UNITED STATES ATOMIC ENERGY COMMISSION

AECU-2737

CONTINUOUS COUNTERCURRENT ION EXCHANGE
WITH TRACE COMPONENTS

Technical Report Number 5

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June 24, 1953

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Subject Category, CHEMISTRY

Work performed under Contract No. AT(11-1)-110 -

Project Agreement No. 1, Report No. 30.

Approved: L. M. Richards, Chairman, Department of Chemistry

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PREFACE

During the course of the countercurrent ion exchange program carried out by Stanford Research Institute for the Atomic Energy Commission, an extensive study was made of the moving bed type of resin-solution contactor. This work is described in some detail in the attached report, which covers the process theory, design, operation, and evaluation of this equipment. Some of the preliminary information for the study was reported in Technical Report No. II (May 1, 1952) and is repeated here for continuity.

The report was presented, with the Atomic Energy Commission's approval, at the Cleveland Meeting of the American Institute of Chemical Engineers, December 10, 1952, and was submitted to *Chemical Engineering Progress* for publication.

The major conclusions which can be drawn from the present work are:

1. The moving bed equipment and associated resin valves, described in the report, provide satisfactory countercurrent contact between ion exchange resins and solutions.
2. The modified Colburn equation, in conjunction with the proposed mass transfer correlation, can be used to predict the operation of this unit under trace conditions.

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AECU - 2737

June 24, 1953

Technical Report No. V

**CONTINUOUS COUNTERCURRENT ION EXCHANGE
WITH TRACE COMPONENTS**

ABSTRACT

A design theory was developed for countercurrent ion exchange, under trace conditions, based on kinetic and equilibrium considerations. Equipment was designed to provide continuous countercurrent contact between a moving bed of ion exchange resin and the solutions to be treated. This equipment was evaluated experimentally by the separation of trace ionic components in a feed solution. Contact efficiency was improved with a vibrated screen assembly which was immersed in the moving bed and which produced continual reorientation of the resin particles.

The data were correlated in an equation which related the height of a transfer unit with operating variables and the characteristics of the resin-ion system. The results are given in graphical and tabular form.

INTRODUCTION

Ion exchange separations are normally conducted batchwise by saturating and eluting a fixed bed of resin. This process has the usual disadvantages of a cyclic operation, such as variable effluent concentrations, complex operability, and unfavorable ratio of productive time to unproductive time. In an attempt to overcome the shortcomings of the cyclic process, Stanford Research Institute has undertaken an investigation of continuous ion separation by means of countercurrent contact between resin and solution.

The initial objectives of the investigation were to determine whether continuous countercurrent separation of ions was feasible and whether the theoretical considerations derived to describe such exchange were valid. Once these questions were answered affirmatively, the investigation was directed toward development of the most suitable equipment for continuous countercurrent ion exchange. The principal requirements for this equipment were that it be easily operated and that it make economical use of resin, i.e. provide good contact between resin and solution phases and thus promote rapid ion exchange.

FUNDAMENTAL THEORY

General The separation of ions by ion exchange operates by the transfer of ions between a solid resin phase and a fluid solution phase. The differences in affinities of the resin for the ions to be separated, say ions A and B, leads to an enrichment of the least strongly held, say A, in the fluid phase and of the other, B, in the solid phase. In countercurrent operation, the phases move in opposing directions, and thus the majority of the separated components A and B are carried to opposite ends of the contacting apparatus. In order that both product streams be fluid, it is necessary that ion B in the resin phase be re-transferred to a solution. This requires a third component, say ion G, to elute or remove B from the effluent resin.

Thus in the simplest ion exchange separation system, three components (ions A, B, and G) and two phases (resin and solution) are involved. The only design theory that is presently available to handle this complex

system is the trace theory. As defined by Vermeulen and Hiester (11), the exchange of a trace component takes place when a resin saturated with a gross component (G) contacts a solution containing a very small concentration of component A (and/or B) in the presence of a very large concentration of component G. This leads to a linear relationship between the concentration of component A on the resin and its concentration in solution at equilibrium. The exchange reaction for this case may best be represented as:

with the equilibrium constant, K_{AG} , for this reaction being defined as

$$K_{AG} = \frac{(A \cdot \text{resin}) (G^+)}{(A^+) (G \cdot \text{resin})} \quad (2)$$

Similar relations can be obtained for trace component B.

Mechanism and Rate of Ionic Transfer In the exchange adsorption denoted by the chemical reaction, Equation (1), a sequence of ionic processes is involved in order to replace ion G on the resin by ion A in the fluid. These processes may be grouped into the following three steps:

1. External counter diffusion of A and G through the fluid film surrounding the resin particle.
2. Exchange or "surface reaction" of A and G. This step normally takes place so rapidly that it does not affect the rate of exchange (1).
3. Internal counter diffusion of A and G through the homogeneous gel structure of the resin particle.

The effective rate of exchange will evidently be controlled mainly by the step that exerts the largest resistance to transfer and is therefore inherently the slowest. Obviously, the rate equation is simplified by neglecting all but this rate-controlling resistance, or by combining all of the steps into one effective step with a single apparent rate.

Actually, the rate relation for each of these conditions has the same general mathematical form, differing only in the specific definition of the rate constant, κ_A . The form of the generalized equation, originally

published in reference (11), has been modified to present the resin and solution concentrations as equivalent fractions rather than as normal concentrations directly. In this form the equation is more closely analogous to those derived for other diffusional rate processes:

$$\left[\frac{d(y_A)}{d\tau} \right]_{\text{particle}} = \kappa_A \frac{c_E f_E}{Q \rho_p (1-f_E)} \left(x_A - \frac{y_A}{M_A} \right) \quad (3)$$

where y_A is the equivalent fraction of component A on the resin with respect to Q, the total ionic capacity of the resin per unit weight on an oven-dried basis; τ is the residence time of the resin particle within the contacting zone; κ_A is a generalized transfer coefficient for A exchanging with G, in reciprocal time units; f_E is the void fraction of the total volume of the contacting zone and is equivalent to the fraction of the total volume occupied by solution; conversely, $(1-f_E)$ is the fraction of the total volume occupied by resin in the contacting zone; ρ_p is the density of the resin expressed as oven-dried weight per unit volume of swelled resin; x_A is the equivalent fraction of component A in solution with respect to the total ionic concentration of the solution, c_E ; M_A is the slope of the equilibrium line on an $y-x$ plot as defined below.

Equation (3) may be simplified by the use of the dimensionless distribution ratio or partition coefficient, D , as defined in reference (11).

$$D_A = \frac{M_A Q \rho_p (1-f_E)}{c_E f_E} \quad (4)$$

The modified Equation (3) then becomes

$$\left[\frac{d(y_A)}{d\tau} \right]_{\text{particle}} = \kappa_A \frac{M_A}{D_A} \left(x_A - \frac{y_A}{M_A} \right) \quad (5)$$

In terms of the individual mass transfer coefficients, the corresponding equations are

$$\left[\frac{d(y_A)}{d\tau} \right]_{\text{particle}} = (k_A)_F a_F \frac{M_A}{D_A} \left[x_A - (x_A)_i \right] \quad (6)$$

for fluid film diffusion, and

$$\left[\frac{d(y_A)}{d\tau} \right]_{\text{particle}} = (k_A)_p a_p \left[(y_A)_i - y_A \right] \quad (7)$$

for particle film diffusion, where $(k_A)_F$ and $(k_A)_p$ are the mass transfer coefficients, in velocity units, based on fluid and particle diffusion respectively; a_F and a_p are the transfer areas per unit volume of contacting zone for diffusion through the fluid and particle respectively; and the subscript i denotes the interface. The term M_A/D_A , which is the ratio of the total equivalent capacities in the fluid and in the solid phases, is required in Equations (5) and (6) to put them on a consistent basis, i.e. in terms of the particle. The relations between the generalized overall rate constant κ_A , and the individual transfer coefficients are easily obtained from Equations (5) and (6) or (7), since at the interface,

$$\left[\frac{d(y_A)}{d\tau} \right]_{\text{particle}} = \frac{x_A - y_A/M_A}{\frac{D_A}{M_A} \cdot \frac{1}{\kappa_A}} = \frac{x_A - y_A^*/M_A}{\frac{D_A}{M_A} \cdot \frac{1}{(k_A)_F a_F}} = \frac{y_A^*/M_A - y_A/M_A}{\frac{1}{M_A} \cdot \frac{1}{(k_A)_p a_p}} = \frac{x_A - y_A/M_A}{\frac{D_A}{M_A} \cdot \frac{1}{(k_A)_F a_F} + \frac{1}{M_A} \cdot \frac{1}{(k_A)_p a_p}} \quad (8)$$

and thus

$$\frac{1}{\kappa_A} = \frac{1}{(k_A)_F a_F} + \frac{1}{D_A} \cdot \frac{1}{(k_A)_p a_p} \quad (9)$$

Equilibrium Relations In terms of equivalent fractions, the mass action equilibrium relation, Equation (2) takes the form:

$$K_{AG} = \frac{y_A x_G}{x_A y_G} \quad (10)$$

where $\frac{x_G}{y_G}$ is a constant under trace conditions.

This leads to the equilibrium relations

$$y_A^* = M_A x_A \quad (11)$$

or

$$x_A^* = \frac{y_A}{M_A} \quad (12)$$

where $M_A = \frac{K_{AG} Y_G}{x_G}$. These are Henry's law (or linear isotherm) forms, since M_A , the slope of the equilibrium line or the distribution coefficient, is a constant for a given trace exchange system.

It should be noted that this form is equivalent to that obtained by setting the rate Equation (5) equal to zero, i.e., assuming that the rate of exchange is zero or that the system is in equilibrium.

DESIGN CONSIDERATIONS

Countercurrent Operation In continuous countercurrent practice, a stream of ion exchange resin of constant composition, $(y_A)_{entr}$ is fed into the top of a countercurrent contacting section at a constant volumetric rate of flow, R_p , and is removed from the bottom of the section at the same rate. Simultaneously, a solution stream of constant composition, $(x_A)_{entr}$ is introduced into the bottom of the section at a constant volumetric rate of flow, R_F , and passes up through the column countercurrent to the resin and leaves the top at this same rate. Diagrammatically this is shown in Figure 1 for a column having a height, h , and cross sectional area, S . Here, $(x_A)_{exit}$ is the composition of the effluent solution after having passed through the column, which has a total inventory of resin, $hS(1-f_E)$; and $(y_A)_{exit}$ is the composition of the effluent resin. The residence time for a resin particle in the column is the ratio of the total resin inventory to the resin flow rate.

There are two methods for predicting these exit compositions, the first, or dynamic method, based on the rate Equation (5) where τ is the statistical residence time of a resin particle in the countercurrent section, and the second based on the assumption that the section is made up of a finite number of equilibrium contacts (similar to plates in a distillation column).

Dynamic Method For the dynamic approach, a conservation equation and boundary conditions are needed in addition to the rate equation. At the steady state, i.e., no accumulation or depletion of A at any crosssection in the column, the following differential material balance equation applies:

$$R_p \rho_p Q \frac{d(y_A)}{d\tau} = R_F C_A \frac{d(x_A)}{d\tau} \quad (13)$$

This equation, in conjunction with the generalized rate Equation (5) and the boundaries indicated in Figure 1, is now sufficient to define the behavior of this system. Colburn (3) has given the solution for a set of analogous equations and, in the present case, the result is

$$\frac{E_A}{1-E_A} \ln \frac{E_A(1-\gamma_A)}{E_A-\gamma_A} = \frac{\kappa_A h s f_E}{R_F} = (Nt_A)_{OF} \quad (14)$$

where $(Nt_A)_{OF}$ is the number of overall transfer units, based on the fluid film, as defined by Chilton and Colburn (2), and where γ_A is related to the terminal solution and resin concentrations as follows:

$$\frac{(x_A)_{entr} - (x_A)_{exit}}{(x_A)_{entr} - (x_A^*)_{exit}} = \gamma_A = E_A \cdot \frac{(y_A)_{entr} - (y_A)_{exit}}{(y_A)_{entr} - (y_A^*)_{exit}} \quad (15)$$

Here, $(x_A^*)_{exit} = (y_A)_{entr} / M_A$ from Equation (12)

and $(y_A^*)_{exit} = M_A (x_A)_{entr}$ from Equation (11)

It will be observed that γ_A is the degree of approach to equilibrium transfer of component A in the solution phase, while the degree of approach in the resin phase is γ_A/E_A , because the resin concentrations are expressed on a different basis than that used for solutions.

The value of E_A in Equations (14) and (15) is the ratio of the slope of the equilibrium line to the slope of the operating line on a McCabe-Thiele x - y type plot. In terms of the operating variables concerned, this ratio is defined as

$$E_A = \frac{M_A}{R_F c_A / R_P \rho_P Q} = D_A \frac{R_P / (1-f_E)}{R_F / f_E} \quad (16)$$

It will be noted that the multiplier of D_A , above is the ratio of the linear resin velocity to the linear solution velocity. Using Equation (14) to replace κ_A in Equation (9) it becomes

$$\frac{h s f_E}{R_F} \cdot \frac{1}{(Nt_A)_{OF}} = \frac{1}{(k_A)_F a_F} + \frac{1}{D_A} \cdot \frac{1}{(k_A)_P a_P} \quad (17)$$

By analogy to the definition of the overall number of transfer units, the individual transfer units should be the product of the film coefficient and residence time for the phase of interest. Thus

$$(Nt_A)_F = (k_A)_F a_F \frac{hSf_E}{R_F} \text{ for fluid film diffusion controlling.} \quad (18)$$

$$(Nt_A)_P = (k_A)_P a_P \frac{hS(1-f_E)}{R_P} \text{ for particle film diffusion controlling.} \quad (19)$$

Substituting these into Equation (17) and utilizing Equation (16), the relation between the various transfer units becomes

$$\frac{1}{(Nt_A)_{OF}} = \frac{1}{(Nt_A)_F} + \frac{1}{E_A (Nt_A)_P} \quad (20)$$

Equilibrium Contact Method Where discrete stages are involved in countercurrent contacting of resin and solution, the relations established by Kremser (7) for absorption of lean components can be converted to ion exchange nomenclature. Under the assumption that complete equilibrium is attained in each discrete stage, the relation for the degree of approach to equilibrium transfer is

$$\gamma_A = E_A \frac{E_A^{N_C} - 1}{E_A^{N_C + 1} - 1} \quad (21)$$

where N_C is the number of equilibrium contacts between the two phases.

Rearrangement of Equation (21) gives a more appropriate form for determining N_C from γ_A and E_A

$$N_C = \frac{\ln \left[\frac{E_A - \gamma_A}{E_A (1 - \gamma_A)} \right]}{\ln E_A} \quad (22)$$

The relation between theoretical contacts and transfer units is directly analogous to the relation in distillation, i.e., one theoretical contact produces a change in solution composition equal to the driving force at the point where the resin leaves the section, $x - x^*$, whereas one transfer unit produces a change in solution composition equal to the

average driving force, $(x-x^*)_{av}$. A transfer unit and theoretical contact will be identical only when the slopes of equilibrium line and operating line are the same, i.e. $E = 1$.

An exact relation between the number of transfer units and equilibrium contacts can be obtained by eliminating γ_A between Equations (14) and (22). This gives

$$\frac{(Nt_A)_{OF}}{N_C} = \frac{E_A \ln E_A}{E_A - 1} \quad (23)$$

Design Criteria The McCabe-Thiele graphical method may be applied to the design of equipment for the separation of trace components by counter-current ion exchange. Figure 2, for instance, illustrates the relation between the operating line and equilibrium isotherm when a trace ion, A, is being transferred from the solution phase to the countercurrent resin stream. The horizontal distance between the two lines represents the overall driving force for ionic transfer based on the fluid film. The number of transfer units may be determined graphically, as indicated in Figure 3, by the procedure suggested by Selke and Bliss (9), although the use of Equation (14) to obtain $(Nt_A)_{OF}$ is much more convenient.

The number of equilibrium contacts required to reduce the concentration of A from its feed value to the desired exit concentration may also be found graphically by stepping off the stages in the conventional manner or by using Equation (22).

For ionic transfer from solution to the resin i.e. saturation, the operating line will lie below the equilibrium line. In order to have nearly complete removal of ion A from a feed solution, the entering resin must be nearly free of A, the slope of the equilibrium line must be greater than the slope of the operating line (i.e. $M_A > R_F C_E / R_P \rho_P Q$), and a large number of contacts will generally be required. Conversely, the operating line will be above the equilibrium line for elution or stripping of ions from the resin. Nearly complete regeneration requires an eluting solution free of the component concerned, a large number of contacts, and a slope ratio such that $M_A < R_F C_E / R_P \rho_P Q$.

A hypothetical separation of trace ions A and B is illustrated in Figure 4 for a saturation section having two theoretical contacts. The

two ions are present in equimolar concentrations in the feed, and the entering resin is free of A and B. The operating lines for the two ions are parallel. Because of the greater slope of the equilibrium line for B than that for A, the concentration of the solution is reduced much further in B than in A. Thus the effluent solution is enriched in A, and the effluent resin is enriched in B.

The maximum slope of the operating line, the $R_F C_E / R_P \rho_P Q$ ratio, which will give the desired effluent solution concentration may also be determined graphically as shown by the dashed line in Figure 2.

Method of Correlating Data A correlation of continuous ion exchange data involves the relation of the height of a transfer unit to the Reynolds and Schmidt numbers and other dimensionless parameters. This correlation is based on Equation (17), which relates the overall number of transfer units to the fluid and particle film coefficients k_F and k_P .

The fundamental definitions of the film coefficients are

$$(k_A)_F = \frac{(D_A)_F}{B_F} \quad (24)$$

$$(k_A)_P = \frac{(D_A)_P}{B_P} \quad (25)$$

where $(D_A)_F$ and $(D_A)_P$ are respectively the counter-diffusivities of ions A and G in the fluid and in the particle, and where B_F and B_P are the effective thicknesses of the fluid and particle films.

The effective transfer area per unit volume of bed has been assumed to be identical for both the fluid and particle films, i.e., $a = a_F = a_P$. Moreover, this transfer area has been assumed to be the phase interface or the surface of the resin particle. Using these assumptions Ergun (5) has shown that

$$a = \frac{6(1-f_E)}{d_P} \quad (26)$$

Taking into account Equations (24-26), Equation (17) may then be modified as follows:

$$\frac{h S f_E}{(N t_A)_{OF} R_F} = \frac{d_p}{6(1-f_E)} \cdot \frac{B_F}{(D_A)_F} + \frac{1}{D_A} \cdot \frac{d_p}{6(1-f_E)} \cdot \frac{B_P}{(D_A)_P} \quad (27)$$

After multiplying through by $1/d_p$ to obtain ratios of film thickness to particle diameter and by $[a(D_A)_P D_A]$ to obtain a dimensionless form, rearrangement of terms leads to

$$\left[\frac{h}{(N t_A)_{OF} d_p} \right] \frac{D_A S f_E (D_A)_P 6(1-f_E)}{d_p R_F} = D_A \frac{(D_A)_P}{(D_A)_F} \cdot \frac{B_F}{d_p} + \frac{B_P}{d_p} \quad (28)$$

It has been noted (2,13) that the fluid film thickness ratio, B_F/d_p , varies inversely with the Reynolds and Schmidt numbers, although the particle film thickness ratio, B_P/d_p is assumed to be a constant for spherical particles. Thus

$$\frac{B_P}{d_p} = \text{a constant}, \beta \quad (29)$$

and

$$\frac{B_F}{d_p} = \alpha (Re)^{-m} (Sc)^{-n} \quad (30)$$

where α is a constant of proportionality, m and n denote powers and

$$Re = \frac{r_h u \rho}{\mu} = \frac{[d_p f_E]}{[6(1-f_E)]} \left[\frac{R_F}{f_E} + \frac{R_P}{(1-f_E)} \right] \frac{\rho}{\mu} = \frac{d_p R_F \rho}{6(1-f_E) S \mu} \left[1 + \frac{R_P/(1-f_E)}{R_F/f_E} \right] \quad (31)$$

and

$$Sc = \frac{\mu}{\rho (D_A)_F} \quad (32)$$

The terms involved in the basic Reynolds and Schmidt groups have the usual definitions: r_h being the hydraulic radius, u the true average point velocity, ρ the solution specific gravity, and μ the solution viscosity, all in consistent units. The specific definition of the hydraulic radius is that proposed by Ergun (5); it is equivalent to the ratio of the volume occupied by the fluid in the bed to the total surface wetted. The point velocity for countercurrent operation was taken as the sum of the fluid and particle velocities.

Combining Equations (28-30) and multiplying the numerator and denominator of the left hand side by $(D_A)_F$, the correlation equation becomes

$$D_A \frac{(D_A)_P}{(D_A)_F} \left[\frac{h f_E}{(Nt_A)_{OF} d_P} \right] \left[\frac{6(1-f_E)S(D_A)_F}{d_P R_F} \right] = \alpha D_A \frac{(D_A)_P}{(D_A)_F} (Re)^{-m} (Sc)^{-n} + \beta \quad (33)$$

Graphically the relation may be represented by a straight line if the left hand side is plotted as the ordinate; against

$D_A \frac{(D_A)_P}{(D_A)_F} (Re)^{-m} (Sc)^{-n}$ as the abscissa. The resultant line will have a slope α and an intercept β .

EQUIPMENT

General As in any process development, the physical design of the separation apparatus changed as experience was gained and ideas were evolved. The current equipment reflects the best features of three earlier models of continuous countercurrent column apparatus.

The first model was a glass column in which the resin was transferred by means of a water operated venturi jet. In the second model improvements were made to reduce dilution due to the water transporting the resin. A mechanical screw lift was used for transferring resin in the third model, but too much solution was pumped by the screw lift and the resin attrition rate was high.

A new resin transfer device was developed to replace and to overcome the disadvantages of the screw lift. This was the resin metering and dewatering valve shown in Figures 5 and 6. The design of this valve was based on a metering device used by Stanton (10) in his studies of countercurrent ion exchange. Made largely of acrylic resin, the valve consisted of a cylindrical rotor and a case. Through the center of the rotor and perpendicular to its longitudinal axis, a hole was bored. A glass disc containing a multitude of small holes was retained at the center of this bore. The case was made to fit the rotor with a close tolerance and was provided with six channels between the periphery of the rotor and the outside of the case.

As the rotor turned in a clockwise direction, the following sequence of operations occurred: starting with the bore of the rotor in a vertical position, an aliquot of resin slurry flowed into the upper half of the bore through the inlet nipple. The resin was retained on the glass disc, and some of the solution in the slurry drained through the perforations to the bottom outlet. As the bore of the rotor passed under the right air inlet, air pressure was applied to this inlet by means of a cam arrangement which actuated a solenoid air valve. The air pressure forced the residual interstitial solution out of the resin into the slot on the opposite side and thence out the same bottom outlet. Just as the bore passed beyond the right air inlet, the cam arrangement caused the solenoid valve to close. This prevented air leakage around the rotor. The bore next became aligned with the resin outlet and, at the opposite end, with the flush solution inlet. This solution, under a constant head, carried the resin slug from the valve as a slurry. The flushing operation left the bore partially filled with washout solution, which was displaced when the new top of the bore rotated under the left air inlet, to which the air flow was also controlled by the cam arrangement. The surge of air blew the residual solution from the bore into the slot opposite the air inlet and thence out the same slurry outlet. This completed one cycle, the next operation being the filling of the new upper half of the rotor bore. Therefore, there were two complete cycles per revolution of the valve rotor.

The rotor was driven by a 1/4 hp motor through a variable speed torque converter and reduction gears. The rate of resin transfer was proportional to the speed of rotation of the rotor, as shown in Figure 7. The performance of the valve was evaluated experimentally, and no measurable carry over of the solution originally in the feed slurry to the discharged slurry was found, other than what the filtered resin would normally carry.

Experimental Unit Two of these resin valves were incorporated into a column assembly for evaluating the effect of a number of variables on continuous countercurrent ion exchange in a single column. In this column only one phase at a time of the cyclic operations involved in the completely continuous separation of ions was studied (e.g., the saturation of G resin with B and A ions) since the column variables which

affect the saturation step similarly affect the elution or regeneration step and other phases of the cyclic process.

The column assembly is indicated schematically in Figure 8 and is pictured in Figure 9. The Pyrex shell was 9.5 cm. i.d., and the distance between the feed inlet and the overflow ring was 122 cm. The feed solution was introduced through a 7.5 cm. ring of glass tubing having an upper surface of porous fritted glass. The distributor was provided with an inlet tube which extended through the wall of the column.

At the top of the column the exhausted solution spilled into the overflow ring and was collected. The resin was introduced into the top of the column from an overhead slurry storage through one of the metering and dewatering valves. A corresponding valve served to remove the resin from the bottom of the column. To avoid accumulation or depletion of the resin inventory in the column, the resin throughput rates of the two resin valves were always equalized.

Solution was pumped from near the top of the column to a small overhead reservoir. This solution was used to wash the resin from the upper valve into the top of the column. Thus the washout solution, which was of substantially the same composition as the exhausted feed, was recycled.

The solution drained from the resin entering the lower valve was recycled to the column. This solution re-entered the column at the base of the lower taper into an expanded bulb which minimized disturbance within the column.

Contact between the resin and solution was obtained by a moving bed process in which the resin was the continuous phase and the solution the discontinuous phase. The column contained a dense bed of resin through which the solution flowed. As a layer of this resin bed was removed from the bottom of the column by the lower valve, it was replaced with a layer of resin at the top of the bed, resulting in a net downward flow of the resin. In making a run the column was first filled with feed solution, which then was metered in at a constant rate, entering through the fritted glass ring and overflowing at the top at the same rate. Resin from the overhead supply was metered into the top of the column at a constant rate and fell to the top of the moving resin bed. This was maintained at the desired height, above the solution feed distributor, by removal of the resin from the base of the column at the same rate it was supplied.

A column insert, termed the tapped screen and illustrated in Figure 10, was designed to promote better contact between resin and solution under moving bed conditions. It consisted of 5 discs of 16-mesh monel screen spaced 5 cm. apart and supported with monel rods. A central rod passed through the screens and was attached to them with washers. A light hammer, actuated by a motor driven cam, tapped the central rod 50 to 200 times per minute; for higher rates, a vibrator, which gave a tapping frequency of greater than 1000 per minute, was used. These impacts were transferred to the screens. With this assembly in place in the column, conventional moving bed runs were made in which one or more of the screens was contained within the moving bed of resin. The vibration of the screens tended to cause reorientation of the resin particles and redistribution of the fluid, thus reducing channeling.

Some attrition of the resin was observed during its passage through the resin valves and the tapped screen. With new resin this amounted to about 0.1% per passage. More detailed information on resin attrition is contained in Appendix A.

Multi-unit Operations The studies described above have been concerned largely with only one phase of a continuous ion separation process, namely, the transfer of the ions trace or otherwise, from the feed solution to the resin. This has been termed saturation. As in the more familiar fixed bed processes, the resin must undergo alternate saturation and elution. The simplest system for continuous ion separation involves two countercurrent contacting units, one for saturating and one for eluting the resin.

Such a system is indicated schematically in Figure 11. In operation, a feed stream containing a mixture of ions A and B would be introduced into the bottom of the saturation section. The ion, say A, least strongly held by the resin would be carried largely by the rising solution. Thus the effluent solution (or upper product) from the saturating section would be enriched in ion A and the effluent resin from this section would be enriched in ion B. The transfer of ion B to the solution phase would involve another exchange process in which the spent resin (enriched in B) would be passed through the second countercurrent contactor comprising the eluting section. The spent elutant from this section would then be enriched in B and could be considered as a lower product stream. The

resin removed from the regenerating section, now eluted, would be returned as feed resin for the saturating section, which would thus permit continuous recirculation of the solid phase. This two-section unit will be discussed in detail in a companion paper (6).

Other possibilities are apparent in the arrangement not only of these two sections, but in the arrangement of three and four-section units. Although it is possible to apply the principle of reflux with the two-section unit, the more complex units are designed specifically to provide reflux of a portion of the ions from one or both product streams into the sections from which the respective streams emerged. Dickel (4) has discussed this principle of reflux in countercurrent ion exchange separations. An example of a possible four-section arrangement is shown in Figure 12.

EXPERIMENTAL PROCEDURE

General The experimental work was based on the separation of Li^+ and K^+ in trace concentrations, with respect to the H^+ carrier or gross component. Elution was also conducted with H^+ . This particular system was selected for several reasons: the three ions are equivalent, thus simplifying the exchange mechanism; Li^+ and K^+ are both available in pure forms at reasonable costs, may be analyzed readily by flame photometry, and being the first and third elements in the alkali metal series, differ sufficiently to make separation feasible; and H^+ is used as the carrier and elutant because of its ease of analysis. The Li^+ is least strongly held by the resin and thus corresponds to A ion in the general discussion above, K^+ corresponds with the hypothetical B ion and H^+ is the G ion.

Chempro C-20 cation exchange resin was used throughout the studies. It is a sulfonated polystyrene base type of resin. The resin was wet screened 16 to 35 mesh, so the average wet particle diameter was 0.07 cm. The solution diffusivities for Li^+ , K^+ and H^+ were taken from the International Critical Tables and were averaged for the ion pairs concerned. This led to $(D_{\text{Li}})_F = 1.85 \times 10^{-5}$ and $(D_{\text{K}})_F = 2.18 \times 10^{-5}$ sq.cm./sec. The ratio of the resin and solution average diffusivities, $(D_A)_P / (D_A)_F$, was found by several of the present authors (12) to be ~ 0.19 for univalent ions and this type of resin. The resulting resin diffusivities would then be $(D_{\text{Li}})_P = 3.46 \times 10^{-6}$ and $(D_{\text{K}})_P = 4.08 \times 10^{-6}$ sq.cm./sec. The

settled resin had a void fraction, f_E , of 0.39 and a density, ρ_p , of 0.64 g. oven-dried weight per cc. of true wet resin volume.

Methods of Analysis The following analytical procedures were developed to assess the concentration of lithium, potassium, and hydrogen ions in the solutions and on the resins. These cations were present in the solutions as chlorides.

The solutions were analyzed for the alkali metal content with a Beckman DU spectrophotometer with a flame attachment. Lithium was determined at 673 $m\mu$ and at a slit width of 0.15 mm, while potassium was read at 771 $m\mu$ and at a slit width of 0.06 mm. It was necessary to make corrections for interference (by reinforcement) of the HCl on the emission, and for mutual interference of the metal ions. The H^+ correction was made by analyzing the unknown solutions against lithium and potassium standard solutions containing 1.0 N HCl, since this was the H^+ concentration in nearly all the experimental solutions. If the H^+ content of the unknown differed from 1.0 N by more than 10%, the solution was adjusted to 1.0N by the addition of measured volumes of distilled water or HCl as required, and was then analyzed for the metal ions. Corrections for the mutual interference of the metal ions were made with the aid of a number of calibration curves, which had been prepared by the experimental determination of the degree of interference over a very wide range and ratio of concentrations. The exact H^+ concentrations were determined with a Beckman automatic titrator. Concentrations in solution were reported as meq/cc.

Resin samples were analyzed by eluting water-washed aliquots of about 25 cc. with 250 ml of 2 N HCl. The resulting elutants were diluted to 1.0N H^+ , and were analyzed for metallic ion concentrations as described above. The eluted aliquots were oven-dried, and resin concentrations were reported as meq/g.* The H ion concentration on the resin,

*Where necessary, as in resin flowrates, settled volumes were converted to a weight basis by means of a density factor. This factor, 0.39 g. dry resin/cc settled volume, was determined experimentally for a number of samples, and was found to have a maximum deviation of about 1%.

although seldom of interest in trace studies, was obtained as the difference between the ultimate capacity of the resin and the total metal ion concentration.

Resin Behavior The ultimate capacity of the resin represents the total number of ion exchange positions available on a unit quantity of resin. This was determined by first converting a portion of resin entirely to the hydrogen form by complete elution of metal ions. Then a portion of this resin was contacted in a fixed bed with a large quantity of CaCl_2 solution to displace the H^+ . The effluent solution was titrated for the H^+ concentration, and the total millequivalents of H^+ removed were calculated. The resin aliquot was oven-dried, and the ultimate capacity was then reported as meq/g. on the dry basis. This procedure is similar to that suggested by Kunin and Myers (8). For the resin used, this capacity was 5.11 meq/g.

The distribution coefficients for the Li^+-H^+ , and K^+-H^+ pairs under study were determined by batch contacting. Separate portions of a resin sample in the hydrogen form were equilibrated by shaking for about 8 hours with solutions containing various trace concentrations of Li and K ions in 1.0 N HCl. The equilibrated resin and solution samples were then separated and analyzed by the above procedures. The results, plotted as equivalent fraction of the trace ion on the resin, based on the ultimate capacity, vs. equivalent fraction of this ion in the solution, based on total ionic concentration, gave the curves shown in Figure 13. The slope of the Li^+ curve, which is the distribution coefficient, M_{LiH} , is 0.87. Similarly, the potassium-hydrogen distribution coefficient, M_{KH} , is 3.30.

At the higher solution flow velocities used for most of the later runs, expansion of the resin bed was encountered. This affected the external void fraction. The measurement of bed expansion was difficult because of the oscillating level of the resin at high throughputs. The data obtained from the experimental runs and from special hydraulic tests are indicated in terms of the external void fraction in Figure 14. Up to 0.035 cm/sec, no effect on the void fraction was observed. Beyond that solution velocity, an average curve was drawn through the points, and the smoothed data were used in the interpretation of the experimental results. Above 0.35 cm/sec, resin was carried out the top of the column at a substantial rate.

Operation of Equipment All the experimental runs were made under quite similar conditions. In most of the runs, the column was operated as a saturation section. The prepared resin, essentially in the hydrogen form, was metered into the top of the column at 0.2 to 0.7 cc/sec and was withdrawn at the same rate through the lower resin valve. Feed solutions usually were made up to have the approximate composition: 0.03 N Li^+ , 0.03 N K^+ and 1.0 N H^+ , and the exact composition was then determined by analysis. Solution flow rates, measured with a rotometer, ranged from 0.8 to 16.5 cc/sec, equivalent to superficial velocities of 0.01 to 0.23 cm/sec. through the column. Elution runs were also made in which resin, partially saturated with Li^+ and K^+ , was passed counter-currently to an acid feed solution.

Each run was started with the column full of feed solution and with the inventory of resin in the base of the column at the level to be maintained during the run. Both resin valves were started simultaneously when the solution began to overflow at the top of the column. Every 15 minutes (5 minutes at the higher flowrates), the effluent solution and the slurry of exhausted resin were collected. The volumes of the effluent solution and the slurry, and the settled volume of the resin in the slurry (obtained by tapping the graduate) were recorded. In addition, a portion of the resin was vacuum filtered and held for analysis. Samples of the effluent solution and supernatant slurry solution were also retained.

A run was continued until there was reasonable assurance from past experience that the steady state had been attained. The length of the runs varied from 1 to 3 hours.

The concentrations of the metal ions in all the samples and the concentration of H^+ in the solution samples were determined by the procedures described.

The runs were made with the top level of resin maintained constant between 6 and 28 cm. above the feed solution inlet. The feed resin entering the column fell freely through the rising solution to the top of the moving bed of resin. The residence time of a resin particle in the moving bed was 10 to 45 minutes, and the solution residence time was 1 to 4 minutes. The experimental procedure for those runs in which the

tapped screen was used to improve contact did not differ from that for the simple moving bed runs except in the continuous operation of the tapping hammer.

The operating conditions for the runs are listed in Table I.

INTERPRETATION OF RESULTS

Treatment of Data The experimental data were obtained in terms of flowrates and concentrations (later converted to equivalent fractions). A typical set of data is represented in Figure 15. These data were obtained in Run 1. The upper portion of Figure 15 shows the change in the equivalent fractions of the trace ions in the effluent resin with time, and the lower set of curves relates the corresponding changes on the effluent solution to the time of operation.

The equivalent fraction of the trace ions in the effluent solution and resin at the steady state were used to determine γ from Equation (15). For a given run, four values of γ were obtained: one based on the change in the fraction of Li^+ in solution, one based on the change in the fraction of K^+ in the solution, and the two corresponding values obtained from the resin concentration information. The two γ values based on Li^+ were averaged, as were the two γ values based on K^+ . This was done to compensate for the deviation of the output-input balance for each ion from 100%. Balances ranged from 89% to 111% with an average deviation of 3%. The E ratio for each ion was calculated from the distribution coefficient and the equivalent flow rates according to Equation (16).

Then, the numbers of overall transfer units and equilibrium contacts were calculated by Equations (14) and (22), respectively, from the E values and averaged γ values for each ion. The results for several of the runs showed nearly complete approach to equilibrium transfer, i.e. $\gamma \rightarrow 1$ or $\gamma/E \rightarrow 1$, and thus apparently an infinite N_c or N_t . This, of course, is impossible so the results must reflect the experimental uncertainties. The proper interpretation of the results is certainly that a very large number of contacts or transfer units were obtained, the exact number being difficult to determine because of the limit of analytical accuracy. In the case of Run 2, for instance, an average γ_K value of 1.00 was obtained, indicating equilibrium. If this γ_K had been 0.99 at the same equivalent flowrates, the following values would have been

indicated: $(N_C)_K = 7.9$, $(Nt)_K = 10.6$. Since E_{Li} the ratio of the distribution coefficient to slope of the material balance line, was less than one, it represented the limiting value of γ_{Li} for this run. The experimental $(\gamma/E)_{Li} = 1.00$ showed that the maximum possible transfer of the Li ions was obtained. Here, if $(\gamma/E)_{Li}$ had been 0.99, the $(N_C)_{Li}$ would have been 4.7 and the $(Nt)_{Li} = 3.0$. These finite values are estimates, and were inserted in Table I in place of the apparently infinite N_C and Nt indicated directly by the actual data.

The results of the experimental runs are given in Table II in terms of overall numbers of transfer units and contacts, and the enrichment and recovery factors. The values were calculated to the second decimal place and rounded to the first. The estimated values are indicated by asterisks.

Correlation of Data It was not possible to make direct use of the proposed correlation relation (33), because the experimental data did not permit a conclusive choice of the powers for the Reynolds and Schmidt numbers.

However, several of the present authors (12) have shown that, for fixed bed ion exchange under trace conditions, a modified form of Equation (33) also applies, i.e.,

$$D_A \frac{(D_A)_P}{(D_A)_F} \left[\frac{h f_E}{S_A d_P} \right] \left[\frac{6(1-f_E)S(D_A)_F}{d_P R} \right] = \alpha' D_A \frac{(D_A)_P}{(D_A)_F} (Re)^{-m} (Sc)^{-n} + \beta' \quad (34)$$

where S is the number of fixed bed transfer units and R is the solution flow rate.* They found that the best fit to data available in the literature was obtained with $m=n=0.5$, $\alpha'=0.29$ and $\beta'=0.04$.

It will be noticed that the above relation is identical with Equation (33) except for the two terms peculiar to fixed bed exchange and defined above.

* Obviously the Reynolds number used here is the same as that in Equation (31) except the R_p is zero and R_p has been replaced by R so that the average point velocity is now $R/f_E S$.

In view of these fixed bed results, the power of both the Re and Sc numbers was selected as 0.5 for the correlation of the moving bed data. Initially only one set of related moving bed data was used. This was obtained in the runs for which the tapped screen assembly was operated at a tapping rate of 200/min., and in which the bed expansion was negligible; it was the largest group of such related data. The experimental results for these runs were plotted as

$$D_A \frac{(D_A)_P}{(D_A)_F} \left[\frac{h f_E}{(Nt_A)_{OF} d_p} \right] \left[\frac{6(1-f_E)S(D_A)_F}{d_p R_F} \right] \text{ vs } D_A \frac{(D_A)_P}{(D_A)_F} (Re)^{-0.5} (Sc)^{-0.5}$$

on linear coordinates as shown in Figure 16. The method of averages was used to locate the correlation line, and its slope and intercept, α and β , were found to be 1.6 and 0.6 respectively.

A replot of this correlation line on log-log coordinates, Figure 17, reveals more clearly the two diffusional regions.

The horizontal portion of the curve, below abscissa values of 0.03, is the region where internal diffusion controls; above abscissa values of 3.0 the 45° line represents the region where external diffusion controls.

In this figure the experimental data for all the moving bed runs are represented, including runs at high and low flowrates, at high and low tapping rates, and those in which the screen assembly was omitted. As can be seen, the original correlation line represents these data equally well except for the one run (No.1) made without the tapped screen assembly at the low flowrate.

It is apparent that most of the present runs fall in the transition region. The deviations of the data from the curve are attributed largely to the uncertainties of the experimental results. As pointed out above, wherever the approach to equilibrium indicated by the data was 1.0 or higher, the Nt value was calculated on the assumption that the actual approach was 0.99. These adjusted data are identified by the underlined points in Figure 16.

For the moving bed runs, involving either the tapped screen or high flowrates, the data can best be represented by

$$D_A \frac{(D_A)_P}{(D_A)_F} \left[\frac{hf_E}{(Nt_A)_{OF} d_p} \right] \left[\frac{6(1-f_E)S(D_A)_F}{d_p R_F} \right] = 1.6 D_A \frac{(D_A)_P}{(D_A)_F} (Re \cdot Sc)^{-0.5+0.6} \quad (35)$$

Since the Reynolds and Schmidt numbers have been assumed to have the same powers, their product, the Peclet prime number, can be used where required,

$$Re \cdot Sc = \left[\frac{d_p R_F}{6(1-f_E)S(D_A)_F} \right] \left[1 + \frac{R_P/(1-f_E)}{R_F/f_E} \right] = Pe', \quad (36)$$

thus eliminating ρ and μ from the expression.

For convenience, Equation (35) can be rearranged into a transfer height form, since $Ht=h/Nt$

$$\left[\frac{(Ht_A)_{OF}}{d_p} \right] = \frac{1.6}{f_E (Re \cdot Sc)^{0.5}} \left[\frac{d_p R_F}{6(1-f_E)S(D_A)_F} \right] + \frac{1}{E_A} \cdot \frac{0.6}{(1-f_E)} \left[\frac{d_p R_P}{6(1-f_E)S(D_A)_P} \right] \quad (37)$$

where $\frac{1}{E_A} \cdot \frac{R_P/(1-f_E)}{R_F/f_E}$ has been utilized to replace $\frac{1}{D_A}$

An analogous form

$$\frac{(Ht_A)_{OF}}{d_p} = \frac{(Ht_A)_F}{d_p} + \frac{1}{E_A} \cdot \frac{(Ht_A)_P}{d_p} \quad (38)$$

can be obtained by multiplying equation (20) by h/d_p . Upon comparison of the two forms, the factors affecting the individual transfer heights become readily apparent.

Because of the limitations in the experimental equipment and analytical techniques, it was difficult to obtain results which fell definitely in either the internal or external diffusion controlled area. For this reason it should be emphasized that the constants given in the above relation are tentative, since the data do not cover a wide enough range of the abscissa to show that the relation would hold at the extremes of

the indicated curve. More confidence may be placed on the 0.6 value for β than the other constants, because as may be seen from Figure 16, any reasonable adjustment of the curve will not affect the intercept to any great extent.

In an attempt to extend the range of the data, and perhaps to obtain better contact between the resin and solution, two other means of contact within the column were evaluated: first, by free fall of the resin and second, with a stirred contactor insert. Very little success was achieved with either because of difficulties in accurately assessing numbers of transfer units, void fractions, and (for the stirred contactor) the Reynolds numbers. These aspects of the program are described in more detail in Appendices B (free fall) and C (stirred contactor).

Discussion of Results At the low solution flowrates (< 3 cc/sec) the tapped screen unit was most effective in promoting good resin-solution contact, i.e. in reducing channeling. This will be observed by comparing the greater transfer heights of Run No.1, which was made without the tapped screen (solid circles in Figure 17), with the others in this range, which involved tapping. On the other hand, there was no significant effect on the results when the tapping frequency was varied between 50 and about 1000 per minute.

With further reference to Figure 17, it is obvious that at the higher flowrates (> 7 cc/sec) the tapped screen assembly offered no advantage. Apparently, under high flowrate conditions, the greater turbulence not only reduced the fluid film resistance as anticipated, but also decreased channeling as much as did the tapped screens. Since the higher flowrates are of more commercial interest, it is advantageous that good contact can be obtained without the tapped screen unit and its attendant mechanical complexities.

It will be noted that the difference between the α and β values for the fixed bed and moving bed correlation relations indicates a displacement between the two curves. This is attributed to a difference in the contact efficiencies, the fixed bed having the greater efficiency. The factors contributing to this contact efficiency have not been established, but they may be related to differences between upflow and downflow, to the column diameter-particle diameter ratio, to the Reynolds number, and for the current study, to the tapping frequency of the screen assembly.

Some of these factors were studied qualitatively in a short series of fixed bed runs made at low flowrates. Here, upflow was less efficient than downflow, but the tapped screen increased the upflow efficiency. A column of smaller diameter was found to be more effective than one of large diameter. More detail concerning these fixed bed runs is given in Appendix D.

ACKNOWLEDGMENTS

The authors wish to express their appreciation for the invaluable technical advice of Prof. Theodore Vermeulen of the University of California, of Dr. Edward R. Tompkins of the Naval Radiological Defense Laboratory and of Mr. Jack J. Gordon of Stanford Research Institute. Portions of the experimental work were conducted by Mr. Raymond K. Cohen and Mrs. Lydia Peters of the Institute, and their assistance is gratefully acknowledged.

NOTEBOOK REFERENCES

The basic experimental data from which these results were obtained have been permanently recorded in Stanford Research Institute Notebooks No. 658, 788, 1062, 1095, 1148, 1225, 1245, 1259, 1266, 1268, 1279, 1301, 1340, 1378, 1392, and 1423.

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Presented at the 45th Annual Meeting, A. I. CH. E., Cleveland, Ohio

NOMENCLATURE

- a = effective transfer area of film, sq. cm./cc. of contacting zone.
- A,B,G = trace components A,B, and gross component G.
- B = effective thickness of resistance film, cm.
- c_i = total ionic level in the solution phase in meq./cc., equal to the sum of the ionic concentrations of components, A,B, and G.
- d_p = mean diameter of resin particles, cm.
- D = distribution or partition parameter, dimensionless.
- D = effective ionic diffusivity for a trace component diffusing against the carrier component, sq. cm./sec.
- E = ratio of the slope of the equilibrium line to the slope of the operating line, dimensionless.
- f_E = ratio of void space outside resin particles to total volume of contacting zone, dimensionless.
- Ht = height of contact zone equivalent to a transfer unit, cm. Given by relation, $Ht = h/Nt$.
- h = height of the contacting zone, cm.
- k = mass transfer coefficient, cm./sec.
- K = chemical equilibrium constant for exchange, dimensionless.
- M = slope of the equilibrium line, dimensionless.
- N_c = number of equilibrium contacts.
- Nt = number of transfer units.
- Pe' = Peclet prime number for the fluid, $Pe' = Re \cdot Sc$.
- Q = total ionic concentration of the resin or the ultimate capacity, meq./g. oven-dried resin.
- r_h = hydraulic radius, cm.
- R = volumetric flow rate, cc./sec.
- Re = Reynolds number for the fluid.
- s = number of fixed bed transfer units.
- S = cross-sectional area of column, sq. cm.
- Sc = Schmidt number for the fluid.
- u = point velocity, cm./sec.
- x = equivalent fraction of a component in solution with respect to the total ionic level of the solution, dimensionless.

- x^* = equivalent fraction in the solution in equilibrium with a given equivalent fraction on the resin, dimensionless, $x^* = y/M$.
- y = equivalent fraction of a component on the resin with respect to the total capacity of the resin, dimensionless.
- y^* = equivalent fraction on the resin in equilibrium with a given equivalent fraction in the solution, dimensionless, $y^* = x \cdot M$.
- γ = degree of approach to equilibrium transfer for a component, dimensionless.
- κ = generalized transfer coefficient, reciprocal sec.
- μ = viscosity of the solution, poise.
- τ = residence time in contacting zone, sec.
- ρ = specific gravity of the solution, g./cc.
- ρ_p = density of resin, g. oven-dried resin per cubic cm. of true resin volume saturated with the carrier component.

Subscripts

- A, B, G = components A, B, and G.
- entr = feed composition
- exit = effluent composition
- f = fluid (or solution) phase
- i = interface values
- OF = over-all value based on the fluid film
- p = particle (or resin) phase

APPENDIX A

Resin Attrition

Several experimental evaluations of resin attrition in the continuous column were made at various times over an extended period of time. The procedure involved the determination of the fines produced in passing the resin through the column.

At the beginning of the program, when a recently received resin was passed through the two resin transfer valves and the column filled only with solution, 0.1% fines were produced per pass. After nine months of intermittent use, this resin showed a production of 1.2% fines per pass under the same conditions. A similar test performed after four months of use gave an intermediate value. When the tapped screen was used during these tests, the attrition rate was slightly, perhaps insignificantly, higher.

A small part of the increase in attrition rate with time may have been due to some deformation of the plastic resin valves. However, at the end of the experimental program, a fresh sample of resin was found to show one-sixth the attrition rate of the old resin under the same test conditions. It is not clear whether this observed increase in resin fragility was a result of intermittent cycling or of nearly continuous exposure to 1.0 N HCl solutions. In either case, one would expect to reach some plateau of fragility.

In any case, the present authors found, in an economic study to be reported later, that resin replacement costs represent a very small part of the total operating costs of a countercurrent ion exchange plant, even when quite high attrition rates (4% per pass) were assumed. Also, with larger scale resin transfer valves, the ratio of resin exposed to contact with the wall of the case would be much less, and correspondingly less attrition would be expected. Thus, the interest in attrition is primarily academic.

APPENDIX B

Free Fall Runs

Description One free fall experiment was carried out in the 9.5 cm diameter column. The resin was allowed to fall freely (as the dispersed phase) from the upper resin transfer valve to the base of the column (44 cm) against a rising stream of solution. A small inventory of resin was carried at the base of the column below the solution inlet to assure proper operation of the lower resin valve.

In an associated experiment, the resin slurry from the upper valve was conducted through a 2 cm diameter tube which extended below the solution feed position to 1 cm above the level of the resin bed. Here then, there was no countercurrent flow of the resin and solution streams, and any ion exchange which did occur was caused by end effects (resin-solution contact within the upper resin valve and below the solution feed position).

Data and Results The data for these two runs are tabulated below:

A. Experimental Conditions

Run	Total Ionic Conc. C_{Σ} meq./cc	Void Fraction f_E	Volumetric Flowrates		E Values	
			Solution R_F cc/sec.	Resin R_P cc/sec.	E_{Li}	E_K
Free Fall	1.081	0.9995	2.06	0.173	0.221	0.837
End Effects	1.056	0.9995	1.37	0.219	0.419	1.58

B. Experimental Results

Run	Number and Height of Over-all Transfer Units				Number of Equil. Contacts	
	$(Nt)_{Li}$	$(Nt)_K$	$(Ht)_{Li}$ cm.	$(Ht)_K$ column height	$(N_C)_{Li}$	$(N_C)_K$
Free Fall	0.25	0.55	175	80	0.59	0.60
End Effects	0.25	0.56	-	-	0.40	0.43

It will be noted that nearly identical Nt values were obtained for both runs. It is apparent then that the end effects were responsible for a large part of the overall exchange observed for the free fall run. Therefore, the Ht values indicated for the free fall run were no doubt fictitious, and, for the actual exchange within the free fall zone, the Ht values were probably extremely high.

The void fraction in the free fall zone could not be determined accurately because of the small amount of resin present. Since the void fraction and Ht values were questionable, the data were not evaluated for the moving bed mass transfer correlation.

APPENDIX C

Stirred Contactor Runs

Description The stirred contact insert, pictured in Figure C-1, was designed to fit with close tolerances within the previously described column. The design was based on a liquid-liquid contactor described by Oldshue and Rushton, (Chem. Eng. Prog. 48 (297) 1952). It consisted of four baffled compartments in each of which a turbine circulated the resin slurry. These turbines, mounted on a central shaft, were driven by a variable speed motor at 900 to 2000 RPM. The overall height within the contacting zone was 20.3 cm. By inserting fitted discs, the diameter of the openings between compartments could be reduced from 5 cm to 2.5, thereby increasing the resin hold-up. Figure C-2 shows the stirred contactor fitted with only two of these discs, so that the baffle opening at the bottom of the two upper compartments is 2.5 cm, while the opening is 5 cm at the bottom of the two lower compartments. Under operating conditions, the resin inventory is visibly greater in the upper half of the unit.

As in the free fall run (see Appendix B), only a small quantity of resin was retained in the base of the column, well below the solution inlet. Except for the operation of the agitators, the runs were conducted like those previously delineated.

Data and Results The information gained from four runs with the stirred contactor is tabulated below:

A. Experimental Conditions

Run No.	Total Ionic Conc. C_i meq. / cc.	Volumetric Flowrate		E' Values		Void Fraction f_E	Diameter of openings between Compartments cm
		Solution	Resin				
		R_F	R_P				
		cc / sec.	cc/sec.	E_{Li}	E_K		
1	1.004	1.39	0.220	0.452	1.72	0.984	5
2	1.013	1.38	0.195	0.427	1.62	0.958	2.5
3	1.050	1.38	0.208	0.411	1.56	0.984	5
4	1.101	1.37	0.221	0.418	1.58	0.969	2.5

B. Experimental Results

Run No.	Number and Height of Over-all Transfer Unit				Number of		Stage	
	$(Nt)_{Li}$	$(Nt)_K$	$(Ht)_{Li}$ cm	$(Ht)_K$ cm	Equil. Contacts $(Nc)_{Li}$	$(Nc)_K$	Efficiency $(Nc)_{Li}$ 4	$(Nc)_K$ 4
1	0.56	1.12	36	18	0.86	0.83	22%	21%
2	0.56	0.87	36	23	0.93	0.72	23%	18%
3	0.45	0.96	45	21	0.72	0.59	18%	15%
4	0.59	1.65	34	12	0.96	1.35	24%	34%

Several factors precluded further work with this device: (1) the stage efficiency was poor (and Ht values high), (2) the mechanical complexity was undesirable, and (3) an appreciable amount of fine resin was observed carrying over in the effluent solution. In addition, the data could not be used in the moving bed correlation, first, because the effective Reynolds number was not known, and second, because the resin inventory was so small that it was difficult to evaluate, with sufficient accuracy, the fraction of the total volume occupied by the resin.

Resin attrition tests were made with and without the stirred contactor in the column, and the attrition rate was found to be twice as high with the stirred contactor present.

APPENDIX D

Fixed Bed Runs

Description As was pointed out in the manuscript report, there is a difference in contact efficiency between fixed and moving bed runs. Since the first type of runs involved solution downflow in small diameter columns, and the countercurrent runs were made with upflow at large diameters, it was postulated that both the type of flow and the column diameter might contribute to the observed effects.

This suggestion was tested by operating fixed beds under these varying conditions. Of the four fixed bed runs in the large column, two were made with downflow and two with upflow; one of the latter with the tapped screen in use. The results of the fixed bed run made in a 2.5 cm column (reported in Technical Report No. I) are also given below for comparison.

A conventional experimental procedure was used involving the passage of a trace feed solution, at a uniform flowrate, through a bed of hydrogen-form resin. The effluent was collected in measured volumes and analyzed to obtain the trace ion breakthrough curve. The calculations for the number of transfer units were made according to Hiester and Vermeulen, (Chem. Eng. Prog. 48 (505)(1952).)

Data and Results

Run No	Bed Height	Column Diameter	Total Ionic Conc.	Solution Flowrate	Number of Transfer Units		Direction of Flow
	h cm	d _w cm	c _z meq./c.c.	R/S cm./sec.	s _{Li}	s _K	
1	6.1	9.5	1.08	0.0217	1.3	2.0	upflow
2	7.6	9.5	1.01	0.0296	-- ²	19	downflow
3	7.6	9.5	1.07	0.0195	4.5	25	downflow
4 ¹	7.6	9.5	1.05	0.0202	--	7.9	upflow
TR No.1	12.7	2.5	0.09	0.102	19	--	downflow

¹ Tapped screen assembly used at tapping rate of 200/min.

² The absence of transfer unit information indicates either that the particular ion was not present in the system or that the experimental results were too poor for evaluation.

Qualitatively, the results indicate more efficient resin - solution contact in downflow than in upflow (compare Runs 1 and 3). Also, better contact occurred in the smaller diameter column. These results explain in part the displacement between the moving bed and fixed bed correlation curves, since the fixed bed correlation was based largely on data obtained in small diameter columns under downflow conditions, as opposed to the larger diameter columns and upflow operation of the moving bed runs.

Further, the fixed bed data confirmed the effectiveness of the tapped screen assembly in improving resin-solution contact at low flowrates with upflow operation.

Table I 36

EXPERIMENTAL CONDITIONS

RUN NO.	BED HEIGHT h cm	TOTAL IONIC CONCENTRATION C_z meq/cc	VOLUMETRIC FLOWRATES		E VALUES		VOID FRACTION f_E	TAPPING RATE Taps min
			SOLUTION	RESIN				
			R_F cc/sec	R_P cc/sec	E_{Li}	E_K		
1	12.7	1.00	2.07	0.221	0.306	1.16	0.39	*
2	12.7	1.06	1.37	0.212	0.419	1.59	0.39	200
3	7.6	1.08	1.36	0.214	0.436	1.65	0.39	200
4	7.6	1.08	1.38	0.380	0.721	2.74	0.39	200
5	6.8	2.13	1.97	0.218	0.148	0.561	0.39	200
6**	7.6	1.03	0.78	0.347	1.23	4.65	0.39	200
7	7.6	1.00	1.58	0.204	0.374	1.42	0.39	50
8	6.4	1.10	1.61	0.330	0.539	2.04	0.39	200
10	28.0	1.04	15.05	0.742	0.135	0.512	0.50	200
11	21.6	1.00	15.40	0.651	0.121	0.458	0.54	200
12	16.5	1.04	8.69	0.705	0.223	0.845	0.53	200
13	17.8	1.06	7.73	0.732	0.228	0.866	0.52	*
17	21.0	0.98	16.48	0.562	0.100	0.379	0.60	*
19	21.6	1.06	13.92	0.642	0.124	0.470	0.56	*
20	16.5	1.08	8.83	0.698	0.210	0.796	0.49	*
21	7.6	0.70	2.66	0.291	0.442	1.68	0.39	1000

* Tapped screen assembly omitted.

** Elution run.

Table II

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EXPERIMENTAL RESULTS

RUN NO.	ENRICHMENT OF Li^+ IN EFFLUENT SOLN. $(x_{\text{Li}}/x_{\text{K}})_{\text{effluent}}$ $(x_{\text{Li}}/x_{\text{K}})_{\text{feed}}$	RECOVERY OF Li^+ IN EFFLUENT SOLN. $(x_{\text{Li}})_{\text{effluent}}$ $(x_{\text{Li}})_{\text{feed}}$	NUMBER AND HEIGHT OF OVERALL TRANSFER UNITS				NUMBER OF EQUIL. CONTACTS		STEADY STATE OUTPUT/INPUT RATIO	
			$(Nt)_{\text{Li}}$	$(Nt)_{\text{K}}$	$(Ht)_{\text{Li}}$	$(Ht)_{\text{K}}$	$(N_c)_{\text{Li}}$	$(N_c)_{\text{K}}$	Li^+	K^+
					cm. bed height					
1	4.7	0.71	0.79	2.2	16	5.8	1.5	2.1	0.94	1.00
2	10.1	0.55	3.0*	10.6*	4.2	1.2	4.7*	7.9*	0.98	1.11
3	6.9	0.56	2.0	5.8	3.8	1.3	3.1	4.5	0.91	1.03
4	3.1	0.41	1.8	7.2*	4.2	1.1	2.2	4.1*	1.00	1.07
5	1.6	0.84	0.8*	1.2	8.8	5.7	2.3*	1.6	1.01	0.98
6**	—	—	3.2	5.5*	2.4	1.4	3.6	2.8*	0.89	0.99
7	6.9	0.62	1.1	3.5	6.8	2.2	1.9	2.9	0.99	0.99
8	6.2	0.50	1.7	3.6	3.7	1.8	2.1	2.6	0.97	0.98
10	1.6	0.88	0.32	1.9	88	15	1.0	2.7	1.02	1.03
11	1.4	0.90	0.25	1.1	86	21	0.8	1.6	1.02	0.94
12	2.5	0.82	0.45	2.2	37	7.5	1.0	2.7	1.06	1.00
13	2.6	0.78	0.98	2.8	18	6.4	1.8	2.9	1.01	0.99
17	1.4	0.90	0.47	1.1	45	19	1.9	1.9	0.99	0.99
19	1.1	0.90	0.27	0.81	80	27	0.9	1.6	1.02	1.02
20	2.0	0.82	0.51	1.8	32	9.3	1.2	2.0	0.90	0.99
21	7.2	0.65	1.16	3.3	6.5	2.3	1.8	2.5	0.99	0.91

* Based on assumption that $\gamma = 0.99$ or $\gamma/E = 0.99$.

** Elution run.

FIG. 1

SIMPLE COUNTERCURRENT OPERATIONS

IA-CU337-38

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FIG. 2
McCABE - THIELE DIAGRAM FOR
TRACE COUNTERCURRENT ION EXCHANGE

IA-CU337-41

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FIG. 3
GRAPHICAL DETERMINATION OF NUMBER OF
TRANSFER UNITS

IA-CU337-37

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FIG. 4

SEPARATION OF TRACE COMPONENTS WITH TWO THEORETICAL CONTACTS

IA-CU337-40

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FIG. 5
SCHEMATIC DIAGRAM OF
RESIN METERING AND DEWATERING VALVE

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FIG. 6

RESIN METERING AND DEWATERING VALVE

P-CU337-89

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FIG. 7
PERFORMANCE OF RESIN METERING VALVE

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FIG. 8
SCHEMATIC DIAGRAM OF COLUMN ASSEMBLY
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FIG. 9 - COLUMN ASSEMBLY
P-CU337-90

FIG. 10
TAPPED SCREEN ASSEMBLY

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FIG. II
COUNTERCURRENT OPERATIONS IN
A TWO-SECTION UNIT

1A-CU337-43

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FIG. 12
FOUR-SECTION ION SEPARATION UNIT

1A-CU337-39

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FIG. 13
EQUILIBRIUM ISOTHERMS

1A-CU337-42A

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FIG. 14
EFFECT OF FLOWRATE ON VOID FRACTION

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FIG. 15
EFFLUENT COMPOSITIONS VS. TIME FOR RUN 1

1A-CU337-49

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FIG. 16
LINEAR CORRELATION PLOT

A-CU337-84

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FIG. 17
LOGARITHMIC CORRELATION PLOT

A-CU337-85

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FIG. C-1
STIRRED CONTACTOR

P-CU337-92

AT REST
NO RESIN

IN OPERATION
RESIN BEING FED

FIG. C-2
EFFECT OF BAFFLE OPENING ON RESIN HOLDUP
P-CU337-93

June 24, 1953

Report No. 30
Technical Report No. V

**CONTINUOUS COUNTERCURRENT ION EXCHANGE
WITH TRACE COMPONENTS**

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S R I Project No. CU-337

Prepared for

Reactor Development Division
U.S. Atomic Energy Commission
Under Contract AT(11-1)-110

Project Agreement No. 1

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