

CONTINUOUS SEPARATION USING AN ANNULAR CHROMATOGRAPH WITH ROTATING INLET AND OUTLET

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Key Words: Chromatography, Continuous Preparative Separation, Annular Chromatograph, Crossflow, Ion Exchange Resin, Ion Exclusion

A continuous rotating annular chromatograph is developed for preparative separation. An annular bed is fixed while a feed nozzle and product collectors are rotated at the same speed. To evaluate the performance of this device, sodium chloride and methanol were separated by the action of ion exclusion. The rotation speed and feed rate were varied. The theoretical model predicted well the experimental concentration profile. Dispersion in the angular direction was negligible. The separation was efficiently achieved and the concentration of products was almost as high as that in the feed. The HETP was determined from the concentration profile and the contribution of respective mass transfer resistance was evaluated. The system was found to be a promising process for preparative chromatographic separation.

Several techniques have been proposed for continuous chromatographic systems in preparative separations. Use of moving chromatographic beds permits continuous introduction of feed and continuous withdrawal of products. The systems may operate in counterflow or crossflow fashion. Counterflow systems were used industrially almost 40 years ago.²⁾ Simulated counter-current systems were also established.⁵⁾ However, most counterflow systems are restricted to two-component separation.

In crossflow systems the chromatographic bed moves perpendicularly in the direction of fluid motion within the bed. The crossflow systems have no restriction on the number of components to be separated. The annular chromatograph is one of the two-dimensional separation systems.⁸⁾ An annular chromatograph rotating with respect to a feed stream and product collection points was first proposed by Martin.⁶⁾ Fox *et al.*³⁾ applied the system to separation of biological mixtures. Recently, Begovich *et al.*¹⁾ used a rotating annular bed with stationary feed stream and product collection ports. Their device was operated with an overpressure of gas and gradient elution as well as isocratic elution. A series of works has been performed for the separation of metal ions.

The continuous rotating annular chromatograph (abbreviated as CRAC) developed in this work consists of a stationary annular bed and rotating feed nozzle and product collectors. It is the opposite of the device of Begovich *et al.*¹⁾ A device of this type has

advantages as follows. Since a weighty bed need not be rotated, rotating power can be saved and scaling-up of the device is easy. The bed can be easily kept at constant temperature with a thermostat jacket. This is important especially for biological separations which require accurate temperature control.

The principle of the CRAC is shown schematically in Fig. 1. Feed is introduced at one rotating point and eluent fluid is supplied everywhere else. The products are collected by collectors which rotate at the same angular rate as the feed point. As elution proceeds,

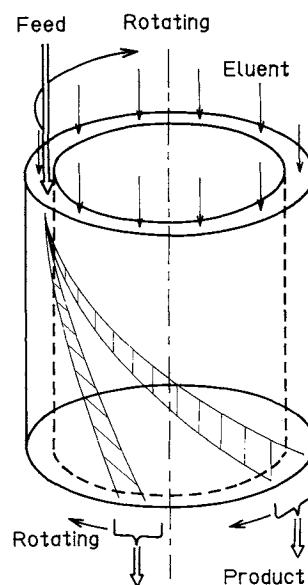


Fig. 1. Principle of continuous rotating annular chromatography.

Received April 22, 1987. Correspondence concerning this article should be addressed to M. Goto.

solutes progress down the annulus, giving the appearance of helices as the feed point rotates. The more strongly retained solutes exit from the annulus bottom at a greater distance from the feed point. Thus, steady-state multicomponent separation is accomplished with simultaneous movement in the two spatial directions.

An ion exclusion system was applied to the CRAC using a cation exchange resin as adsorbent. The separation of sodium chloride and methanol was chosen. A kinetic analysis of the system was made in the previous paper.⁴⁾ Since their equilibrium relations are linear, a theoretical analysis of the system can be easily obtained.

1. Theory

The mathematical description of the CRAC is similar to that of conventional column chromatography. The mass balance on a differential element in the CRAC yields the following equation, when radial gradients in velocity and concentration are assumed to be negligible.

$$\omega \frac{\partial C}{\partial \theta} + \frac{u}{\varepsilon_B} \frac{\partial C}{\partial z} + \frac{3\bar{D}(1-\varepsilon_B)}{R_p \varepsilon_B} \frac{\partial \bar{C}}{\partial r} \bigg|_{r=R_p} = D_L \frac{\partial^2 C}{\partial z^2} + D_\theta \frac{1}{R_a^2} \frac{\partial^2 C}{\partial \theta^2} \quad (1)$$

Mass balance in the particle gives

$$\bar{D} \left(\frac{\partial^2 \bar{C}}{\partial r^2} + \frac{2}{r} \frac{\partial \bar{C}}{\partial r} \right) = \omega \frac{\partial \bar{C}}{\partial \theta} \quad (2)$$

The boundary conditions are

$$\bar{D} \frac{\partial \bar{C}}{\partial r} \bigg|_{r=R_p} = k_f(C - C^*) \quad \text{at } r = R_p, \quad \theta > 0 \quad (3)$$

$$\frac{\partial \bar{C}}{\partial r} = 0 \quad \text{at } r = 0, \quad \theta > 0 \quad (4)$$

$$C = \bar{C} = 0 \quad \text{at } z \geq 0, \quad \theta = 0 \quad (5)$$

$$C = C_0 \quad \text{at } z = 0, \quad 0 \leq \theta \leq \theta_F \quad (6)$$

$$C = 0 \quad \text{at } z = 0, \quad \theta_F < \theta \leq 2\pi \quad (7)$$

where θ_F is given by $2\pi Q_F / (Q_E + Q_F)$.

If the angular dispersion which appears in the second term of the right-hand side in Eq. (1) is neglected, these equations are transformed into the equations for the conventional one-dimensional column system by the replacement of $\theta/\omega \rightarrow t$. In the case of the linear equilibrium relation shown in the following equation, the analytical solution was obtained by Rasmuson *et al.*⁷⁾

$$\bar{C} = KC^* \quad (8)$$

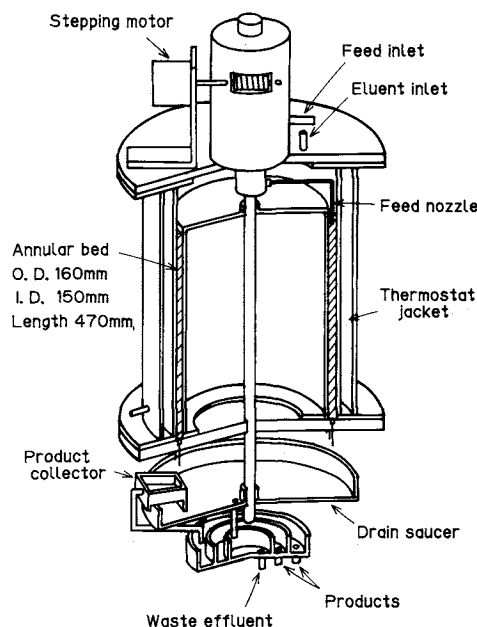


Fig. 2. Continuous rotating annular chromatograph apparatus.

2. Experimental

2.1 Apparatus

The continuous chromatograph apparatus is shown in Fig. 2. The annulus was formed from three acrylic cylinders. The two outer cylinders were attached to flanges. The inner cylinder and the outer ones were clamped concentrically to a polyvinyl chloride base plate. The cylinders were cut from 150 mm O.D. \times 142 mm I.D., 170 mm O.D. \times 160 mm I.D. and 200 mm O.D. \times 188 mm I.D. acrylic tubes. The annulus was 5.0 mm wide and 490 mm long, with an outside diameter of 160 mm. The exit holes were 90 in number, drilled equidistantly on a circumference in the center of the columnar space between two cylinders. Each of the exit holes was covered with porous plastic to prevent the falling of resins through the holes. Capillary tubes of stainless steel were inserted into the bottoms of the exit holes to collect the effluent liquid.

The feed inlet device consisted of a rotating rod of 30 mm O.D. and 125 mm length and a stationary cylinder of 45 mm I.D. and 80 mm O.D. Sealing was accomplished by two rubber seal rings (oil seal) contained in the annular space. The device was developed with some contrivances to supply feed solution from the stationary inlet port to the rotating feed nozzle. The feed nozzle was a 1.5 mm O.D. stainless steel pipe placed in the center of the annulus and immersed in the fixed bed. The depth was typically about 30 mm.

The effluent from the bottom of the column drips into a rotating drain saucer under the column. The product collectors are placed on the drain saucer. The

collected product and waste effluent flow into a stationary saucer which is concentrically divided into three parts. The products flow to product reservoirs and waste effluent flows to a drain or recirculating eluent reservoir.

The rotating feed device and drain saucer are fixed to a stainless steel shaft which is rotated by a stepping motor.

2.2 Operation

The separation of sodium chloride and methanol by ion exclusion was studied in order to evaluate the performance of the CRAC and verify the mathematical model. Since the exclusion equilibrium relations are almost linear for this separation system, the mathematical equations can be solved easily.

Degassed distilled water was continuously fed into the column. Feed solution consisted of 100 mol/m³ sodium chloride and 2000 mol/m³ methanol. The cation exchange resin Dowex 50W-X8 in the sodium form was packed to a depth of 470 mm. The resin was sieved in distilled water and a portion of average diameter 0.14 mm was adopted. The concentrations were measured by conductivity meter for sodium chloride and by differential refractometer for methanol.

To obtain the concentration profile at the bottom of the bed, a sampling device consisting of 30 evenly spaced sampling tubes of 3×10^{-6} m³ volume was used in place of the product reservoirs described above. After steady state was reached, the sampling device was put into place and the concentrations of the solution in the tubes were measured.

3. Results

3.1 Comparison between the continuous rotating annular chromatograph and the conventional column chromatograph

A chromatogram for sodium chloride and methanol mixture was obtained using a conventional one-dimensional column. The inside diameter of the column was 6.0 mm and the bed length was 438 mm. Figure 3 shows a comparison between the CRAC and the column chromatograph for the same operating condition. The solid lines indicate the column chromatogram, while circles indicate the concentration profile for the CRAC. The abscissa is the dimensionless elution position $tu/L\epsilon_B$ or $\theta u/\omega L\epsilon_B$. Sodium chloride was eluted first by ion exclusion and then methanol was eluted later. The elution position is given by the following equation.

$$\bar{\theta} = \omega L/u \{ \epsilon_B + (1 - \epsilon_B)K \} \quad (9)$$

The profile for the CRAC coincided well with that for the column system. This coincidence indicates that angular dispersion in the CRAC may be negligible, as mentioned by Begovich *et al.*¹⁾

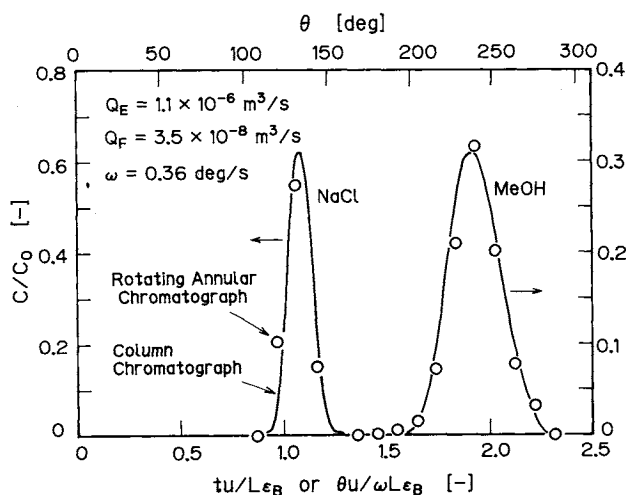


Fig. 3. Comparison between CRAC and column chromatograph.

3.2 Effect of rotation speed

Figure 4 shows the effect of rotation speed on the concentration profile while keeping the ratio of feed rate to rotation speed and the ratio of eluent rate to rotation speed constant. The solid lines indicate calculated results using the analytical solution for Eqs. (1)–(8). In the theoretical calculation, kinetic parameters determined in the previous paper⁴⁾ were used. These values are indicated in Table 1.

The peak concentration and width increased slightly with increasing rotation speed, as shown in Fig. 4. This can be explained by the increasing effect of intraparticle diffusion resistance as the liquid linear velocity increases. Agreement between the calculated curves and the experimental concentration profiles is excellent. Therefore, angular dispersion may be negligible for these operating conditions, because angular dispersion was assumed to be negligible in the theoretical calculation.

3.3 Effect of feed rate

Figure 5 shows the effect of feed rate on the concentration profile while the rotation speed and eluent rate were held constant. The peak concentration and bandwidths increased as the feed rate increased. The theoretical model was able to predict the experimental concentration profile satisfactorily.

4. Discussion

4.1 Resolution

The resolution between two chromatographic peaks is defined as the ratio of the distance between the two peaks to their average bandwidth.

$$R_s = 2(\bar{\theta}_2 - \bar{\theta}_1)/(W_1 + W_2) \quad (10)$$

where subscript 1 or 2 indicates the first or second peak on the chromatogram, respectively. The resolutions were calculated from the concentration pro-

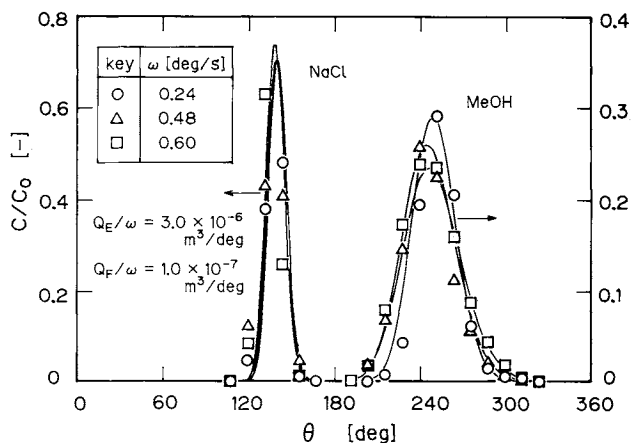


Fig. 4. Effect of rotation speed on concentration profile of CRAC.

Table 1. Kinetic parameters for ion exclusion separation

	K [—]	\bar{D} [m²/s]	Pe [—]
NaCl	0.0269	2.10×10^{-10}	0.241
MeOH	0.515	4.72×10^{-10}	0.126

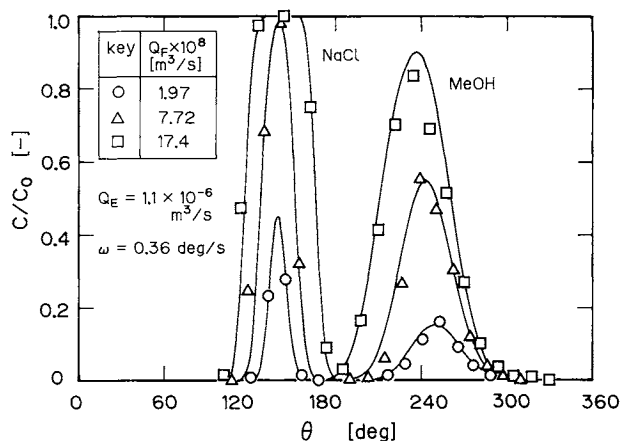


Fig. 5. Effect of feed rate on concentration profile of CRAC.

file of the CRAC. **Figure 6** shows the effect of feed rate on resolution. The circles indicate the resolution obtained from experimental data for a rotation speed of 0.36 deg/s. The solid lines indicate theoretical curves for various rotation speeds. Agreement between experiment and theory at $\omega = 0.36$ deg/s was good. The resolution decreased as the bandwidth increased with the feed rate for a constant total flow rate. The higher resolution was obtained for lower rotation speed because of low flow rate.

4.2 Limitation of feed rate

To apply the preparative chromatograph to industrial scale, throughput of the feed solution has to be increased. As shown in Fig. 6, resolution decreases as feed rate increases because of the increase in bandwidth. Therefore, feed rate is restricted by the

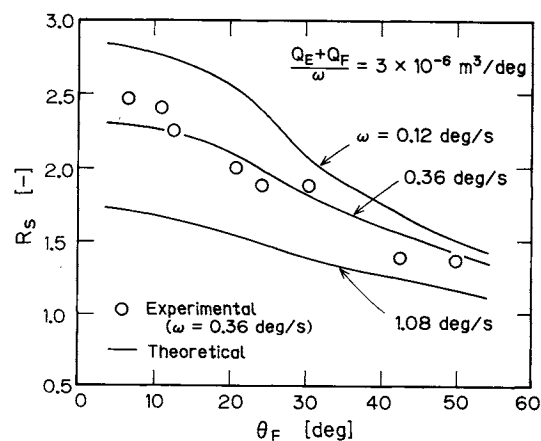


Fig. 6. Effect of feed rate on resolution.

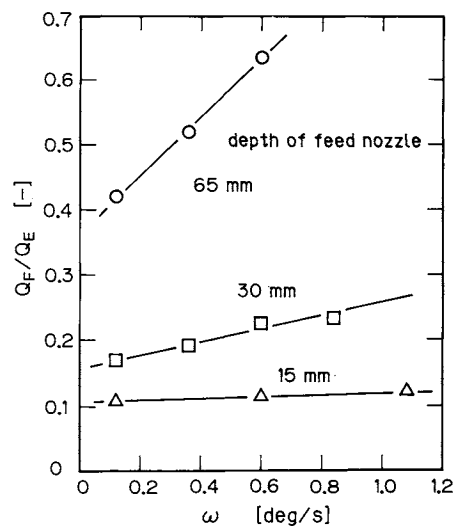


Fig. 7. Limitation of feed rate.

resolution desired for the system.

When the feed is injected at a low feed rate, feed materials flow downward together with the eluent. On the other hand, when the feed rate increases gradually for a given eluent rate, it is suddenly observed at a certain flow rate that the feed solution cannot flow down the column. In that case, part of the feed solution streams upward from the feed nozzle and then feed materials mix with the eluent liquid over the top of the bed. The upper limit of feed rate depends on the depth of the feed nozzle under the top of the fixed bed. **Figure 7** shows the influence of the depth of the feed nozzle on the limit of feed rate. The limit of feed rate increased as the rotation speed increased. The limit of feed rate was influenced significantly by the depth of the feed nozzle. The deeper the feed nozzle, the larger the feed rate. However, the resistance to moving the nozzle in the resin bed will increase as the depth of the nozzle increases. Therefore, an appropriate depth of the feed nozzle must be chosen.

4.3 HETP

The height equivalent to a theoretical plate (HETP) for the CRAC can be evaluated by the following equation,⁴⁾ using the parameters in Table 1.

$$\text{HETP} = \frac{2u}{\varepsilon_B} \left\{ \frac{1-\varepsilon_B}{\varepsilon_B} \frac{KR_p^2}{\bar{D}} \left(\frac{1}{15} + \frac{\bar{D}K}{3R_p k_f} \right) \times \left(1 + \frac{1-\varepsilon_B}{\varepsilon_B} K \right)^{-2} + \frac{D_L \varepsilon_B^2}{u^2} \right\} \quad (11)$$

To determine the rate-controlling step in the CRAC, the contribution of respective mass transfer resistance to the HETP was evaluated as described in the previous paper⁴⁾ and is shown in Fig. 8. For the flow-rate region in this work, $u = (1.0-10) \times 10^{-4}$ m/s, liquid film mass transfer resistance was negligible. While axial dispersion was dominant for lower flow rates, both axial dispersion and intraparticle diffusion were dominant for higher flow rates in this work. If higher flow rate is required to increase the throughput, using smaller particles of adsorbent may be effective for higher resolution. Because smaller particles increase the pressure drops in the bed, however, the appropriate particle size depends on the system.

4.4 Efficiency of the continuous annular chromatograph

Fox *et al.*³⁾ reported that the efficiency of operation of the continuous system was considerably lower—only 1/10 as compared with the conventional column. The efficiency was defined as the amount of eluent required for a given volume of feed solution, that is, Q_F/Q_E . The low efficiency of their results may be due to the feed injection nozzle being set at the top of the bed, thus preventing increase of feed flow rate because of mixing of feed materials with eluent liquid.

The efficiency in this work was almost the same as that of the conventional column, because the ratio of feed to eluent flow rate could be large enough for practical operation and because the angular dispersion effect was negligible.

To increase the efficiency of the column, the whole bed should be used for separation all the time. For this separation system, the efficiency can be increased by reducing the distance between the tailing of the last peak and the rising of the first peak. Figure 9 shows an example of operation under the more efficient condition.

The feed rate in Fig. 9 is almost the limiting value for the nozzle with the 30 mm depth. When it is desired to increase the feed rate over the limit, a device with multifeed points is one approach to overcoming the problem. Figure 10 shows the calculated results in the case of two feed points located in opposite directions. The throughput can be duplicated as compared with the single-feed point system, and efficient separation was achieved.

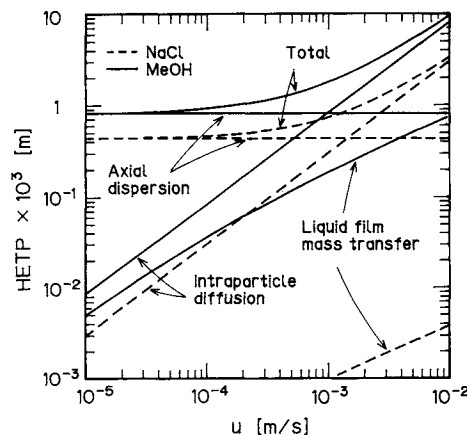


Fig. 8. Contribution of respective mass transfer resistance to HETP.

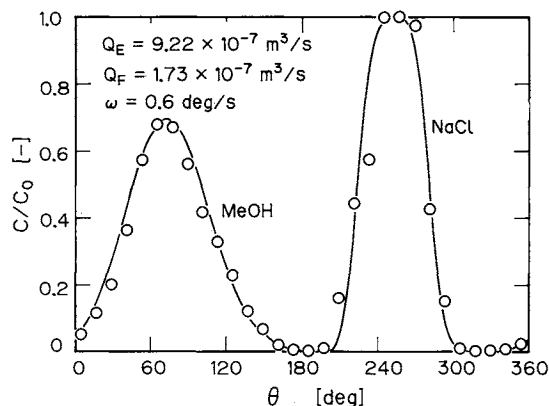


Fig. 9. Concentration profile under efficient condition.

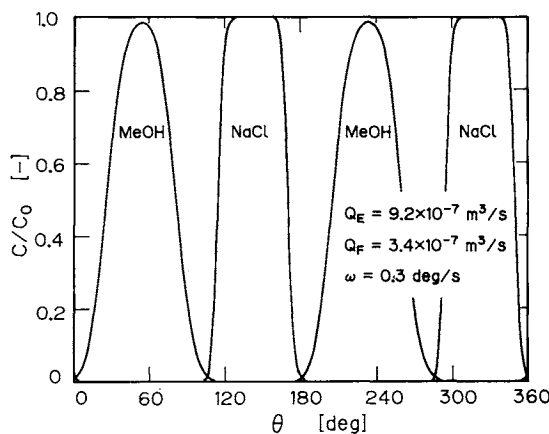


Fig. 10. Concentration profile for two-feed nozzle system.

Conclusion

The separation of sodium chloride and methanol in a continuous rotating annular chromatograph was studied. The chromatogram obtained was similar to that of a conventional column and the angular dispersion effect was negligible. The continuous rotating annular chromatograph was shown to be effective for preparative separation. The mathematical model de-

veloped for the one-dimensional column chromatograph was able to describe the CRAC system by using simple replacement from time to angular position.

Nomenclature

C	= liquid-phase concentration	[mol/m ³]
\bar{C}	= resin-phase concentration	[mol/m ³]
C_0	= feed concentration	[mol/m ³]
C^*	= equilibrium concentration	[mol/m ³]
\bar{D}	= intraparticle diffusivity	[m ² /s]
D_L	= axial dispersion coefficient	[m ² /s]
D_θ	= circumferential dispersion coefficient	[m ² /s]
K	= exclusion equilibrium constant	[m ³ /m ³]
k_f	= liquid film mass transfer coefficient	[m ² /s]
L	= bed length	[m]
Pe	= Peclet number ($= 2uR_p/\varepsilon_B D_L$)	[—]
Q_E	= eluent rate	[m ³ /s]
Q_F	= feed rate	[m ³ /s]
R_a	= radius of annular bed	[m]
R_p	= radius of adsorbent particle (= 0.07 mm in this study)	[m]
R_s	= resolution	[—]
r	= radial coordinate	[m]
t	= time	[s]

u	= superficial velocity	[m/s]
W	= bandwidth	[rad or deg]
z	= axial coordinate	[m]
ε_B	= interparticle void fraction in the bed (= 0.397 in this study)	[—]
θ	= angular coordinate	[rad or deg]
θ_F	= angular distance of feed injection	[rad or deg]
$\bar{\theta}$	= solute peak position	[rad or deg]
ω	= rotation speed	[rad/s or deg/s]

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(Presented at 52nd Annual Meeting of The Society of Chemical Engineers, Japan, at Nagoya, April 1987.)

VARIABLE-PRESSURE/VARIABLE-RATE EXPRESSION OF SEMISOLID MATERIALS

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Key Words: Solid Liquid Separation, Expression, Semisolid, Variable Pressure, Variable Rate, Dewatering, Korean Kaolin

In a batchwise variable-pressure/variable-rate expression process, the expression pressure is increased to a predetermined maximum pressure and then held constant until final equilibrium compression is obtained. For analyzing the variable-pressure/variable-rate expression process, the following assumption is made: the internal condition of compressed cake under the instantaneous pressure p in a variable-pressure/variable-rate operation is close to that in a constant-pressure operation under such a pressure p when the same volume of liquid is removed from the same amount of original materials in both operations. Using this assumption, the changes of sample thickness with expression time can be calculated from the analytical equation for the constant-pressure process based on the Terzaghi-Voigt combined model. The match between experiment and theory was satisfactory for the expression of semisolid Korean kaolin.

Introduction

Expression under variable pressure is often encountered in industry, in both batchwise and con-

tinuous operations. However, relatively little work has been reported in connection with variable-pressure/variable-rate expression. Shirato *et al.* presented both a simplified analytical theory,²⁾ which treated the modified consolidation coefficient as constant, and a more rigorous numerical method³⁾ which

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