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Pressurized Continuous Chromatography

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PRESSURIZED CONTINUOUS CHROMATOGRAPHY

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ABSTRACT

A pressurized continuous annular chromatograph has been developed for preparative separations. This device utilizes a slowly rotating annular bed of sorbent material, fixed multiple feed points, and fixed withdrawal locations. Most of our investigations have been performed with a 28-cm-diam column, but a larger model is being designed and constructed. The separation of copper, nickel, and cobalt components from a carbonate solution has been studied in detail. This solution simulates the leach liquor from the Caron process for recovering nickel and cobalt from laterite ores. Use of continuous gradient elution has been demonstrated. Recent studies have investigated several separations, including that of zirconium and hafnium (necessary for the production of zirconium for use in nuclear reactors), on a preparative scale. This system, because of its continuous feed and product withdrawal, its adaptability to large-scale operations, and its ability to separate many components, is expected to make chromatography a more competitive process in the industrial sector.

INTRODUCTION

Application of chromatography to industrial preparative operation has been hampered by several factors. The necessity of batch operation and the channeling occurring with large-diameter columns have been major reasons for the avoidance of ion-exchange separation methods in the chemical processing industry. Its use has been largely restricted to low throughput systems and for processing sensitive materials for which unit operations methods are not suitable. Attempts to develop a continuous chromatograph have been made in the past (1-5), but with only limited success. Several researchers used an annular rotating chromatograph but were not able to solve the operational difficulties associated with such a device. The apparatus used by Dunnill and Lilly was capable of making relatively simple biochemical separations but could only operate with gravity or low-pressure flow. The design of this system was not compatible with gradient elution techniques.

We have developed a rotating annular chromatograph that can be operated under pressure and can utilize gradient elution techniques. This device consists of a rotating annular bed of sorbent material moving past stationary feed entry points and stationary product collection points (Fig. 1). As the bed rotates, it receives feed material for a short period of time, then it is exposed to the eluent for a somewhat longer time period. As the downward flow of eluent produces separation among the various constituents of the feed, they are carried circumferentially with the bed as it rotates. Consequently, the separated constituents appear as helical bands within the bed. Since the feed point is fixed and the time spent in the column is a constant for a given feed constituent, the angular displacement experienced by that constituent is also a constant. Therefore, the various products can be collected at stationary points around the chromatograph exit. Material with the largest distribution coefficient will remain in the column longest and will therefore experience the largest angular displacement from the feed point.

We have used two models of the continuous annular chromatograph (CAC), and a third is being fabricated. Most of our data have been obtained on a device (CAC-II) with annulus outside diameter of 27.9 cm and annulus width of 1.27 cm. The cross-sectional area

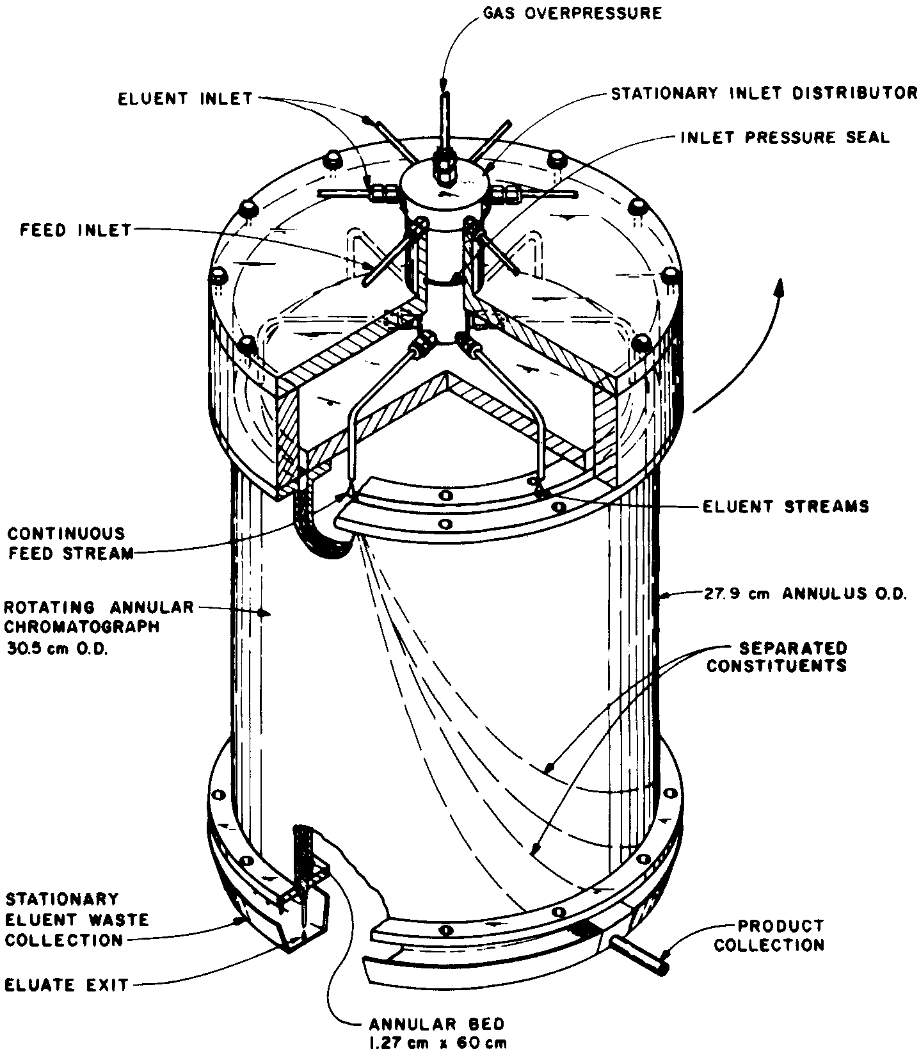

FIGURE 1. Pressurized, continuous annular chromatograph (CAC-II).

of the bed is 106 cm^2. Bed depth is approximately 60 cm, and the bed is supported by a solid-steel plate with a v-groove machined below the annulus. There are 180 exit holes drilled thorugh this plate at the bottom of the groove, each plugged with porous Teflon above the exit tube. This configuration gives 180 discrete exit points located at 2° intervals around the circumference. Samples can be collected from individual tubes (or several tubes to collect an entire band), or an analytical instrument (e.g., spectrophotometer) can be connected to any tube to produce a conventional chromatogram.

The inlet distributor is a 2-in. steel pipe that is held stationary while the chromatograph rotates. Seal is accomplished by two O-rings contained in the top flange. Two feed entry points (180° apart) and four eluent entries are provided in this distributor. Four manifolds, each with six nozzles, have been fabricated to allow operation in the gradient elution mode. Each manifold supplies eluent to one-quarter of the column, resulting in 24 nozzles, equally spaced around the column, which are capable of feeding four different eluents. This system is constructed of Plexiglas so that visual observations of the separation can be made and operates at a maximum pressure of 30 psi. Further details on its construction can be found in papers by Scott et al. (6) and Canon and Sisson (7). A smaller device (CAC-ME) has also been constructed of Plexiglas and has been operated. Its annulus outside diameter is 8.9 cm, and annulus width is 0.64 cm; the bed depth is 60 cm, and bed cross-section is 16.5 cm^2. This model has proved particularly useful in testing new separations on a small scale. Its smaller size enables rapid change of eluents and feeds without requiring large volumes of these solutions. The CAC-ME can be operated at pressures as high as 90 psi.

A third device is now being fabricated and is expected to provide scaling data and to prove the concept on a relatively large scale. This device (CAC-III) is constructed of Carpenter 20 alloy steel and will be rated for operation at 150 psi. The annulus outside diameter is 59.7 cm, and annulus width is 4.45 cm. Total cross-sectional area of the bed is 771 cm^2, more than seven times the area of CAC-II. This device (Fig. 2) will have the capability of operation with multiple feed points and operation in the gradient elution mode with a wide variety of eluents.

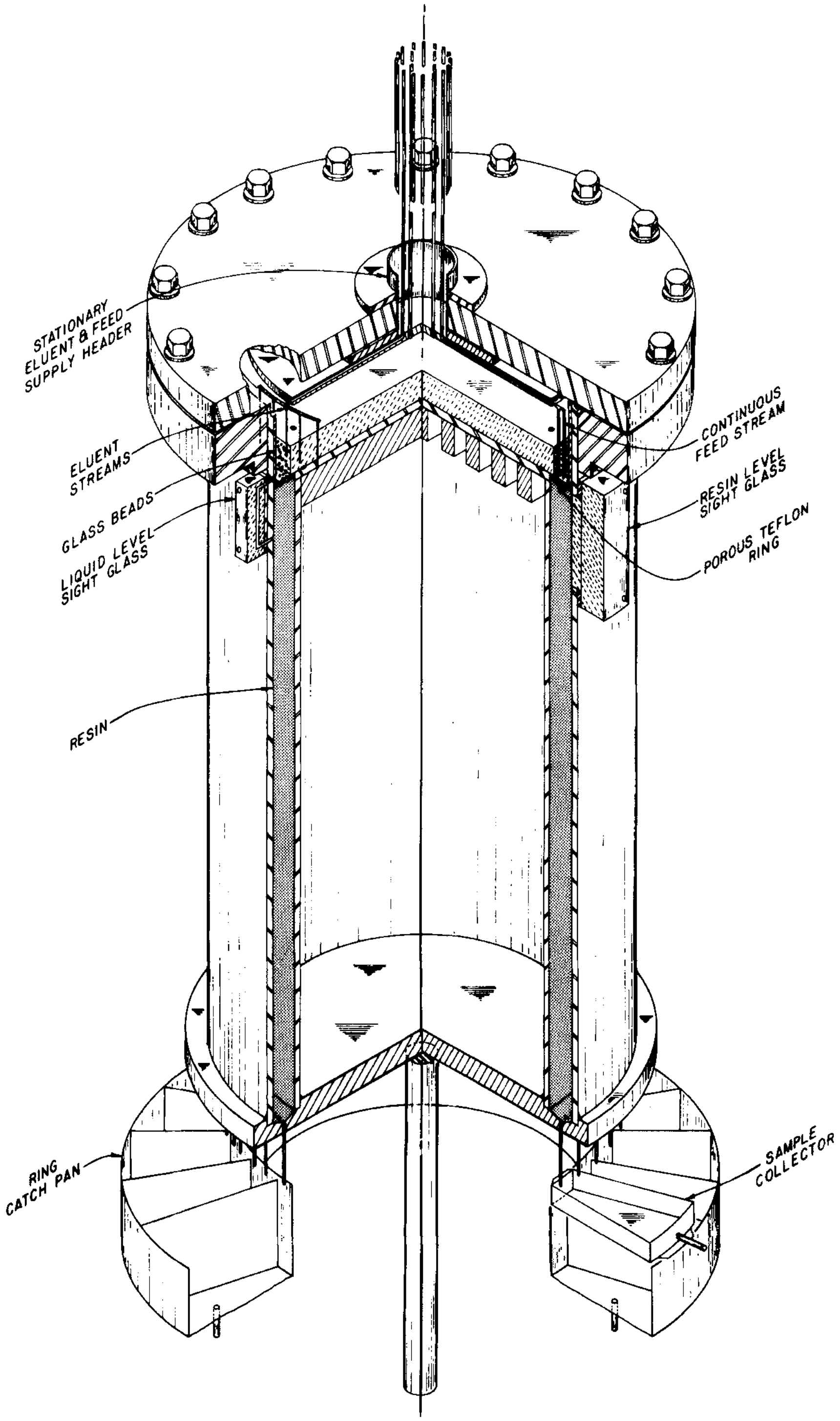

FIGURE 2. Pressurized, continuous annular chromatograph (CAC-III).

METHODS

Isocratic Operation

Operation with a single eluent is accomplished by the use of a conductivity-type liquid-level controller operating the eluent pump. A constant gas overpressure is maintained to force liquid through the bed while the controller maintains a liquid head above the top of the bed. Feed material is injected continuously by another pump into a 3-cm-deep layer of small glass beads above the sorbent material. Because the bed is rotated relative to the feed point, fresh sorbent is constantly receiving feed material. That part of the bed not receiving feed at a given time is undergoing either elution or regeneration.

A spectrophotometer has been connected directly to one of the rotating exit tubes to measure the separation. Angular displacement of any point measured from the feed point is analogous to time on a conventional column chromatograph; therefore, as the exit tube rotates to a greater angular displacement, it receives material that has been in the column longer. As a result, any tube can be used and will eventually pass under all the separated bands, giving a conventional-type chromatogram.

Gradient Elution Operation

Gradient elution chromatography with the CAC is equivalent to that in a conventional column but with significant operational difficulties to overcome. Since angular displacement (from the feed point) is equivalent to time, different eluents must be flowing simultaneously through various vertical sections of the column. (These are imaginary sections, because the annulus is not partitioned.) Since a liquid head of eluent cannot be tolerated, special changes in operation (from the isocratic mode) are required. The glass beads allow us to maintain a liquid head (to prevent forcing air through the bed) and avoid mixing of the eluents. A differential pressure controller measures the liquid head and adjusts the gas overpressure to maintain the liquid level just below the top of the glass beads layer. Four different eluents can be used simultaneously. The eluent manifolds are used to confine each eluent to a specific angular portion of the column (90° when four are used) at the point of introduction. The eluents then flow through the column with little mixing at the interfaces. The eluent manifold nozzles extend into the glass beads, thus avoiding most of the mixing which would occur with a liquid head. Each manifold is fed from a separate metering pump, and each nozzle receives 1/6 of the total manifold flow. When all eluent pumps are set to give equal flows, the controller is allowed to seek the equilibrium gas overpressure that will prevent liquid accumulation or depletion above the top of the glass beads. This makes it possible to increase the number of eluents without further complication to the control system. Small variations in gas pressure (<1%), and therefore liquid velocity in the column, are sufficient to control the system.

RESULTS

Although many sorbent materials could be used in the CAC, all studies reported here used Dowex 50W-X8 cation exchange resin with a wet size range of 50 to 60 μm. Data were obtained on the 28-cm-diam column (CAC-II) for several systems.

Copper-Nickel-Cobalt System

The separation of copper, nickel, and cobalt from a synthetic process liquor has been investigated as an ion-exchange separation of potential utility. In the Caron process for nickel recovery from oxide ores, an ammonia-rich process liquor is produced that contains copper and nickel complex ions and as many as three cobalt complex ions, which are referred to as Cu, Ni, Co-1, Co-2, and Co-3. Hurst (8) identified the nickel and cobalt complexes and studied the effect of eluent concentration and pH upon their distribution coefficients. He concluded that a high-resolution ion-exchange separation could be used for the final purification step in the Caron process, with recovery of both nickel and cobalt. In such a process, a continuous chromatograph would be most useful.

Dowex 50W-X8 cation-exchange resin (50 to 60 μm) was used in CAC-II to separate the components in a synthetic feed liquor containing Cu, Ni, Co-1, and Co-2. The third cobalt species was not included since it can be easily removed prior to the CAC using a stationary ion-exchange column. The eluent was 1 M $(NH_4)_2CO_3$ buffered to a pH of 7.8 using carbon dioxide. Since all four solutes are colored substances, the separation could be readily followed by a spectrophotometer. Copper and nickel bands were measured at 644 nm while Co-1 and Co-2 were measured at the absorption maxima, 523 and 510 nm, respectively.

Use of in-line instruments with this device has made accurate determinations of the resolution possible. Resolution, R, is defined as

$$R = \frac{2(\theta_2 - \theta_1)}{W_1 + W_2} ,$$

where θ_1 and θ_2 are the angular displacements (from the feed point) of the maximum concentrations of constituents 1 and 2, and W is the constituent bandwidth. A resolution value of unity indicates no dead volume between peaks but virtually no overlapping. A series of experiments were conducted to determine the effect of feed rate on resolution for a given feed concentration. Data for copper, nickel, cobalt-1 and cobalt-2 are shown in Fig. 3. Resolutions greater than unity could be maintained at feed rates as high as 2.5% (6.7 cc/min) of the total eluent flow for all but the copper-nickel separation. Since this device is intended for large-scale preparative chromatography, it is desirable to operate near the maximum feed rates. Loss of resolving power is the limiting factor for feed rate and determines this maximum.

Another inducement to operate near the maximum is the reduction in dilution at high flow rates. Ideally, one would like to separate

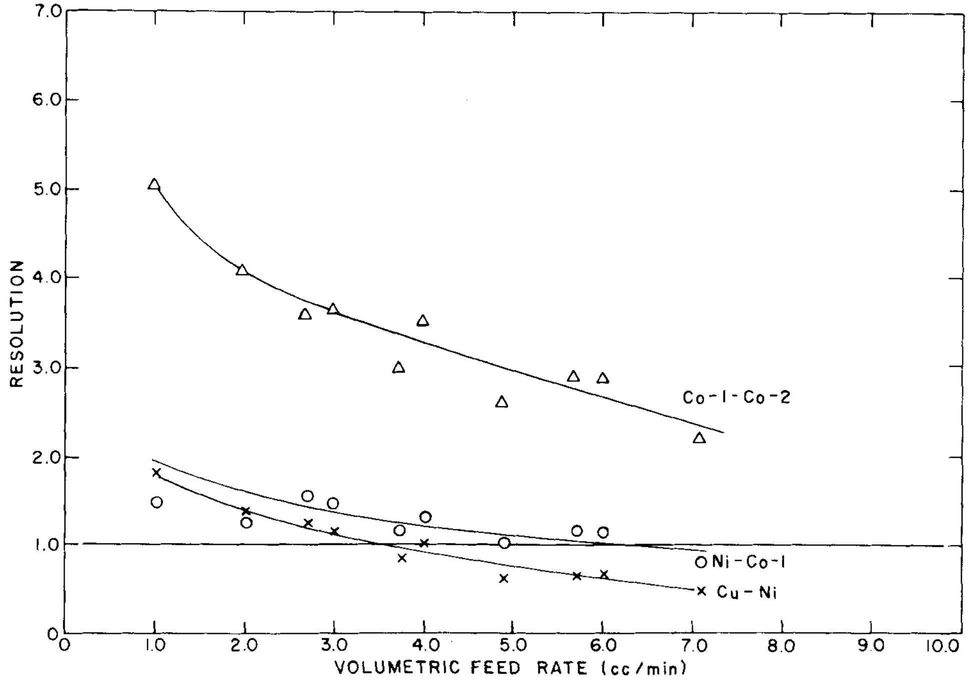

FIGURE 3. CAC resolution vs volumetric feed rate for the Cu-Ni-Co system in $(NH_4)_2CO_3$.

the constituents with no dilution. While this is not possible, one can sometimes approach this condition. Figure 4 shows the reduction in dilution which occurs with increasing feed rate. At 2.5% of eluent flow, the dilution is a factor of 6 for Co-2 and less than 4 for the other components.

In a preparative device the feed rate could be easily manipulated to achieve the desired separation with the maximum throughput. However, one might also be able to change the feed concentration if there was sufficient benefit to be gained. Consequently, we have investigated the effect of feed concentration on resolution and dilution for the same carbonate system. The ratios of the concentrations of the species in the feed were held

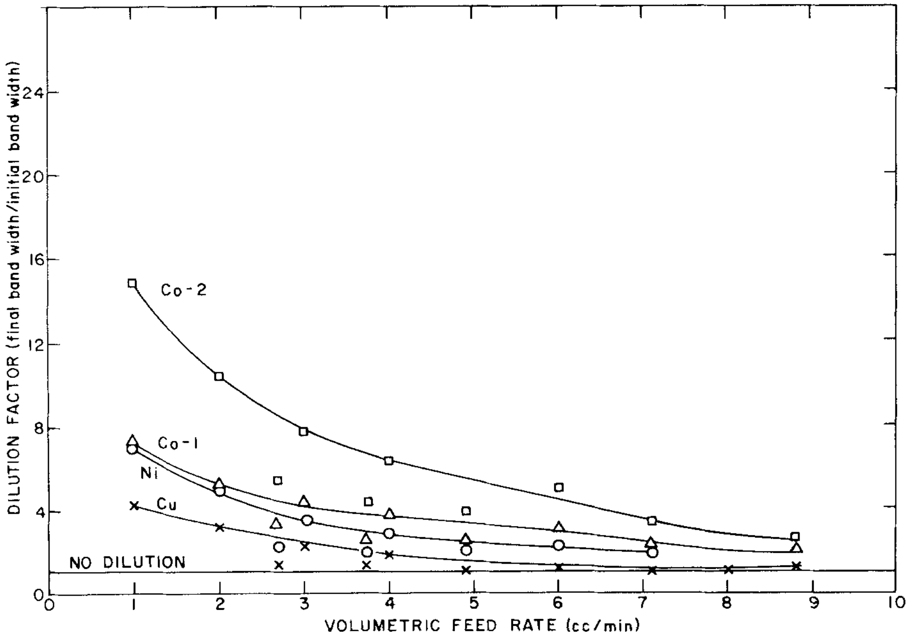

FIGURE 4. Dilution factor as a function of volumetric feed rate for the Cu-Ni-Co system.

constant, as would be the case if evaporation or dilution were used. These experiments did not show (Fig. 5) a drastic reduction in resolution with an increase in feed concentration. In general, resolution was only reduced by about 20% for a six-fold increase in the total metal concentration of the feed. The dilution factor behaved somewhat unexpectedly, showing a slight increase (20 to 40%) over the same concentration range (Fig. 6). These results demonstrate the advantages of operating at high feed concentrations and the maximum flow rate possible while still maintaining the desired resolution.

Gradient Elution with Copper-Nickel-Cobalt

Although gradient elution techniques are not required to perform separation of the Cu-Ni-Co system, its colored constituents

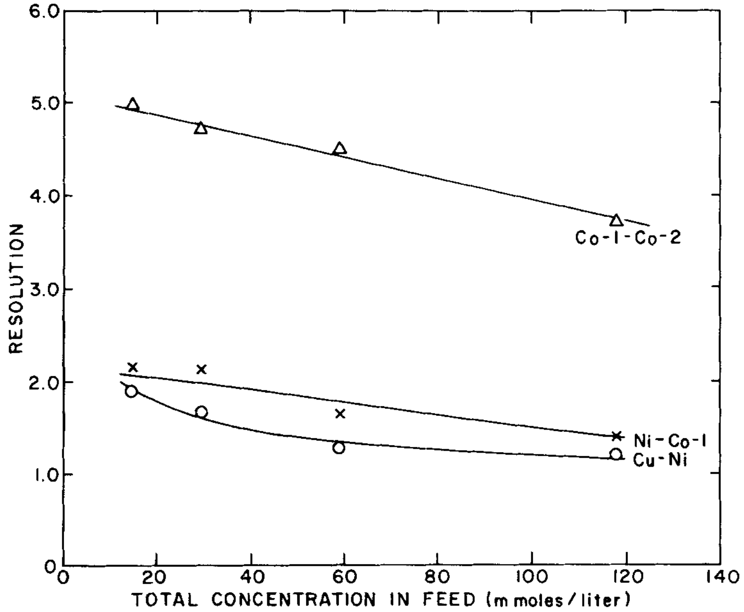

FIGURE 5. Effect of the total feed concentration on resolution for the Cu-Ni-Co system.

graphically illustrate the method. Figure 7 is a photograph of CAC-II operating in the gradient elution mode with Cu, Ni, and Co-2 in the feed. A pH gradient was used, with the quadrant containing the feed point receiving 1 M $(NH_4)_2CO_3$ at pH 9.4, while the adjacent quadrant received 1 M $(NH_4)_2CO_3$ at pH 7.8. The interface between these eluents is clearly marked by the change in slope of the copper and nickel bands. The Cu, Ni,and Co-2 have approximately the same distribution coefficient in the high pH eluent, but they are markedly different at low pH. The interface is very sharp and its position is stable, indicating little eluent mixing and no significant flow variations in the column.

Iron-Aluminum System

Our research and development efforts in resource recovery (9) have produced acid liquors (from the acid leaching of coal ash)

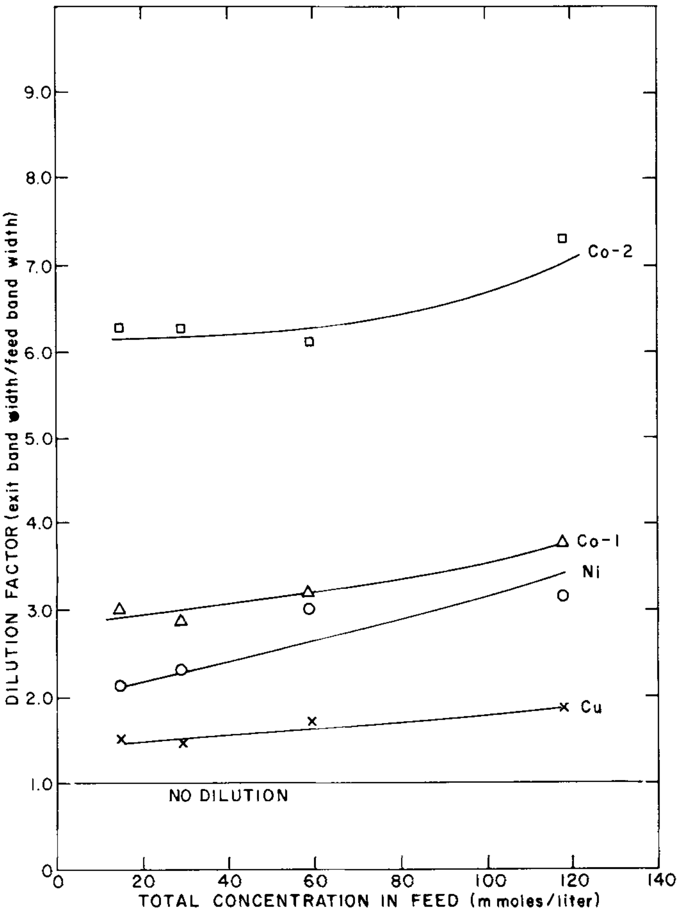

FIGURE 6. Effect of the total feed concentration on dilution factor for the Cu-Ni-Co system.

that contain significant amounts of iron and aluminum, as well as smaller quantities of many other metals. Efficient separation of these metals has not yet been demonstrated by other methods, therefore continuous chromatography is being examined for this application. It may also have utility in separating or partitioning the many trace metals found in these solid residues.

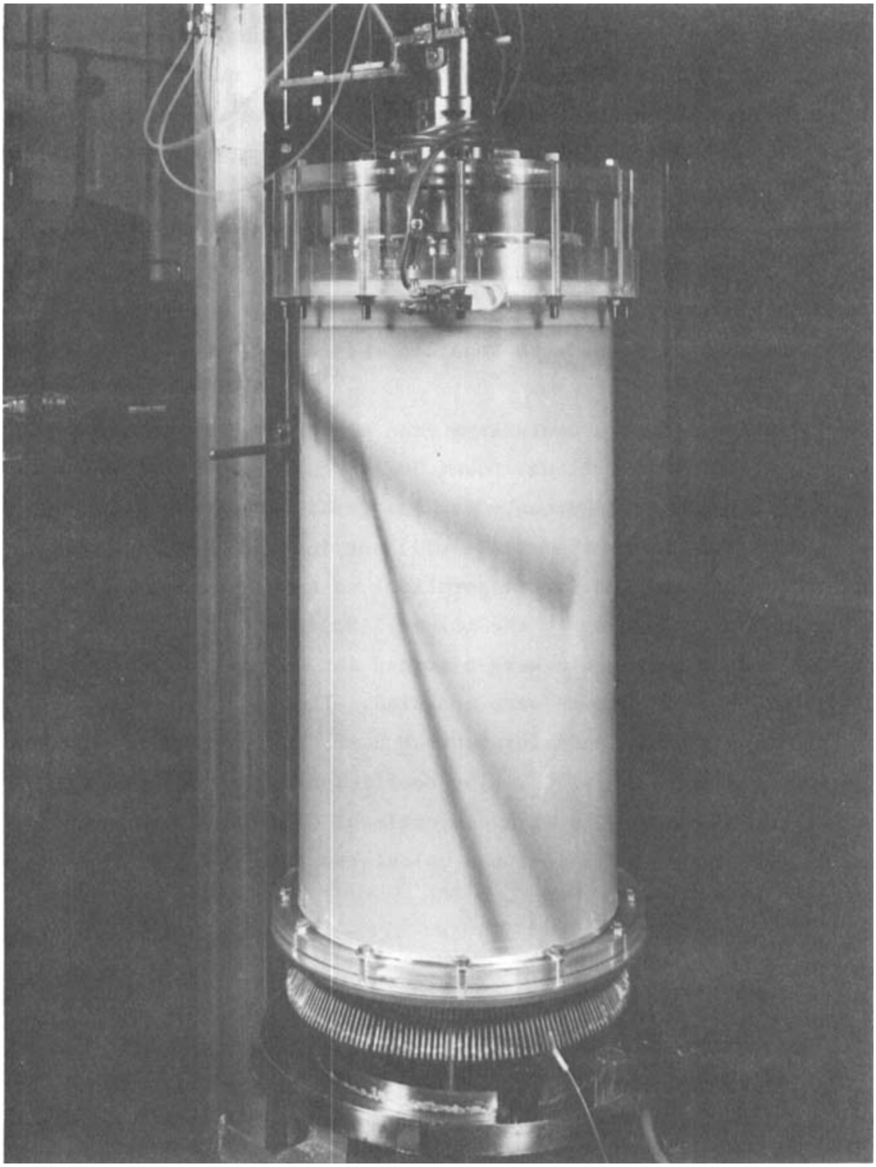

FIGURE 7. Use of a pH gradient in the separation of Cu-Ni-Co with 1 $\underline{M}$ $(NH_4)_2CO_3$.

The literature gives methods for the separation of a large number of these metals via conventional ion exchange. However, these are analytical methods, suitable for small quantities, but not for preparative-scale work. They involve use of many eluents, including HCl, H_2SO_4, and methanol in various concentrations and combinations. The resin specific volume changes occurring with these eluents prohibit the use of this system in the continuous chromatograph. Therefore, a new system was sought to separate these metals in an acid solution. Since aluminum and iron are the major components, methods to separate these metals were given first priority.

Simulated liquors containing iron and aluminum nitrates were used for the feed solutions. Dowex 50W-X8 cation exchange resin, the same resin used previously for the Co-Ni-Cu system, was used for all tests. Since the metals will not load from the high-acid liquor, neutralization (or evaporation) to a pH of about 1.4 is required before feeding to the column. Solutions of ammonium sulfate and sulfuric acid were examined for use as eluents and distribution coefficients were measured. Figure 8 shows the distribution coefficients for 0.025 $\underline{M}$ H_2SO_4 and various concentrations of $(NH_4)_2SO_4$. The coefficients were determined from column measurements on a conventional 0.50-in.-diam column. The distribution coefficient was calculated from

$$K = \frac{V_R - V_0}{V_T - V_0} ,$$

where

V_R = volume of eluent used to elute the solute at peak concentration,

V_0 = void volume of the column,

V_T = total volume of the column.

Several experiments were performed with a single eluent with relatively poor results. With low concentrations of $(NH_4)_2SO_4$ in the eluent, dilution of aluminum was high, while higher

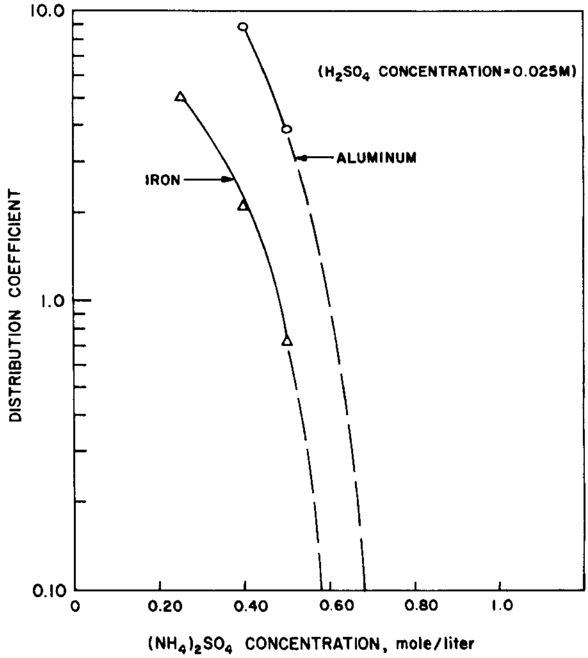

FIGURE 8. Distribution coefficients of aluminum and iron in 0.025 M H_2SO_4 as a function of $(NH_4)_2SO_4$ concentration.

$(NH_4)_2SO_4$ concentrations (>0.50 M) would not give separation. Consequently, a gradient elution in the CAC-II was used. The separation is shown in Fig. 9, with a feed containing 4.0 g Fe/l and 7.0 g Al/l. Angular displacements were measured from the feed point. With the feed point at 0°, the area receiving 0.5 M $(NH_4)_2SO_4$ and 0.025 M H_2SO_4 extended from 303 to 123° and the remainder received 1.0 M $(NH_4)_2SO_4$ and 0.025 M H_2SO_4. The rotation rate was 210°/hr; the feed rate was 4.05 cm^3/min; and the superficial eluent velocity was 2.29 cm/min. These conditions were chosen to enable the iron to elute simultaneously with the arrival of the second (higher concentration) eluent. The second eluent then eluted the aluminum quickly, compressed the band, and

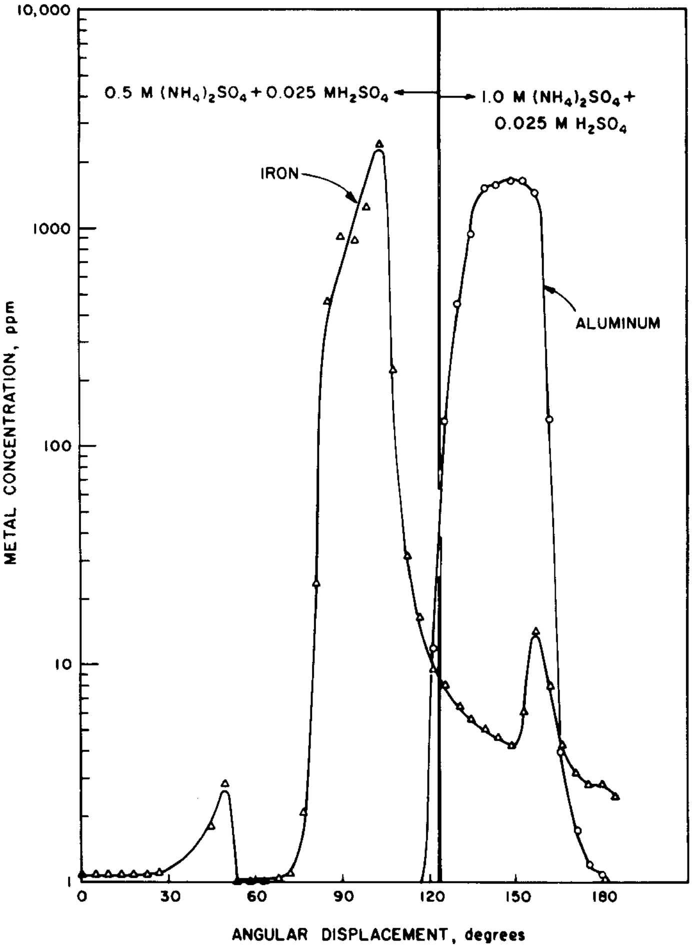

FIGURE 9. Continuous separation of iron and aluminum with gradient elution chromatography. The vertical line represents the interface of the two eluents.

significantly reduced the amount of dilution. Table 1 shows a comparison of isocratic and gradient elution. Dilution (concentration in the feed/concentration in the eluted band) was reduced spectacularly for aluminum and significantly for iron. Recovery (g metal fed per minute/g metal recovered in the product

TABLE 1

Comparison of Isocratic and Gradient Elution Results for Iron and Aluminum

Run no./conditions	Dilution		% recovery		% cross contamination	
	Fe	Al	Fe	Al	Al in Fe	Fe in Al
FEA-1/isocratic	19.3	51.5	80	78	0.069	1.00
FEA-18/gradient	7.4	8.5	92	98	0.029	0.66

band per minute) was also significantly improved and cross contamination was reduced slightly. Cross contamination refers to the concentration of the contaminant (minor) metal in the product metal after the product stream is reduced to the metal. Thus, the aluminum produced from the product in run FEA-18 would contain 0.66 wt % iron.

These results indicate that aluminum and iron can be separated using continuous ion exchange methods with gradient elution techniques. Investigations on this system are continuing, and the system will be expanded to include titanium, manganese, and other metals. However, the real utility of the process may prove to be in separating or isolating the many trace metals found in these leach liquors, especially those known to be hazardous. Additional studies will also be required to improve further the separation of the major components.

Zirconium-Hafnium System

All naturally occurring zirconium ores typically contain about 3% (by weight of the zirconium) hafnium. Due to the similarity of their atomic and ionic radii and their electron structures, the separation of zirconium and hafnium is a very difficult and complex task. The primary incentive for obtaining pure components has come from the field of nuclear technology, where the low neutron capture cross section of zirconium makes it attractive as fuel cladding in nuclear reactors, and the high cross section of hafnium makes it useful for control rod applications. As the production rates of zirconium and hafnium are increased, however, a number of other applications are likely to be found. For example, hafnium may well prove to be useful in the construction of jet engines since it can absorb and give up heat at more than twice the rate of zirconium or titanium. Hafnium may also find uses in electronics, the optical industry, and as catalysts.

Current commercial technology for the separation of zirconium and hafnium centers on two liquid extraction methods. The first involves the extraction of the thiocyanate complexes of zirconium and hafnium using isobutyl methyl ketone, while the other method uses the tributyl phosphate extraction of the nitrate complexes. Both of these methods are complex and expensive; this provided our motivation for attempting the separation on a continuous basis using cation exchange resin in the CAC. Using a conventional column packed with Dowex 50W-X8 cation exchange resin, Hurst (10) determined the distribution coefficients of both zirconium and hafnium in the sulfate form as a function of the sulfuric acid eluent concentration. Over an acid concentration range of 0.5 to 2 *N*, the ratio of the distribution coefficients decreased from 9 to 4.5.

For continuous separations, the CAC-II was packed to a depth of 60 cm with Dowex 50W-X8 cation exchange resin. Sulfuric acid, with concentrations ranging from 0.9 to 1.5 *N*, has been used as the eluent at a typical flow rate of 250 ml/min. The zirconium and hafnium feed liquor is simulated by dissolving commercially available zirconium sulfate ($ZrOSO_4 \cdot H_2SO_4 \cdot 3H_2O$) in water. This material has not been processed to remove hafnium, so these metals are present in the same ratio as found in the original ore. Feed solutions containing up to 135 g Zr/l and 4.1 g Hf/l have been prepared in this manner.

A typical experimental result is shown in Fig. 10. The first peak, at approximately 10°, corresponds to a species with zero distribution coefficient. Although for this peak the ratio of hafnium to zirconium is reduced slightly from the ratio in the feed, this zero distribution coefficient indicates that the feed contains a small amount of material which does not interact with

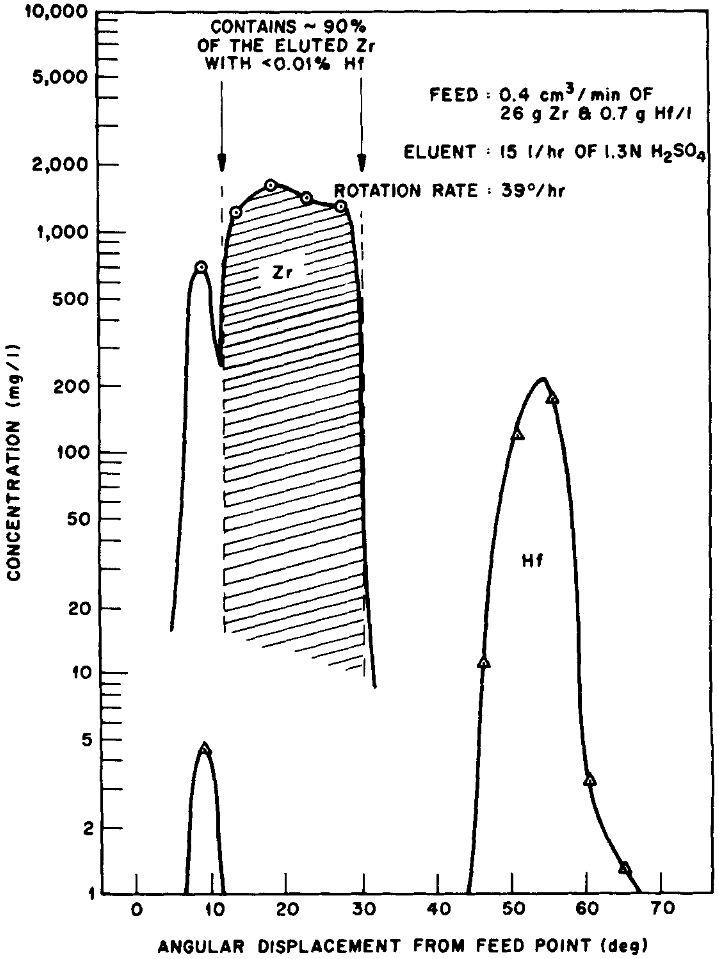

FIGURE 10. Continuous separation of zirconium and hafnium with CAC-II.

the resin. For the case shown in the figure, approximately 10% of the zirconium is tied up in this first peak and is contaminated with hafnium. However, the remaining 90% of the zirconium is eluted in the second peak, and contains less than 0.01% hafnium, which qualifies it as pure zirconium for nuclear use. The zirconium content of the third peak, which is primarily hafnium, is not well known since the lower limit of analytical detection is approximately 1 ppm.

Figure 10 also shows that the entire separation takes less than one quadrant of the chromatograph. Thus it would be a simple matter to put in three more feed lines and space the feed inlet points 90° apart. For four feed points and the conditions described in the figure, the small-scale CAC-II would be able to produce over 20 kg of pure zirconium per year. Furthermore, it appears entirely feasible that both the feed rate and the feed concentration can be increased significantly, raising the potential production of this small unit towards 1000 kg of pure zirconium per year.

Scale-up of the Continuous Annular Chromatograph

As mentioned previously, all of the systems studied to date have been run in the 28-cm-diam CAC-II or the 9-cm-diam CAC-ME. A 60-cm-diam unit, CAC-III, is presently being fabricated. To obtain the proper scale-up factor, the copper-nickel-cobalt system was run on the CAC-II and the CAC-ME, using the same eluent velocity in both units.

The results are shown in Figs. 11 and 12. The abscissa in both figures is the ratio of the volumetric feed and eluent flow rates (reduced feed rate). Since the eluent velocity was held constant, the annular cross-sectional area is the scaling factor for the two figures, and as they show, it appears to be approximately the correct scaling factor. Data for the two devices generally agree for the limiting separations. The resolution is slightly better in the CAC-ME which is probably to be expected due to its

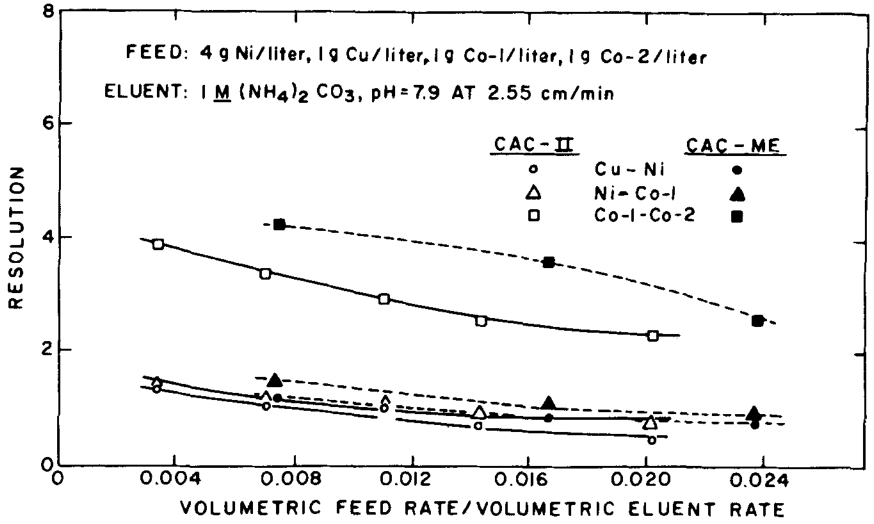

FIGURE 11. Effect of reduced feed rate on resolution in the copper-nickel-cobalt system.

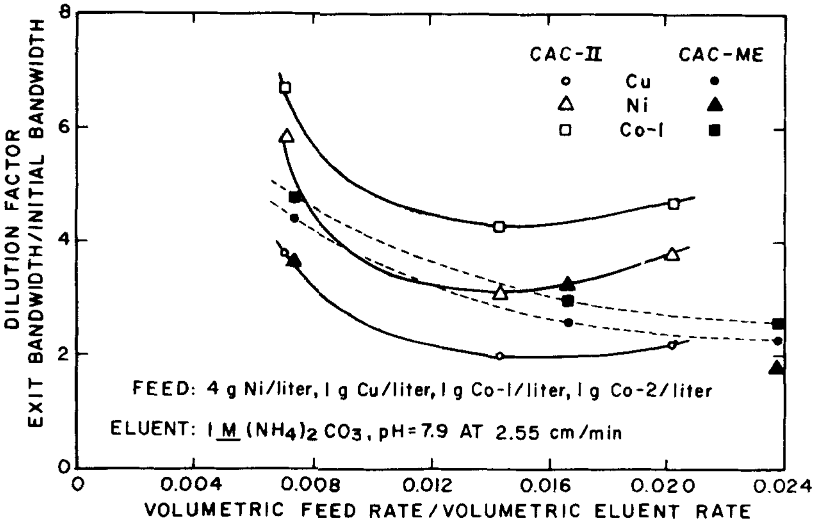

FIGURE 12. Effect of reduced feed rate on product dilution in the copper-nickel-cobalt system.

smaller annular width. Similarly, the dilution factor is on the same order in both units, with the smaller chromatograph generally having a slightly lower product dilution.

Based on these results, the annular cross-sectional area has been used as the initial scale-up factor for the design of the CAC-III. Additionally, experiments are planned to determine the effect of eluent velocity on the resolution of the feed component species so that the column length can be set. Using Fig. 10 as a guide for the zirconium-hafnium system, a 60-cm-long CAC-III, operating at 150 psig could produce approximately 1 metric ton of pure zirconium per year, with the possibility of achieving 50 metric tons per year if the feed rate and concentration can be increased as now appears feasible. This would compare quite favorably to the U.S. demand, which was 1900 metric tons in 1973 (11).

CONCLUSIONS

The continuous annular chromatograph has been demonstrated to hold great potential for performing separations on a preparative scale in the metals industry. The separation of copper, nickel, and cobalt from an ammoniacal leach liquor has been thoroughly explored and can be easily performed by the CAC. Investigations on the acid liquors obtained in the leaching of low-grade ores are continuing to show promise for the CAC in that area. This system requires gradient elution techniques and demonstrates the power of the device when operating in such a manner. Its adaptability to gradient elution without serious complication of its operation tremendously increases its potential in the processing industries. Its most immediate impact, however, may be in the separation of zirconium and hafnium. This separation is critical to the nuclear industry and its difficulty can be judged from the description of these metals, by one handbook (12), as being the two most difficult elements to separate. Scaling to produce 2.5% of the U.S. demand on a device only 60 cm in diameter demonstrates a very powerful technique. Much larger devices could be quite easily constructed and operated. Investigations with the CAC-III will be performed to prove its potential for utility as a large-scale separations device in the processing industry.

ACKNOWLEDGMENTS

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