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# AN EXPERIMENTAL STUDY OF THE PERFORMANCE CHARACTERISTICS OF A CONTINUOUS COUNTERCURRENT ION EXCHANGE COLUMN

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Knoxville 16, Tennessee

March, 1957

CONTRACT W-7405 ENG 26, S-783

UNION CARBIDE NUCLEAR COMPANY

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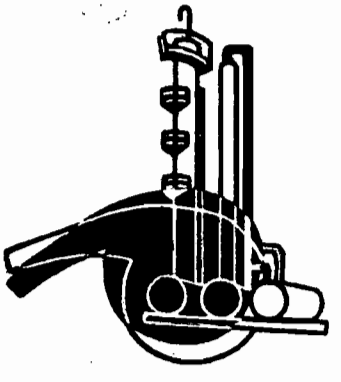

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## SUMMARY

A continuous countercurrent ion exchange column has been designed, constructed, and tested for preliminary performance data using the ion exchange system Dowex-50W, calcium, and sodium. The ion exchange column contained both loading (adsorption) and stripping (regeneration) sections with the two sections separated by isolation zones of zero dynamic pressure differential. The resin was moved through the column in a dense bed countercurrent to liquid contamination and regeneration streams and performance tests were carried out to show the feasibility of this type of column operation, to determine typical values of the equilibrium stage heights, and to measure the ion exchange attrition rates. This investigation constitutes one phase of a project concerned with the development of continuous ion exchange equipment now in progress at The University of Tennessee. The work is supported by Union Carbide Nuclear Company through a sub-contract, W-7405 eng. 26, S783, with the University.

The ion exchange column was constructed of four-inch glass pipe and was approximately thirteen feet in overall height. The performance tests were made with resin having particle diameters predominantly between 840 and 1100 microns when wet. The calcium feed solution concentrations were

varied between 4000 and 15000 ppm equivalent $CaCO_3$ and the regenerant solutions used for all tests were one per cent by weight sodium chloride. Data are reported for tests in which the liquid flow rates were between 40 and 75 gallons per hour per square foot, based on the empty column cross-section. The column was actually operated successfully at liquid flow rates of 100 gallons per hour per square foot. This liquid flow rate is very near that corresponding to fluidization of the ion exchange resin particles. Attempts to eliminate fluidization within the column by means of the pressure drop across a cocurrent flow section at the top of the column, referred to by Jury (9) as the hydraulic ram, have not been completely successful to date.

An automatic pneumatic control system was used to maintain the zero dynamic pressure differential conditions across the isolation zones separating the liquid feed streams to the exchange sections of the column. Three independent tests were conducted to verify the effectiveness of the isolation zones for separating the exchange sections. These tests involved the use of colored feed solutions for the observation of liquid flow behavior in the column, measurement of pressure profiles across the column to show the absence of hydraulic driving forces in the isolation zones, and material balance calculations from the ion exchange runs.

Column performance data are reported for seven runs.

In each of the runs the column was operated for specific liquid and resin flow rates and specific liquid feed compositions. Samples of the liquid feed and product streams and of resin at the terminals of each exchange section were analyzed to show the approach to steady state conditions. Such data were used to determine the number of theoretical equilibrium stages by the McCabe-Thiele (13) graphical method, and stage heights were computed from the actual exchange section heights. Typical values of the height equivalent to a theoretical stage, HETS, ranged from 0.3 to 1.0 foot. These values are approximately ten times the corresponding values obtained by integration of the ion exchange rate equation developed by Anderson (2) in work on another phase of this investigation. This disagreement is attributed to nonuniform flow effects in the column.

Resin attrition rate measurements indicated approximately 0.02 per cent fines (diameter less than 840 microns) accumulation per pass through the ion exchange column, based on the total resin inventory of the column. The value was obtained using a manually adjusted plug-type valve to regulate the resin flow rate. When a motor driven rotating feeder was used to regulate the resin flow rate, the accumulation of fines was much greater, 2 per cent per pass through the column.

It is concluded from these studies that the operation of a continuous countercurrent ion exchange column using a moving dense bed of ion exchange resin particles is satisfactory at liquid flow rates up to that corresponding to fluidization. Further work is needed for the effective utilization of the hydraulic ram principle as a means of maintaining dense bed operations above the fluidization velocity of the resin particles.

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# CHAPTER I

# INTRODUCTION

## General

A wide variety of chemical industries is currently using and planning further future applications for a relatively new unit operation known as ion exchange. Since 1935, when the first synthetic ion exchange resin was prepared by Adams and Holmes (1), there have been many advances made in the field of ion exchange technology with the direct result being the everyday high quality of many commercial products such as television tubes, storage batteries, glycerine, sugar, streptomycin, penicillin, vitamins, paper, dyes, etc. However, until recently, most commercial ion exchange operations had been carried out with batch or fixed bed equipment. An appreciation of the desirability of obtaining strictly continuous ion exchange as a replacement for the intermittent operations inherent in batch and fixed bed operations has brought recognition of the real need and value of continuous ion exchange throughout the chemical industry.

Shortly after World War II a program of continuous ion exchange development was undertaken by the Oak Ridge National Laboratory to provide continuous ion exchange equipment needed for the commercial processing of low-grade

Western uranium ores. In order to expedite this program, portions of the development work were contracted to outside agencies (3). The current investigation was carried out as a part of the outside development work under a subcontract between The University of Tennessee and Union Carbide Nuclear Company, a prime contractor with the U. S. Atomic Energy Commission and operator of the Oak Ridge National Laboratory. It is the objective of the project at the University to develop a method of continuous ion exchange and to carry out performance tests for the purpose of obtaining characteristic operating data. An ion exchange system consisting of a calcium chloride or a sodium chloride solution in the liquid phase and Dowex-50W, a synthetic ion exchange resin, in the solid phase was chosen for the performance tests on the basis of convenience since analytical methods were already available for the rapid and accurate analysis of test samples (10). An integral part of this overall investigation, the theoretical and experimental development of a "rate equation" for the ion exchange reaction and other equilibrium relationships, has been reported by Anderson (2) for the same ion exchange system. Another part of the overall investigation was to be devoted to the mechanics of a continuous column and the carrying out of performance tests on the equipment. This problem was undertaken by the author and is the subject of this thesis.

## Literature Survey

In this section no attempt has been made to present a complete survey of all the studies in the field of ion exchange for the reason that only a portion of these studies is pertinent to the present work. The prime concern of this survey is with continuous ion exchange and as such is exclusive, for the most part, of other types of ion exchange methods and equipment.

During the past few years the interest in ion exchange as a basic unit operation has been developing primarily along the lines of a continuous process and the equipment required to carry out continuous ion exchange operation. There have been at least ten workable laboratory models and one commercial unit for continuous ion exchange reported in the literature. A particularly interesting point relating these various methods is their proposed method for overcoming the liquid flow rate limitation caused by the fluidization of a resin bed within the ion exchange column.

Stanton (18) used a pair of rotating plug-type valves for transferring incremental quantities of resin from an experimental column. This method provided for liquid-resin contact to occur in a dense bed which had a net downward motion by virtue of the continuous addition of resin at the top and its net withdrawal from the bottom of the column.

This method of resin flow control served to eliminate the limit on liquid feed rate. Both resin saturation and regeneration were carried out within a single column. Sieve plates were added to the regeneration section to improve the liquid-resin contact. Several separations of copper and zinc were made with the equipment.

Mihara and Terasaka (14) developed a method of continuous ion exchange using an endless wire mesh coated with ion exchange resin which was circulated through adjacent saturant and regenerant tanks. Similarly, Selke and Muendel (17) developed a method of continuous ion exchange using an endless belt of phosphorylated cotton. A third method along these same lines, developed by McCormack and Howard (11), employed the use of resin enclosed in permeable casings which were conveyed like a continuous string of sausages through the ion exchange system. All three of these methods employ essentially the same method of circumventing the fluidization problem, i.e., each has placed the resin (or exchange media) in or on some rigidly fixed conveyor where it is unaffected by the liquid flow rate.

Swinton and Weiss (20) modified a commercial ore-dressing jig for a continuous ion exchange system and found the system, using sodium chloride and calcium chloride, to have a contact efficiency of approximately one-fourth that reported by Selke (16). Because of the flexibility,

ruggedness, and ease of maintenance of equipment the system appeared to be quite economical. The fluidization problem was overcome with a series of plates and downcomers connected with a diaphragm whereby the resin moved essentially horizontally most of the time.

Moir, Ross, and Weiss (15) developed a froth-flotation method which may be feasibly applied to continuous ion exchange on an industrial scale when special adsorbents have been devised. This method avoids the fluidization problem rather uniquely. The proposed exchange is to occur on the surface of bubbles containing a special exchange adsorbent.

Higgins and Roberts (8) devised a method utilizing solution downflow and resin upflow. The upward motion of the resin was created by hydraulic impulses applied at the base of the resin bed. At the time of the resin movement upward the liquid flow was temporarily interrupted. Therefore the system was not completely continuous, although the interruptions were brief enough to make the system closely approximate continuous behavior. The problem of fluidization was eliminated entirely since the liquid flow only occurred through a fixed bed.

Hiester, Cohen, Phillips, and Radding (5) at Stanford Research Institute devised a method requiring rotating valves to meter the resin input at the top of the column and to remove the resin at the bottom. A column insert and tapped-

screen assembly was used to promote better contact between resin and solution under moving-bed conditions.

McIlhenny and McConnel (12) invented a continuous method for concentrating the magnesium ions in sea water. This method involved the use of two columns constructed beside each other with interconnecting flow lines. One of the columns was used for exchange and the other for regeneration. Both columns contained perforated plates to aid in preventing fluidization. Along with the column invention several interesting control methods were indicated in the patent, such as: (a) a photoelectric cell, (b) a refractometer, and (c) a star valve metering device.

A commercial water softening unit, Dorr's Hydro Softener (7), has proven acceptable during pilot plant operation and although it still uses some fixed bed concepts, it does provide continuous operation since the large "fixed" bed is being regenerated constantly in an auxiliary column.

Hiester (6) and Selke (15) independently arrived at the conclusion that continuous ion exchange columns are less efficient than a fixed bed operating under the same conditions but that the resin and equipment requirements for a continuous column are much less than for an equivalent fixed bed unit.

The studies in continuous ion exchange have not included any extensive resin attrition measurements and only three groups have indicated even approximate resin attrition

rates. The Dorr Hydro-Softener (7) has an approximate ten per cent per year resin replacement requirement due to attrition. Arehart, Bresee, Hancher, and Jury (3) reported results of attrition tests which indicated that attrition rates become very significant after six months of operation and are also a function of the resin used. Hiester, Fields, Phillips, and Radding (5) reported that approximately 0.1 per cent attrition of resin within their column occurred per passage.

Arehart, Bresee, Hancher, and Jury (3) recently reported performance data on a Higgins (8) type contactor. These data are useful for scale-up of this type of contactor and for comparison with other performance data obtained with continuous ion exchange columns. In addition, they also suggested the use of a cocurrent flow "hydraulic ram" section to prevent resin fluidization and pressure balances to obtain solution isolation within the column in designing a continuous ion exchange unit. However, they did not describe the operation of a column incorporating these design features.

Summary

The basic problems that must be met in designing a continuous ion exchange column are: (a) overcoming the "fluidization" velocity of the liquid which limits the unit capacity, (b) devising a method of passing the exchange

resin and liquid through a column countercurrently to make optimum use of concentration gradients, and (c) developing methods of flow control for both liquid and resin. In most of the work reviewed the methods of flow control were fairly well standardized, with rotameters being used on the liquid streams and mechanical valves used to regulate the resin flow. Other methods of resin control were indicated, but they had not been extensively tested. The methods used to pass the resin countercurrent to the liquid and the methods of overcoming the limiting liquid velocities were primarily mechanical with the exception of a completely hydraulic control system suggested by Arehart, Bresee, Hancher, and Jury (3). This system, as proposed for hydraulic control, versus the mechanically controlled systems has the interesting prospects of (a) lowering the resin attrition rate and (b) simplifying the mechanical features of the equipment.

## Present Investigation

The experimental design suggested by Arehart, Bresee, Hancher, and Jury (3) which had a "hydraulic ram" and pressure balances for controlling isolation zones as its main design features was the basis of the column design tested in this investigation. The objectives of this investigation were: (a) to develop a method of continuous ion exchange,

(b) to study the mechanical aspects related to operating the experimental ion exchange column developed, and (c) to obtain performance data from the experimental ion exchange column for scaling up its design to industrial sized models.

# CHAPTER II

## BASIC RELATIONSHIPS

Ion exchange is probably best explained on the basis of its physical nature. On this basis, a definition of ion exchange may be stated as:

> the reversible exchange of ions between a solid and a liquid in which there is no substantial change in the structure of the solid. (7)

By this definition one of the ions must always be bound to the immobile solid and is therefore not carried away by the solution. This fact embodies the principal advantage of the process of ion exchange.

### Equilibrium Relations

The chemical reaction for the cationic exchange occurring in the system studied in this investigation is:

$$2\ Na \cdot (Resin) + Ca^{++} \rightleftharpoons Ca \cdot (Resin)_2 + 2\ Na^{+} \quad (1)$$

where: $Na \cdot (Resin)$ = sodium form of resin

$Ca \cdot (Resin)_2$ = calcium form of resin

The application of the law of mass action, which governs this reaction, results in the following equation for the equilibrium constant (K) in terms of concentrations:

$$K = \frac{[Ca \cdot (Resin)_2] \cdot [Na^+]^2}{[Na \cdot (Resin)]^2 \cdot [Ca^{++}]} \qquad (2)$$

where: $[Ca \cdot (Resin)_2]$ = concentration of calcium form of resin

$[Na \cdot (Resin)]$ = concentration of sodium form of resin

$[Na^+]$ = ionic concentration of sodium in liquid

$[Ca^{++}]$ = ionic concentration of calcium in liquid

## Rate Equation

Anderson (2), as a part of the ion exchange program of study at The University of Tennessee, developed a rate equation from experimental data and theoretical considerations. This rate equation provides a basis for interpreting column performance data. The differential form of the equation is:

$$\frac{-R\,dy}{\frac{\pi D^2}{4}(1-\alpha)\rho_s dZ} = \frac{aC_o x(1-y)^2 - \frac{C_o^2 y(1-x)^2}{K}}{\frac{a(1-y)^2 + \frac{2C_o y(1-x)}{K}}{k_L} + \frac{2C_o x(1-y) + \frac{C_o^2(1-x)^2}{Ka}}{k_R}} \qquad (3)$$

where: R = resin flow rate, grams dry resin per minute

D = diameter of exchange bed, cm.

$\alpha$ = void fraction of resin = 0.50 for Dowex-50W (16)

$\rho_s$ = density of resin, grams per cu. cm.

Z = exchange resin bed height, cm.

K = equilibrium constant for exchange system

a = total ionic capacity of resin, meq ($Ca^{++}$ + $Na^{+}$) per gram

P = meq $Ca^{++}$ per gram dry resin

y = P/a

$C_o$ = total ionic concentration of liquid, meq ($Ca^{++}$ + $Na^{+}$) per ml.

x = $\frac{\text{Calcium ionic concentration of liquid, meq } Ca^{++}/\text{ml}}{C_o}$

$k_R$ = the solid phase diffusion constant, minutes$^{-1}$

$k_L$ = the liquid film diffusion constant, minutes$^{-1}$

The two diffusion constants were related to the flow conditions in the dense resin bed by the empirical equations:

$$k_R = 0.278 + 0.162\ Re$$

$$k_L = 31.32\ Re^{0.643}$$

Here Re is the Reynolds number based on the particle diameter and the superficial liquid velocity in the resin bed.

The differential equation is of little use as such, but the integral form may be used to determine theoretical exchange bed height requirements. The integral form is obtained directly from equation (3).

$$\int_o^Z dZ = \frac{-Ra}{\frac{\pi D^2}{4}(1-\alpha)\rho_s} \int_{y(o)}^{y(Z)} \left[ \frac{\frac{a(1-y)^2 + \frac{2C_o y(1-x)}{K}}{k_L} + \frac{2C_o x(1-y) + \frac{C_o^2(1-x)^2}{Ka}}{k_R}}{aC_o x(1-y)^2 - \frac{C_o^2 y(1-x)^2}{K}} \right] dy \quad (4)$$

The values of x in equation (4) are found as a function of x(o), y(o), and y by taking a material balance with respect to calcium over a hypothetical section of the ion exchange column.

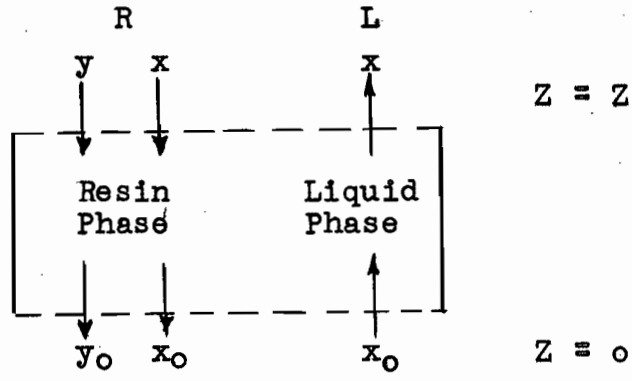


Figure 1. Hypothetical Section of the Ion Exchange Column

The material balance equation is:

$$Ray(o) + \frac{R\alpha\rho_L C_o x(o)}{(1-\alpha)\rho_s} + LC_o x = Ray + \frac{R\alpha\rho_L C_o x}{(1-\alpha)\rho_s} + LC_o x(o) \quad (5)$$

where: $Ray(o)$ = the Calcium leaving with the resin at Z = o

$\frac{R\alpha\rho_L C_o x(o)}{(1-\alpha)\rho_s}$ = the Calcium leaving with the liquid in the resin voids at Z = o

$LC_ox$ = the Calcium leaving with the liquid at Z = Z

Ray = the Calcium entering with the resin at Z = Z

$\frac{R\alpha\rho_s C_o x}{(1-\alpha)\rho_s}$ = the Calcium entering with the liquid in the resin voids at Z = Z

$LC_ox(o)$ = the Calcium entering with the resin at Z = o

Z = exchange section height

$\rho_L$ = liquid density, grams per ml.

L = liquid flow rate, ml. per minute

The evaluation of equation (4) with equation (5) can be carried out by numerical methods which are readily applied once the data are obtained. Calculated bed heights determined by the preceding method should prove advantageous in evaluating the experimental performance data from a continuous ion exchange unit.

## Theoretical Stages

The relations established by McCabe and Thiele (13) for the graphical determination of the number of equilibrium contact stages can be applied to ion exchange where discrete steps are involved in countercurrent contacting of resin and solution. Figure 2, for instance, illustrates the relation between the operating line and the equilibrium curve when an ion A is being transferred from the resin stream to the countercurrent solution phase. The horizontal distance between

the two lines represents the overall driving force for ionic transfer based on the liquid film. The number of equilibrium contacts required to reduce the concentration of A in the resin phase from its entering value to the desired exit concentration may be found graphically by stepping off the stages in the conventional manner by applying the McCabe-Thiele method (13).

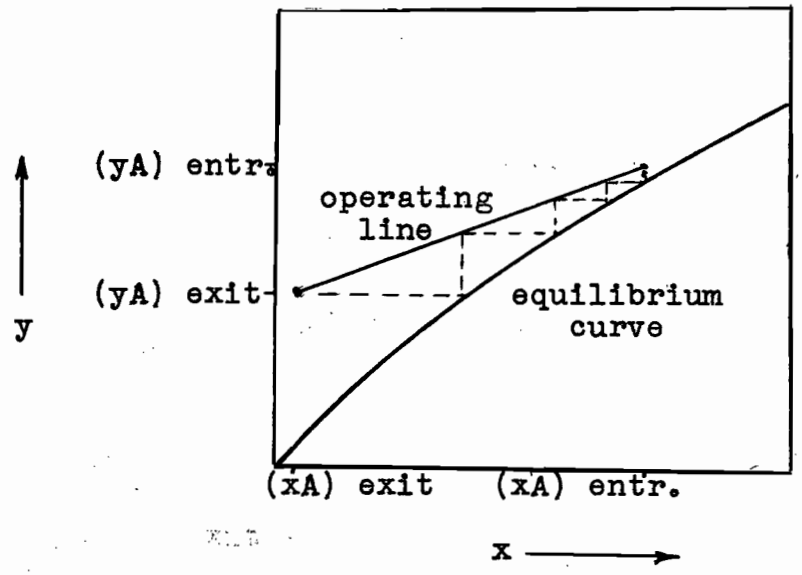


Figure 2. McCabe-Thiele Diagram for Counter-current Ion Exchange

For ionic transfer from the resin to solution, i.e., stripping, the operating line will be above the equilibrium line. In order to have nearly complete removal of ion A from the resin, the entering solution must be nearly free of A, the slope of the operating line must be greater than the slope of the equilibrium curve, and a large number of contacts

will generally be required. Conversely, the operating line will be below the equilibrium curve for loading ions onto the resin. Nearly complete saturation of the resin requires that the solution be free of the second component, have a large number of contacts, and have an operating line with a slope less than that of the equilibrium curve.

# CHAPTER III

# EXPERIMENTAL EQUIPMENT

## General

The equipment used in this investigation consisted of an ion exchange column, containing both loading and stripping sections, and the necessary accessories required for the operation and testing of the column. The basic column design and construction were flexible enough to allow the changing of parts and the incorporation of new ideas into the experimental design. The experimental column details were not altered throughout most of the performance tests made after the initial experimentation. This was done to eliminate unnecessary variations that might have occurred in the column performance.

## Column

The column, containing the two exchange sections, was constructed of 4-inch ID glass pipe sections rigidly flanged together with bolts and gasket sections. Pipe lengths varying from ten inches to two feet were used in the column construction to obtain the desired positions for the pressure taps, the liquid feed streams, and the liquid removal streams.

For most of the tests the column height was approximately thirteen feet.

The schematic diagram, Figure 3, and the equipment photograph, Figure 4, show the relative importance of the column in the overall equipment layout. Both loading and stripping were carried out in the single experimental column. As indicated in Figure 3, the resin is carried from the bottom of the column to the top by a liquid jet lift. From the top of the column the resin then moves toward the bottom of the column due to gravitational attraction of its own mass and the action of the cocurrent flow hydraulic ram. As the resin moves through the column from the top to the bottom it passes through these sections: (a) a zone of resin immediately above the loading section in which no exchange occurs, (b) the loading zone where the resin picks up calcium ions from the liquid feed and loses sodium ions, (c) an isolation zone of constant hydraulic pressure in which no liquid flows, (d) the stripping section where the resin loses calcium ions to the liquid and picks up sodium ions, (e) a wash section where the liquid contained in the void spaces of the bed is washed out and replaced by wash water, and (f) a second isolation zone of constant hydraulic pressure to prevent any liquid flow, either up or down, at the bottom of the column.

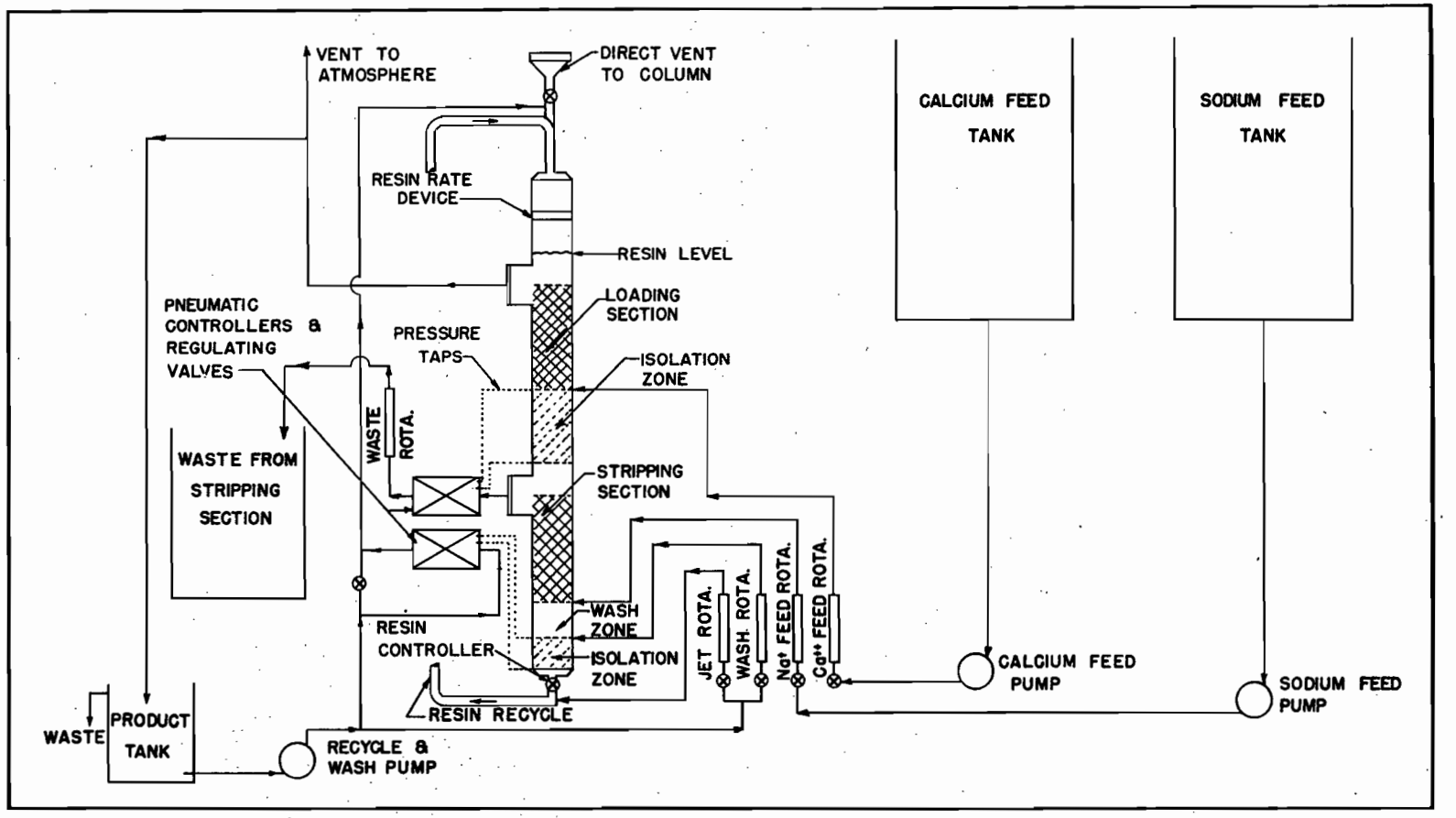


Figure 3. Schematic Layout of Experimental Apparatus

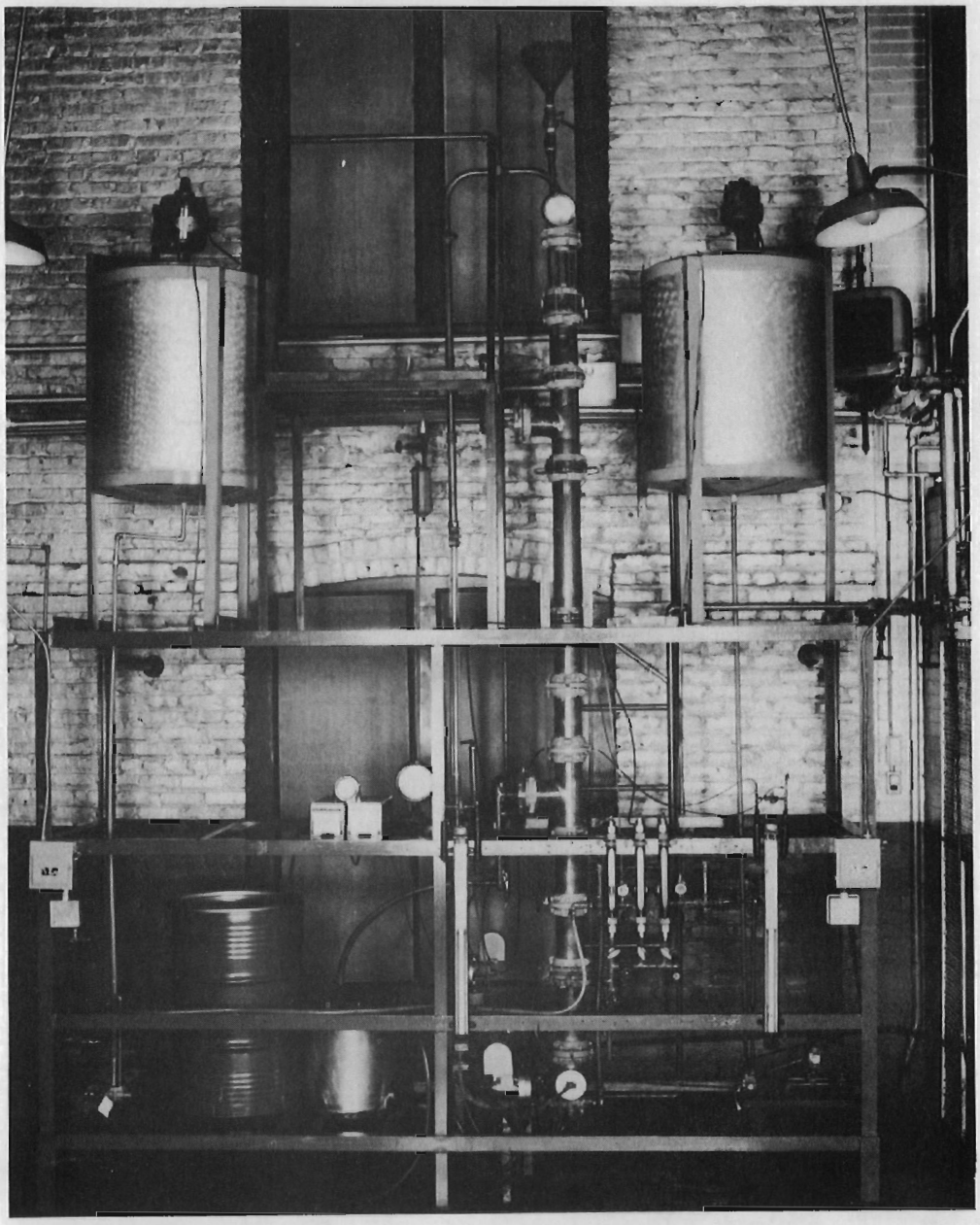

Figure 4. Experimental Apparatus for Continuous Countercurrent Ion Exchange

## Resin System

The exchange medium was Dowex-50W (8 per cent cross-linkage) supplied by the Dow Chemical Company and screened by the Illinois Water Treating Company. The exchange capacity, found experimentally, was 4.818 meq per gram of dry resin. The density of the resin was 1.3177 grams per cubic centimeter in the hydrogen form and wet (2). Ninety-five per cent of the resin supplied to the column was made up of particles with diameters between 840 and 1100 microns when wet. The remainder of the resin was made up of fines (particles with diameters less than 840 microns when wet).

The exchange system was closed with respect to resin and there was only one initial charge of resin made to the column. The liquid jet lift provided the necessary force required to move the resin in the system and an adjustable control valve was used (See Figure 5) to control the quantity of resin carried in the jet lift. A butterfly type metering device and timer were used to determine the "dry-resin" flow rate without removing resin from the system. A special resin sampling device for removing approximately one gram of resin from the column cross section was built and found satisfactory (See Figure 6). Before obtaining the resin sample from the column it was necessary to fill the sampling device with liquid to prevent air from entering the

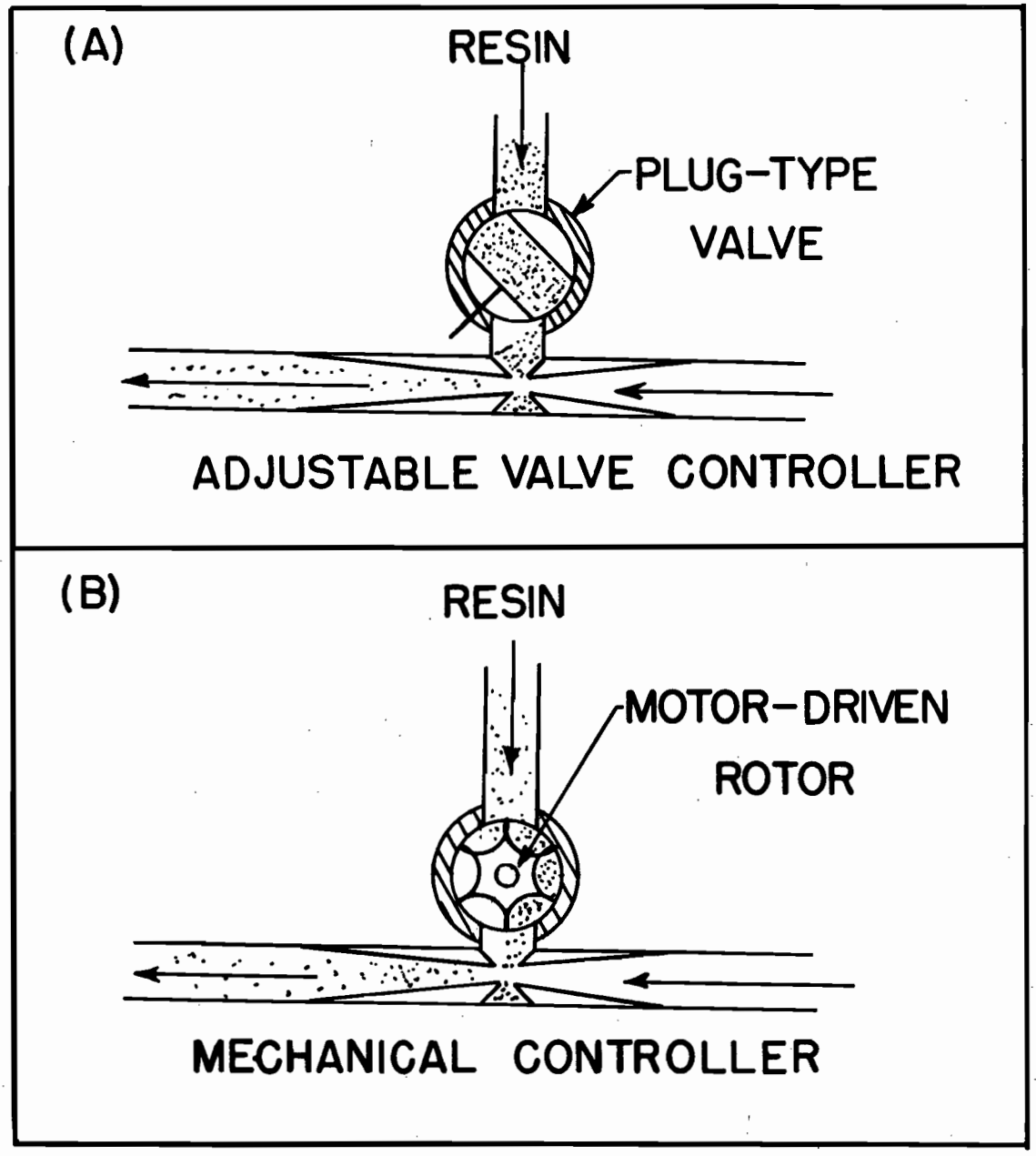


Figure 5. Resin Rate Controlling Devices

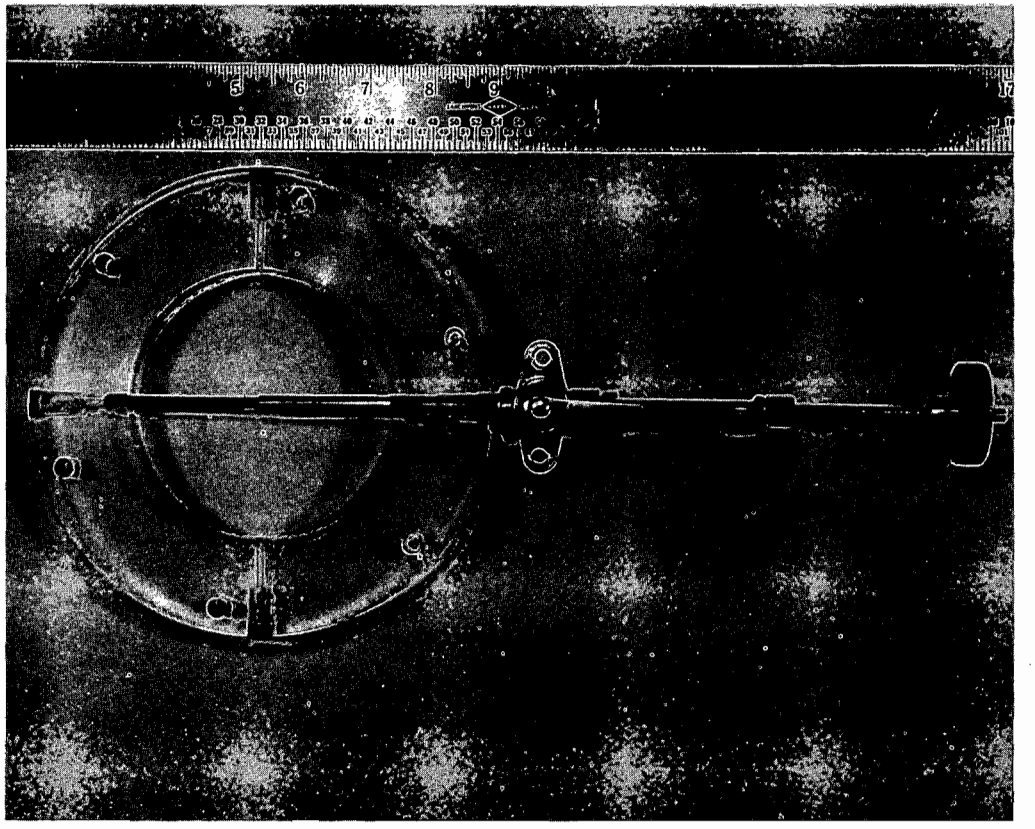


Figure 6. Resin Sampling Device

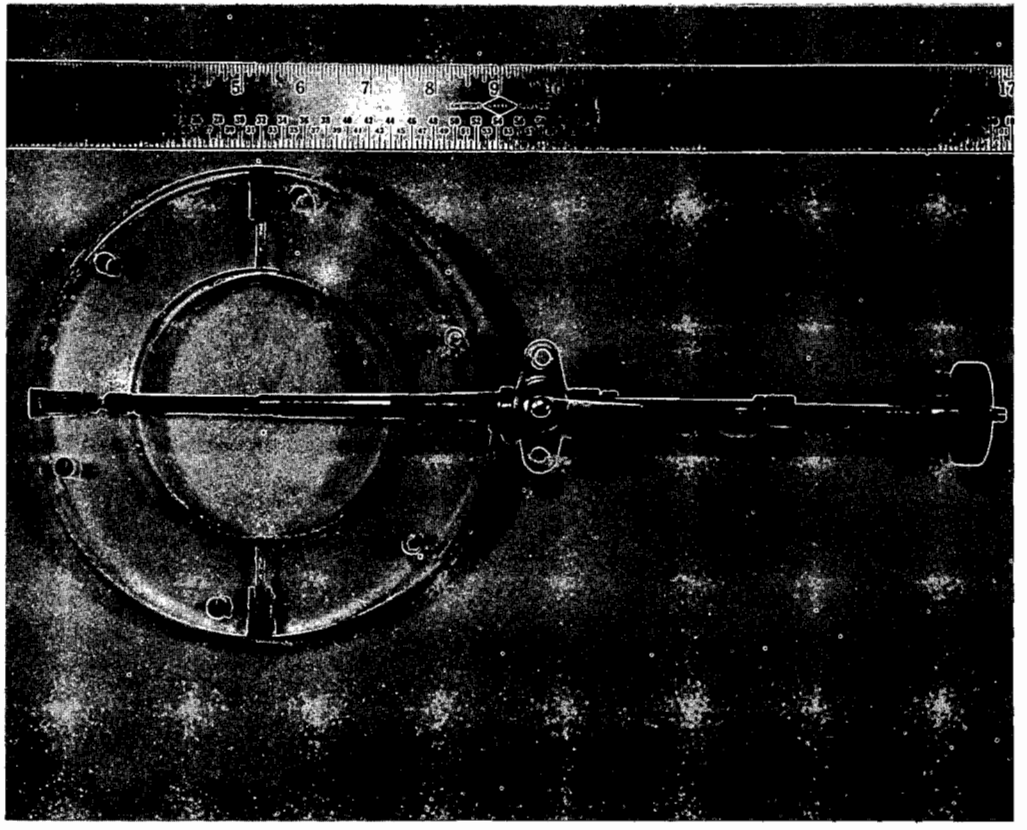

Figure 6. Resin Sampling Device

exchange column.

## Liquid System

The liquid system was rather elaborate, as shown in Figure 3. It consisted of four feed streams and two "product" streams. These streams were:

(1) a calcium chloride solution. This solution was fed to the loading section and had been made up from city water and a commercial grade calcium chloride. The composition of this solution was reported in terms of equivalent $CaCO_3$ hardness. For the various performance tests solutions containing 4000 to 15000 ppm were used for the feed to the loading section.

(2) a sodium chloride solution. This solution was fed to the stripping section and had been made up from city water and a commercial grade of sodium chloride. Each sodium chloride solution was made up as one per cent by weight NaCl and analyzed for equivalent $CaCO_3$ hardness and NaCl concentration.

(3) a wash stream. This stream was "softened" liquid from the loading section used to displace the liquid carried along with the resin from the stripping section.

(4) a jet lift stream. The jet feed, recycled from the product effluent, served to lift the regenerated resin

back to the top of the column.

(5) product stream (loading section). This stream was the "softened" calcium feed stream after it had passed through the loading section.

(6) waste stream (stripping section). This stream was the "hardened" sodium feed stream after it had passed through the stripping section.

Flow rates for all the liquid streams except the product stream from the loading section were measured with rotameters.

In order to obtain uniform liquid feed to the exchange sections a feed ring was constructed with a series of "slotted tubes," one-eighth inch in diameter. These tubes were arranged in the feed ring as shown in Figure 7. Both the product from the loading section and the waste from the stripping section were withdrawn from the column through take-off sections. These take-off sections were glass "T" pipe sections with a 30 mesh screen inserted between the flanges in the horizontal arm to allow the passage of liquid and to retain the resin within the column.

In order to remove resin from the low pressure space at the bottom of the column and lift the resin to the top of the column a venturi-type jet was used. This venturi-jet is shown schematically in Figure 5 and its characteristic measurements include: (a) a 5/32 inch throat, (b) a five

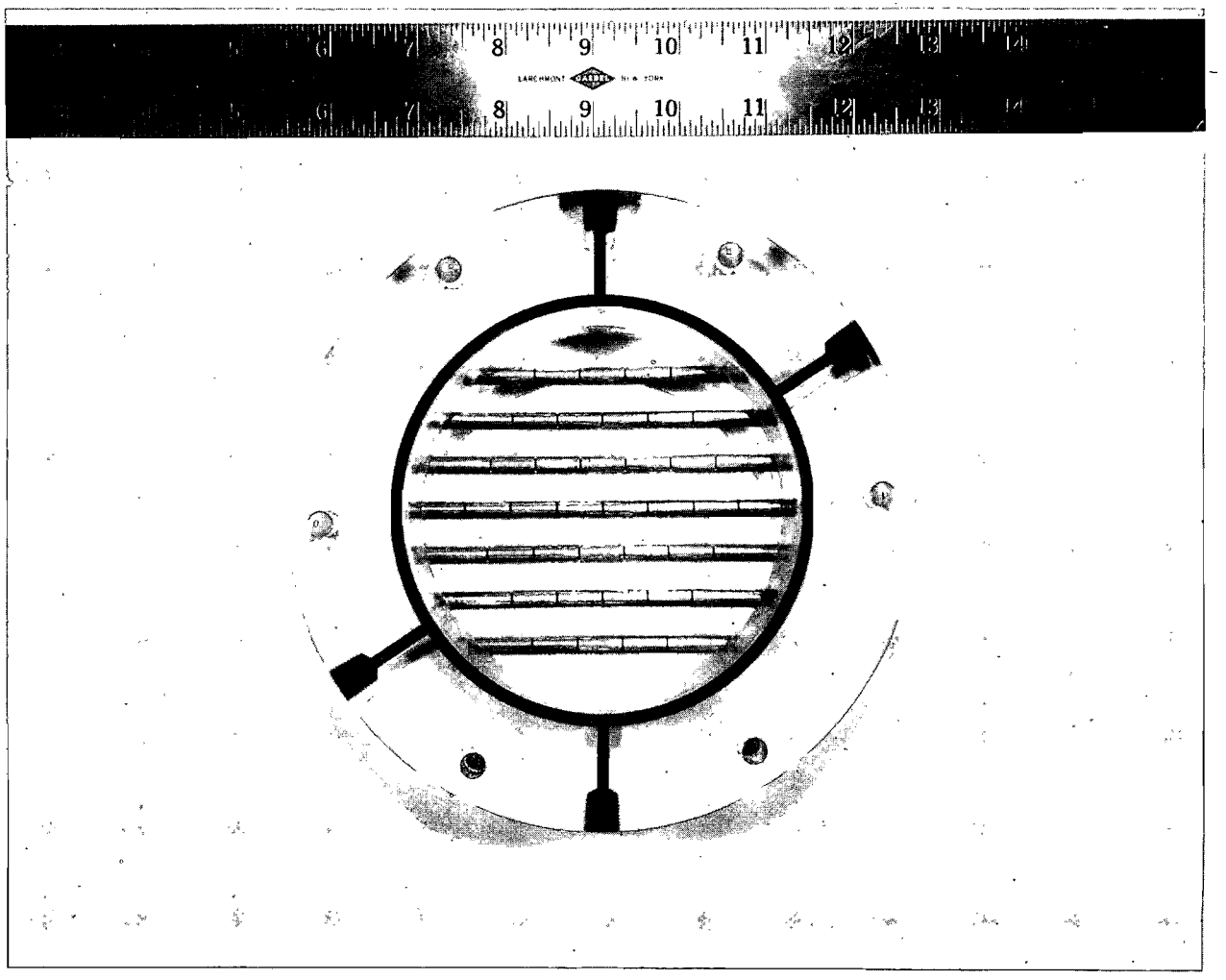

Figure 7. Liquid Feed Ring

degree angle of taper, and (c) a 3/8 inch opening for the resin.

Two 116 gallon aluminum tanks were used to make up and store the calcium and sodium feed solutions until they could be used in the column. Propeller-type agitators were used in each tank for mixing the solutions.

The isolation zones were maintained by pneumatically controlled valves. The primary sensing elements of the controllers were Foxboro D.P. cells, range: 0-50 inches of water, modified by the Instrument Section at the Oak Ridge National Laboratory to give an operating range of ± 6 inches of water. The pneumatic signals from the D.P. cells were supplied to Foxboro controllers, Model 58P4, which actuated Foxboro Regulator valves, Type V-4.

## Pumping System

Three pumps were required for the operation of the experimental column during test runs. They were: (a) the calcium feed pump, (b) the sodium feed pump, and (c) the recycle and wash feed pump. The calcium and sodium feed pumps were positive displacement pumps and the recycle and wash pump was a centrifugal pump. The positive displacement pumps were coupled with air-bubble fluctuation dampers to provide uniform feed rates to the column. The recycle and

and wash feed pump was used to recycle the product from the loading section as wash and for the jet lift. (See Figure 3.)

# CHAPTER IV

# EXPERIMENTAL PROCEDURE

## General

The primary objectives of this investigation were to (a) design and build a continuous ion exchange column and (b) obtain performance data for scaling up the experimental column to industrial type equipment. The early parts of the investigation were primarily concerned with building and developing a workable experimental ion exchange system. After the development work on the continuous countercurrent ion exchange equipment had proven it to be operable, performance tests were made to evaluate the system and obtain pertinent data for future ion exchange equipment design.

## Column Development

The initial experimental column was essentially the same as shown in Figure 3 and described in the preceding chapter without the automatic pressure control system for the isolation zones. The operation of the initial experimental column depended upon the manual maintenance of the two constant pressure zones to isolate the loading and stripping sections. This was later modified to one manually controlled zone and a pneumatically controlled zone because

of the difficulties encountered in making frequent manual adjustments. Even one manually controlled zone proved to be a control problem, so a second pneumatic control unit was installed. The use of two controlling units made the operation of the column considerably simpler since the operational manpower requirements were reduced to a single operator where two and sometimes three operators had been required to maintain manual operational conditions. Some other changes were made in the column development, as follows:

(1) Positive displacement pumps were installed in the feed lines. This change was made to provide more uniform feed rates than had been obtained with a pair of centrifugal pumps used earlier. The first pair of pumps used was also oversized and significant heating of the feed solutions resulted. There was some question about the effect of temperature upon the exchange reaction at the time of the change, although no extensive investigation was made along these lines.

(2) A special take-off section was designed, built, and subsequently removed. The take-off section used in most of the testing in this investigation consisted of the "T" section with a screened cross section described in the preceding chapter; however, it was felt that a design which would allow the removal of the liquid from the center of the exchange column would give a better sample for testing

purposes. The second take-off section consisted of a tube inserted into the center of the column and covered with a hemispherical screen, one and one-half inches in diameter. Because of large pressure build-ups within the column and the subsequent packing of resin around the take-off this design was rejected. Further work is planned along these lines.

(3) A mechanical resin rate controller embodying the use of a variable speed, motor driven gear in controlling the resin flow rate was installed in the column. See Figure 5. This controller had the desirable feature of easily established, uniform resin flow rates. However, this advantageous feature was outweighed by the greatly increased resin attrition rate and the mechanical controller was removed.

## Operational Procedure

It was necessary to decide upon a set of operating conditions before making each performance test. Conditions for providing data for performance evaluation were estimated from experimental observations and mass balance calculations.

The approximate calcium solution concentration to be fed to the loading section was first decided upon. The calcium feed solution concentrations used throughout this

investigation were considerably higher than normally associated with water softening processes. Because of the limit on liquid feed rates imposed by the fluidization of the resin at flow rates near 100 gallons per hour per square foot it was necessary to use concentrated (from 4000 to 15000 ppm equivalent calcium carbonate) calcium feed solutions to load calcium ions onto the resin in the loading section at rates sufficiently high to allow the attainment of steady state conditions in reasonably short operational time periods.

The sodium chloride solutions fed to the stripping section in all performance tests were made up of one per cent (by weight) sodium chloride to conserve the reagent. An accurate analysis of the sodium feed solution was made with standard silver nitrate solutions to determine the chloride and thereby the sodium ion concentration.

These were rather unorthodox conditions for water softening by ion exchange methods, but they provided a good basis for obtaining performance data for the evaluation of the ion exchange equipment.

The essential steps in operating the experimental column and obtaining data were as follow below. (See Figure 3.)

1) Fill empty column with liquid to remove air.

2) Close the resin control valve.

3) Fill the column with wet resin.

4) Start pumps (but not feeds).

5) Start jet feed (the resin control valve is still closed at this point).

6) Open pneumatic control valves to the system by opening the manual control valve in series with them.

7) Gradually open the resin control valve until the approximate desired resin flow rate is obtained.

8) Start feeding solutions to the column (calcium, sodium, and wash) at the desired flow rates.

9) Make adjustments on jet feed rate to the final reading.

10) Adjust the resin rate to the desired value by "trial-and-error" manipulation of the adjustable control valve and the resin rate measuring device.

11) Adjust the liquid feed rates to the final desired rates.

12) At sampling points (product from loading section and waste from stripping section) adjust the sampling valves to obtain "drip" samples and begin taking samples.

13) Periodically check all feed rates and make the necessary adjustments.

14) Take regular liquid samples and test for equivalent $CaCO_3$ hardness.

15) After the liquid sample concentrations (from the loading and stripping sections) become approximately constant begin taking resin samples at (a) the top of the loading section, (b) the middle of the isolation zone between the loading and stripping sections, and (c) the bottom of the stripping section.

16) Analyze the resin sample for calcium content.

From ten to twelve hours (4 to 5 resin cycles) were required to obtain regular and consistent data on most test runs following the preceding outline.

## Liquid Sample Analysis

The method of liquid sample analysis was a standard one for determining water hardness and was obtained from the Civil Engineering Department (10) at The University of Tennessee. This method requires the use of reagents prepared commercially by the Hach Chemical Company of Ames, Iowa. The analysis requires the specific use of the following commercial reagents:

a) Standard Versenate Solution - 1.00 ml. is equivalent to 1.00 mg. $CaCO_3$.

b) UniVer - an indicator, buffer, and inhibitor powder.

The actual analytical procedure is as follows:

Pipette 50 cc. of liquid sample into a 250 ml. Erlenmeyer flask. Add approximately one gram of UniVer powder and titrate with Standard Versenate Solution until the color changes from red to blue. Shake while titrating.

The total hardness expressed as ppm $CaCO_3$ is calculated by multiplying the ml. of the Versenate solution required in the titration by twenty. Within experimental limits, the sample size may be altered provided the corresponding calculation factors are also changed.

## Resin Sample Analysis

The calcium content of the resin was measured

indirectly. The resin samples were dried and weighed accurately and then placed into Erlenmeyer flasks containing 100 ml. (accurately measured) of saturated sodium chloride solution. The samples were then placed upon a shaker, for twenty-four hours or more, until the resin and liquid had reached equilibrium. Under these conditions the resin was almost entirely converted into the sodium form and all of the calcium ions were transferred to the liquid. Thus, with a liquid sample analysis and the resin sample weight, it was possible to calculate the calcium content of the resin in terms of meq $CaCO_3$ per gram dry resin.

# CHAPTER V

# PRESENTATION OF DATA AND RESULTS

## Data

The data obtained from the operation of the experimental ion exchange column were fundamentally those required for establishing material balances around the stripping and loading sections. Complete sets of liquid samples and flow rate data were taken at regular time intervals (30 minutes to one hour) from the time of start-up to the end of each experimental test run. Complete tabulations of data as steady state was approached and other pertinent experimental results are recorded in notebooks entitled "Original Record of Research" on file in the Chemical Engineering Department at The University of Tennessee. These records are on pages 650 to 660, 10001 to 10050, 15551 to 15600, and 21101 to 21128, inclusive.

The concentrations of the product from the loading section and the waste from the stripping section are plotted as a function of operation time for four experimental runs in Figure 8 as steady state conditions were approached. The average values of the various concentrations and flow rates were estimated for approximate steady state conditions and are tabulated in Table I for seven test runs. The concen-

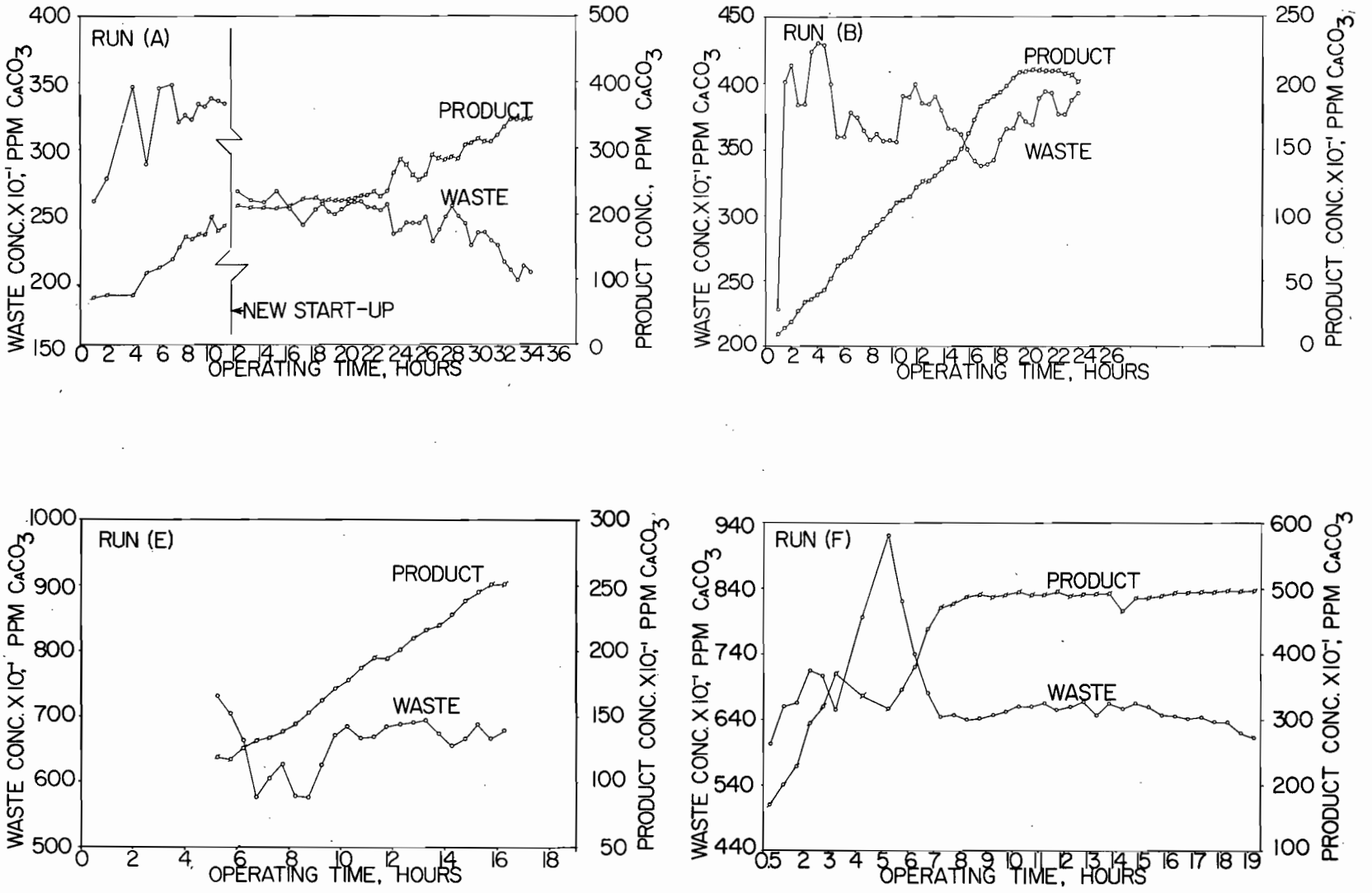


**Figure 8. The Calcium Concentration Variation in the Product and Waste Streams as Steady State Conditions Are Approached**

TABLE I

SUMMARY OF PERFORMANCE DATA

| Run (1) | $Ca^{++}$ Feed, ppm $CaCO_3$ (2) | $Na^{+}$ Feed Hardness ppm $CaCO_3$ (3) | $Na^{+}$ Feed Hardness meq NaCl ml. (4) | Avg. Conc. at Steady State, ppm $CaCO_3$ Prod. (5) | Avg. Conc. at Steady State, ppm $CaCO_3$ Waste (6) | $Ca^{++}$ Content of Resin at Steady State, meq $CaCO_3$/gm. Dry Resin Top of Column (7) | $Ca^{++}$ Content of Resin at Steady State, meq $CaCO_3$/gm. Dry Resin Mid. of Column (8) | $Ca^{++}$ Content of Resin at Steady State, meq $CaCO_3$/gm. Dry Resin Bot. of Column (9) | Resin Rate gm. Dry Resin per min. (10) |
|---|---|---|---|---|---|---|---|---|---|
| A | 2800 | 200 | - | 225 | 2580 | 2.97 | 3.16 | 2.94 | 61.7 |
| B | 5800 | 170 | - | 2090 | 3850 | - | - | - | 84.2 |
| C | 6300 | 135 | 0.1850 | 490 | 4500 | 3.07 | 4.50 | 2.90 | 15.4 |
| D | 6680 | 145 | 0.1820 | 860 | 5400 | 3.17 | 4.29 | 3.24 | 19.8 |
| E | 8155 | 215 | 0.1885 | 2510 | 6680 | 3.92 | 4.28 | 3.26 | 16.1 |
| F | 8850 | 205 | 0.1900 | 4980 | 6600 | 4.16 | 4.42 | 3.17 | 20.1 |
| G | 15050 | 175 | 0.1926 | - | 9500 | 4.38 | 4.44 | 3.43 | 20.1 |

| Run (1) | Avg. Liq. Flow Rates, ml. per min. $Ca^{++}$ Feed (11) | Avg. Liq. Flow Rates, ml. per min. $Na^{+}$ Feed (12) | Avg. Liq. Flow Rates, ml. per min. Wash Feed (13) | Avg. Waste Take-off Rate, ml./min. (14) | $Cl^{-}$ Conc. in Liquid Streams, meq $Cl^{-}$ per ml. $Ca^{++}$ Feed Loading Section (15) | $Cl^{-}$ Conc. in Liquid Streams, meq $Cl^{-}$ per ml. Prod. from Loading Section (16) | $Cl^{-}$ Conc. in Liquid Streams, meq $Cl^{-}$ per ml. $Na^{+}$ Feed Stripping Section (17) | $Cl^{-}$ Conc. in Liquid Streams, meq $Cl^{-}$ per ml. Waste from Stripping Section (18) |
|---|---|---|---|---|---|---|---|---|
| A | 325 | 285 | 39.5 | 363 | - | - | - | - |
| B | 325 | 285 | 39.5 | 252 | - | - | - | - |
| C | 325 | 285 | 39.5 | 355 | - | - | - | - |
| D | 325 | 285 | 39.5 | 278 | 0.1409 | 0.1465 | 0.1818 | 0.1813 |
| E | 385 | 235 | 39.5 | 272 | 0.1660 | 0.1665 | 0.1885 | 0.1885 |
| F | 385 | 235 | 39.5 | 252 | 0.1806 | 0.1806 | 0.1907 | 0.1912 |
| G | 350 | 285 | 39.5 | 301 | - | - | 0.1936 | 0.2128 |

tration data consist of the hardness (in terms of equivalent $CaCO_3$ hardness) of (a) the calcium feed, (b) the sodium feed, (c) the product from the loading section, and (d) the waste from the stripping section , plus the calcium content of the resin at three points within the column. The liquid samples were also analyzed for their chloride concentrations as a check on the cross-flow of liquids in the isolation zone.

The rate data include measurements of the resin rate, in terms of grams dry resin per minute, and all liquid rates with the exception of the product from the loading section, in terms of ml. per minute. These data were obtained from calibrated rotameter readings.

The liquid pressures within the column were studied as a function of height and column design under various operating conditions. A typical pressure profile of the column as a function of height with the column design as it existed for most of the data reported is shown in Figure 9. Data for this profile are tabulated in Table II.

## Results

The results of this investigation may be divided into the sections that follow.

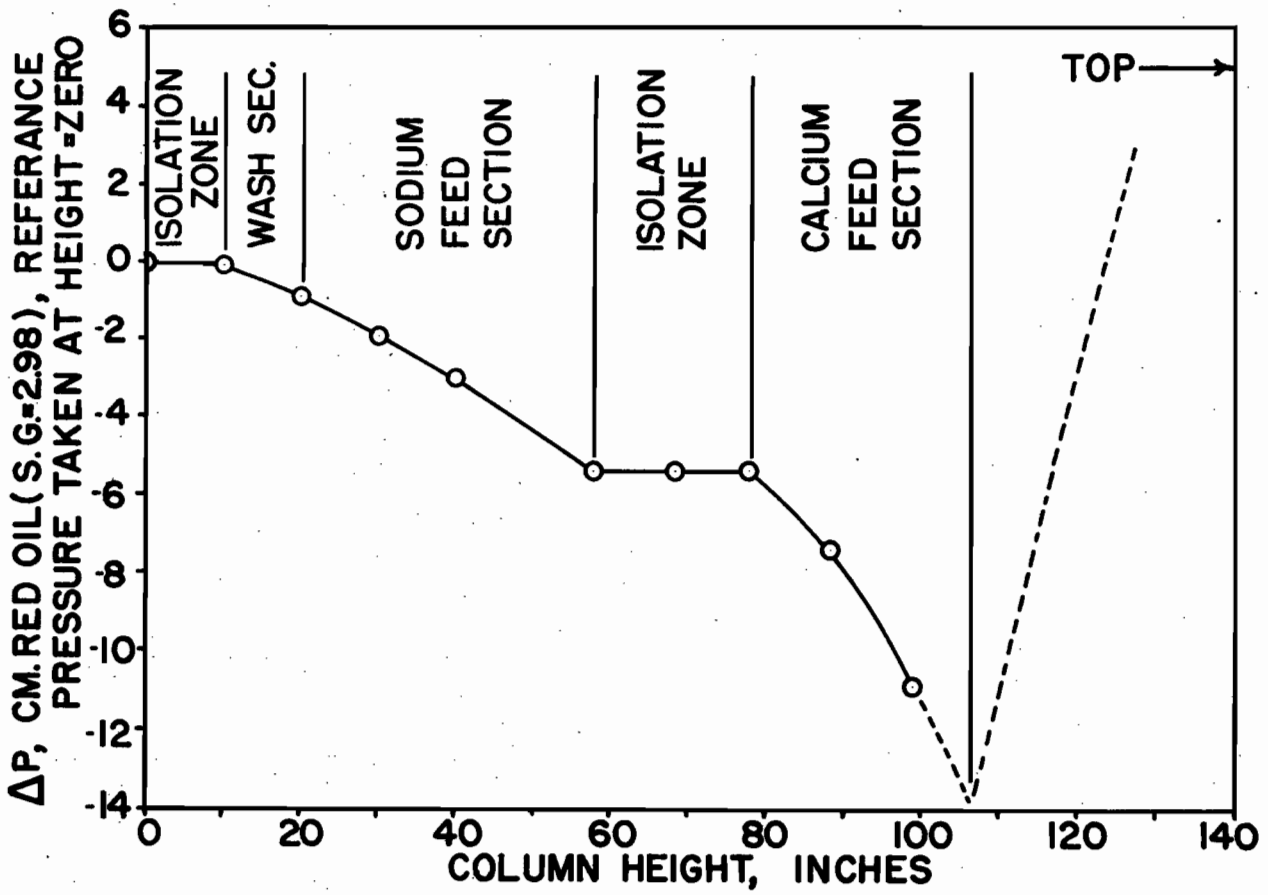


Figure 9. Typical Pressure Profile as a Function of Column Height

TABLE II

TYPICAL PRESSURE PROFILE DATA

| Height of Column, inches | P, cm. of No. 3 Red Oil above Reference |
|---|---|
| 0 | 0.0 |
| 10 | - 0.1 |
| 20 | - 0.9 |
| 30 | - 1.9 |
| 40 | - 3.0 |
| 58 | - 5.4 |
| 68 | - 5.4 |
| 78 | - 5.4 |
| 88 | - 7.4 |
| 98 | -10.9 |
| 140 | 50.0 |

## The Ion Exchange Column Design

The design and construction of the ion exchange column for laboratory experimentation were significant parts of this investigation. Figures 3 and 4 show the experimental equipment as it appeared at the end of this phase of the investigation. The experimental equipment developed fulfills the following desirable basic design requirements of continuous ion exchange operation.

(1) The system is completely closed with respect to resin, i.e., there are no additions of resin after the initial charge.

(2) The resin is regenerated (or stripped) in one section of the column simultaneously as it is being contaminated (or loaded) in another section.

(3) The resin inventory requirements are small.

(4) The stripping and loading sections are isolated from each other.

(5) The exchange resin and liquid feed streams flow countercurrently to obtain effective use of the concentration gradients as driving forces for the ion exchange reaction.

Advantageous aspects of the continuous countercurrent ion exchange column studied and developed throughout this investigation were: (a) the adoption of an automatic pressure control system to the column design to maintain two

hydraulically balanced isolation zones, (b) the total absence of any mechanical device which could be a serious source of resin attrition, and (c) the partial application of the "hydraulic ram" principle, through which momentum is transferred from a liquid stream to the resin by frictional drag.

Experimental Ion Exchange

A summary of the data required for computing theoretical bed heights is presented in Table III. Most of the data in Table III were calculated directly from Table I, the original performance data. The items obtained elsewhere were the resin density, ($\rho_s$) (2), and the resin void fraction, ($\alpha$) (19). The ion exchange capacity of the Dowex-50W resin, (a), and the equilibrium constant, (K), for the chemical system used in this investigation (calcium, sodium, and Dowex-50W resin) were calculated from experimental work carried out by Young (21). The data and calculations required to evaluate these values (a and K) are tabulated in Table IV and the extrapolated curve is shown in Figure 10. The equilibrium constant evaluated for these data is

$$K = 1.336 \text{ gram of dry resin per gram of solution}$$

and the total ion exchange capacity of the resin is

TABLE III

SUMMARY OF DATA NECESSARY FOR CALCULATION OF THEORETICAL BED HEIGHTS

| Run | C | | D | | E | | F | | G |
|---|---|---|---|---|---|---|---|---|---|
| Item | Strip. Sec. (1) | Load. Sec. (2) | Strip. Sec. (3) | Load. Sec. (4) | Strip. Sec. (5) | Load. Sec. (6) | Strip. Sec. (7) | Load. Sec. (8) | Strip. Sec. (9) |
| R, $\frac{\text{gm. dry resin}}{\text{min.}}$ | 15.4 | 15.4 | 19.8 | 19.8 | 16.1 | 16.1 | 20.1 | 20.1 | 20.1 |
| L, $\frac{\text{ml. feed solu.}}{\text{min.}}$ | 324.5 | 325 | 324.5 | 325 | 274.5 | 385 | 274.5 | 385 | 285 |
| a, $\frac{\text{meq}}{\text{gm. dry resin}}$ | 4.818 | 4.818 | 4.818 | 4.818 | 4.818 | 4.818 | 4.818 | 4.818 | 4.818 |
| $C_o$, $\frac{\text{meq}}{\text{ml. feed solu.}}$ | 0.1813 | 0.1260 | 0.1783 | 0.1336 | 0.1885 | 0.1631 | 0.1878 | 0.1770 | 0.1926 |
| $\rho_s$, $\frac{\text{gm. resin}}{\text{ml. resin}}$ | 1.3177 | 1.3177 | 1.3177 | 1.3177 | 1.3177 | 1.3177 | 1.3177 | 1.3177 | 1.3177 |
| $\rho_L$, $\frac{\text{gm. liquid}}{\text{ml. liquid}}$ | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| $\alpha$, void fraction | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 |
| $Y_{(o)}$, resin conc. at feed pt. | 0.602 | 0.934 | 0.672 | 0.890 | 0.677 | 0.888 | 0.658 | 0.917 | 0.709 |
| $X_{(o)}$, liq. conc. at feed pt. | 0.085 | 1.00 | 0.025 | 1.00 | 0.059 | 1.00 | 0.095 | 1.00 | 0.020 |
| $Y_{(Z)}$, resin conc. at take-off | 0.934 | 0.637 | 0.890 | 0.658 | 0.888 | 0.814 | 0.917 | 0.863 | 0.922 |
| $X_{(Z)}$, liq. conc. at take-off (exp) | 0.496 | 0.078 | 0.606 | 0.121 | 0.721 | 0.319 | 0.703 | 0.563 | 0.995 |
| $X_{(Z)}$, liq. conc. at take-off (cal) | 0.519 | 0.401 | 0.402 | 0.466 | 0.390 | 0.906 | 0.610 | 0.920 | 0.417 |

TABLE IV

EVALUATION OF THE EQUILIBRIUM CONSTANT AND THE TOTAL ION EXCHANGE CAPACITY OF THE RESIN

| Point No. (1) | P (2) | $C_o$ (3) | Final meq $Ca^{++}$ per ml. solu. (4) | X, (4)/(3) (5) | 1-X, 1-(5) (6) | $(1-X)^2$, $(6)^2$ (7) | $C_oP$ (2)·(3) (8) | $\frac{C_oP(1-X)^2}{X}$, (7)·(8)/(5) (9) | $\left[\frac{C_oP(1-X)^2}{X}\right]^{\frac{1}{2}}$ $(9)^{\frac{1}{2}}$ (10) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.137 | 0.3249 | 0.16500 | 0.5078 | 0.4922 | 0.2423 | 1.3441 | 0.6413 | 0.801 |
| 2 | 3.898 | 0.2367 | 0.08201 | 0.3465 | 0.6535 | 0.4270 | 0.9227 | 1.1371 | 1.066 |
| 3 | 3.574 | 0.1736 | 0.03460 | 0.1993 | 0.8007 | 0.6412 | 0.6204 | 1.9960 | 1.413 |
| 4 | 3.258 | 0.1432 | 0.01750 | 0.1222 | 0.8778 | 0.7705 | 0.4665 | 2.9414 | 1.715 |
| 5 | 2.908 | 0.1208 | 0.00806 | 0.0667 | 0.9333 | 0.8710 | 0.3513 | 4.5875 | 2.142 |
| 6 | 2.841 | 0.1157 | 0.00654 | 0.0565 | 0.9435 | 0.8900 | 0.3287 | 5.1778 | 2.276 |
| 7 | 2.646 | 0.1087 | 0.00440 | 0.0405 | 0.9595 | 0.9204 | 0.2876 | 6.5359 | 2.551 |
| 8 | 2.415 | 0.0944 | 0.00266 | 0.0282 | 0.9718 | 0.9445 | 0.2280 | 7.6364 | 2.764 |
| 9 | 2.046 | 0.0792 | 0.00122 | 0.0154 | 0.9846 | 0.9696 | 0.1620 | 10.1997 | 3.194 |
| 10 | 0.000 | - | - | - | - | - | - | extrapolated - | 5.57 |

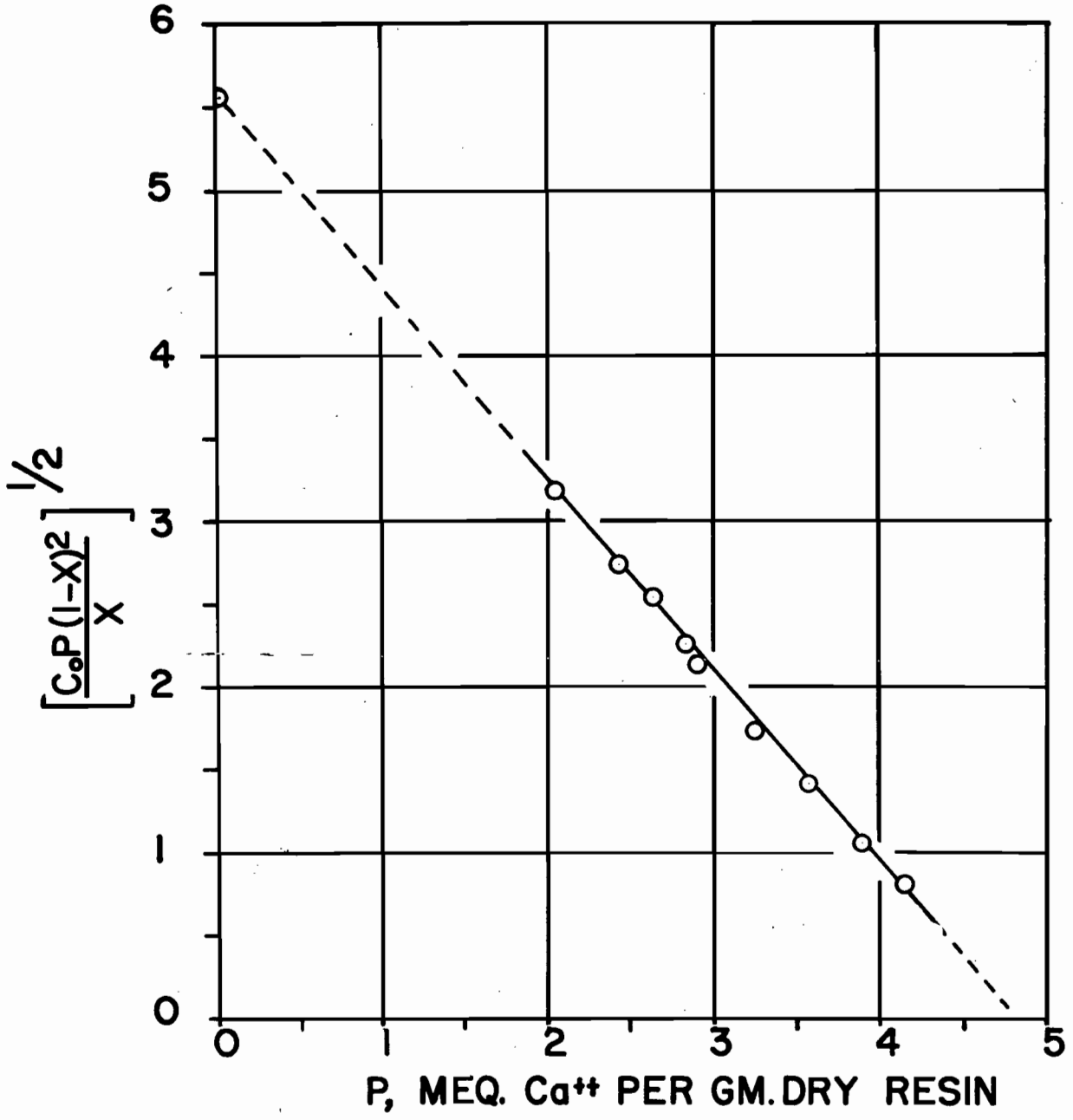


Figure 10. Curve for the Extrapolation of Data to Determine the Equilibrium Constant and Total Ionic Capacity of the Resin

$$a = 4.818 \text{ meq } (Ca^{++} + Na^{+}) \text{ per gram of dry resin}$$

The experimental equilibrium constant (K) and the total ion exchange capacity (a) were used to compute the data necessary for the establishment of a general correlation of the equilibrium liquid and resin concentrations as a function of the total ionic concentration of the liquid. Data for this general correlation are tabulated in the Appendix. The equilibrium curves obtained by interpolation of these data and experimental data for the stripping section, from Table III, were plotted on Figure 11 for the graphical determination of the number of theoretical equilibrium stages required for the separation. The number of theoretical equilibrium stages is tabulated in Table V. Results of the numerical integration of the rate equation, using data from Table III, are also tabulated in Table V. These theoretical and experimental data were used to compare the column performance in terms of theoretical versus actual HETS (height equivalent to a theoretical stage).

Exchange Section Isolation

The typical pressure profile data presented in Table II and Figure 9 were the result of one of the isolation zone studies. These data were taken in an attempt to prove that the isolation zones did not allow a liquid stream to

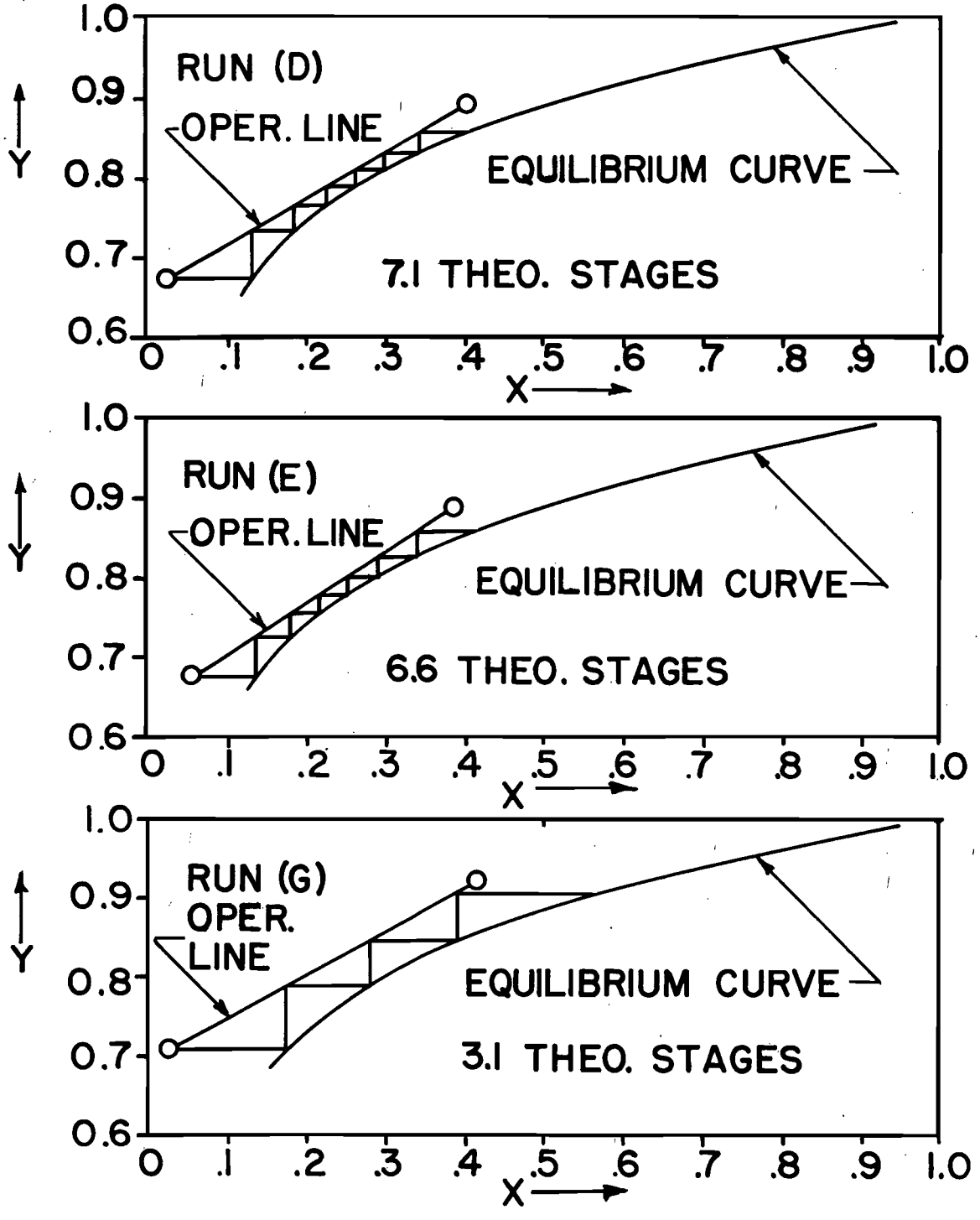


Figure 11. The Graphical Determination of the Number of Theoretical Equilibrium Stages from Experimental Data

TABLE V

THEORETICAL AND EXPERIMENTAL RESULTS COMPARED

| Run | No. of Equilibrium Stages (Graphically) | Resin Bed Height | | Stage Height | | % Bed Effectiveness |
|---|---|---|---|---|---|---|
| | | Actual (cm.) | Calc. (cm.) | Actual cm./stage | Theoret. cm./stage | |
| (1) | (2) | (3) | (4) | (3)/(2) (5) | (4)/(2) (6) | (7) |
| D, stripping | 7.1 | 74.930 | 7.125 | 10.564 | 1.004 | 9.51 |
| E, stripping | 6.6 | 74.930 | 6.549 | 11.353 | 0.992 | 8.74 |
| G, stripping | 3.1 | 74.930 | 2.167 | 24.171 | 0.699 | 2.89 |

flow between the two exchange sections. Similarly, the liquid test samples were analyzed for their chloride concentration in an effort to show that there was a chloride balance around the individual exchange sections. These data are tabulated in Table I. A third method used in studying the isolation zone involved the study of liquid flow patterns with colored feed solutions. Observations made during these tests indicated that zones of zero pressure gradient did serve to isolate the exchange sections.

Resin Attrition

Two types of resin rate control systems were used and their effect upon resin attrition rates was compared. The particle size distributions are shown in Figure 12 and Table VI for (a) the original resin supply, (b) the resin after 1000 hours of operation with the adjustable control valve, and (c) the resin after 100 hours of operation using the mechanical controller.

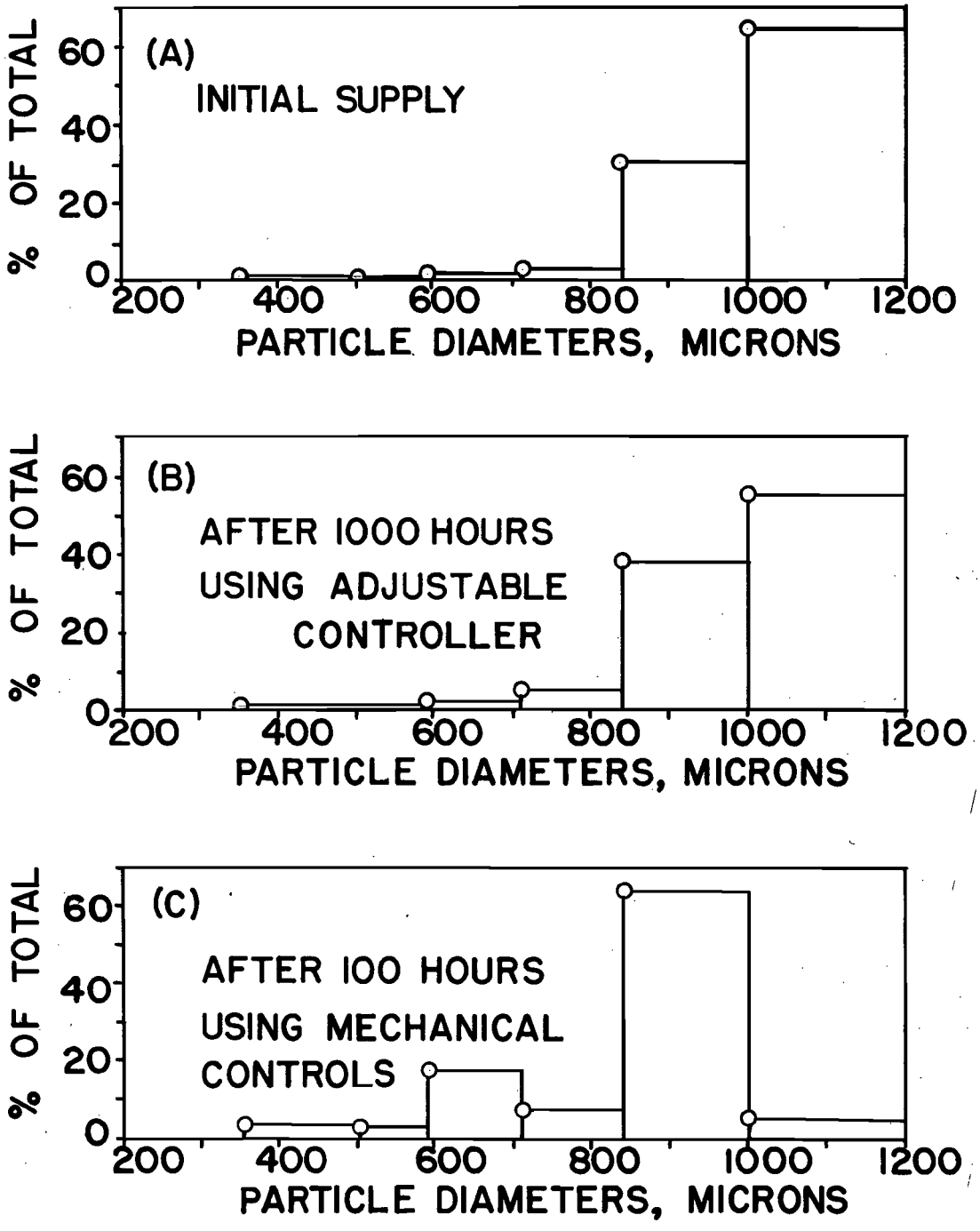


Figure 12. Resin Attrition Test Results

TABLE VI

RESIN ATTRITION TEST DATA

| Screen Size, microns | Supply Resin, % Resin on Screen | Resin after 1000 hrs. Use with Adj. Controller, % Resin on Screen | Resin after 100 hrs. Use with Mech. Controller, % Resin on Screen |
|---|---|---|---|
| 1000 | 64.7 | 54.8 | 5.7 |
| 840 | 30.3 | 38.1 | 63.8 |
| 710 | 2.8 | 4.9 | 7.0 |
| 590 | 1.5 | 1.7 | 17.7 |
| 500 | 0.3 | - | 2.4 |
| 350 | 0.4 | 0.5 | 3.4 |

# CHAPTER VI

# DISCUSSION OF RESULTS

## The Ion Exchange Column Design

The original design of a continuous countercurrent ion exchange for this investigation centered around two basic design features. These features were (a) hydraulically balanced isolation zones to separate the exchange sections and (b) a hydraulic ram to transfer momentum from the liquid to the resin by frictional drag. The experimental equipment embodying these design features essentially verified the soundness of the design insofar as the investigation was extended. Until December 1956 the experimental investigation had been centered about the hydraulic balance system with little extensive investigation having been made of the "hydraulic ram" feature. To a limited extent, however, the "hydraulic ram" feature was utilized in all of the runs, since the jet stream was pumped directly to the top of the column as either resin lift liquid or for pressure balance liquid. However, it was not possible to increase the liquid upflow in the column significantly above 100 gallons per hour per square foot even with a pressure drop of 50 psi across the cocurrent flow "hydraulic ram" section.

Several miscellaneous equipment tests were carried out in attempts to improve the column operability and the system control. The results of most of these tests proved informative in the negative sense only, i.e., they led to direct conclusions as to what was not applicable to the experimental system. Two examples were:

(1) The experiment with a mechanical resin rate controller showed that such devices greatly increase the resin attrition rate.

(2) The attempt to alter the take-off section design showed that the liquid flow area could not be reduced much without greatly increasing the pressure within the column.

The major development in the experimental design was the installation of two pneumatic control valves to control the isolation zones. Extensive test runs and static tests of the control instruments indicated that good control, within $\pm$ 0.2 inch of water, could be expected from the control instruments. This variation was small relative to many of the fluctuations caused by upsets in liquid feed rates, resin flow rates, concentration changes, etc.

## Experimental Ion Exchange

No attempt was made to analyze the experimental data for the loading section of the column because (a) the

resin sample was taken from the top of the resin bed and not at the top of the loading section and (b) the product sample from the loading zone included the recycle liquid. It was interesting to note in Table I that the resin picked up calcium from the time it left the bottom of the stripping section and the time it arrived at the top of the ion exchange bed for each run (item (7) and Item (9), Table I).

The sharp disagreement between theoretically calculated ion exchange bed heights and the actual experimental bed heights in Table V cast some doubt upon the theoretical calculation upon initial examination. However, Herrmann (4) suggested, for fixed ion exchange beds, that only a fraction of the total bed height is actually used for a particular ion exchange. It is his hypothesis that the actual ion exchange bed height may be quite small if the ion exchange is considered to occur in the following fashion: (a) there is a "dead" or completely loaded section of the resin bed in which no ions can be further exchanged, (b) there is an "active" section of the resin bed in which all of the ion exchange occurs, and (c) there is an "active" section of the resin bed which does not contact an "active" liquid (i.e., all the exchange ions have been removed). Application of this concept to continuous ion exchange indicates that the actual exchange bed height requirements may be of the order of magnitude of the theoretically calculated heights.

Consequently it is concluded that the experimental bed height requirements are high because of other factors, possibly channeling and nonuniform flow conditions within the exchange section.

The calculated stage heights, based upon the graphical theoretical stage concept, ranged from 0.3 to 1.0 foot for the actual experimental conditions. These stage heights were considerably lower than the 2.7 feet per stage reported for the stripping section in the literature (3). This discrepancy was difficult to explain since the other investigators used a different chemical system in addition to a differently designed continuous ion exchanger.

The values of the equilibrium constant and the total exchange capacity of the resin are both higher than recently reported values (2). Comparison of experimental resin capacities obtained in this investigation with the total resin exchange capacity obtained by Anderson (2) and from Young's (21) data indicated that (a) Anderson's value was low and (b) the value obtained from Young's data was probably slightly high. At the present it appears that the value from Young's data is the best available.

## Exchange Section Isolation

The constant dynamic pressure throughout the isolation

zones (See Figure 9 and Table II) indicated that there was no hydraulic driving force present for causing the flow of liquid in these zones. The visual evidence afforded by colored solutions fed into the column during operation verified the pressure profile data. A chloride analysis was made on each of the liquid streams moving through the column to verify, by mass balance considerations, the isolation of the two exchange sections. The chloride analysis data (see Table I) indicated that little, if any, of the feed streams actually crossed through the isolation zone. This isolation feature is necessary for the satisfactory performance of the continuous ion exchange column.

## Resin Attrition

On the basis of a visual inspection after only 100 hours of operation the attrition caused by the mechanically driven resin rate controller appeared to be large enough to warrant the determination of the resin particle size distribution and hence show the extent of resin attrition. For control purposes similar particle size distributions were determined for the supply resin and the resin after 1000 hours operation with the adjustable control valve. The screening tests verified the visual observation. After approximately 1000 hours of operation with the adjustable

control valve the percentage fines, i.e., particles of diameter less than 840 microns, had increased from 5.0 per cent to 7.1 per cent, approximately 0.02 per cent increase per pass through the column. After only 100 hours of operation with the mechanical controller there had been an increase in the percentage fines from 5.0 per cent to 30.5 per cent, approximately 2 per cent per pass. The rate of attrition with the mechanical controller is excessive for commercial applications. However, the rate of attrition with the adjustable control valve is comparable to that reported for Dorr's Hydro-Softener, a commercial continuous water softening unit.

# CHAPTER VII

## CONCLUSIONS AND RECOMMENDATIONS

The conclusions made from this study on the performance of a continuous countercurrent ion exchanger are:

(1) The numerical integration of Anderson's (2) rate equation gives a good first estimate of the bed height requirements for a given exchange.

(2) The experimental stage heights evaluated for the stripping section in this investigation ranged from 0.3 to 1.0 foot. These values are significantly smaller than values reported by other investigators.

(3) The pneumatically controlled isolation zones are effective in separating the exchange sections.

(4) From four to five resin cycles are required to approach steady state operating conditions because of the time required for the resin to reach equilibrium with the various liquid streams.

(5) The hydraulic ram concept has not been effectively utilized in this investigation.

(6) The elimination of all contact between the resin and moving valves within the column is necessary to minimize the rate of resin attrition.

Recommendations for further study are:

(1) Develop experimental methods of resolving the

observed discrepancy between actual and calculated ion exchange bed heights into terms experimentally evaluated.

(2) For the further determinations of performance characteristics modify the present equipment to use: (a) constant (known) composition resin feed, (b) constant (known) composition liquid feed, and (c) distilled water jet and balance system. This would enable the investigator to reach steady state in much less time than closed-system operation allows.

(3) Consider the possiblity of cocurrently regenerating the resin in a jet lift stream since experimental data indicated that significant ion exchange can be carried out in this manner.

(4) Obtain basic information on the frictional characteristics of the ion exchange resins in order to apply the "hydraulic ram" principle for overcoming the fluidization velocity limit on the countercurrent operation.

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# APPENDIX

## SAMPLE CALCULATIONS (A)

For most of the investigation a wash stream was used in conjunction with the regeneration stream. This required that (a) an average ionic concentration, (b) an average calcium hardness, and (c) a total liquid feed rate to the stripping section be calculated. The following is a sample calculation for Run E of the original data in Table I and Table III.

Assume:

The total ionic concentrations in the sodium feed solution equal to the sum of the calcium and sodium ion concentrations of the stream.

$$(C_o)_{Brine} = (C_o)_{Na} + (C_o)_{Ca}$$

where: $(C_o)_{Brine}$ = the total ionic strength of the sodium feed solution

$(C_o)_{Na}$ = the sodium ionic concentration in the sodium feed solution

$(C_o)_{Ca}$ = the calcium ionic concentration in the sodium feed solution

$$(C_o)_{Brine} = [\text{Item (4), Table I}] + [\text{Item (3), Table I}] \cdot [\text{conversion factor}]$$

$$= 0.1885 + (215)(2 \times 10^{-5}) = 0.1928 \ \frac{\text{meq} \cdot (Ca^{++} + Na^{+})}{\text{ml. solution}}$$

The feed rates are obtained from Item (12) and Item (13), Table I.

$L_{Brine}$ = 235 ml./min. = sodium feed rate

$L_{Wash}$ = 39.5 ml./min. = wash feed rate

$L_{Total} = L_{Brine} + L_{Wash}$

$= 235 + 39.5 = 274.5$ ml./min., which is listed as L under Item 5, Table III

$(C_o)_{Wash} = (C_o)$ product $= (C_o)_{Ca^{++}}$ feed = Item (2), Table I $\cdot$(conversion factor)

= the total ionic concentration of the wash stream

$= (8155)(2 \times 10^{-5}) = 0.1631$ meq/ml.

$(C_o)_{Avg}$ = the average value of the total ionic concentration in the feed to the stripping section

$$= \frac{(C_o)_{Brine} \cdot (L_{Brine}) + (C_o)_{Wash} \cdot (L_{Wash})}{L_{Total}}$$

$$= \frac{(0.1928) \cdot (235) + (0.1631) \cdot (39.5)}{274.5}$$

$= 0.1885 \dfrac{\text{meq}(Ca^{++} + Na^{+})}{\text{ml. feed}}$, which is listed as $C_o$ under Item (5), Table III

hf = average hardness of feed stream

$$= \frac{(\text{hardness of sodium feed}) \cdot (L_{Brine}) + (\text{hardness of product}) \cdot (L_{Wash})}{L_{Total}}$$

$$= \frac{(0.0043)\cdot(235) + (0.0502)\cdot(39.5)}{274.5}$$

$$= 0.0112 \ \frac{\text{meq } Ca^{++}}{\text{ml. solution}}$$

$$X_o = \frac{hf}{(C_o)_{Avg}} = \frac{0.0112}{0.1885} = 0.0594,$$ which is listed as $X_o$ under Item (5), Table III

The remaining items listed in Table III are obtained as follows for Column (5):

<u>Item</u>

$R = \frac{16.1 \text{ gm. dry resin}}{\text{min.}}$, Item (10, Table I

$a = 4.818 \ \frac{\text{meq } (Ca^{++} + Na^{+})}{\text{gm. dry resin}}$, from Table IV and Figure 10

$\rho_s = 1.3177 \ \frac{\text{gm. resin}}{\text{ml. resin}}$, data by Anderson (2)

$\rho_L = 1.000 \ \frac{\text{gm. liquid}}{\text{ml. liquid}}$, density assumed to be approximately that of water

$\alpha = 0.500$, data by Straker (21)

$Y_{(o)} = 0.677, \ \frac{\text{Item (9), Table I}}{a}$

$Y_{(Z)} = 0.888, \ \frac{\text{Item (8), Table I}}{a}$

$X_{(Z)}$, exp. $= 0.721, \ \frac{\text{Item (6), Table I}}{(C_o)_{Avg}}$

$X_{(Z)}$, calc. $= 0.390$, calculated by equation (5) and the preceding data

The items listed in Table III for the loading zones are obtained similarly, except that the corrections for the wash section are not required.

For example, for Column (6), Table III:

<u>Item</u>

R, a, $\rho_S$, $\rho_L$, and $\alpha$ are the same as in Column (5), Table III

$L = 385 \ \frac{ml.}{min.}$, Item 11, Table I

$C_o = 0.1631 \text{ meq } \frac{Ca^{++} + Na^{+}}{ml.}$, Item (2), Table I $\cdot$ (conversion factor)

$= (8155) \cdot (2 \times 10^{-5})$

$Y_o = 0.888$, $\frac{\text{Item 8, Table I}}{a}$

$X_o = 1$, $\frac{\text{Item (2), Table I}}{\text{Item (2), Table I}}$, since calcium ions alone are present

$Y_{(Z)} = 0.814$, $\frac{\text{Item (7), Table I}}{a}$

$X_{(Z)}\text{exp.} = 0.319$, $\frac{\text{Item (5), Table I}}{\text{Item (2), Table I}}$

$X_{(Z)}\text{calc.} = 0.906$, calculated by equation (5) and the preceding data

## SAMPLE CALCULATIONS (B)

The equilibrium constant in equation (2) must be evaluated from experimental data. The following outline is a proposed method of making this evaluation.

Let: $P$ = meq $Ca^{++}$ per gram dry resin

Thus:

$$[Ca^{++}] = C_o X$$

$$[Na\cdot(Resin)] = a(1-Y)$$

$$[Na^{+}] = C_o(1-Y)$$

$$[Ca\cdot(Resin)_2] = ay = P$$

and equation (2) becomes

$$K = \frac{[C_o(1-X)]^2\cdot(aY)}{(C_o X)\cdot[a(1-Y)]^2} = \frac{C_o}{a}\cdot\frac{(1-X)^2}{(1-Y)^2}\cdot\frac{Y}{X} \qquad (2a)$$

$$Ka(1-P/a)^2 = \frac{C_oP}{a}\cdot\frac{(1-X)^2}{X}$$

$$K^{\frac{1}{2}}a(1-P/a) = \left[\frac{C_oP(1-X)^2}{X}\right]^{\frac{1}{2}} = K^{\frac{1}{2}}a - K^{\frac{1}{2}}P$$

Therefore, a plot of $\left[\frac{C_oP(1-X)^2}{X}\right]^{\frac{1}{2}}$ versus P should be linear with a slope of $(-K^{\frac{1}{2}})$ and an intercept at P = o of $(aK^{\frac{1}{2}})$.

In evaluating (K) and (a) for the experimental system the preceding method was used. The experimental data and calculations are tabulated in Table IV. Considering the calculations for point (1), the items are:

Item

(1) = point number

(2) $= 4.137 \frac{\text{meq } Ca^{++}}{\text{gm. resin}} = P$, experimental data

(3) $= 0.3249 \frac{\text{meq } Ca^{++}}{\text{ml. solu.}} = C_o$, experimental data

(4) $= 0.16500 \frac{\text{meq } Ca^{++}}{\text{ml. solu.}}$, final = experimental data

(5) $= 0.5078 = X =$ (4) divided by (3)

(6) $= 0.4922 = 1-X = 1 - (5)$

(7) $= 0.2423 = (1-X)^2 = (6)^2$

(8) $= 1.3441 = C_oP = (2)\cdot(3)$

(9) $= 0.6413 = \frac{C_oP(1-X)^2}{X} = \frac{(7)\cdot(8)}{(5)}$

(10) $= 0.801 = \left[\frac{C_oP(1-X)^2}{X}\right]^{\frac{1}{2}} = (9)^{\frac{1}{2}}$

Item (10) for point 10 is extrapolated graphically as shown on Figure 10 to obtain (a).

Therefore:

$$K = \left[- \text{slope}\right]^2$$

$$= \left[- \frac{5.57-0}{0-4.83}\right]^2 = \left[-1.156\right]^2 = 1.336$$

and

$$a = \frac{\text{intercept}}{K^{\frac{1}{2}}} = \frac{5.57}{1.156} = 4.818 \frac{\text{meq } (Ca^{++} + Na^{+})}{\text{gm. resin}}$$

## SAMPLE CALCULATIONS (C)

Sample calculations for Run D, stripping, Table V follow.

Item

(1) = D, stripping, experiment identification

(2) = 7.1 theoretical stages, obtained graphically from Figure 11

(3) = 74.930 cm., measured value

(4) = 7.125 cm., obtained by numerical integration of rate equation - See Table IX, Appendix D, page 76

(5) = 10.564 = (3) divided by (2)

(6) = 1.004 = (4) divided by (2)

(7) = 9.51% = $\frac{(6)}{(5)} \times 100$

## SAMPLE CALCULATIONS (D)

The equation (2a) must be evaluated for various values of $C_o$ in order to establish an equilibrium relationship graphically.

$$K = \frac{C_o}{a} \cdot \frac{(1-X)^2 Y}{(1-Y)^2 X} \tag{2a}$$

Definition of $\phi$, $\beta$, $\gamma$ according to:

$$(1-X)^2 = \phi \tag{6}$$

$$X = \beta \tag{7}$$

$$\frac{a}{C_o} K = \gamma \tag{8}$$

and solution for Y gives

$$Y = \frac{2\gamma\beta + \phi}{2\gamma\beta} \pm \left[\left(\frac{2\gamma\beta + \phi}{2\gamma\beta}\right)^2 - 1\right]^{\frac{1}{2}}$$

For this case, the only root of use is

$$Y = \frac{2\gamma\beta + \phi}{2\gamma\beta} - \left[\left(\frac{2\gamma\beta + \phi}{2\gamma\beta}\right)^2 - 1\right]^{\frac{1}{2}}$$

An equilibrium relationship can be easily established for any $C_o$ using this relationship. Table VII shows the calculation for this relationship. In explanation of this table, the items for the value of $X = 0.05$ are as follows:

TABLE VII

CALCULATION OF THE EQUILIBRIUM CURVE, $C_o$ = 0.190 meq/gm.

| $X$, $\beta$ (1) | $(1-X)^2$, $\phi$, $1-(1)^2$ (2) | $2\gamma\beta$, 67.765(1) (3) | $2\gamma\beta+\phi$ (3) (2) (4) | $\frac{2\gamma\beta+\phi}{2\gamma\beta}$, (4)/(3) (5) | $\left(\frac{2\gamma\beta+\phi}{2\gamma\beta}\right)^2$, $(5)^2$ (6) | $\left(\frac{2\gamma\beta+\phi}{2\gamma\beta}\right)^2-1$, (6)-1 (7) | $\left[\left(\frac{2\gamma\beta+\phi}{2\gamma\beta}\right)^2-1\right]^{\frac{1}{2}}$, $(7)^{\frac{1}{2}}$ (8) | $Y$, (5)-(8) (9) |
|---|---|---|---|---|---|---|---|---|
| 0.05 | 0.9025 | 3.3878 | 4.2903 | 1.266397 | 1.60376 | 0.60378 | 0.7769 | 0.4895 |
| 0.10 | 0.8100 | 6.7756 | 7.5856 | 1.119547 | 1.25339 | 0.25339 | 0.5034 | 0.6162 |
| 0.20 | 0.6400 | 13.5512 | 14.1912 | 1.047228 | 1.09669 | 0.09669 | 0.3109 | 0.7363 |
| 0.30 | 0.4900 | 20.3268 | 20.8168 | 1.024106 | 1.04879 | 0.04879 | 0.2208 | 0.8033 |
| 0.40 | 0.3600 | 27.1024 | 27.4624 | 1.013283 | 1.02674 | 0.02674 | 0.1637 | 0.8495 |
| 0.50 | 0.2500 | 33.8780 | 34.1280 | 1.007380 | 1.01481 | 0.01481 | 0.1217 | 0.8856 |
| 0.60 | 0.1600 | 40.6536 | 40.8136 | 1.003936 | 1.00789 | 0.00789 | 0.0888 | 0.9151 |
| 0.70 | 0.0900 | 47.4292 | 47.5192 | 1.001898 | 1.00380 | 0.00380 | 0.0616 | 0.9303 |
| 0.80 | 0.0400 | 54.2048 | 54.2448 | 1.000738 | 1.00148 | 0.00148 | 0.0384 | 0.9623 |
| 0.90 | 0.0100 | 60.9804 | 60.9904 | 1.000164 | 1.00033 | 0.00033 | 0.0181 | 0.9821 |
| 0.95 | 0.0025 | 64.3684 | 64.3707 | 1.000039 | 1.00008 | 0.00008 | 0.0088 | 0.9912 |

Item

(1) = 0.05 = X or $\beta$

(2) = 0.9025 = $(1-X)^2$ or $\phi$

(3) = 3.3878 = $2\gamma\beta$ = (constant) • (1)

(4) = 4.2903 = $2\gamma\beta + \phi$ = (3) + (2)

(5) = 1.266397 = $\left(\frac{2\gamma\beta + \phi}{2\gamma\beta}\right)$ = (4) divided by (3)

(6) = 1.60376 = $\left(\frac{2\gamma\beta + \phi}{2\gamma\beta}\right)^2$ = $(5)^2$

(7) = 0.60376 = $\left(\frac{2\gamma\beta + \phi}{2\gamma\beta}\right)^2 - 1$ = (6) - 1

(8) = 0.7769 = $\left[\left(\frac{2\gamma\beta + \phi}{2\gamma\beta}\right)^2 - 1\right]^{\frac{1}{2}}$ = $(7)^{\frac{1}{2}}$

(9) = 0.4895 = Y = (5) - (8)

A summary of five such tabulations is given in Table VIII.

The numerical integration involved in estimating the exchange bed height is carried out in Table IX for Run D. The increments of Y were made equal and even in number so that Simpson's rule for approximating plane area could be used. Substitution of the numerical values from Table III into equation (4) gives the following.

$$Z = -1.7869 \int_{(0.6920)}^{(0.8900)} \left\{ \frac{\left[(0.22445)(1-Y)^2 + (0.012435)(1-X)Y + (0.966136)X(1-Y) + (0.013338)(1-X)^2\right]}{\left[(0.85905)X(1-Y)^2 - (0.023796)(1-X)^2 Y\right]} \right\} dY \quad (9)$$

TABLE VIII

TABULATIONS OF X VERSUS Y AS A FUNCTION OF $C_o$

| X | Y | | | | |
|---|---|---|---|---|---|
| | $C_o$=0.1260 meq/ml. | $C_o$=0.1385 meq/ml. | $C_o$=0.1631 meq/ml. | $C_o$=0.1770 meq/ml. | $C_o$=0.140 meq/ml. |
| 0.05 | 0.5566 | 0.5367 | 0.5148 | 0.5013 | 0.4895 |
| 0.10 | 0.6733 | 0.6606 | 0.6281 | 0.6265 | 0.6162 |
| 0.20 | 0.7791 | 0.7698 | 0.7529 | 0.7432 | 0.7363 |
| 0.30 | 0.8355 | 0.8293 | 0.8162 | 0.8094 | 0.8033 |
| 0.40 | 0.8759 | 0.8702 | 0.8599 | 0.8546 | 0.8495 |
| 0.50 | 0.9058 | 0.9016 | 0.8936 | 0.8895 | 0.9956 |
| 0.60 | 0.9303 | 0.9271 | 0.9211 | 0.9180 | 0.9151 |
| 0.70 | 0.9511 | 0.9488 | 0.9445 | 0.9425 | 0.9303 |
| 0.80 | 0.9692 | 0.9677 | 0.9650 | 0.9636 | 0.9623 |
| 0.90 | 0.9852 | 0.9846 | 0.9833 | 0.9827 | 0.9821 |
| 0.95 | 0.9928 | 0.9924 | 0.9918 | 0.9915 | 0.9912 |

TABLE IX

NUMERICAL INTEGRATION OF RATE EQUATION FOR DETERMINING THEORETICAL BED HEIGHT - RUN D, STRIPPING SECTION

| Y (1) | (1-Y) 1-(1) (2) | $(1-Y)^2$ $(2)^2$ (3) | X (4) | (1-X) 1-(4) (5) | $(1-X)^2$ $(5)^2$ (6) | (1-Y)X (2)•(4) (7) | $(1-Y)^2X$ (3)•(4) (8) | (1-X)Y (1)•(5) (9) | $(1-X)^2Y$ (1)•(6) (10) | $-f(Y_i)$ (11) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.6720 | 0.3280 | 0.10758 | 0.0247 | 0.9753 | 0.9512 | 0.00810 | 0.002657 | 0.6554 | 0.6392 | 4.08815 |
| 0.7156 | 0.2844 | 0.08088 | 0.1000 | 0.9000 | 0.8100 | 0.02844 | 0.008088 | 0.6440 | 0.6796 | 9.41971 |
| 0.7592 | 0.2408 | 0.05798 | 0.1752 | 0.8248 | 0.6803 | 0.04219 | 0.010158 | 0.6262 | 0.5165 | 19.82955 |
| 0.8028 | 0.1972 | 0.03889 | 0.2505 | 0.7495 | 0.5918 | 0.04940 | 0.009742 | 0.6017 | 0.4510 | 30.22183 |
| 0.8464 | 0.1536 | 0.02359 | 0.3357 | 0.6643 | 0.3313 | 0.05156 | 0.007919 | 0.5623 | 0.3735 | 32.61666 |
| 0.8900 | 0.1100 | 0.01210 | 0.4010 | 0.5990 | 0.3588 | 0.04411 | 0.004852 | 0.5331 | 0.3193 | 16.54641 |

$$= -1.7869 \int_{0.6920}^{0.8900} f(Y)dY$$

Since Re = 0.47036 and $k_R$ = 0.3552

$k_L$ = 19.2104

Equation (5) reduces to (10) upon substituting numerical values.

$$X = 1.7258\ Y - 1.1350 \qquad (10)$$

These two equations, (9) and (10), give the numerical values of

$$\left(\frac{dZ}{dY}\right)_{Y=Y_i} = C\ f(Y_i)$$

Therefore, the tabulation in Table IX gives a numerical value of Z when Simpson's Rule is applied.

For Y = 0.6720, the items in Table IX are as follows.

<u>Item</u>

(1) = 0.6720 = Y

(2) = 0.3280 = 1 - (1) = (1-Y)

(3) = 0.10758 = $(2)^2$ = $(1-Y)^2$

(4) = 0.0247 = (constant)•(1) - (constant) = X

<u>Item</u>

(5) = 0.9753 = 1 - (4) = $(1-X)$

(6) = 0.95121 = $(5)^2$ = $(1-X)^2$

(7) = 0.00810 = (2)•(4) = $(1-Y)X$

(8) = 0.002657 = (3)•(4) = $(1-Y)^2X$

(9) = 0.65540 = (1)•(5) = $(1-X)Y$

(10) = 0.63921 = (1)•(6) = $(1-X)^2Y$

(11) = 4.08815 = - f(Y), obtained by substituting Items (1) through (10) into equation (9)

$$Z = -1.7869 \int_{0.6920}^{0.8900} f(Y_i)\, dY$$

$$= -1.7869 \left[ \frac{0.0436}{3} \left\{ 4.08815 + 16.54641 + 4(39.64154) + 2(52.44621) \right\} \right]$$

$$= 7.125 \text{ cm.}$$

# NOMENCLATURE

# NOMENCLATURE

$a$ = total ion capacity of resin

$\alpha$ = void fraction of resin

$\beta$ = symbol for simplification = X

Ca = calcium ion concentration in liquid

$Ca \cdot (Resin)_2$ = calcium form of resin

$C_o$ = total ionic concentration of liquid

D = diameter of column

f(Y) = a function of Y simplification symbol

$\gamma$ = symbol for simplification = $\frac{a}{C_o} K$

$h_f$ = calcium hardness or ionic concentration

K = equilibrium constant

$k_L$ = liquid film diffusion constant

$k_R$ = solid phase diffusion constant

L = liquid flow rate

Na = sodium ion concentration in liquid

$Na \cdot (Resin)$ = sodium form of resin

P = calcium content of resin

$\phi$ = symbol for simplification = $(1-X)^2$

R = resin flow rate

Re = Reynolds number

$\rho_L$ = liquid density

$\rho_S$ = resin density

X = calcium ion concentration of liquid divided by $C_o$

Y = P divided by a

Z = ion exchange bed height