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A Dynamic Model for Radiotracer Determination of Solute Residence Time Distribution in Counter-Current, Pulse Column Solvent Extraction Processes

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ABSTRACT

A radiotracer method for the measurement of the mass holdup of a solute being processed in a counter-current pulse column using the average residence time distribution is presented and investigated by mathematical modelling. Typical solutions to the model for impulse tracer injections of the solute at the inlet show that while the number and volume of stages have a significant effect on the response of the system, the amount of backmixing has little effect, particularly for small systems. The system response to impulse tracer injections under various conditions was simulated with this model and model parameters were extracted from these simulated results by using a nonlinear least squares method to demonstrate the approach.

INTRODUCTION

One of the techniques that would be useful in the real time determination of the uranium holdup in operating countercurrent pulse column solvent extraction processes is the determination of the average residence time distribution (RTD) by the impulse tracer method. The mass holdup of uranium in the column is identically the uranium mass flow rate through the column times the average residence time of the uranium. This approach would be even more attractive if a dynamic model of the process with adjustable parameters were available so that the average residence time could be determined by the least-squares fitting of data. This approach would allow much shorter measurement times than those dictated by using the numerical integration of data that requires taking data for very long times to fully characterize the long tail of the RTD (1,2). This is the primary incentive for the present work on the development of a suitable dynamic model for this process.

A schematic diagram of the pulse column configuration of interest here is shown in Figure 1. Note that the organic and inorganic phases are fed at opposite ends of the column with corresponding product streams at the other ends. Laboratory scale apparatus of this type is presently being built for the initial experimental studies that are planned.

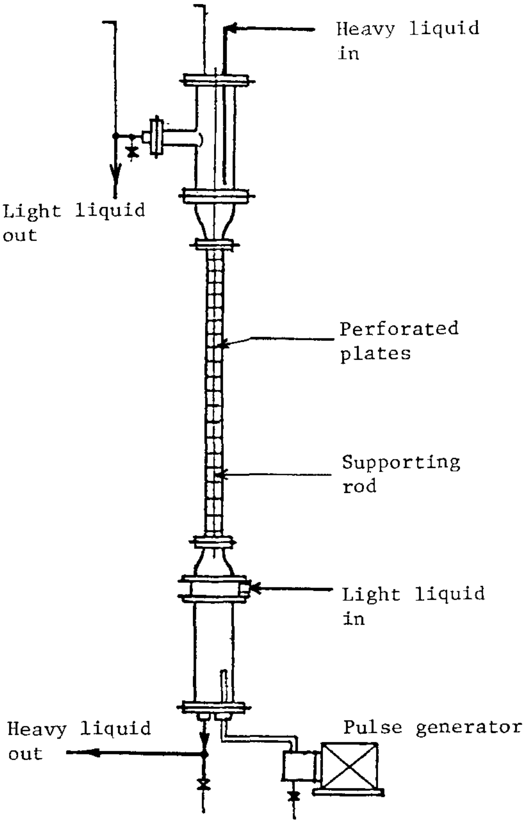

Fig. 1. Schematic diagram of the pulse column

The choice of modelling approaches to this problem were influened partly by our previous success with the cross flow finite stage models that have been employed with ball mill processes (3,4) and the flotation process (5,6) and by the literature survey made by Burkhart (7), the paper by Ricker, Nakashio, and King (8), and the paper by Biery and Boylan (9).

The basic model employed here is almost identical to that of Ricker, Nakashio, and King (8) except that here the dynamic case is considered instead of the steady-state case to obtain the tracer profile at the exits as a function of time. The major assumption in this case is that each phase is adequately modelled by a series of N perfectly mixed tanks of equal volume in series with backmixing. Interphase mass transfer is accounted for by allowing transfer from one phase to the other at each cell. Biery and Boylan (9) previously treated this problem dynamically on a differential basis to predict the time required to reach system steady state, assuming plug flow of the solute in the aqueous phase and negligible longitudinal turbulent diffusion. A paper by Hartland and Mecklenburg (10) compared the differential and stagewise treatments of counter-current extraction processes with backmixing for cases where there is a linear equilibrium relationship. They show that the expressions obtained for both approaches are remarkably similar and that they are identical when the number of stages N in the staged model approaches infinity. However, their paper treats only the steady state case which cannot be applied to the impulse tracer injection. Britsch and Ebert (11) reported their work using radiotracers to determine the longitudinal mixing in both phases. They utilized different radiotracers to study each phase separately. A similar work was carried out by Bensalem, Steiner, and Hartland (12) who used chemical and dye tracers to study axial dispersion.

MODEL DERIVATION

The pulse column shown in Figure 1 has been represented by a stagewise process as shown in Figure 2. For simulation of the pulse column in the time domain, the basic material balance equations for the tracer solute in the ith stage of each phase are given by the following relations (7)

aqueous phase

$$v_x dx_i/dt = (1+\alpha)G(x_{i-1}-x_i) + \alpha G(x_{i+1}-x_i) - q_i \qquad (1a)$$

organic phase

$$v_y dy_i/dt = (1+\beta)H(y_{i+1}-y_i) + \beta H(y_{i-1}-y_i) + q_i \qquad (1b)$$

with

$$q_i = (K_x a)v(x_i-x_i^*) = (K_y a)\ (y_i^*-y_i) \qquad (2)$$

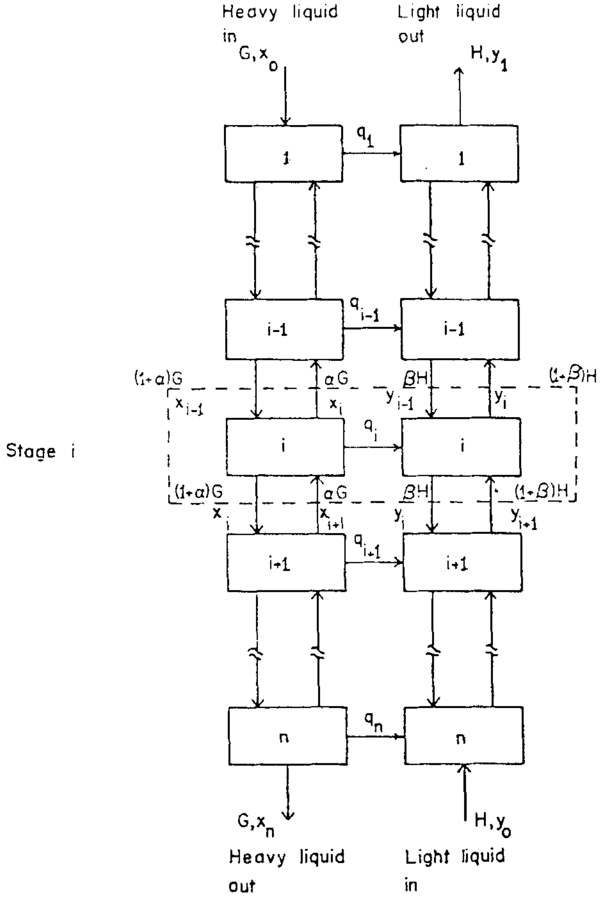

Fig. 2. Finite stage model of the pulse column

The assumptions in deriving this model are that there is perfect mixing within each stage of each phase, the volume of each stage is constant with constant backmixing coefficients in both phases, and there is a constant mass transfer coefficient. It is further assumed that there is an equal number of stages in each phase and that the amount of solute transfer between phases is negligible compared to the total volumes in each stage of each phase and the total flow rates involved.

Since;

$$v_x = F_x V / N$$

$$v_y = F_y V / N \qquad (3)$$

and $$F_x + F_y = 1.$$

there is a set of eight independent parameters that completely describe the system, namely G, H, N, V, $(K_x a)$ or $(K_y a)$, F_x, α, and β. The flow rates G and H are usually independently known, so there are six parameters that must be determined in using the model.

MODEL PREDICTIONS

The model is used to obtain the dynamic response of the pulse column from an impulse input of tracer under the various conditions listed in Table 1. The response of the system (sum of concentrations at the extract and raffinate multiplied by their respective flow rates) are plotted as a function of time after an impulse input of the tracer at the inlet of the aqueous phase and are shown in Figures 3 and 4. A constant value of 2.5 is used for the distribution constant K_D. Equations 1a and 1b were solved numerically using a fourth order variable step Runge-Kutta method. The computer program for this method is given by Gear (13). It solves a system of ordinary differential equations and incorporates a self correction technique for minimizing the error buildup in the numerical solution.

DETERMINATION OF MODEL PARAMETERS

When a tracer is injected at the heavy phase input and measured at the light and heavy phase outputs using two detectors, the total response of the system is given by

$$R(t) = [Y_1 G x_N(t) + Y_2 H y_1(t)] f(t) + R_B \qquad (4)$$

Where the function f(t), which can be obtained by an off-line measurement (3), takes into account the radioactive decay of the tracer. The detector yields Y_1 and Y_2 and the background counting rate R_B are known linear parameters. The heavy and light phase output concentrations, $x_N(t)$ and $y_1(t)$, are the solution of Equations 1a and 1b, respectively, and contain the parameters describing the system. A

TABLE 1

Assumed Values for the Simulation of Data

CASE	N	V(cm^3)	$K_x a$(hr^{-1})	F_x	α	β
1	2	200	2.0	0.5	0.01	0.01
2	2	200	2.0	0.5	0.4	0.01
3	2	200	2.0	0.3	0.01	0.01
4	4	400	2.0	0.5	0.01	0.01
5	4	400	2.0	0.5	0.4	0.01
6	4	400	2.0	0.3	0.01	0.01

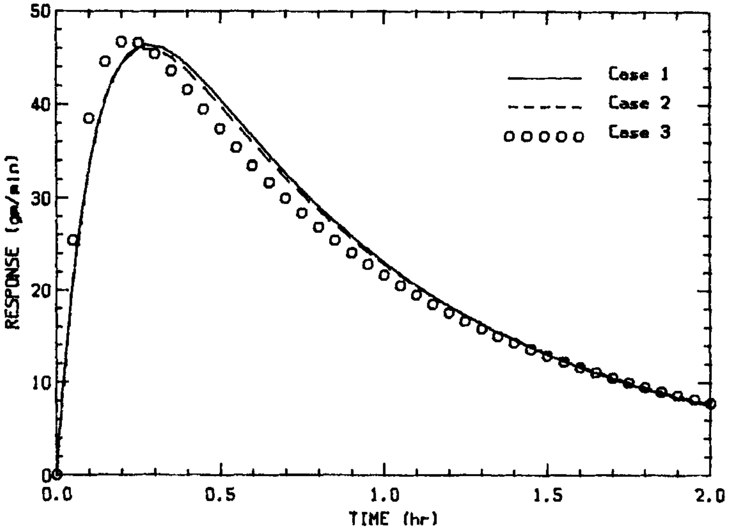

Fig. 3. DYNAMIC BEHAVIOR OF PULSE COLUMN

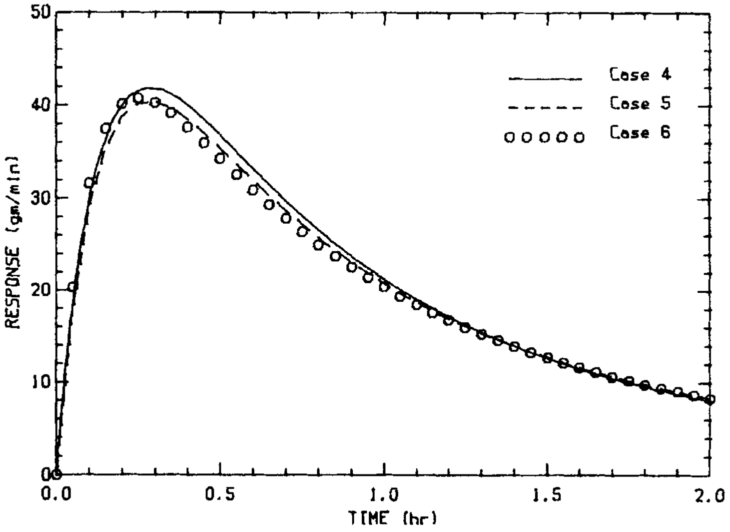

Fig. 4. DYNAMIC BEHAVIOR OF PULSE COLUMN

nonlinear least squares search can be used to determine these parameters using Equation 4 to fit the experimental detector response R(t) to model values. A computer program called CURCON (14), a modified version of one given by Bevington (15), has been developed to determine the optimum values of the searched parameters by minimizing the reduced Chi-square values with respect to each of the parameters simultaneously. It utilizes the combined gradient search and parabolic extrapolation algorithm derived by Marquardt (16).

Data Simulation

Simulated detector response curves that would be obtained with a radioactive tracer are generated in order to investigate the accuracy and sensitivity of the computer programs written for applying the method. Assuming the values of the parameters as given in Table 1, counting rates are calculated as a function of time after tracer injection. Simulated detector responses are then generated by assuming that the counting rates are Gaussian distributed with stand-standard deviations equal to the square root of the counting rate divided by the time over which the counting rate is determined as would be the case for actual counting rates. The detector yields were taken to be equal to unity and a negligible background response was assumed. The searched parameters for the various conditions are given in Table 2 and the detector response R(t) for Case 3 is plotted as a function of time in Figure 5 comparing the simulated and fitted data.

TABLE 2

Values Found in the Search for the Model Parameters

CASE	N	$V(cm^3)$	$K_xa(hr^{-1})$	F_x	α	β	χ_ν^2
1	2	199.88	2.0041	0.5108	0.0001	0.0256	22.65
2	2	200.04	2.0616	0.5589	0.2525	0.1108	20.98
3	2	198.46	1.9900	0.3122	0.1004	0.0287	20.81
4	4	394.77	1.9590	0.5094	0.0789	0.0214	22.67
5	4	396.68	1.9645	0.5102	0.3393	0.0372	23.08
6	4	400.53	2.0138	0.3075	0.0310	0.0102	21.04

Heavy-phase flow rate (G) = 50 (cm^3/hr)

Light-phase flow rate (H) = 100 (cm^3/hr)

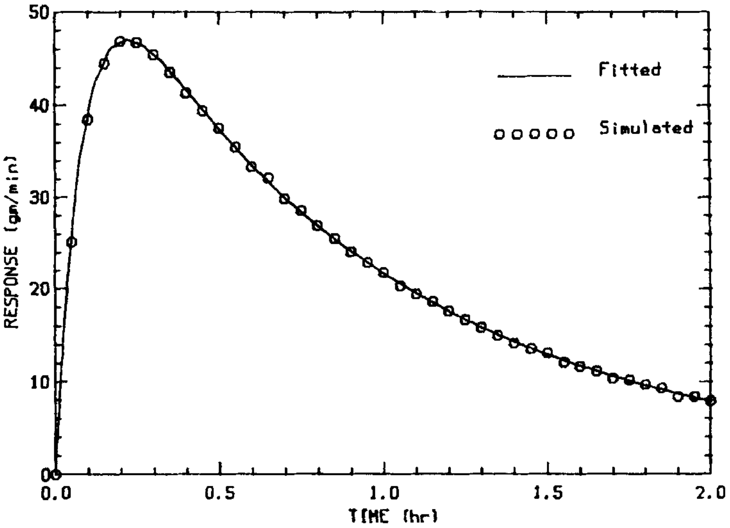

Fig. 5. TRACER IMPULSE RESPONSE OF PULSE COLUMN

Mass Holdup

In a pulse column operating at steady state, with a constant inventory of material over a time interval T, the in-process inventory can be determined knowing the average residence time τ as follows,

$$I = \tau F \qquad (5)$$

The residence time distribution (RTD) is given as,

$$E(t) = R(t)/\int_0^\infty R(t)dt \qquad (6)$$

where R(t) is given by equation 4. The average residence time τ is obtained from:

$$\tau = \int_0^\infty tE(t)\, dt \qquad (7)$$

Note that the integrals in equations 6 and 7 have an upper inte-integration limit on time of infinity. In the usual case where the net counting rate R(t) approaches zero asymtomatically as time approaches infinity and a non-negligible background counting rate exists, the numerical integration process without a model is very inaccurate and requires that data be taken for a long time so that the tail of the counting rate curve is well characterized. When a model is available that is not integrable, the problem of taking data for a long time can be avoided, but numerical integration still contains considerable inaccuracy. To avoid this inaccuracy problem and to reduce the time required for taking data to the minimum possible, one would like to have a mathematical model of R(t) and E(t) that can be integrated analytically. The model need not contain all of the parameters that describe the process; a phenomenological or semi-empirical model with a few adjustable parameters will suffice. In that regard the model described and used here probably is too detailed. We are presently investigating other staged models (17) that yield analytical models for E(t) to be used in place of equations 1a, 1b, and 2.

The average residence time obtained for each case listed in Table 1 and Table 2 is tabulated in Table 3. Equation 7 is solved numerically as the solution of the model since R(t) presented in this paper must be obtained numerically at the present time.

DISCUSSION AND CONCLUSIONS

It is clear from Figure 3 that the backmixing coefficients have little effect on the operation of the pulse column (Case 1 with α = 0.01 and Case 2 with α = 0.4) as compared to the holdup ratio of the two phases (Case 1 with F_x = 0.5 and Case 3 with F_x = 0.3). However, the effect is more prominent for a larger system (Figure 4, Case 4 with α = 0.01 and Case 5 with α = 0.4). Table 2 shows that the search method developed and used here is very sensitive for all the parameters except the backmixing coefficients. The insensitivity of the pulse column operation to the backmixing coefficients makes it difficult to search for these parameters. The parameter search

TABLE 3

Average Residence Time

CASE	Residence Time (hr)	
	Using Assumed Parameters	Using Searched Parameters
1	1.01973	1.02058
2	1.03058	1.03095
3	1.06758	1.06795
4	1.28858	1.30094
5	1.35667	1.35736
6	1.36809	1.36949

results for Case 3 are plotted in Figure 5 comparing the simulated (actual) and fitted (model with searched parameters) data. Table 3 also shows that the average residence time of the solute is not a strong function of backmixing, particularly for small systems, while the holdup ratio of the two phases greatly effects this parameter.

The insensitivity to backmixing parameters suggests that other simpler models might be employed which could yield analytical expressions for tracer response.

NOMENCLATURE

a = interfacial area per unit volume (cm^2/cm^3)

F = feed rate of solute material (kg/hr)

F_x = volume fraction of one stage of the heavy phase

F_y = volume fraction of one stage of the light phase

G = heavy phase total flow rate (cm^3/hr)

H = light phase total flow rate (cm^3/hr)

K_D = equilibrium distribution constant

K_x = mass transfer coefficient based on the x phase (cm/hr)

K_y = mass transfer coefficient based on the y phase (cm/hr)

V = total effective volume of the system (cm^3)

v = volume of both phases in stage i (cm^3)

v_x = volume of heavy phase (cm^3)

v_y = volume of light phase (cm^3)

x_i = heavy phase solute concentration in stage i (gm/cm^3)

x_i^* = concentration of x in equilibrium with y (gm/cm^3)
($x_i^* = y_i / K_D$)

y_i = light phase solute concentration in stage i (gm/cm^3)

y_i^* = concentration of y in equilibrium with x (gm/cm^3)
($y_i^* = K_D\, x_i$)

Greek Letters

α = fraction of heavy phase flow rate flowing backwards
(the heavy phase backmixing coefficient)

β = fraction of light phase flow rate flowing backwards
(the light phase backmixing coefficient)

τ = average residence time (hr)

χ_ν^2 = reduced chi-square value

Subscript

i = stage number

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