ELUTION REQUIREMENTS FOR ION-EXCHANGE SEPARATION OF URANIUM ISOTOPES

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SUMMARY

The necessary flow rate and the effective bed length for the ion-exchange separation of uranium isotopes have been calculated using ROSEN's theory. The applicability of ROSEN's theory was verified using the isotope exchange of ^{235}U-^{238}U between the anion-exchange resin bed and 8.4 M hydrochloric acid. The effective feed rate and the estimated column bed length were 8.6×10^{-3} cm/sec and 3.4×10^2 cm, respectively, for the linear isotherm system of U(IV) using 8.4 M hydrochloric acid and the anion-exchange resin, Diaion SA10.

INTRODUCTION

Breakthrough operation has been frequently used for ion-exchange separation of isotopes since TAYLOR AND UREY[1] used the method to separate lithium isotopes with an inorganic ion exchanger, Zeolite. A method to estimate the degree of separation was derived for the breakthrough operation system by GLUECKAUF[2] who introduced "the number of theoretical plates" as the number of stages in the fixed resin bed in equilibrium with the eluent. GLUECKAUF's theory is expressed in eqn. 1 as the relative concentration of effluent, C/C_0,

$$\frac{C}{C_0} = \frac{1}{2} - A_\varepsilon \left\{ \frac{N-M}{\sqrt{M}} \right\} + \exp(2N) \left[\frac{1}{2} - A_\varepsilon \left\{ \frac{N+M}{\sqrt{M}} \right\} \right] \quad (1)$$

Here, $A_\varepsilon(t)$ is the area of the normal curve of error defined by

$$A_\varepsilon(t) = \frac{1}{\sqrt{2\pi}} \int_0^t \exp\left(-\frac{t^2}{2}\right) dt \quad (2)$$

N is the number of theoretical plates up to the point x,

M is the number of theoretical plate elution volumes contained in volume V.

However, GLUECKAUF's theoretical equation with a linear isotherm estimates neither the number of theoretical plates nor the degree of separation without first using practical separation.

A more rigorous theoretical expression for breakthrough curve for the linear equilibrium system had been derived earlier by ROSEN[3] who considered the presence

of both the fluid film and intraparticle diffusion resistance. ROSEN's expression uses the time required for the fluid to flow a distance and the time measured from an instant point reached by the fluid.

$$\frac{C}{C_0} = \frac{1}{2} + \frac{2}{\pi}\int_0^{\infty}\exp\{-XH_1(\lambda, \nu)\}\sin\{Y\lambda^2 - xH_2(\lambda, \nu)\}\frac{d\lambda}{\lambda}$$

$$H_1(\lambda, \nu) = \frac{H_1(\lambda) + \nu\{H_1(\lambda)\}^2 + \nu\{H_2(\lambda)\}^2}{\{1 + \nu H_1(\lambda)\}^2 + \{\nu H_2(\lambda)\}^2}$$

$$H_2(\lambda, \nu) = \frac{H_2(\lambda)}{\{1 + \nu H_1(\lambda)\}^2 + \{\nu H_2(\lambda)\}^2} \tag{3}$$

$$H_1(\lambda) = \frac{\lambda(\sinh 2\lambda + \sin 2\lambda)}{\cosh 2\lambda - \cos 2\lambda} - 1$$

$$H_2(\lambda) = \frac{\lambda(\sinh 2\lambda - \sin 2\lambda)}{\cosh 2\lambda - \cos 2\lambda}$$

The relative concentration can be given as a function of the three dimensionless parameters as follows:

$$\nu = \frac{D_s K}{r k_F}, \quad X = \frac{3D_s K(1 - \varepsilon)}{r^2} \cdot \frac{z}{u}, \quad Y = \frac{2D_s}{r^2}\left(t - \frac{z}{u/\varepsilon}\right) \tag{4}$$

The nomenclature is shown in Table I.

In this paper, the applicability of ROSEN's equation is discussed to predict the column performance of the isotopes of U(IV) in 8.4 M hydrochloric acid with an

TABLE I

EXPERIMENTAL CONDITIONS

Symbols	Nomenclature	U (IV)	Methods or formulae
R	radius of column	1.27/2 (cm)	
	ion-exchange resin	Diaion SA10A	
		(50 ~ 100 mesh)	
r	radius of resin particles	1.09 × 10⁻² (cm)	
z	bed length	90.0 (cm)	
ε	void fraction	0.3 (—)	
C_0	inlet concentration of solute in liquid	22.7 (g/l)	
	concentration of hydrochloric acid	8.4 M	
u	linear velocity	4.53 × 10⁻³	
		1.78 × 10⁻² (m/sec)	
t	temperature	30 (°C)	
q	concentration of U in resin	192 (g/l-resin)	
K	equilibrium constant	8.45 (—)	q/C_0
ϱ	density of fluid	1.15 (—)	
μ	viscosity of fluid	1.38 × 10⁻² (g/ml sec)	Ostwald's method
D_L	diffusivity of solute in liquid	1.80 × 10⁻⁶ (cm²/sec)	Ref. 11
a_v	surface area of particle per unit volume of bed	1.80 × 10² (cm²/ml)	$4\pi r^2/\frac{4}{3}\pi r^3$
Re	Reynolds number	8.24 × 10⁻³	
		3.24 × 10⁻² (—)	$Ru\varrho/2\mu$
Sc	Schmidt number	6.67 × 10³ (—)	$\mu/\varrho D_L$
k_F	fluid film mass transfer coefficient	2.95 × 10⁻⁴	
		5.88 × 10⁻⁴ (—)	$1.15\,(Re/\varepsilon)^{-1/2}Sc^{-2/3}\mu$

anion-exchange system. Some effects of isotope separation have been previously found in this system[4].

EXPERIMENTAL

A column (100 cm long, 1.27 I.D.) was used. A jacket was installed around the column to keep the experimental temperature constant, with 30° water circulating from a thermostat. The anion-exchange resin, Diaion SA10 (made by Mitsubishi Kasei Co. Ltd., Tokyo; corresponding to Dowex 1 X8), was employed. The experiments were carried out on the linear adsorption isotherm system of U(IV). 8.4 M hydrochloric acid was passed through the ion-exchange resin bed prior to each experiment. Feed solution I containing depleted uranium (the isotope fraction of ^{235}U = 0.355%) was fed into the column until a uranium solution having the same concentration as feed solution I was eluted from the column. Feed solution II containing natural uranium (the isotope fraction of ^{235}U = 0.730%) was fed into an anion-exchange resin column pre-saturated with feed solution I. The concentrations of uranium and H^+ in solutions I and II were made equal to each other, within analytical errors. The Reynolds number, the Schmidt number and the coefficient for fluid film mass transfer are necessary for the discussion of the applicability of ROSEN's equation. These values and their calculation are listed together with other experimental values and conditions in Table I. The void fraction is the value measured on the column saturated with depleted uranium. The surface area of the particle per unit volume of the bed was calculated from the mean radius of the resin particles used and the void fraction. The diffusivity value of U(IV) in 8.4 M hydrochloric acid was used instead of the self-diffusivity.

A solution of natural uranium tetrachloride was prepared by dissolving pure metal chips in hydrochloric acid under cooling after washing the chips with ethanol, dilute nitric acid and water. A solution of depleted uranium tetrachloride was prepared by the electrical reduction of the uranyl chloride solution. These uranium tetrachloride solutions were refined by passing them through an anion-exchange resin bed to remove uranyl chloride. Uranous ion concentration was analyzed by titration with potassium bichromate. The isotope ratios were determined by thermoionization, using an Atlas mass spectrometer model CH4 equipped with a single collector[5].

RESULTS AND DISCUSSION

The process in which natural U(IV) is substituted for depleted U(IV) pre-saturated by passing through the ion-exchange resin bed is as follows;

$$^{235}U(IV) + ^{238}\bar{U}(IV) \rightleftharpoons ^{238}U(IV) + ^{235}\bar{U}(IV)$$
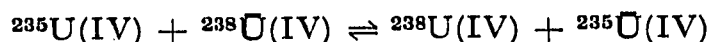
ROSEN's theoretical breakthrough curve was given by the relative effluent concentration expressed as a function of time, Y/X, for bed length X, and for film resistance v/X. Several numerical solutions were computed for the several values of bed length and film resistance selected by ROSEN[6]. The film resistance parameter v/X of this study can be calculated from the experimental data listed in Table I. The approximate value of the bed length was obtained from the curve fitting the numerical solutions which had been computed for various values of the bed length with OKITAC 9050

by KAWAZOE *et al.*[7]. The effective diffusion coefficient of U(IV) in spherical particles assumed constant by ROSEN was calculated from the value of X obtained from the curves. The effective diffusion coefficient of U(IV) was calculated as 1.5×10^{-9} cm^2/sec for the linear velocities, 4.5×10^{-3} and 1.8×10^{-2} cm/sec used in this study. Therefore, the applicability of ROSEN's theoretical equation to the systems employed in this study was confirmed. The experimental breakthrough curves of natural uranium were obtained from the isotope ratios of the effluent. The experimental points and the breakthrough curves calculated with the effective diffusion coefficients obtained are shown in Fig. 1.
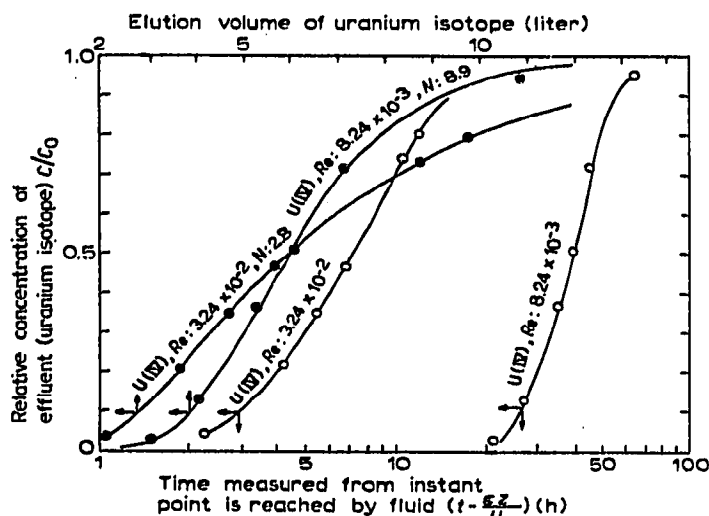

Fig. 1. Breakthrough curves of uranium isotopes. ○ and ●, observed points; ————, theoretical line.

For $X \geqq 50$ and $\nu \leqq 0.01$, the following expression, accurate to 1%, can be obtained directly from the integral of eqn. 3.

$$\frac{C}{C_0} = \frac{1}{2}\left[1 + \mathrm{erf}\left\{\frac{3Y/2 - X}{2\sqrt{X/5}}\right\}\right] \tag{6}$$

Substituting parameter E for $(3Y/2 - X)/2\sqrt{X/5}$ in eqn. 6, the following equation is obtained.

$$t - \frac{z}{u/\varepsilon} = \sqrt{\frac{4Kz\,(1 - \varepsilon)\,r^2}{15uD_s}}\,E + \frac{K\,(1 - \varepsilon)\,z}{u} \tag{7}$$

The parameter E can be calculated from the relative effluent concentration of natural uranium, using eqn. 6. The numerical values in the square root of eqn. 7 are constant, so that the effective diffusion coefficient can be evaluated from the slope obtained, plotting E *vs.* time, $t - \varepsilon z/u$. Fig. 2 is the graphical representation of the parameter E *vs.* time for the U(IV) system. The effective coefficients obtained were 1.4×10^{-9} and 1.6×10^{-9} cm^2/sec for the linear flow velocities of 4.5×10^{-3} and 1.8×10^{-2} cm/sec, respectively. These values agreed well with that obtained from the exact solution.

For $N > 3$, the second term of eqn. 1 becomes almost negligible. Eqn. 1 therefore is given by

$$\frac{C}{C_0} = \frac{1}{2} - A_\varepsilon \left\{ \sqrt{N} \frac{\bar{V} - V}{\sqrt{\bar{V}V}} \right\} \tag{8}$$

where $\bar{V}$ is the elution volume of the center of the S-shaped elution curve ($C = C_0/2$). We read the value of $\bar{V}$ and also the column volume V' of the concentration given by

$$\frac{C}{C_0} = \frac{1}{2} - A_\varepsilon \{1\} = 0.1587 \tag{9}$$

Then, the number of theoretical plates is obtained from eqn. 10.

$$N = \frac{\bar{V}V'}{(\bar{V} - V')^2} \tag{10}$$

The values obtained from the breakthrough curve which is represented by the effective effluent concentration of U(IV) *versus* the effluent volume in Fig. 1 were 2.8 and 8.9 for the linear flow velocities of 4.5×10^{-3} and 1.8×10^{-2} cm/sec, respectively. The breakthrough curves calculated using these numbers of theoretical plates, fitted the experimental points well. ROSEN's approximate equation and also GLUECKAUF's equation were verified to be possible within their assigned requirements.
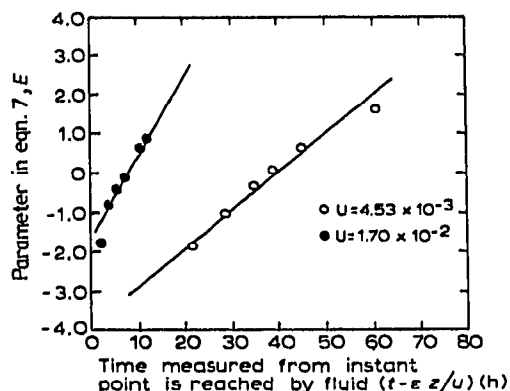

Fig. 2. Applicability of ROSEN's approximation (eqn. 4).

The ion-exchange separation factor of isotopes, a, is given by the ratio of the ion-exchange equilibrium constants of isotopes. Introducing an ion-exchange separation factor as follows,

$$a = \frac{K_2}{K_1} - 1 = \frac{X_2}{X_1} - 1 \tag{11}$$

one can estimate the separation factor and also the degree of separation for a linear equilibrium system by the method of LONDON[8]. A local enrichment factor, S, will be estimated by the following equation derived by substituting a for the effective bed length X in eqn. 6, on the assumption that the effective diffusion coefficients of isotopes are identical.

$$^1_2 S = \frac{^1C}{^1C_0} \cdot \frac{^2C_0}{^2C} = \frac{1 + \text{erf} \{(3Y/2 - X_1)/2\sqrt{X_1/5}\}}{1 + \text{erf} \{(3Y/2 - X_2)/2\sqrt{X_2/5}\}} = \frac{1 + \text{erf} (t_1)}{1 + \text{erf} (t_2)} \tag{12}$$

$$t_2 = \frac{1}{\sqrt{1 + a}} \{t_1 - a\sqrt{5X_1}/2\} \doteq t_1 - (\sqrt{5X_1}/2)a$$

The parameter $\sqrt{5}\overline{X}_1/2$ corresponds to the number of theoretical plates given by GLUECKAUF. The parameter is superior to that used by GLUECKAUF since it is expressed by the quantities exactly measurable as shown by eqn. 4.

Usually, for ion-exchange separation of isotopes, one employs the ion-exchange resin particles of 50–100 mesh of which the mean radius is 1×10^{-2} cm. The linear ion-exchange equilibrium constant of U(IV) using the anion-exchange resin SA10 and 8.4 M hydrochloric acid was measured as 40 up to 0.002 M U(IV). Substituting the values of the mean radius of the resin particles, the linear ion-exchange equilibrium constant and the effective diffusion coefficient of U(IV), 1.5×10^{-9} cm^2/sec, for the parameters, v and X, which are expressed by eqn. 4 and satisfy the requirements of eqn. 6, the following are obtained.

$$k_F \geqq 6 \times 10^{-4}, \quad z/u \geqq 4 \times 10^4 \tag{13}$$

Rewriting the coefficient of fluid film mass transfer with the Reynolds number and the Schmidt number[9], the above expression for k_F of ROSEN's approximate equation is described as follows.

$$1.15 \, (\varrho/\mu)^{1/6} \, (2/\varepsilon R)^{1/2} \, D_L{}^{2/3} \, u^{1/2} \geqq 6 \times 10^{-4} \tag{14}$$

The feed rate and the effective column bed length are calculated from eqns. 12–14, using the experimental data listed in Table I. The following results are obtained.

$$u \geqq 8.6 \times 10^{-3} \text{ cm/sec}, \quad z \geqq 3.4 \times 10^2 \text{ cm} \tag{15}$$

The number of theoretical plates is inversely proportional to the feed rate, so that an estimated feed rate of 8.6×10^{-3} cm/sec and a calculated effective column bed length of more than 3.4×10^2 cm are optimal. The longitudinal diffusion will be neglected for the isotope separation system mentioned above so far as the estimated effective feed rate is employed[10].

CONCLUSIONS

The elution requirements for the separation of uranium isotopes were estimated by ROSEN's theory and verified by the use of ^{235}U–^{238}U exchange in the linear equilibrium system between the anion-exchange resin and the hydrochloric acid. The optimal linear flow velocity and the effective length of the column bed could be determined from an invariable Schmidt number and a variable Reynolds number fixed experimentally. This study showed the applicability of ROSEN's theory to the pre-computation of a local enrichment factor along the eluted partitions from a column.

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