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Separation and Recovery of Nickel and Molybdenum Using Continuous Rotating Annular Chromatography

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ABSTRACT

A continuous rotating annular chromatograph was developed for preparative separation of nickel and molybdenum. Dowex 50W-8X cation resin (hydrogen form) was packed in a 505-mm long and 10-mm wide stationary annular column. The feed solution was continuously introduced at the top of the bed by a rotating feed nozzle and was carried down through the annular column with an eluent of 10% sulfuric acid. The products were collected by a rotational tray rotating at the same speed as the feed nozzle. To evaluate the performance of this device, the effect of feed flow rate and rotational speed of feed nozzle were measured. Experimental results were compared with results calculated using model-plate theory. It was found that the optimum feed flow rate, at a constant eluent flow rate of 48.8 mL/min and a rotational speed of 4.5 degree/min, was 3.5 mL/min.

INTRODUCTION

Solutions containing significant quantities of nickel with some molybdenum contaminant are produced by the sulfuric acid leaching of spent hydrotreating catalysts (1). Subject to the demands of the metal market, there is potential value in the separation and recovery of the nickel from the catalyst leach solutions (2). Several methods, such as solvent extraction and precipitation, have been used to separate and purify nickel. However, chromatographic separation is one of the better separation methods

since it requires little energy, produces almost no heat, and has extremely high separation efficiencies. The method lacks the high throughput rates needed to make it a competitive separation technique on a preparative or industrial scale.

A number of investigators have studied the development of continuous chromatographic systems for use in preparative scale separations. Martin (3) was apparently the first to conceptualize a rotating annular chromatograph with respect to fixed continuous feed and product streams. Later Giddings (4) reported that a large capacity is theoretically possible in an annular device with the same resolution as a conventional column. A semicontinuous chromatographic unit consisting of an assembly of 100 conventional columns was reported by Dinellic et al. (5) and Barker et al. (6). Fox et al. (7) applied the rotational bed system to the separation of biological mixtures. However, these devices cannot be regarded as annular chromatographs operating in a continuous separation mode.

Since the initial development in 1974, a truly continuous chromatograph with a rotating annulus apparatus has been constructed and tested at Oak Ridge National Laboratory (ORNL). Most of these studies have been reported by Scott, Sisson, Begovich, Canon, and Byers (8–12). The apparatus consisted mainly of a rotating annular bed which was operated by an overpressure of gas and involved gradient elution as well as isocratic elution. The applications of the equipment for the separation of metals ions are summarized in Table 1.

Although the method has been advocated by ORNL's research team, it is still a relatively new area of research and warrants further improvement. The improvement of continuous rotating annular chromatography (CRAC) in the current study has been the use of a rotating feed nozzle rather then a rotating annular column. This approach was originally proposed and tested by Dunhill et al. (14) and Andrew (15), but their flow

TABLE 1
Summary of Metal Separation Using Annular Chromatography

Components separated	References
Hg/Cd/Cu	13
Ca/Fe	13
Blue dextran/Co	8
Al/Fe	10
Cu/Ni/Co	10, 12
Hf/Zr	11
Fe/Cr	17
Rare earths	18, 19

rates were very low. Takahashi et al. (16) used the system to separate amino acids on a preparative scale using gel as sorbent.

The present studies were concerned with the design, fabrication, and testing of a novel CRAC device using mixtures of nickel and molybdenum salts in solution. These were intended to simulate solutions produced by leaching spent hydrotreating catalysts. The separation of Ni/Mo was tested to confirm the merits of the CRAC device. The influences of rotational speed of feed nozzle and feed flow rate were determined. A stage model (plate theory) was used to predict the separation performance.

PRINCIPLE AND THEORY OF CRAC

The principle of the CRAC is shown schematically in Fig. 1. Feed solution is continuously introduced by a rotational feed nozzle at the top of

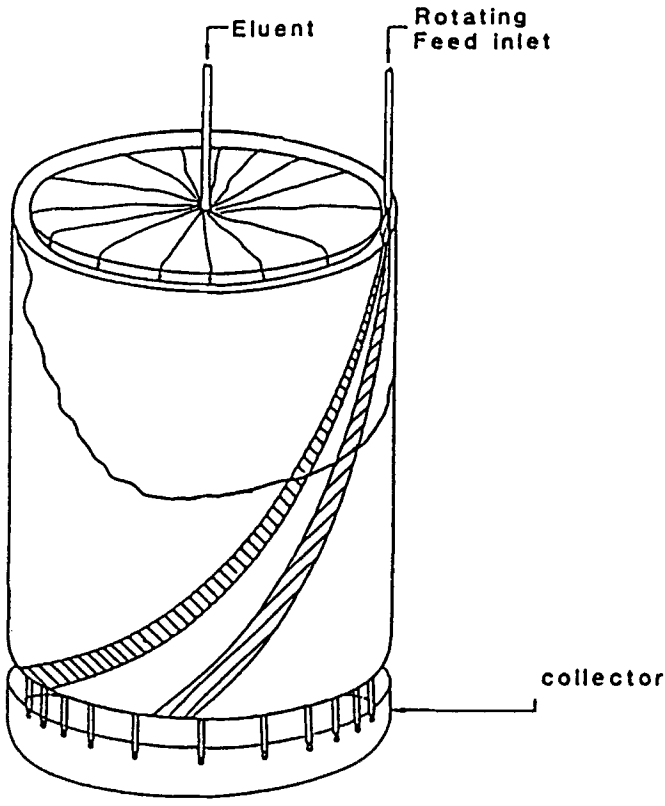

FIG. 1 Simplified schematic of the annular chromatograph with rotating feed nozzle.

the annular bed while eluent flows over the entire annulus bed. The feed is carried down through the bed by the eluent. The slope of the helical component bands depends on the distribution coefficient, eluent velocity, and rotational speed. At steady state, the component bands form helices between the top and bottom of the annular column. The separation products are collected by collectors which rotate at the same angular rate as the feed nozzle.

Conventional plate theory has been extended to rotating annular chromatography (8) and can be used to predict the separation performance of a CRAC if prior knowledge of the distribution coefficients and plate heights is available (9–12). The relevant equations are as follows:

$$\bar{\theta} = \omega \frac{L}{U} [\epsilon + (1 - \epsilon)K] \tag{1}$$

$$W = \sqrt{W_0^2 + 16 \frac{\overline{\theta^2}}{N}} \tag{2}$$

$$W_0 = 360 \frac{Q_F}{(Q_F + Q_E)} \tag{3}$$

$$R = \frac{2(\bar{\theta}_2 - \bar{\theta}_1)}{W_2 + W_1} \tag{4}$$

APPARATUS AND OPERATION

The CRAC apparatus is shown in Fig. 2. The apparatus consists of an annular bed of Dowex 50W-8X cation-exchange resin (100–200 mesh) packed in the space between two concentric Plexiglas cylinders (95 mm i.d. × 100 mm o.d. and 70 mm i.d. × 75 mm o.d.). The annulus is 10 mm wide and 505 mm long. The resin was sieved to 100–200 mesh in the 10 (v/v)% H_2SO_4 eluent. A porous wash support was placed on top of the resin bed to prevent disturbance of the resin, and a 80-mm layer of glass beads (0.5 mm o.d.) was placed on the wash support to minimize band broadening of the feed stream.

There were 36 tapered exit holes, drilled equidistant on the circumference in the center of the annulus bottom. Standard stainless steel tubes (⅛″) were inserted into the exit holes, and the tubes were plugged with porous Teflon to retain the ion-exchange resin while permitting effluent liquor to pass through the holes with minimal pressure drop.

The rotating feed nozzle was a plastic pipe of 2 mm diameter. Simultaneous rotation of the feed nozzle and collector (tray) was achieved from a variable speed ac motor linked to a 200:1 reduction gearbox. The actual

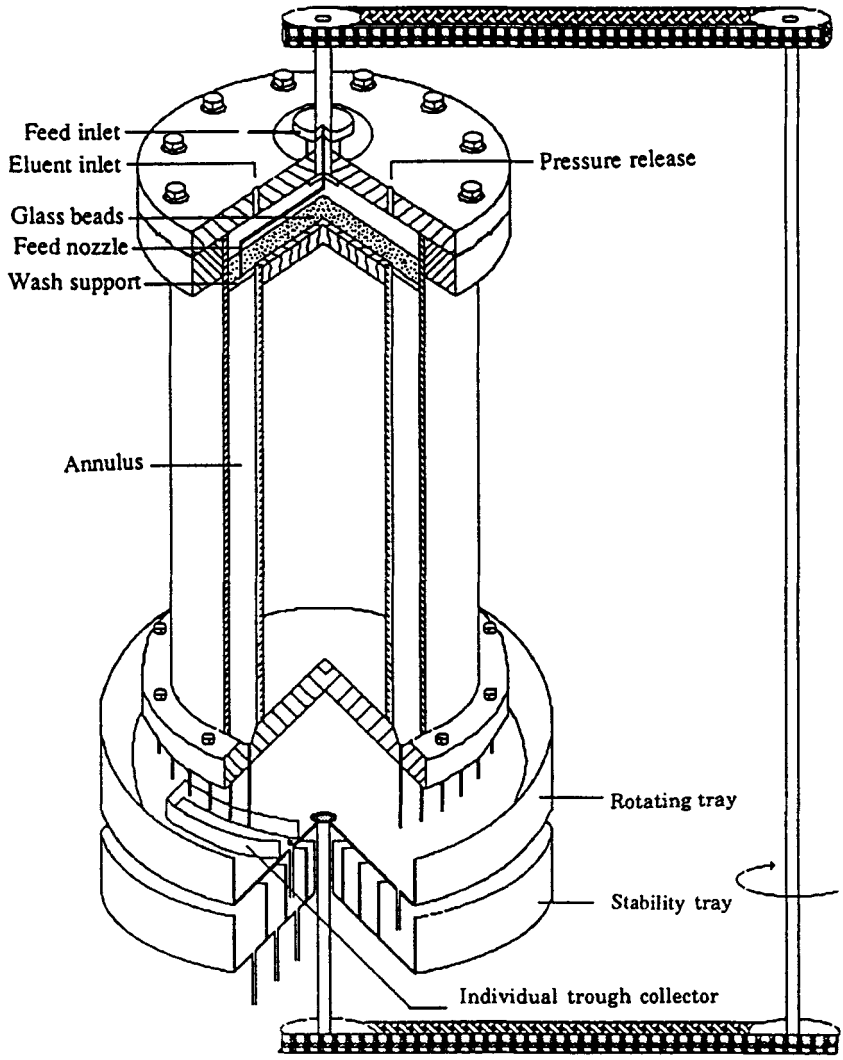

FIG. 2 Continuous rotating annular chromatograph apparatus.

rotational speed was controlled using a speed control instrument system and could be varied as required. Feed solutions and 10 (v/v)% H_2SO_4 eluent solution were supplied through a distribution port on the top of the annular column by two peristaltic pumps. The flow rate from both pumps was checked at frequent intervals. A pressure gauge and pressure release valve were also constructed on the eluent distributor.

TABLE 2
Typical Experiment Conditions

Variable	Setting
Feed rate (Q_F mL/min)	2.0
Eluent rate (Q_E mL/min)	48.8
Rotational speed (ω degree/min)	4.5
System pressure (KPa)	37
Temperature (°C)	Ambient temperature (22–24)

The feed concentration used contained 1.2 (w/v)% molybdenum as MoO_3^{2-} and 6 (w/v)% nickel as Ni^{2+}. The feed solution was continuously introduced through a rotational feed nozzle and was carried down through the bed by the eluent. Spent eluent was collected at the bottom of the annular column by a rotating collection tray. Positioned on this tray were two separate collection troughs for collection of the molybdenum and nickel fractions. Location of the troughs was dependent on the band position of nickel and molybdenum. The void fraction of the annular bed ($\epsilon = 0.701$) was determined using 1% blue dextran which is not retained by the column. The chromatogram was obtained by collecting samples of the effluent and subjecting them to atomic absorption spectroscopy analysis. Typical experimental conditions are given in Table 2.

RESULTS AND DISCUSSION

The separation obtained using the typical experimental conditions of Table 2 is shown in Fig. 3. Molybdenum and nickel are seen to be completely separated by more than 80° at the exit of the CRAC. Thus the physical collection of each component using a tray rotating at the same speed as the feed nozzle is simple and effective.

The effect of bed length on the separation of nickel and molybdenum is shown in the upper half of Fig. 3. For this particular separation, resolution is obviously better than required. To maximize resin bed utilization, it could be possible either to use a shorter resin bed or to increase the feed flow rate.

The molybdenum peak position in the lower half of Fig. 3 was at approximately 94° from its feed point (zero degree represents the point at which the given feed solution was injected onto the annular column). This result corresponds to a species with a zero distribution coefficient (blue dextran) and is to be expected in that, under the given experimental conditions, molybdenum exists as an anionic species and would not be retained

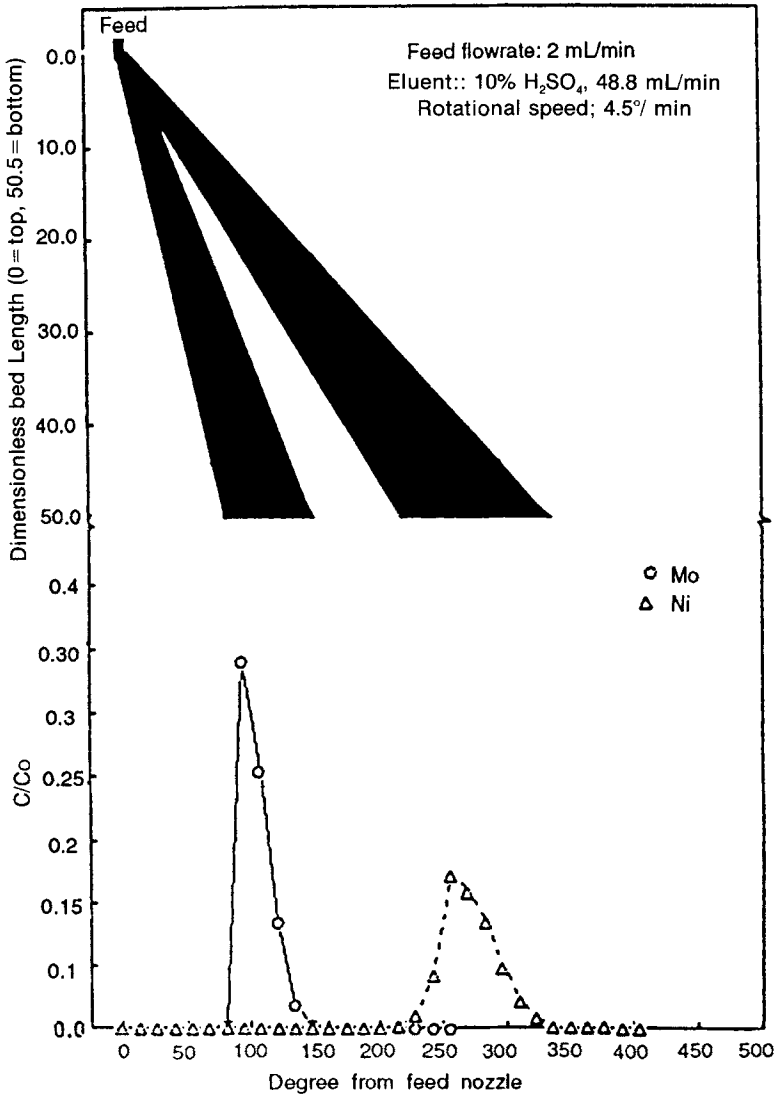

FIG. 3 Typical chromatogram for the conditions given in Table 2.

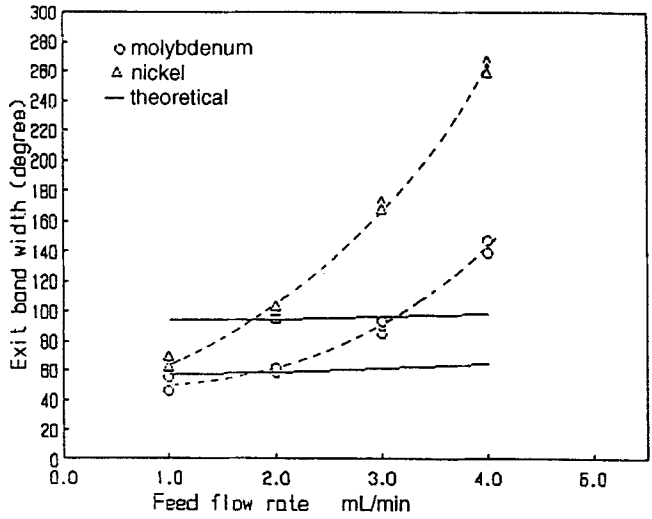

FIG. 4 The effect of feed flow rate on the exit bandwidth of Mo and Ni.

by the cation column. Nickel was retained by the cation column and its calculated distribution coefficient was 5.3.

The effect of feed flow rate on the separation of nickel and molybdenum is shown in Figs. 4–6. As predicted by the plate theory (Eq. 1), the change of the feed flow rate from 1 to 4 mL/min was found not to influence the position of the nickel and molybdenum bands. Figure 4 shows that, as the feed flow rate was increased, an increase in exit bandwidth occurred. The graph shows that for both metals the increase in bandwidth is nonlinear. According to the plate theory (Eq. 2), any increase in exit bandwidth should be due only to an increase in the initial feed bandwidth. Figure 5 shows that as the feed flow rate was increased from 1 to 4 mL/min, initial bandwidth increased as predicted. The linear increase of initial feed bandwidth as the feed flow rate increased did not result in a linear increase in exit bandwidth. Thus the nonlinear increase in exit bandwidth must be the result of factors additional to the change in inlet bandwidth, such as nonlinear adsorption and desorption, dispersion and diffusion, etc.

Figure 6 shows the effect of feed flow rate on the resolution between molybdenum and nickel. Resolution falls linearly as the feed flow rate is increased. According to Eq. (4), the experimental results do not correspond to the theoretical prediction. In preparative chromatography, a resolution of 1 is considered adequate (6–9). For the current separation, resolution values fell below 1 when the feed flow rate exceeded about 3.5

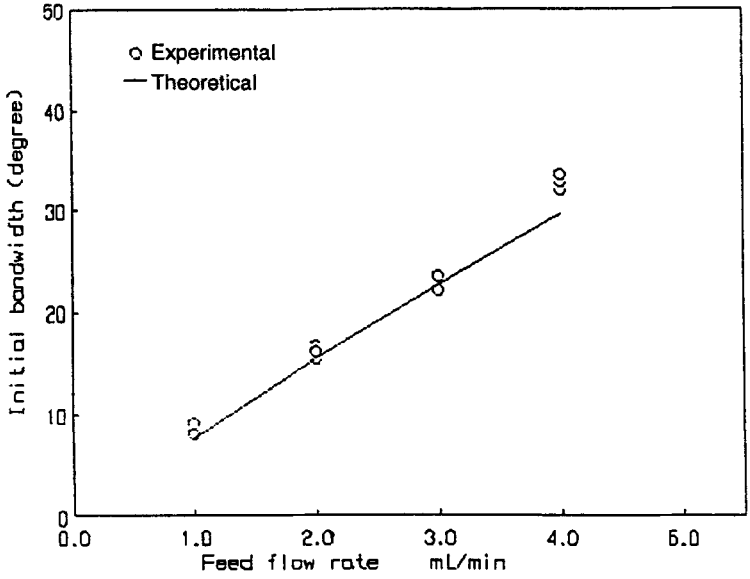

FIG. 5 The effect of feed flow rate on the initial bandwidth.

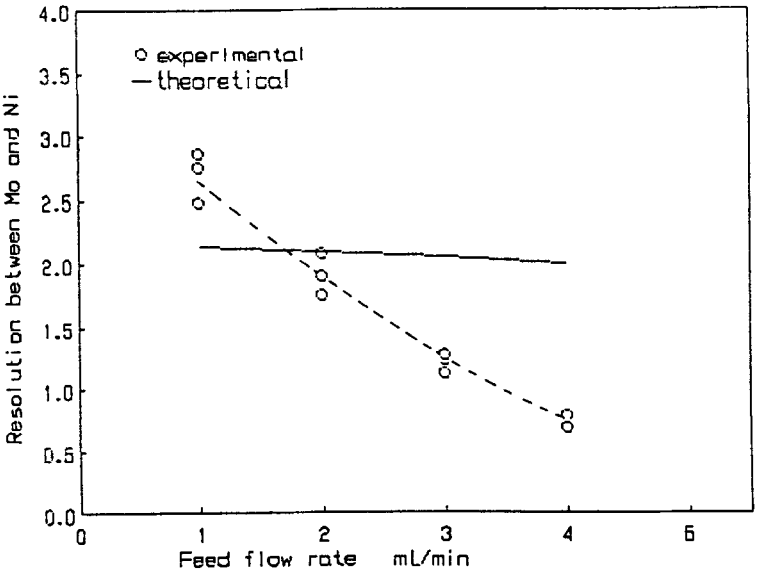

FIG. 6 The effect of feed flow rate on the resolution between Mo and Ni.

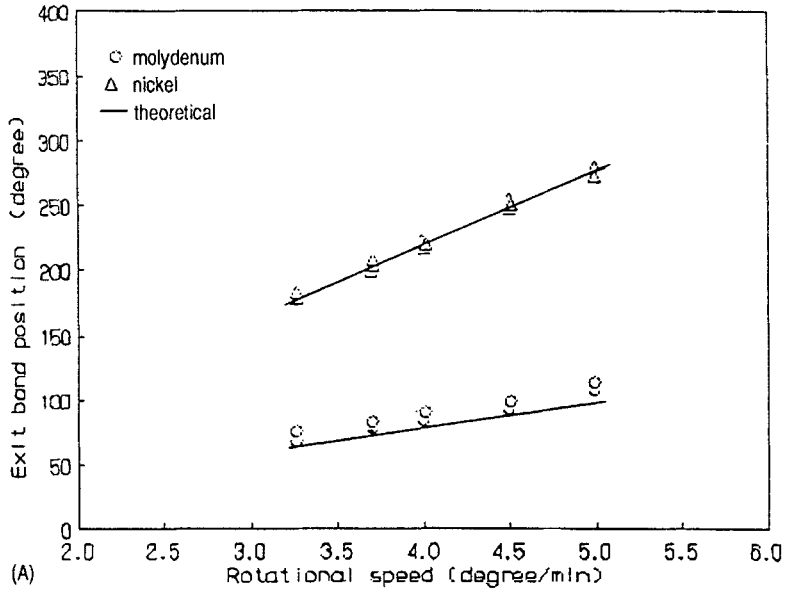

FIG. 7A The effect of rotational speed on the exit band position of Mo and Ni.

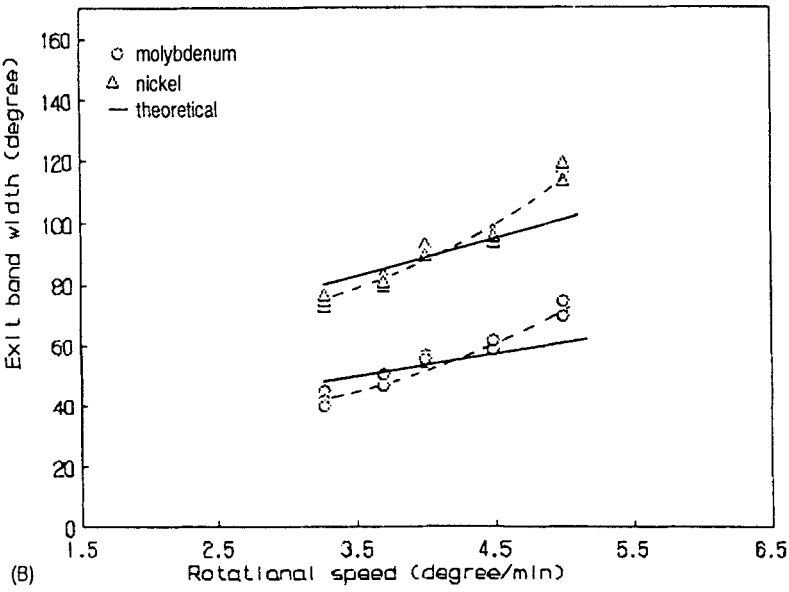

FIG. 7B The effect of rotational speed on the exit bandwidth of Mo and Ni.

mL/min ($Q_F/Q_E = 7.2 \times 10^{-2}$). Thus a feed flow rate of 3.5 mL/min can be considered to be the maximum throughput at the rotation speed and eluent flow rate given in Table 1.

Figure 7A shows a linear increase in eluent band position as the rotation speed of the feed nozzle is increased. This result corresponds to that predicted by Eq. (1) in that the band position is proportional to the rotational speed. Figure 7B shows the effect of rotational speed on the exit bandwidth of molybdenum and nickel. The results show that as rotation speed is increased, there is a nonlinear increase in exit bandwidth. Thus Eq. (3) was unable to predict the exit bandwidth with an increase of rotating speed of the feed nozzle.

Figure 8 shows the effect of feed nozzle rotational speed on resolution with eluent and feed rate held constant. At high rotational speed, the resolution was nearly a constant value, but resolution decreased as the rotational speed decreased from 3.7°/min. This decrease of resolution with decreasing rotational speed can be explained by considering the two parameters which affect the resolution: exit position and exit bandwidth. As the rotational speed increased, the exit band position increased proportionally while the exit bandwidth did not increase by the same amount. The net result is that the resolution falls off.

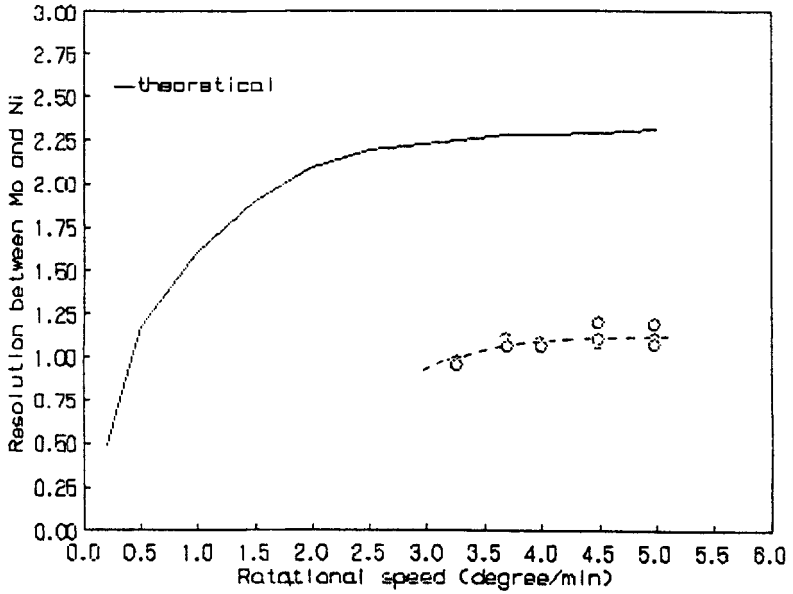

FIG. 8 The effect of rotational speed on the resolution between Mo and Ni.

CONCLUSIONS

These studies have demonstrated the successful application of a novel CRAC device to separate a solution containing nickel and molybdenum salts. The CRAC device uses a rotating tray for physical collection of products and a rotational feed nozzle for continuous injection. It is a very effective device for separation of dissolved salts as illustrated by efficient separation of the two salts. The throughput of this device at constant eluent flow rate and rotational speed of feed nozzle is 3.5 mL/min.

Plate theory was compared with experimental results obtained using the CRAC device. The results are in agreement with the data of Begovich et al. (9–12). Plate theory of the linear operating region can successfully predict the exit band position but not the exit bandwidth. Since molybdenum is essentially unretained on the column, it would appear that solute diffusion rather than nonlinear adsorption–desorption processes is responsible for the excessive band broadening.

NOMENCLATURE

W	bandwidth at baseline (degree)
W_0	initial feed bandwidth (degree)
R	resolution
Q_F	feed flow rate (mL/min)
Q_E	eluent flow rate (mL/min)
N	number of theoretical plates
K	linear distribution coefficient
L	bed length (cm)
U	eluent superficial velocity (cm/min)

Greek Letters

$\bar{\theta}$	exit band position (degree)
ω	rotational speed (degree/min)
ϵ	bed void fraction

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