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A High-Capacity Pressurized Continuous Chromatograph

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ABSTRACT

Multicomponent liquid chromatographic separations have been achieved by using a slowly rotating annular bed of sorbent material. The feed material is continuously introduced at a stationary point at the top of the bed, and eluent is allowed to flow everywhere else around the annulus. The rotation of the sorbent bed causes the separated components to appear as helical bands, each of which has a characteristic, stationary exit point; hence the separation process is truly continuous.

The concept has been developed primarily on a 279-mm-diam by 0.6-m-long device with a 12.7-mm-wide annulus. The effects of annulus width and diameter have been studied using the same device with annulus widths up to 114.3 mm. With this largest width, approximately 96% of the area available within the outer cylinder is devoted to the rotating sorbent bed. Further annulus-width studies have been pursued on units with 89- and 445-mm diameters. These geometric extensions to the basic concept allow extremely large capacity increases with minimal loss in separation and no increase in chromatograph diameter.

The effects associated with increased feed concentration have also been studied. In this effort as well as in the annulus-width program, the separation of copper, nickel, and cobalt components from a carbonate solution was studied in detail. The nickel and cobalt components are found in the leach liquor of the Caron process for recovering nickel and cobalt from laterite ores. Nominally 50- μ m-diam Dowex 50W-X8 cation exchange resin was used

as the bed material. The nickel concentration of the feed was varied tenfold, from 136.1 to approximately 1400 meq/L. The combined effects of the bed loading and annulus width were studied and compared with nonlinear theory.

INTRODUCTION

With its near universal applicability, versatility, and high resolution capabilities, chromatography has lacked only throughput capacity to make it an ultimate separation technique. Typical chromatographic separations are made in fixed columns and, as such, are inherently batch in nature. Various attempts have been made to increase the capacities of chromatographic devices either through cyclic operation of large-diameter columns or through continuous feeding of a mixture and continuous removal of the components in moving-bed systems (1). This work focuses on the rotating annular chromatograph, which is a cross-flow moving-bed type of system.

Martin (2) was the first to propose the concept of an annular chromatograph rotating with respect to a continuous feed stream and product collection points. In practice, the sorption bed results from packing the annular space formed between the two concentric cylinders. This entire bed (shown in Fig. 1) is slowly rotated while the feed material to be separated is continuously introduced from a fixed entry at the top of the bed with eluent fed uniformly everywhere else around the annulus. As the eluent and sorption medium cause the feed mixture to separate in the vertical direction, the rotation of the sorbent bed causes the feed components to also separate in the circumferential direction, resulting in the appearance of different helical bands. Each of the bands exits at a stationary point which is dependent on three factors: (i) the distribution coefficient of the species under the given feed, eluent, and sorbent bed conditions; (ii) the residence time of the eluent; and (iii) the rotation rate of the annulus. As long as these three factors remain constant, the elution time of each constituent, and hence its angular displacement from the fixed entry, will also remain constant. With a fixed entry assembly for the

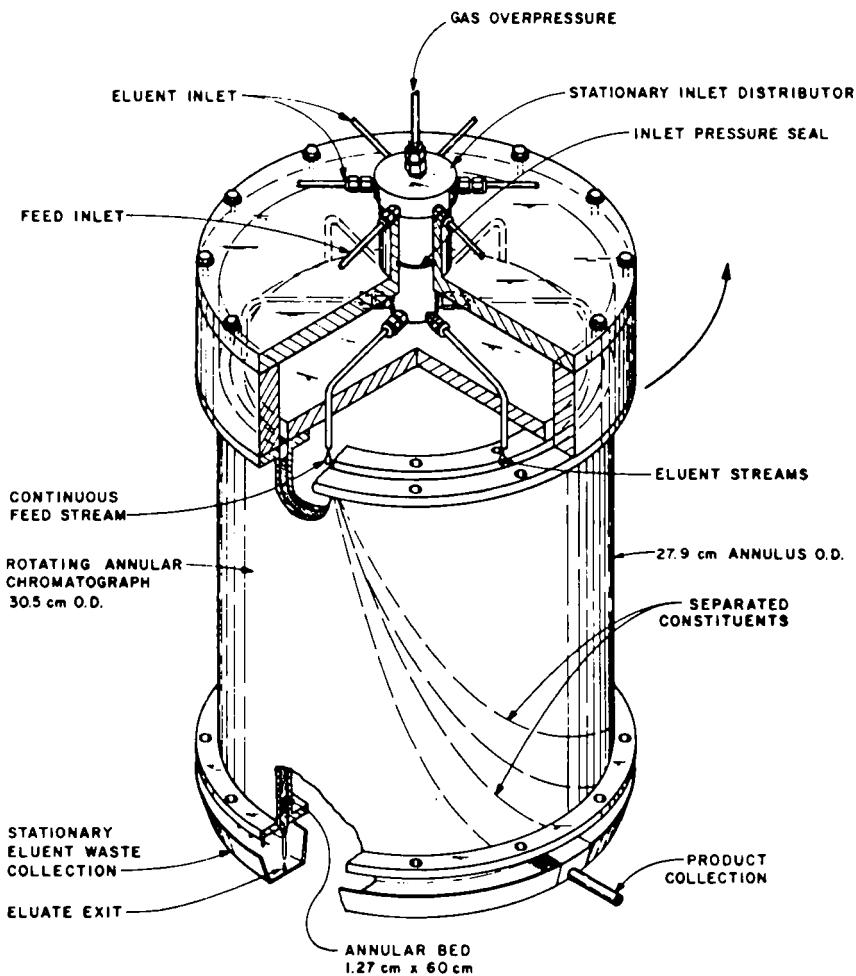


FIGURE 1. Schematic of the 279-mm-diam continuous annular chromatograph (CAC-III).

feed and constant angular displacement of each constituent during elution, constituent product collectors are also at fixed locations, despite the fact that the sorbent bed is moving. That part of the bed not receiving feed at any given time is undergoing either elution or regeneration. Thus, feed is continuously pumped into the device, and the separated components are continuously withdrawn by stationary collectors.

Scott and co-workers (3) were the first group to assemble a continuous annular chromatograph (CAC) capable of pressurized operation. Following this work, Canon and Sisson (4) described some equipment modifications which not only improved the consistency of the data, but also allowed a gradient elution mode of operation. The gradient elution technique was colorfully demonstrated in the separation of copper, nickel, and cobalt from ammonium carbonate solutions and was also applied to the separation of iron and aluminum from ammonium sulfate-sulfuric acid solutions (5). Begovich and Sisson (6) utilized the CAC in the difficult separation of zirconium and hafnium and studied the effects of feed flow rate and feed concentration on the separation of these two metals. They also presented experimental results detailing the effect of column size on CAC performance (7). Torres et al. (8), using the same equipment, studied the effects of rotation rate, eluent rate, and bed loading on ion exchange separation performance with the copper-nickel-cobalt system. In addition, some preliminary feed concentration experiments were performed.

In conjunction with experimental work, models of increasing sophistication have been applied to the CAC. Plate theory, an extremely useful modeling tool of conventional chromatography, was extended to the CAC by Scott et al. (3). Shah et al. (9) attempted a numerical solution after initializing their computational grid using the analytical solution for a conventional column (10). Bratzler and Begovich (11) extended the analytical solution of Rhee et al. (12) to a CAC, taking account of the saturability of a sorbent and the interactions present between solutes during multi-

component separations. Using a large body of experimental data, Begovich (13) extended this idealized analytical solution to incorporate the important effect of dispersion in a chromatograph. This extended model was then compared, along with the predictions of plate theory, to actual CAC experimental results (14). A complete description of the background of annular chromatography can be found in (13).

EXPERIMENTAL

Some of the physical characteristics of the basic CAC units used in this work are detailed in Table 1. A schematic of the 279-mm-diam unit, with its annulus width of 12.7 mm, is presented in Fig. 1. The annulus is formed from two concentric open cylinders, both of which are flanged at the bottom and sealed with O-rings. The inner cylinder is closed at its top, effectively making it a spacer. The outer cylinder extends approximately 80 mm above the inner cylinder and is appropriately flanged and sealed. The sorbent bed is placed within the annulus to a level just below (30 to 40 mm) the top of the inner cylinder; a layer of glass beads on top of the resin makes up the remainder of the annular bed. Eluent, feed, and gas driving pressure are introduced through a stationary inlet distributor which extends through the top flange and is sealed by two O-rings contained in the flange. This distributor is physically held stationary by support brackets, while the rest of the device is rotated via a drive shaft attached to the bottom plate. A digital-speed drive system with feedback control and forward- or reverse-direction capability, along with the appropriate gear reducers, allows the CAC to be rotated over a wide range of rates. Typical rotation rates have ranged from 15 to 275 deg/h.

Each of the three basic CAC units listed in Table 1 was fabricated similarly. The CAC-ME and CAC-II are made primarily of plastic, which limits their normal operating pressure to 274 kPa (25 psig), while the metal construction of the CAC-III allows a normal operating pressure of 1135 kPa (150 psig).

TABLE 1
Physical Characteristics of the CAC Units Used in this Study

Designation	Annulus Width, Δr (mm)	Outer Annulus Radius, r_o (mm)	$\Delta r/r_o$	Annular Bed Cross-Sectional Area (cm ²)	% Available Area*
CAC-ME	6.4	44.5	0.14	16.5	26.5
	12.7		0.29	30.4	48.9
	22.2		0.50	46.6	74.9
	31.8		0.71	57.0	91.6
CAC-II	12.7	139.7	0.09	106.4	17.3
	50.8		0.36	364.8	59.5
	114.3		0.82	592.8	96.7
CAC-III	31.8	222.3	0.14	411.7	26.5

*% available area is the cross-sectional area of the annular bed divided by the maximum possible area based on r_o .

The effect of annulus width on separation performance was tested in both the CAC-ME and the CAC-III by decreasing the diameter of the inner cylinder in each unit. As the inner diameter was decreased, while the outer diameter was held constant, the annulus width was increased. This resulted in an increased annular cross-sectional area; therefore, a larger volumetric flow rate had to be used for the same pressure driving force (i.e., same eluent velocity). The annulus widths for the CAC-ME-2 and -3 and CAC-II-2 were changed by inserting inner cylinders of varying diameter into the CAC units, while leaving all other components of the units (including their bottom plate) intact. Since the exit holes through these bottom plates were spaced evenly on diameters of 82.6 and 267 mm for the CAC-ME and CAC-II, respectively, each inner cylinder was machined with an outward flare at the bottom to allow the effluent to flow smoothly through the exit holes. This flare, which started approximately 38 mm above the bottom plate, extended from the desired inner diameter out to the original inner diameter of 76 mm for the CAC-ME and 254 mm for the CAC-II.

Some new components, which more closely resemble the probable industrial-scale configuration, were required for the CAC-II-3 because of its large annulus width (114 mm). A schematic of this unit is shown in Fig. 2. Besides the 51-mm-diam inner cylinder, a new feed system and bottom plate had to be fabricated. The bottom plate, which was designed to evenly drain the annulus, contained three exit circles, each containing 72 holes with 5-deg spacing. The three exit circles had 3.2-, 4.3-, and 5.2-mm-diam holes on radii of 44, 83, and 121 mm, respectively. The diameter ratio of these exit holes of $1.65/1.36/1$ implies that each circle should drain the CAC's cross-sectional area in the following ratio: $2.71/1.86/1$.

Three feed nozzles were used to evenly distribute the feed at the top of the annulus. These nozzles were positioned at the same radii as the exit circles (44, 83, and 121 mm). Each of the nozzles was fed using a metered feed pump in the same ratio

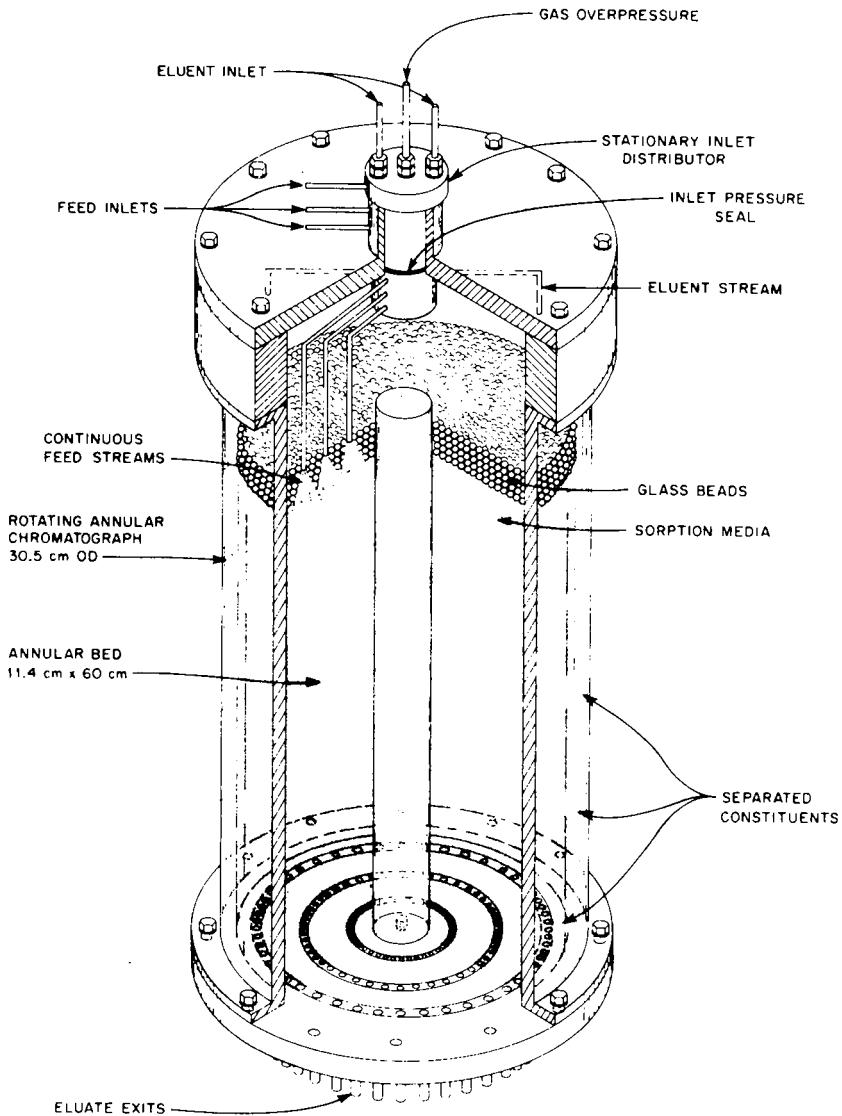


FIGURE 2. Schematic of the 114-mm-wide annulus CAC-II-3.

as the cross-sectional areas drained by their respective exit circles. In this way, an attempt was made to distribute the feed over a constant degree of arc (or wedge) across the entire annulus width.

A synthetic feed mixture containing copper, nickel, and two cobalt species (designated Cu, Ni, Co-1, and Co-2, respectively)

in ammonium carbonate solution was used in all of these experiments. The nickel and cobalt species in this mixture simulated the leach liquor produced in the Caron (15) process for nickel and cobalt recovery from laterite oxide ores. The solutes were normally eluted using 0.8 M ammonium carbonate buffered to a pH of 7.9 using carbon dioxide. Under these conditions, the elution sequence was Cu, Ni, Co-1, and Co-2.

The effect of feed concentration on the separation performance was studied by proportionally increasing the concentrations of the four species in the mixtures from baseline levels of 1 g Cu/L, 4 g Ni/L, and 1 g/L for each cobalt species to four times these levels. The highest concentration is near the saturation condition at the pH (7.9) selected for this investigation.

THEORY

Much of the theoretical development necessary for the current investigation has been discussed in previous papers in this series (3, 11, 13, 14). The steady-state material balance for a rotating continuous annular chromatograph may be written as follows:

$$\omega \frac{\partial c}{\partial \theta} + \omega \left(\frac{1 - \epsilon}{\epsilon} \right) \frac{\partial n}{\partial \theta} - D_\theta \frac{\partial^2 c}{\partial \theta^2} - \frac{D_r}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) = D_z \frac{\partial^2 c}{\partial z^2} - \frac{V}{\epsilon} \frac{\partial c}{\partial z}, \quad (1)$$

where the boundary conditions are:

$$(1) \text{ for } \theta = 0, \text{ all } z, \text{ all } r \quad : \quad c = n = 0$$

$$(2) \text{ for } z = 0, 0 < \theta < \theta_f \quad : \quad c = c_f \\ \text{all } r \\ \theta_f < \theta < 360 \text{ deg} : \quad c = 0$$

$$(3) \text{ at } z = \infty, 0 < \theta < \theta_f \quad : \quad c = c_f \\ \text{all } r \\ \theta_f < \theta < 360 \text{ deg} : \quad c = 0$$

$$(4) \text{ at } z = \infty, \text{ all } \theta, \text{ all } r \quad : \quad c = 0$$

$$(5) \text{ at } r = r_i, \text{ all } z, \text{ all } \theta \quad : \quad \frac{\partial c}{\partial r} = 0$$

$$(6) \text{ at } r = r_o, \text{ all } z, \text{ all } \theta \quad : \quad \frac{\partial c}{\partial r} = 0.$$

Of the three dispersion coefficients, it is anticipated that only the axial component, D_z , will be significant in the annular chromatograph. Indeed, in work with narrow annuli, Begovich (13) has shown that angular dispersion is negligible. Further, if the feed has a uniform radial distribution, no effect of radial dispersion will be observed. This last condition, which is readily obtained in narrow annuli, may prove more difficult in wide-annulus devices. Nonuniform distribution detracts from efficiency and therefore is avoided where possible. Hence it is usual to ignore any radial contributions to dispersion, leaving axial dispersion as the only important contribution to the mass balance.

Rhee et al. (12) obtained an analytical solution to Eq. (1) for the case of no dispersion

$$\omega \frac{\partial c}{\partial \theta} + \omega \left(\frac{1 - \epsilon}{\epsilon} \right) \frac{\partial n}{\partial \theta} + \frac{V}{\epsilon} \frac{\partial c}{\partial z} = 0 , \quad (2)$$

where the dimensional translation from time to angular position (i.e., $\theta = wt$) has been made. It was assumed that local adsorption equilibrium exists throughout the bed and that one may apply nonlinear Langmuir competitive solute-resin binding isotherms to many separation processes, as follows:

$$n_i = \frac{\frac{N_c K_{Li} c_i}{m}}{1 + \sum_{j=1}^m K_{Lj} c_j} . \quad (3)$$

As the concentration of solute increases, the equation describes a tendency to saturate the sorbent. It is postulated that a finite number of binding sites exists and the tendency of any particular solute to bind decreases as sites become filled. In multicomponent chromatography, this means that the presence of a solute with a higher affinity for the sorbent (and thus a larger K_L value) will effectively displace solutes with lower sorbent affinities. At low liquid solute concentrations, the Langmuir isotherms reduce to linear uncoupled equations.

With this relation between solid- and liquid-phase compositions substituted into Eq. (2), the m coupled partial differential equations may be posed as a Riemann's problem and solved in terms of m generalized Riemann invariants. Bratzler and Begovich (11) brought numerical tractability to the problem through computer solution of this idealized problem as applied to the annular chromatograph. This theory allows good prediction of exit solute band position but, because dispersion is ignored, underpredicts bandwidth and the shape of the exit solute peaks.

The foregoing model was extended by Begovich (13) by superimposing a variance (i.e., dispersion) onto the predicted idealized concentration profile. This approach involves an assumption of linearity which will be applicable in cases where dispersion makes a small-to-moderate contribution and where concentrations are low. A full solution to Eq. (1) will require a large matrix computer method. The variance for a Gaussian curve can be related to a vessel dispersion number (VDN) as follows (16):

$$\sigma^2 = 2\epsilon D_L/VL = 2 \cdot VDN . \quad (4)$$

Best-fit variances were found for the observed concentration profiles of a large number of runs involving several chromatographs and a wide variety of operating conditions. Regression of the averaged solute VDN values against eluent Reynolds numbers yielded the following correlation:

$$\overline{VDN}_x = 1.06 \times 10^{-2} \cdot Re^{0.77} . \quad (5)$$

When this dispersion correction was applied to the idealized model, the experimental results gave a correlation coefficient of 0.9.

As discussed earlier, a known system (copper, nickel, and cobalt) was used in the current study. Therefore, both the distribution coefficients and the dispersion coefficient correlation are known. The zero-dispersion model is used to predict band

position. Dispersion is added through the VDN prediction, and new concentration profiles are generated using a computer program which has been written for this purpose.

The resolution of two components is of particular interest in assessing the performance of a chromatograph. If the angular displacements of the peaks of the exit bands of components 1 and 2 are $\bar{\theta}_1$ and $\bar{\theta}_2$, respectively, and the baseline widths of the two peaks are W_1 and W_2 , then their resolution is defined as

$$R \equiv 2(\bar{\theta}_2 - \bar{\theta}_1)/(W_1 + W_2) . \quad (6)$$

For Gaussian-shaped profiles, unit resolution indicates no dead volume between peaks, but with essentially no overlap either. Optimal use is made of a bed when a resolution value of 1 is obtained. Since all of the parameters that contribute to resolution may be computed using the generalized model, the resolution may also be predicted.

EXPERIMENTAL RESULTS AND DISCUSSION

In all of the experiments reported here, Dowex 50W-X8 cation exchange resin with a wet-size diameter range of 44 to 74 μm was used to separate the mixture of Cu, Ni, Co-1, and Co-2. The concentration of each species could be measured as a function of θ for all experiments (and radial position in the case of the largest CAC-II annulus) by use of an in-line spectrophotometer.

Earlier publications (7, 14) have shown a comparison of concentration profiles for each of the four species with the extended theory, using narrow-annulus results. Agreement between theory and experiment was excellent in all cases, indicating that the proposed theory is valid. Indeed, a critical test of the theory is its prediction of the shape of the concentration profile. A comparison was made of a typical experiment in the current wide-annulus series. A concentration profile taken from the middle circle of sample ports in the CAC-II-3 was selected as a typical comparison. Feed concentrations for all species were at the base-

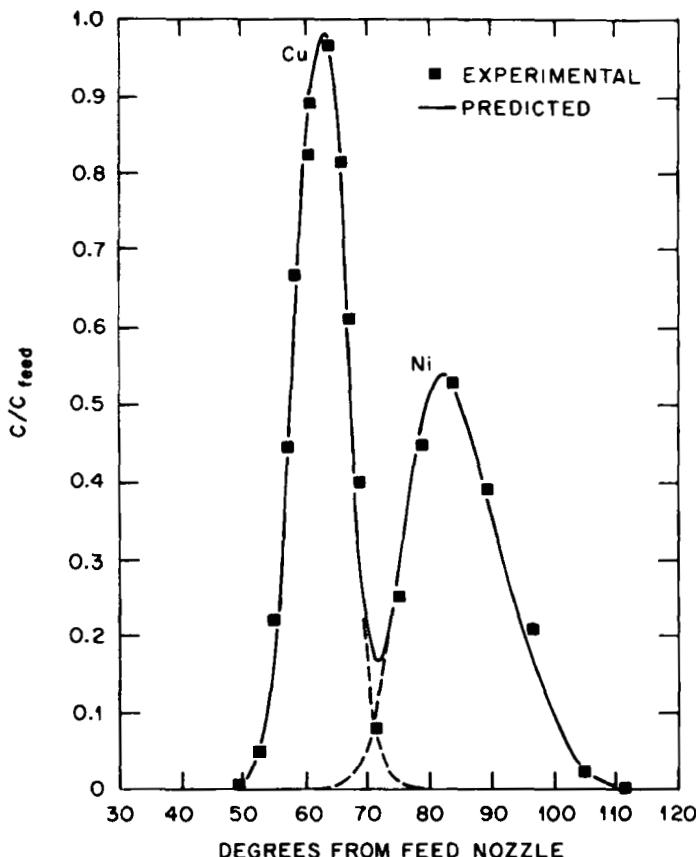


FIGURE 3. Copper and nickel concentration profiles from the CAC-II-3 central exit port.

line levels; the feed-to-eluent ratio was 0.03, and the rotation rate was 90 deg/h. Figure 3 shows predicted profiles for copper and nickel with experimental data points superimposed. Since almost perfect agreement was obtained between experiment and theory for most of the chromatogram, only a few points were selected for illustration from the continuous spectrophotometer output. The cobalt peaks, not shown in this chromatogram, manifest similar agreement between experiment and theory. Indeed, all of the baseline concentration level results show qualitatively similar agree-

ment. Theory and experiment appear to deviate only in the area where substantial overlap of the peaks occurs. This disagreement is possibly caused by the different response that equal concentrations of copper and nickel have in the spectrophotometer.

Effect of Annulus Width

The single largest equipment change one can make to increase the capacity of a given outside diameter CAC is to increase its annulus width by using a smaller-diameter central insert. In conventional chromatographs, however, increasing the diameter for the sake of capacity often leads to decreased resolution. Theory predicts that, with proper feed distribution (constant feed/eluent ratio as a function of radial position), there should be no effect of radius since radial dispersion is being manifested only under conditions of nonuniform feed distribution. Two chromatographs of different outside radii were used to explore the effect of annulus width: the CAC-ME ($r_o = 44.5$ mm) and the CAC-II ($r_o = 139.7$ mm). As is shown in Table 1, the area inside r_o dedicated to the resin bed ranged from 26.5 to 91.6% for the smaller chromatograph and from 17.3 to 96.7% for the larger unit. These percentages represent 3.5-fold and 5.5-fold increases, respectively. In each case, the increase is realizable at the cost of the added resin required to fill the wider annulus.

The effect of annulus width on the resolution of the components in a mixture for comparable feed, flow, and other operating conditions is an important figure of merit for performance of a high-capacity chromatograph. Figure 4 presents such conditions for the four annulus widths used in the smaller chromatographic unit (CAC-ME). Resolution is shown as a function of the loading on the column (i.e., the percentage feed-to-eluent rate). Since no functionality in radial position (i.e., no radial dispersion) is built into the theory, a single, solid line describes the predicted resolution-loading relationship. Within the expected experimental error, a single curve predicts the resolution behavior of the copper-nickel pair. The somewhat anomalous behavior observed for

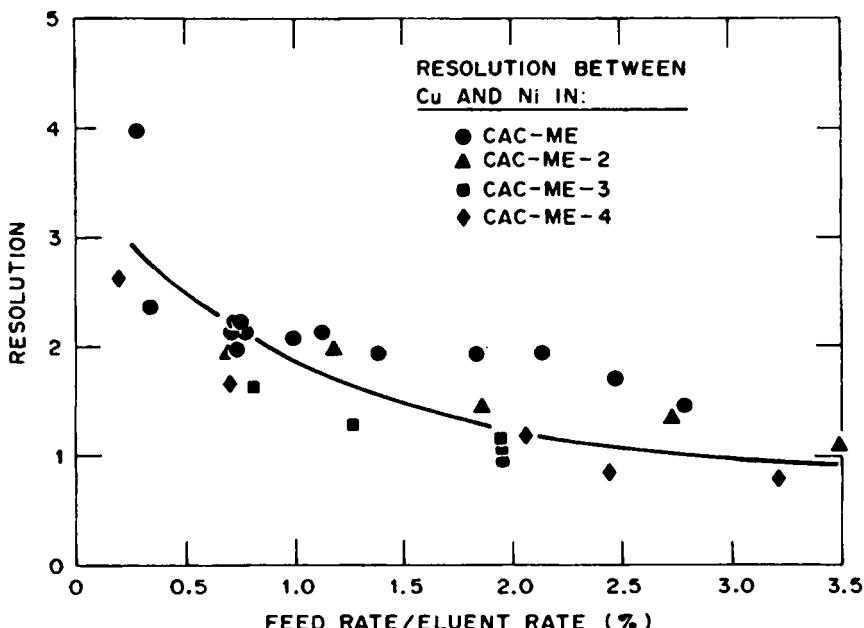


FIGURE 4. Resolution between copper and nickel for four annulus widths in CAC-ME.

the narrowest-annulus CAC (circles on graph) can probably be explained by the fact that these data points were obtained at a slightly different pH from the others. Separation is a sensitive function of pH in this chemical system (17). Similar agreement between theory and experiment was found with the other component pairs.

In performing similar experiments with the CAC-II unit, there was some concern about obtaining uniform distribution of the feed at the largest annulus width. Therefore, three feed points and three take-off locations were used (see Fig. 2). A single feed and a single take-off location were used in the two narrow-annulus experiments. Several experiments were performed at all three annulus widths, and the data are compared in Fig. 5 on a resolution-vs-loading curve. In this case, a wider range of loadings was

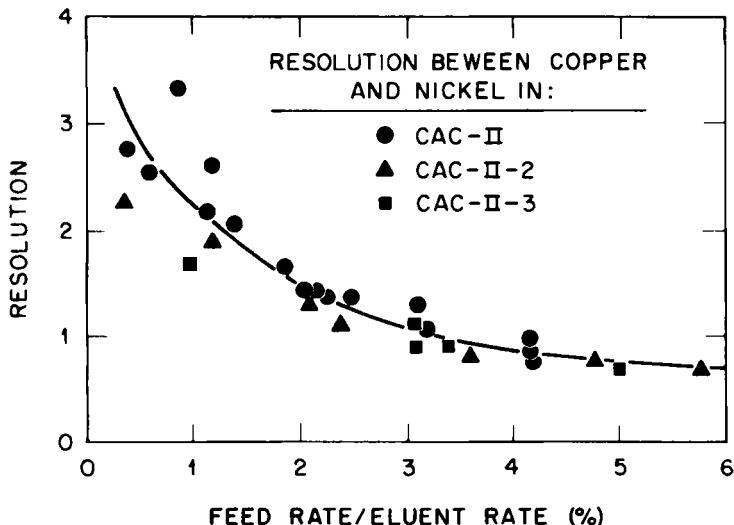


FIGURE 5. Resolution between copper and nickel for three annulus widths in CAC-II.

obtained and better control of the pH was maintained. The resulting agreement between experiments is substantially improved over Fig. 4. The points for the widest annulus are flow-average resolutions for the three exit streams. Comparable results were obtained for the other component pairs.

The only evidence of any radial effects appears in the low loading region (below 2%), where the results for the wide-annulus unit are generally substantially below those for the narrower-annulus unit. This departure appears to increase with annulus width. A possible explanation is that the feed mixture enters through a small tube in the section and is assumed to take on the shape of the wedge of bed into which it enters. Viewed from the top, the stream enters in circular form and only approaches a wedge shape if it is sufficiently large to be impeded by the walls of the annulus or an adjacent feedstream. Low flows apparently fall victim to this effect and hence are subject to radial redistribution, as well as having an effectively higher loading than is

calculated for ideal distribution. An ideal distribution may be approached by providing several feed ports across the annulus.

In the widest-annulus case for CAC-II, the three feed nozzles were positioned as shown in Fig. 6. Feed rates which would theoretically give a uniform flow distribution were then calculated. This standard flow distribution yielded a substantial skew in resolution toward the outside radius. Based on these initial resolutions, the flow distribution was redistributed to account

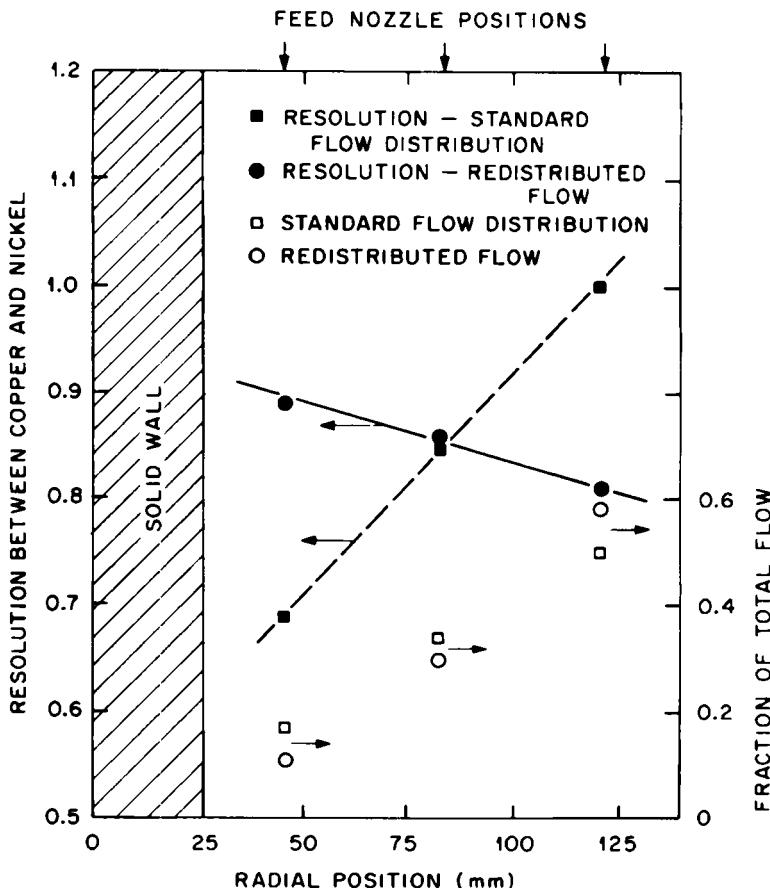


FIGURE 6. Copper-nickel resolution as a function of feed flow distribution.

for the loading imbalance (outside flow increased, others decreased). The resulting performance is much closer to uniform, although a slight overcorrection is apparent.

It is evident that at least 96% of the total area within the annulus may be used. Total removal of the insert is probably inadvisable because of possible radial effects that could cause transport of solute across the center line. Second, the central post lends some physical support to the bed.

Effect of Feed Concentration

Many investigations to determine the effect of feed concentration have been performed recently. Canon et al. (5) explored feed concentrations both below and slightly above the normal values selected for the current study and in the same pH region. A recent review of these data (13) indicated that the results could be predicted using the linearized theory modified for dispersion. The objective of our current study is to test the concentration limits of the extended theory and to observe the effect of concentration on chromatographic performance.

To allow a sufficiently wide range of feed concentrations, copper was omitted from the feed mixture and a pH of 9.0 was selected (8). The band positions of nickel and Co-1 were switched as a result of the pH change. Feed concentrations up to ten times higher than normal were used in experiments in the CAC-II-1 at a loading of 0.5% and a rotation rate of 90 deg/h. The results for band position are shown in Fig. 7, while resolution data as a function of feed concentration are given in Fig. 8. The analytical model for interacting isotherms was compared with the band position data. The trends of all three components are predicted throughout the concentration range. Further, this prediction depends only on distribution coefficients obtained in the low concentration-noninteracting region.

Prediction of the resolution can be expected to be more difficult. As concentration increases, it may be expected that solid-phase resistance to adsorption may become significant in addition

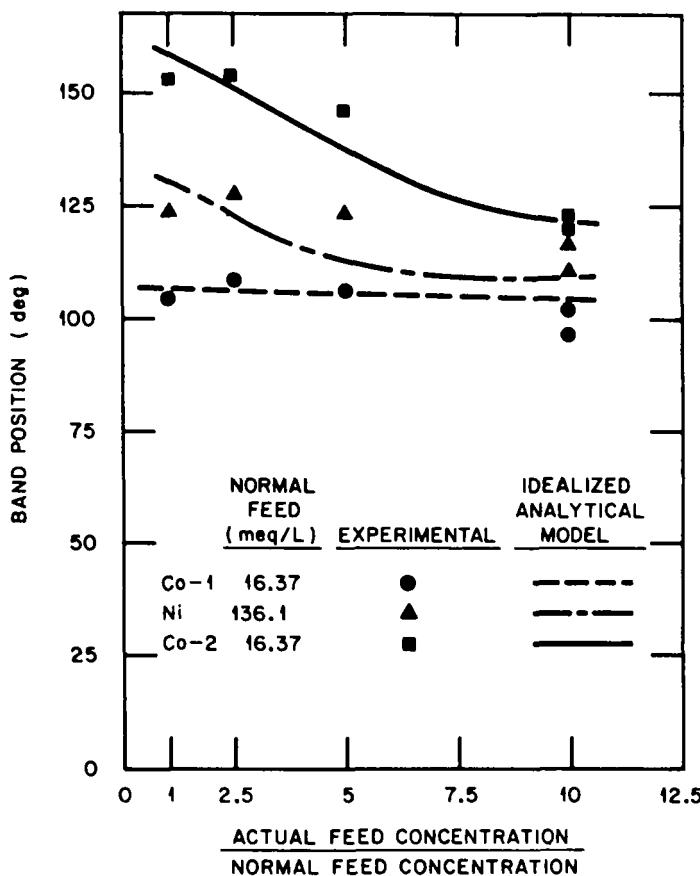


FIGURE 7. Band position as a function of feed concentration using a nickel-cobalt feed mixture and an eluent of pH 9.0.

to the fluid dispersion. Also, the linear approximations of the interactive Langmuir isotherm [Eq. (3)] will become more inaccurate. With these possibilities in mind, the dispersion model was applied to the current resolution data. The Ni-Co-1 resolution data were omitted for the sake of clarity since they were similar to those plotted on the other two curves. In all three cases, the estimates only departed grossly from experiment in the concentra-

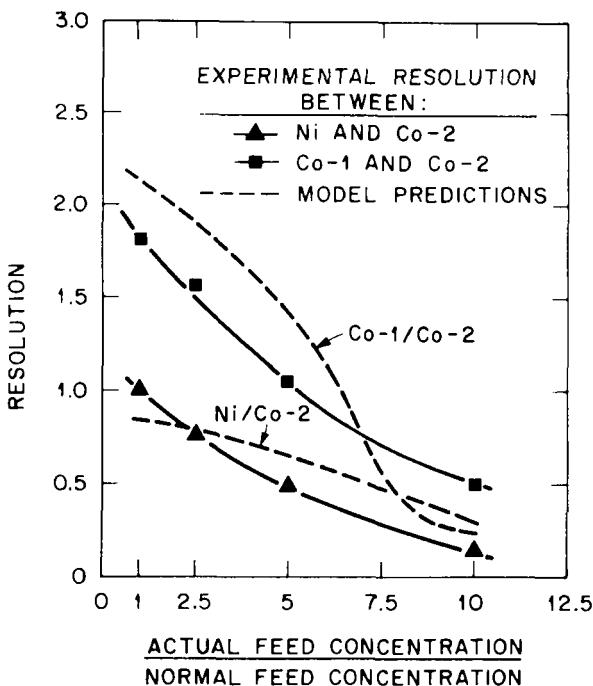


FIGURE 8. Resolution as a function of feed concentration using a nickel-cobalt feed mixture and an eluent of pH 9.0.

tion range above five times normal, a region where resolutions for this chemical system are quite low and where experimental results as well as theoretical predictions may be open to question. More study would be required to identify the sources of the deviations.

Overall, chromatographic performance tends to deteriorate with increasing concentration primarily because of competition for adsorption sites, which results in smaller separation of peak positions. This is predicted by the analytical theory extended to account for dispersion.

Combined Effects of Annulus Width and Concentration

The feed concentration was increased by a factor of 4 over the normal concentration by using the four-species mixture at a pH

of 7.9. The behavior of mixtures with concentrations twice and four times normal was observed in the wide-annulus chromatograph (CAC-II-3). A constant loading of 3% and a rotation rate of 90 deg/h were used throughout this series of experiments. Resolution results for the copper-nickel pair are shown in Fig. 9 as a function of concentration for the three radial positions on the apparatus. Obviously, the same distribution problem existed in this series, as was examined earlier (Fig. 6). Assuming that the center-position distribution is close to that typically observed for a properly adjusted position, it can be seen that the theoretical prediction of the extended dispersion model gives a good indi-

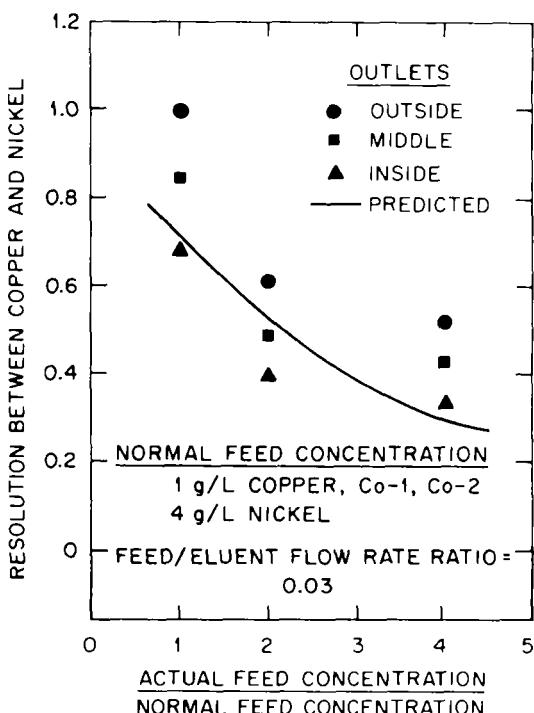


FIGURE 9. Resolution as a function of feed concentration in CAC-II-3 using a copper-nickel-cobalt feed mixture and an eluent of pH 7.9.

cation of chromatographic performance. Again, it is conservative and slightly underpredicts the resolution at high concentration.

CONCLUSIONS

The results of this study show that an excellent opportunity exists for enhancing the capacity of the continuous annular chromatograph by increasing its annulus width to the point where the center core is almost completely eliminated. Performance depends on an adequate distribution of feed and, perhaps, on independent product ports at various radial positions.

The model that has been developed on the basis of an idealized interactive isotherm to which has been superimposed a dispersion term appears to describe the system well and leads us to the conclusion that radial and θ -direction dispersion coefficients are unnecessary at this stage in the development of CAC technology.

The performance of both wide- and narrow-annulus chromatographs at high concentration is semiquantitatively predicted by the dispersion theory. As expected, resolution improves with decreasing concentration, suggesting that the normal concentration established for the program described here is probably optimal for this system.

NOTATION

c = solute concentration in the liquid phase, mol/m^3 solution
c_f = liquid-phase feed concentration, mol/m^3 solution
d = sorbent particle diameter, m
D_r = radial dispersion coefficient, m^2/s
D_z = axial dispersion coefficient, m^2/s
D _{θ} = circumferential dispersion coefficient, deg^2/s
K_L = Langmuir isotherm parameter, m^3 solution/mol
L = bed length, m
m = number of components
n = solute concentration in the solid phase, mol/m^3 sorbent
N_c = sorbent capacity, mol/m^3 sorbent

r = radial coordinate, m
 r_i = annulus inner radius, m
 r_o = annulus outer radius, m
 R = resolution
 Re = $\rho dV/\epsilon \mu$ = eluent Reynolds number
 t = time, s
 V = superficial eluent velocity, m/s
 VDN = $\epsilon D_z/VL$ = vessel dispersion number
 VDN_x = $D_z \bar{\theta}/\omega L^2$ = solute vessel dispersion number
 W = solute baseline bandwidth, deg
 z = axial coordinate, m

Greek Letters

ϵ = bed void fraction, $\text{m}^3 \text{ voids}/\text{m}^3 \text{ bed}$
 θ = angular coordinate, deg
 $\bar{\theta}$ = solute peak position, deg
 θ_f = angle feed is applied to column, deg
 μ = eluent viscosity, $\text{kg}/\text{m}\cdot\text{s}$
 ρ = eluent density, kg/m^3
 σ^2 = variance
 ω = rotation rate, deg/s

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REFERENCES

1. M. V. Sussman, "Continuous Chromatography," *CHEMTECH* 6(4), 260-264 (1976).
2. A. J. P. Martin, "Summarizing Paper," *Discuss. Faraday Soc.* 7, 332-336 (1949).
3. C. D. Scott, R. D. Spence, and W. G. Sisson, "Pressurized Annular Chromatograph for Continuous Separations," *J. Chromatogr.* 126, 381-400 (1976).

4. R. M. Canon and W. G. Sisson, "Operation of an Improved, Continuous Annular Chromatograph," *J. Liq. Chromatogr.* 1(4), 427-441 (1978).
5. R. M. Canon, J. M. Begovich, and W. G. Sisson, "Pressurized Continuous Chromatography," *Sep. Sci. Technol.* 15(3), 655-678 (1980).
6. J. M. Begovich and W. G. Sisson, "Continuous Ion Exchange Separation of Zirconium and Hafnium Using an Annular Chromatograph," *Hydrometallurgy* 10, 11-20 (1983).
7. J. M. Begovich and W. G. Sisson, "A Rotating Annular Chromatograph for Continuous Metal Separations and Recovery," *Resour. Conserv.* 9, 219-229 (1982).
8. R. J. Torres, C. S. Chang, and H. A. Epstein, "Fundamental Studies in Continuous Annular Chromatography," Massachusetts Institute of Technology, School of Chemical Engineering Practice, Report ORNL/MIT-329, Oak Ridge, Tenn. (1981).
9. R. Y. Shah, J. H. Austin, and L. M. Burelle, "Comprehensive Model for an Annular Continuous Chromatograph," Massachusetts Institute of Technology, School of Chemical Engineering Practice, Report ORNL/MIT-205, Oak Ridge, Tenn. (1974).
10. L. Lapidus and N. R. Amundson, "Mathematics of Adsorption in Beds. VI. The Effect of Longitudinal Diffusion in Ion Exchange and Chromatographic Columns," *J. Phys. Chem.* 56, 984-988 (1952).
11. R. L. Bratzler and J. M. Begovich, "A Mathematical Model for Multicomponent Separations on the Continuous Annular Chromatograph," Oak Ridge National Laboratory Report ORNL/TM-6706, Oak Ridge, Tenn. (1980).
12. H. K. Rhee, R. Aris, and N. R. Amundson, "On the Theory of Multicomponent Chromatography," *Trans. Roy. Soc.* A267, 419-455 (1970).
13. J. M. Begovich, "Multicomponent Separations Using a Continuous Annular Chromatograph," Ph.D. Dissertation, University of Tennessee (1982); also available as Oak Ridge National Laboratory Report ORNL-5915 (1982).
14. J. M. Begovich and W. G. Sisson, "A Rotating Annular Chromatograph for Continuous Separations," accepted for publication by *AIChE J.* (1983).
15. M. H. Caron, "Fundamental and Practical Factors in Ammonia Leaching of Nickel and Cobalt Ores and Separation of Nickel

and Cobalt," *Trans. Amer. Inst. Min. Metall. Eng.* 188, 67-103 (1950).

16. O. Levenspiel, Chemical Reaction Engineering, 2nd ed., Wiley, New York (1972).
17. F. J. Hurst, "Separation of Cobalt from Nickel in Ammonia-Ammonium Carbonate Solutions Using Pressurized Ion Exchange," *Hydrometallurgy* 1, 319-338 (1976).