

# EFFECTS OF LIQUID PULSATION ON THE PERCENT USE OF AN ION-EXCHANGE BED

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Ion exchange can be intensified by oscillating the liquid in a long bed of material, which considerably increases the time between two regenerations.

The rate of ion exchange is determined either by external diffusion or by internal diffusion [1]. Internal diffusion processes are the more rapid; use of hydrodynamic features allows one to accelerate the external diffusion considerably and to bring the rate near to that for internal diffusion [2].

Kinetic equations have been given [3] for KU-2 cation exchange resin in a short bed with liquid pulsating, and it was shown that such motion provides an efficient means of accelerating the ion exchange; an appropriate pulsation velocity  $\omega A$  resulted in an internal-diffusion state.

In industrial practice, a given degree of exchange is obtained by operating with a long bed; periods of ion exchange alternate with ones of exchanger regeneration, and the first period ends when a certain level of breakthrough begins. Completion of this period does not mean that the exchanger in the bed has been fully utilized; the degree of utilization is related to the mode of exchange. This is maximal if the diffusion is of internal type, and breakthrough will set in later than in external diffusion. The ratio of exchange times to breakdown characterizes the relative increase in the exchange duration  $\alpha$ . If, for instance, it is possible in some way to raise  $\alpha$  to 2, this means that a bed of exchanger of given quality and given length will operate twice as long before breakthrough than when the other mode of operation is employed, and the exchange capacity will be much better utilized. Pulsating motion corresponds to this requirement.

It might seem that solution to the problem consists in increasing the speed of the liquid and thus transferring the process to the internal-diffusion range; but this method is sometimes inapplicable, because it leads to a considerable reduction in the dimensionless length  $\omega^*$ :

$$\omega^* = \frac{\sigma H (D_{1c} + \Gamma D_{1a})}{u R^2 m} \quad (1)$$

and hence to transformation of the bed into a short one, which offers little protection. The method of oscillating the liquid is better also in that it enables one to increase the Biot number without altering the dimensionless length of the layer.

Rosen [4, 5] has considered mass transfer in the motion of a liquid through a layer of spherical particles, while particles of other shapes have been considered in [6]. Apart from exact solutions, which are troublesome for direct use, approximate solutions have also been derived that enable one to determine the relative liquid concentration  $\Delta = c_1/c_0$  at the exit from the layer with a set degree of accuracy.

We use the approximate solutions of [4-6] to find  $\alpha$ :

$$\alpha = \frac{1 + \sqrt{\frac{4}{15 \omega^*} \operatorname{erf}^{-1}(2\Delta - 1)}}{1 + \sqrt{\frac{4}{3 \omega^*} \left( \frac{1}{\operatorname{Bi}^*} + \frac{1}{5} \right) \operatorname{erf}^{-1}(2\Delta - 1)}} \quad (2)$$

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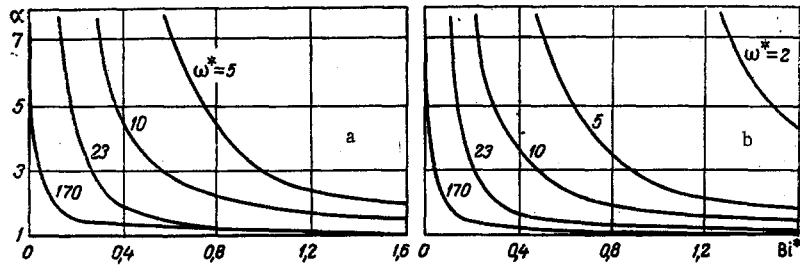


Fig.1. Relative increase in duration of ion exchange  $\alpha$  against  $Bi^*$  for various  $\omega^*$ .

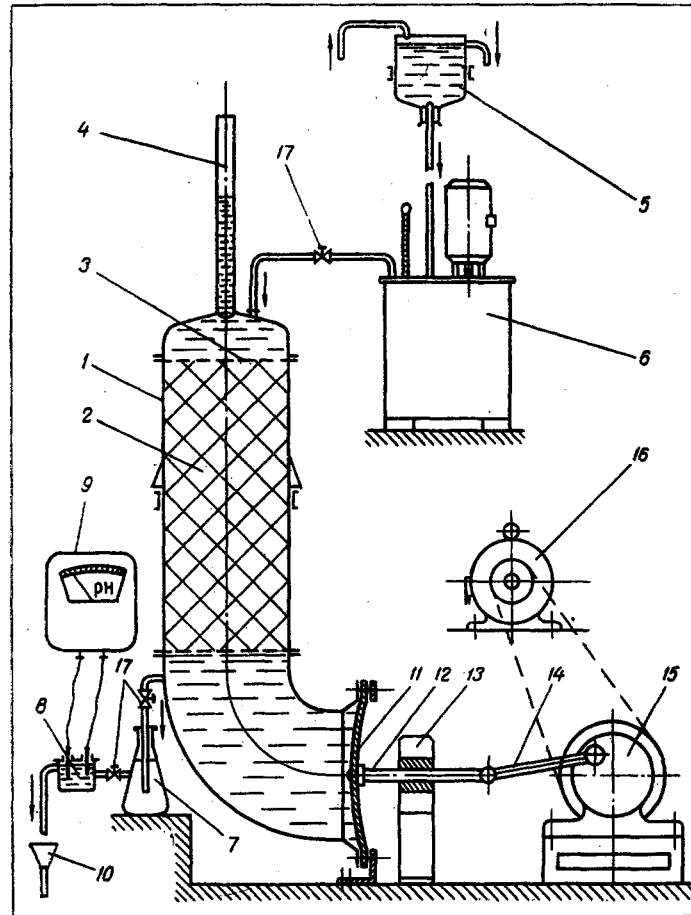


Fig.2. Apparatus with long layer of cation-exchange material: 1) column; 2) layer; 3) grid; 4) piezometric tube; 5) pressure tank; 6) thermostat; 7) intermediate tank; 8) electric cell; 9) pH-meter; 10) funnel; 11) membrane; 12) rod; 13) directing plug; 14) connecting rod; 15) eccentric; 16) electric drive; 17) tap.

In (2)

$$Bi^* = \frac{kR}{D_{1c} + \Gamma D_{1a}} \quad (3)$$

We see from (2) that for certain values of  $Bi^*$  and  $\omega^*$  the denominator becomes 0, and  $\alpha \rightarrow \infty$ ; for a layer with a given  $\omega^*$  we can determine the  $Bi^*_{\min}$  for which  $\alpha \rightarrow \infty$ :

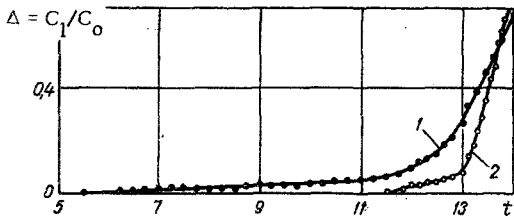


Fig. 3. Output kinetic curves: 1)  $\omega A = 0$ ; 2)  $\omega A = 1.12$  cm/sec; t, h.

$$Bi_{\min}^* = \frac{5}{\frac{15}{4} \omega^* \frac{1}{(\text{erf}^{-1})^2 (1 - 2\Delta)} - 1} \quad (4)$$

Expression (4) shows that one cannot use (2) to calculate  $\alpha$  for an arbitrary  $\omega^*$  when  $Bi^*$  is close to  $Bi_{\min}^*$ ; as industrial ion-exchange sorption is often operated at low filtration rates [1], where  $Bi^*$  is small, we have only restricted use for (2).

The most suitable solution for practical purposes is the general one for mass transfer between a stationary bed and in infiltrating liquid [7]; in our symbols, that solution takes the form

$$\Delta = \exp(-\omega^* B_1 \mu_1^2) \left[ \exp(-\mu_1^2 \tau) I_0(2\mu_1^2 \sqrt{\omega^* B_1 \tau}) + \mu_1 \int_0^\tau \exp(-\mu_1^2 \theta) I_0(2\mu_1^2 \sqrt{\omega^* B_1 \tau}) d\theta \right], \quad (5)$$

where

$$\begin{aligned} \text{tg } \mu_1 &= \frac{1}{Bi^* - 1} \mu_1; & B_1 &= \frac{6Bi^{*2}}{\mu_1^2 (\mu_1^2 + Bi^{*2} - Bi^*)}; \\ \tau &= \tau' - (1 - B_1) \omega^*; & \tau &= D^* t / R^2; & \tau' &= D^* t' / R^2. \end{aligned}$$

See [8] for values of  $\mu_1$ ,  $B_1 = f(Bi^*)$ .

Figure 1 shows calculated  $\alpha$  as derived via (5) for  $\Delta = 0.005$  and  $\Delta = 0.01$ ; here  $\alpha$  was found as the ratio of the  $\tau'$  derived for internal-diffusion conditions ( $Bi^* = \infty$ ) to the  $\tau'$  corresponding to the given  $Bi^*$ .

The above arguments may be applied to our experiments with a long bed (Fig. 2). We used KU-2 cation exchange resin, and the initial solution was tap water, in which calcium is the dominant cation. The initial concentration in the solution was  $c_0 = 7.12 \cdot 10^{-3}$  g-eq/liter, which corresponds to  $\Gamma = 2.1 \cdot 10^3$  on the equilibrium curve [3]. The initial solution passed from the head tank 5 via the thermostat 6 to the column 1 containing a long layer 2 between the grids 3; the pulsation was produced by a membrane device and the drive of parts 11-16. The outgoing solution passed through the intermediate vessel 11, the electrode cell 8 to the funnel 10; the pH meter 9 recorded the pH directly. The pressure tube 4 was used to measure the amplitude of the oscillations.

Figure 3 shows dilution curves, where curve 1 was for a uniform flow ( $\omega A = 0$ ) with a flow speed of  $0.153 \cdot 10^{-2}$  m/sec, while Fig. 2 was for the same speed but with pulsation ( $\omega A = 1.12$  cm/sec), which led to internal-diffusion conditions. Figure 3 shows that the exchange in the pulsation condition for  $\Delta = 0.01$  was 1.75 times greater than that for uniform motion.

We have to determine  $\omega^*$  and  $Bi^*$  in order to compare theory with experiment (Fig. 1).

In accordance with [3], in the region  $\Gamma \gg 1$ ,  $D_{1c} \ll D_{1a}$ , while  $D_a = D^*$ ; then

$$\omega^* = \frac{\sigma H D^* \Gamma}{u R^2}; \quad Bi^* = \frac{k R}{\Gamma m D^*}.$$

The quantities appearing in  $\omega^*$  and  $Bi^*$  were determined by experiment; for instance, for the above experimental conditions (Fig. 3)  $\sigma = 0.14$ ,  $H = 0.26$  m,  $D^* = 0.75 \cdot 10^{-10}$  m<sup>2</sup>/sec,  $m = 0.23$ ,  $R = 0.406 \cdot 10^{-3}$  m,  $\omega^* = 23$ .

To find  $k$  we can use a general graphical relationship [2]

$$Nu = f(Re, Pr);$$

$$Nu = \frac{k d}{D_l}; \quad Re = \frac{u d \rho}{\varepsilon \mu}; \quad Pr = \frac{\mu}{\rho D_l}, \quad (6)$$

for 298°K,  $\rho = 997$  kg/m<sup>3</sup>,  $\mu = 0.8937 \cdot 10^{-3}$  N·sec/m<sup>2</sup>,  $\varepsilon = 0.4$ ,  $D_l = 0.676 \cdot 10^{-9}$  m<sup>2</sup>/sec,  $Re = 3.47$ ,  $Pr = 1325$ ,  $Nu = 37.1$ ,  $Bi^* = 0.35$ .

Figure 1b shows  $\omega^*$  and  $Bi^*$  for  $\alpha = 1.8$ .

The pulsating motion therefore leads to considerable acceleration of the ion exchange, which is seen as an overall increase in the ion-exchange time for the same regeneration time.

#### NOTATION

$Bi^*$	is the Biot number;
$Nu$	is the Nusselt number;
$Re$	is the Reynolds number;
$Pr$	is the Prandtl number;
$\omega^*$	is the dimensionless length of bed;
$t, t'$	are the time calculated from the moment of liquid arrival at given point and beginning of process;
$\tau, \tau'$	are the dimensionless time;
$D_{lc}, D_{la}$	are the mass conductivities in liquid and adsorption phases;
$m$	is the porosity of exchanger;
$D_a = D_{la}/m;$	
$D^*$	is the effective diffusivity;
$\Gamma$	is the mean slope of equilibrium isotherm in the given concentration range;
$R$	is the radius of exchanger particle;
$d = 2R;$	
$k$	is the mass-transfer coefficient;
$H$	is the height of bed;
$u$	is the interstitial velocity;
$\varepsilon$	is the porosity of layer;
$\sigma$	is the pore volume per unit layer volume;
$c_0$	is the initial concentration of liquid;
$c_1$	is the concentration of liquid flowing out of ionite layer;
$\omega$	is the fluctuation frequency;
$A$	is the amplitude of pulsations;
$\rho$	is the density of solution;
$\mu$	is the dynamic viscosity of solution;
$D_l$	is the diffusivity of $Ca^{2+}$ ions in solution;
$y = \text{erf}^{-1}x$	is the inverse function of $x = \text{erf}y$ ;
$\mu_1$	is the first root of characteristic equation;
$B_1$	is the coefficient;
$I_0$	is the modified Bessel function of the first kind of the zeroth order.

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