ν = kinematic viscosity
ρ = density
N_{Le} = Lewis number
N_{Nu} = Nusselt number
N_{Pr} = Prandtl number
N_{Ra_c} = concentration Rayleigh number, Equation (1)
N_{Ra_T} = thermal Rayleigh number, Equation (1)
N_{Sc} = Schmidt number
N_{Sh} = Sherwood number

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Fixed Bed Sorption with Recycle

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There are several types of processing operations in which a stream is taken from a source, fed to a sorbent bed, and then recycled back to the source. One such situation is shown in Figure 1, where a sorbent bed is being used to remove a desired product B from a reacting mixture. Unreacted component A is recycled back to the reactor. Besides recovering product, the sorbent bed ensures that the reaction mixture remains low in B. Therefore, if the reaction is reversible, the reverse reaction is suppressed and nearly complete conversion of A is obtained.

A second example of sorption with recycle is the sorbent artificial kidney system discussed by Cooney (2) and Cooney and Mace (3). The sorbent bed in this case consists of microcapsules containing activated carbon particles, ion exchange resin particles, and urease enzyme solution. This type of device, which has been developed in rudimentary form and is now beginning to be tested on animals (*1*) would remove the major toxic metabolites (urea, uric acid, creatinine) from the blood of a person suffering from lack of kidney function.

In recycle sorption systems, the economic point for bed replacement or regeneration often is not the point at which the first detectable breakthrough of the sorbable species is observed. Rather it may be the time when maximum capacity of the bed has been reached, that is, when more solute is leaving the bed than is entering. In any event, whether breakthrough or maximum capacity is the chosen criterion, it is necessary to determine the shape of the solute concentration profile in the bed as a function of time in order to establish when the sorber should be taken off stream. Unfortunately, no general analytical theories exist which give the proper profile descriptions when there is recycle (that is, when the boundary condition at the bed inlet is a function of time). Analytical solutions *may* be possible for linear equilibria, but have not yet been obtained.

The most general approach to solving such problems is via numerical integration of the pertinent differential equations. For the sorbent bed we have, neglecting axial dispersion

$$v\frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \frac{1-\epsilon}{\epsilon}\frac{\partial q}{\partial t} = 0 \qquad (1)$$

$$\frac{\partial q}{\partial t} = f(q^*, q, c^*, c) \qquad (2)$$

$$q^* = f(c) \qquad (3)$$

These are the continuity equation for the solute, a mass transfer rate law, and an equilibrium distribution function, respectively. For the source we would have, if it were a single perfectly mixed tank

$$F(c_{\text{out}} - c_{\text{in}}) + R = V\frac{dc_{\text{in}}}{dt} \qquad (4)$$

where R is a production term (sometimes zero). Note that the subscripts here refer, as shown in Figure 1, to the *bed* inlet and outlet concentrations, not to the *source* inlet and outlet concentrations. Because the behavior of sorption systems with recycle has not been considered in any detail in the previous literature, and because there are features about such systems which are unique and interesting, we wish to present information for the case of a reaction product recovery system and thereby illustrate the basic phenomena involved.

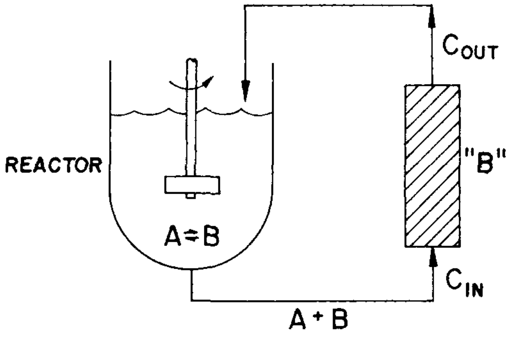

Fig. 1. Reactor-sorber system with recycle.

REACTION PRODUCT RECOVERY SYSTEM

Let us consider the arrangement presented in Figure 1 with the following values of the system parameters

reactor volume, $V = 5$ liters
recycle flow rate, $F = 60$ cu.cm./min.
initial concentration of B in the reactor
$= 3.0$ g./liter
bed size = 6-cm. wide by 40 cm. long

Since component A is present in very large excess, and product B will be continually removed by the sorbent bed, the reverse reaction of B may be neglected. The net production rate of B by reaction will thus be essentially equal to the forward reaction rate. Because the concentration of A will be nearly constant, the reaction rate may be assumed to be also nearly constant. A production rate of 6 g./(liter) (day) was selected for the present case. Of course, there is no extra computational difficulty in allowing for significant reverse reaction, if one desires.

The residence time of the fluid in the circuit external to the reactor is short enough to permit one to assume that no reaction takes place outside of the reactor. Also, it may be additionally assumed for this case that the volume of fluid in the reactor is constant, since the amount of product formed and removed over any reasonable length of time is very low compared to the total mass in the reactor (see Figure 4 below).

It will be noted that the initial concentration level of B implies that recycle of fluid to the sorbent bed is begun only after a certain degree of reaction has already occurred. The purpose in assuming this is to make more emphatic the basic dynamic behavior of the reactor—sorbent bed interaction, as will be shown by figures to be presented later. Such a situation does have a practical counterpart—for example, when a uremic person is first connected to a sorbent artificial kidney, his metabolite levels would most likely be elevated far above desirable values.

The sorption isotherm for the present case was assumed to be linear and of the form $q^* = (40/3)c$. The proportionality constant was selected from among typical data on organic solute sorption on activated carbon at low concentrations. Computationally, any type of isotherm can be treated with no unusual difficulties. A linear mass transfer rate law of the form

$$\frac{\partial q}{\partial t} = K_p\, S_0(q^* - q) \qquad (5)$$

was used, with values of $K_p = 1.2 \times 10^{-4}$ cm./sec. and $S_0 = 100$ cm.$^{-1}$, typical solid-liquid sorption system values. The adequacy of a linear rate law of this form has been established by many investigators.

SOLUTION METHOD

The isotherm and rate law discussed above were solved along with Equations (1) and (4). Partial derivatives were replaced by simple first order finite differences and concentrations were computed at each point in a z-t grid in the fashion shown by Lapidus (*4*), for example. Equation (4) representing the reactor was treated using second-order Runge-Kutta formulas. The step sizes, Δz and Δt, required to yield a sufficiently accurate solution were determined in the usual manner of successive reduction until no further significant effect on the solution was noted.

RESULTS

Figures 2, 3, and 4 summarize the major features of the numerical work. We may arbitrarily divide the system behavior into several time periods, which are:

Period I. From Time Zero Until Solute Breakthrough

Following initiation of feed, a saturation wave progresses continuously through the column. Recycle of solute-free fluid from the bed outlet to the source simultaneously produces an increasing dilution of the source concentration. Since the bed inlet concentration is continually falling, an elution, or desorption, wave develops behind the saturation, or sorption, front. Between the sorption and desorption zones there exists a peak, whose height can be seen to progressively diminish with the distance traveled.

Period II. Breakthrough Until Time of Minimum Inlet Concentration

As c_{out} begins to rise, the rate at which the feed (source) concentration has been falling will begin to taper off. At some point c_{out} will be large enough to reverse the downward fall of c_{in}. This point, the point of minimum inlet concentration, will be reached when

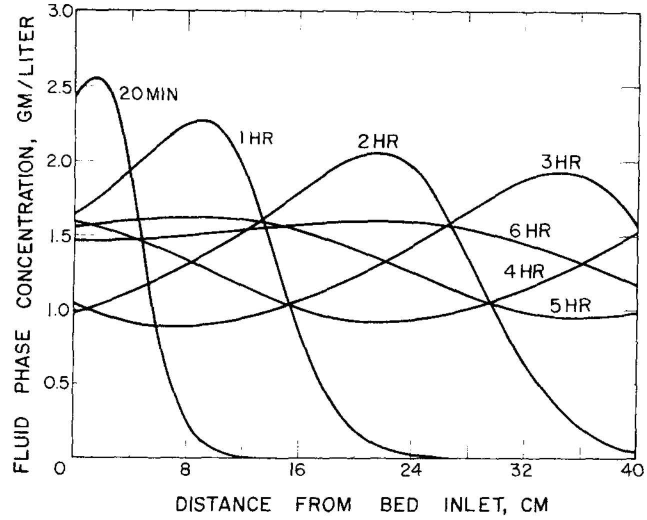

Fig. 2. Sorbent bed concentration profiles for reaction product recovery system: early stages.

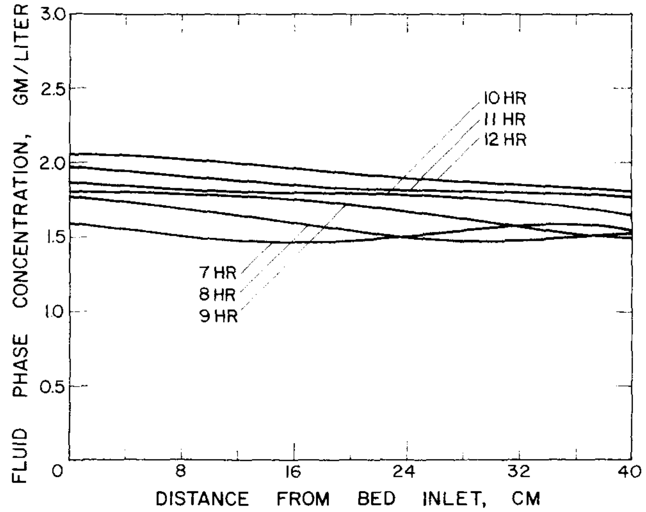

Fig. 3. Sorbent bed concentration profiles for reaction product recovery system; later stages.

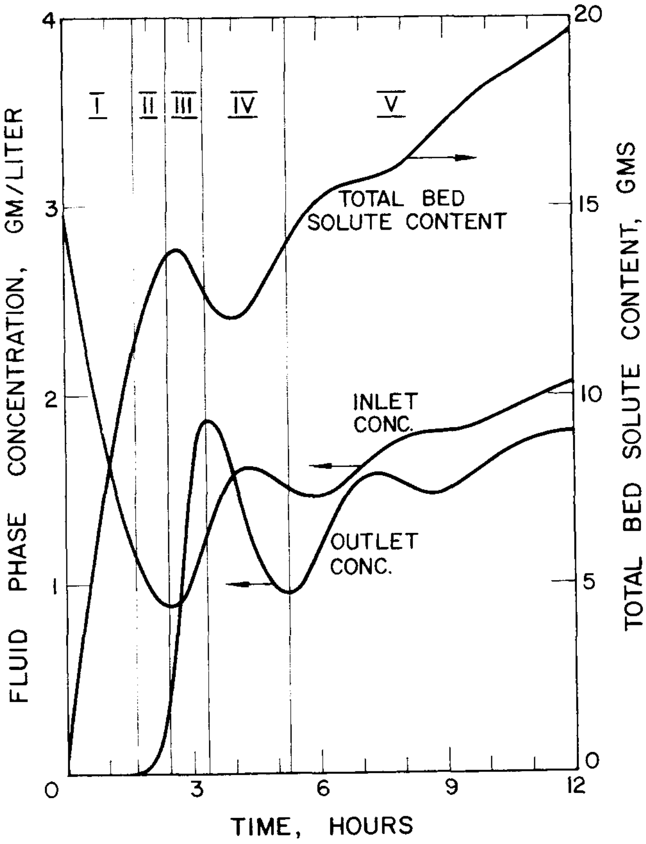

Fig. 4. Variation of bed inlet and outlet concentrations and total bed solute content with time in reaction product recovery system.

$$F(c_{\text{out}} - c_{\text{in}}) + R = 0 \qquad (6)$$

that is, when c_{out} has reached the level $(c_{\text{in}} - R/F)$.

Period III. Time of Minimum Inlet Concentration Until Emergence of the First Peak

At the start of this time period, c_{in} has just begun to rise. At some moment later, the inlet and outlet concentrations of the bed will become equal. When this occurs the total solute content of the bed will exhibit a local maximum. This would be one logical time when one might wish to take the sorber off stream. Beyond this point, $c_{\text{out}} > c_{\text{in}}$ (although both are increasing) and the total bed solute content must therefore decline.

Period IV. From Peak Emergence Until Minimum Outlet Concentration

After the peak which separates the first pair of sorption-desorption waves reaches the end of the bed, c_{out} starts to drop. When c_{out} becomes equal to c_{in} there occurs a local minimum in the total solute content of the bed. Thereafter, $c_{\text{in}} > c_{\text{out}}$ and the total bed solute content rises anew.

At the point where c_{out} has dropped to a level R/F units *below* c_{in}, the rate of solute accumulation becomes zero [see Equation (4)] and c_{in} shows a maximum. Beyond this point both c_{in} and c_{out} fall, with c_{in} falling slower by virtue of the fact that the source is suffering a net loss of solute.

Period V. The Later Stages of the Process

The plotted results show very plainly how the oscillatory behavior of the system gradually damps out. The profiles in Figure 3, for example, suggest that ultimately a state will be reached where no oscillations exist and where the profile is smooth and fairly flat, being somewhat higher near the inlet and decreasing monotonically to a lower value at the outlet. With increasing time this profile will not *overlap* the profile for an earlier time but will simply shift upward over its whole length.

Discussion of these latter features of the process is interesting but to some extent not completely relevant, since the sorbent bed would normally be taken off stream before this time. However, it is certainly possible that in some situations one might want to leave the sorbent bed on stream for a long period. Since the sorbent capacity increases right along with the system solute concentrations (especially for a linear isotherm), one might wish to let the sorbent bed become rather heavily loaded with the desired product before removal.

SUMMARY

The recycle system considered here has been shown to consist, basically, of alternating sorption and desorption waves of progressively smaller amplitude traveling through the sorbent bed, and bed inlet and outlet concentrations which cycle in a damped fashion. The total bed solute content was seen to exhibit a local maximum and local minimum, followed by a steady rise.

It is clear that all of the basic features of these concentration—time patterns are influenced by bed length, sorption capacity, flow rate, the initial concentration of the removable species, etc. Therefore, many types of oscillating patterns could be created by assuming different combinations of the system properties and parameters. In the present paper, we have attempted in choosing only *one* representative case to illustrate the primary characteristics of recycle systems. Although the behaviors shown by our example system should not be considered to be completely general, we do feel that they are typical. We intend to explore the effects of choosing other parameter values in the future.

NOTATION

c = fluid phase concentration, g./cc.
F = volumetric fluid phase flow rate, cc./sec.
K_p = overall stationary phase mass transfer coefficient, cm./sec.
q = stationary phase concentration, g./cc.
R = solute production rate in source, g./sec.
S_0 = sorbent particle specific surface area, cm.$^{-1}$
t = time, sec.
v = interstitial fluid phase velocity in sorbent bed, cm./sec.
V = volume of source, cc.
z = axial distance in sorbent bed from inlet, cm.
ϵ = void fraction in sorbent bed, dimensionless

Subscripts and Superscripts

$*$	denotes an equilibrium concentration
in	denotes concentration at sorbent bed inlet
out	denotes concentration at sorbent bed outlet

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