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Periodic Operation for Desalination with Thermally Regenerable Ion-Exchange Resin. Dynamic Studies

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Abstract

A new periodic operation in which a thermally regenerable ion-exchange resin in a basket is alternatively immersed in cold and hot reservoirs is proposed for desalting water. Dynamic behaviors are studied to decrease the concentration of salt in the cold reservoir to as small a value as possible within a limited period. Comparison between experimental and calculated values is made for the periodic operation.

INTRODUCTION

An effective desalination process referred to as Sirotherm process (*1*) has been developed by using thermally regenerable ion-exchange resins such as Sirotherm TR-10, TR-20, and Amberlite XD-2 (*2*). The regeneration of salt-loaded resins is achieved with hot water rather than with chemicals. Since hot water may be available in effluents from heat exchangers, it offers an inexpensive method of desalting low-salinity water. It is also free from secondary pollution problems. Therefore this process is competitive with other processes, such as reverse osmosis, electrodialysis, and conventional ion-exchange. However, it is not suitable for direct desalination of seawater, which has a salt content of about 600 mol/m^3, because the resins cannot be regenerated by hot water for such a concentrated salinity water.

The operation principle of the Sirotherm process is basically the same as that of conventional ion-exchange processes, so it may be applicable to present fixed- and moving-bed plants. In a previous paper (*3*), however, we proposed a more advantageous operation; that is, a periodic operation in which a thermally regenerable ion-exchange resin in a basket was alternately immersed in cold and hot reservoirs. A graphical solution for mass balance equations was presented together with analytical solutions for special cases. The experimental results indicated that this operation was simple and effective for desalting water. For each cycle of the periodic operation, the concentration in the resin phase was assumed to be equilibrated with that in the bulk liquid phase. Thus the basket had to be left for a long time to attain the equilibrium state.

In this paper, dynamic behaviors are studied to enhance the efficiency of the periodic operation; that is, to decrease the concentration of salt in the cold reservoir as much as possible within a limited period. The adsorption isotherms and the effective surface diffusivity are determined for predicting unsteady-state behavior of periodic operation.

THEORY

A thermally regenerable ion-exchange resin consists of a mixture of weak-acid and weak-base resins to adsorb salt from a solution at low temperature. The resin is subsequently regenerated by leaching out the salt with hot water.

The process depends on the reversibility of equilibrium in which both H^+ and OH^- ions dissociated from water act as the driving force:

$$R_AH + R_B + NaCl \underset{\text{Hot}}{\overset{\text{Cold}}{\rightleftarrows}} R_ANa + R_BHCl$$

where R_AH is the acidic resin and R_B the basic resin.

To utilize this characteristic feature, a new periodic operation is proposed as shown in Fig. 1. A basket made of wire gauze contains a thermally regenerable ion-exchange resin which has a higher adsorption capacity for salt in cold water than in hot water. The basket is first immersed in the cold reservoir to adsorb the salt in the water for a period t_c. This is the cold

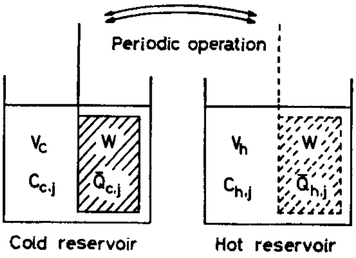

FIG. 1. Schematic of periodic operation for desalting water.

half of the first cycle. Then the basket is moved and immersed in the hot reservoir to desorb salt from the resin into the water for a period t_h. This is the hot half of the first cycle. This operation is repeated until a specified total time T.

Mass balance equations may be written for the end of each half cycle. For the cold half of cycle j, we have

$$W(\bar{Q}_{c,j} - \bar{Q}_{h,j-1}) = V_c(C_{c,j-1} - C_{c,j}) \tag{1}$$

and for the hot half of cycle j,

$$W(\bar{Q}_{h,j} - \bar{Q}_{c,j}) = V_h(C_{h,j-1} - C_{h,j}) \tag{2}$$

The values of $\bar{Q}_{h,0}$, $C_{c,0}$, and $C_{h,0}$ should be given as initial conditions.

The average concentration in the resin phase at the end of the cold half, $\bar{Q}_{c,j}$, is given by

$$\bar{Q}_{c,j} = 24 \int_0^{d_p/2} Q_{c,j}(r) r^2 \, dr / d_p^3 \tag{3}$$

where $Q_{c,j}(r)$ is a local concentration at the radial coordinate in the resin particle r at the end of the cold half of cycle j. $\bar{Q}_{h,j}$ is given in a similar way. The temperature and concentration in the bulk liquid phase are kept constant throughout each reservoir by mechanical stirring.

When both t_c and t_h are rather long, the concentrations in the resin phases, $\bar{Q}_{c,j}$ and $\bar{Q}_{h,j}$, may be assumed to be equilibrated with those in the bulk liquid concentration, $C_{c,j}$ and $C_{h,j}$, respectively. A graphical solution for this case was presented in the previous paper (*3*).

If the concentration in the resin is not equilibrated with that in the bulk liquid phase due to t_c being too small, unsteady-state mass balance equations for the concentrations in both bulk liquid and resin phases, $c_{c,j}(t)$ and $q_{c,j}(t)$, should be solved to obtain the concentration profile at the end of each half cycle, $Q_{c,j}(r)$ and then $\bar{Q}_{c,j}$ in Eq. (3). It is assumed that the rate of ion-exchange is expressed in terms of the effective surface diffusivity within particles and that the interphase mass transfer resistance is negligible.

For the cold half of cycle j, we have

$$\frac{\partial q_{c,j}(r,t)}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_s r^2 \frac{\partial q_{c,j}(r,t)}{\partial r}\right) \tag{4}$$

$$\frac{\partial c_{c,j}(t)}{\partial t} = -\frac{6WD_s}{V_c d_p}\left.\frac{\partial q_{c,j}(r,t)}{\partial r}\right|_{r=d_p/2} \tag{5}$$

The initial and boundary conditions are

$$q_{c,j}(r,0) = Q_{h,j-1}(r) \tag{6}$$

$$c_{c,j}(0) = C_{c,j-1} \tag{7}$$

$$q_{c,j}(d_p/2, t) = f(c_{c,j}(t)) \tag{8}$$

On the assumption of negligible interphase mass transfer, Eq. (8) holds, which means that there is equilibrium of the liquid phase with the resin phase at the surface.

By rearranging Eq. (5) in terms of Eq. (4) and integrating the resultant equation, we have

$$V_c(c_{c,j}(0) - c_{c,j}(t)) = W(\bar{q}_{c,j}(t) - \bar{q}_{c,j}(0)) \tag{9}$$

where

$$\bar{q}_{c,j}(t) = 24 \int_0^{d_p/2} q_{c,j}(r, t) r^2 \, dr/d_p^3 \tag{10}$$

Equation (9) means that the removal of salt from the liquid phase is identical to the gain in the resin phase.

Equations (9) and (10) will be used instead of Eq. (5) for numerical calculations described later because of their simplicity.

When Eqs. (4), (9), and (10) with conditions (6)–(8) are solved, the values of $Q_{c,j}(r)$ and $C_{c,j}$ at the end of the cold half of cycle j, $t = t_c$, can be obtained by

$$q_{c,j}(r, t_c) = Q_{c,j}(r) \tag{11}$$

$$c_{c,j}(t_c) = C_{c,j} \tag{12}$$

Thus the average concentration $\bar{Q}_{c,j}$ may be calculated by Eqs. (3) and (11).

In a similar way, we have equations for the hot half of cycle j.

EXPERIMENTAL

A schematic drawing of the apparatus is shown in Fig. 2. A basket (1) was made of 100 mesh stainless steel wire gauze. Sirotherm TR-20, manufactured by ICI Australia Ltd., was used as the thermally regenerable resin. The swollen resin was sieved in water, and the fraction of particles from 16 to 20 mesh (average diameter, $d_p = 9.2 \times 10^{-4}$ m) was packed into the basket. The weight fraction of water content in the swollen resin was 0.637, which was obtained from the differences of weight between swollen and dry resins. Two glass flasks (2) were used as the cold and hot reservoirs and were set in the thermostat (3) at 10 and 70°C, respectively. The reservoirs contained water which was distilled and further deionized. A weighed quantity of NaCl (more than 99.9% purity) was added to the reservoirs to obtain a given concentration of salt.

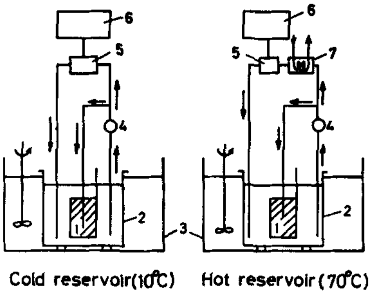

FIG. 2. Schematic drawing of experimental apparatus. 1: Basket. 2: Flask. 3: Thermostat. 4: Pump. 5: Conductivity cell. 6: Recorder. 7: Heat exchanger.

Solutions in the reservoirs were recycled by pumps (4) to make the concentration and temperature constant. The concentration change of NaCl with time was measured continuously by a flowthrough electric conductivity cell (5) with a recorder (6). Since the direct measurement of electric conductivity was unstable at 70°C, the solution in the hot reservoir was cooled to 10°C by a heat exchanger (7).

The resin in the basket was first immersed in the cold reservoir for 10, 20, and 50 min. Then the resin was moved into the hot reservoir and immersed for 10 min. This periodic operation was repeated to decrease the concentration of NaCl in the cold reservoir.

The solution and resin particles in the basket in both cold and hot reservoirs were mixed by recycling flows enough to neglect the liquid-to-particle mass transfer resistances.

RESULTS

Equilibrium Resin Capacities

Test tubes which contained swollen resins and NaCl solutions were immersed in thermostats at 10 and 70°C for about 10 h. The concentration of NaCl solution was measured by an electric conductivity cell. The capacities were calculated from the difference between initial and final concentration of NaCl in the liquid phase:

$$q_\infty = q_0 + V(c_0 - c_\infty)/W \qquad (13)$$

As shown in the log-log plots of Fig. 3, the results may be correlated by Freundlich-type isotherms within certain concentration ranges.

At 10°C, we have

$$q_\infty = 635.8 c_\infty^{0.216}, \qquad 5.0 \leq c_\infty \text{ (mol/m}^3\text{)} \leq 60.0 \qquad (14)$$

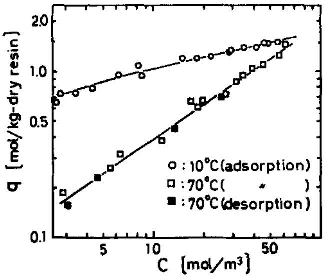

FIG. 3. Equilibrium resin capacities at 10 and 70°C.

and at 70°C,

$$q_\infty = 81.3 c_\infty^{0.687}, \qquad 3.0 \leqq c_\infty\ (\text{mol/m}^3) \leqq 60.0 \tag{15}$$

As the concentration of NaCl increases, the isotherm at 70°C becomes close to that at 10°C. Thus, when $c > 50$ mol/m^3, the resin cannot be regenerated any more.

Desorption experiments ($q_\infty < q_0$) as well as adsorption experiments ($q_\infty > q_0$) were carried out at 70°C to compare both cases. The results in Fig. 3 show a good agreement within the range of this experiment.

Surface Diffusivity, D_s

To estimate the dynamic behavior of periodic operation, it is necessary to investigate the rate of mass transfer into the resin particles. The fresh resin ($q_0 = 0$) in the basket was immersed in the solution of NaCl at 10 or 70°C until the concentration of resin equilibrated with that of the liquid phase.

The solid lines in Fig. 4 show the concentration changes of NaCl with time at 10 and 70°C. The equilibrium was almost attained after 40 min at 10°C, while it was attained within 10 min at 70°C.

Equations (4)–(10) for only the first cold half of the cycle [that is, $j = 1$, $Q_{h,j-1}(r) = q_0 = 0$, and $C_{c,j-1} = c_0$] were numerically solved for various values of D_s. The partial differential equation, Eq. (4), was rewritten to a difference equation for computations. The dotted lines in Fig. 4 are the calculated results for values of D_s which gave the minimum square residue between experimental and calculated results.

It is evident from Fig. 4 that the estimated values of D_s are dependent on the initial concentrations in the liquid phase c_0.

The dependence was correlated by using the average of initial and final concentrations, $c_{av} = (c_0 + c_\infty)/2$. Figure 5 shows the correlation together with experimental points.

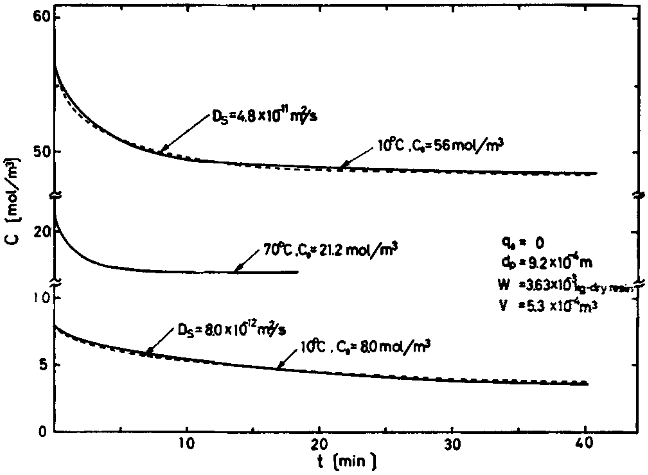

FIG. 4. Typical time–concentration curves for NaCl.

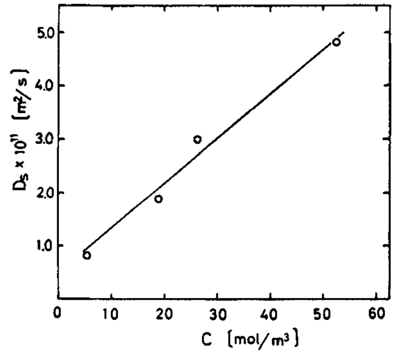

FIG. 5. Surface diffusivity vs concentration of NaCl solution.

$$D_s = 4.1 \times 10^{-12} + 8.62 \times 10^{-13} c_{av}, \quad \text{at } 10^\circ\text{C} \tag{16}$$

The same dependence of effective surface diffusivity D_s was reported for the adsorption of organics in an aqueous phase on activated carbon by Sudo et al. (*4*). They discussed the possibilities of several mechanisms: (1) increase of unit hopping distance of hopping model; (2) change of the ratio of the chemical potential gradient to the gradient of the amount adsorbed with the increase with q; and (3) decrease of heat of adsorption with q.

However, it seems difficult to discriminate the mechanisms. In this study, although the surface diffusion is assumed to be only a single rate-determining step, other steps such as pore diffusion and the ion-exchange reaction rate may influence the overall rate of mass transfer.

As shown in Fig. 4, the concentration in the liquid phase at 70°C approaches equilibrium very quickly. Therefore it is not necessary to study unsteady states at 70°C in the periodic operation. This is discussed in the following section.

Periodic Operation for Desalting Water

In experimental runs the adsorption time t_c in the cold half of the cycle at 10°C was varied from 10 to 50 min to study the dynamic behavior of periodic operation. On the other hand, the desorption time t_h in the hot half of the cycle at 70°C was fixed at 10 min in which equilibrium between resin and liquid phase was already attained as shown in Fig. 4.

Figure 6 shows the experimental results for $t_c = 10$ min together with the predicted ones for both $t_c = 10$ min and ∞. In the case of $t_c = \infty$, since we can assume equilibrium in both cold and hot reservoirs, the graphical method in the previous paper (*3*) can be used for the prediction, and the points C_1, H_1, C_2, H_2, etc. are obtained. In the case of $t_c = 10$ min, Eqs. (1)–(12) must be solved for the cold half of the cycle by a computer. The function for the equilibrium in Eq. (8), $f(c_{c,j}(t))$, is given by Eq. (14) or (15), which was determined from experiments. The surface diffusivity D_s in Eq. (4) is calculated by Eq. (16) as a function of the concentration in the liquid phase. Since equilibrium can be assumed for the hot half of the cycle at $t_h = 10$ min in any case, the points H_j'' ($j = 1, 2, \ldots$) in Fig. 6 are on the isotherm at 70°C. On the other hand, the

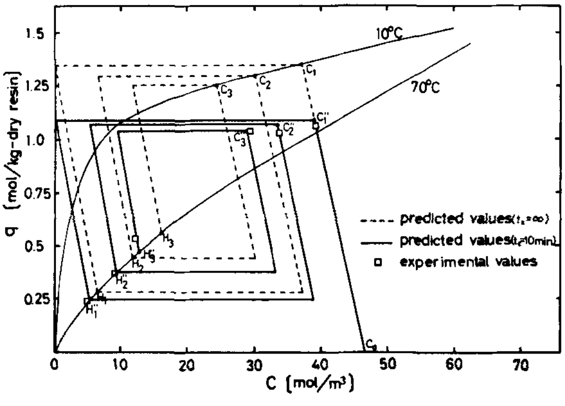

FIG. 6. Periodic operation for $C_{c,0} = 46.5\ \mathrm{mol/m^3}$, $\bar{Q}_{h,0} = C_{h,0} = 0$, $V_c = 5.3 \times 10^{-4}\ \mathrm{m^3}$, $V_h = 6.0 \times 10^{-4}\ \mathrm{m^3}$, $W = 3.63 \times 10^{-3}$ kg dry resin.

points C_j'' ($j = 1, 2, \ldots$) for the cold half of the cycle at $t_c = 10$ min are in the middle of two isotherms at 10 and 70°C. Agreement between experimental and predicted values is fairly good as seen in Fig. 5.

The concentration changes with time in the cold reservoir are shown in Fig. 7 for periodic operations with three runs of $t_c = 10$, 20, and 50 min. Experimental results, indicated by solid lines, are in good agreement with calculated ones (dotted lines) although there are some differences for the case of $t_c = 50$ min. It is evident from Fig. 7 that the concentration in the cold reservoir decreases rapidly as the adsorption time t_c is decreased. To demonstrate this trend more clearly, Fig. 8 shows the effect of t_c on the concentrations in the cold reservoir at the specified total time of $T = 180$ or 360 min. Dotted lines indicate the calculated results for $C_{c,0} = C_{h,0}$

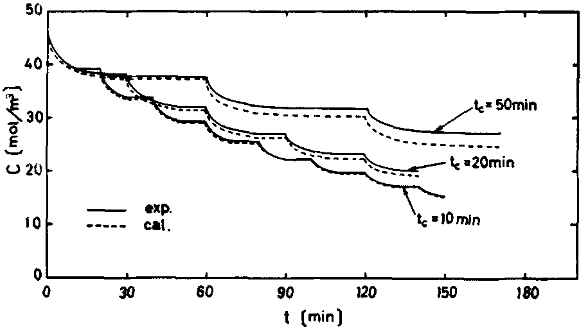

FIG. 7. Concentration changes with time for periodic operation: $C_{c,0} = 46.5$ mol/m^3, $\bar{Q}_{h,0} = C_{h,0} = 0$, $V_c = 5.3 \times 10^{-4}$ m^3, $V_h = 6.0 \times 10^{-4}$ m^3, $W = 3.63 \times 10^{-3}$ kg dry resin.

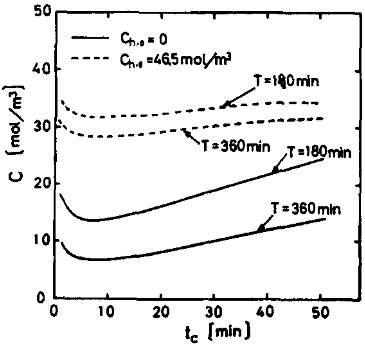

FIG. 8. The effect of adsorption time on the concentration in the cold reservoir for $C_{c,0} = 46.5$ mol/m^3, $\bar{Q}_{h,0} = 0$, $V_c = 5.3 \times 10^{-4}$ m^3, $V_h = 6.0 \times 10^{-4}$ m^3, $W = 3.63 \times 10^{-3}$ kg dry resin.

$= 46.5\ \mathrm{mol/m^3}$. For industrial use, since the feed water to both cold and hot reservoirs may be contaminated by salt, this case would be more practical than the case of $C_{c,0} = 46.5\ \mathrm{mol/m^3}$ and $C_{h,0} = 0$ (indicated by solid lines) although the efficiency for desalination is lower. It is seen from Fig. 8 that the optimum adsorption time is about 8 min for any case. If $t_c < 8$ min, the efficiency becomes lower because the adsorption is too short to decrease the concentration in the cold reservoir compared with the desorption time of $t_h = 10$ min. The cost of periodic operation which is required to move the basket between reservoirs is not considered in this optimization. Therefore, in the application of this periodic operation for desalting water on an industrial scale, the optimization must be considered from this point of view.

CONCLUSION

A new periodic operation has been proposed for desalting water by using a thermally regenerable ion-exchange resin. The adsorption isotherms at 10 and 70°C were expressed by the Freundlich type. The surface diffusivity D_s was evaluated from batchwise data and was found to be dependent on the concentration in the liquid phase. Comparison between experimental and calculated results of periodic operation was made for adsorption time $t_c = 10$, 20, and 50 min and desorption time $t_h = 10$ min. It was revealed from the calculations for periodic operations that the optimal adsorption time t_c was about 8 min when the desorption time t_h was fixed at 10 min. With respect to the optimization of desalting water, we must still investigate the adsorption isotherms and rates with various conditions such as temperature and salt concentrations. Costs such as the movement of the basket must also be considered for practical purposes.

SYMBOLS

C	concentration of salt in the liquid phase at the end of half cycle ($\mathrm{mol/m^3}$)
c	concentration of salt in the liquid phase in the period of half cycle ($\mathrm{mol/m^3}$)
D_s	effective surface diffusivity ($\mathrm{m^2/s}$)
d_p	diameter of swollen resin (m)
Q	concentration of salt in the resin phase at the end of half cycle (mol/kg dry resin)
$\bar{Q}$	average concentration of salt in the resin phase at the end of half cycle, defined by Eq. (3)
q	concentration of salt in the resin phase in the period of half cycle

	(mol/kg dry resin)
$\bar{q}$	average concentration of salt in the resin phase in the period of half cycle, defined by Eq. (10)
r	radial coordinate in the resin particle (m)
T	specified total time (min)
t	time (s or min)
V	volume of solution (m^3)
W	weight of dry resin (kg)

Subscripts

c	cold
h	hot
j	cycle number
0	initial
∞	final or equilibrium

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