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Periodic Operation for Desalting Water with Thermally Regenerable Ion-Exchange Resin

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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 developed to desalt water. A graphical solution for mass balance equations is presented together with analytical solutions for special cases. Experiments were performed. This operation may have some advantages over conventional fixed-bed and moving-bed operations.

INTRODUCTION

A new, promising process for desalting water has been developed by utilizing thermally regenerable ion-exchange resins. Since the regenerant is hot water rather than acids and alkalis for conventional resins, this process is free from secondary pollution problems. A mixture of weak-acid and weak-base resins is used to adsorb salt from a solution at low temperature, and the resin is subsequently regenerated by leaching out the salt with a relatively small volume of hot water. The process depends on the reversibility of the equilibrium

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

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

This process was referred to as the Sirotherm process by Weiss et al.

(*1–5*) who extensively investigated the resins with thermal regeneration. The theoretical model was developed to describe the thermal regeneration of ion-exchange resins by Hamann (*6*, *7*). Ackerman et al. (*8*) introduced Amberlite XD-2 resin as a novel ion-exchange resin with thermal regeneration.

Parametric pumping, which is an adsorptive separation technique based on periodic, synchronous, coupled transport actions, has experimentally been investigated for the NaCl–H_2O–resin system (*9–13*). However, since an alternative repetition of heating and cooling is required, the consumption of heat energy may be very high.

In this paper a new periodic operation in which a thermally regenerable ion-exchange resin in a basket is alternatively immersed in cold and hot reservoirs is investigated to desalt water. This operation may have some advantages over conventional fixed-bed and moving-bed operations.

THEORY

The schematic of periodic operation is shown in Fig. 1. A basket made of wire gauze contains a thermally regenerable ion-exchange resin which has higher adsorption capacity for salt in cold water than in hot water. The basket is first immersed in the cold reservoir to adsorb salt in water and then moved into the hot reservoir to desorb salt from the resin to water. This operation is repeated to decrease the concentration of salt in the cold reservoir. For the cycle *j*, mass balance equations can be written as follows.

For the cold reservoir we have

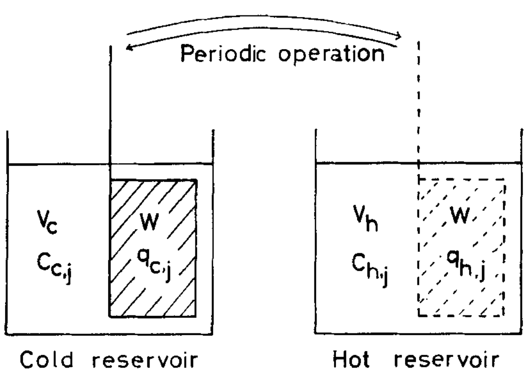

FIG. 1. Schematic of periodic operation for desalting water.

$$C_{c,j-1}V_c + q_{h,j-1}W = C_{c,j}V_c + q_{c,j}W \tag{1}$$

and for the hot reservoir we obtain

$$C_{h,j-1}V_h + q_{c,j}W = C_{h,j}V_h + q_{h,j}W \tag{2}$$

For both cold and hot reservoirs, the concentrations in the resin phase, $q_{c,j}$ and $q_{h,j}$, are assumed to be equilibrated with the concentrations in the bulk liquid phase, $C_{c,j}$ and $C_{h,j}$, respectively. The temperature and concentration are kept constant throughout each reservoir by mechanical stirring.

The theory for this periodic operation may be related to that for the equilibrium staged model of the cycling zone technique for countercurrent distribution (*14*).

Graphical Solution

In general, resin capacities in equilibrium with cold and hot salt solutions may be given as shown in Fig. 2. Operation line equations are

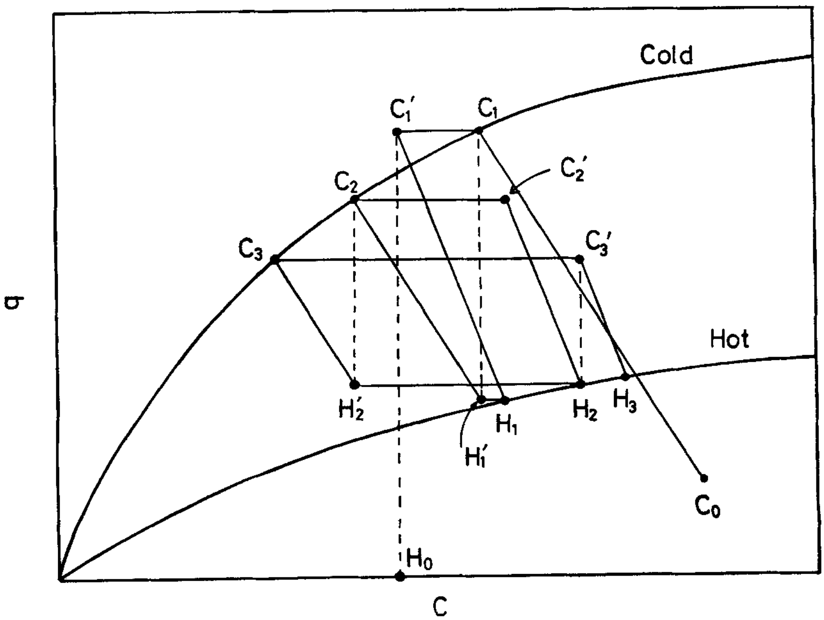

FIG. 2. Graphical solution method for concentrations in the cycle *j*.

obtained by rewriting Eqs. (1) and (2):

$$q_{c,j} = q_{h,j-1} - (V_c/W)(C_{c,j} - C_{c,j-1}) \tag{3}$$

and

$$q_{h,j} = q_{c,j} - (V_h/W)(C_{h,j} - C_{h,j-1}) \tag{4}$$

A graphical solution is given by the following procedure. (1) Draw a straight line with slope $-V_c/W$ through the initial point C_0 $(C_{c,0}, q_{h,0})$ and obtain the intersection of this line and the curve of resin capacity in equilibrium with cold salt solution. This intersection corresponds to the point C_1 $(C_{c,1}, q_{c,1})$. (2) Draw a straight line with slope $-V_h/W$ through the point C_1' $(C_{h,0}, q_{c,1})$. The intersection of this line and the curve of resin capacity in equilibrium with hot salt solution corresponds to the point H_1 $(C_{h,1}, q_{h,1})$.

This procedure is repeated in order to obtain the points C_2 $(C_{c,2}, q_{c,2})$, H_2 $(C_{h,2}, q_{h,2})$, C_3 $(C_{c,3}, q_{c,3})$, H_3 $(C_{h,3}, q_{h,3})$, etc. as shown in Fig. 2. This graphical solution technique is similar to that for single-stage parametric pumping (*15*, *16*).

Analytical Solutions for Special Cases

If q is independent of C or q is proportional to C, we can obtain analytical solutions. Two cases are considered in this section.

Case I. $q_c = K_c$ and $q_h = K_h$ $(K_c > K_h)$. For this case, Eqs. (1) and (2) may be rewritten

$$C_{c,j} - C_{c,j-1} = -(W/V_c)(K_c - K_h), \qquad j = 1, 2, 3, \ldots \tag{5}$$

$$C_{h,j} - C_{h,j-1} = (W/V_h)(K_c - K_h), \qquad j = 1, 2, 3, \ldots \tag{6}$$

Summations of the cycle from 1 to j in Eqs. (5) and (6) yield, respectively,

$$C_{c,j} = C_{c,0} - (jW/V_c)(K_c - K_h) \tag{7}$$

$$C_{h,j} = C_{h,0} + (jW/V_h)(K_c - K_h) \tag{8}$$

It is evident from Eq. (7) that $C_{c,j}$ becomes zero if cycle j is greater than $C_{c,0}V_c/\{W(K_c - K_h)\}$.

Case II. $q_c = K_c'C_c$ and $q_h = K_h'C_h$ $(K_c' > K_h')$. In this case, Eqs. (1) and (2) may be rewritten as

$$C_{h,j} = \{(K_c'W + V_c)C_{c,j+1} - V_cC_{c,j}\}/(K_h'W), \quad j = 1, 2, 3, \ldots \quad (9)$$

$$C_{c,j} = \{(K_h'W + V_h)C_{h,j} - V_hC_{h,j-1}\}/(K_c'W), \quad j = 1, 2, 3, \ldots \quad (10)$$

By substituting Eq. (9) into Eq. (10), we have

$$(K_c'W + V_c)(K_h'W + V_h)C_{c,j+2} - \{(K_c'W + V_c)V_h + (K_h'W + V_h)V_c + K_c'K_h'W^2\}C_{c,j+1} + V_cV_hC_{c,j} = 0, \quad j = 1, 2, 3, \ldots \quad (11)$$

The solution of Eq. (11) is given as

$$C_{c,j} = a_1 + a_2[V_cV_h/\{K_c'W + V_c)(K_h'W + V_h)\}]^{j-1}, \quad j = 2, 3, \ldots \quad (12)$$

where

$$a_1 = \frac{K_h'(C_{c,0}V_c + q_{h,0}W + C_{h,0}V_h)}{(K_c'K_h'W + V_hK_c' + V_cK_h')} \quad (13)$$

$$a_2 = \frac{K_c'V_h(C_{c,0}V_c + q_{h,0}W) - K_h'V_hC_{h,0}(K_c'W + V_c)}{(K_c'W + V_c)(K_c'K_h'W + V_hK_c' + V_cK_h')} \quad (14)$$

As the cycle j increases, $C_{c,j}$ tends to a_1 because the value of $V_cV_h/\{(K_c'W + V_c)(K_h'W + V_h)\}$ is always less than unity.

For the Cycle 1, that is, $j=1$, from Eq. (1) we have

$$C_{c,1} = (C_{c,0}V_c + q_{h,0}W)/(K_c'W + V_c) \quad (15)$$

On the other hand, the value of $C_{h,j}$ can be obtained from substitution of Eq. (12) into Eq. (9).

EXPERIMENTAL

Sirotherm TR-20, manufactured by ICI Australia Limited, was used as the thermally regenerable resin. The swollen resin was sieved in water and the fraction of particles from 16 to 20 mesh (the average diameter, $d_p = 0.092$ cm) was used for our experiments. The fraction of water content in the swollen resin was 0.637, which was obtained from the differences of weight between dry and swollen resins. The resin was packed in the basket made by 100 mesh stainless steel wire gauze. Two glass flasks were used as the cold and hot reservoirs and were set in the thermostats at 10 and 70°C, respectively. The reservoirs contained water which was distilled and further deionized. NaCl was added in the reservoirs to obtain given concentrations of salt. Constant concentrations and temperatures in the reservoirs were maintained by magnetic stirring.

The resin in the basket was first immersed in the cold reservoir at 10°C for 120 min and then moved into the hot reservoir at 70°C for 90 min. This operation was repeated to decrease the concentration of NaCl in the cold reservoir.

RESULTS

To obtain equilibrium resin capacities at 10 and 70°C, test tubes which contained swollen resins and NaCl solution were immersed in the thermostats for about 10 hr. The capacities were calculated from the differences between initial and final concentrations of NaCl in the liquid phase and are shown in Fig. 3.

Experimental results for periodic operations are shown in Figs. 4 and 5. Since these results are in good agreement with equilibrium resin capacities at 10 and 70°C, the assumption of $q_{c,j}$ and $q_{h,j}$ in equilibrium with $C_{c,j}$ and $C_{h,j}$, respectively, may be valid for our experimental conditions of periodic operations. The values predicted from the graphical

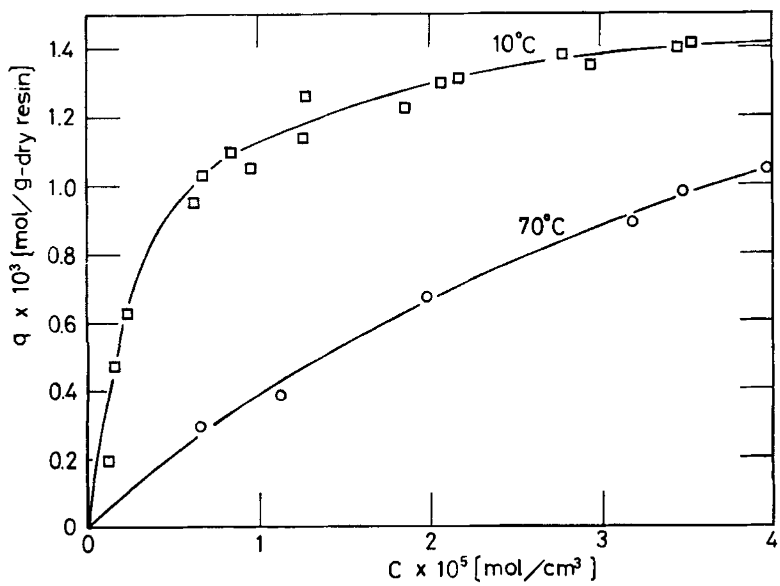

FIG. 3. Equilibrium resin capacities at 10 and 70°C.

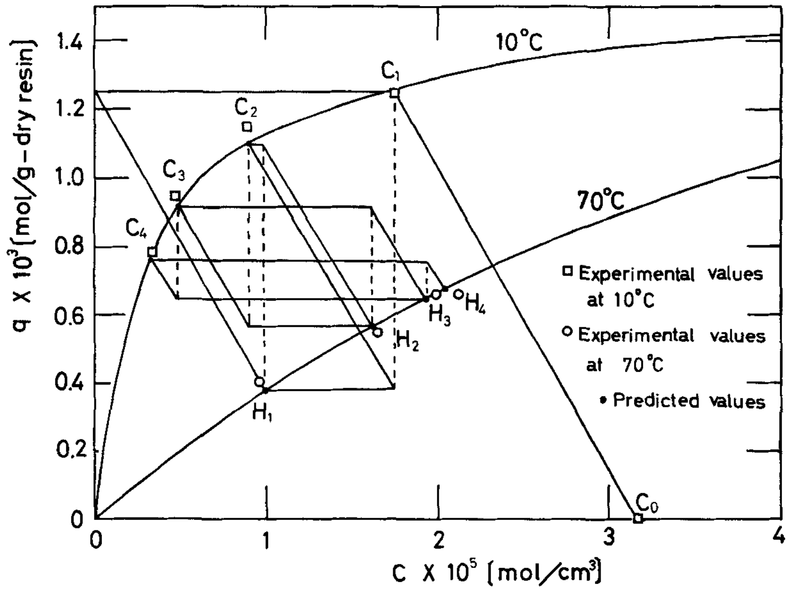

FIG. 4. Experimental results of periodic operation for $C_{h,0} = 0$. Other conditions: $V_c = V_h = 320\ \text{cm}^3$, $W = 3.63$ g-dry resin, $q_{h,0} = 0$, $C_{c,0} = 3.17 \times 10^{-5}$ mole/cm³.

solution technique are also shown in Figs. 4 and 5. The agreements between experimental and predicted values are fairly good. Figure 4 shows the case of $C_{h,0} = 0$, that is, the initial concentration in the hot reservoir was zero. The concentration of NaCl in the cold reservoir at Cycle 4, $C_{c,1}$, is about 1/5 times that at Cycle 1, $C_{c,1}$. Figure 5 shows the case of $C_{h,0} \doteqdot C_{c,1}$, that is, the initial concentration in the hot reservoir was adjusted to the concentration in the cold reservoir at Cycle 1. In this case, $C_{c,4}$ is about 1/2.5 times $C_{c,1}$. For industrial use, since the feed water to both cold and hot reservoirs may be contaminated by salt, the case of Fig. 5 would be more probable than the case of Fig. 4.

CONCLUSIONS

The new periodic operation proposed in this paper may have some advantages over conventional fixed-bed and moving-bed operations for the following reasons.

A fixed-bed operation where cold and hot water are alternatively flowed

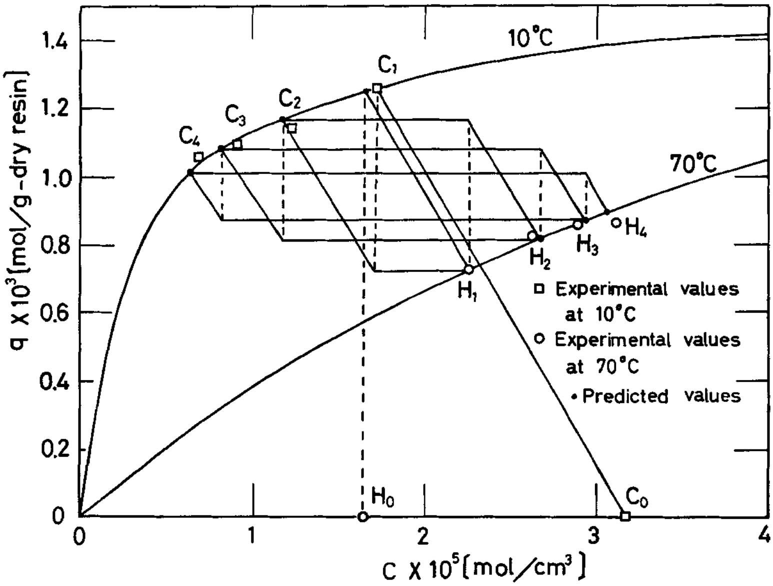

FIG. 5. Experimental results of periodic operation for $C_{h,0} \fallingdotseq C_{c,1}$. Conditions: $V_c = V_h = 320\ \text{cm}^3$, $W = 3.67$ g-dry resin, $q_{h,0} = 0$, $C_{c,0} = 3.17 \times 10^{-5}$ mole/cm³, $C_{h,0} = 1.64 \times 10^{-5}$ mole/cm³.

through a bed packed with a thermally regenerable resin may require larger amounts of hot water for the regeneration of resin and produce smaller amounts of cold water with a decreased concentration of salt because a transient state is rather long when the flow is changed.

A moving-bed operation where the resin is moved through cold and hot columns is troublesome for a separation of water and resin between two columns. Also, an attrition loss due to the moving action of resin may be high because the resin is not rigid.

On the other hand, the proposed periodic operation where only the resin in a basket is alternatively immersed in the cold and hot reservoirs is simple and effective for desalting water as indicated in our experimental results.

SYMBOLS

C concentration of salt in the liquid phase, mole/cm³

K constant for equilibrium resin capacity in Case (I), mole/g

K' constant for equilibrium resin capacity in Case (II), cm^3/g
q concentration of salt in the resin phase, mole/g dry resin
V volume of reservoir, cm^3
W weight of dry resin, g

Subscripts

c cold
h hot
j cycle number

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