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PROCESSING OF PLUTONIUM BY ION EXCHANGE IV.
THE SEPARATION OF PLUTONIUM
FROM WEAKLY SORBED IMPURITIES

Printed in USA. Price $ 0.75 Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

LA-3040
UC-10, CHEMICAL SEPARATIONS
PROCESSES FOR PLUTONIUM AND
URANIUM
TID-4500, 28th Ed.

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REPORT WRITTEN: January 1964

REPORT DISTRIBUTED: April 29, 1964

PROCESSING OF PLUTONIUM BY ION EXCHANGE IV.

THE SEPARATION OF PLUTONIUM FROM WEAKLY SORBED IMPURITIES

By

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Contract W-7405-ENG. 36 with the U. S. Atomic Energy Commission

ABSTRACT

Sorption of plutonium(IV) on anion-exchange resin from 7$\underline{M}$ nitric acid is an excellent method for its purification. Only a limited number of other elements are sorbed, and most of these only weakly. The fate of such weakly sorbed impurities in this purification process is discussed theoretically for several degrees of approximation to the actual system. A numerical computer calculation closely duplicates the experimental behavior of four selected impurity elements.

ACKNOWLEDGEMENTS

The authors wish to thank the personnel of Group CMB-1 who performed the radiochemical analyses and those in the recovery section of Group CMB-11 who assisted with the large column experiment.

In the purification of plutonium by anion exchange a nitric acid solution is percolated through an anion-exchange column. The resin has a much greater affinity for the plutonium than for the impurities. Essentially all the plutonium is held by the anion-exchange resin, while the impurities may partially pass through the column during this loading operation. The column is then washed with plutonium and impurity-free nitric acid solution which removes the impurities from the column. This report describes some theoretical and experimental investigations aimed at estimating the separation obtained.

The separation of ions in an ion-exchange column has been thoroughly studied in the case of no interaction between the various ions. We shall review the results briefly in several degrees of approximation and computational complexity. The possibility of interactions between ions in the resin phase makes the problem more complex mathematically, and numerical solutions are necessary. The behavior of weakly sorbed impurities may be affected by the presence of plutonium. The presence of large amounts of sorbed plutonium may not only reduce the amount of impurities that are sorbed at equilibrium,[1] but may also affect their rates of diffusion through the resin phase.

As a zero-order approximation we may assume that the impurities behave completely independently of the plutonium and of each other and that equilibrium is instantaneously achieved. Then if an impurity is distributed uniformly at a molar concentration c_o in the feed solution of volume V_F, the material will begin to load the column as a "square wave" (see Fig. 1) with constant composition c_o in the solution phase and $\bar{c}^*$ in moles per liter of resin solid in the resin phase.† Equilibrium concentrations in the resin phase are related by the distribution coefficient λ,

$$\bar{c}^* = \frac{c_o \lambda}{1 - \epsilon} , \qquad (1a)$$

or

$$\bar{x}^* = c_o \lambda , \qquad (1b)$$

where $\bar{x}^*$ is equilibrium concentration in the resin phase in moles per liter of resin bed and ϵ is the fraction of this bed which is void. It should be noted that $\bar{c}^*/c$ is constant for a given resin while λ depends upon ϵ, which varies with packing efficiency.

Since the capacity of the column is

$$V_c \bar{x}^* + \epsilon V_c c_o = V_c c_o (\lambda + \epsilon) , \qquad (2)$$

where V_c is volume of the column (solution plus solid), the impurity will appear at the bottom of the column when a volume

$$V_B = V_c (\lambda + \epsilon) \qquad (3)$$

has been fed to the column. The front of the wave moves at a velocity

$$v_w = \frac{v}{\lambda + \epsilon} \qquad (4)$$

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† The definitions of all symbols are listed at the end of this report.

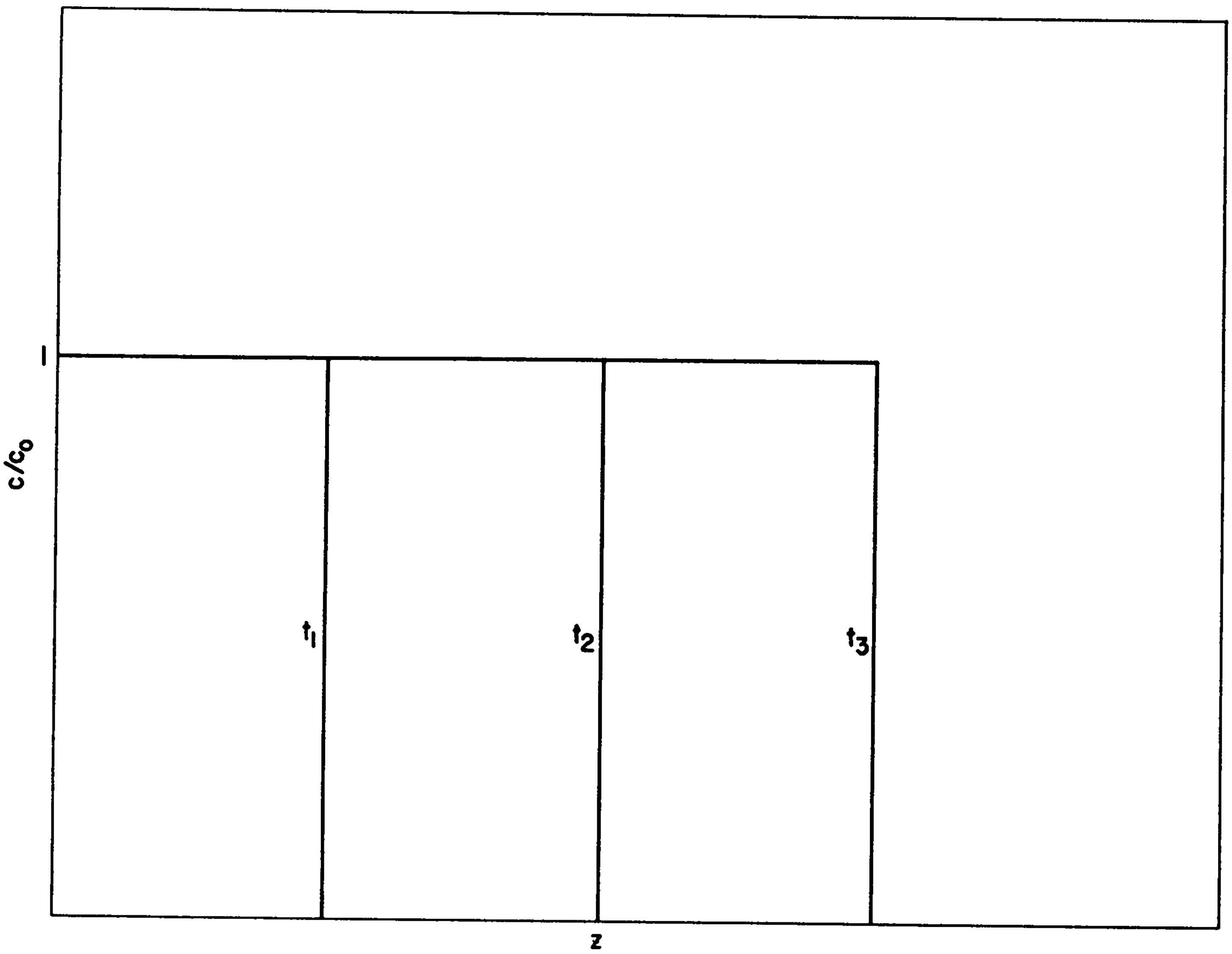

Fig. 1. Development of Wave During Feed Step with Instantaneous Equilibrium

where v is the velocity of the solution outside the column. Equation (4) holds whether feed or wash solution is being run into the column; in the latter case the rear boundary of the wave will also move with velocity v_w. Equation (4) also holds whether breakthrough takes place before or after the wash begins. If λ is equal to or less than a particular value, say λ_k, then the breakthrough of the impurity will occur during the loading step.

$$\lambda_k = \frac{V_F}{V_c} - \epsilon . \qquad (5)$$

Since under our assumptions of instantaneous, independent equilibrium the raffinate after breakthrough is always at concentration c_o, the impurity will be eluted exactly V_F liters after breakthrough. This can all be summarized by plotting the fraction of the total amount of the impurity remaining in the column as a function of raffinate volume (see Fig. 2). While the assumptions with this model are very sweeping, the controlling rate processes for the impurities are usually quite rapid compared to those for plutonium, and the above model comes close to the actual situation.

The next level of approximation is the standard ion-exchange-column theory[2] based on a mass balance for a quasi-steady state; it accounts for rate effects of diffusion in the resin and solution by the "theoretical plate" concept. The column is treated as a countercurrent system, and the "height of a theoretical plate" is the height of a segment of the column where the resin leaving it is in equilibrium with the solution entering it. This theoretical plate height, H, is given by the sum of four terms representing the effects of finite particle size, diffusion in the solid phase, diffusion in the static layer of solution around the beads, and longitudinal diffusion in the moving solution phase. In the typical processing conditions which we have considered, the first and

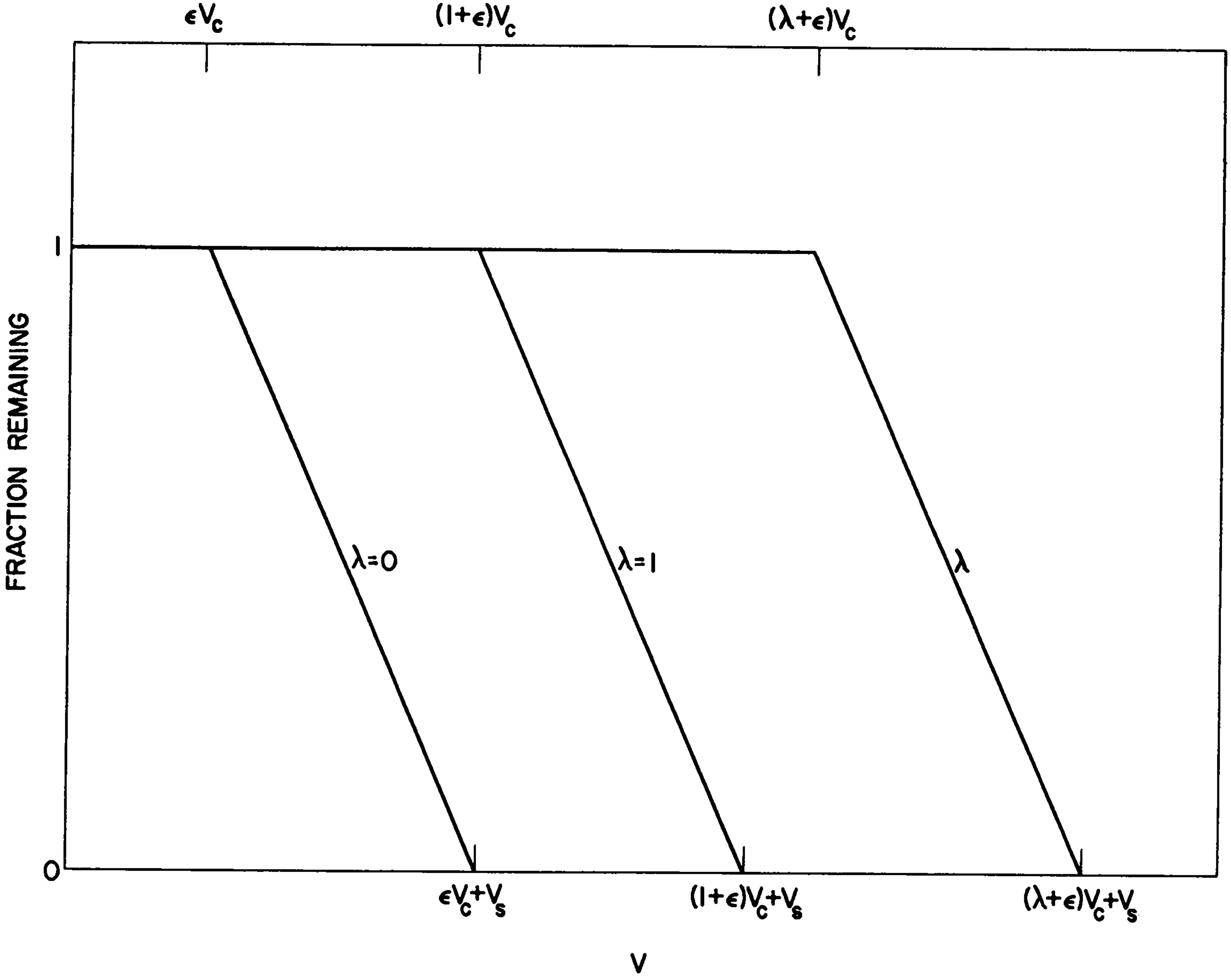

Fig. 2. Fraction of Impurity Remaining

last terms are negligible, and the resin diffusion usually predominates. If we consider only resin diffusion as significant, then

$$H = \frac{0.14r^2v\lambda}{\overline{D}(\lambda + \epsilon)}, \tag{6}$$

where $\overline{D}$ is the diffusion coefficient in cm^2/sec, and r is the average radius of the beads. The diffusion equation, which describes the solution concentration with the column, takes the form (for constant λ)

$$\frac{\partial c}{\partial z} + a(\lambda + \epsilon)\frac{\partial c}{\partial V} - \frac{H}{2}\frac{\partial^2 c}{\partial z^2} = 0 , \tag{7}$$

where z is distance along the column and a is the cross-sectional area of the column. The solutions of Equations (6) and (7) are simplest in terms of the number of plates,

$$N = \frac{z}{H} , \tag{8}$$

and the number of plate elution volumes,

$$M = \frac{V}{(\lambda + \epsilon)aH} . \tag{9}$$

The solution under constant feed into an empty column for $N > 3$ is

$$\frac{c}{c_o} = \frac{1}{2} - A_\epsilon\left(\frac{N - M}{\sqrt{M}}\right), \tag{10}$$

where A_ϵ is the error integral

$$A_\epsilon(y) = \frac{1}{\sqrt{2\pi}} \int_0^y e^{-y^2/2}\, dy \, . \tag{11}$$

The loading will proceed with a constantly spreading wave front (see Fig. 3), which is characteristic of a linear isotherm (constant λ). In our case we have a wash step also, during which the input concentration is zero. The solution can be written as the sum of two terms, each based on Equations (10) and (11), but with one displaced in volume by V_F. Defining M_F by replacing V with V_F in Equation (10), the complete solution, valid for $M > M_F$, is

$$\frac{c}{c_0} = A_\epsilon\left(\frac{N - M + M_F}{\sqrt{N - M_F}}\right) - A_\epsilon\left(\frac{N - M}{\sqrt{M}}\right). \tag{12}$$

The elution curve is shown in Fig. 4. The rectangle is the result of the zero-order approximation discussed earlier, and it has a width of V_F. If ΔV is the extra volume of wash required to remove the impurity over that necessary for the case in which instantaneous equilibrium is assumed, then from Fig. 4,

$$\Delta V \approx (\lambda + \epsilon) a \sqrt{\frac{\pi}{2} ZH} \, , \tag{13}$$

where Z is the length of the column. Actually, at an elution volume of $(\lambda + \epsilon)V_c + V_F + \Delta V$, the value of c/c_0 is not zero but about 0.1, and 1 or 2 percent of the impurity remains in the column. Most of this is eluted in the next $\Delta V/2$, so a better approximation for the total elution volume is

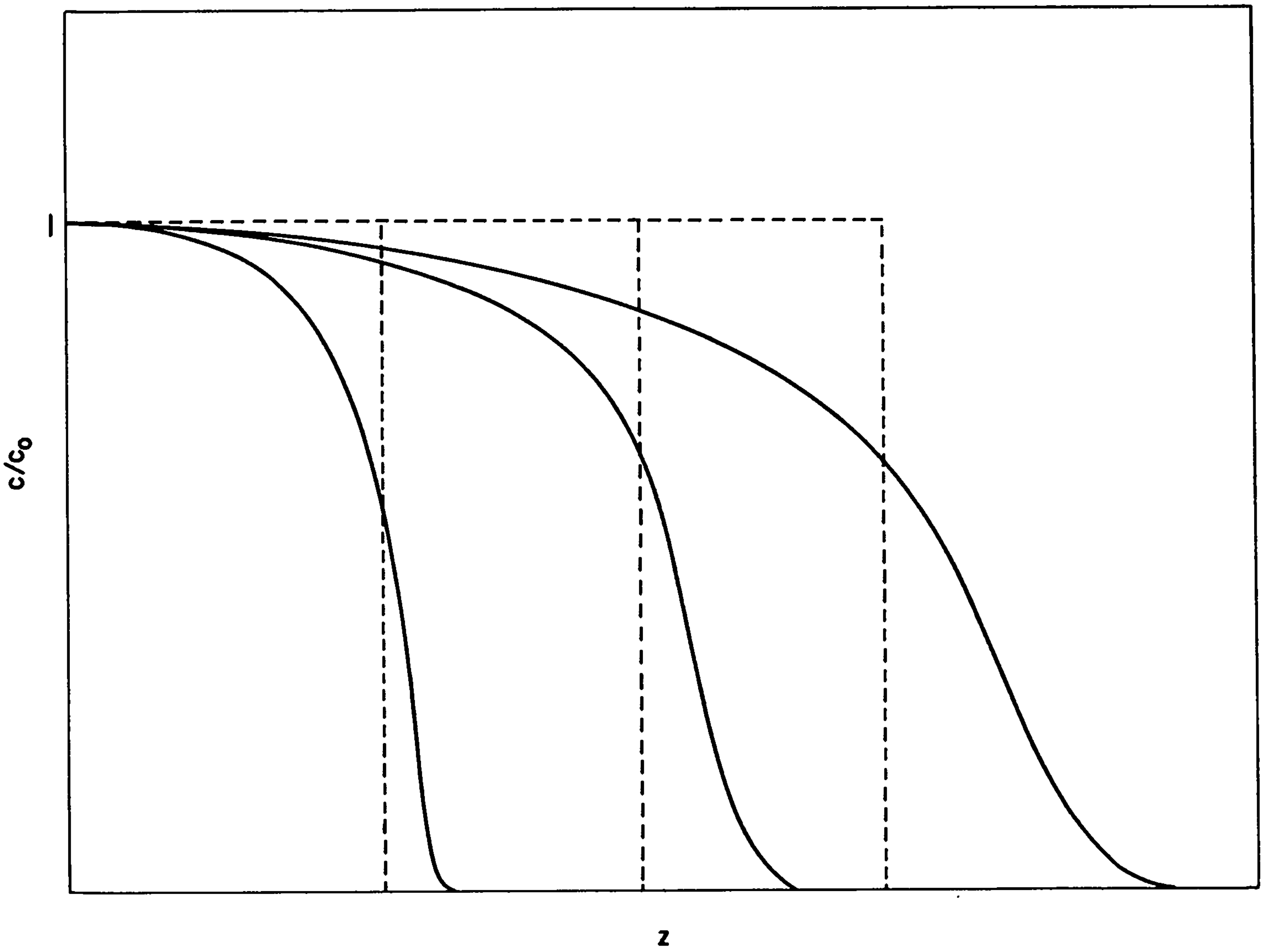

Fig. 3. Development of Wave During Feed Step with Finite Diffusion Rates

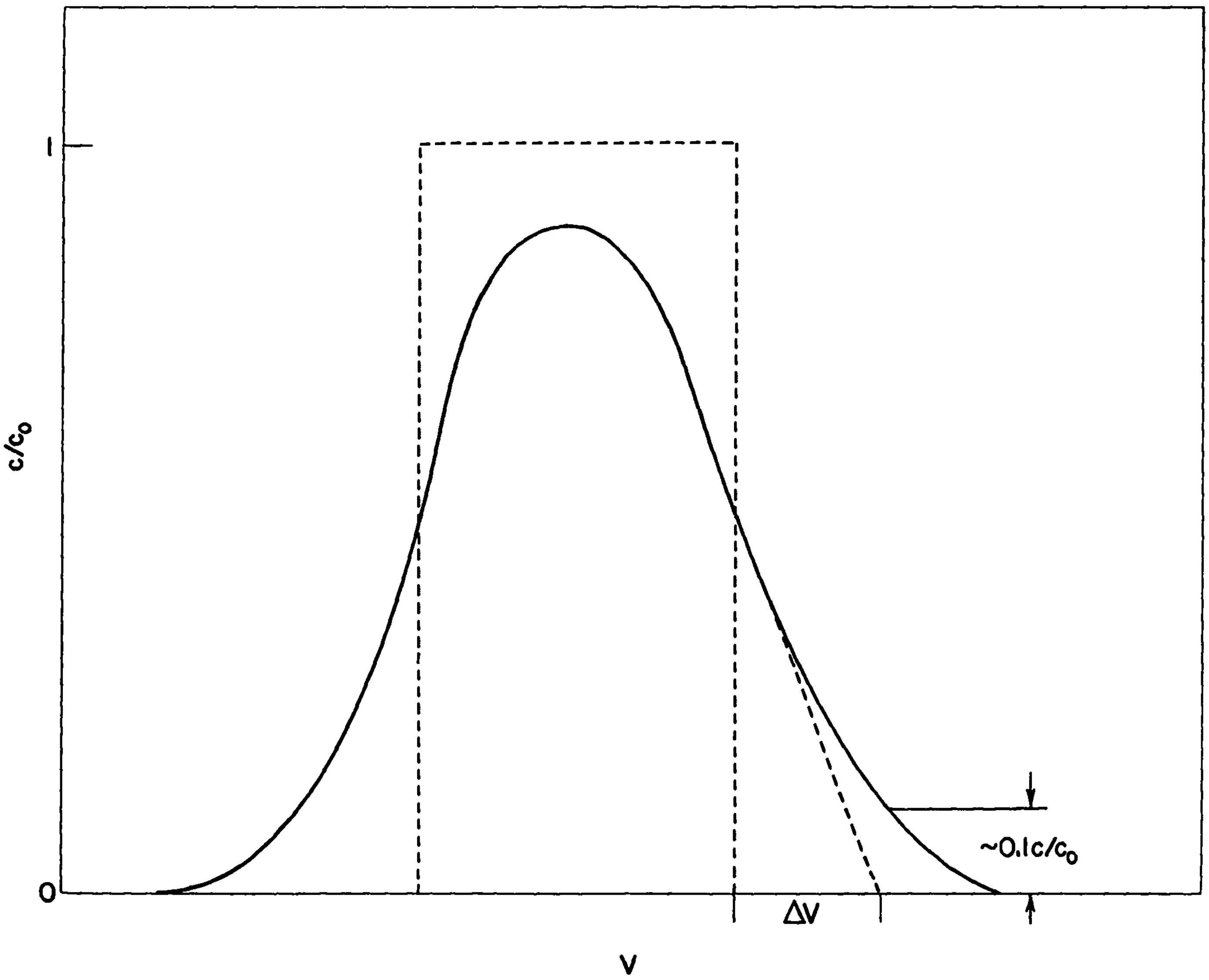

Fig. 4. Elution Curve

$$V_T = V_F + (\lambda + \epsilon)(V_c + 2a\sqrt{ZH}). \qquad (14)$$

Equation (14) is valid only for a constant feed concentration. The problem of a variable feed concentration can be handled by considering only the feed concentration just prior to the wash step. The amount of wash necessary to remove an infinitesimal amount of this feed is then added to the total feed volume, V_F. This problem was also considered by Glueckauf.[2] He computed the width W of the wave at a concentration of e^{-1} of the maximum concentration in the wave to be

$$W = V_c(\lambda + \epsilon)\sqrt{\frac{8}{N}} \; . \qquad (15)$$

We are interested in the half-width, ΔV, for the more general case where the concentration is down to $e^{-\eta}$ of the maximum. This is

$$\Delta V = V_c(\lambda + \epsilon)\sqrt{\frac{2\eta}{N}} \; . \qquad (16)$$

This leads to the result in Equation (14) when $\eta = 2$. Hence we see that Equation (14) is completely general for impurities that do not interact with the plutonium in either phase and load such a small fraction of the exchange sites that λ is constant.

We now consider a model that approximately describes the behavior of impurities in the presence of plutonium, as found by a detailed numerical calculation.[3] The behavior of plutonium in anion-exchange systems was the subject of Reference 4. We shall consider only that case where the impurities are present at a concentration which will allow them to load only a trace amount of the resin sites, so that they do not affect the behavior of the plutonium. We shall allow for a possible reduction in both $\bar{D}$ and λ of each impurity, caused by the presence of strongly bound plutonium.

James[1] showed that the trace level loading distribution coefficient of an impurity should be reduced by a factor

$$\left(1 - \frac{\bar{c}_{Pu}}{\bar{C}_{Pu}}\right)^2 = \frac{\lambda}{\lambda_o} , \qquad (17)$$

where $\bar{C}_{Pu}$ is the capacity of the resin for plutonium as calculated from the capacity for anions, $\bar{c}_{Pu}/\bar{C}_{Pu}$ is the fraction of sites occupied by plutonium, and λ_o and λ are the distribution coefficients in the absence and presence of plutonium, respectively. However, this equation was found not to hold for several impurities when thorium was used instead of plutonium. In fact, λ/λ_o was found to be greater than unity for several elements for $0 < \bar{c}_{Th}/\bar{C}_{Th} < 0.5$.

Reference 4 showed empirically that the resin diffusion coefficient for plutonium is given by

$$\bar{D}_{Pu} = \bar{D}^o_{Pu} \, e^{-k\bar{c}_{Pu}/\bar{C}_{Pu}} , \qquad (18)$$

with $\bar{D}^o_{Pu} = 1.5 \times 10^{-9} cm^2/sec$ and $k = 5.5$. We therefore assumed that the impurity diffusion coefficients would be reduced by a factor $\exp(-k\bar{c}_{Pu}/\bar{C}_{Pu})$. The diffusion coefficients of several weakly sorbed impurity elements were measured in the absence of plutonium. These experiments are described in the appendix. The diffusion coefficients were 30 to 75 times higher than that of plutonium.

With these factors in mind an approximate analytical model was formed. The impurities move down the column much faster than the plutonium, and at the normal process flow rates they approach equilibrium behavior (the zero-order approximation). It was shown earlier that for equilibrium behavior the concentration of impurities in the solution in the column should be a square wave (see Fig. 1). However, as the plutonium is sorbed on top of the impurities, if Equation (17) applies, the impurity distribution coefficients should be reduced and the impurities forced out of the resin by the advancing plutonium wave. The impurities displaced from the resin would be added to c_o and the concentration of the impurities should rise above that of the feed solution in the region ahead of the advancing plutonium wave. This is described by Fig. 5 (A and B).

From Fig. 5, by assuming there is a negligible amount of impurity in the resin, the concentration of the impurity in the solution phase ahead of the advancing plutonium wave is

$$c = c_o \left[1 + \frac{\lambda z_P}{(\lambda + \epsilon) z_i}\right] \qquad (19)$$

and

$$z_i = \frac{V_F}{a(\lambda + \epsilon)} - z_P \; . \qquad (20)$$

The length of the plutonium wave, z_P, is determined independently.[3] Combination of Equations (19) and (20) yields

$$\frac{c}{c_o} = 1 + \frac{a\lambda z_P}{V_F - a z_P(\lambda + \epsilon)} \; . \qquad (21)$$

When the wash operation is initiated, z_P remains constant, and the impurity in the solution over the plutonium wave moves ahead, adding Δz_i to the front of the wave (see Fig. 5C). A material balance gives

$$\Delta z_i = \frac{\epsilon z_P z_i}{(\lambda + \epsilon) z_i + \lambda z_P} \; . \qquad (22)$$

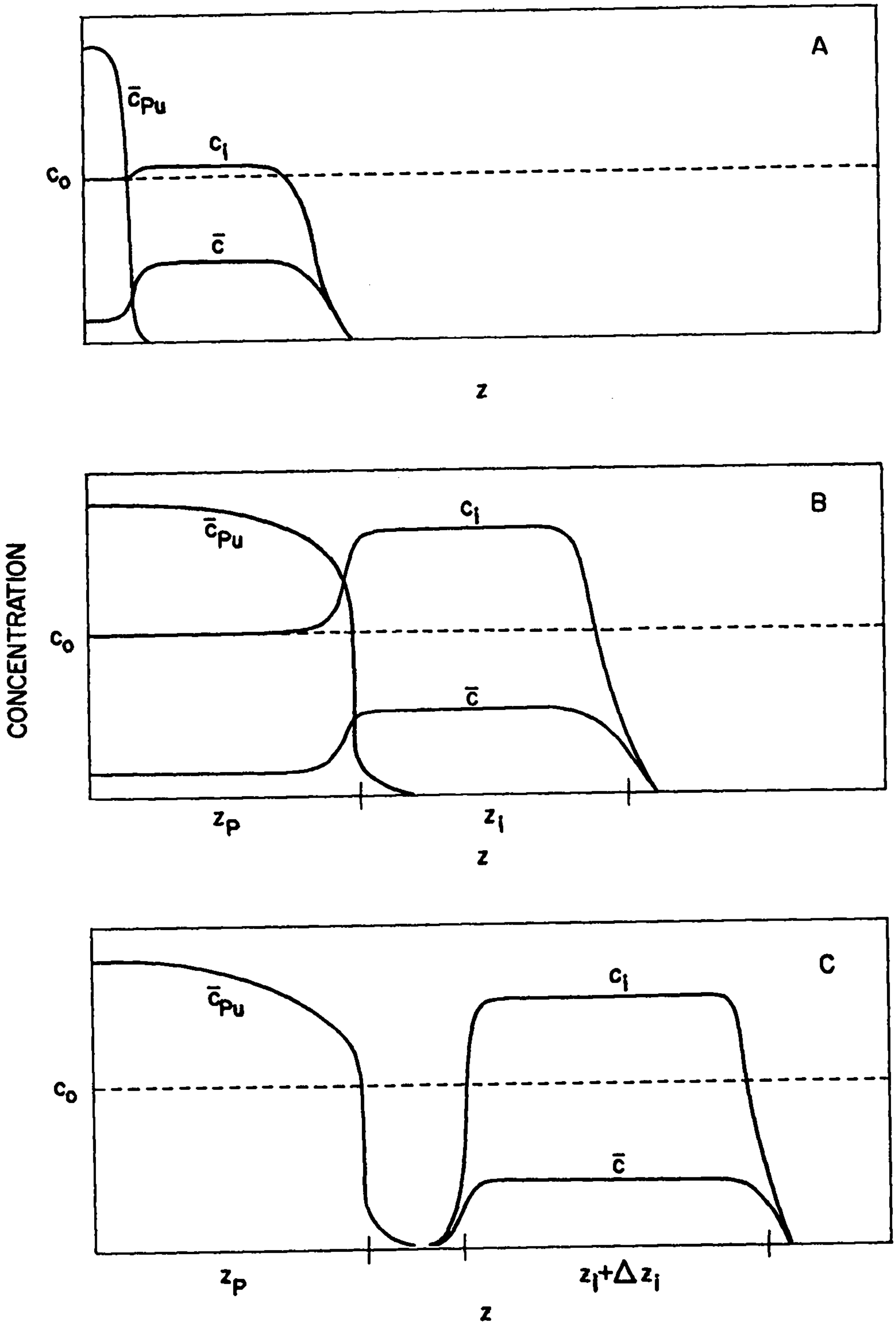

Fig. 5. Plutonium Exclusion of an Impurity

The impurity wave then separates from the plutonium wave, moving independently as described earlier, except that c is greater than the feed concentration.

This simple model begins to fail for large λ (say >3) when z_1 becomes quite small, and the impurity concentration is not flat but peaked at the front of the plutonium wave. Also the only effect due to the plutonium was caused by the reduction of λ, Equation (17). Inclusion of an exponential effect on the diffusion coefficient would trap a small amount of impurity in the plutonium wave. This would be released slowly, and the impurity wave would develop a long tail as it separated from the plutonium wave during the wash step.

An experiment, described in the appendix, was conducted using Ag, Hg, Bi, and U as impurities. The concentration of impurities in the eluate was measured. The results are shown by the data points in Fig. 6. While the long tails are apparent, the effect of Equation (17) is apparently absent, except possibly for Ag. The initial and boundary conditions of this experiment were applied to a numerical calculation, described in Reference 3. The inclusion of Equation (17) in the calculation produced impurity breakthrough concentrations, which rose several times higher than the feed concentrations. This effect was certainly not observed. In the absence of specific experimental data for the effect of plutonium on the impurity distribution coefficients, it was assumed that they are not affected, and this calculation produced a more reasonable result. The inclusion of an exponential effect on the diffusion coefficients in the calculation duplicated the observed tailing.

A final approximate correction was made in the code for the effect of diffusion in the film of static solution surrounding the beads of resin. Of course, no data are available for the diffusion coefficients, but they usually range from 10^{-6} to $10^{-5} cm^2/sec$. The lower value gave much better fits to the leading portion of the elution curves for the

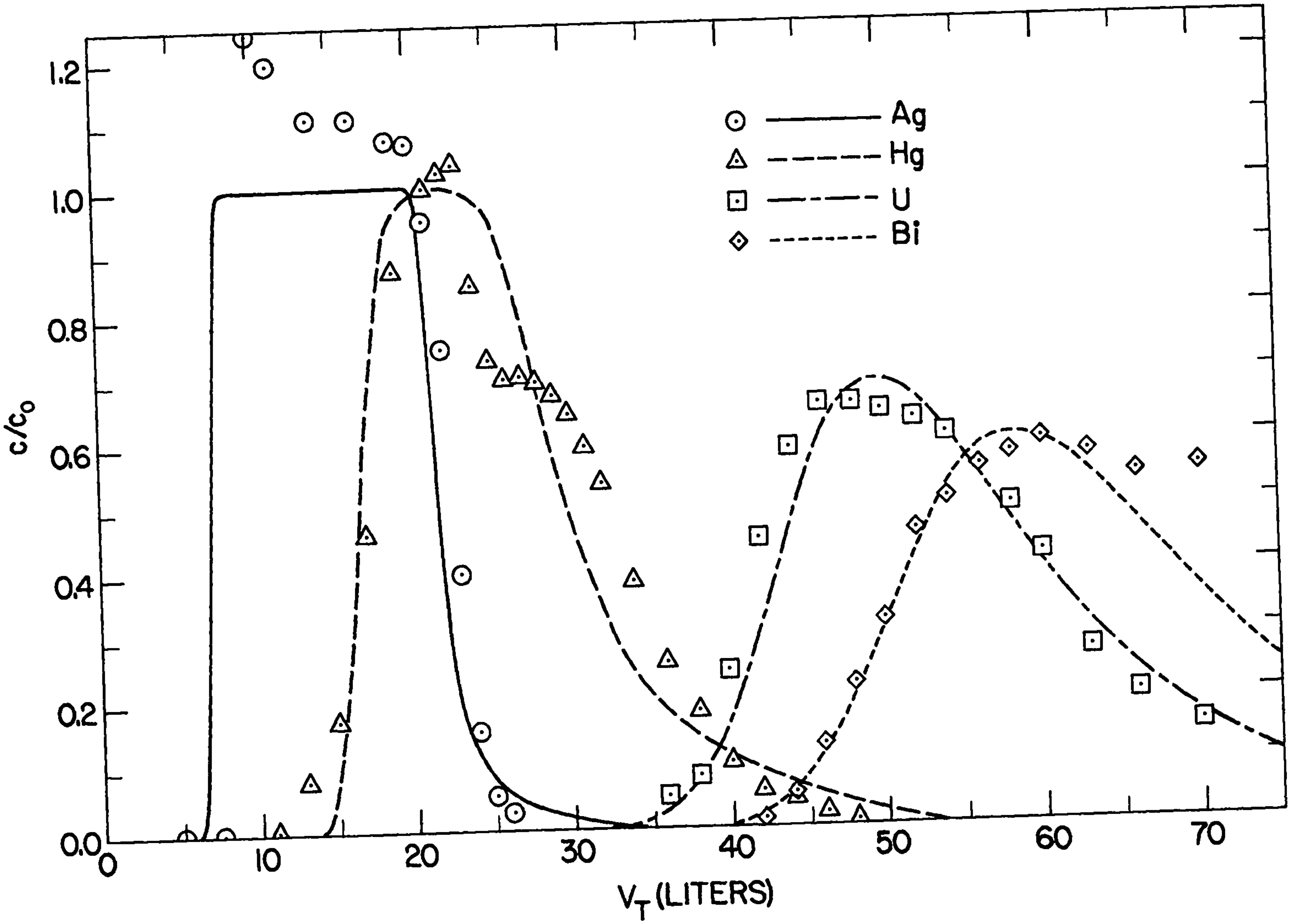

Fig. 6. Impurity Breakthrough Curves

elements with larger λ. In all cases the film correction had a negligible effect on the total volume of wash required to elute the impurity. The results of the numerical calculation with these modifications are given by the curves in Fig. 6.

Probably the quantity of greatest importance in this separation is the volume of wash solution necessary to remove a certain fraction of the impurity from the column. This is presented in Fig. 7. The abscissa is the wash volume (total raffinate minus V_F) divided by ϵV_c sufficient to leave the fraction in the column given by the ordinate. The curves are somewhat dependent upon V_F, $\bar{D}^o$ of the impurity, v, V_c, and the capacity of the column, but these are secondary effects. The computation was made for a column similar to the one described in the appendix. The feed contained sufficient plutonium to load the column about half full of plutonium.

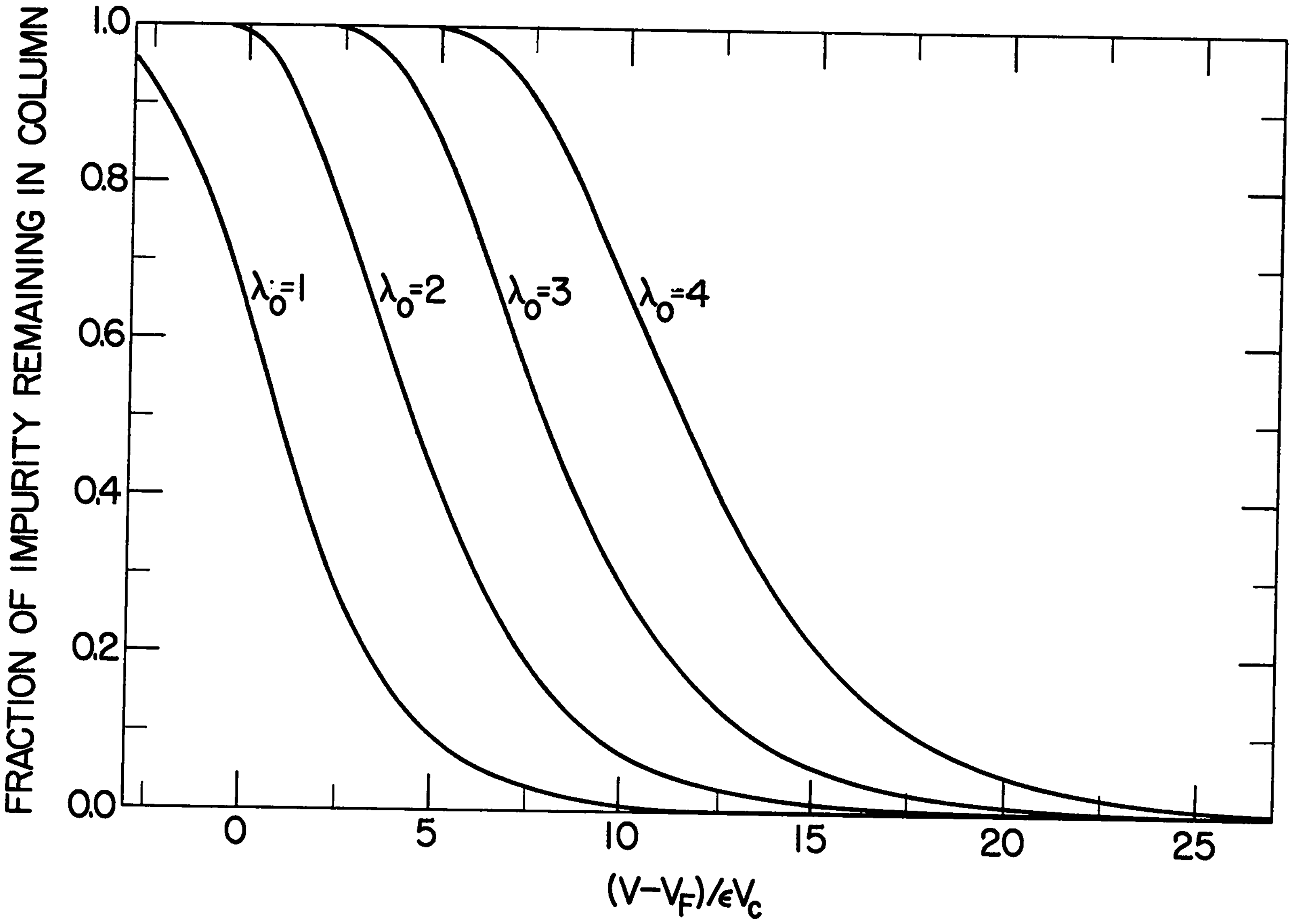

Fig. 7. Fraction of Impurity Remaining on Column

APPENDIX

In systems where solid diffusion is rate-controlling, $\bar{D}^o$ can be determined by following the progress of a very short wave of sorbed material as it is eluted down a very long column. This is easily done by scanning the column with a shielded GM tube and using a radioactive isotope of the element to be investigated. The apparatus for such experiments was described earlier.[5]

From Glueckauf,[2]

$$N = 2\pi \left(\frac{c_{max}}{m} V \right)^2 , \qquad \text{(A1)}$$

where c_{max} is the maximum concentration in the wave, m is the total amount of sorbed species in the wave, and V is the volume of solution necessary to move the band N plates. However, the scanning device measures the height, h, of the wave as recorded on a moving-chart recorder and the area, α, under this recorded wave. The quantity h/α is measured in the dimensions of centimeters of column length, so by dimensional analysis,

$$\frac{c_{max}}{m} = \frac{hd}{\alpha V} \quad , \qquad (A2)$$

where d is the distance the maximum of the wave has moved. Therefore, Equation (A1) takes the form,

$$N = 2\pi \left(\frac{hd}{\alpha}\right)^2 . \qquad (A3)$$

The number of theoretical plates between two successive measurements of the progress of the band is

$$N_2 - N_1 = \frac{2\pi}{\alpha^2} \left[(h_2 d_2)^2 - (h_1 d_1)^2\right] . \qquad (A4)$$

Using Equation (6) and the fact that $H = (d_2 - d_1)/(N_2 - N_1)$ we obtain,

$$\bar{D}^{o} = \frac{0.284\pi r^2 v \lambda^{o}[(h_2 d_2)^2 - (h_1 d_1)^2]}{(\lambda^{o} + \epsilon)\alpha^2(d_2 - d_1)} . \qquad (A5)$$

Of course, λ^{o} is also easily determined from [5]

$$\lambda^{o} = \frac{V_2 - V_1}{(d_2 - d_1)a} - \epsilon . \qquad (A6)$$

By measuring h, d, V, v, α, and a and using Equations (A5) and (A6), the diffusion coefficients of several elements were determined. The results are shown in Table AI.

Table AI

Particle-Diffusion Coefficients

Isotope	$\bar{\bar{D}}^o (\times 10^8)\ cm^2/sec$
^{46}Sc	8
^{90}Y	7
$^{152-154}Eu$	10
^{141}Ce	9
^{203}Hg	4
^{110}Ag	7

The accuracy is probably no better than ±50 percent.

The column used in the experiment reported earlier (Ag, Hg, Bi, and U trace elements) was assembled from a 2-foot section of 6-inch-inside-diameter glass pipe. A weighed amount of resin was loaded into the column in the moist state and contacted with 7M nitric acid. A second section of 6-inch glass pipe was secured to the top of the column. The resin bed was raised (backwashed) by forcing 7M nitric acid into the column through the screen from below. The resin was allowed to slowly settle back to the screen, and the entire operation repeated. A weighed sample of the moist resin that was loaded in the column was washed, dried, and weighed to determine that 4150 g of "oven-dry" resin were added to the column. The capacity of the column, $\bar{C}_{Pu}$ = 1.11 moles/l of solid resin or 3.82 equivalents per "oven-dry" gram, was determined as described before.[5] Weight and volume measurements of a sample of resin that was compacted as above gave a value for ϵ of 0.31. In the column the resin was 54 cm high.

Five millicuries each of ^{110}Ag and ^{203}Hg were obtained from Oak Ridge National Laboratory, along with 10 mc of ^{210}Bi. These isotopes were diluted as received to 9.9 l with a 7M nitric acid solution containing 1 g/l each of silver, mercury, and bismuth. This solution was added to a plutonium solution to give 15.2 l of feed solution which contained 20.4 g_{Pu}/l. The feed solution was passed over the column at 5 l/hr and was followed by a 7M nitric acid wash at 12 l/hr. Samples of the raffinate were analyzed for the three isotopes above and for ^{237}U which was also present in the feed from the alpha decay of the plutonium. The results were plotted against volume of raffinate, and an integration gave the total amount in the raffinate. This was used to calculate the feed concentration.

The values of λ^o that were used in this calculation are

$$\lambda^o_{Ag} = 0.18$$

$$\lambda^o_{Hg} = 0.85$$

$$\lambda^o_{U} = 2.8$$

$$\lambda^o_{Bi} = 3.4$$

These agree reasonably well, after correction for the different ϵ, with values reported by James,[5] except for uranium; we can offer no explanation for this difference.

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NOMENCLATURE

A_ϵ	error integral (dimensionless)
a	cross-sectional area of the column (cm^2)
$\bar{C}_{Pu}$	total capacity of the resin for plutonium if all resin sites are occupied (moles/l of resin solid)
$\bar{c}$	concentration in the resin phase (moles/l of resin solid)
$\bar{c}^*$	equilibrium concentration in the resin phase (moles/l of resin solid)
c	concentration in the solution phase (moles/l of solution)
c_{max}	maximum concentration in the solution phase (moles/l of solution)
c_o	concentration in the feed solution (moles/l of solution)
$\bar{D}$	solid diffusion coefficient (cm^2/sec)
$\bar{D}^o$	solid diffusion coefficient (cm^2/sec)
H	height of a theoretical plate (cm)
h	height of recorded wave (cm)
k	empirical constant
M	number of theoretical plate elution volumes (dimensionless)
M_F	number of theoretical plate elution volumes per feed volume (dimensionless)
m	total amount of sorbed material on the column (moles)

Nomenclature (cont'd)

N	number of theoretical plates (unitless)
r	average radius of the resin particles (cm)
t	time (sec)
V	volume of solution phase passed (l)
V_c	column volume, or aZ (l)
V_F	volume of the feed solution (l)
V_T	total volume of solution passed (l)
v	solution velocity inside the column (cm/sec)
v_w	velocity of the wave front (cm/sec)
W	width of the elution wave (l)
$\bar{x}$	concentration in the resin phase (moles/l of resin solid)
$\bar{x}^*$	concentration in the resin phase under equilibrium conditions (moles/l of resin solid)
Z	length of the column (cm)
z	distance along the column (cm)
z_i	length of the impurity wave (cm)
z_P	length of the plutonium wave (cm)
α	area under recorded wave (cm^2)
ϵ	fraction of a settled bed of resin that is solution (dimensionless)
η	parameter (dimensionless)
λ	distribution coefficient or $\bar{x}/c$ (moles/l of resin bed per moles/l of solution phase)