A comparative study of kinetic models for the extraction of uranium by strong-base anion-exchange resins

by C. A. FLEMING*, Ph.D. and
M. J. NICOL*, Ph.D. (Visitors)

SYNOPSIS

This paper examines the kinetics of the extraction of uranium from acid sulphate solutions by strong-base anion-exchange resins. Parameters such as the concentration of uranium in solution, the agitation of the resin beads in solution, the size of the resin beads, and the degree of cross-linking within the resin matrix were varied, and the effects on the kinetics are reported. The applicability of various empirical kinetic models to the description of the data is assessed, and an attempt is made at the modelling of the rate data in terms of established theories about the diffusion of ions through films of stagnant liquid and through spherical beads of resin.

SAMEVATTING

Hierdie referaat ondersoek die kinetika van die ekstraksie van uraan uit suur sulfaatoplossings met sterkbasis-anioonruilharse. Parameters soos die konsentrasie van uraan in oplossing, die roering van die harspêrels in die oplossing, die grootte van die harspêrels en die mate van kruisbinding binne die harsmatriks is gevarieer en daar word verslag gedoen oor die uitwerking daarvan op die kinetika. Die toepaslikheid van verskillende empiriese kinetiese modelle op die beskrywing van die data word geëvalueer en daar word gepoog om 'n model van die data oor die tempo op te stel in terme van bestaande teorieë oor die diffusie van ione deur lae stagnante vloeistof en deur bolvormige harspêrels.

Introduction

The continuous countercurrent ion-exchange process for the recovery of uranium from acidic leach liquors has, in recent years, become accepted as an attractive alternative to solvent extraction. There are several operating continuous ion-exchange plants in South Africa, and the process design and description of a typical plant has been reported[1]. The design and operating conditions for the continuous ion-exchange process are dependent on a quantitative understanding of the factors governing the thermodynamics and kinetics of the absorption and elution of uranyl ions by beads of anion-exchange resin.

Many ion-exchange processes are used in industry, and the rates of such processes are almost always controlled by diffusion through a film of stagnant liquid adjacent to the solid ion-exchanger (film diffusion), or through the pores of the ion-exchanger itself (particle diffusion), or by a combination of both. Very few ion-exchange interactions are known in which the rate of the chemical reaction between the exchanging ion and the functional group on the ion-exchanger is the slow step of the process[2]. Those interactions generally involve chelating resins, and are not considered here.

Film diffusion can be expected to prevail when resins of high capacity, low degree of cross-linking, and small particle size are in contact with inefficiently agitated dilute solutions. Conversely, particle diffusion should predominate when highly cross-linked low-capacity resins of large diameter are contacted with rapidly moving concentrated solutions. It is naturally expected that the initial stages of an ion-exchange process are controlled by film diffusion and the latter stages by particle diffusion.

As pointed out by Helfferich[3], diffusion in ion-exchangers is necessarily slower, for several reasons, than that in solution. Firstly, part of the cross-section of the ion-exchanger is occupied by the framework and is not available for diffusion, which necessarily must take place in tortuous pores. Secondly, the mobility of large ions may be impeded by the framework. Thirdly, interactions (electrostatic or otherwise) with the fixed ionic groups can retard diffusion. Finally, the generation of local electric fields in the ion-exchanger by virtue of the unequal rates of diffusion of the exchanging ions results in electrical transference (Nernst–Planck model). From these observations it can be concluded that the intraparticle diffusion coefficient is a function of the ionic composition of the ion-exchanger, and is generally not a constant parameter in the rate equation. It is for this reason that simple models of ion-exchange kinetics are often found to apply only to a limited range of solution and exchanger concentrations. This is particularly true of exchange reactions involving ions of greatly differing mobilities, such as those involving uranium.

The complexity of a full kinetic description in terms of the Nernst–Planck model has resulted in the widespread use of various empirical models in the design and operation of continuous ion-exchange equipment. This paper describes the results obtained during a laboratory study of the kinetics of the absorption of uranium onto various anion-exchange resins. The various empirical models that have been employed for design purposes were used in a comparative analysis of the data. In addition, an attempt was made, by variation of the experimental conditions, to isolate and distinguish the areas in which the rate of the process is controlled by either film diffusion or particle diffusion. The results were analysed in terms of the following simplified models.

*National Institute for Metallurgy, Randburg, Transvaal.

(1) The simple linear driving-force model[4,5] in terms of which the rate is proportional to the extent of the departure of the system from equilibrium. Thus, for particle diffusion,

$$d[U]_t/dt = k([U]_e - [U]_t) \quad \ldots\ldots\ldots \quad (1)$$

or, in the integrated form,

$$\ln\left(\frac{U_e - U_t}{U_e - U_o}\right) = -kt.$$

$[U]_e$ denotes the concentration of uranium in the resin at equilibrium with a solution having a uranium concentration $[U]_s$, and $[U]_t$ and $[U]_o$ are the concentrations of uranium in the resin at time t and at time o, and the constant k is a function of the diffusion coefficient of uranyl ions in the bead and the size of the bead.

(2) A quadratic driving-force equation, derived by Vermeulen[6] and used by Jagger[7], and subsequently used in the design of the NIMCIX plant[1], in terms of which the rate can be expressed as

$$\frac{d[U]_t}{dt} = \frac{D\pi^2}{r^2}\left[\frac{[U]_e^2 - [U]_t^2}{2[U]_t - [U]_o}\right].$$

D is an average intradiffusion coefficient and r is the radius of the resin bead. For $[U]_o = 0$ and $[U]_e$ a constant, integration of the above equation yields

$$\log\left[[U]_e^2 - [U]_t^2\right] = \frac{D\pi^2 t}{r^2} + \log\left[[U]_e^2\right] \quad \ldots \quad (2)$$

(3) The ash-layer or shell progressive model, which is known to describe the rate of many heterogeneous processes involving the diffusion of reactants into particles and the formation of a spherical reaction zone that spreads inwards. Moving boundaries of this sort have been observed microscopically in many ion-exchange processes. Schmuckler[2] et al. have, with considerable success, applied this model to simple ion-exchange processes. The relevant equation for rates controlled by particle diffusion is

$$t = \frac{r^2[IX]}{6D[U]_s}\left\{3 - 3\left(1 - \frac{[U]_t}{[U]_e}\right)^{2/3} - \frac{2[U]_t}{[U]_e}\right\}, \quad \ldots \quad (3)$$

where $[IX]$ is the concentration of exchangeable groups in the resin. These simplified models describe rate data under conditions in which control by particle diffusion is dominant. Model (3) can, at the expense of additional mathematical complexity, accommodate film-diffusion control, as discussed below. Under conditions of film-diffusion control only, the rate equation can be written

$$\frac{d[U]_t}{dt} = k_{MA}\left[[U]_s - [U]_s^e\right],$$

where $[U]_s^e$ is the concentration of the uranium at the bead surface, where it will be in equilibrium with the resin having an average concentration of $[U]_t$. For low $[U]_s$, the absorption isotherm can be approximated to a linear dependence of $[U]_e$ on $[U]_s$, and substitution of the $[U]_s$ and $[U]_s^e$ terms in the above equation by those involving $[U]_t$ and $[U]_e$ yields an equation of the same form as (1). Thus, model (1) can be expected to describe the kinetics under conditions in which the rate is controlled by film diffusion.

The results are discussed in terms of these three models, the functional forms of which are referred to as f(1), f(2), and f(3).

Experimental Method

Unless stated otherwise, all the experiments were carried out at room temperature with sized samples of resin that had been converted to the sulphate form by treatment with 1M sodium sulphate and washed with distilled water. The resins used were an experimental high-density strong-base resin, BRS 76, prepared at the National Institute for Metallurgy, and conventional strong-base resins containing various amounts of the cross-linking agent divinylbenzene (DVB) prepared by Diaprosim. In addition, the commercial strong-base resins A101 DU and IRA 400 were examined.

The rate of loading of uranium was studied in an all-glass fluidized-bed reactor[8], the experimental procedure being the same as that described in detail elsewhere[9]. Briefly, uranium solution is pumped through a reactor, which fluidizes the resin, and then through an optical flowcell located in the sample compartment of an ultraviolet spectrophotometer. The wavelength of the spectrophotometer is adjusted to give a convenient absorbance with the desired uranium solution circulating in the apparatus. As uranium is extracted by the resin, the ultraviolet absorbance decreases and sufficient concentrated uranium is added to the reactor from an external source to restore the original absorbance level. The volume of concentrated solution added, when plotted as a function of time, produces a kinetic profile of the reaction.

Solutions were prepared that contained 50, 100, 200, or 500 p.p.m. of U_3O_8 (as uranyl sulphate) and 30 g/l sodium sulphate. Unless stated otherwise, all the solutions were adjusted with sulphuric acid to a pH value of 1,8. All the concentrations of uranium are quoted in terms of U_3O_8 content, and the volumes of resin as wet-settled volume in bisulphate form.

Experimental Results

The effects of the various parameters on the rate of uptake of uranium are given below, and the data are analysed in such a way that comparisons can be made between the three kinetic models described above.

The Effect of Particle Size

Three size fractions, 420 to 500 μm, 500 to 590 μm, and 590 to 842 μm, of the resin BRS 76 were obtained by wet-screening, and the rates of extraction by these resins from solutions in the concentration range 50 to 500 p.p.m. of uranium were measured. An analysis of the rate data in terms of the slopes of the plots of functions f(1), f(2), and f(3) is presented in Table I. Instead of numerous graphical plots of f(x) versus time, a qualitative assessment of the linear relationships was made, and these relationships are denoted in Table I as good, fair, poor, or non-linear. The non-linear assessment (Nl) was applied only when no straight line could reasonably be drawn through any portion of the data points.

TABLE I

THE EFFECT OF SIZE OF RESIN BEADS ON THE KINETICS OF URANIUM EXTRACTION FROM VARIOUS SOLUTIONS ONTO A STRONG-BASE ANION-EXCHANGE RESIN, BRS 76, RESIN WELL FLUIDIZED (≈ 200% BED EXPANSION)

U_3O_8 p.p.m.	420 to 500 μm				500 to 590 μm				590 to 842 μm			
	U_3O_8 capacity g/l	Slope × 10⁵, s⁻¹ f(1)	f(2)	f(3)	U_3O_8 capacity g/l	Slope × 10⁵, s⁻¹ f(1)	f(2)	f(3)	U_3O_8 capacity g/l	Slope × 10⁵, s⁻¹ f(1)	f(2)	f(3)
50	18,0	12,7 Good	— Nl	8,4 Fair	20,0	11,2 Good	— Nl	7,1 Fair	19,0	9,3 Good	— Nl	6,7 Poor
100	27,0	20,0 Good	— Nl	14,5 Poor	28,5	12,9 Fair	8,8 Poor	7,8 Fair	26,0	11,5 Fair	8,1 Poor	7,0 Fair
200	38,0	14,3 Good	13,1 Poor	9,7 Fair	38,1	14,3 Fair	12,4 Fair	10,2 Good	40,5	11,3 Fair	9,4 Poor	7,1 Fair
500	60,0	— Nl	20,5 Fair	17,1 Good	60,1	17,3 Fair	14,4 Fair	10,8 Good	60,0	10,7 Fair	8,9 Good	7,3 Good
		Linearity	Linearity	Linearity		Linearity	Linearity	Linearity		Linearity	Linearity	Linearity

TABLE II

THE EFFECT OF DVB CONTENT ON THE KINETICS OF URANIUM EXTRACTION FROM VARIOUS SOLUTIONS ONTO A STRONG-BASE ANION-EXCHANGE RESIN, BRS 76, RESIN SIZE 500 TO 590 μm, RESIN WELL-FLUIDIZED (≈ 200% BED EXPANSION)

U_3O_8 p.p.m.	2% DVB				4,5% DVB				8% DVB			
	U_3O_8 capacity g/l	Slope × 10⁵, s⁻¹ f(1)	f(2)	f(3)	U_3O_8 capacity g/l	Slope × 10⁵, s⁻¹ f(1)	f(2)	f(3)	U_3O_8 capacity g/l	Slope × 10⁵, s⁻¹ f(1)	f(2)	f(3)
50	2,5	31,6 Good	24,4 Poor	8,0 Poor	9,5	17,9 Good	14,0 Poor	12,3 Fair	20,0	8,8 Fair	9,0 Poor	6,6 Fair
100	8,5	38,5 Good	29,0 Poor	24,4 Poor	18,0	21,4 Good	— Nl	14,4 Fair	31,0	11,2 Good	— Nl	6,4 Poor
200	17,0	39,4 Good	— Nl	25,8 Fair	29,0	35,9 Good	33,9 Poor	23,8 Fair	44,0	13,2 Good	11,4 Poor	8,5 Fair
500	23,0	107,2 Good	85,0 Fair	65,9 Fair	42,0	38,4 Good	34,4 Good	22,0 Good	62,0	15,9 Poor	13,6 Fair	10,0 Good
		Linearity	Linearity	Linearity		Linearity	Linearity	Linearity		Linearity	Linearity	Linearity

Attention is drawn to the following points.

(i) In dilute uranium solution (50 p.p.m.), the kinetics are best described by the function f(1) in all three size fractions. This is consistent with theory, since film-diffusion control is favoured by low concentrations of exchange ions, and, as shown above, f(1) can also be used to describe film diffusion under these conditions.
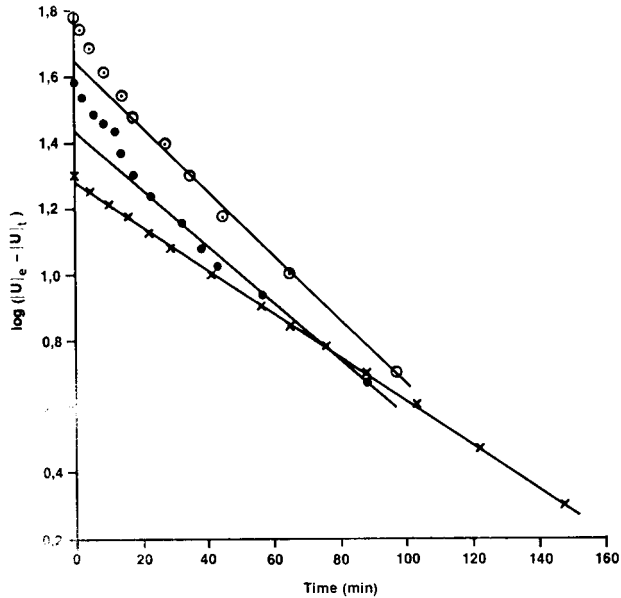
(ii) The kinetics of extraction from solutions containing 500 p.p.m. of uranium are best described by the functions f(2) and f(3). This, too, fits the theory, since these models best describe diffusion within the resin bead, and intraparticle diffusion control is most likely at high values of $[U]_s$.
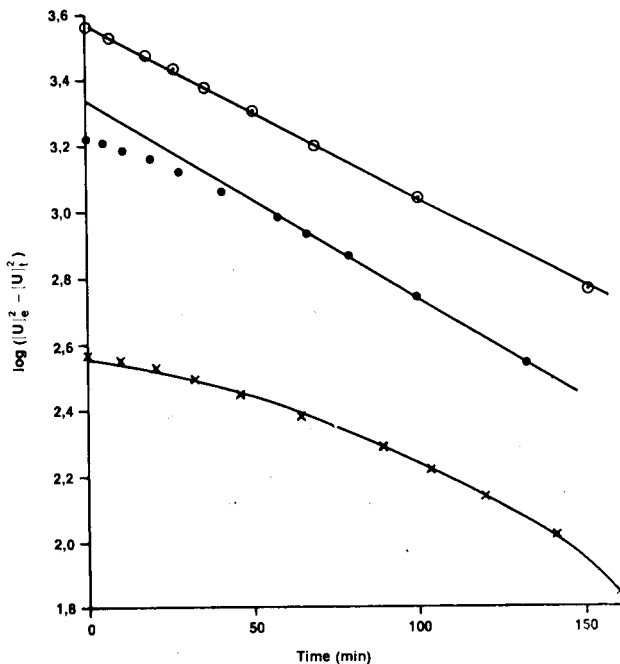
(iii) In the intermediate concentration range, 100 to 200 p.p.m., f(1) apparently fits the data best when the beads are small, and f(3) when the beads are large. Since film diffusion is favoured by small beads and particle diffusion by large beads, this result is also consistent with prediction.

These effects are illustrated graphically in Figs. 1 to 3. In Fig. 1, the kinetic data are plotted as a function of f(1), and a good linear relationship is found only when $[U]_s=50$ p.p.m. The same data are plotted as a function of f(2) in Fig. 2, and as a function of f(3) in Fig. 3. In the last two cases, the linear relationships are good when $[U]_s=500$ p.p.m., fair when $[U]_s=200$ p.p.m., and poor when $[U]_s=50$ p.p.m.

(iv) The theory of ion-exchange kinetics[3] predicts that the rate of exchange will vary inversely with the radius of the resin bead in the case of film-diffusion control, and inversely with the radius squared in the case of particle-diffusion control. The rate data are plotted as a function of the mean bead radius in Fig. 4, as log–log relationships. Only the two extremes, $[U]_s=50$ p.p.m. and $[U]_s=500$ p.p.m., are considered, and when $[U]_s=50$ p.p.m. the slopes of the log–log relationships are close to 1, whereas slopes of close to 2 are encountered when $[U]_s=500$ p.p.m. These results, and those presented above, all point to particle-diffusion rate control in concentrated (500 p.p.m.) uranium solutions, and film-diffusion control in dilute (50 p.p.m.) solutions.

The Effect of Resin Structure

Three resins that had DBV concentrations of 2 per cent, 4,5 per cent, and 8 per cent were compared. DVB is a reagent that promotes cross-linking of the resin matrix, and the density of exchange sites in the resin therefore increases with increasing DVB; alternatively, increased DVB leads to decreased swelling of the resin.
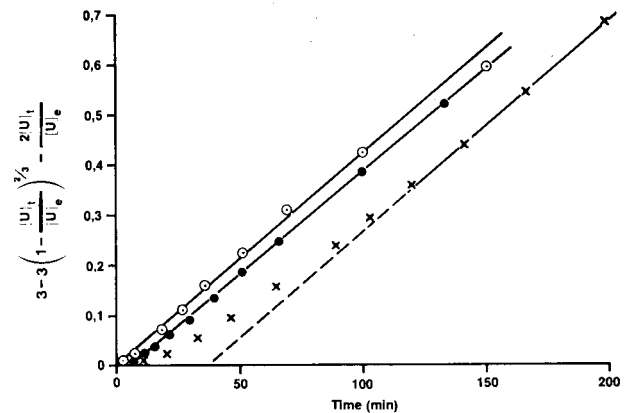

Fig. I—The kinetics, f(I), of uranium extraction by a strong-base anion-exchange resin, BRS 76. (Uraniun concentration in solution: 500 p.p.m. (○), 200 p.p.m. (●), and 50 p.p.m. (✗). Resin size: +500—590 μm.)

Fig. 2—The kinetics, f(2), of uranium extraction by a strong-base anion-exchange resin, BRS 76. (Uranium concentration in solution: 500 p.p.m. (○), 200 p.p.m. (●), and 50 p.p.m. (✗). Resin size: +590—842 μm.)

Fig. 3—The kinetics, f(3), of uranium extraction by a strong-base anion-exchange resin, BRS 76. (Uranium concentration in solution: 500 p.p.m. (○), 200 p.p.m. (●), and 50 p.p.m. (✗). Resin size: +590—842 μm.)
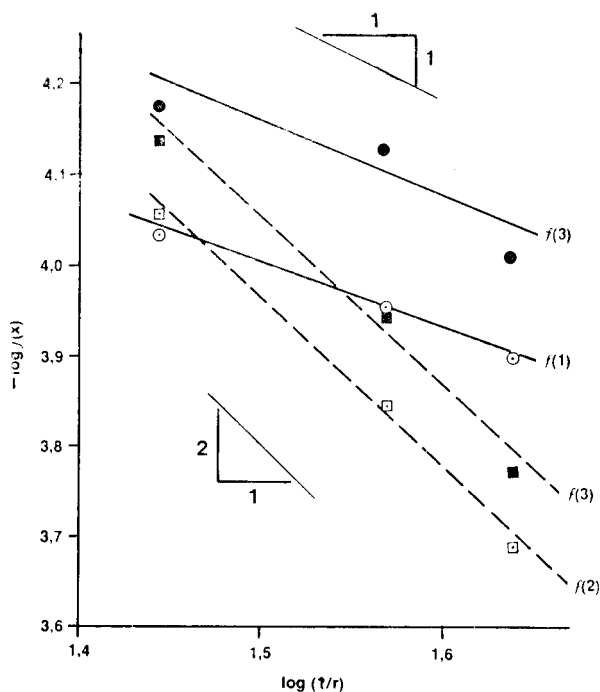
Fig. 4—The effect of size of the resin bead on the rate of uranium extraction by a strong-base resin, BRS 76. (Broken lines: [U]$_s$=500 p.p.m. Unbroken lines: [U]$_s$=50 p.p.m.)

However, while an increase in DVB improves the capacity of a resin, the kinetics of absorption are adversely affected since an increase in cross-linking decreases the intraparticle diffusion coefficient of the exchange ions. On this basis, film-diffusion control should be dominant for low-DVB resins, and particle-diffusion control for high-DVB resins.

The data collected in Table II and Fig. 5 fulfil these predictions adequately. Thus, the broken curves in Fig. 5 show a uniform decrease in kinetics with increasing DVB, whereas the full-line curves show an approximately linear increase in capacity with increasing DVB. Attention is drawn to a number of other features of Fig. 5 and Table II.

(a) The effect on the kinetics of the uranium concentration in solution, [U]$_s$, is far greater for the 2 per cent DVB resin, when film diffusion should predominate, than for the 8 per cent DVB resin, when particle-diffusion control might be expected. This is in line with the Vermeulen approximation, f(2), which predicts that the rate will be independent of [U]$_s$ under conditions of particle-diffusion control.

(b) Theoretically, the DVB content of the resin will influence the rate only when particle diffusion is rate controlling. This is consistent with Fig. 5, which shows that the DVB content has a far greater effect on the rate when [U]$_s$=500 p.p.m. than when [U]$_s$=50 p.p.m.

(c) Finally, on the basis of the qualitative assessments of the linearity of functions f(1), f(2), and f(3), the following generalizations can be made:

(1) film diffusion is predominant when the 2 per cent DVB resin is used, irrespective of [U]$_s$;

(2) when the 4,5 per cent DVB resin is used, film-diffusion control is significant when 50 p.p.m. $\leqslant$ [U]$_s$ $\leqslant$ 200 p.p.m. Both film diffusion and particle diffusion participate at [U]$_s$=500 p.p.m.; and

(3) in the 8 per cent DVB resin, the rate is controlled by particle diffusion at [U]$_s$=500 p.p.m., and probably by a combination of film diffusion and particle diffusion at lower concentrations of uranium.

These observations are consistent with the considerations outlined in the Introduction.

Effect of Interruption of the Absorption Process

A convenient experimental technique by which control by film diffusion can be distinguished from that by particle diffusion involves the interruption of the absorption process for a period during which the loading ion can distribute itself within the resin beads by diffusion into the interior. With particle-diffusion control, the rate immediately after the interruption should be higher than that before the interruption, whereas, with film-diffusion control, the interruption should have no effect on the rate (because no concentration gradients exist in the bead).

The results of interruption tests conducted under various conditions are presented in Figs. 6 and 7. In Fig. 6, the conditions chosen favour film diffusion: low DVB content, small bead size, and light agitation. The results confirm that, at [U]$_s$ $\leqslant$ 200 p.p.m., film diffusion is, in fact, rate controlling. In the experiments illustrated in Fig. 7, conditions favour particle-diffusion control, and the results indicate that, even at [U]$_s$=50 p.p.m., particle diffusion is significant.

Effect of Agitation

Semi-quantitative information on the effect of agitation on the rate of loading was obtained when the flow through the fluidized-bed reactor was varied. The results of experiments in which the flow was varied so as to provide various expansions on the height of the
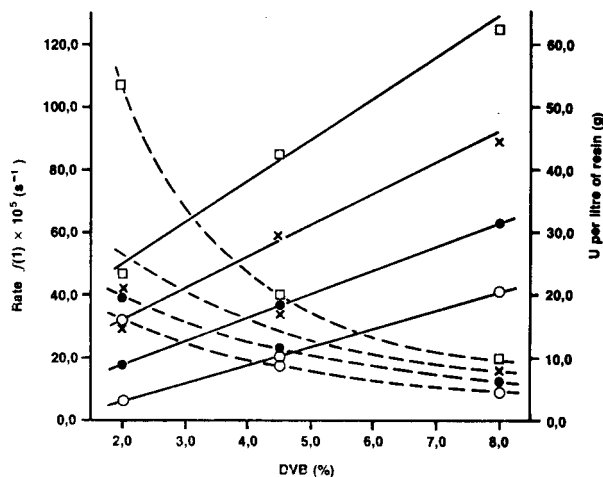

Fig. 5—The effect of DVB content on the kinetics (broken-line curves), and capacity (full-line curves) of strong-base anion-exchange resins for uranium. (Uranium concentration in solution: 50 p.p.m. (◯), 100 p.p.m. (●), 200 p.p.m. (X), and 500 p.p.m. (☐).)

packed bed are presented in Table III. As in Tables I and II, an assessment is given of the linearity of functions f(1), f(2), and f(3) with respect to reaction time. This assessment indicates that, irrespective of agitation, film-diffusion control predominates at $[U]_s = 50$ p.p.m., and particle-diffusion control at $[U]_s = 500$ p.p.m. The behaviour for $[U]_s = 100$ or 200 p.p.m. is somewhat intermediate. This observation fits well with expectations. It should be borne in mind that, in the correlation of rate with fluid velocity, the appropriate velocity is the linear velocity. This, of course, is not proportional to the volumetric flow-rate since the free cross-sectional area for flow changes with the bed expansion.

An interesting feature of these results is that the rate apparently goes through a maximum at between 75 and 100 per cent bed expansion. Normally, the effect of fluid velocity on mass transfer is characterized by a uniform dependence of the rate on fluid velocity when film diffusion is rate controlling (low fluid velocities) and independence of the rate on fluid velocity when particle diffusion is rate controlling. The results in Table III, however, indicate that the rate actually decreases at bed expansions of more than 100 per cent. This may be due to a slipstream effect, in which the thickness of the film on the front edge of the bead decreases but the stagnant slipstream at the rear edge of the bead increases as the bead moves more rapidly through the solution. Alternatively, at high bed expansions, decreasing interparticle interactions will decrease mass transfer, whereas, at very low bed expansions (packed beds), certain areas will be shielded from flow. On this basis too, therefore, a maximum mass-transfer coefficient at intermediate bed expansions might be expected. This maximum was also observed recently by Petkova et al.[10], who studied the kinetics of sulphuric acid sorption on a strong base resin. They suggest that this effect may be
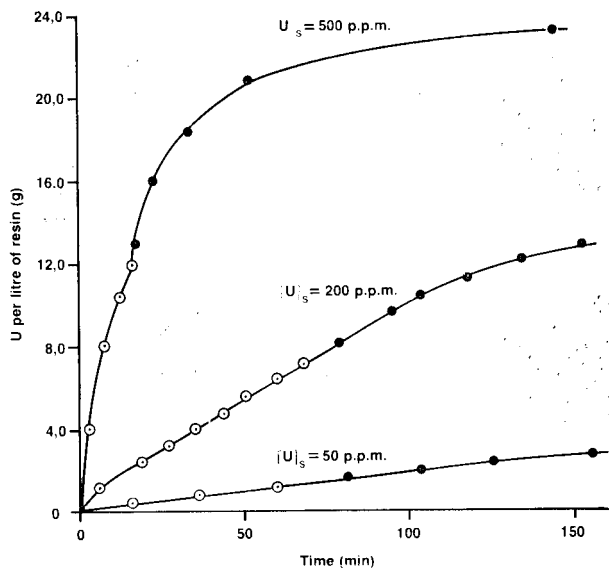

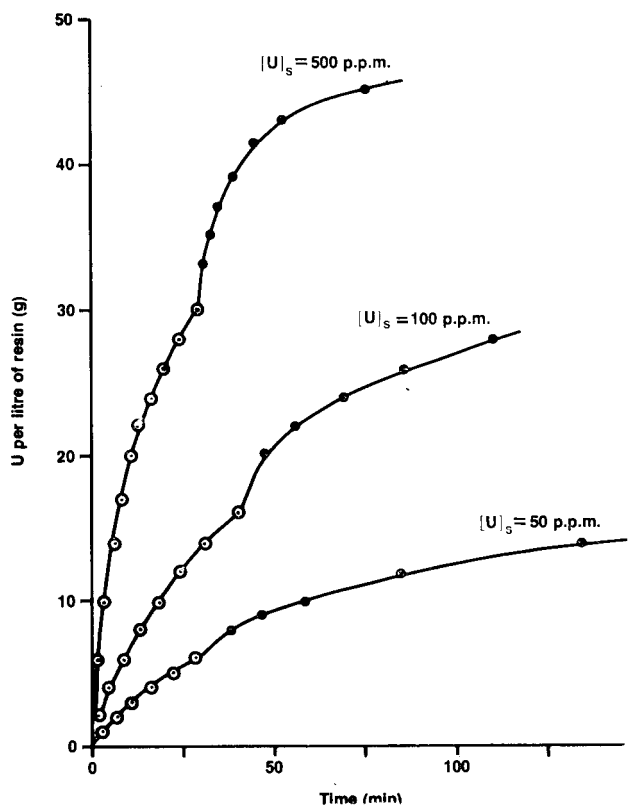
Fig. 6—The effect of an hour's interruption on the loading rate of uranium from solutions of concentration $[U]_s$ onto a strong-base resin containing 2 per cent DVB. (Resin size: +500−590μm. Fluidization: 50 per cent bed expansion. Symbols: (○) data points before interruption, (●) data points after interruption.)

Fig. 7—The effect of an hour's interruption on the loading rate of uranium from solutions of concentration $(U)_s$ onto the strong-base resin, BRS 76. (Resin size: +590−842μm. Fluidization: 200 per cent bed expansion. Symbols: (○) data points before interruption, (●), data points after interruption.)

due to longitudinal diffusion at low superficial velocities, which allows more time for the concentration profile in the column to become diffuse.

It is significant that the maxima were observed only at uranium concentrations of less than 200 p.p.m. (Table III), when film-diffusion control is expected to be significant. In the 500 p.p.m. solution, the effect of fluid velocity on the rate of reaction is not regular.

The Effect of pH

As shown by the results in Table IV, a variation in the pH value of the solution from 1,25 to 2,0 had no noticeable effect on the rate from 100 p.p.m. of U_3O_8 solution onto IRA 400 resin. The slope of the plots of function f(2) are presented in Table IV, but the same conclusions can be drawn whichever model is used.

Discussion

Before the above results are discussed in detail, an attempt is made to estimate the maximum possible rate of exchange, which is given by the maximum rate of transport of uranium ions to the surface of the bead. This can be calculated from the following relationship:

$$\frac{d[U]_t}{dt} = k_M[U]_s \left(\frac{\text{bead surface area}}{\text{bead volume}} \right) \text{mg.cm}^{-3}.\text{s}^{-1},$$

A rough estimate of the rate of mass transfer to the beads can be obtained by calculation of an approximate mass-transfer coefficient (k_M) from the data obtained by Harriott[11]. He found that, above about 200 μm, the size

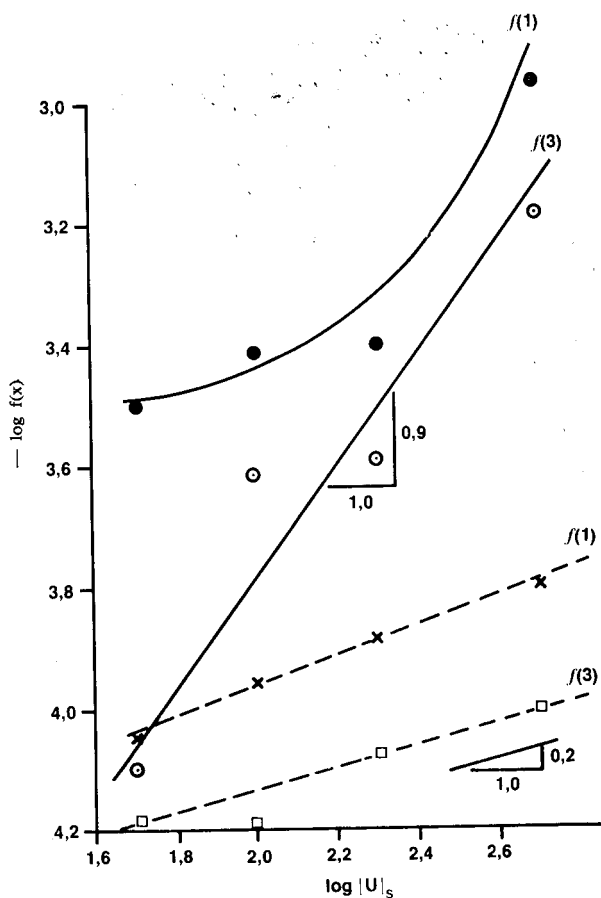## TABLE III

U_3O_8 p.p.m.	U_3O_8 capacity g/l		25% Slope $\times 10^5$, s^{-1}			50% Slope $\times 10^5$, s^{-1}			75% Slope $\times 10^5$, s^{-1}			100% Slope $\times 10^5$, s^{-1}			150% Slope $\times 10^5$, s^{-1}		
			f(1)	f(2)	f(3)	f(1)	f(2)	f(3)	f(1)	f(2)	f(3)	f(1)	f(2)	f(3)	f(1)	f(2)	f(3)
50	19,0	Slope	6,6	—	3,7	7,8	—	4,6	9,7	—	6,9	7,8	5,7	4,9	7,8	6,6	4,9
		Linearity	Good	Nl	Poor	Good	Nl	Poor	Good	Nl	Poor	Good	Fair	Fair	Good	Fair	Fair
100	26,0	Slope	7,5	—	—	10,3	5,3	—	11,0	6,5	4,7	13,2	7,4	6,5	9,7	7,1	6,2
		Linearity	Good	Nl	Nl	Good	Poor	Nl	Good	Poor	Poor	Fair	Poor	Fair	Fair	Fair	Fair
200	40,5	Slope	8,5	4,4	3,8	9,8	6,7	5,7	11,2	8,9	7,0	6,0	5,3	4,5	6,8	5,7	4,3
		Linearity	Poor	Poor	Poor	Fair	Poor	Poor	Good	Poor	Fair	Fair	Good	Fair	Fair	Good	Fair
500	60,0	Slope	10,9	7,8	7,1	9,0	7,0	5,8	—	6,9	5,9	12,3	9,3	8,0	11,5	8,7	7,4
		Linearity	Poor	Poor	Good	Poor	Good	Good	Nl	Fair	Fair	Poor	Fair	Good	Fair	Good	Good

Fig. 8—The effect of the uranium concentration in solution on the rate of extraction by strong-base anion-exchange resins. (Resin size: +500−590μm. Symbols: (●) and (○) 2 per cent DVB resins, (X) and (□) 8 per cent DVB resins.)

$360~\mu$m from a solution containing 50 p.p.m. of U_3O_8, one can calculate from the equation above that the maximum rate should be $6,0\times10^{-3}$ mg.cm^{-3}.s^{-1}. Measurement of the initial slope of the curve in Fig. 7 gives rates equivalent to $5,6\times10^{-3}$ or $8,0\times10^{-3}$ mg.cm^{-3}.s^{-1} depending on the assumed packing density for the 50 p.p.m. solution. This is in excellent agreement with the calculated maximum rate and indicates that, in dilute solutions of 50 p.p.m. of uranium or less, mass transfer to the bead surface is rate controlling.

From these calculations and the discussion above, it is apparent that the diffusion of uranyl ions is considered to be rate controlling. Ideally, the contribution from the diffusion of sulphate ions both in the resin and in solution should be considered, especially at a bulk sulphate concentration of as high as 30 g/l. Experiments show that, in the absence of background electrolyte, an increase of approximately 20 per cent in the rate of uranium extraction is obtained, irrespective of whether film diffusion or particle diffusion is predominant. This indicates that the diffusion of sulphate ions does contribute to the rate, but no attempt is made here to quantify these results.
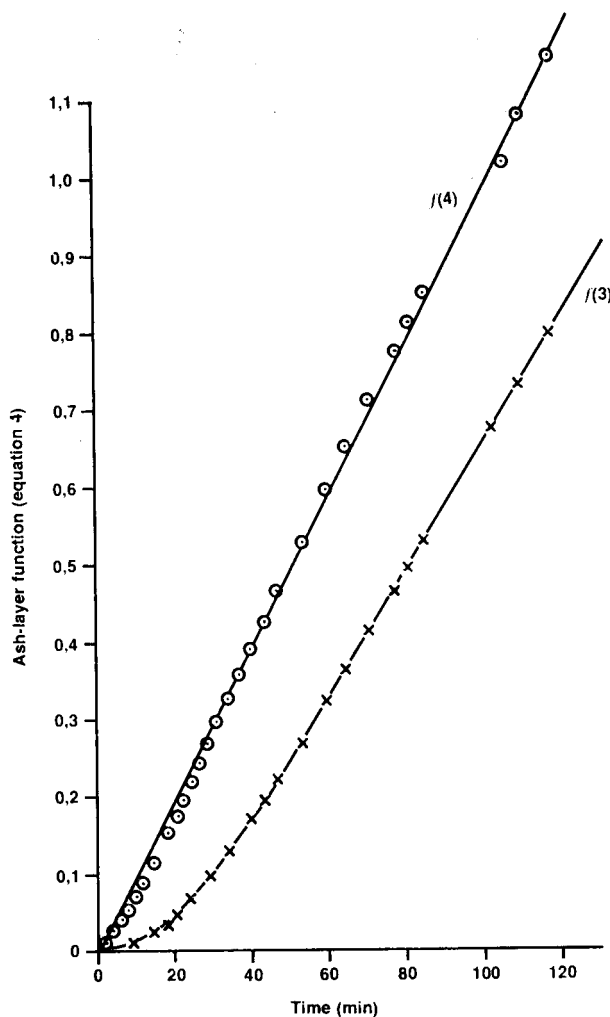
It is also possible to obtain an estimate from the

of the particle had very little effect on the mass-transfer coefficient, which had a value of about 0,01 cm.s^{-1} for the exchange of sodium ions for protons on a cation-exchange resin. Correction for the difference between the diffusion coefficient of the uranyl ions (assumed to be 2×10^{-6} cm^2.s^{-1}) and that of the sodium ions resulted in a mass-transfer coefficient for the uranyl ions of $1,7\times10^{-3}$ cm.s^{-1}. In the calculation of the rate of exchange, the actual volume of the resin in a given packed-bed volume of resin has to be estimated, and this in turn is determined by the efficiency of packing. There is a theoretical maximum in a hexagonal closely packed bed that has a unit cell volume of $5,66r^3$ (26 per cent voidage). A theoretical minimum exists when each bead in the packed bed is located vertically above the bead beneath it, and the unit cell volume is $8r^3$ (48 per cent voidage). For the loading onto beads of mean radii

TABLE IV

EFFECT OF pH ON EQUILIBRIUM AND RATE OF LOADING

pH	U_3O_8 on resin g/l	f(2) × 10⁵ s⁻¹
1,25	11,4	14,8
1,50	22,9	11,3
1,80	40,5	12,2
2,00	46,2	13,2

Fig. 9—The kinetics of uranium extraction based on the ash-layer model. ([U]s: 200 p.p.m. DVB: 4,5 per cent. Resin size: +500−590μm. f(3): $D(rk_{MA})^{-1}=0,00$. f(4): $D(rk_{MA})^{-1}=0,183$.)

data of the diffusion coefficient under conditions of particle-diffusion control. Thus, for a mean slope of about $10^{-4}.s^{-1}$ (Tables I to III) and a mean bead radius of about 0,025 cm, the function f(2) yields a value of 6×10^{-9} $cm^2.s^{-1}$ for the intraparticle diffusion coefficient of the uranyl ion. This is in good agreement with values reported by Barnes et al.[12]. Uncertainty about the effect of $[U]_s$ on particle diffusion (see below) precludes more accurate calculation of diffusion co-efficients from the rate data.

From the above, it is apparent that the initial stages of loading onto resin from dilute (50 p.p.m.) solutions are likely to be controlled by film diffusion. This supports the results of the experiments presented above, which show that in solutions of 50 p.p.m. of uranium

(1) the extraction rate is inversely proportional to bead radius (Fig. 4),
(2) the effect of the DVB content in the resin is minimal (Fig. 5), and
(3) the kinetics are best described by a first-order rate law of the type f(1).

All this evidence points to film-diffusion control. In low-DVB resins film-diffusion control is likely to be significant until the resin is loaded almost to capacity (Fig. 6), whereas in high-DVB resins there is evidence (Fig. 7) to suggest a contribution from particle-diffusion control in the partially loaded resin.

Absorption from 100 p.p.m. and 200 p.p.m. solutions of uranium is almost certainly controlled by film diffusion in the early stages of loading, especially in small low-DVB resins. The curve of $[U]_s=200$ p.p.m. in Fig. 6 shows no evidence of particle-diffusion control, even after 50 per cent loading has been achieved.

Finally, the data for 500 p.p.m. uranium solutions are best fitted by the ash-layer model, f(3), even during the initial stages of loading. This points to particle diffusion as the main resistance to mass transfer, and this conclusion is supported by the interruption tests (Figs. 6 and 7) and the effect of bead radius on the rate (Fig. 4). All the results presented above for extraction from 500 p.p.m. solutions suggest that the ash-layer model is far more versatile than the Vermeulen approximation, f(2), in describing intraparticle rates of mass transfer. However, one problem with the ash-layer model is that it predicts a first-order dependence of the rate on $[U]_s$. Results taken from Table II and plotted as log–log relationships (Fig. 8) indicate that, whereas orders of close to 1 are found when the 2 per cent DVB resin is used (film-diffusion control prevailing), an order of 0,2 is found when the 8 per cent DVB resin is used. This is more in line with the Vermeulen model, which predicts that the rate should be independent of $[U]_s$ under conditions of particle-diffusion control.

The difficulty in modelling the performance of a continuous ion-exchange column can be attributed to the sensitivity of the kinetic mechanism to changes in $[U]_s$ and to changes in the extent of loading of the resin. Thus, in the last one or two stages of a continuous ion-exchange process, when freshly stripped resin is contacted with dilute uranium solution, film-diffusion control is expected. On the other hand, in the first few stages of the column, fairly concentrated uranium solution

(≈ 200 p.p.m.) is treated with partially loaded resin, and here particle-diffusion control will undoubtedly be significant. Since these two rate-determining steps have different functional dependencies on the uranium concentration, the extent of loading, and the physical characteristics of the resin bead, it is not surprising that a simple rate-expression based on one or the other does not adequately describe the performance of a continuous ion-exchange column.

The ash-layer model does, however, incorporate a term for the contribution from film-diffusion control, and therefore offers the best compromise. The full equation[2] can be written

$$t = \frac{r^2[IX]}{6D[U]_s}\left\{ \frac{2[U]_t}{[U]_e}\left[\frac{D}{rk_{MA}}-1\right]+ \right.$$

$$\left. \left[3-3\left(1-\frac{[U]_t}{[U]_e}\right)^{2/3}\right]\right\} \qquad \cdots \cdots \quad (4)$$

D is the average intraparticle diffusion coefficient, and k_{MA} is the mass-transfer coefficient in the stagnant film around the bead. Under conditions of particle-diffusion control, $rk_{MA} \gg D$, and equation (4) is reduced to equation (3).

A qualitative impression of the improvement offered by this model is given in Fig. 9. The kinetic data refer to the extraction of uranium from a 200 p.p.m. solution by a 4,5 per cent DVB resin. The results presented above indicate that film diffusion plays a significant part in determining the rate under these conditions, especially at low loading. In fact, when film diffusion is ignored, a poor linear fit of the data is obtained, curve f(3). However, when film diffusion is considered and a value of $D/rk_{MA}=0,183$ is substituted in equation (4), a good linear relationship, denoted by f(4), is obtained. However, the slope of f(3) tends to the same value as the slope of f(4), and this indicates that particle-diffusion control prevails at high loading.

The data presented in Fig. 10 refer to the extraction of uranium from a 100 p.p.m. solution by a 2 per cent DVB resin. In this instance, as diffusion inside the resin bead is faster than in the 4,5 per cent DVB resin, the contribution to the rate from intraparticle diffusion will be even less. This is illustrated in Fig. 10, which shows that neither f(3) ($D/rk_{MA}=0$) nor f(4) ($D/rk_{MA}=0,183$) describes the kinetics adequately. A good linear relationship, f(5), is obtained only when a value of $D/rk_{MA}=0,450$ is substituted in the general equation. On this basis, the contribution from particle-diffusion control increases by a factor of 2,6 from the 2 per cent DVB resin to the 4,5 per cent DVB resin (on the assumption that rk_{MA} does not change), and these values correspond closely to the DVB contents.

Finally, data on the extraction of uranium from a 500 p.p.m. solution by BRS 76 are presented in Fig. 11. The data presented in Tables I and II suggest that particle-diffusion control predominates throughout the absorption process under these conditions, and this is confirmed in Fig. 11. Thus, a good linear relationship between time and f(3) (the line through the origin) is obtained, and this implies that D/rk_{MA} is approximately equal to 0 and that film diffusion can be ignored.

For these results to be quantified and applied to continuous ion exchange, D, the average intraparticle diffusion coefficient would have to be determined for the resin in use. Thus, in the case of A101 DU, which has a low DVB content, a function similar to f(4) or f(5) would probably describe the kinetics best. In the case of IRA 400, f(3) would probably suffice. It is not clear at this stage whether this model could be scaled up to accommodate the performance of a continuous ion-exchange column. The model requires that D should not vary considerably from its mean value throughout the length of the column (or it would not be possible to treat D/rk_{MA} as a constant). It also requires that, at a time t, $[U]_t$ should be approximately constant. Whereas this may be true in the experiments reported here, in which one is dealing essentially with a single-stage column, it is not likely to be true in a multiple-stage continuous ion-exchange column. Finally, the effect of $[U]_s$ would need to be characterized more thoroughly. Thus, the results presented in Fig. 8 suggest that a rate law of the form

$$t = \frac{r^2[IX]}{6D}\left\{\frac{2[U]_t}{[U]_s[U]_e}\left[\frac{D}{rk_{MA}}-1\right]+\right.$$

$$\left.\frac{1}{[U]_s^{0,2}}\left[3-3\left(1-\frac{[U]_t}{[U]_e}\right)^{2/3}\right]\right\}$$

would be more suitable than equation (4).

The only other practical implication of this work is the observation that the rate improves as the size of the resin bead decreases, and this effect will be most significant at the lower end of a continuous ion-exchange column, where particle diffusion is rate controlling. As shown by Harriott[11], the mass-transfer coefficient is relatively independent of bead size above about 200 μm, and changes only slightly with fluid density. Harriott also found that the mass-transfer coefficient varies only slowly with the degree of agitation above that necessary to keep the particles in free suspension. Finally, the results presented above suggest that the attainment of highly expanded fluidized beds will probably have a deleterious effect on the kinetics.

Conclusions

The kinetic data indicate that film diffusion is significant in determining the rate at uranium concentrations of 50 p.p.m. or less. Under limiting conditions, the linear driving-force model, f(1), accommodates film diffusion, and good correlation of the rate data is therefore obtained in dilute uranium solutions when f(1) is used. However, this model yields a poor fit of the data at higher concentrations of uranium, when intraparticle-diffusion control is rate limiting.

The ash-layer model, (f(3)), provides the best linear fit of the data at uranium concentrations of greater than 100 p.p.m., when particle-diffusion control is dominant. However, this model yields a poor fit of the rate data in dilute uranium solutions, when film-diffusion control is significant.
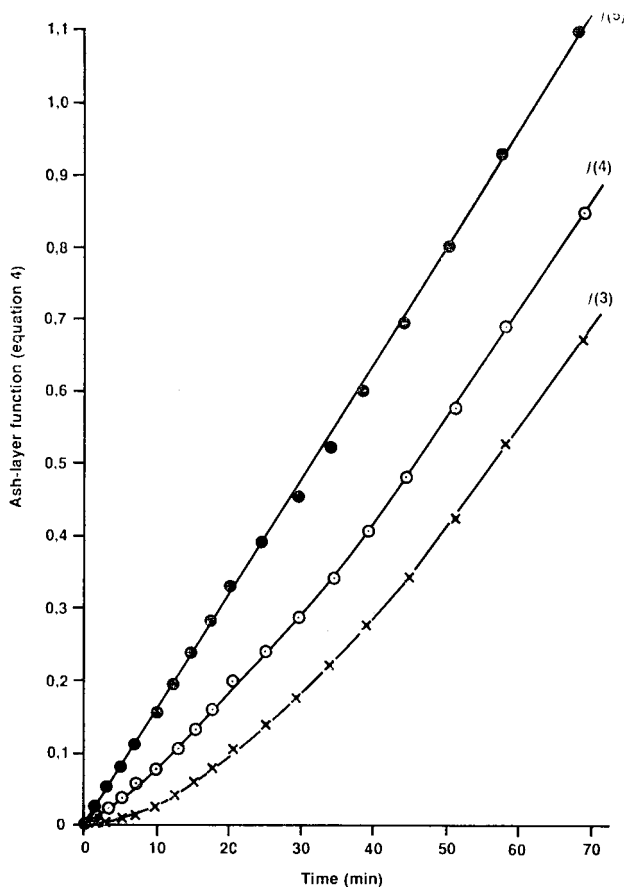
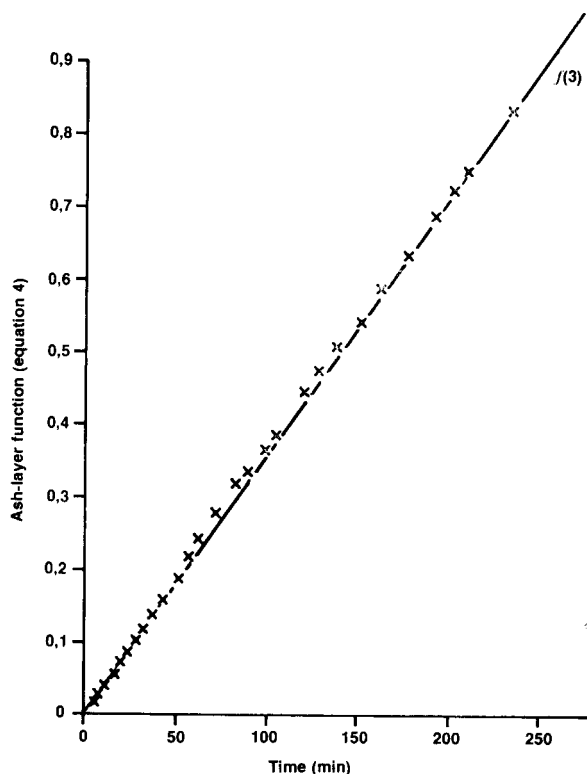Therefore, neither model would be expected to fit the

Fig. 10—The kinetics of uranium extraction based on the ash-layer model. ([U]$_s$: 100 p.p.m. DVB: 2 per cent. Resin size: +500−590μm. f(3): $D(rk_{MA})^{-1}=0,00$. f(4): $D(rk_{MA})^{-1}=0,183$. f(5): $D(rk_{MA})^{-1}=0,450$.)

Fig. 11—The kinetics of uranium extraction based on the ash-layer model. ([U]$_s$: 500 p.p.m. Resin BRS 76. Resin size: +590−842μm. f(3): $D(rk_{MA})^{-1}=0,00$.)

data well in a situation such as a continuous ion-exchange operation, where both film and particle diffusion contribute to limiting the rate. In this case, the best compromise is offered by an extended ash-layer model, f(4), which accommodates the contribution from film diffusion.

Acknowledgement

This paper is published by permission of the National Institute for Metallurgy.

References

1. HAINES, A. K. The development of continuous fluidized-bed ion-exchange in South Africa, and its use in the recovery of uranium, *J. S. Afr. Inst. Min. Metall.*, vol. 78. 1978. p. 303.
2. SCHMUCKLER, G., NATIV, M. and GOLDSTEIN, S. The theory and practice of ion exchange. *Soc. Chem. Ind.*, 1976. p. 17.1.
3. HELFFERICH, F. *Advances in ion exchange.* Marinsky (ed.), vol. 1, chap. 2. New York, McGraw-Hill, 1962.
4. MARCHELLO, J. M., and DAVIS, M. W. Theoretical investigation of agitated ion exchange beds. *I. & E.C. Fundamentals*, vol. 2. 1963. p. 27.
5. SLATER, M. J. Continuous ion-exchange in fluidized beds. *Can. J. Chem. Engng*. vol. 52. 1974. p. 43.
6. VERMEULEN, T. *Ind. Eng. Chem.*, vol. 45. 1953. p. 1664.
7. JAGGER, N. D. The formulation and testing of a mathematical model for the description of the rate of ion-exchange in uranyl sulphate solutions. Thesis, University of Natal, 1973.
8. HARRIS, P. J. Johannesburg, National Institute for Metallurgy. *Report no.* 1414, 1973.
9. FLEMING, C. A., and HANCOCK, R. D. *J. S. Afr. Inst. Min. Metall.*, vol. 79, no. 11. Jan. 1979. p. 334.
10. PETKOVA, E. N., VASSILEV, H., and SHKODROVA, V. M. Kinetics of sulphuric acid sorption on a strong base Wofatit SBW anion exchange resin. *Hydrometallurgy*, vol. 4, 1979. p. 269.
11. HARRIOTT, P. *A.I. Ch.E. J.*, vol. 9. 1962. p. 93.
12. BARNES, C. D., DA SILVA NEVES, R. A., and STREAT, M. Anion exchange of uranium from aqueous sulphuric acid solution: diffusion kinetics. *J. Appl. Chem. Biotechnol.*, vol. 24. 1974. p. 787.

Spotlight series

In a series of feature articles entitled 'Spotlight on . . .', which will be published from time to time, we hope to highlight recent metallurgical and mining events of interest, processes that are novel or of new significance, and developments that cast a new light on old ideas. We plan to include descriptions of new equipment and processes, reviews of recent achievements, and accounts of interesting colloquia, symposia, vacation schools, congresses, and visits. Such articles might bear titles like 'Spotlight on carbon-in-pulp', 'Spotlight on stainless steel in South Africa', 'Spotlight on new drilling rig', 'Spotlight on strip mining symposium'.

Readers will be invited to contribute to this series by submitting such accounts (maximum 3000 words) accompanied by suitable illustrations. As with all contributions to the *Journal*, publication will depend on the recommendations of the referees concerned, the contribution will be edited before being published, and the author will be required to cede his copyright to the Institute.

A set of guidelines has been drawn up for the writing of feature articles in this series, and prospective authors, if they so wish, can obtain copies from the S.A.I.M.M., P.O. Box 61019, Marshalltown 2107 (telephone 834-1271).