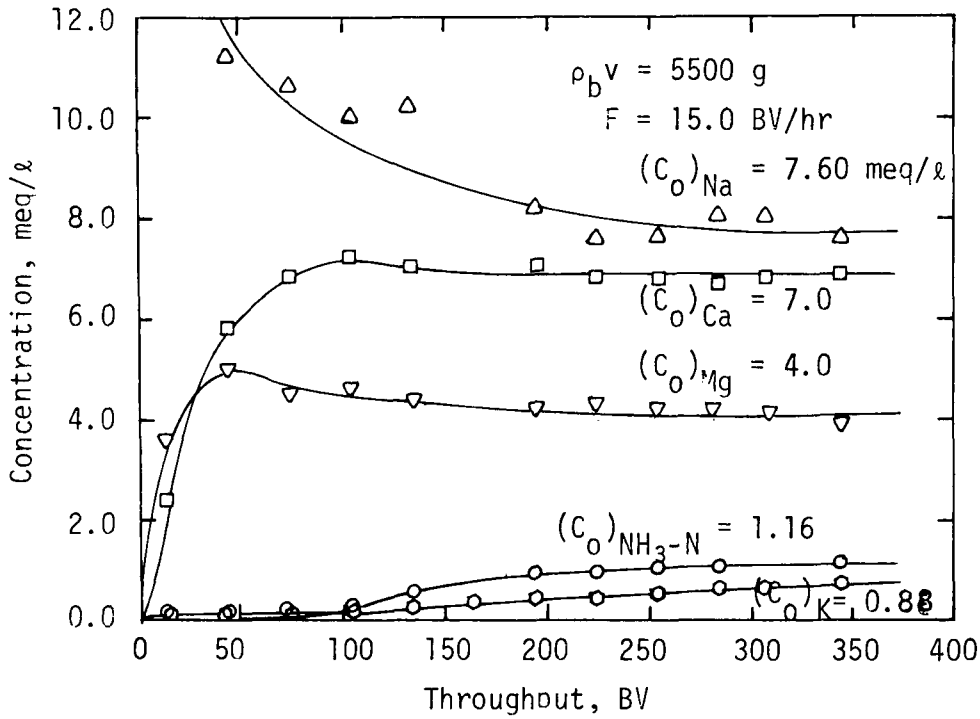


FIGURE 5. EFFECT OF WATER COMPOSITION ON AMMONIA EXCHANGE CAPACITY — RUN 6

APPENDIX C

AMMONIA CONCENTRATION HISTORIES — EFFECT OF pH ON AMMONIA EXCHANGE

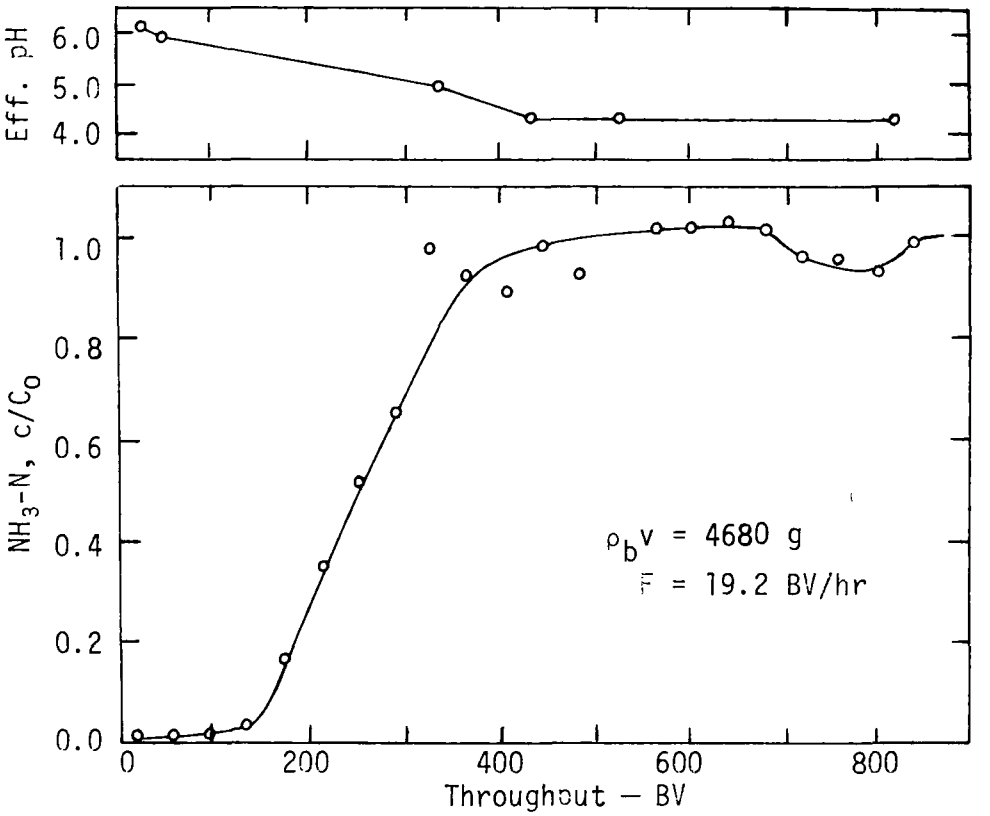


FIGURE 1. AMMONIA CONCENTRATION HISTORY — pH 4.0

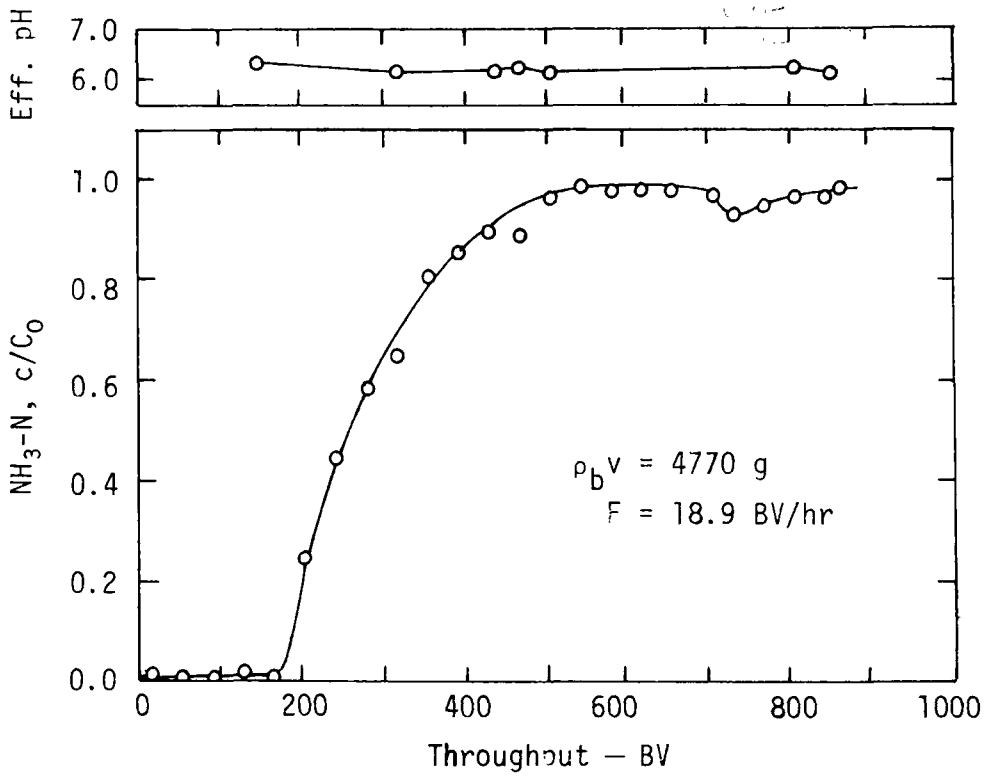


FIGURE 2. AMMONIA CONCENTRATION HISTORY — pH 6.0

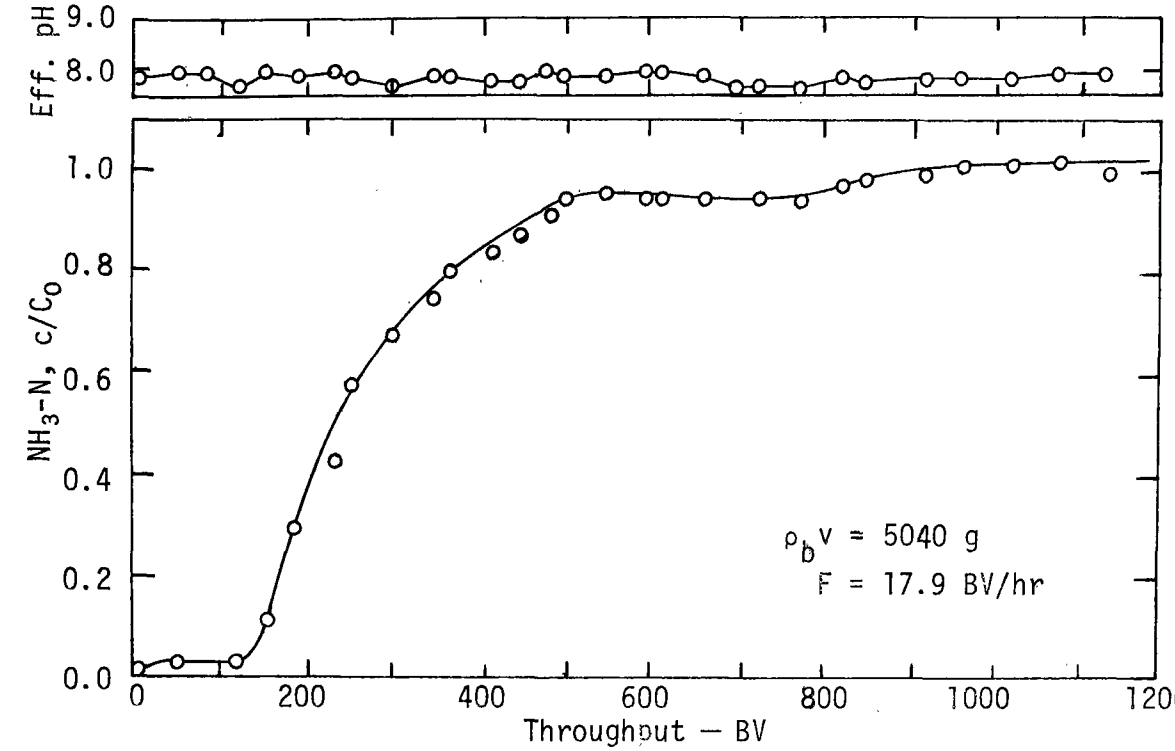


FIGURE 3. AMMONIA CONCENTRATION HISTORY — pH 8.0

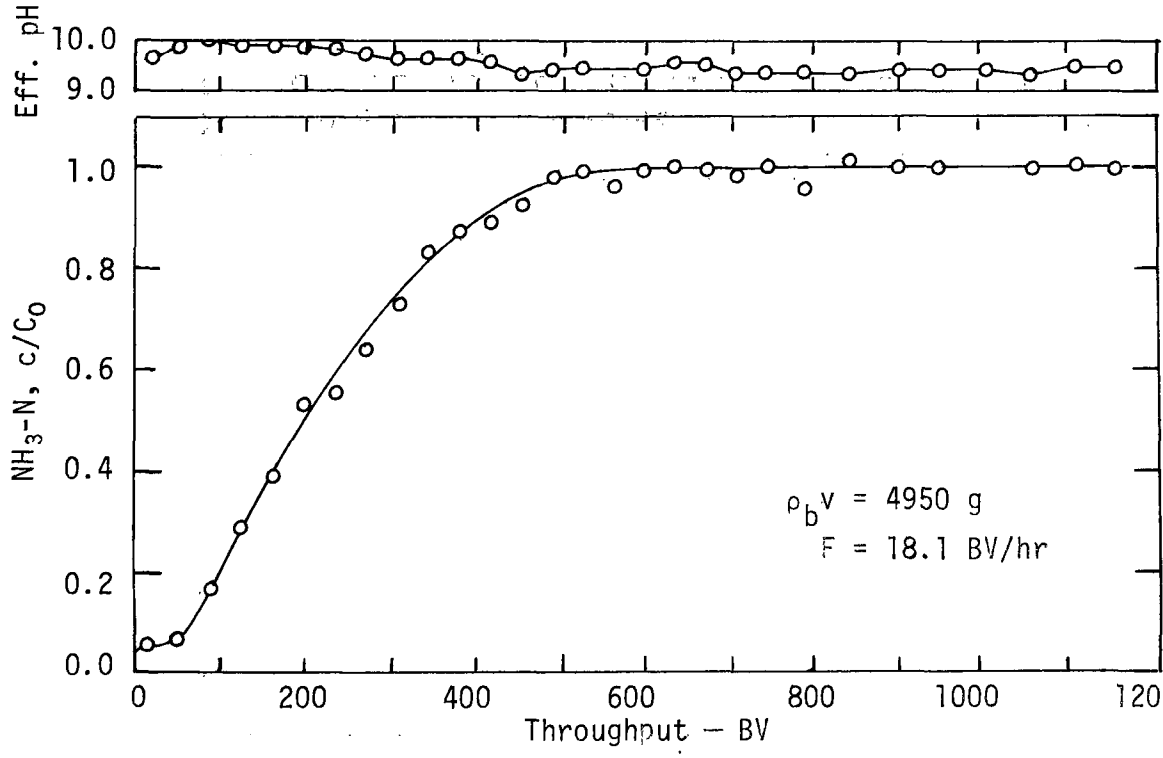


FIGURE 4. AMMONIA CONCENTRATION HISTORY — pH 9.5

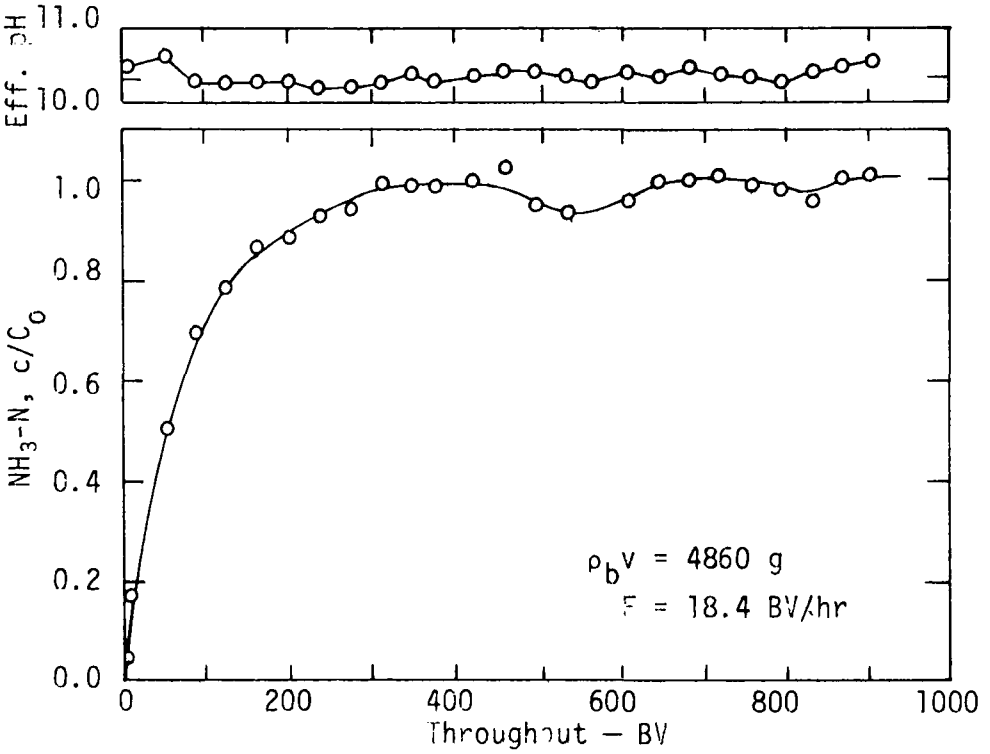
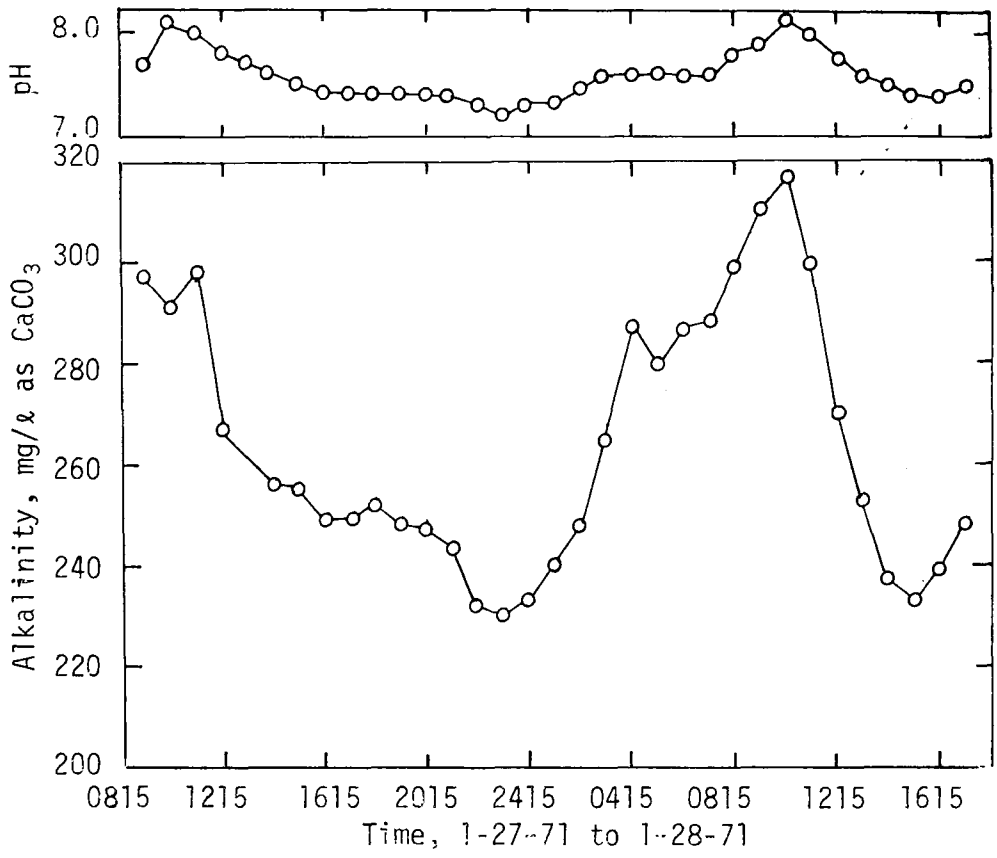


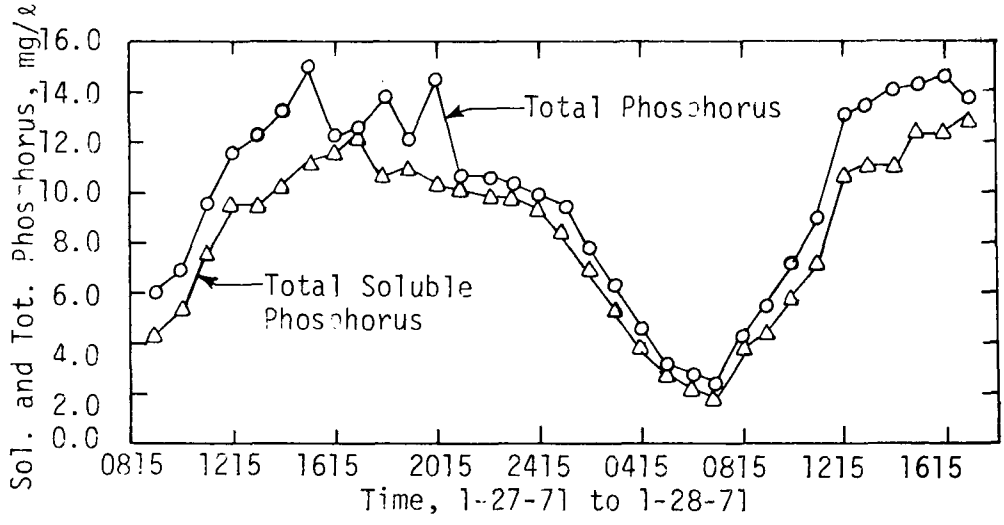
FIGURE 5. AMMONIA CONCENTRATION HISTORY — pH 10.0

APPENDIX D

WASTEWATER CHARACTERIZATION

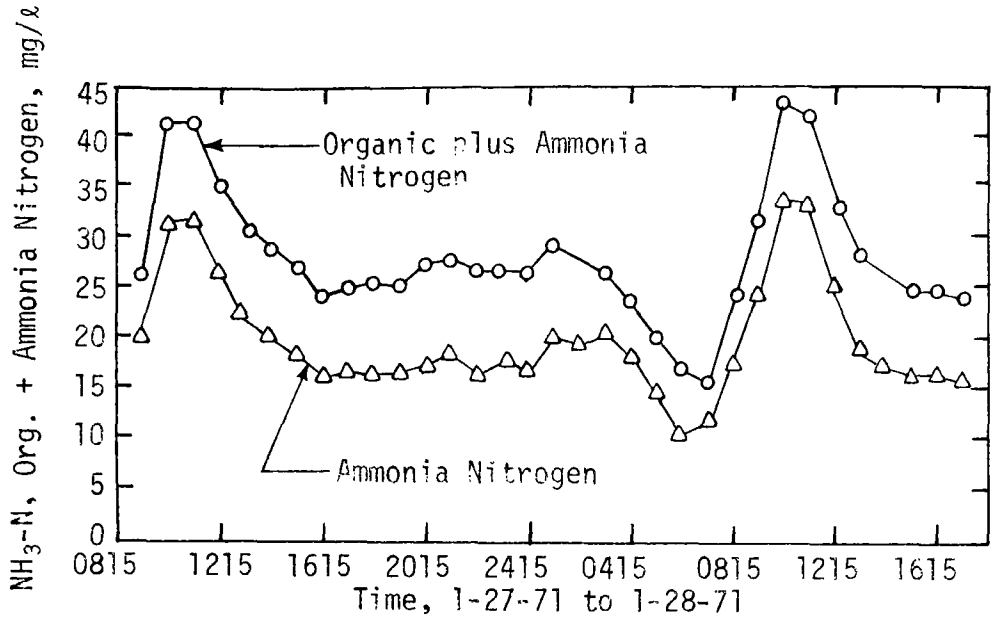


a. ALKALINITY, pH

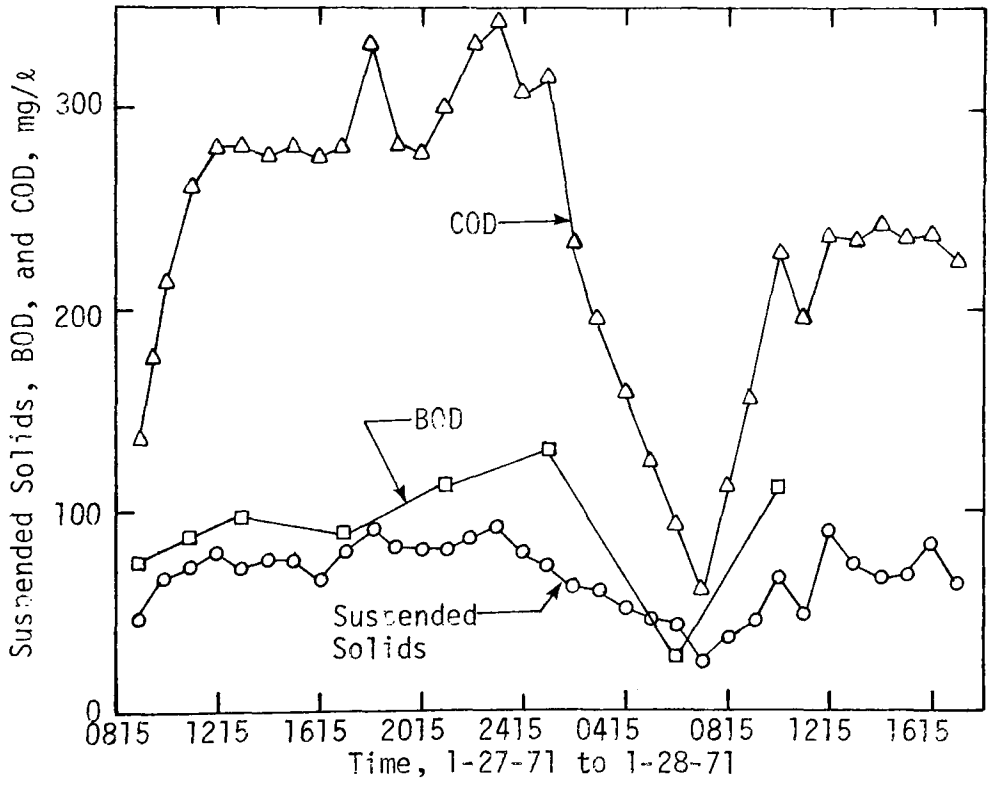


b. TOTAL AND TOTAL SOLUBLE PHOSPHORUS

FIGURE 1. WASTE CHARACTERIZATION — SERL PRIMARY EFFLUENT

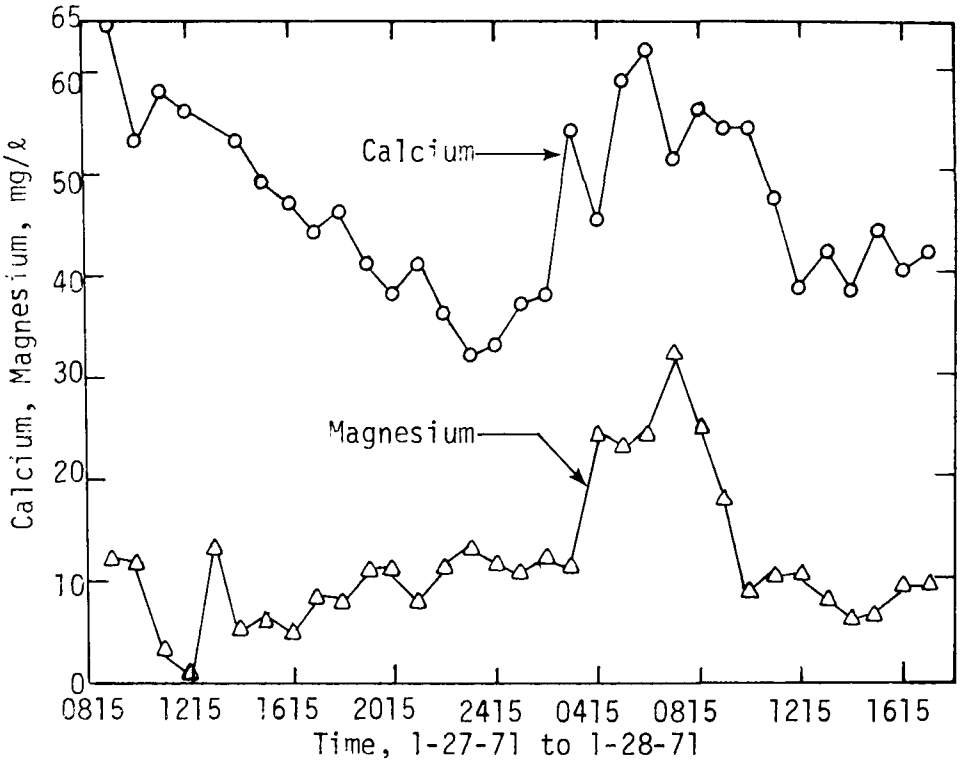


c. AMMONIA NITROGEN, ORGANIC PLUS AMMONIA NITROGEN

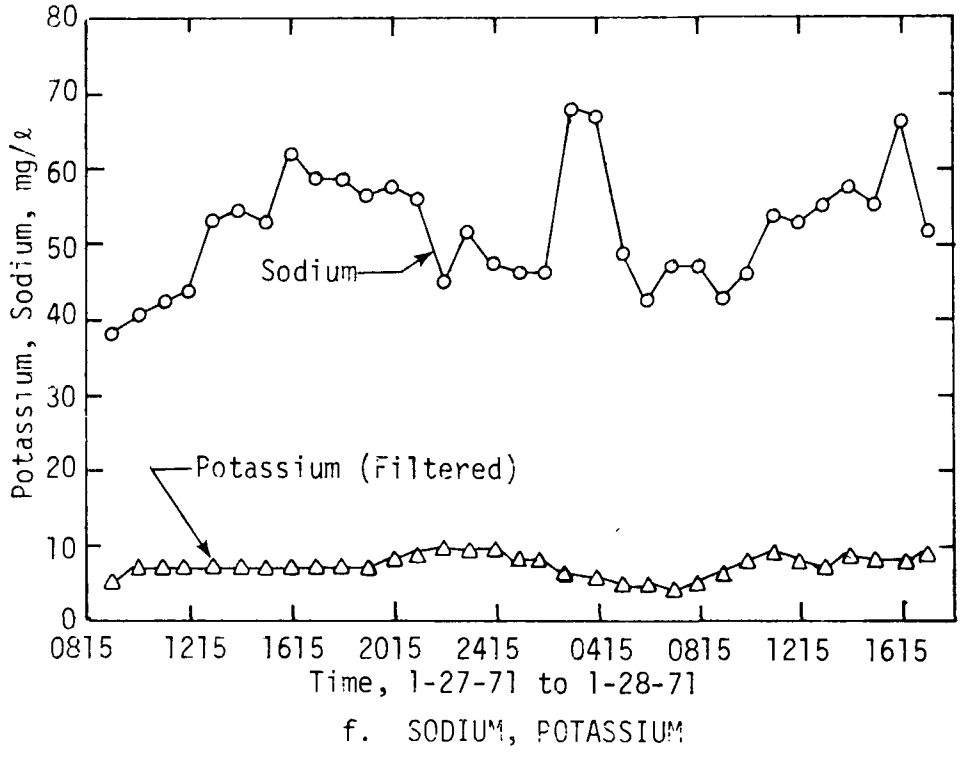


d. SUSPENDED SOLIDS, BOD, COD

FIGURE 1 (Continued). WASTE CHARACTERIZATION — SERL PRIMARY EFFLUENT



e. CALCIUM, MAGNESIUM



f. SODIUM, POTASSIUM

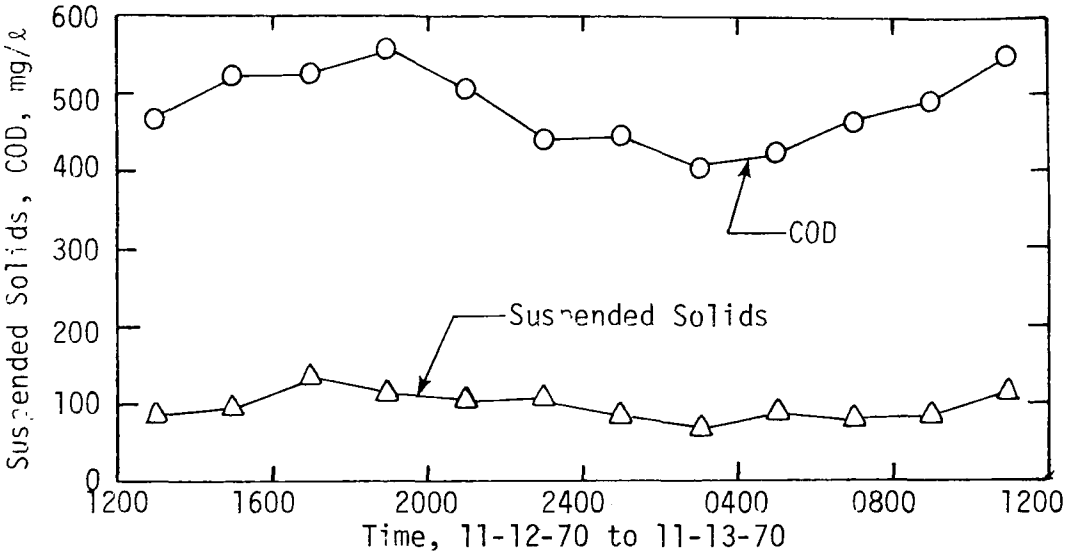
FIGURE 1 (Continued). WASTE CHARACTERIZATION — SERL PRIMARY EFFLUENT

TABLE 1

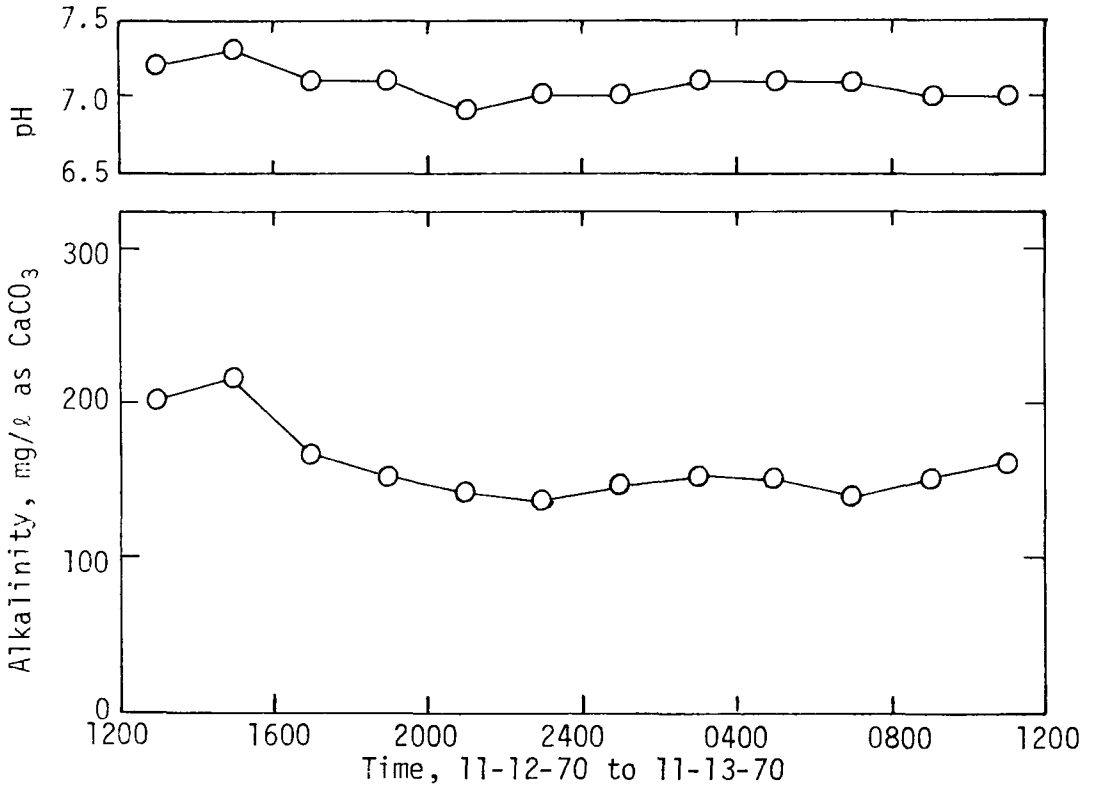
COMPOSITION OF SERL PRIMARY EFFLUENT

Analysis	24-hr Average Concentration[a]
COD, mg/ℓ	239
BOD, mg/ℓ	86
Suspended Solids, mg/ℓ	66.5
Alkalinity, mg/ℓ as $CaCO_3$	262
Soluble Phosphorus, mg/ℓ	7.8
Total Phosphorus, mg/ℓ	9.2
Org. + Ammonia Nitrogen, mg/ℓ	26.5
NH_3-N, mg/ℓ	18.8
Sodium, mg/ℓ	51.1
Potassium (filtered), mg/ℓ	6.8
Calcium, mg/ℓ	47
Magnesium, mg/ℓ	12
pH	7.6

[a]Average for first 24 samples of 33 samples taken.

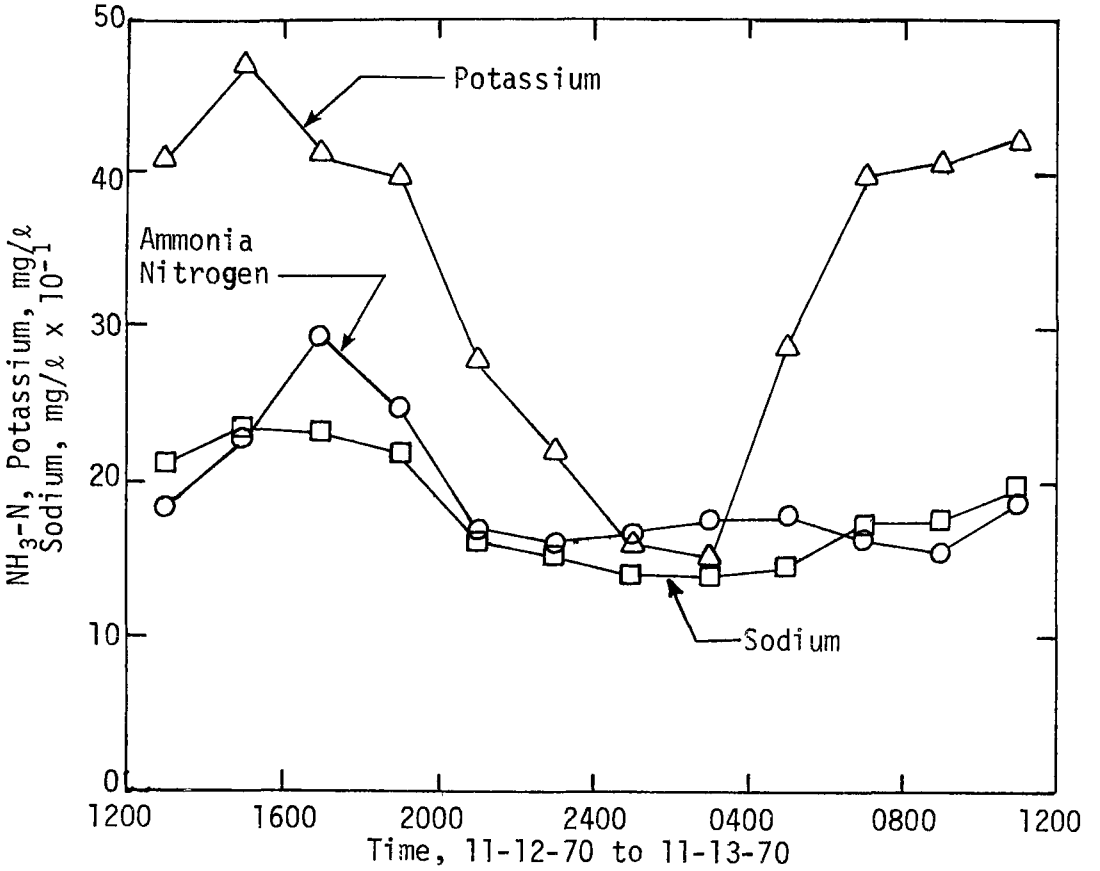


a. SUSPENDED SOLIDS, COD

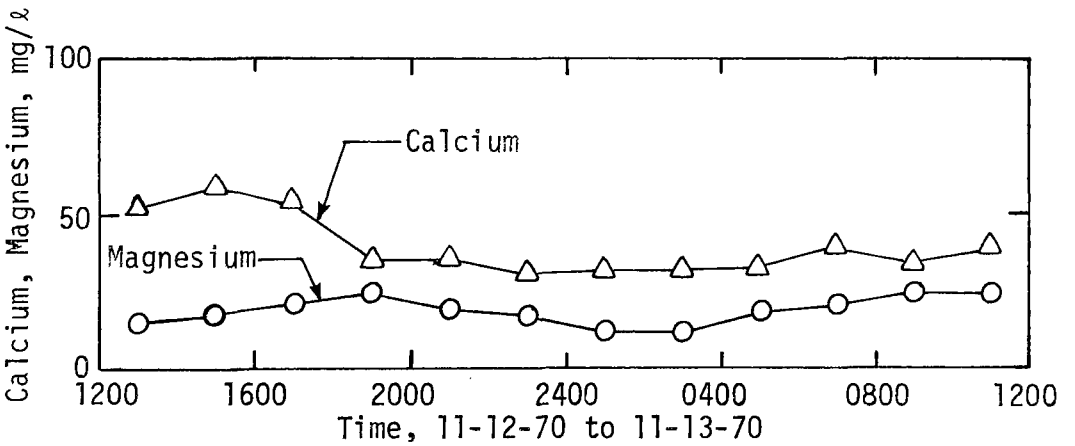


b. ALKALINITY, pH

FIGURE 2. WASTE CHARACTERIZATION — EBMUD PRIMARY EFFLUENT



c. AMMONIA, SODIUM, POTASSIUM



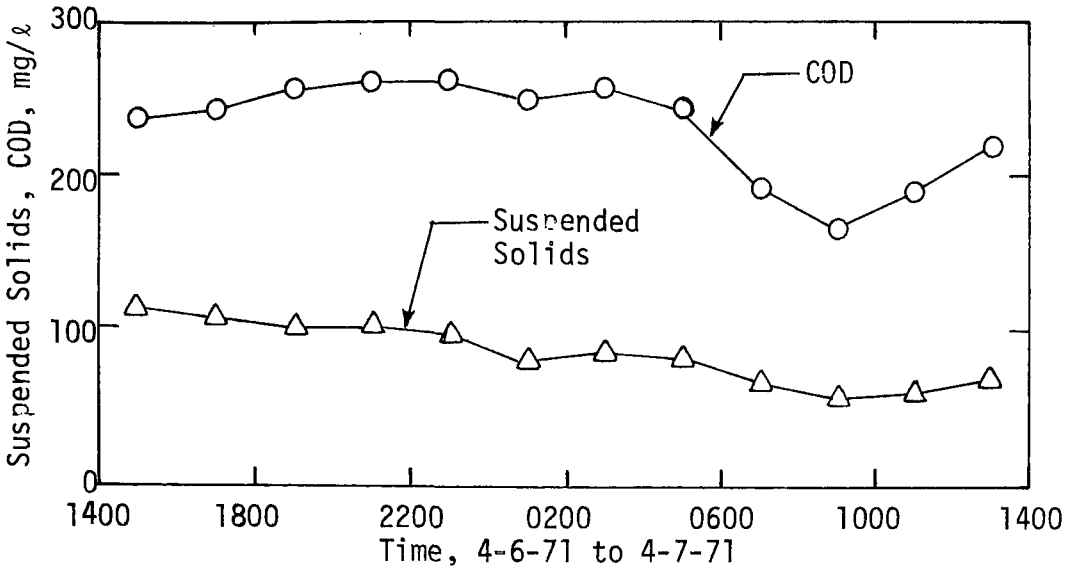
d. CALCIUM, MAGNESIUM

FIGURE 2 (Continued). WASTE CHARACTERIZATION — EBMUD PRIMARY EFFLUENT

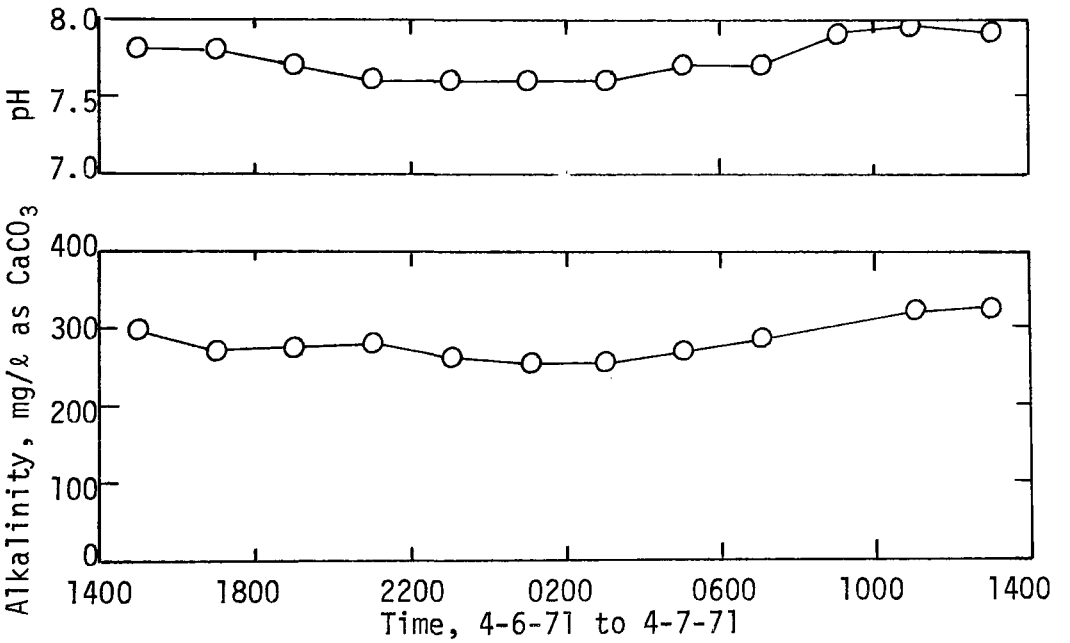
TABLE 2

COMPOSITION OF EBMUD PRIMARY EFFLUENT

Analysis	24-hr Average Concentration
COD, mg/ℓ	484
Suspended Solids, mg/ℓ	94
Alkalinity, mg/ℓ as $CaCO_3$	160
NH_3-N, mg/ℓ	19.2
Sodium, mg/ℓ	183
Potassium, mg/ℓ	33.4
Calcium, mg/ℓ	39
Magnesium, mg/ℓ	12
pH	7.1

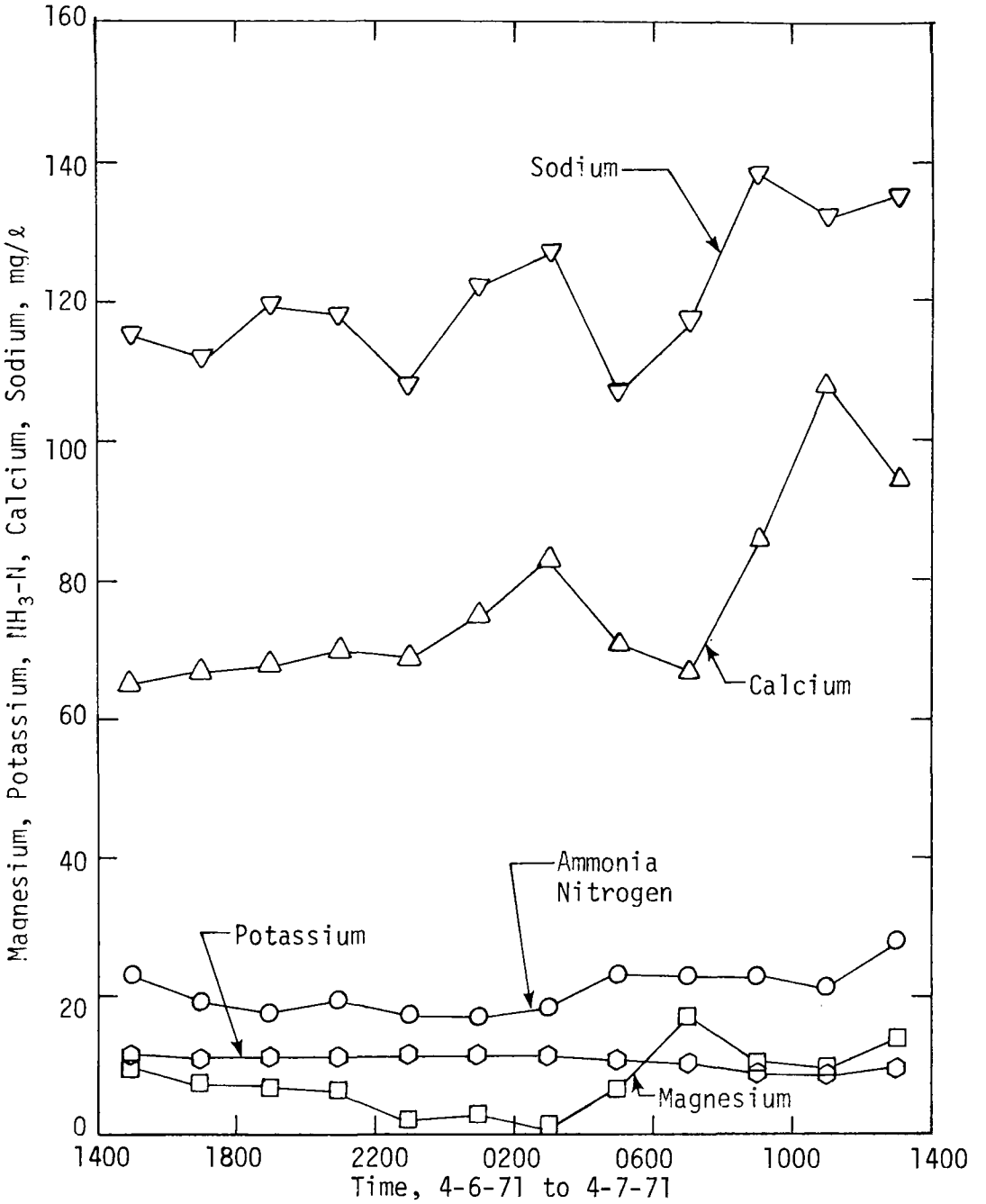


a. SUSPENDED SOLIDS, COD



b. ALKALINITY, pH

FIGURE 3. WASTE CHARACTERIZATION — CCCSD PRIMARY EFFLUENT



c. Ammonia, Sodium, Potassium, Calcium, Magnesium

FIGURE 3. WASTE CHARACTERIZATION — CCCSD PRIMARY EFFLUENT

TABLE 3

COMPOSITION OF CCCSD PRIMARY EFFLUENT

Analysis	24-hr Average Concentration
COD, mg/ℓ	222
Suspended Solids, mg/ℓ	83
Alkalinity, mg/ℓ As $CaCO_3$	281
NH_3-N, mg/ℓ	20.9
Sodium, mg/ℓ	121
Potassium, mg/ℓ	10.8
Calcium, mg/ℓ	77
Magnesium, mg/ℓ	8
pH	7.7

APPENDIX E

SUPPLEMENTARY OPERATING DATA

TABLE 1

SERL SERIES I SUPPLEMENTARY DATA[a]

Run	Date 1970	Treatment	COD mg/ℓ	SS mg/ℓ	Turb. JTU	pH	Tot. P mg/ℓ	Tot. Sol. P mg/ℓ	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ
1	8-25	Pri. Eff.	248	76		7.3	10.4		17.9			48	8
		Act. Sludge	107	32		7.0	15.7	9.8				50	6
		Ppt. Eff.	27	1.2	4.4	8.0		0.6	15.1	59.8	9.8	79	6
		Col. Eff.	25	1.4	3.0	8.3	0.6	0.6	0.77	108	2.2	57	6
2,3	8-26	Pri. Eff.	260	90	280	7.4	10.4		21.6				
		Act. Sludge	79	49	70	7.2	10.4	9.6	15.5				
		Ppt. Eff.	24	1.2	1.1	7.8		0.5	15.2	59.8	9.8	89	6
		Col. Eff.	21	<1.0	2.2	8.0	0.6	0.5	1.50	108	1.8	63	7
4,5	8-27	Pri. Eff.	132	36[b]	175[b]	7.5	6.1		24.2			70[b]	7[b]
		Act. Sludge	99	49	112	7.1	9.8	8.5	15.4				
		Ppt. Eff.	27	<1.0	2.9	7.5		0.5	15.2	54.5	9.4	89	5
		Col. Eff.	25	<1.0	1.6	7.9	0.5	0.5	0.47	104	2.3	67	6
6,7	8-28	Pri. Eff.	229	84	160	7.2	12.6		24.1				
		Act. Sludge	78	37	65	7.0	13.0	11.7	14.2			48	8
		Ppt. Eff.	19	<1.0	3.7	7.8		0.5	13.6	57.0	9.4	93	3
		Col. Eff.	18	1.2	1.3	7.8	0.6	0.5	0.66	92.5	2.1	74	9
8	8-29	Pri. Eff.	272	82	312	7.5	12.6		23.3			58	8
		Act. Sludge	62	20	52	7.4	10.1	9.6	15.7			50	12
		Ppt. Eff.	26	<1.0	2.0	8.3	0.5	0.5	15.6	53.9	9.4	81	10
		Col. Eff.	24	<1.0	2.6	8.5	0.5	0.5	0.06	105	3.0	72	4

[a]Treatment: primary sedimentation, activated sludge, chemical precipitation at pH 11.0, ammonia sorption. Activated sludge loading rate averaged 0.4 lb BOD/lb MLVSS-day.

[b]Analysis of grab sample.

TABLE 1 (Continued)

SERL SERIES I SUPPLEMENTARY DATA[a]

Run	Date 1970	Treatment	COD mg/ℓ	SS mg/ℓ	Turb. JTU	pH	Tot. P mg/ℓ	Tot. Sol. P mg/ℓ	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ
9,10	9-1	Pri. Eff.	278	84	360	7.5	12.1		22.3			53	
		Act. Sludge	94		328				16.1				
		Ppt. Eff.	44	4.1	17	8.2	1.8	1.7	15.2			59	
		Col. Eff.	39	1.0	5.5	8.6	1.7	1.5	0.37			47	
11,12	9-2	Pri. Eff.	297	84	360	7.5	11.9		20.2				
		Act. Sludge	77	37	86	7.6	10.4	10.4	17.0				
		Ppt. Eff.	35	2.9	10	8.1	1.9	1.7	15.7	60.3	9.4		
		Col. Eff.	31	1.2	5.4	8.3	1.8	1.8	0.29	110	2.0		
13,14	9-3	Pri. Eff.	238	69	210	7.4							
		Act. Sludge	64	19	41	7.1							
		Ppt. Eff.	33	<1.0	8.4	8.1			15.4	60.3	9.4		
		Col. Eff.	31	<1.0	0.4	8.2			0.27	109	1.0		
15,16	9-4	Pri. Eff.	252	66	305	7.4			22.8				
		Act. Sludge	85	36	54	7.1			14.6				
		Ppt. Eff.	34	2.6	10	8.2			13.0	55.2	9.4		
		Col. Eff.	32	<1.0	0.5	8.6			0.12	104	1.9		
17,18	9-5	Pri. Eff.							21.1			35	14
		Act. Sludge							21.0				
		Ppt. Eff.			13				18.6			54	13
		Col. Eff.			5.1				0.18			57	14

[a]Treatment: primary sedimentation, activated sludge, chemical precipitation at pH 9.5, ammonia sorption. Activated sludge loading rate averaged 0.4 lb BOD/lb MLVSS-day.

TABLE 1 (Continued)

SERL SERIES I SUPPLEMENTARY DATA[a]

Run	Date 1970	Treatment	COD mg/ℓ	SS mg/ℓ	Turb. JTU	pH	Tot. P mg/ℓ	Tot. Sol. P mg/ℓ	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ
19	9-16	Pri. Eff.	238	65	210	7.3	10.8	8.7	18.5			48	7
		Ppt. Eff.	79	5.6	49	8.1	0.3	0.3	18.6	51.8	9.8	70	3
		Col. Eff.	70	6.4	45	8.2	0.3	0.3	0.28	104	4.1	50	3
21,22	9-17	Pri. Eff.	255	76	200	7.3	11.1	8.7	19.4			52	2
		Ppt. Eff.	77	5.7	38	8.0	0.2	0.2	18.9	51.8	10.2	76	2
		Col. Eff.	62	6.7	41	8.0	0.2	0.2	0.48	106	2.0	58	4
23,24	9-18	Pri. Eff.	256	89	270	7.4	11.1	8.7	20.8			50	4
		Ppt. Eff.	73	6.7	76	7.9	0.2	0.2	16.9	48.8	9.6	75	2
		Col. Eff.	62	6.6	43	8.0	0.2	0.2	0.19	115	1.6	46	3
25,26	9-19	Pri. Eff.	294	95		7.3	13.9	11.3	21.6			38	10
		Ppt. Eff.	61	7.7	30	7.8	0.3	0.2	21.0	50.6	9.4	71	3
		Col. Eff.	47	5.3	28	7.8	0.2	0.2	0.32	110	1.1	52	5
27	9-20	Pri. Eff.										43	5
		Ppt. Eff.							17.5	61.7	11.3	60	2
		Col. Eff.							0.20	123	4.7	40	3

[a]Treatment: primary sedimentation, chemical precipitation at pH 11.0, ammonia sorption.

TABLE 1 (Continued)

SERL SERIES I SUPPLEMENTARY DATA[a]

Run	Date 1970	Treatment	COD mg/ℓ	SS mg/ℓ	Turb. JTU	pH	Tot. P mg/ℓ	Tot. Sol. P mg/ℓ	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ
28,29	9-22	Pri. Eff.	272	76	310	7.2	12.6	9.8	17.2				
		Ppt. Eff.	94	13	44	7.6	0.2	0.2	18.8	58.0	8.8	82	3
		Col. Eff.	90	4.4	32	7.7	0.2	0.2	0.19	128	0.6	51	3
30,31	9-23	Pri. Eff.	247	66	310	7.3	10.6	8.2	20.5			47	4
		Ppt. Eff.	72	5.9	80	7.7	0.1	0.1	17.9	48.3	9.0	83	3
		Col. Eff.	68	4.5	32	7.9	0.1	0.1	0.15	113	0.6	58	4
32,33	9-24	Pri. Eff.	265	79	310	7.6	12.6	9.6	22.8			48	4
		Ppt. Eff.	70	3.0	49	7.3	0.2	0.2	20.0	52.0	9.5	88	4
		Col. Eff.	64	3.0	29	7.6	0.2	0.2	0.36	102	1.6	78	4
34,35	9-25	Pri. Eff.	256	22	310	7.5	10.8	8.3	21.2			47	5
		Ppt. Eff.	84	1.5	18	7.3	0.4	0.4	19.5	47.9	8.8	77	4
		Col. Eff.	73	3.3	29	7.5	0.3	0.3	0.25	106	1.2	64	5
36	9-26	Pri. Eff.	201	37		7.4			24.8			43	8
		Ppt. Eff.	70	1.4		7.3			19.4			64	4
		Col. Eff.	51	8.8		7.4			0.62			60	5

[a]Treatment: primary sedimentation, chemical precipitation at pH 11.0, ammonia sorption.

TABLE 1 (Continued)

SERL SERIES I SUPPLEMENTARY DATA[a]

Run	Date 1970	Treatment	COD mg/ℓ	SS mg/ℓ	Turb. JTU	pH	Tot. P mg/ℓ	Tot. Sol. P mg/ℓ	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ
38	9-29	Pri. Eff.	251	62		7.4	11.7	9.4	16.4			50	4
		Ppt. Eff.	110	4.4		7.8	1.0	0.1	17.6	56.3	8.8	54	5
		Col. Eff.	102	5.8		7.8	0.7	0.7	0.28	80.5	1.1	56	8
39,40	9-30	Pri. Eff.	233	6.7	270	7.4	10.2	8.7	20.7			41	9
		Ppt. Eff.	94	4.1	38	7.2	0.9	0.8	20.0	49.5	8.4	50	8
		Col. Eff.	80	8.8	50	7.4	0.6	0.6	0.24	99.0	0.9	53	11
41,42	10-1	Pri. Eff.	275	84	340	7.4	11.3	9.4	19.8			40	8
		Ppt. Eff.	103	11.5	90	7.3	0.7	0.7	20.8	51.8	8.8	48	8
		Col. Eff.	90	7.6	51	7.6	0.6	0.5	0.38	126	0.7	27	11
43,44	10-2	Pri. Eff.	245	71	290	7.3	10.4	8.6	19.6			42	8
		Ppt. Eff.	94	3.1	36	7.3	0.6	0.5	20.2	53.0	8.4	53	4
		Col. Eff.	68	5.5	35	7.6	0.5	0.5	0.42	111	0.9	34	4
45,46	10-3	Pri. Eff.	235	72		7.3			16.6			46	7
		Ppt. Eff.	76	3.8	37	7.4			18.5	53.0	8.0	50	7
		Col. Eff.	47	7.9	25	7.5			0.37	113	0.8	39	6

[a]Treatment: primary sedimentation, chemical precipitation at pH 9.5, ammonia sorption.

TABLE 2

SERL SERIES II SUPPLEMENTARY DATA[a]

Run	Date 1971	Treatment	COD mg/ℓ	SS mg/ℓ	Turb. JTU	pH	Tot. P mg/ℓ	Tot. Sol. P mg/ℓ	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ
47,48	2-17	Pri. Eff.	198	46	230	7.5	9.4	8.0	19.7			56	4
		Ppt. Eff.	98	1.4		7.3	0.7	0.7	19.8	50.6	10.5	70	3
		Col. Eff.	100	3.0		7.6	0.5	0.5	3.4	84.0	3.5	62	5
49,50	2-18	Pri. Eff.	216	51	230	7.4	9.2	7.9	19.5	58.6[b]	8.6[b]	45	11
		Ppt. Eff.	100	1.1	24	7.0	0.6	0.6	17.9	62.1	10.2	66	6
		Col. Eff.	95	2.0	16	7.5	0.5	0.5	1.16	100	1.6	57	8
51,52	2-19	Pri. Eff.	196	42	240	7.4			20.0			54	4
		Ppt. Eff.	83	3.3		7.0			18.2	49.4	8.6	65	5
		Col. Eff.	87	2.9		7.5			1.89	109	1.6	53	6
53	2-20	Pri. Eff.	218	84	240	7.6			20.9			54	5
		Ppt. Eff.	68	5.5		7.1			20.2			66	4
		Col. Eff.	70	9.6		7.4			0.98	105	1.6	59	5
54	2-21	Pri. Eff.	278	101	130	7.4			24.5			43	7
		Ppt. Eff.	77	6.8		6.7			20.8	48.3	7.8	62	6
		Col. Eff.	69	6.8		7.2			0.60	112	0.4	55	5
55	2-23	Pri. Eff.	296	102	330	7.4			17.4			41	11
		Ppt. Eff.	92	5.0		7.0			18.6	59.8	10.2	69	4
		Col. Eff.	115	3.6		7.4			0.67	112	0.5	62	5

[a]Treatment: primary sedimentation, chemical precipitation at pH 11.0, ammonia sorption.

[b]Sample composited over period 2-17 to 2-21.

TABLE 2 (Continued)

SERL SERIES II SUPPLEMENTARY DATA[a]

Run	Date 1971	Treatment	COD mg/ℓ	SS mg/ℓ	Turb. JTU	pH	Tot. P mg/ℓ	Tot. Sol. P mg/ℓ	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ
56,57	2-24	Pri. Eff.	238	67	290	7.4	9.8	8.4	18.1			45	7
		Ppt. Eff.	75	4.8		7.4	0.7	0.5	18.3	55.2	9.0	75	3
		Col. Eff.	77	2.8		7.7	0.6	0.5	1.26	105	0.8	67	3
58,59	2-25	Pri. Eff.	242	59	330	7.5	8.5	7.8	20.6	55.2[b]	8.6[b]	52	5
		Ppt. Eff.	80	4.2		7.3	0.5	0.4	20.6			74	3
		Col. Eff.	81	4.4		7.7	0.5	0.3	2.38			62	5
60,61	2-26	Pri. Eff.	236	66	360	7.4			21.6			40	12
		Ppt. Eff.	68	3.8		7.0			22.0	49.4	10.2	76	4
		Col. Eff.	88	7.2		7.6			1.11	100	0.8	74	3
62,63	2-27	Pri. Eff.	250	66	310	7.2			22.8			34	11
		Ppt. Eff.	78	5.8		7.2			21.9	54.0	8.2	80	3
		Col. Eff.	71	8.8		7.3			1.42	106	1.6	35	8
64	2-28	Pri. Eff.	276	108	340	7.1			23.1			35	11
		Ppt. Eff.	82	7.6		7.1			22.0	52.9	9.0	86	1
		Col. Eff.	81	11.0		7.4			0.53	126	0.4	58	
66	3-1	Pri. Eff.		90	300	7.2			21.1			32	12
		Ppt. Eff.		4.8		7.3			22.4	58.6	9.4	94	2
		Col. Eff.		15		7.8			4.06	102	1.6	44	

[a]Treatment: primary sedimentation, chemical precipitation at pH 11.0, ammonia sorption.

[b]Sample composited over period 2-23 to 2-28.

TABLE 3

EBMUD SUPPLEMENTARY DATA[a]

Run	Date 1970	Treatment	COD mg/ℓ	SS mg/ℓ	pH	Tot. P mg/ℓ	Tot Sol. P mg/ℓ	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ
1	11-26	Pri. Eff.	346	83	7.0			12.3			31	9
		Ppt. Eff.	166	26	7.2			10.7			96	2
		Col. Eff.	127	12	7.2			1.33			96	6
2	11-27	Pri. Eff.	311	70	8.1			14.8			38	8
		Ppt. Eff.	116	17	7.1			14.3			84	9
		Col. Eff.	109	8.0	7.0			3.2			98	6
3	11-30	Pri. Eff.	200	88	7.5	4.0	2.7	5.7			39	10
		Ppt. Eff.	92	30	6.9	2.3	1.7	5.3			90	10
		Col. Eff.	51	7.7	6.9	0.9	0.7	0.41				
4	12-1	Pri. Eff.	266	180	7.3	5.6	3.7	8.8			43	9
		Ppt. Eff.	94	8.1	7.1	0.9	0.6	8.5			120	6
		Col. Eff.	98	13.6	7.3	0.9	0.7	0.32			92	8
5	12-2	Pri. Eff.	273	100	7.1	4.4	1.9	9.7			33	15
		Ppt. Eff.	112	7.9	7.6	0.8	0.3	8.5	110	12.9	88	14
		Col. Eff.	84	6.6	7.3	0.5	0.3	0.26	110	2.7	96	5
6	12-3	Pri. Eff.	409	190	7.0	7.1	3.7	9.2				
		Ppt. Eff.	113	14	7.2	0.8	0.4	8.8	92.0	12.5		
		Col. Eff.	95	5.4	7.1	0.7	0.3	0.31	131	2.3		
7	12-4	Pri. Eff.	414	227	7.2	7.5	3.7	9.7			36	11
		Ppt. Eff.	158	58	7.2			8.1	78.2	12.1	110	5
		Col. Eff.	99	4.2	7.1	0.7	<0.1	0.51	120	2.7	86	4

[a]Treatment: primary sedimentation, chemical coagulation, filtration, ammonia sorption.

TABLE 3 (Continued)

EBMUD SUPPLEMENTARY DATA[a]

Run	Date 1970	Treatment	COD mg/ℓ	SS mg/ℓ	pH	Tot. P mg/ℓ	Tot. Sol. P mg/ℓ	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ
8	12-8	Pri. Eff.	353	90	7.0			12.6			33	13
		Ppt. Eff.	309	136	7.4			14.4	117	21.1	97	4
		Col. Eff.	196	18	7.4			0.29	177	3.5	87	6
9	12-9	Pri. Eff.	352	72				13.2			37	11
		Ppt. Eff.	175	5.0				12.6	105	25.0	100	
		Col. Eff.	161	2.5				0.83	136	3.5	97	3
10	12-10	Pri. Eff.	374	84		7.0	4.7	16.1			44	8
		Ppt. Eff.	182	81		0.7	0.3	16.5	129	23.5		
		Col. Eff.	165	12		0.5	0.3	0.62	192	3.5	94	4
11	12-11	Pri. Eff.	453	120		7.6	3.3	15.2			32	17
		Ppt. Eff.	197	15		0.8	0.2	15.8	117	27.4	110	5
		Col. Eff.	175	8.1		0.8	0.3	2.19	184	3.5	96	4

[a]Treatment: primary sedimentation, chemical precipitation, filtration, ammonia sorption.

TABLE 3 (Continued)

EBMUD SUPPLEMENTARY DATA[a]

Run	Date 1970	Treatment	COD mg/ℓ	SS mg/ℓ	pH	Tot. P mg/ℓ	Tot. Sol. P mg/ℓ	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ
12	12-14	Pri. Eff.		84	7.3						35	8
		Ppt. Eff.		9.9	8.2			16.1	138	10.6	104	9
		A.C. Eff.	22	8.5	8.4							
		Col. Eff.		2.4	8.3			0.19	184	3.5	75	4
13	12-15	Pri. Eff.	339	147	7.1	7.5	4.6	16.7			47	7
		Ppt. Eff.	162	8.4	7.9	0.6	0.5	15.1	143	18.8		
		A.C. Eff.	57	1.7	7.9	0.5	0.4	14.8				
		Col. Eff.	76	2.1	8.0	0.4	0.4	0.56	184	3.1		
14	12-16	Pri. Eff.	352	93	7.2			12.6			44	3
		Ppt. Eff.	169	14	8.0			13.3	117	20.7		
		A.C. Eff.	100	3.0	8.1							
		Col. Eff.		3.4	8.0			0.31	193	3.5		
15	12-17	Pri. Eff.	242	70	7.2	4.5	2.8	10.5			36	8
		Ppt. Eff.	140	27	7.2	1.4	0.8	11.2	95.5	17.2	102	3
		A.C. Eff.	72	9.1	7.9	0.7	0.8	11.1			105	4
		Col. Eff	56	3.3	8.4	0.4	0.3	0.35	168	1.6	70	3

[a]Treatment: primary sedimentation, chemical precipitation, filtration, carbon sorption, ammonia sorption.

TABLE 3 (Continued)

EBMUD SUPPLEMENTARY DATA[a]

Run	Date 1970	Treatment	COD mg/ℓ	SS mg/ℓ	Turb. JTU	pH	Tot. P mg/ℓ	Tot. Sol. P mg/ℓ	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ
16	12-19	Pri. Eff.	243	52		7.3			11.3			41	9
		Ppt. Eff.	135	32		7.3			9.7	102	19.1	104	4
		Resin Eff.	90	7.7		7.2						98	4
		Col. Eff.	77	11		7.3			0.76	126	1.1	95	5
17	12-20	Pri. Eff.	243				6.4	3.6	12.0			36	9
		Ppt. Eff.	86		112		0.7	0.3	12.0	107	16.8	91	6
		Resin Eff.	67				1.6	1.3	11.5				
		Col. Eff.	60		46		1.3	1.0	0.25	138	2.0	82	4
18	12-21	Pri. Eff.	147	86		7.4			8.1			42	3
		Ppt. Eff.	49	17	23	7.6			8.3	78.2	6.2		
		Resin Eff.	34	3.3		8.1			8.6			98	4
		Col. Eff.	28	2.8	15	8.3			0.35	113	1.6	90	2
19	12-22	Pri. Eff.	247	76		7.0	4.9	2.7	10.5			52	3
		Ppt. Eff.	134	16	64	7.9	1.0	0.6	9.7	106		126	3
		Resin Eff.	64	8.2		7.8	0.8	0.6	9.8			116	2
		Col. Eff.	81	4.6	17	7.9	0.7	0.5	0.55	133		106	2

[a]Treatment: primary sedimentation, chemical coagulation, filtration, macroporous resin sorption, ammonia sorption.

TABLE 4

CCCSD SUPPLEMENTARY DATA[a]

Run	Date 1971	Treatment	COD mg/ℓ	SS mg/ℓ	pH	Tot. P mg/ℓ	Tot. Sol. P mg/ℓ	NH_3-N mg/ℓ	Na mg/ℓ	K mg/ℓ	Ca mg/ℓ	Mg mg/ℓ
1	4-26	Part. Set. Sew.										
		Ppt. Eff.	77	9.6	6.8			18.5	95	10.9	62	11
		Col. Eff.	68	8.7	6.9			1.18	143	3.9	53	8
2	4-27	Part. Set. Sew.	262	118	7.2	12.7	10.5	21.1	112	10.9	64	8
		Ppt. Eff.	72	11	6.7	1.5	0.9	19.1	98	10.9	74	4
		Col. Eff.	63	7.5	6.8	1.3	0.9	0.52	138	3.1	78	1
3	4-28	Part. Set. Sew.	320	141	7.5			18.8	113	11.7	50	14
		Ppt. Eff.	64	9.1	6.8			20.2	113	12.5	72	2
		Col. Eff.						0.26				
4	4-29	Part. Set. Sew.	330	142	7.3			23.1	117	11.7	57	9
		Ppt. Eff.	68	6.5	6.5			20.1	115	11.7	71	3
		Col. Eff.	52	6.9	6.9			0.25	139	3.9	76	5
5	4-30	Part. Set. Sew.	284	123	7.2	13.3	9.8	23.5	102	11.7	54	11
		Ppt. Eff.	74	9.6	6.3	1.0	0.2	19.3	102	11.7	71	4
		Col. Eff.	54	6.8	6.8	0.6	0.5	0.27	139	3.9	74	3
6	5-1	Part. Set. Sew.	260	108	7.4			18.0	103	12.1	57	11
		Ppt. Eff.	104	33	9.1			22.9	113	11.7	70	3
		Col. Eff.	58	9.3	9.0			9.3	138	2.3	48	4

[a]Treatment: partial sedimentation, chemical coagulation at pH 10.5-10.8, filtration, ammonia sorption.

TABLE 5

BIOCHEMICAL OXYGEN DEMAND
mg/ℓ

Location	Date	Pri. Eff.	Ppt. Eff.	Col. Eff.
SERL-I	8-28-70	99[a]	3	3
	9-3-70	121[a]	5	2
	9-17-70	108	30	28
	9-24-70	121	32	27
	10-1-70	127	65	40
SERL II	2-18-71	92	43	49
	2-25-71	96	26	30
	3-8-71	121	47	43
EBMUD	11-25-70	260	136	123
	12-2-70	185	56	48
	12-11-70	217	127	121
	12-16-70	167	112[b]	99
CCCSD	4-27-71	112[c]	29	29
	4-30-71	130[c]	20	14

[a]Primary effluent received activated sludge treatment prior to chemical precipitation; BOD of activated sludge effluent equalled 53 mg/ℓ on 8-28-70 and 24 mg/ℓ on 9-3-70.

[b]Precipitated effluent passed through 3 ft of activated carbon prior to ammonia sorption; BOD of carbon effluent equalled 85 mg/ℓ.

[c]Partially settled sewage.

TABLE 6

ORGANIC PLUS AMMONIA NITROGEN

mg/ℓ

Location	Date	Pri. Eff.	Ppt. Eff.	Col. Eff.
SERL-I	8-29-70	33.8[a]	18.1	6.1
	9-3-70	31.2[a]	18.7	7.5
	9-18-70	29.9	23.5	5.3
	9-22-70	27.7	22.0	2.1
	9-30-70	28.0	23.2	3.4
SERL II	2-18-71	28.1	24.6	5.5
	2-25-71	30.0	23.5	5.0
EBMUD	11-24-70	34.6	31.1	10.2
	12-1-70	18.1	15.7	4.5
	12-3-70	23.4	14.4	3.1
	12-8-70	31.4	23.9	7.4
	12-10-70	32.9	24.9	6.6
	12-15-70	27.6	22.5[b]	2.7
	12-17-70	20.0	16.9[b]	3.1
	12-20-70	21.3	18.8[c]	2.8
	12-22-70	20.2	17.1[c]	3.5
CCCSD	4-25-71	35.6[d]	22.4	9.0
	4-27-71	32.8[d]	29.4	3.6
	4-29-71	36.4[d]	24.9	2.9
	4-30-71	36.7[d]	23.8	2.4

[a]Primary effluent received activated sludge treatment prior to chemical precipitation; Org.-N + NH_3-N of activated sludge effluent equalled 20.5 mg/ℓ on 8-29-70 and 20.2 mg/ℓ on 9-3-70.

[b]Precipitated effluent passed through 3 ft of activated carbon prior to ammonia sorption; Org.-N + NH_3-N of carbon effluent equalled 18.5 mg/ℓ on 12-15-70 and 15.5 mg/ℓ on 12-17-70.

[c]Precipitated effluent passed through 3 ft of macroporous resin prior to ammonia sorption; Org.-N + NH_3-N of resin effluent equalled 18.1 mg/ℓ on 12-20-70 and 15.5 mg/ℓ on 12-22-70.

[d]Partially settled sewage.

SELECTED WATER RESOURCES ABSTRACTS
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16. Abstract

The zeolite ion exchanger clinoptilolite was investigated with the objective of optimizing its application to ammonia removal from wastewaters. The study included multiple cycle pilot plant operations at three municipal sewage treatment plants. Particular attention was given to cation interference with exhaustion performance and with minimum cost regeneration.

The ammonia capacity of clinoptilolite was found to be nearly constant over the pH range of 4 to 8, but diminished rapidly outside this range. In regeneration the pH was critical in determining the NaCl requirements, a higher pH favoring lesser amounts of salt. However, at a pH over 12.5 zeolite attrition became excessive and exchanger makeup contributed significantly to operating costs.

An average ammonia removal of 95.7% was obtained in demonstration studies on three municipal wastes having an NH_3-N content of about 20 mg/ℓ. The cost of ammonia removal using clinoptilolite for a 10-mgd plant operating under these conditions was estimated to be $0.082/1000 gal. Ammonia removals down to less than 0.5 mg/ℓ NH_3-N is technically feasible, but only with shorter exhaustion runs and greater regenerant requirements.

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17a. Descriptors: *Cation exchange, *Ammonia, *Zeolites, *Tertiary Treatment, Nitrogen, Waste Water Treatment, Water Reuse, Cost Analysis.

17b. Identifiers: *Clinoptilolite, *Advanced Wastewater Treatment, Chemical-Physical Treatment of Wastewater.

17c. COWRR Field & Group: 05D

18. Availability

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