Mass Transfer in a Continuous-flow Mixing Vessel

D. W. HUMPHREY and H. C. VAN NESS

Purdue University, Lafayette, Indiana

Mass transfer coefficients have been determined for the dissolution of $Na_2S_2O_3 \cdot 5H_2O$ crystals in water under conditions of turbulent agitation in a mixing vessel. The dissolution was carried out in a steady-flow process in which the area of salt crystals and the concentration of the solution in the mixing vessel were constant during each run. A comparison is made with previously unpublished results for batch runs in a similar system, and a method is developed for calculating the surface area of salt particles suspended in the mixing vessel under steady-flow conditions.

Relatively little attention has been given in recent years to the problem of determining mass transfer coefficients for the dissolution of solids in liquids in agitated systems. A major portion of the work reported on this subject has been done by Hixson and coworkers (*1* to *5*), and Wilhelm, Conklin, and Sauer (*10*) and Mack and Marriner (*8*) have also published experimental results. Most recently Johnson and Huang (*7*) described a series of experiments designed for a basic study of rates of dissolution of solids from a flat surface into liquids under turbulent agitation in a mixing tank.

All these experiments have been carried out in batch systems wherein the agitated liquid is brought in contact with an initial quantity of salt. As dissolution occurs, the surface area of the solid phase and the concentration of the agitated solution change continuously from the beginning to the end of a run. Since the rate of mass transfer from solid to liquid depends on both surface area and concentration, it also varies continuously with time. This obviously complicates the taking of data and the calculation of mass transfer coefficients for such systems, and it may partly explain why so few experimental investigations have been made of this subject.

One method of obviating these difficulties is to design a steady-flow system in which salt and solvent are continuously added to an agitated solution in a mixing tank while the solution is continuously withdrawn. At steady state the surface area of the solid and the concentration of the solution remain constant. The concentration of the solution can then be readily measured, and the surface area of the solid can be calculated by a method to be described. The objective of the present research was to investigate the use of such a system for the purpose of determining mass transfer coefficients.

D. W. Humphrey is at present with Research Laboratories, Standard Oil Company of Indiana, Whiting, Indiana, and H. C. Van Ness is at Rensselaer Polytechnic Institute, Troy, New York.

Table 1. Approximate Experimental Conditions

	Propeller	Turbine
Impeller speed, rev./min.	From 400 to 1,300	From 200 to 600
Water-flow rate, gal./min.	1.3	1.3
Feed rate of hydrated salt, g./min.	105	From 75 to 125
Initial surface area of salt, sq. ft./lb.	15.6	From 9.0 to 15.6

The salt used for this purpose was sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) in the form of commercial *Hypo rice*, and tap water was used as the solvent. Hypo rice was selected because of its ready availability, its regular crystalline form, and the relative ease with which it may be suspended in water.

EXPERIMENTAL

A schematic diagram of the equipment is shown in Figure 1. The mixing vessel was a flat-bottomed, cylindrical can, 1 ft. in diameter and 15 in. high. It contained four symmetrically located baffles which extended 1 in. from the side of the vessel. Two impellers were used, one a three-blade, 4-in.-diam., marine-propeller type and the other a six-blade (flat), 4-in., radial-flow turbine manufactured by The Mixing Equipment Company. Both were mounted centrally and vertically in the mixing tank three in. from the bottom, speed control being obtained by a pulley system between the shaft and the motor. The liquid depth in the tank was maintained at 12 in.

Water was fed to the mixing vessel from a constant-head tank. Solution flowed from the mixing tank through an overflow tap in the side of the tank. The outlet was covered with a 40-mesh screen to prevent salt particles from leaving the tank. The water line and the overflow line were fitted with quick-closing valves so that flow in both might be stopped simultaneously. The overflow line also contained an orifice and a conductivity cell for indicating flow rate and concentration, which were used merely to show when steady state was reached.

The salt feeder consisted of a rotating wheel fitted with small buckets, which lifted the salt crystals from a bin and dumped them into the tank. In a steady state system the feed rate is, of course, equal to the rate of solution.

The approximate experimental conditions are given in Table 1. Original experimental data are given by Humphrey (*6*).

THE MASS TRANSFER COEFFICIENT

According to the film theory, the mass transfer of salt from the surface of a salt particle to the main body of a turbulent liquid is treated as if it occurred by molecular diffusion through a laminar layer of liquid surrounding the salt particle, the layer being thick enough to contain all the concentration gradient. Since the degree of agitation affects the rate of mass transfer, it is assumed to control the thickness of this laminar layer. The rate of mass transfer by diffusion through the laminar layer is given by the equation

$$(N_s)_d = -D_s A_s \frac{dC_s}{dy} \qquad (1)$$

Mass transfer by bulk flow also occurs in the laminar film, however, because the solvent diffuses toward the solid-liquid interface under the influence of the concentration gradient and can be removed only by bulk flow of solution from the interface to the main body of the liquid. The rate of diffusion of solvent toward the interface is given by an equation analogous to Equation (1):

$$(N_f)_d = D_f A_s \frac{dC_f}{dy} \qquad (2)$$

The picture is further complicated by the fact that the salt used in this work ($Na_2S_2O_3 \cdot 5H_2O$) contained water of hydration, which can be transferred to the main body of the aqueous solution only by bulk flow. Bulk flow refers only to the movement of solution as a unit away from the interface, and thus it accomplishes transfer of salt as well as solvent from the interface to the main body of the solution. The total rate of transfer of salt is the sum of the rates of transfer by molecular diffusion and by bulk flow:

$$(N_s)_t = (N_s)_b + (N_s)_d \qquad (3)$$

Similarly, the rate of transfer of water from the interface to the main body of solution is

$$(N_f)_t = (N_f)_b - (N_f)_d \qquad (4)$$

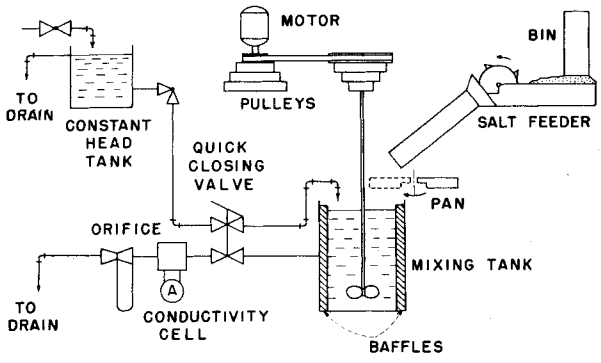

Fig. 1. Schematic diagram of equipment.

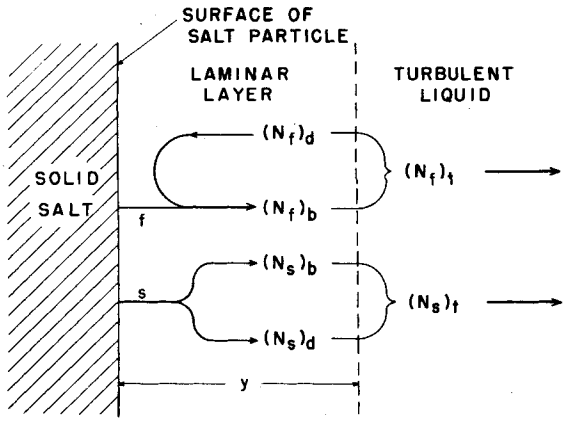

Fig. 2. Mechanisms of mass transfer.

These various transfer mechanisms are illustrated schematically in Figure 2.

Since bulk flow amounts to transporting the solution as a whole, the total rate of bulk flow of salt plus water at any point in the laminar film is

$$\frac{(N_f)_b}{1 - x_s} = \frac{(N_s)_b}{x_s} \tag{5}$$

where x_s is the mole fraction of salt in the laminar film at any point.

Furthermore, the over-all result of all transfer operations is to put the hydrated salt in solution. Thus:

$$\frac{(N_s)_t}{z_s} = \frac{(N_f)_t}{1 - z_s} \tag{6}$$

where z_s is the fraction of the total transfer that is salt, i.e., the mole fraction of salt ($Na_2S_2O_3$) in the hydrate ($Na_2S_2O_3 \cdot 5H_2O$).

Equations (1) through (6) may be combined to give the total rate of transfer of salt at any point in the laminar film:

$$(N_s)_t = \frac{z_s A_s}{z_s - x_s}\left[x_s D_f\left(\frac{dC_f}{dy}\right) - (1 - x_s)D_s\left(\frac{dC_s}{dy}\right)\right] \tag{7}$$

If the concentrations in Equation (7) are replaced by

$C_s = (\rho/M)x_s$ and $C_f = (\rho/M)(1 - x_s)$

after suitable rearrangement it becomes

$$(N_s)_t = -\frac{z_s A_s D_s(\rho/M)}{(z_s - x_s)}\left(\frac{dx_s}{dy}\right) + \frac{z_s A_s x_s(D_f - D_s)}{z_s - x_s} \cdot\left[(1 - x_s)\frac{d(\rho/M)}{dy} + (\rho/M)\frac{dx_s}{dy}\right] \tag{8}$$

In most instances the second term on the right of Equation (8) is small compared with the first term, and in the interest of simplicity it may be neglected. The reason for this is that x_s is usually small even for saturated solutions, and for sodium thiosulfate its maximum value at room temperature is 0.065. Also, this term will vanish if D_f and D_s are the same. Although this is true for ideal gases, it is not necessarily true for liquids. Neglecting this term, leads to an equation analogous to that used for gaseous diffusion:

$$(N_s)_t = -\frac{z_s A_s D_s(\rho/M)}{(z_s - x_s)}\left(\frac{dx_s}{dy}\right) \tag{9}$$

Since $(N_s)_t$ is constant, integration of Equation (9) from the interface to the bulk conditions gives

$$(N_s)_t = \frac{z_s A_s D_s(\rho/M)_m}{y} \cdot \ln\left[\frac{z_s - (x_s)_2}{z_s - (x_s)_1}\right] \tag{10}$$

where the subscript 2 indicates bulk conditions and 1, the saturation value at the interface. If the mass transfer coefficient is defined as $K' = D_s/y$, Equation (10) becomes

$$(N_s)_t = K' z_s A_s(\rho/M)_m \cdot \ln\left[\frac{z_s - (x_s)_2}{z_s - (x_s)_1}\right] \tag{11}$$

where $(\rho/M)_m$ is the arithmetic mean of the values at the interface and in the bulk of the solution. Equation (11) was used in this work for the calculation of values of K'. For $Na_2S_2O_3 \cdot 5H_2O$, z_s has a value of $\frac{1}{6}$. If z_s is unity and if $(x_s)_2$ and $(x_s)_1$ are small, this equation reduces to the more common form:

$$(N_s)_t = K(\rho/M)A_s(x_{s_1} - x_{s_2}) = KA_s(C_{s_1} - C_{s_2})$$

SURFACE AREA DETERMINATION

The calculation of mass transfer coefficients by Equation (11) requires that the surface area of the suspended salt particles be known. This area was calculated from the weight of suspended salt particles and their initial area, the weight being determined by stopping all flows simultaneously at the end of a run and measuring the increase in concentration of the solution caused by the dissolution of the suspended salt. In all cases concentrations were determined by titration with a standardized iodine solution.

Consider the dissolution of a single salt particle having an instantaneous weight W_i and area A_i. If it is assumed that the shape of the particle does not change as it dissolves, then

$$W_i = E^3 Q^3 \tag{12}$$

and

$$A_i = \alpha E^2 Q^2 \tag{13}$$

where Q = equivalent diameter of the particle, i.e., the diameter of a sphere equal in volume to the salt particle, and E and α = constants depending on the density and shape of the particle.

Equation (11) may be written for an individual salt particle as it dissolves in a system at steady state:

$$\frac{1}{M_s}\left(\frac{dW_i}{d\theta}\right) = A_i(\rho/M)_m K' z_s \cdot \ln\left[\frac{z_s - (x_s)_2}{z_s - (x_s)_1}\right] \tag{14}$$

If W_i and A_i are eliminated by Equations (12) and (13) and the resulting equation is integrated for steady-flow conditions, the result is

$$Q = Q_0 - \frac{\theta\alpha M_s(\rho/M)_m K' z_s}{3E} \cdot \ln\left[\frac{z_s - (x_s)_2}{z_s - (x_s)_1}\right] \tag{15}$$

This equation shows that the equivalent diameter of a single salt particle Q is a linear function of the time after it was introduced, as all other quantities in the equation are independent of time.

Therefore at any time during the steady-flow process a series of sizes of salt particles will be present in the mixing tank, one size for each different moment a particle was added to the tank. Since the salt particles were added at a regular period, and all were of approximately the same size initially, the sizes which exist in the tank at the moment a particle is added are

$$\frac{Q_0}{s}, \frac{2Q_0}{s}, \frac{3Q_0}{s}, \cdots, \frac{jQ_0}{s}, \cdots, \frac{sQ_0}{s}$$

Of course, at other times the sizes will be slightly different, but this series of sizes is adequate for an excellent approximation of the surface area when s is large. The area of all salt particles in the mixing tank is calculated by summing the areas of all sizes of the series. For this purpose it is convenient to relate the total area of the salt particles suspended in the mixing tank to some collective property such as their total weight:

$$A_s = BW_s \qquad (16)$$

The coefficient B was evaluated from Equations (16), (12), and (13) as follows:

$$B = \frac{A_s}{W_s} = \frac{\sum_{j=0}^{s} \alpha E^2 (jQ_0/s)^2}{\sum_{j=0}^{s} E^3 (jQ_0/s)^3}$$

$$= \frac{s\alpha \sum_{j=0}^{s} j^2}{EQ_0 \sum_{j=0}^{s} j^3}$$

$$B = \left(\frac{s\alpha}{EQ_0}\right)\left[\frac{(s)(s+1)(2s+1)/6}{s^2(s+1)^2/4}\right]$$

$$= \frac{2\alpha}{3EQ_0}\left(2 - \frac{1}{s+1}\right)$$

For large values of s (In the present work s was about 500.) this becomes

$$B = \frac{4}{3}\left(\frac{\alpha}{EQ_0}\right) \qquad (17)$$

but

$$\frac{A_0}{W_0} = \frac{\alpha E^2 Q_0^2}{E^3 Q_0^3} = \frac{\alpha}{EQ_0} \qquad (18)$$

Equations (16), (17), and (18) may be combined to give

$$A_s = (4/3)(A_0/W_0)W_s \qquad (19)$$

The equation for the surface area of suspended salt particles at steady state was developed on the assumption that all salt particles added to the solution were initially of the same size and shape. Actually this was only approximately true. However, Equation (19) should be valid for a small range of initial particle sizes and shapes if a representative mean value is used for A_0/W_0. Since the crystals used in this work were approximately cylindrical in shape, the initial area was determined from their average linear dimensions.

RESULTS

The mass transfer coefficients as calculated by Equation (11) were correlated by an equation of the type suggested by Hixson and Baum (*2*):

$$\frac{K'd}{D_s} = a\left(\frac{\mu}{\rho D_s}\right)^{0.5}\left(\frac{nd^2\rho}{\mu}\right)^b \qquad (20)$$

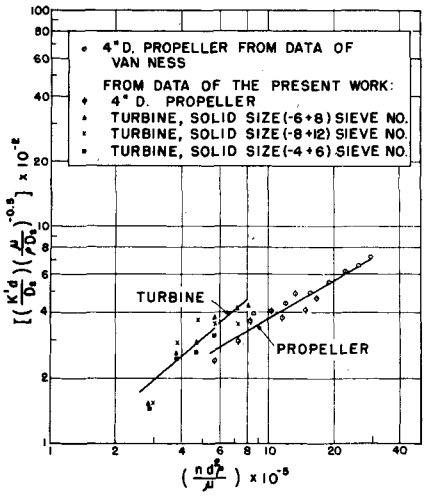

Fig. 3. Correlation of mass transfer coefficients.

The 0.5 power on the Schmidt group has been established both by Hixson and Baum (*2*) and by Johnson and Huang (*7*). The power b on the Reynolds number varies from system to system, as does the coefficient a. In the present work the results for the propeller showed a to be 0.13 and b to be 0.58. Results for the turbine gave a as 0.0032 and b as 0.87. These results were determined from the lines shown on Figure 3.

Included on this plot are some results obtained a number of years ago by one of the authors (*9*) for batch experiments in an identical system with the same propeller that was employed in the present work. No runs were made at that time with the turbine. It is seen that the results for the batch runs with this propeller correlate well with the results of the steady-flow runs of the present investigation for the same propeller.

DISCUSSION

The most significant result of this research is the agreement of the steady-flow results with the batch results reported by Van Ness (*9*) for the same system. This appears to demonstrate the validity of the method used to calculate surface area in the steady-flow experiments.

Only one size of salt particle was used for the propeller runs: particles passing a 6-mesh screen and collecting on an 8-mesh screen. For the turbine runs several sizes of particles were used, as shown on Figure 3. While the results scatter somewhat, there is no correlation of K' with respect to particle size. This further confirms similar conclusions reached by Wilhelm, Conklin, and Sauer (*10*) and by Van Ness (*9*).

The rather poor precision of results shown in Figure 3 is caused by a fundamental difficulty in making steady-flow runs. The weight of salt suspended under steady conditions was calculated from a *difference* between two very nearly equal concentrations. Thus small errors in concentration measurements can cause rather large errors in the value of W_s and hence A_s, the weight and area of suspended salt. Precision could no doubt be improved by refinements in technique. The only other disadvantage of the flow method is that rather large quantities of salt are used.

The anticipated advantages of the steady-flow method were well demonstrated in practice. Sampling of the solution is a simple matter, and the necessity of integrating the rate equation with time is avoided.

NOTATION

a = coefficient in Equation (20)
A_s = surface area of suspended salt at steady state, sq. ft.
A_i = instantaneous surface area of a single salt particle dissolving under steady state conditions, sq. ft.
A_0 = initial surface area of an individual salt particle, sq. ft.
b = exponent in Equation (20)
B = coefficient in Equation (16)
C_f = concentration of solvent, lb. moles/cu. ft.
C_s = concentration of salt, lb. moles/cu. ft.
d = size factor, taken as tank diameter, ft.
D_f = diffusivity of the solvent, sq. ft./hr.
D_s = diffusivity of the salt, sq. ft./hr.
E = a constant in Equations (12) and (13)
K' = mass transfer coefficient in Equation (11), lb. moles/(hr.)(sq. ft.)/(lb. mole/cu. ft.)
M = molecular weight of solution
M_s = molecular weight of the salt as the solid hydrate
n = rotational velocity of impeller, rev./min.
$(N_s)_t$ = total rate of mass transfer of salt, lb. moles/hr.
$(N_f)_t$ = total rate of mass transfer of solvent, lb. moles/hr.
$(N_s)_d$ = rate of mass transfer of salt by diffusion, lb. moles/hr.
$(N_f)_d$ = rate of mass transfer of solvent by diffusion, lb. moles/hr.
$(N_s)_b$ = rate of mass transfer of salt by bulk flow, lb. moles/hr.
$(N_f)_b$ = rate of mass transfer of solvent by bulk flow, lb. moles/hr.
Q = equivalent diameter of salt particle, ft.
Q_0 = initial equivalent diameter of salt particle, ft.
s = number of different sizes of salt particles suspended at steady state
W_s = weight of suspended salt particles at steady state, lb.
W_i = instantaneous weight of a single salt particle dissolving under steady state conditions, lb.

W_0 = initial weight of a single salt particle, lb.
x_s = mole fraction of salt in solution
y = thickness of the laminar film, ft.
z_s = fraction of total mass transfer which is salt, mole basis
α = constant in Equation (13)
θ = time, hr.
μ = viscosity of solution, lb./(hr.)(ft.)
ρ = density of solution, lb./cu. ft.

LITERATURE CITED

1. Hixson, A. W., and G. A. Wilkens, *Ind. Eng. Chem.*, **25**, 1196 (1933).
2. Hixson, A. W., and S. J. Baum, *ibid.*, **33**, 478 (1941).
3. *Ibid.*, **34**, 120 (1942).
4. *Ibid.*, 194 (1942).
5. Hixson, A. W., T. B. Drew, and K. L. Knox, *Chem. Eng. Progr.*, **50**, 592 (1954).
6. Humphrey, D. W., M.S. thesis, Purdue University, Lafayette, Ind. (1956).
7. Johnson, A. I., and C. J. Huang, *A. I. Ch. E. Journal*, **2**, 412 (1956).
8. Mack, D. E., and R. A. Marriner, *Chem. Eng. Progr.*, **45**, 545 (1949).
9. Van Ness, H. C., M.S. thesis, Univ. Rochester, Rochester, N. Y., (1946).
10. Wilhelm, R. H., L. H. Conklin, and T. C. Sauer, *Ind. Eng. Chem.*, **33**, 453 (1941).

Presented at A.I.Ch.E. Pittsburgh meeting

Ion Exchange Separation of Gram Quantities of Americium from a Kilogram of Lanthanum

D. E. ARMSTRONG, L. B. ASPREY, J. S. COLEMAN, T. K. KEENAN, L. E. LaMAR, and R. A. PENNEMAN

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico

The separation of 4.5 g. of americium from approximately a kilogram of light rare earths (primarily lanthanum) was achieved on a pilot plant scale by chromatographic displacement of the mixture from Dowex-50 resin with 0.1% ammonium citrate at *p*H 8 into hydrogen-form Dowex-50. The americium collected into a narrow band and was eluted free from lanthanum but contained an equal weight of cerium. A 6- and a 2-in.-diam. column were used in tandem. Use of a final column with a much smaller diameter would have permitted a cleaner separation from cerium, but this was left for a laboratory-scale separation by a different process. Precipitation, which was observed in the columns during the first runs, was later avoided entirely by use of high flow rates both initially and during the transfer between columns. No adverse effects were noted from ~15 curies of alpha activity.

The success of Spedding and Powell (*1*, *2*) in separating kilogram quantities of rare earths by displacement from Dowex-50 using 0.1% ammonium citrate at *p*H 8 suggested that this technique could be applied advantageously to the separation of americium from gross quantities of lanthanum, provided that gram amounts of trivalent americum behaved like a rare earth of intermediate atomic number and, in addition, that several curies of alpha activity would not interfere. Tracer-scale work (*3*) had shown that americium eluted at about the same position as promethium in the elution analysis of a mixture of trivalent rare earths and americium using ammonium citrate and Dowex-50. Thus, in the displacement of a mixture of americium and lanthanum from Dowex-50 using 0.1% ammonium citrate at *p*H 8, the elution positions should be in the aforementioned order after attainment of equilibrium. Furthermore, one would expect that moving the rare earth-americium band through a relatively few equivalent lengths of resin would achieve separation since the problem is essentially that of separating two light rare earths separated by four atomic numbers.

When a macro mixture of rare earths is displaced from Dowex-50 resin with 0.1% ammonium citrate at *p*H 8 into additional hydrogen-form Dowex-50, a series of head-to-tail bands develops, each band containing a substantially pure rare earth with overlap only at the boundaries (*1*, *2*). Furthermore, after equilibrium band lengths are attained, the length of a band is invariant, and elution through additional resin achieves no further separation. Obviously therefore it is preferable to have rare earth bands long with respect to their width, so that cross-contamination by overlap is minimized. This behavior is quite different from that of a mixture of rare earths under *elution analysis* conditions, where bell-shaped rather than flat bands develop and increasing the length of the column increases the distance between adjacent elution peaks.

EXPERIMENTAL

A limit of ⅓ kg. of lanthanum per run was imposed for several reasons: (1) there were restrictions due to the neutron and gamma activity from the americium associated with this amount of lanthanum; (2) ⅓ kg. of lanthanum would load a 2½-ft. resin bed, 6 in. in diameter, to 25% capacity originally and to half its length when the rare earth band had stretched out to equilibrium; (3) some such limit was suggested by the reported (*1*) formation of a precipitate when the initial loading of light rare earths exceeded 1.2 g./sq. cm. of column cross section; (4) exploratory work with a 5-cm. I.D. column and a resin-bed height of 70 cm. showed that lanthanum and americium were separated when the column was loaded to 22% capacity with a portion of the lanthanum-americium mixture to be separated. However, near the leading edge of the original absorbed band precipitation occurred, causing a portion of the americium to be held up. This precipitate dissolved and caught up with the main americium band before its elution.

It has been reported (*2*) that precipitation of the heavier rare earths can be avoided even with very high loading of the resin bed if high initial flow rates are used during spreading out of the rare earth band. After the rare earth band is spread out to its equilibrium length, the flow rate can be lowered. With 0.1% ammonium citrate at *p*H 8 used, the attainment of this equilibrium length involves lengthening of the band from its original absorbed length, in which nearly all the exchange sites are occupied by rare earth, to approximately twice this length (*1*).

There was available about a kilogram of light rare earths, consisting primarily of lanthanum with 5% cerium, in which americium was present to ~0.5 wt. % (4.5 g. of Am^{241}). Consequently, ⅓ kg. of lanthanum would contain only 1.5 g. of americium or ~18.5 meq. of trivalent americium. On a 2-in.-diam. column (20 sq. cm. area), with a resin capacity of 2 meq./cc., the final americium band would theoretically be only ~0.9 cm. long. (With 0.1% ammonium citrate, *p*H 8, the composition of the resin within the equilibrium band is divided about equally between ammonium and rare earth form.) Obviously, with such a length-to-width ratio, one could not anticipate a clean separation from the beginning edge of the rare earth immediately following. Nevertheless, if banding of the americium were obtained comparable to that reported for the rare earths, then adequate separation of the americium from the bulk of impurities would be achieved.

The combination of a 6- and a 2-in.-