THE EXCHANGE ZONE HEIGHT OF A

FIXED-BED CATION EXCHANGER

by

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Thesis submitted to the Graduate Faculty of the

Virginia Polytechnic Institute

in candidacy for the degree of

MASTER OF SCIENCE

in

CHEMICAL ENGINEERING

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June 1958

Blacksburg, Virginia

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I. INTRODUCTION

Great progress has been made in the field of ion exchange during the past few years. New applications have been proposed and tried, novel methods of operation have been investigated, and a variety of resins have been made available. Theory has advanced rapidly, also. Theoretical equations have been derived which express the behavior of all known cases of ion exchange operation, and explanations of the mechanism of the reactions involved have been advanced.

In contrast to this progress, however, exchange equipment is still being designed on an empirical basis. The mechanism of ion exchange involves both mass transfer and reversible chemical reactions; further, ion exchange is more frequently used in batch rather than continuous systems. The resulting design equations have therefore been mathematically complex and difficult to use, both for the correlation of data and for the design of ion exchange installations.

A few years ago, a new approach to the problem of design methods for ion exchangers was proposed, which, while not very general in its scope of applicability, is simple enough to be of practical use for many of the

more common cases of ion exchange operation. The novel
idea in this method of design is the exchange zone
concept.

This investigation is a further study of the
application of the exchange zone concept to the design
of fixed-bed ion exchangers. The purpose of this
investigation was to determine the relationship between
the influent sodium chloride concentration and flow rate,
and the exchange zone height for a fixed-bed ion exchange
column of Nalcite HCR.

II. LITERATURE REVIEW

The following section reviews some of the more important literature on ion exchange. Ion exchange history, applications, and mechanism theories are considered first. A brief review of alternate design methods and a more detailed review of the exchange zone method complete this section.

History

Ion exchange was discovered by two English soil scientists, Way and Thompson[30], in the course of their investigations on the action of water-soluble fertilizers in soils. They noted the curious fact that certain soluble salts, such as ammonium sulfate, were not easily leached out of the soil by rain water.

The first attempt at an application of this phenomenon was not made until some sixty years later. In 1910, the German chemist Gans[4] used alumino-silicates for the softening of hard water. Because the capacity of both natural and synthetic alumino-silicates was low, studies were made on the synthesis of higher capacity exchangers. These studies[17]

eventually led to the discovery of sulfonated coal
cation exchangers.

Since then, the history of ion exchange has been
characterized by the numerous uses to which it has been
put. Today, it is mentioned in such diverse fields as
medicine and atomic energy, analytical chemistry and
chemical processing, sugar refining, and waste disposal.

Applications

The broad field of ion exchange applications may
be divided into the following general classes:
purification, separation, exchange, and pH control.
Examples of each of these applications are numerous
and several general review articles on these applications
are available[11,12,13].

Purification. Purification refers to the removal
of undesired components from substances with which it
is associated. If the impurity is ionizable, or may be
made to combine with an ionizable compound, then, ion
exchange techniques may be applied to the purification
process. The de-ionization or demineralization of
water to yield a product with a purity comparable to

that of triple-distilled water[3] and the treatment of
sugar juice[21] to remove compounds which decrease the
yield of sucrose are examples of the applications of ion
exchange to purification processes. Other substances for
which ion exchange purification has been proposed are
glycerine and other polyalcohols, and whey[7].

Separation. Ion exchange separation techniques
depend upon differences in the relative affinities of
ions for exchange resins. Most of the applications for
which ion exchange separation techniques have been
proposed involve mixtures whose components are not
easily separable by more conventional methods.
Examples of such mixtures are the rare earths, amino
acids, and proteins.

Separation studies have been made on the mineral
gadolinite. Spedding and Powell[29], using ion exchange
techniques, were able to separate 82 per cent of the
erbium and 50 per cent of the ytterbium to purities
greater than 99.9 per cent in a single operation on a
crude concentrate of gadolinite.

Techniques appropriate for the separation of the
amino acids, peptides and proteins have been described
by Partridge[26]. These techniques were developed for

the isolation and study of the components commonly found in proteins or biological extracts.

Closely related to the amino acid separations are the numerous uses proposed for ion exchange resins in the field of analytical chemistry. As of 1954, Osborn[23] reported a total of more than two thousand papers dealing with the use of ion exchange resins in analytical separations. Among the subjects treated in these papers[24] were the dissociation of normally insoluble salts like barium and strontium sulfates, the separation of ionized from un-ionized substances in solution, and the separation of the amphoteric group of cations.

Exchange. Exchange refers to the substitution of one ion for another in a solution. Such a substitution may be desired in order to remove a deleterious substance from a solution, or to recover a valuable component from a waste stream. The removal of deleterious substances from a solution is, in many respects, similar to purification. In purification, however, the techniques are generally more elaborate, since the complete removal of an impurity is involved, while in exchange, the harmful substance is merely replaced by another substance which does not have the

undesired properties. The softening of water[19], and
the de-ionization of water[20] illustrate this
difference, the former being an example of an exchange
reaction while the latter is an example of purification.

Most of the therapeutic applications of ion
exchange cited by Osborne[25] fall under the exchange
classification. Among such therapeutic applications are
the control of the electrolyte content of the human body
to correct abnormalities brought about by kidney and
heart diseases. Other medical uses are also cited by
Black[1].

Ion exchange techniques have also been proposed and
employed in waste treatment and recovery[27]. Specific
examples of these are the recovery of copper from waste
waters of the cupprammonium rayon process[5], and the
recovery of plating metals from spent plating baths[16].

Control of pH. The use of ion exchange resins for
pH control is based on the fact that these resins furnish
hydrogen or hydroxyl ions when in contact with a polar
liquid. Their chief advantage over other pH controlling
substances lies in the ease with which solid resins may
be separated from liquid media when desired[14]. Among
the uses for which ion exchange resins have been

proposed for pH control are in the catalysis of the
esterification reactions between organic acids and
alcohols, and the hydrolysis of sucrose and other water
soluble complex sugars[14].

Ion Exchange Theories

Ion exchange theories may be divided into two broad
classes: those that are concerned with explaining and
predicting equilibrium phenomena, and those that attempt
to analyse the transport process for the formulation of
rate relationships.

Equilibrium Theory. The following is a brief
summary of ion exchange equilibrium theory[15,18].

When ion exchange resins are brought into contact
with a solution of an electrolyte, a reversible
interchange of ions takes place between the solution
and the solid resin. Experiments have shown that the
equilibrium relationships depend to a great extent on
the interchanging pair of ions.

Initial attempts at an explanation of the latter
phenomena used the mass action concept and defined an
equilibrium constant based on ionic concentrations in
the solution and in the resin analogous to those for

other reversible chemical reactions. This equilibrium constant served to measure the relative affinities of the different ions for a particular resin. Considerable attention was placed on correlating the relative affinities of different ions with their other properties such as atomic weight and crystal radius. These attempts, however, did not meet with any success.

A few years later, refined experimental techniques proved that the equilibrium constant based on ionic concentrations was not actually constant. This required redefining the equilibrium relationship in terms of ionic activities. Since then, refinements have been added to the theory to account not only for the activity energies but also for the swelling energies involved when the resin imbibes some of the solvent in which it is placed.

Transport Process Theory. According to Treybal[31], the transport process may be broken down into the following steps: diffusion of ions from the liquid bulk to the external surface of the exchanger particle; inward diffusion of ions through the solid to the exchange sites; exchange of ions; outward diffusion of the released ions to the solid surface; and diffusion

of the released ions from the solid surface to the liquid bulk. The rate of ion exchange will therefore depend on the resistances offered by these five steps. Hiester[8] has derived rate equations based on these resistances using ionic concentrations as the driving force. These equations are presented in the following section.

Alternate Design Methods

Most of the design equations[6,8,9,10] proposed for ion exchangers are based on an analysis of the transport process involved. These equations differ in their final forms depending on the particular applications for which they are intended. Hiester[8] has derived relationships which cover all of these applications, and a summary of his work is given below.

The system considered by Heister[8] consists of ions $\underline{A}$, $\underline{B}$, and $\underline{G}$, all of the same valence, and the

exchange resin. For the reaction on the resin surface, the rate equation is given by:

$$(dq_A/dt)_p = k_{AG\ kin}\ (c_A)(q_G) - (1/K_{AG})(q_A)(c_G)$$

$$+ (k_{AB\ kin})(c_A)(q_B) - (1/K_{AB})(q_B)(c_B)$$

where:

q_A = concentration of A in resin, milli-equivalents per gram

t = time, minutes

$k_{AG\ kin}$ = specific reaction rate constant for the reaction between ion A and ion G, milliliters per milli-equivalent per minute

c_A = concentration of A in solution, milli-equivalents per milliliter

q_G = concentration of G in resin, milli-equivalents per gram

K_{AG} = exchange reaction equilibrium constant for A and G

c_G = concentration of G in solution, milli-equivalents per milliliter

$k_{AB\ kin}$ = specific reaction rate constant for the reaction between A and B, milliliters per milli-equivalent per minute

q_B = concentration of B in resin, milli-equivalent per gram

K_{AB} = exchange reaction equilibrium constant for A and B

c_B = concentration of B in solution, milli-equivalents per milliliter

p = denotes that the equation is over a given particle.

Considering now the liquid phase outside the resin,
the two diffusion processes may be combined into a counter-
diffusion process, for which the rate equation is:

$$(dq_A/dt)_p = k_{FA}\, a_F\, f_e\, (c_A - c_A{}^*)/s$$

where:

q_A = concentration of A in the resin, milli-
equivalents per gram

t = time, minutes

k_{FA} = mass transfer coefficient of A,
1/centimeter - minutes

a_F = transfer area per milliliter of bulk
volume

f_e = fraction of external void space in
the resin bed

c_A = concentration of A in solution, milli-
equivalents per milliliter

$c_A{}^*$ = concentration of A in the portion of
the fluid adjacent to and in
equilibrium with the solid, milli-
equivalents per milliliter

s = resin bulk density, grams per milliliter

p = denotes that the equation is over a
given particle.

The equilibrium relation is given by:

$$c_A^* \quad \frac{(c_o - c_B^*)\, q_A}{(Q - q_B)\, K_{AG} + (1 - K_{AG})\, q_A}$$

where:

c_A^* = concentration of A in the portion of the fluid adjacent to and in equilibrium with the solid, milli-equivalents per milliliter

c_o = sum of the concentrations of A, B, and G, in the fluid phase, milli-equivalents per milliliter

c_B^* = concentration of B in the portion of the fluid adjacent to and in equilibrium with the solid, milli-equivalents per milliliter

q_A = concentration of A in the resin, milli-equivalents per gram

K_{AG} = equilibrium constant for the exchange reaction between A and G.

Equations similar to these three may be written for component B.

For the internal counter-diffusion of the ions inside the pore fluid, or through the solid phase, depending on the characteristic properties of the resin, the rate equation is:

$$(dq_A/dt)_p = k_{SA} \, a_S \, (q_A^* - q_A)$$

where:

q_A = concentration of $\underline{A}$ in the resin, milli-equivalents per gram

t = time, minutes

k_{SA} = mass transfer coefficient for $\underline{A}$ in the solid phase, 1/centimeter - minute

a_S = transfer area per milliliter of volume

q_A^* = concentration of $\underline{A}$ in the outer layer of particles adjacent to and in equilibrium with the fluid, milli-equivalents per gram

p = denotes that the equation is over a given particle.

The equilibrium relationship will be analogous to that for the liquid phase. Again, similar rate and equilibrium relationships will hold for component $\underline{B}$.

The application of the preceding equations to a particular design problem requires the integration of the rate equations and their simultaneous solution with the equilibrium relationships.

The special case of ion exchange in a fixed-bed, where the two counter-diffusion processes may be assumed to be controlling was studied by Gilliland and Baddour[6]. The integrated form of the equation which they used is given in the following paragraph. This equation was originally derived for the exchange of sodium ions for hydrogen ions in an aqueous solution.

$$c/c_0 = \frac{1}{1 + G \, e^{(K - 1)(Kv - u)/K}}$$

where:

    c = bulk concentration of sodium ions in the liquid phase, milli-equivalents per milliliter

    c_0 = influent solution concentration, milli-equivalents per milliliter

    K = equilibrium constant for the sodium-hydrogen exchange reaction

    e = base of natural logarithms.

The quantities $\underline{G}$, $\underline{v}$, and $\underline{u}$ are defined as follows:

$$G = \frac{g(Kv,\ u/K)}{1 - g(v,\ u)}$$

where:

$$g(u,\ v) = e^{-v} \int_0^u e^{-a} I_0(2\ \sqrt{v\ a})\ da$$

where:

  e = base of natural logarithms

  I_0 = modified Bessel function, first kind, zero order, of $\underline{a}$.

The quantity $\underline{u}$ is defined by the relationship:

$$u = k\ c_0\ y/V$$

where:

  k = mass transfer coefficient

  c_0 = influent solution normality, milli-equivalents per milliliter

  y = volume of solution passed through the bed

  V = flow rate through the bed,

the units for $\underline{k}$, $\underline{y}$, and $\underline{V}$ being any consistent set to make $\underline{u}$ a dimensionless number.

The quantity $\underline{v}$ is defined by the relationship:

$$v = kx/KV$$

where:

k = mass transfer coefficient

x = total exchange capacity of the bed

K = equilibrium constant for the exchange reaction between sodium and hydrogen ions

V = flow rate through the bed,

the units for the above quantities being any consistent set that will make $\underline{v}$ a dimensionless number.

The equilibrium constant for the exchange reaction between sodium and hydrogen ions used in the preceding equations is given by the relationship:

$$K = (c_{av})(c_o - c)/(c)(1 - c_{av})$$

where:

K = equilibrium constant for the exchange reaction between sodium and hydrogen ions

c_{av} = average mol fraction of sodium ions in resin particles

c_o = normality of influent solution, milli-equivalents per milliliter

c = sodium ion concentration in the bulk of the solution phase, milli-equivalents per milliliter.

The Exchange Zone Method

Michaels[22] developed the following method in order
to overcome the mathematical complexity of the procedures
previously proposed. The concepts, definitions, and
limitations involved, as well as the mathematical
development of the relationships to be used are reviewed
in the following paragraphs.

Concepts, Definitions, and Limitations. The exchange
zone method is applicable only to those systems where
sorption of the ion in solution is highly preferred. An
example of such a system is a strong acid-type cation
resin (e. g., Dowex 50 or Nalcite HCR) operating on the
hydrogen cycle and removing a metal ion from solution.
The reverse operation of regeneration is obviously not
within these limitations. Because of this high
preferential sorption, the exchange reaction is fairly
rapid. Consequently, the individual exchange reactions
take place within a small portion of the exchanger
apparatus.

The portion of the exchanger bed in which, at any
particular time, the exchange reactions are taking place
is what Michaels calls the exchange zone. The height of
this zone is called the exchange zone height.

Purely as a matter of convenience, Michaels[22] defined the limits of this zone in the following manner: the upper boundary of the zone is that part of the bed in which at steady state, the cation concentration in the solution phase is 95 per cent of the initial cation concentration in the influent solution; the lower boundary of the zone is that part of the bed in which, at steady state, the cation concentration in the solution phase is five per cent of the initial cation concentration in the influent solution.

At the start of the exchange cycle, the solution is stripped of the ions it carries at the very top of the column. As more solution is passed, the exchange zone forms, and then descends down the column at a constant velocity. When the lower boundary is at the bottom of the column, the concentration of the effluent solution is five per cent of the influent concentration. This condition is referred to as the "break-through." If more solution is passed, the zone begins to leave the column, and when the effluent concentration is 95 per cent of the influent concentration, the zone is just out of the column. This condition is referred to as "exhaustion."

The condition of the resins within the exchange zone varies from almost complete exhaustion at the upper boundary, to almost complete unsaturation at the lower boundary. Thus the zone, as a whole, may be considered as being unsaturated to a fractional degree $\underline{F}$.

The zone itself separates the saturated upper layers of resin from the unused lower layers. The assumption is made that as far as equilibrium is concerned, the two layers thus separated have no effect on each other.

Development of Relationships. In order to make the derived equations more general, no units will be specified for the different quantities involved. Any set of units may be used for the final equation, the only effect of which will be to change the value of the dimensional constant appearing in the final equation.

Consider the system composed of an ion exchange resin bed, with total height $\underline{h_t}$, and cross-sectional area $\underline{A}$, and a solution with an original concentration of $\underline{X_o}$, flowing through the bed with a superficial velocity of $\underline{Q}$. As the solution flows through the bed, exchange takes place initially at the top of the bed, resulting in the formation of the exchange zone after a length of time $\underline{\Theta_f}$, the zone formation time. As more

solution is passed, the zone descends down the column with a constant linear velocity U_z. When the volume of solution passed totals V_b, the lower boundary of the zone is at the bottom of the bed, the effluent concentration X is equal to 0.05 X_o, and the total elapsed time from the beginning of the cycle is θ_b. If more solution is now passed, the zone begins to leave the column, until a volume V_t of solution has been passed, at which time, the upper boundary of the zone is at the bottom of the column, the effluent concentration X is equal to 0.95 X_o, and the total time measured from the start of the cycle is θ_t.

During this exchange cycle, the zone moves a total distance equal to h_t, for a length of time equal to the cycle time θ_t minus the zone formation time θ_f.

The relationship, which is based on the definition of rate, is given by the equation:

$$U_z = h_t / (\Theta_t - \Theta_f)$$

where:

U_z = linear rate of zone descent through the column

h_t = total height of the resin bed

Θ_t = total cycle, or exhaustion point time

Θ_f = zone formation time,

and the units may be any consistent set.

From the break-through time Θ_b to the exhaustion time Θ_t, the zone is moving out of the column with the same linear velocity U_z. The distance which the zone travels during this time interval is evidently equal to its own height, that is, the exchange zone height h_z.

From the definition of rate, the following relationship is obtained:

$$h_z = U_z (\theta_t - \theta_b)$$

where:

h_z = exchange zone height

U_z = linear rate of zone descent through the column

θ_t = total cycle, or exhaustion point time

θ_b = break-through time,

and the units are the same consistent set.

The combination of the two equations yields the relationship:

$$h_z = (h_t)(\theta_t - \theta_b)/(\theta_t - \theta_f)$$

where:

h_z = exchange zone height

h_t = total height of the resin bed

θ_t = total cycle, or exhaustion point time

θ_b = break-through time

θ_f = time of zone formation,

and the units are the same consistent set used above.

Thus, for a given bed height h_t, θ_t and θ_b may be
determined experimentally, and h_z calculated from the
preceding equation, if θ_f is known. An approximate
method for the determination of θ_f, the zone formation
time, is outlined in the next paragraph.

As mentioned in the previous section, the exchange
zone may be thought of as being composed of a fraction F,
which is still unused, and a fraction $(1 - F)$, which has
already entered into the exchange reaction. During the
time the zone is moving out of the column, that is, from
break-through to exhaustion, the portion of the zone that
enters into the exchange reaction is the unused fraction F.
The concentration of effluent leaving the column during
this period of time depends, therefore, on the
instantaneous value of the fraction F at the bottom
of the column, the exchange reaction proceeding only
to the extent that the zone can still accommodate. The
total amount of ions which the unused fraction of the
zone can remove is obviously the total amount of ions

removed from the solution from break-through to exhaustion. This relationship is shown by the equation:

$$M = \int_{V_b}^{V_t} (X_0 - X)\ dV$$

where:

M = total amount of ions removed from break-through to exhaustion

V_t = volume of solution passed up to exhaustion

V_b = volume of solution passed up to break-through

X_0 = influent concentration

X = instantaneous value of effluent concentration

V = volume of solution passed corresponding to an effluent concentration $\underline{X}$,

and the units are the same consistent set used in the preceding.

If the resins in the exchange zone had been completely unused, then the zone would have removed an amount of ions equal to $X_o(V_t - V_b)$, from break-through to exhaustion. Hence, the fraction of the zone that was still unused is:

$$F = M/(X_o)(V_t - V_b)$$

where:

F = fraction of the zone still unused at steady state

M = total amount of ions removed by the zone from break-through to exhaustion

X_o = influent concentration

V_t = volume of solution passed at exhaustion

V_b = volume of solution passed at break-through,

and the units are the same consistent set used before.

Experimentally, the value of the fraction F may be determined by analysing the effluent for cation concentration X, at specific values of the effluent volume V. The quantity of ions removed from solution from break-through to exhaustion may then be computed by graphical integration.

If the zone had been completely saturated at steady state, and could remove no more ions, that is, $F = 0$, then the time of zone formation, θ_f, would be very nearly equal to the time from break-through to exhaustion, $(\theta_t - \theta_b)$. If the zone, on the other hand, had been completely unsaturated at steady state, that is, $F = 1$, then the zone formation time would be equal to zero.

When a linear relationship satisfying these limiting conditions is assumed, the following equation may be written:

$$\theta_f = (1 - F)(\theta_t - \theta_b)$$

where:

θ_f = zone formation time

F = fraction of the zone still unused at steady state

θ_t = total cycle, or exhaustion point time

θ_b = break-through time,

the units being the same consistent set used before.

The final relationship, relating the zone height to quantities which may be experimentally determined is therefore given by the equation:

$$h_z = (h_t)(\theta_t - \theta_b)/[\theta_t - (1 - F)(\theta_t - \theta_b)]$$

where:

h_z = exchange zone height

h_t = total height of the resin bed

θ_t = total cycle, or exhaustion point time

θ_b = break-through time

F = fraction of the zone still unused at steady state,

and the units are the same consistent set used in the foregoing derivation.

The simplifications made in the preceding derivation were indirectly verified by the good reproducibility of results Michaels obtained in his experimental investigation[22].

Summary of Michaels' Experimental Results. Michaels used the system Na-H-Cl-Nalcite HCR, for beds 22 millimeters in diameter, and of various heights. Flow rates were varied from 0.5 centimeter per second to 0.77 centimeter per second, while bed heights used were from 22.5 to 43.8 centimeters. A fixed concentration

of 0.12 mol per liter of sodium chloride was used for
all the tests. The experimental results showed that
the height of the exchange zone is independent of the
total column height, but is dependent on the rate of
flow of solution through the bed. The correlation
presented by Michaels for his results was of the form:

$$h_z = a \ U_1^{0.5}$$

where:

h_z = exchange zone height

U_1 = linear rate of solution flow through
the bed

a = dimensional constant, whose value
depends on the units used
for $\underline{h_z}$ and $\underline{U_1}$.

Factors Affecting the Exchange Zone Height. The
exchange zone height is related to that of the "transfer
unit" in the mass transfer operations. The zone height,
in effect, is a measure of the rate of ion exchange under
an average driving force. The factors affecting the
exchange zone height should therefore be the same factors
affecting the over-all rate. These factors are: the
temperature of the system, through its effect on mass
transfer and reaction rates; the nature of the system;

the ion concentrations; and the rate of solution flow
through the bed, through its effect on mass transfer
rates. It should also be apparent from the foregoing
that the total bed height and the bed diameter would
have no effect on the zone height. Michaels' work has
shown at least the former to be the case.

III. EXPERIMENTAL

The purpose of this investigation, the plan of experimentation, a description of the materials and apparatus used and the test procedures followed, the data and results obtained, and sample calculations are presented in this section.

Purpose of Investigation

The purpose of this investigation was to determine the relationship between the influent sodium chloride concentration and flow rate, and the exchange zone height for a fixed-bed ion exchange column of Nalcite HCR.

Plan of Experimentation

The investigation consisted of the following phases: review of literature, analysis of the variables involved, design and construction of the experimental equipment, performance of the tests, and analysis and correlation of the experimental results.

Review of Literature. The literature review covered published works in various fields of ion

exchange. The history of ion exchange development, ion exchange applications, as well as mechanism theories were studied first, in order to gain a general background on the subject. Design literature for the exchange zone and other methods were then reviewed more comprehensively, since these had a direct connection with this investigation.

Analysis of the Variables Involved. Based on previous work and theoretical considerations the more important variables in this study were expected to be: the temperature of the system, which varied within the range of 60 to 70 degrees Fahrenheit with ambient variations; the nature of the system, which was restricted to the Na-H-Cl-Nalcite HCR system; the rate of solution flow, which was selected as one of the variables to study; and influent ion concentration, which was also selected as a variable to study.

Design and Construction of Equipment. The experimental equipment was designed and constructed taking into consideration both current practice and the peculiar requirements of this experiment. The principal item, the exchange column, consisted of a vertically-mounted pyrex glass pipe, 48 inches long

and two inches in diameter, provided with means for introducing and withdrawing liquids and resin both at the top and at the bottom. Accessory equipment included a micrometer needle valve, which served as a flow rate regulator, a constant volume liquid pump, storage tanks for feed and waste solutions and resin, and miscellaneous laboratory glassware.

Preliminary Tests. Preliminary tests were made on the column to determine its flow and exchange characteristics, and to develop techniques to be used in the experimental tests. Information on flow rates which could be obtained from the pump, data on the approximate length of each test, and an indication of the number of effluent samples which should be taken for each test were obtained from these preliminary tests.

Experimental Tests. Tests were made at each of four different cation concentrations in the influent and at each of four different flow rates. Two replications were made for each test condition, the tests being performed in a random order within each set of replications. The cation concentrations tested were 0.10 N, 0.15 N, 0.20 N, and 0.25 N, and the flow rates

used for each of these concentrations were 2.66, 4.23, 5.32 and 7.14 gallons per minute per square foot of bed area.

Analysis and Correlation of Results. The data and results obtained were analysed to determine the effect of the rate of solution flow on the exchange zone height at each of the concentrations tested. A correlation of the relation between the exchange zone height and both concentration and solution flow rate was tested with experimental data from this test and from the literature and found to represent the data satisfactorily.

Materials

The following materials were used in this investigation.

Hydrochloric Acid. Reagent grade, 36 per cent. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to prepare acid rinsing solutions for the resin bed.

Phenolphthalein Indicator. Phenolphthalein indicator solution prepared by the Department of Chemistry, Virginia Polytechnic Institute. For analytical purposes. Used as an end-point indicator in acid base titrations.

Potassium Chromate Indicator. One molar potassium chromate aqueous solution. Obtained from the Department of Chemistry, Virginia Polytechnic Institute. Used as an end-point indicator in chloride titrations.

Resin, Cation Exchange. Nalcite HCR, hydrogen form, 20/50 mesh, batch L-4381-27. Obtained from the National Aluminate Corporation, Chicago, Illinois. Used as the exchange resin in the fixed-bed cation exchanger.

Silver Nitrate. Reagent grade, meets ACS
specifications, lot No E-286. Obtained from Fisher
Scientific Company, Silver Spring, Maryland. Used to
prepare silver nitrate solutions for chloride
titrations.

Sodium Chloride. Commercial table grade salt.
Obtained from Radford Brothers Store, Blacksburg,
Virginia. Used to prepare feed solutions.

Sodium Hydroxide. Reagent grade, 0.93 normal
stock solution. Obtained from the Department of
Chemistry, Virginia Polytechnic Institute. Used to
prepare 0.05 normal solutions for the titration of
test samples.

Water, Distilled. Distilled water obtained from
the Department of Chemistry, Virginia Polytechnic
Institute. Used for the preparation of feed and acid
rinse solutions, for the backwashing and washing of the
resin bed, and for the analytical work of the
investigation.

Apparatus

The following apparatus and equipment were used during the course of this investigation.

Beam Balance. Ohaus, 600 grams capacity, 100 milligram sensitivity. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in the preparation of feed solution.

Glassware. Assorted pyrex glassware such as beakers, erlenmeyer flasks, 50 milliliter burets, graduated cylinders, funnels, pipets, and volumetric flasks. Obtained from the supply room, Department of Chemical Engineering, Virginia Polytechnic Institute. Used in the preparation of feed and acid rinse solutions, and for the analytical work of the investigation.

Ion Exchange Column. The ion exchange column consisted of a vertically mounted glass pipe and was assembled from the standard equipment listed in the following paragraphs.

Flange Assembly. Standard two-inch Corning flange, complete with rubber insert, nuts and bolts. Two used. Obtained from the Sentinel Glass Company, Hatboro, Pennsylvania. Used to hold rubber stopper cap in place.

Flange. Brass, 1/4 inch thick flange to fit Corning standard two-inch pipe flange. Two used. Obtained from the stock room, Department of Chemical Engineering, Virginia Polytechnic Institute. Used to hold rubber stopper cap in place.

Glass Pipe. Double tough, pyrex, 48 inches long, two inches inside diameter. Obtained from the Sentinel Glass Company, Hatboro, Pennsylvania. Used to hold the resin bed.

Rubber Stoppers. Size No 11. One two-hole, one four-hole used. Obtained from the Department of Chemistry, Virginia Polytechnic Institute. Used to cap the ends of the glass pipe.

Motor. Electric, Master Gearhead motor, 115/230 v, 60 cy, single phase, 3.4/1.7 amp, 378 rpm. Obtained from the stock room, Department of Chemical Engineering, Virginia Polytechnic Institute. Used to drive the feed pump.

Pinch Cock. Screw type, brass. Four used. Obtained from the stock room, Department of Chemical Engineering, Virginia Polytechnic Institute. Used to open and close solution flow lines.

Planimeter. Keuffel and Esser planimeter
No F-4236, serial No 557-79. Obtained from the
Department of Mechanical Engineering, Virginia
Polytechnic Institute. Used to integrate effluent
concentration-time curve areas.

Pump. Sigmamotor, model T-8. Obtained from
Sigmamotor, Incorporated, Middleport, New York. Used
to introduce feed, acid rinse, backwash, and wash
solutions into the exchange column.

Tank. Open end, 25-gallon capacity, aluminum.
Obtained from the stock room, Department of Chemical
Engineering, Virginia Polytechnic Institute. Used as
feed tank.

Tank. Aluminum, 50-gallon capacity. Obtained from
the stock room, Department of Chemical Engineering,
Virginia Polytechnic Institute. One used as distilled
water storage, another as feed stock solution storage.

Timer. Electric "Time-IT", metal case, one-tenth
second units, 10,000 seconds total capacity. Obtained
from the stock room, Department of Chemical Engineering,
Virginia Polytechnic Institute. Used to determine
sample withdrawal time.

Tubing. Flexible tygon tubing, 1/4 and 3/16-inch outside diameters. Obtained from Sigmamotor, Incorporated, Middleport, New York. Used to transport solutions from pump to column.

Valve. Needle valve, threaded, 1/4-inch nominal size, Alpha 101 unplasticized polyvinyl chloride body and parts. Obtained from Alpha Plastics, Incorporated, Livingston, New Jersey. Used to control the effluent flow rate.

Methods of Procedure

The methods of procedure followed in the experimental phase of this investigation are divided into preliminary tests, pre-test procedure, and experimental test procedure.

Preliminary Tests. The preliminary tests consisted of the calibration of the pyrex column, determination of the column hold-up, pump rate studies, calibration of the feed tank, preparation of feed stock solution, and operational procedure studies.

Pyrex Column Calibration. A length of 16 inches was measured from the bottom support of the bed with a folding rule, and this length was marked on the glass column.

Determination of Column Hold-up. The procedure used in the determination of the column hold-up may be followed on Figure 1, page 42, which is the schematic diagram of the ion exchange apparatus.

Fresh resin was placed in the column up to the 16-inch mark, backwashed with water, and then allowed to settle. Minor adjustments were then made in the amount of resin in the column in order to make the bed come up to the 16-inch mark.

FIGURE I. SCHEMATIC DIAGRAM EXPERIMENTAL ION EXCHANGE APPARATUS
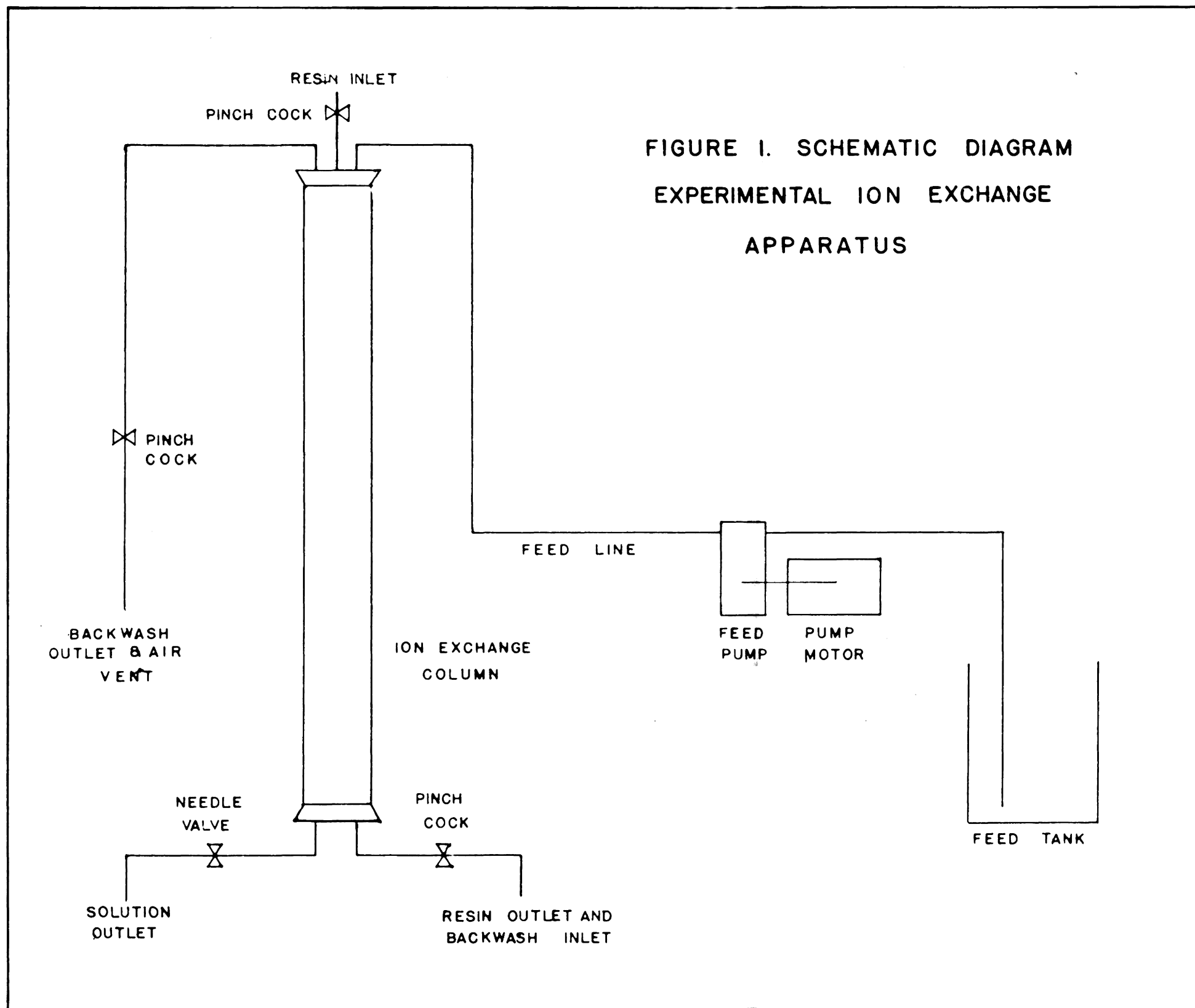
Water was then pumped into the column through
the feed line with different levels of water above
the resin bed in order to determine the minimum
water level above the bed that would prevent the
influent from disturbing the bed. This minimum
water level was found to be approximately three
inches above the top surface of the resin, and was
likewise marked on the column. The influent was
then shut off, and the column and lines drained
of water, the drained water being collected in
a 500-milliliter graduated cylinder. Several
similar tests gave the average volume of water
hold-up as 495 milliliters. This hold-up volume
includes the volume of water above and in the bed,
and in the flow lines.

Pump Rate Studies. A Sigmamotor model T-8
pump was used to introduce feed solution into the
ion exchange column as shown in Figure 1, page 42.
The pump was equipped with two pieces of tygon
tubing 1/4 inch in diameter, and one piece of
tygon tubing 3/16 inch in diameter. Using various
combinations of these three, distilled water as
well as feed solution was pumped into freshly

prepared beds, and the time required for the pump
to deliver one liter of effluent through the bed
in each case was determined. The best spacing of
rates was found to be 2.66, 4.23, 5.32, and 7.14
gallons per minute per square foot of bed area.
These rates were also found to be reproducible
within a range of about plus or minus 0.6 per cent.
The setting of the micrometer needle valve
required for each of the above flow rates was
determined at the same time and marked on the
valve body.

Feed Tank Calibration. Measured volumes of
water were placed in the feed tank shown in
Figure 1, page 42, and the water level marked on
the gage glass at five-liter intervals. The tank
was calibrated up to a volume of 80 liters.

Preparation of Feed Stock Solution. Three
thousand nine hundred grams of sodium chloride
were weighed on a pan balance and placed into one
of the 50-gallon tanks. Approximately 50 gallons
of distilled water were then added, ten gallons
at a time, and the solution agitated with
compressed air after each ten-gallon addition.

Twenty-five milliliter samples were taken with a pipet and analysed for chloride content using the Mohr method outlined by Pierce and Haenisch[28]. The stock solution was again agitated for several minutes and another sample titrated. After three consecutive titrations gave practically constant results, these results were then averaged to give the normality of the stock solution. This concentration was found to be 0.348 normal.

Operational Procedure Studies. These studies were made on freshly prepared resin beds, each bed being backwashed, acid-rinsed, and then water-washed before being used for a test. Tests were made at flow rates of 2.66 and 7.14 gallons per minute per square foot of bed area, using feed solutions with sodium chloride concentrations of 0.1 and 0.2 normal at each rate. With each test, various methods of checking flow rate and withdrawing effluent samples were tried. Peculiarities of the flow characteristics of the bed were observed and noted. From these tests, the approximate limits of the time required for each test, the number of samples to be withdrawn, the volume of samples to

be withdrawn, and minor operating details were
determined.

Pre-Test Procedure. The pre-test procedure refers
to the operations required before each experimental test
was made. These operations may be followed with the aid
of Figure 1, page 42, which is the schematic diagram of
the ion exchange apparatus used.

Spent resin from the previous test was first removed
from the column through the resin draw-off, and the empty
column was then rinsed with distilled water in order to
remove any traces of sodium chloride that might have
been left in the column. After the rinsing operation,
about two liters of distilled water were then placed in
the column, and fresh resin charged through the resin
inlet. The resin bed was then backwashed with distilled
water, allowed to settle, and adjusted to the 16-inch
mark by the addition or removal of resin. The adjusted
resin bed was next rinsed with about three liters of one
normal hydrochloric acid, in order to insure that the
bed was totally in the hydrogen form. The acid rinse was
stopped as soon as the wash effluent concentration was
the same as the influent concentration. A final
distilled water rinse then followed in order to remove

acid from the bed. The height of the water level above
the bed was then adjusted to the water level line
marked on the glass column.

During the acid and water washing periods, feed
solution was prepared, as required, by measuring the
needed volume of feed stock solution into the feed tank,
and diluting with distilled water to the desired
concentration. Each time such a dilution was made, the
resulting solution was checked for sodium chloride
content by the Mohr method[28].

Experimental Test Procedure. After completion of
the pre-test operations, the actual experimental tests
were started. A schematic diagram of the apparatus used
in these experimental tests is shown in Figure 1,
page 42.

The air vent was closed, and solution was pumped
into the column through the influent inlets. The
initial effluent was collected in a 500-milliliter
graduated cylinder, and the electric timer switched
on when the hold-up volume of 495 milliliters had
passed out of the column. Effluent samples were then
collected in 250-milliliter erlenmeyer flasks according
to the following schedule: for tests at 7.14 and 5.32

gallons per minute per square foot of bed area, every
100 seconds, for ten seconds each; and for tests at the
other two rates, every 200 hundred seconds, for
20 seconds each.

Towards the end of each experimental test, every
other sample was titrated as soon as it was taken in
order to determine if the exhaustion point had been
reached. One or two additional samples were taken
beyond the sample indicating that the exhaustion point
had been reached as a precaution. For the tests in the
first set of replicates, the approximate exhaustion
point time was taken as the time required to pass the
volume of solution that would completely exhaust the
resin in the column, as calculated from the results of
the operational procedure studies. For the tests in the
second set of replicates, the approximate exhaustion
point was determined from the results of the corresponding
tests in the first set of replicates.

Rates were checked at the beginning and end of each
test by noting the time required for one liter of
effluent to pass through the column.

Each sample taken was then analysed for acid content
by standard base titration methods. Five-milliliter

portions, measured by a pipet, were used for each
titration. Duplicate titrations were made in each case,
a third titration on the same sample being made only
if the first two did not give reasonably close results.
Standardised 0.05 normal sodium hydroxide solution was
used as the titrating agent, with phenolphthalein
solution as the indicator.

From the results of these titrations, the sodium
chloride content of the samples was computed, this
concentration being the difference between the original
sodium chloride normality of the influent, and the acid
normality of the effluent. A plot of sodium chloride
normality of the effluent against time was then
prepared for each test.

In order to eliminate variability of results
because of bed regeneration, each spent bed was
withdrawn from the column, and a fresh resin bed was
prepared for each test.

Data and Results

The data and results of this investigation are
presented in both tabular and graphical form in the
following sections.

Operational Data. The data and computational
results obtained from the 32 tests made on the ion
exchange column are presented in Table I, page 51.

Exchange Zone Height Data. Table II, page 52,
shows the results obtained for the exchange zone
height at the flow rates and influent concentrations
tested. The same data are presented graphically in
Figures 2 to 5, pages 53 to 56. In these figures, the
exchange zone height is shown as a function of the
solution flow rate, at each of the influent
concentrations studied. To facilitate comparison,
these four curves are shown plotted on a single set
of coordinate axes in Figure 6, page 57. The points
were omitted from the latter figure for clarity.
Figure 7, page 58, shows the least squares curves for
the exchange zone height as a function of the influent
concentration, with the solution flow rates as
parameters. The least squares curves shown in
Figures 2 to 7 do not represent the final correlation

TABLE I

Summary of Operational Data

Bed Dimensions: 16 inches long by two inches in diameter
Temperature: 60 to 70 degrees Fahrenheit
Solution: Aqueous sodium chloride
Resin: Nalcite HCR, 20/50 mesh, hydrogen form

Solution Flow Rate, gal/min/sq ft Q	Influent Concentration, mols/liter C	Exhaustion Point Time, sec θ_t	Break-through Point Time, sec θ_b	Sodium Fraction $(1 - F)$	Exchange Zone Height, inches h_z
7.14	0.25	860 890	300 360	0.445 0.425	14.70 12.76
	0.20	960 980	420 410	0.422 0.425	11.80 12.30
	0.15	1240 1250	570 590	0.430 0.475	11.30 11.30
	0.10	1800 1820	1030 1050	0.460 0.465	8.53 8.44
5.32	0.25	1150 1130	540 570	0.460 0.428	11.20 10.40
	0.20	1220 1190	600 580	0.468 0.475	10.70 10.85
	0.15	1650 1640	870 870	0.463 0.455	9.66 9.55
	0.10	2470 2500	1400 1450	0.470 0.550	8.70 8.75
4.23	0.25	1370 1410	740 780	0.485 0.421	9.42 8.80
	0.20	1460 1480	790 770	0.446 0.502	9.24 10.10
	0.15	1940 1940	1110 1120	0.400 0.430	8.26 8.25
	0.10	3120 3090	1940 1960	0.475 0.456	7.36 7.04
2.66	0.25	2190 2210	1250 1250	0.435 0.440	8.45 8.30
	0.20	2300 2250	1380 1340	0.450 0.440	7.81 7.85
	0.15	3050 3100	1950 1920	0.470 0.480	6.97 7.45
	0.10	4600 4630	3150 3200	0.425 0.440	5.77 5.71

TABLE II

The Effect of Flow Rate on the Exchange Zone Height at Various

Influent Solution Concentrations

Flow Rates, gal/min/sq ft	7.14	5.32	4.23	2.66
Concentration, mols per liter	Exchange Zone Height, inches			
0.25	14.70 12.76	11.20 10.40	9.42 8.80	8.45 8.60
0.20	11.80 12.30	10.70 10.85	9.24 10.10	7.81 7.85
0.15	11.30 11.30	9.66 9.55	8.26 8.25	6.97 7.45
0.10	8.53 8.44	8.70 8.75	7.36 7.04	5.77 5.71

Data obtained from thirty-two tests on a Nalcite HCR bed, sixteen inches high and two inches in diameter, with sodium chloride solutions.

FIGURE 2. EXCHANGE ZONE HEIGHT, SODIUM -
HYDROGEN-CHLORINE - NALCITE HCR SYSTEM

SOLUTION CONCENTRATION: 0.10 NORMAL

FIGURE 3. EXCHANGE ZONE HEIGHT, SODIUM -

HYDROGEN - CHLORINE - NALCITE HCR SYSTEM

SOLUTION CONCENTRATION: 0.15 NORMAL
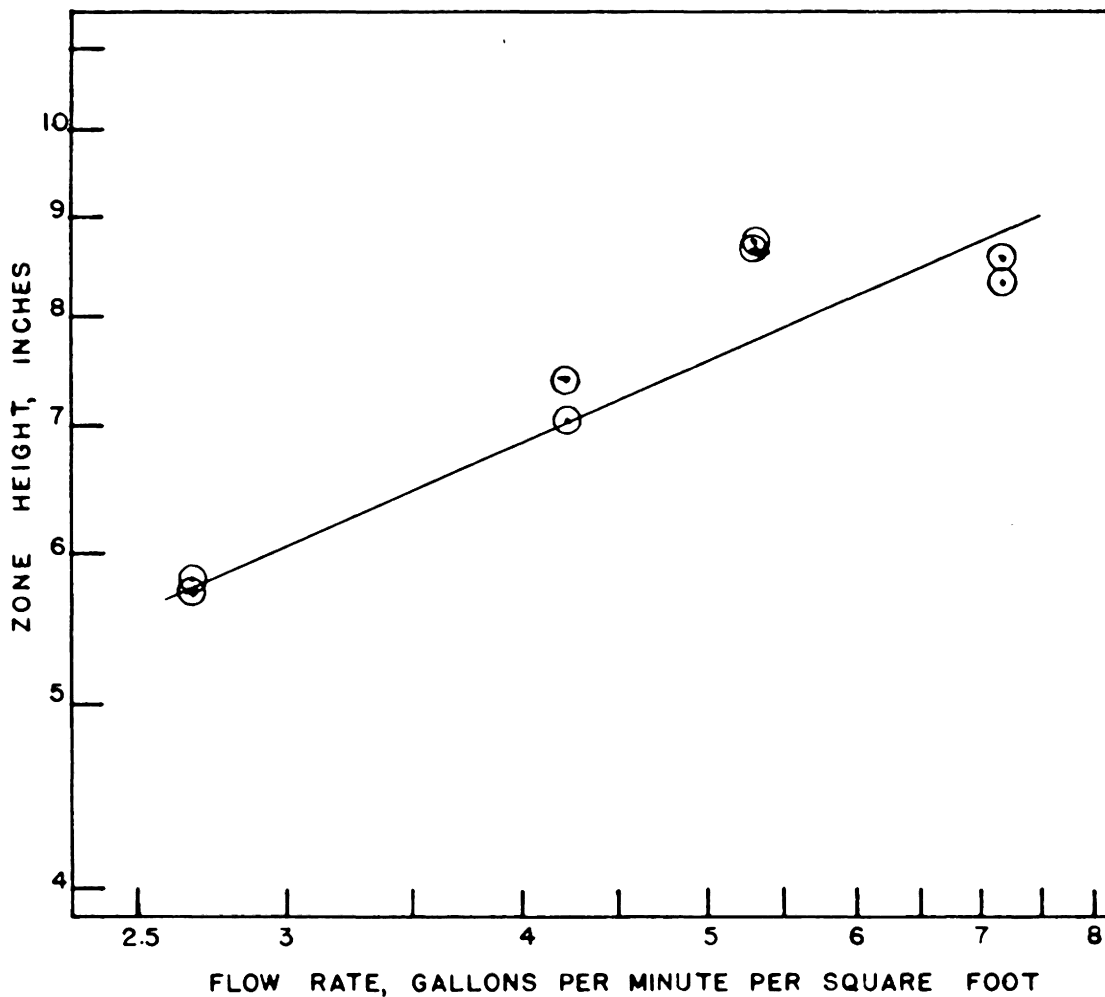
FIGURE 4. EXCHANGE ZONE HEIGHT, SODIUM-

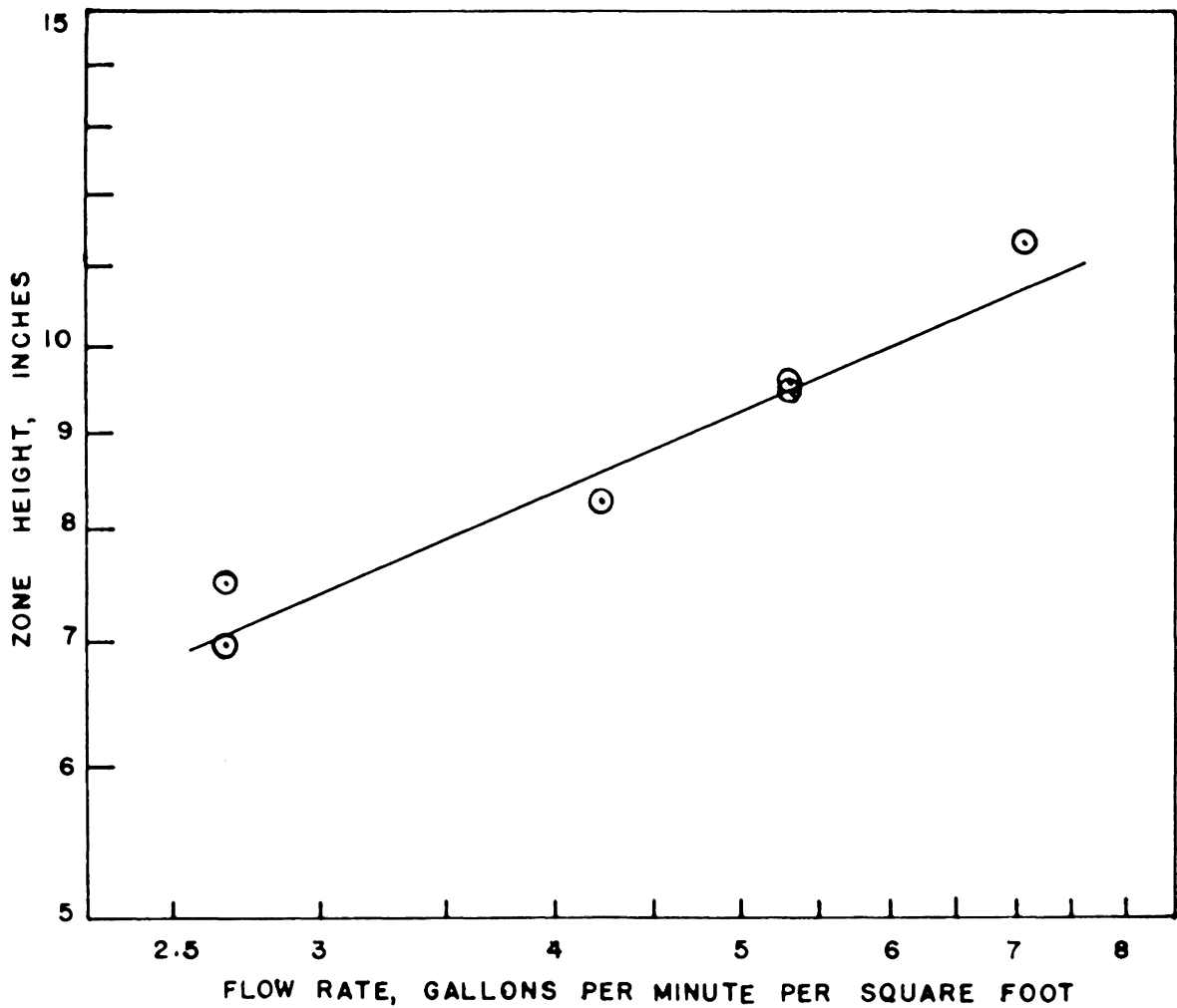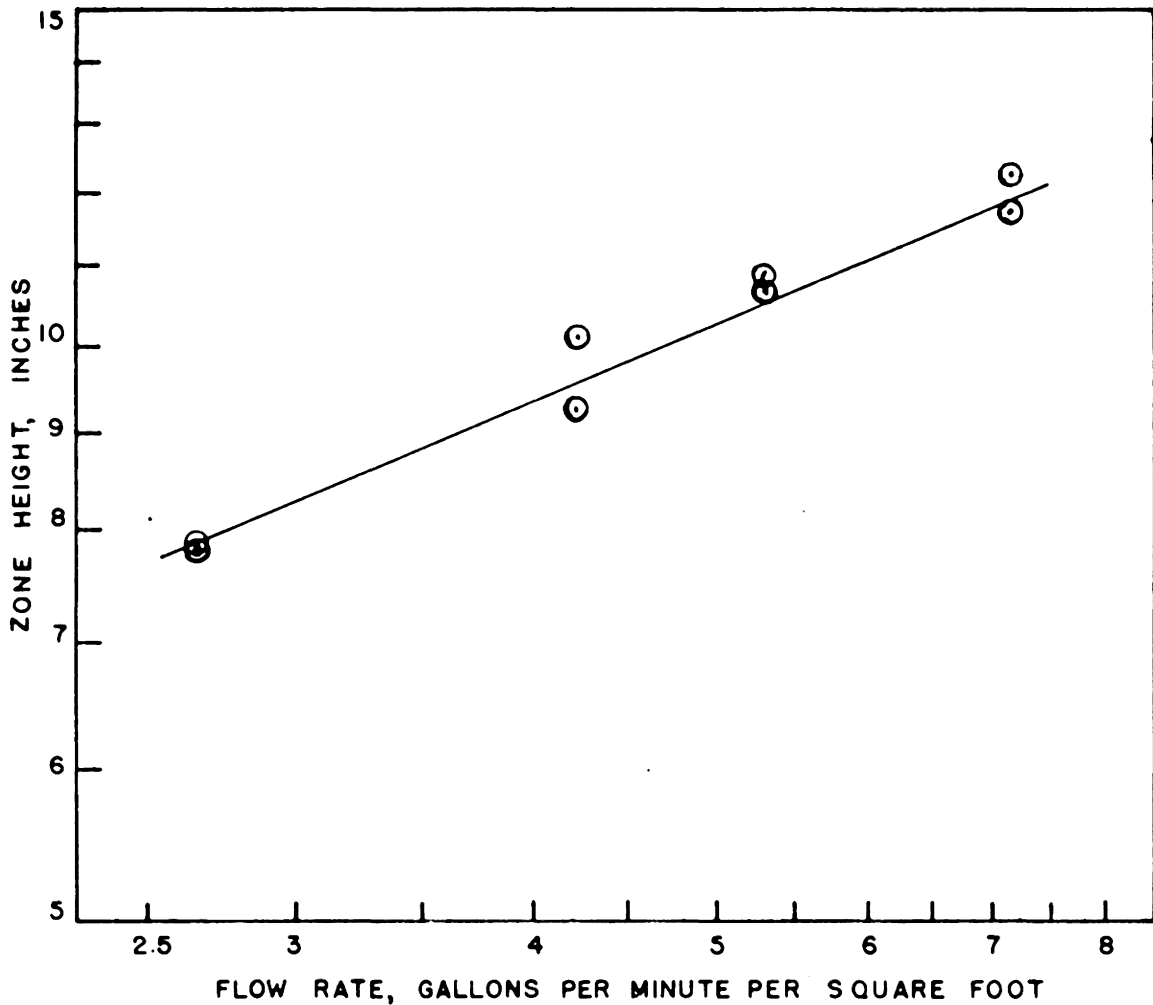HYDROGEN-CHLORINE-NALCITE HCR SYSTEM

SOLUTION CONCENTRATION: 0.20 NORMAL
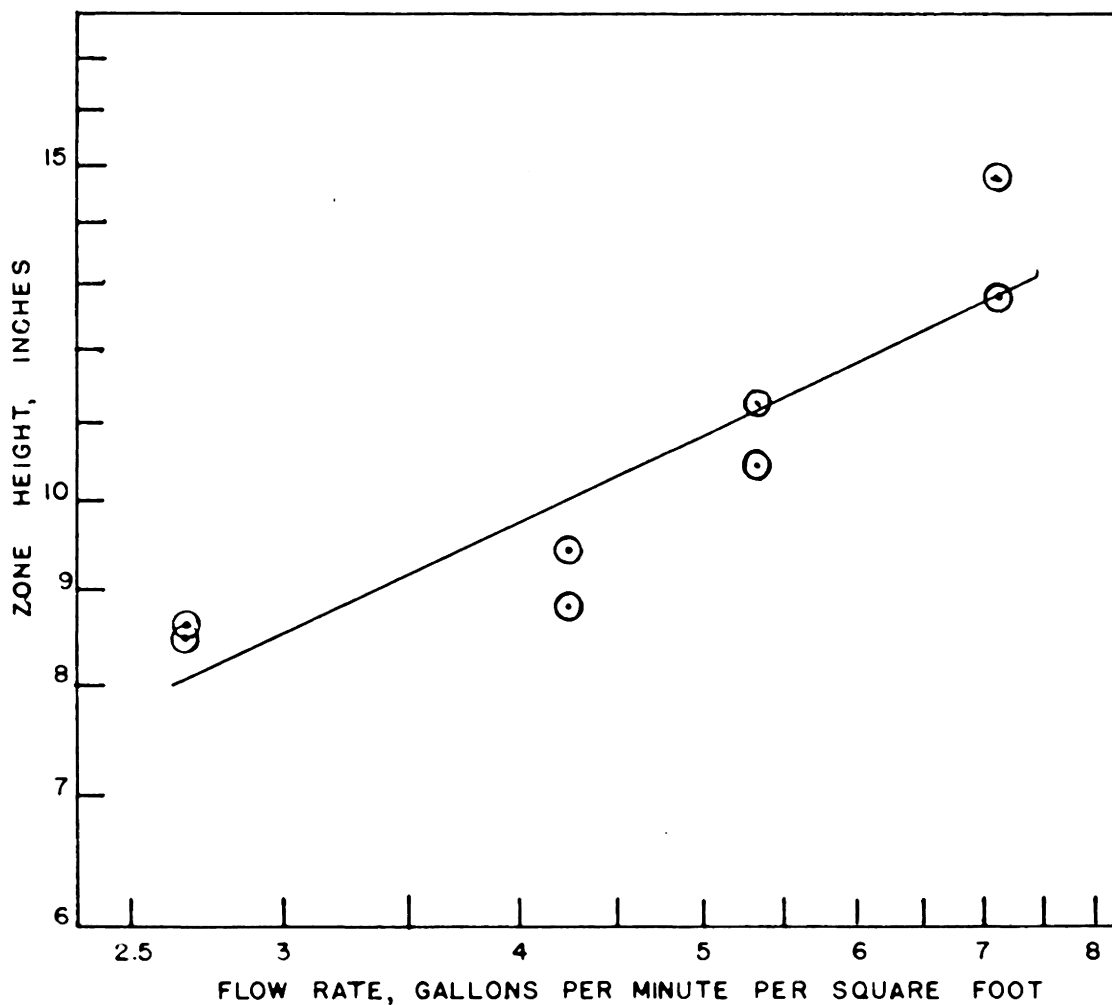
FIGURE 5. EXCHANGE ZONE HEIGHT, SODIUM-

HYDROGEN- CHLORINE -NALCITE HCR SYSTEM

SOLUTION CONCENTRATION: 0.25 NORMAL
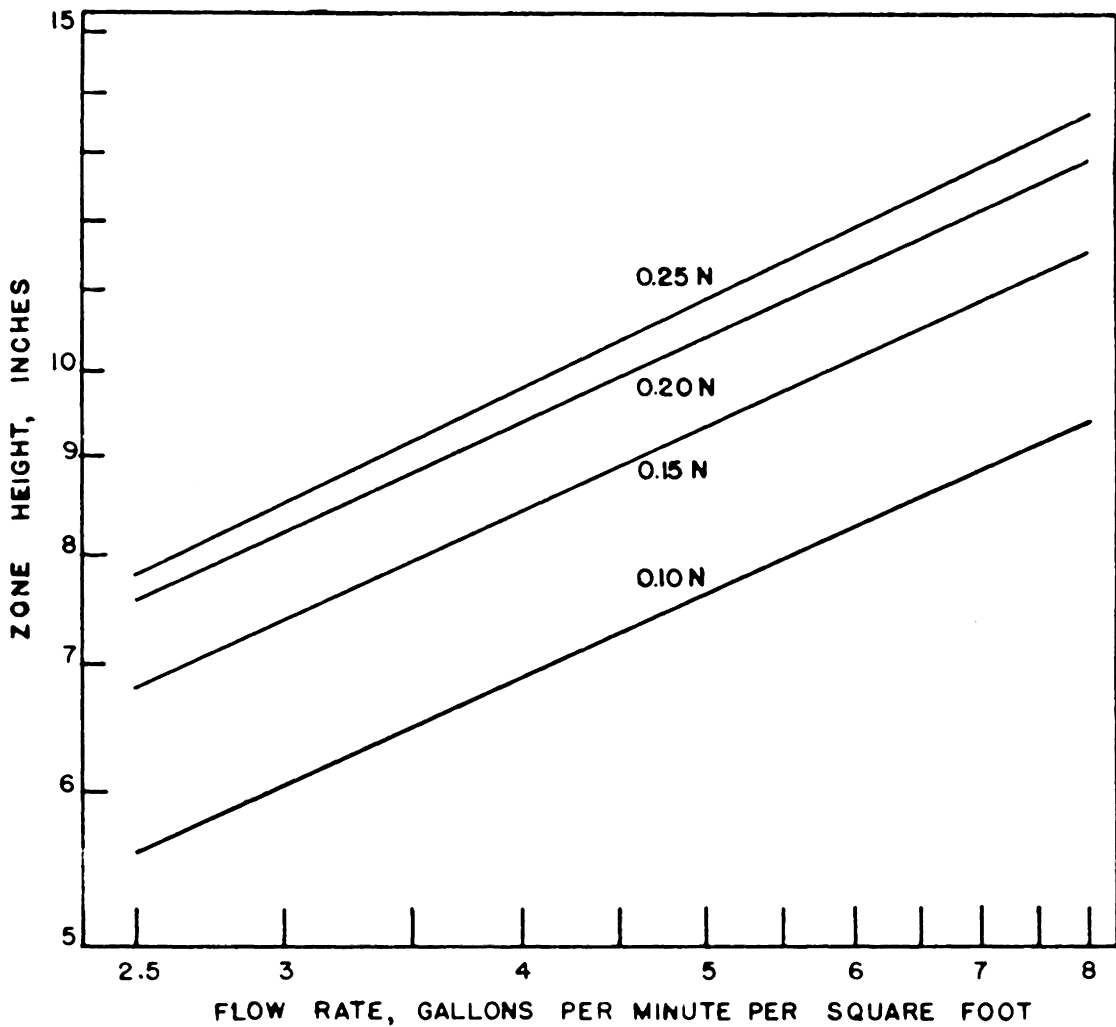
FIGURE 6. EXCHANGE ZONE HEIGHT, SODIUM - HYDROGEN- CHLORINE - NALCITE HCR SYSTEM
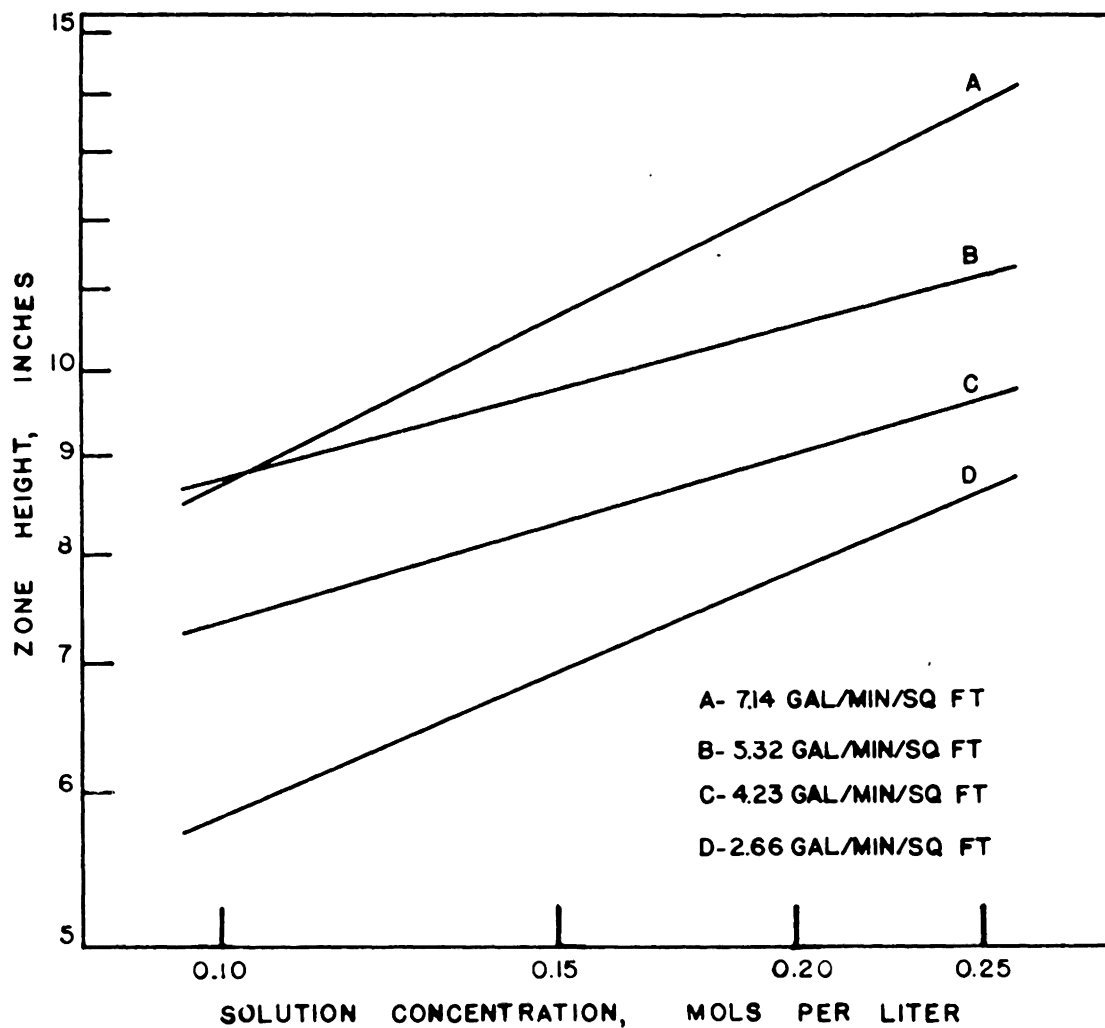
FIGURE 7. EXCHANGE ZONE HEIGHT, SODIUM —

HYDROGEN-CHLORINE - NALCITE HCR SYSTEM

equation for the results obtained in this investigation.
The final correlation equation, as well as the least
squares equations used for the curves shown in Figures 2
to 7 are summarized in Table III, page 60, together with
their corresponding correlation coefficients.

The analysis of variance tables for the height and
the logarithm of the height of the exchange zone are
presented in Tables IV and V, pages 61 and 62.
Table VI, page 63, is a condensed analysis of variance
table for the regression equations shown in Table III,
page 60.

Sodium Fraction Data. Table VII, page 64, gives
the results obtained for the sodium fraction, (1 - F),
of the exchange zone, for each of the 32 tests made on
the experimental ion exchange column. An analysis of
variance table for these data is presented in
Table VIII, page 65.

TABLE III

Regression Equations for the Exchange Zone Height

of the System Na-H-Cl-Nalcite HCR

Equation	Conditions of Restraint	Correlation Coefficient
Individual Single Variable Equations		
$h_z = 5.06\ Q^{0.47}$	C = 0.25 N	0.905
$h_z = 5.12\ Q^{0.44}$	C = 0.20 N	0.987
$h_z = 4.49\ Q^{0.46}$	C = 0.15 N	0.978
$h_z = 3.85\ Q^{0.43}$	C = 0.10 N	0.936
$h_z = 27.60\ C^{0.50}$	Q = 7.14	0.959
$h_z = 15.80\ C^{0.25}$	Q = 5.32	0.950
$h_z = 14.50\ C^{0.30}$	Q = 4.23	0.879
$h_z = 15.60\ C^{0.42}$	Q = 2.66	0.981
Final Correlation Equation		
$h_z = 8.94\ Q^{0.45}\ C^{0.37}$	C from 0.10 to 0.25 N Q from 2.66 to 7.14	0.927

h_z = exchange zone height, inches
Q = solution flow rate, gal/min/sq ft of bed area
C = solution concentration, mols per liter

TABLE IV

Analysis of Variance Table

Exchange Zone Height

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Computed F Value	Tabular [a] F Value
Solution Flow Rate	3	73.60	24.530	125.0	3.24
Concentration of Influent	3	41.60	13.870	70.7	3.24
Interaction	9	9.20	1.020	5.2	2.54
Error	16	3.14	0.196		
Total	31	127.54			

[a] F values at the five per cent level
Standard Mathematical Tables, 11th ed., p. 247
Chemical Rubber Publishing Co., Cleveland, Ohio, 1957

TABLE V

Analysis of Variance Table

Logarithm of the Exchange Zone Height

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Computed F Value	Tabular [a] F Value
Solution Rate of Flow	3	0.16200	0.05400	192.40	3.24
Concentration of Influent	3	0.09900	0.03300	117.60	3.24
Interaction	9	0.01140	0.00127	4.52	2.54
Error	16	0.00449	0.00028		
Total	31	0.27689			

[a] F values at the five per cent level
Standard Mathematical Tables, 11th ed., p. 247
Chemical Rubber Publishing Co., Cleveland, Ohio, 1957

TABLE VI

The Analysis of Variance on

Regression Equations

Regression Equation	Regression Mean Square	Residual Mean Square	Computed F Value	Test [a] Value
$h_z = 5.06\ Q^{0.47}$	0.043936	0.001603	27.5	13.74
$h_z = 5.12\ Q^{0.44}$	0.038090	0.000170	224.0	13.74
$h_z = 4.49\ Q^{0.46}$	0.041104	0.000315	130.0	13.74
$h_z = 3.85\ Q^{0.43}$	0.036878	0.000870	42.5	13.74
$h_z = 27.60\ C^{0.50}$	0.044560	0.000646	69.0	13.74
$h_z = 15.80\ C^{0.25}$	0.011174	0.000207	54.0	13.74
$h_z = 14.50\ C^{0.30}$	0.015563	0.000745	20.9	13.74
$h_z = 15.60\ C^{0.42}$	0.032019	0.000194	165.0	13.74
$h_z = 8.94\ Q^{0.45}\ C^{0.37}$	0.128390	0.000700	184.0	5.52

[a] F values at the one per cent level
   Standard Mathematical Tables, 11th ed., p. 247
   Chemical Rubber Publishing Co., Cleveland, Ohio, 1957

TABLE VII

Data on the Exchange Zone Sodium Fraction

Flow Rates, gal/min/sq ft	7.14	5.32	4.23	2.66
Concentration, mols per liter	Sodium Fraction			
0.25	0.445	0.460	0.485	0.435
	0.425	0.428	0.421	0.440
0.20	0.422	0.468	0.446	0.450
	0.425	0.475	0.502	0.440
0.15	0.430	0.463	0.400	0.470
	0.475	0.455	0.430	0.480
0.10	0.460	0.470	0.475	0.425
	0.465	0.550	0.456	0.440

Data obtained from thirty two tests on a Nalcite HCR bed, sixteen inches high and two inches in diameter, with sodium chloride solutions.

TABLE VIII

Analysis of Variance Table

Sodium Fraction

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Computed F Value	Tabular [a] F Value
Solution Flow Rate	3	0.0036	0.0012	2.01	3.24
Concentration of Influent	3	0.0027	0.0009	1.51	3.24
Interaction	9	0.0102	0.0011	1.85	2.54
Error	16	0.0095	0.0006		
Total	31	0.0260			

[a] F values at the five per cent level
Standard Mathematical Tables, 11th ed., p. 247
Chemical Rubber Publishing Co., Cleveland, Ohio, 1957

Sample Calculations

The method of calculation used in this investigation is shown in this section. The data for Test 303, presented in full for convenience in Table IX, page 67, will be used to illustrate all the calculations used in this thesis.

Calculation of the Sodium Fraction of the Exchange Zone. The first four columns under "Sample Titration," Table IX, were direct observations made during the course of the test. The figures in the fifth column, "Sample Acid Normality," were computed by the following equation illustrated using sample 10:

$$N_a = (V_b)(N_b)/(V_s)$$

where:

N_a = acid normality of the sample, mols per liter

V_b = volume of the base, milliliters

N_b = concentration of the base, mols per liter

V_s = volume of sample used, milliliters

N_a = (19.5)(0.05)/(5)

= 0.195 mol per liter.

TABLE IX

Reproduction of Data Sheet for

Test Number 303

Test No. 303   March 6, 1958
Bed Height - 16 inches   Temperature - 68° F
Influent Concentration - 0.20 N NaCl
Solution Flow Rate - 4.21 gal/min/sq ft of bed area

Sample Titration

Sample No.	Time, sec	Sample Volume, ml	0.05 N NaOH Volume, ml	Sample Acid Normality	Sample NaCl Normality
10	400	5	19.5	0.195	0.005
20	500	5	19.5	0.195	0.005
30	600	5	19.5	0.195	0.005
40	700	5	19.4	0.194	0.006
50	800	5	18.9	0.189	0.011
60	900	5	17.7	0.177	0.023
70	1000	5	16.0	0.160	0.040
80	1100	5	13.3	0.133	0.067
90	1200	5	8.9	0.089	0.111
100	1300	5	4.4	0.044	0.156
110	1400	5	1.8	0.018	0.182
120	1500	10	1.6	0.008	0.192
130	1600	20	2.0	0.005	0.195

θ_t = 1460 sec $(1 - F)$ = 0.446
θ_b = 790 sec h_z = 9.24 inches

Figures appearing in the sixth column, "Sample NaCl Normality," were calculated from the following relationship illustrated also using sample 10:

$$N_s = N_i - N_a$$

·where:

N_s = sodium chloride concentration in the sample, mols per liter

N_i = sodium chloride concentration in the influent, mols per liter

N_a = acid concentration in the sample, mols per liter

N_s = 0.200 - 0.195

= 0.005 mol per liter.

After all the values for this column were found, these values were plotted on rectangular coordinate paper as a function of the time at which any particular sample was taken. A plot of these values such as were made for each test is shown in Figure 8, page 69.
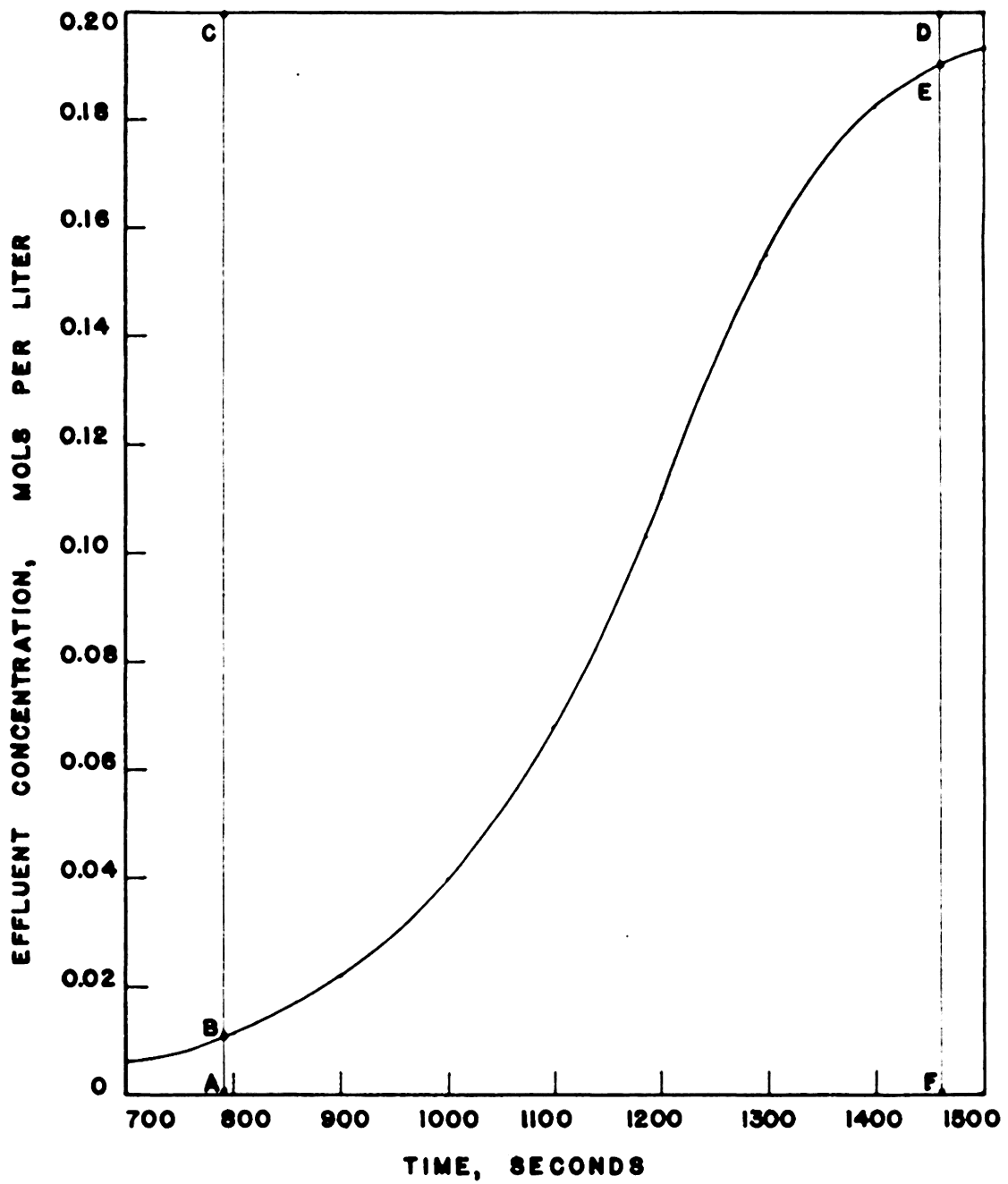
FIGURE 8. EFFLUENT CONCENTRATION-TIME CURVE

On this figure, lines ABC and FDE were next drawn. Line ABC is located on θ_b, the break-through line, which corresponds to a sodium chloride concentration in the effluent equal to five per cent of the sodium chloride concentration in the influent. For this test, the break-through concentration was 0.01 N, and the corresponding break-through time, θ_b, was 790 seconds. Line FDE is the line that passes through θ_t, the exhaustion time, which corresponds to a sodium chloride concentration in the effluent equal to 95 per cent of the sodium chloride concentration in the influent. For this test, this exhaustion concentration was 0.19 N, and the corresponding exhaustion time, θ_t, was 1460 seconds.

With the aid of a planimeter, areas ABEF and ABCDEF were then determined. The sodium fraction, (1 - F), was computed as shown below:

$$(1 - F) = (\text{Area ABEF})/(\text{Area ABCDEF})$$

where:

$$(1 - F) = \text{sodium fraction of the exchange zone}$$

$$(1 - F) = (1519)/(3398)$$

$$= 0.446.$$

Calculation of the Exchange Zone Height. The exchange zone height was calculated by means of the following equation:

$$h_z = (h_t)(\theta_t - \theta_b)/[\theta_t - (1 - F)(\theta_t - \theta_b)]$$

where:

h_z = exchange zone height, inches

h_t = height of the resin bed, inches

θ_t = exhaustion point time, seconds

θ_b = break-through point time, seconds

$(1 - F)$ = sodium fraction of the exchange zone

$$h_z = (16)(1460 - 790)/[1460 - (0.446)(1460 - 790)]$$

$$= 9.24 \text{ inches.}$$

<u>Single Variable Regression Equations</u>. The curves
shown in Figures 2 to 7, pages 53 to 58, were all plotted
by fitting constants to appropriate regression equations
by the method of least squares. All of these equations
were of the form:

$$Y = a + b(x - \bar{x})$$

where:

      Y = regression value of the logarithm
            of the height, in inches, of the
            exchange zone

      a = mean of the logarithm of the observed
            values of the height, in inches, of
            the exchange zone

      b = slope of the regression line

      x = logarithm of the independent variable,
            either the concentration or the flow
            rate

      $\bar{x}$ = mean of the observed values of <u>x</u>.

The constants <u>a</u> and <u>b</u> in the above equations were
evaluated for each of the eight single variable
equations presented in Table III, page 60. The
calculation procedure used in the evaluation of these
constants will be illustrated for the first equation
given in Table III.

The constant _a_ was evaluated by means of the equation:

$$a = Sy/n$$

where:

a = constant in the single variable regression equation

Sy = the sum of all the logarithms of the observed heights, in inches, of the exchange zone

n = number of _y_ values in the summation Sy

$$a = 8.11931/8$$

$$= 1.01490.$$

The constant **b** was calculated by the relationship:

$$b = (nSxy - SySx)/(nSx^2 - \overline{Sx}^2)$$

where:

b = slope of the regression line

Sxy = the sum of the products of corresponding **x** and **y** values

Sy = sum of all the **y** values

Sx = sum of all the **x** values

Sx^2 = sum of the squares of all **x** values

$\overline{Sx}^2$ = square of the sum of all **x** values

n = number of **y** values

$$b = (43.46368 - 42.72057)/(29.25632 - 27.68443)$$

$$= 0.473.$$

The regression equation is, therefore:

$$Y = 1.0149 + (0.473)(x - 0.6577)$$

which gives, after transforming:

$$h_z = 5.06 \, Q^{0.473}$$

where:

h_z = exchange zone height, inches

Q = solution flow rate, gal/min/sq ft.

Final Correlation Equation. The method of calculation used in the determination of the final correlation equation given in Table III, page 60, is shown below.

The proposed equation was:

$$Y = a + bX + cZ$$

where:

Y = regression value of the logarithm of the height, in inches, of the exchange zone

X = logarithm of the flow rate, gal/min/sq ft

Z = logarithm of ten times the influent concentration in mols per liter

a, b, c = regression coefficients to be determined.

The determination of the constants, <u>a</u>, <u>b</u>, and <u>c</u>, of the final correlation equation was done by the solution of the following set of simultaneous equations:

$$S_y = an + bSx + cSz$$

$$Sxy = aSx + bSx^2 + cSxz$$

$$Szy = aSz + bSxz + cSz^2$$

where:

Sy = sum of the logarithms of all observed heights, in inches, of the exchange zone

n = number of observations or tests

Sx = sum of the logarithms of all observed values of the flow rate in gal/min/sq ft

Sz = sum of the logarithms of ten times the concentration, in mols per liter

Sxy = sum of the products of corresponding <u>x</u> and <u>y</u> values

Szy = sum of the products of corresponding <u>z</u> and <u>y</u> values

Sx^2 = sum of the squares of all <u>x</u> values

Sxz = sum of the products of corresponding <u>x</u> and <u>z</u> values

Sz^2 = sum of the squares of all <u>z</u> values

a,b,c = constants to be determined

$$30.69448 = 8.0000\,a + 21.0464\,b + 7.0005\,c$$

$$20.54230 = 21.0464\,a + 14.6282\,b + 4.6042\,c$$

$$6.97626 = 7.0005\,a + 4.6042\,b + 2.2397\,c$$

$$a = 0.5818$$

$$b = 0.4511$$

$$c = 0.3670.$$

The correlation equation is, therefore:

$$Y = 0.5818 + 0.4511 \ X + 0.3670 \ Z$$

which, upon transforming, gives the final correlation equation:

$$h_z = 8.94 \ Q^{0.45} \ C^{0.37}$$

where:

h_z = exchange zone height, inches

Q = solution flow rate, gal/min/sq ft

C = influent concentration, mols per liter.

Analysis of Variance. The regression equations shown in Table III, page 60, were all tested for significance by an analysis of variance. The calculation procedures followed will be illustrated for the first equation in Table III.

The regression sum of squares was calculated using the equation:

$$SSR = (nSxy - SxSy)^2/(n)(nSx^2 - \overline{Sx}^2)$$

where:

SSR = regression sum of squares

n = number of observations

Sxy = sum of the cross products of the corresponding $\underline{x}$ and $\underline{y}$ terms

Sx = sum of all $\underline{x}$ values

Sy = sum of all $\underline{y}$ values

Sx^2 = sum of the squares of all $\underline{x}$ values

$\overline{Sx}^2$ = square of the sum of all $\underline{x}$ values

and the $\underline{x}$ and $\underline{y}$ values being, as previously defined:

x = logarithm of the observed value of the flow rate in gal/min/sq ft

y = logarithm of the height, in inches, of the exchange zone,

$$SSR = (43.46368 - 42.72057)^2/(8)(29.25632 - 27.68443)$$

$$= 0.043936.$$

The regression mean square was then computed using the relationship:

$$MSR = SSR/df$$

where:

MSR = regression mean square

SSR = regression sum of squares

df = degrees of freedom

$$MSR = 0.043936/1$$

$$= 0.043936.$$

The residual sum of squares was calculated as the difference between the total sum of squares and the regression sum of squares, using the equation:

$$SSr = Sy^2 - (Sy)^2/n - SSR$$

where:

SSr = residual sum of squares

Sy^2 = sum of the squares of all y values

Sy = sum of all y values

n = number of observations

SSR = regression sum of squares

$$SSr = 8.29393 - (8.11931)^2/8 - 0.043936$$

$$= 0.009619.$$

The residual mean square was then computed from the relationship:

$$MSr = SSr/dfr$$

where:

MSr = residual mean square

SSr = residual sum of squares

dfr = residual degrees of freedom

$$MSr = (0.009619)/6$$

$$= 0.001603.$$

An F ratio test was used for significance testing, using the values of the regression and residual mean squares found. The F ratio was computed from the equation:

$$F = MSR/MSr$$

where:

F = variance ratio

MSR = regression mean square

MSr = residual mean square

$$F = 0.043936/0.001603$$

$$= 27.5.$$

The tabulated F value at the one per cent level for this case was found to be 13.74. The regression equation constants were therefore significant.

IV. DISCUSSION

In this section, the results obtained in the investigation are discussed, recommendations for future work are made, and the limitations of the study are presented.

Discussion of Results

The results obtained from the 32 tests made in this investigation are analysed with respect to experimental errors and the variables studied. Design applications are also discussed.

Experimental Errors. After considering the theories involved and the experimental procedure followed, it is the author's opinion that the chief sources of error were the following: variations in exchange capacity from test to test; lack of accuracy in the measurement of influent and effluent concentrations, bed height, and flow rate; "end effects;" and calculation procedure.

Exchange Capacity Variation. In order to avoid variability that would be introduced if regeneration were attempted, a new bed of fresh resin was used for each test. Since the resin

bulk is composed of particles of different sizes, and possibly of different exchange activities, each bed made up from it may contain a different number of exchange sites. Furthermore, particle classification in the resin bulk still unused could increase this variability. Precautions were therefore taken to minimize such variability. The bulk of the fresh resin was stored in a dry condition to minimize particle classification, and the bulk was thoroughly mixed before the withdrawal of a batch. Each new bed was also acid-washed before the actual exchange test to insure that all of the exchange sites were in the active hydrogen form.

The operations relative to keeping the bed height constant at 16 inches were another source of exchange capacity variations. The height of each new bed was adjusted after backwashing - that is, after the bed had been to some extent classified. If the height was in excess of 16 inches, resin was drawn off the bottom of the bed, thus altering the particle size distribution of the bed. No practical remedy

could be devised to circumvent this defect.
Fortunately, experience gained in the preliminary
tests minimized the adjustments in bed height
required.

Measurement Errors. Errors in measurement
were probably present in the determination of the
bed height, the influent and effluent concentrations,
and the flow rate.

Bed Height. To avoid repeated direct
measurements of the bed height, and thereby
increase the precision, a mark corresponding
to 16 inches was made on the outside surface
of the glass column. Each new bed was brought
to this mark after backwashing. It was
noticed, however, that the top surface of
the bed did not always settle as a horizontal
plane surface. Repeated backwashing, and
tapping on the column had to be resorted to
whenever this was the case. Even with all
these precautions, however, the uneven
surface presented by the resin particles
made accurate adjustment of the height more
difficult. Nevertheless, the height variation
was probably less than one-eighth of an inch.

Influent and Effluent Concentrations.
The influent and effluent concentrations were
measured by standard methods of volumetric
analysis. Duplicate titrations were made on
effluent samples, further replications being
resorted to only when the duplicate results
did not agree to within a tenth of a
milliliter. For the influent, triplicate
titrations were made throughout, further
replications being resorted to when the
triplicate results did not agree to within
a tenth of a milliliter. It is believed that
precision errors from this source were not
significant.

Flow Rate. Two sources of error were
present in the determination of the flow rate.
These were the measurement of the effluent
volume, and the determination of the time of
flow. The volume of effluent was measured
with a one-liter volumetric flask, while the
time of flow was determined by switching on an
electric timer at the start and switching it
off as soon as the liquid level passed the

mark on the neck of the volumetric flask.
Judging when the liquid level had passed the
mark became progressively more difficult as
the rate of flow increased. The error in
time determination was caused, not by any
lack of sensitivity or accuracy in the timer,
but by the lag in response of the operator.
Flow rate measurements, it is believed, were
precise to within plus or minus three per
cent, the precision being better for the
lower flow rates.

End Effects. End effects in the continuous
operations are usually associated with the unusual
conditions present at the entrance and exit of the
apparatus. In batch operations, such as fixed-bed
ion exchange, an analogous situation may be
present with respect to time. These end effects,
or initial transient effects are considered in the
following paragraphs.

During the preliminary tests made on the
exchange column, it was found out that the resin
bed had to be under a certain height of water at
the start of the test for two reasons. First, if

solution were passed through a bed which had been drained of liquid, small pockets of air were trapped inside the bed. Under such conditions, not all of the resin would be in contact with the solution. Second, without this height of water, the incoming solution disturbed the top portion of the bed. The minimum height of water that would prevent these undesirable conditions was therefore determined, and used in all of the experimental tests.

The presence of this column of water above the resin bed was the chief cause of the end effects. At the start of operations, the incoming solution mixed with this water, so that during an initial period of time, the solution flowing through the exchange bed did not have the desired concentration. Further, at the solid-liquid interface, the transient condition would be present for the period of time required to wash away the water adhering to the surface of the particles and lodged inside the resin pores.

To minimize these effects, the height of the bed could have been increased, so that the transient

time would be a small fraction of the total time of
operation. A more elaborate system of feeding the
solution into the column may also decrease the
height of water required above the bed. Because of
physical limitations, however, these remedies were
not tried. Instead, as stated above, the minimum
height of water required was determined and used
throughout the experiment.

No extensive measurements were made of the
duration of this transient effect. However, for
the two tests made at an influent concentration of
0.25 normal, and a solution flow rate of 7.14
gallons per minute per square foot of bed area,
it was observed that the transient time amounted
to as much as eight per cent of the total time.
This was determined by titrating for chloride
content three effluent samples withdrawn at the
start, and 100 and 200 seconds after the start of
the tests. Using the results of these three
titrations, a plot was made of chloride
concentration in the effluent against time,
taking into consideration that the effluent
concentration would remain constant at the value

-89-

of the influent chloride concentration after
reaching this value. The approximate time when
the effluent concentration reached 0.25 normal,
the chloride concentration in the influent for
these two tests, was read from this plot.

Since these end effects may be expected to be
most pronounced in these two tests, it is believed
that the average variation caused by end effects
for all the 32 tests made was smaller than eight
per cent of the corresponding total cycle times.

Calculation Procedure. The errors referred
to as arising from the calculation procedure are
not those due to mistakes in computation, but
those arising from the inherent inaccuracy of
the method used. Graphical methods of solution
are good examples of these.

The major part of the calculation procedure
used in this investigation was graphical in nature.
Of the four variables used in computing for the
exchange zone height, three were determined
graphically. The sodium fraction, $(1 - F)$, was
determined by graphically integrating the area
under the effluent concentration-time curve.

Likewise, both the exhaustion point and break-through point times were read from this curve. All three were therefore subject to the compound error arising from the inaccuracy in plotting the curve, and the uncertainty in reading values from it.

It is the author's opinion that errors arising from the calculation procedure had a much greater effect on the results of tests made at the higher concentrations, particularly at the higher flow rates. Under these conditions, these errors would represent a much higher fraction of the values of the variables involved.

Miscellaneous Sources of Error. The experiment was also subject to other sources of error such as the variation in temperature of the system, flow rate variations, and the quality of the distilled water used.

No practical means of temperature control was available for the extensive system used. The system temperature consequently varied with the room temperature. During the course of the investigation, room temperature was observed to vary between 60 and 70 degrees Fahrenheit.

Flow rate was under better control. The constant volumetric flow pump performed well during the entire course of the experimentation, flow rate variation being observed to be less than three per cent for all tests. The only precaution that had to be taken was to see to it that the tygon tubing in contact with the pump fingers was still resilient and undeformed.

A considerable amount of distilled water was used in this investigation for making up feed solutions, for washing and backwashing of the resin bed, and for the analytical work. During the preliminary tests, it was observed that the distilled water had an acidity of approximately 1/10,000 normal. While this would be negligible for most purposes, it could have some effect in the titration of the later samples from tests involving the lower concentrations. The precaution was therefore taken of not diluting samples to be titrated with distilled water.

The author believes that with the precautions taken, the last two sources of error had negligible effects on the results of the investigation.

With respect to the temperature, it is believed that its only effect would be on the rate of mass transfer. Previous experiments[6,22] have shown that for the flow rate and concentration values tested in this experiment diffusion is the controlling rate step in the over-all exchange process. Considering the range of temperature variation, changes in the mass transfer rate from this variation should have only a small effect on the results of this investigation.

The sources of error discussed above may be expected to affect both the accuracy and the precision of the experimental results. No way of assessing the effects of error on accuracy is available, and the only practical method of increasing accuracy would be to increase the experimental precision. The statistical analysis gives what is generally considered to be a reasonable estimate of the precision of the experiment. The value found for this investigation was plus or minus 0.442 inch, which amounts to approximately plus or minus five per cent of an observation. It must be emphasized again, however, that most of the sources of error had considerably more effect on tests involving

the higher concentrations and flow rates, a fact which
may be observed from an examination of Figures 2
to 5, pages 53 to 56. Consequently, while the over-all
reproducibility of results is fairly good, any
correlation obtained from these results would still
be subject to some uncertainty.

Effect of Variables Studied. The effect of the
rate of flow of solution, as well as of the influent
concentration on the exchange zone are discussed in
the following paragraphs.

Analysis of Variance. An examination of the
results given in Table II, page 52, and in Figures
2 to 7, pages 53 to 58, will show that there is
an apparent upward trend in the values for the
exchange zone height with increase in solution
flow rate and influent concentration. This
observation is confirmed by the analysis of
variance on both the height and the logarithm
of the height of the exchange zone, as shown in
Tables IV and V, pages 61 and 62. These tables
show that the effects of solution flow rate and
influent concentration on the exchange zone height
cannot be reasonably attributed solely to the

random errors of experimentation but must
represent an actual relationship between these
variables.

Effect of Influent Concentration. Figure 7,
page 58, is a graphical presentation of the effect
of influent concentration on the exchange zone
height. The least squares equations for these
curves, together with the corresponding
correlation coefficients are shown in Table III,
page 60. These equations show that at a fixed
flow rate, the exchange zone height can be
correlated as a power of the concentration. This
power, however, varies arbitrarily from 0.25
to 0.5. Whether the four values obtained for the
concentration exponent represent estimates of the
same true value, or of four different actual values
cannot be safely concluded based on the results of
this investigation alone. The lack of data in this
field makes a comparison with previous work also
impossible. Moreover, the high correlation
coefficients obtained for these equations can
only add to the difficulty of attempting any
explanation. Since, in the absence of strong

evidence to the contrary, one would like to assume
that natural phenomena occur in a well-ordered
pattern, the author believes that it would be
prudent to withhold conclusions regarding the
over-all effect of concentration until more data
are available.

Effect of Solution Flow Rate. Figures 2 to 6,
pages 53 to 57, present the relationship between
the exchange zone height and the solution flow rate
at a fixed influent concentration. The least
squares equations for these curves, and their
corresponding correlation coefficients are shown
in Table III, page 60.

The high values obtained for the correlation
coefficients lend support to the observation that
the exchange zone height is a simple power function
of the solution flow rate. Although this function
appeared to be regular in its change from one
concentration to another, a statistical test of
significance failed to show any significant
differences between the slopes of the regression
lines. Therefore, it may be stated with some
degree of confidence that these lines are

approximately parallel and that the only change in the function is in the proportionality constant and not in the exponent of the solution flow rate when the concentration changes.

In the only previous work in this field, Michaels[22] reported that the exchange zone height was directly proportional to the 0.5 power of the solution flow rate. A statistical test of significance between this value, and 0.45, the mean of the four values obtained in this investigation, failed to show if a difference existed.

The Final Correlation Equation. In order to present the results obtained in this investigation in a form more convenient than the eight separate equations previously discussed, it was decided to find a multiple regression equation for these results. This equation, given in Table III, page 60, is as follows:

$$h_z = 8.94 \, Q^{0.45} \, C^{0.37}$$

where:

h_z = height of the exchange zone, inches

Q = solution flow rate, gallons per minute per square foot of bed area

C = the influent concentration, mols per liter.

The exponents of the solution flow rate and the influent concentration are very nearly the averages of the respective exponents appearing in the separate equations. Likewise, the multiple correlation coefficient, $\underline{R}$, with a value of 0.927, is in the same high range as that of the individual correlation coefficients obtained for the separate equations.

A statistical comparison of the relative effectiveness of the multiple regression equation in correlating the data obtained in this investigation against that of the separate equations showed that the former is slightly better. The results obtained are therefore most conveniently and accurately correlated by this final correlation equation.

A comparison was also made between this final correlation equation and Michaels' equation on the experimental data and results obtained in his investigation[22]. Using both equations, values were calculated for the exchange zone height at the ten test conditions studied by Michaels. The two sets of values were compared with the

experimental values for the exchange zone height
obtained by Michaels. For both equations, four of
the ten computed values were found to differ from
the corresponding experimental values by more than
ten per cent, which was Michaels' estimate of his
experimental error. The largest deviation from
experimental values using Michaels' equation was
17.2 per cent, while the largest deviation using
the final correlation equation for this
investigation was 16.4 per cent. A statistical
test of significance between the error variances
of the two equations, however, showed that no
significant difference existed between the
effectiveness of the two equations in correlating
Michaels' results.

It must be emphasized, however, that the good
statistical results obtained with the final
correlation equation only means that this equation
successfully correlates both the experimental data
from this work and Michaels' work. It does not
necessarily follow that these equations are a good
description of the actual natural behavior. It is
believed that the data available at the present time

are but a very small fraction of that which would be required for such a description.

Mass Transfer Comparisons. An analysis of the definition of the exchange zone height shows that it is analogous to the total height required for a given mass transfer application. As such, therefore, it may be thought of also as being composed of two factors, as shown in the equation below:

$$h_z = (HEU)(NEU)$$

where:

h_z = exchange zone height

HEU = height of an exchange unit

NEU = number of exchange units.

Utilizing mass transfer concepts further, the number of exchange units may be defined as:

$$NEU = \int \frac{dy}{f(y, \; Kr, \; Ke)}$$

where:

NEU = number of exchange units

y = cation concentration in the solution phase

$f(y, \; Kr, \; Ke)$ = the exchange potential, a function of the solution concentration, y; $\underline{Kr}$, the exchange reaction equilibrium constant; $\underline{Ke}$, the mass transfer equilibrium relationships.

The limits of the integration obviously correspond to the lower and upper boundaries of the exchange zone, as previously defined.

Similarly, the height of an exchange unit may be broken up into components as shown below:

$$HEU = HTUs + HRU + HTUr$$

where:

HEU = height of an exchange unit

HTUs = height of a transfer unit, solution phase diffusion

HRU = height of a reaction unit

HTUr = height of a transfer unit, resin phase diffusion.

The breaking up of the height of an exchange unit follows from the series-resistance concept. The HTU terms correspond to the heights required for the diffusion processes in the two phases, while the HRU term corresponds to the height required for the exchange reaction. All three are expressed in terms of height units.

From the definition of the number of exchange units, it is evident that this quantity is independent of flow rate, since none of the factors entering into the definition are affected by changes in the flow rate. Consequently, any changes in the value of the exchange zone height at a fixed concentration, must be due to flow rate effects on the height of the exchange unit. The results of this investigation indicate that this relationship is:

$$ HEU = c \, Q^{0.45} $$

where:

HEU = height of an exchange unit

Q = flow rate

c = proportionality constant, dimensional.

Michaels[22], citing Hougen and Wilke, states that
where the controlling resistance is in the mass transfer
step, the exchange zone height should be proportional to
the 0.51 power of the flow rate. A statistical test
of significance between 0.45, the value found in this
investigation, and 0.51, showed that there was no
significant difference between the two. It appears,
therefore, that in the concentration range tested, the
results may be correlated based on the height of the
transfer unit alone. It must be mentioned, however,
that the Hougen and Wilke correlation cited by Michaels,
as well as other correlations[2] for which the value
of 0.51 has been found, are based on solid-gas transfer
experiments.

Changes in influent concentration have a more
complex effect on the exchange zone height. The number
of exchange units is evidently a function of the
influent concentration. Likewise, the height of the
exchange unit may be affected. Changes in concentration
bring about changes in the viscosity and degree of
ideality of the solution, factors which affect
diffusion rates. The effect of concentration on the
exchange zone height found in this experiment is

therefore a composite effect, and no data are available for analysing this over-all effect into components for the number of exchange units, and the height of the exchange unit.

The Sodium Fraction. The results obtained for the sodium fraction, $(1 - F)$, of the exchange zone are shown in Table VII, page 64. It will be noted that there is considerable variation in the values obtained in this investigation and that the variation does not show any trend. The analysis of variance for the sodium fraction, shown in Table VIII, page 65, confirms the fact that the observed variation is random, and is not significantly above the error variance.

Michaels[22] reports values for an influent concentration of 0.12 normal which are higher than those found in this investigation. The mean of the values found by Michaels was 0.51, while the mean of those found in this experiment is 0.454, a difference of about ten per cent.

Since the sodium fraction measures the relative amounts of the exchanging cations present in the exchange zone, which is the active portion of the bed at any given time, the sodium fraction may be

considered as related to the equilibrium constant for the exchange reaction, provided that it may be assumed that the over-all exchange process is diffusion controlled. Theoretically, therefore, its value should change with concentration. It is the author's opinion, however, that the changes in value for the concentration range studied were small enough to be masked by the variation caused by random errors.

Reproducibility of Data. The experimental data were found to be reproducible between replications to a remarkably high degree, particularly at the lower flow rates and concentrations. The effluent concentration-time curves of replicates gave corresponding points which were surprisingly close together in value. Since both the sodium fraction and the exchange zone height were determined primarily from values read from these curves, it follows that these two should also exhibit the same high degree of reproducibility.

Michaels[22] reports the same observation with respect to the effluent concentration-time curves. No comparison can be made, however, between the reproducibility of the exchange zone height in his work and in this one, since he reported only one value

for each condition tested, at a plus or minus deviation
of ten per cent. The ten per cent figure appears to be
his estimate of the over-all error effects in his
investigation.

The remarkable reproducibility of results suggests
that the method of procedure employed in both
investigations may not be sensitive enough to be
affected by the ordinary errors commonly found in
engineering experiments. It is believed prudent,
therefore, to re-examine the method before it is used
again in experiments of this nature.

Design Applications. The use of the exchange zone
concept in the design of fixed-bed ion exchangers is
shown in the following sections. It must be stressed
here that the exchange zone method is valid only under
conditions where the exchange reaction is highly
favored by the reaction equilibrium constant. This is
generally the case for strong acid type resins, and
solutions of metallic cations.

Capacity Determination. A problem often
encountered concerns the determination of the
capacity of a specific piece of equipment under
certain process conditions. The application of

the exchange zone method to the solution of this problem is illustrated by the following example.

It is desired to use an existing ion exchanger to remove sodium ions from a 0.1 normal sodium chloride solution. The exchanger has a bed space with a cross-sectional area of three square feet and a height of 40 inches. A strong acid type cationic resin having an exchange capacity of 35 equivalents per cubic foot will be used. Solution will be passed through the bed at the rate of five gallons per minute per square foot of bed area, until the effluent sodium chloride concentration reaches five per cent of the influent concentration or 0.005 normal. The bed will then be backwashed, and regenerated with one normal hydrochloric acid. The volume of regenerant to be used is to contain three times as many equivalents of hydrogen ions as that required to replace the sodium ions in the resin bed. Available head limits the solution and regenerant flow rates to five gallons per minute per square foot of bed area. After the regeneration, the bed will be backwashed again, and then placed in the exchange

portion of the cycle. It is estimated that the two backwashing steps, and other minor operations relative to bed preparation will take 30 minutes.

Experimental data indicate that a conservative value for the sodium fraction, $(1 - F)$, is 0.4. Determine the capacity of the bed, in gallons of solution per 24 hours, assuming the applicability of the equation:

$$h_z = 8.94 \, Q^{0.45} \, C^{0.37}$$

where:

h_z = exchange zone height, inches

Q = solution flow rate, gallons per minute per square foot of bed area

C = influent concentration, mols per liter.

The solution of the problem outlined above is given in the following sections. The exchange zone height is determined from the given equation:

$$h_z = 8.94 \, (5)^{0.45} \, (0.1)^{0.37}$$

$$= 7.86 \text{ inches.}$$

Of the total zone height, the fraction (1 - F) is
in the sodium form at the end of the exchange
operation, and is therefore the active or usable
portion of the zone. The unusable portion is
therefore the fraction F, or the hydrogen fraction.
Since (1 - F) is equal to 0.4, F must be equal
to 0.6. The inactive height of the zone is
therefore Fh_z:

$$Fh_z = 0.6(7.86)$$

$$= 4.72 \text{ inches.}$$

It follows that of the 40 inches of bed
height, only (40.00 - 4.72) or 35.28 inches would
be useful for the exchange reaction.

The active or useful volume of resin may now be determined.

$$V_{ra} = (A_r)(h_a)$$

where:

V_{ra} = active, or useful volume of resin, cubic feet

A_r = resin bed cross-sectional area, square feet

h_a = active height of resin bed, feet

$$V_{ra} = (3)(35.28)/12$$

$$= 8.82 \text{ cubic feet.}$$

The actual exchange capacity of the bed is therefore:

$$C_e = (c)(V_{ra})$$

where:

C_e = actual exchange capacity of the bed, equivalents

c = specific exchange capacity of the resin, equivalents per cubic foot

V_{ra} = active volume of resin, cubic feet

$$C_e = (35)(8.82)$$

$$= 309 \text{ equivalents.}$$

Clearly, this is the amount of sodium ions removed
by the resin from solution per exchange cycle.
This volume of solution per cycle is given by the
following relationship:

$$V_s = (C_e)/(3.785)(N_s)$$

where:

V_s = solution volume per cycle, gallons

C_e = actual exchange capacity of the bed, equivalents

N_s = solution concentration, mols per liter

3.785 = conversion factor, liters per gallon

$$V_s = (309)/(3.785)(0.1)$$

$$= 816 \text{ gallons.}$$

The volumetric flow rate of solution is now
determined by the relationship:

$$U = (Q)(A_r)$$

where:

   U = volumetric flow rate, gallons per
       minute

   Q = solution flow rate, gallons per
       minute per square foot of bed area

   A_r = bed cross-sectional area, square feet

   $$U = (5)(3)$$

   $$= 15 \text{ gallons per minute.}$$

To determine the time of the exchange operation
per cycle, the following equation is used.

$$\Theta_e = V_s/U$$

where:

   Θ_e = time of exchange operation per
       cycle, minutes

   V_s = solution volume per cycle, gallons

   U = volumetric flow rate, gallons per
       minute

   $$\Theta_e = (816)/(15)$$

   $$= 54.5 \text{ minutes.}$$

The volume of regenerant solution per cycle is found by the equation:

$$V_{re} = (3)(C_e)/(3.785)(N_r)$$

where:

V_{re} = regenerant volume per cycle, gallons

C_e = actual exchange capacity of the bed, equivalents

N_r = concentration of regenerant, equivalents per liter

3.785 = conversion factor, liters per gallon

3 = ratio of equivalents in regenerant to equivalents in resin, as required by the conditions of the problem

$$V_{re} = (3)(309)/(3.785)(1)$$

$$= 245 \text{ gallons.}$$

The volumetric rate of flow of regenerant will obviously be equal to the volumetric rate of flow of the solution, since both will be passed through the bed at five gallons per minute per square foot

of bed cross-sectional area. The regenerating time
may therefore be found by the relationship:

$$\Theta_r = V_{re}/U$$

where:

Θ_r = regeneration time, minutes

V_{re} = regenerant volume per cycle, gallons

U = volumetric flow rate of both solution and regenerant, gallons per minute

$$\Theta_r = (245)/(15)$$

$$= 16.3 \text{ minutes.}$$

The total cycle time is now determined from the
following:

$$\Theta_c = \Theta_e + \Theta_r + \Theta_d$$

where:

Θ_c = total cycle time, minutes

Θ_e = exchange time, minutes

Θ_d = backwash and minor operations time, minutes

$$\Theta_c = 54.5 + 16.3 + 30$$

$$= 100.8 \text{ minutes.}$$

The number of cycles per 24 hours is therefore equal to (24)(60)/(100.8) or 14.3. Since 816 gallons of solution are treated in one cycle, the total exchange capacity per 24 hours is (14.3)(816) or 11,650 gallons.

Determination of Equipment Size. Problems involving the calculation of equipment size for a given set of process conditions vary in their complexity depending upon the number of process variables fixed. If the number of these variables which are fixed is less than that required to give a specific solution to the problem, other relationships will be required. Optimizing procedures on the economic balance will usually be involved in these cases.

This section will outline the solution of a problem where the required number of process variables has already been fixed. An illustrative problem, and its solution is given below.

Twenty gallons per minute of a solution containing 0.1 normal of sodium chloride are to be treated by ion exchange to replace the

sodium with hydrogen ions in the solution. A resin
of the Nalcite HCR type, having an exchange
capacity of 35 equivalents per cubic foot will be
used. Pressure drop limitations require that both
solution and regenerant flow rates be not more than
five gallons per minute per square foot of bed
area. Two beds will be used - one in the exchange
operation, while the other is being regenerated and
prepared for the next cycle. It is estimated that
the regeneration time will be one-half of the
exchange time, while backwashing and other minor
operations will take 30 minutes per cycle.
Assuming F, the hydrogen fraction, to have a
value of 0.6, determine the dimensions of the bed
required for each column.

Since the beds will be used alternately, the
total time spent in regenerating and preparing one
bed should be equal to the exchange operation time.
The exchange time per cycle may therefore be
determined from the relationship:

$$\Theta_e = \Theta_r + \Theta_d$$

where:

Θ_e = exchange operation time, minutes

Θ_r = regeneration time, minutes

Θ_d = backwash and bed preparation time,
minutes

Θ_e = $(0.5)(\Theta_e) + 30$

= 60 minutes.

The volume of solution to be passed through each bed, per cycle, is therefore equal to 1200 gallons since the volumetric rate of flow of solution is given to be 20 gallons per minute. The equivalents of sodium ions replaced per cycle can now be found by the equation:

$$E_s = V_s N_s \times 3.785$$

where:

E_s = equivalents replaced in solution per cycle, equivalents

V_s = volume of solution treated per cycle, gallons

N_s = solution concentration, mols per liter

3.785 = conversion factor, liters per gallon

$$E_s = (1200)(0.1)(3.785)$$

$$= 455 \text{ equivalents.}$$

This quantity is also the exchange capacity of the active portion of each bed.

The determination of the bed dimensions now follow. The cross-sectional area of the bed may be found by the following relationship:

$$A_r = U/Q$$

where:

A_r = resin bed cross-sectional area, square feet

Q = solution flow rate, gallons per minute per square foot of bed area

U = volumetric flow rate of solution, gallons per minute

$$A_r = 20/5$$

$$= 4 \text{ square feet.}$$

The exchange zone height is given by the equation:

$$h_z = 8.94 \ Q^{0.45} \ C^{0.37}$$

where:

h_z = exchange zone height, inches

Q = solution flow rate, gallons per minute per square foot of bed area

C = solution concentration, mols per liter

$$h_z = 8.94(5)^{0.45} (0.1)^{0.37}$$

$$= 7.86 \text{ inches.}$$

The inactive portion of the zone, F, is 0.6. Of the total zone height of 7.86 inches, (0.6)(7.86) or 4.72 inches, constitute the unusable portion. This quantity, when added to the active bed height will give the total bed height required.

The active bed height may be found by the relationship:

$$h_a = 12\ C_e/(c)(A_r)$$

where:

h_a = active bed height, inches

C_e = total exchange capacity of the active portion of the bed, equivalents

A_r = bed cross-sectional area, square feet

c = specific exchange capacity of the resin, equivalents per cubic foot of resin

12 = conversion factor, inches per foot

$$h_a = (12)(455)/(35)(4)$$

$$= 39\ \text{inches}.$$

The total height of the resin bed is therefore (39.00 + 4.72) or 43.72 inches. The total height of the column itself should be about twice this amount, to allow for bed expansion during backwashing. The bed should therefore be housed in a column that is about 80 inches high.

Recommendations

The following recommendations are made for future studies.

Improvement of the Method of Procedure. The results of this investigation seem to indicate that the method of procedure employed may not be sensitive enough to yield reliable data. It is recommended that the present method be analysed and evaluated before any further work is made using it.

It is also recommended that studies be made on alternate methods of determining the variation of the effluent concentration with respect to time. The titration method is extremely laborious, and is a serious handicap to the extension of data in this field. For this purpose, it is recommended that the use of a continuous recording conductivity or pH meter be studied.

Extension of the Correlation Equation. The correlation equation presented was obtained for relatively low flow rates and high concentrations. It is recommended that further studies be made to extend this equation to flow rates of 15 gallons per minute per square foot of bed area, and concentrations of 0.01 mol per liter.

Extension of the Method to Other Systems. The
exchange zone method for fixed-bed exchanger design
has been investigated only for the Na-H-Cl-Nalcite HCR
system. It is recommended that other systems be used
in future studies, with the aim of eventually
accumulating enough data to determine the effect
of varying the cation exchange pair, the anion, as
well as the resin.

It is recommended that the systems
K-H-Cl-Nalcite HCR, Ca-H-Cl-Nalcite HCR, and
Na-Ca-Cl-Nalcite HCR, as well as variations involving
the anion be studied, after studies have been made
on extending the correlation equation for the
system Na-H-Cl-Nalcite HCR.

Limitations

The limitations of the experimental work in this investigation are presented in the following paragraphs.

Exchange Bed. The exchange bed used in this investigation was two inches in diameter, and had a hydrogen form height of 16 inches. A new resin bed was prepared for each test from fresh, acid-washed resin.

System. The system studied was Na-H-Cl-Nalcite HCR. The resin, which had a 20/50 mesh size was initially in the hydrogen form, the transfer of sodium ions being from the sodium chloride solution to the resin in all tests. No regenerated resins were used in this study.

Variables Studied. The effect of solution flow rate and influent concentration on the exchange zone height was studied in this investigation. Flow rate was varied from 2.66 to 7.14 gallons per minute per square foot of bed area, while the concentration range investigated was from 0.10 to 0.25 mol per liter of sodium chloride. No other variables were studied during the course of this project.

Temperature. All 32 tests made in this study were performed in the temperature range of 60 to 70 degrees Fahrenheit.

V. CONCLUSIONS

The exchange zone height for the system
Na-H-Cl-Nalcite HCR was studied by passing sodium
chloride solutions of 0.10 to 0.25 mol per liter
concentration at flow rates of 2.66 to 7.14 gallons
per minute per square foot of bed area through a bed
of Nalcite HCR resin in the hydrogen form. The resin
bed was two inches in diameter and 16 inches high.
This investigation led to the following conclusions.

1. The exchange zone height may be related to the
influent concentration and solution flow rate by the
equation:

$$h_z = 8.94 \ Q^{0.45} \ C^{0.37}$$

where:

h_z = exchange zone height, inches

Q = solution flow rate, gallons per
minute per square foot of bed
area

C = influent concentration, mols per
liter.

The equation fits the experimental data over the
entire range investigated to within an average
deviation of plus or minus 11 per cent.

2.   The equation given above correlates all other available data with an average deviation of plus or minus ten per cent.

3.   Within the range of variables studied, the sodium fraction of the exchange zone was found to have an average value of 0.454, and an average deviation of plus or minus five per cent.

VI. SUMMARY

During the past several years, great progress has
been made in ion exchange applications, methods of
operation, and theory. In spite of this, however,
equipment is still being designed on an empirical
basis. While a number of design methods have been
proposed, none of them have really become popular due
to their mathematical complexity.

Some four years ago, Michaels introduced the
exchange zone concept, on which he based a simplified
design method. Since that time, literature searches
have shown that no further work has been done on this
method of design for ion exchangers.

It was the purpose of this investigation to study
the exchange zone method further, and thus extend the
conditions for which data for this method are available.
In particular, the effects of solution flow rate and of
influent concentration on the exchange zone height were
investigated for the system Na-H-Cl-Nalcite HCR.

Thirty-two tests were made on a bed of hydrogen
form Nalcite HCR, using sodium chloride solutions of
0.10 to 0.25 normal concentrations, at flow rates of

2.66 to 7.14 gallons per minute per square foot of bed area. The resin bed had a diameter of two inches and a hydrogen form height of 16 inches. No regeneration was employed, each test being made on a new bed made up from fresh, acid-washed resin. All tests were made within the temperature range of 60 to 70 degrees Fahrenheit.

The experimental results were correlated by the following equation:

$$h_z = 8.94 \; Q^{0.45} \; C^{0.37}$$

where:

h_z = exchange zone height, inches

Q = solution flow rate, gallons per minute per square foot of bed area

C = influent concentration, mols per liter.

The equation was found to fit the experimental results to within plus or minus 11 per cent, and all other available data to within plus or minus ten per cent.

The sodium fraction of the exchange zone height was found to have an average value of 0.454, with an average deviation of plus or minus five per cent.

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VIII. ACKNOWLEDGMENTS

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