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Woo K. Park[a]; Edward D. Michaels[ab]
[a] MRC-MQUND, Miamisburg, Ohio [b] O. S. Department of Energy, Monsanto Research Corp,

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SEPARATION OF NITROGEN ISOTOPES BY DISPLACEMENT BAND CHROMATOGRAPHY

Woo K. Park and Edward D. Michaels
MRC-MOUND*
Miamisburg, Ohio 45342

ABSTRACT

A study of the separation of ^{14}N and ^{15}N isotopes via displacement band chromatography was conducted using sulfonated styrene-divinylbenzene resins. Starting with a feed solution of 0.5 N NH_4OH (containing 51% ^{15}N), a band was developed that generated a concentration profile ranging from 11 to 85 % ^{15}N. The separative power and HETP (height equivalent to a theoretical plate) were found to be dependent on the resin characteristics (size, crosslinkage) and operating parameters (superficial velocity, concentration). The use of a 7/10-micrometer-size, high performance resin increased the separative power by a factor of 17 and decreased the HETP by a factor of 10, when compared to a 100/200 mesh Dowex 50W-X12 resin under similar process conditions. The HETP could further be reduced by lowering the superficial velocity and/or eluant concentration.

BACKGROUND

This laboratory is involved in the development of chemical exchange isotope separation processes to enrich isotopes of interest in physical and biomedical research. Since these isotopes are

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often of low natural abundance their separation requires a large number of stages and a high reflux ratio to produce significant enrichments. Cascade dynamics and control considerations dictate that the process holdup (or stage residence time) be held to a minimum. Although liquid-liquid chemical exchange chemistry is generally developed to a higher degree than analogous liquid-solid chemical exchange chemistry, it has been suggested (1) that liquid-solid processes offer more opportunity to minimize stage residence time and hence holdup.

The liquid-solid nitrogen chemical exchange developed by Spedding et.al (2) was selected as a process on which to study the factors which might lead to low stage residence time processes. This chemical exchange process is well characterized and should be analogous in many ways to the metal isotope chemical exchange chemistries which are now the subject of current research (3).

Chemistry

The separation of nitrogen isotopes via displacement band chromatography is accomplished through the formation of an ammonium band and the distribution of nitrogen isotopes within this band. A small amount of ammonium hydroxide solution is fed into a column of resin in the hydrogen state and eluted by a sodium hydroxide solution, forming a moving band, as shown in Figure 1.

Thus, as in a reflux unit, ammonium ions are continuously released from the resin and converted to ammonium hydroxide at the rear boundary of the band. The ammonium hydroxide solution moves down along the band at a velocity faster than that of the band itself until it reaches the front of the band. At the front boundary, on the other hand, the ammonium hydroxide solution is converted to ammonium ions, which are retained in the resin phase and fall behind in the band movement. The controlling reactions are,

at the front of the band;

$$H^+\text{-R} + NH_4OH = NH_4^+\text{-R} + H_2O \qquad (1)$$

where -R denotes resin phase,

within the band;

$$^{14}NH_4^+\text{-R} + {}^{15}NH_4OH = {}^{15}NH_4^+\text{-R} + {}^{14}NH_4OH \qquad (2)$$

at the rear of the band;

$$NH_4^+\text{-R} + Na^+ + OH^- = Na^+\text{-R} + NH_4OH \qquad (3)$$

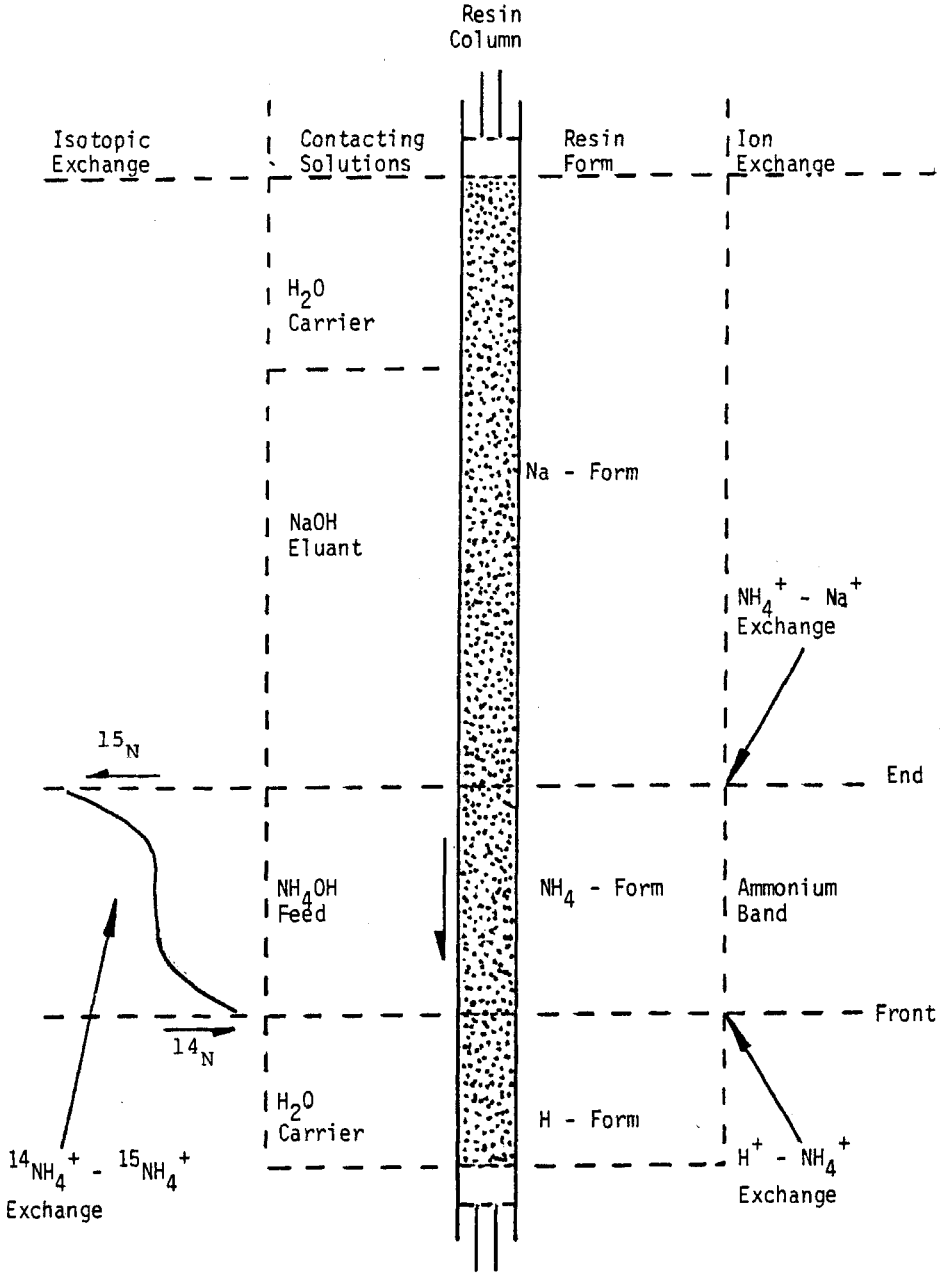

Fig. 1. Process scheme for chromatographic separation of nitrogen isotopes

All three reactions are reasonably fast (2). The equilibrium constants for Reactions (1) and (3) are much greater than one, so that replacement of hydrogen ions by ammonium ions and ammonium ions by sodium ions are quantitative. The equilibrium constant for Reaction (2) is slightly greater than one so that a slight separation of nitrogen isotopes occurs between the resin and aqueous phases. The countercurrent movement of ammonium ions in two phases thus develops a longitudinal isotopic profile within the band. The ^{15}N isotope is enriched in the rear of the band and the ^{14}N isotope in the front.

Resin Characteristics and Operating Parameters

A number of resin characteristics are considered to affect the performance of the resin column for isotope separation. These include the physical and chemical features of the resin such as resin particle size, pore structure, crosslinkage, ionic group and capacity.

Among these characteristics, resin size is considered an important factor because the smaller size resin offers larger specific surface area, shorter diffusion distance, and smaller void volume when packed in a column; this helps separation efficiency.

The degree of crosslinking, represented by the percentage of crosslinking agent in the copolymer matrix, affects both the mobility of ions in the resin (and hence separation) and the physical stability of the resin. The competing effects (hence selecting the crosslinkage) require tradeoff to ensure the desired separation efficiency while maintaining physical stability.

Because of its proven ability to separate nitrogen isotopes, the sulfonated polystyrene-divinyl benzene copolymer was selected as the primary resin type (2). The resins in this category offer several advantages: high chemical and mechanical stability, high exchange capacity, fast exchange rate and wide availability. A total of ten resins with various size and crosslinkage were obtained (from Bio-Rad Laboratories and Benson Co.) and studied. Their performance was rated in terms of separative power, HETP and concentration profile. The effects of operating parameters, flow rate and feed and eluant concentrations were also determined for a representative resin.

EXPERIMENTAL

Apparatus and Procedure

A schematic diagram of the apparatus used for the separation of nitrogen isotopes is shown in Figure 2. In this experimental

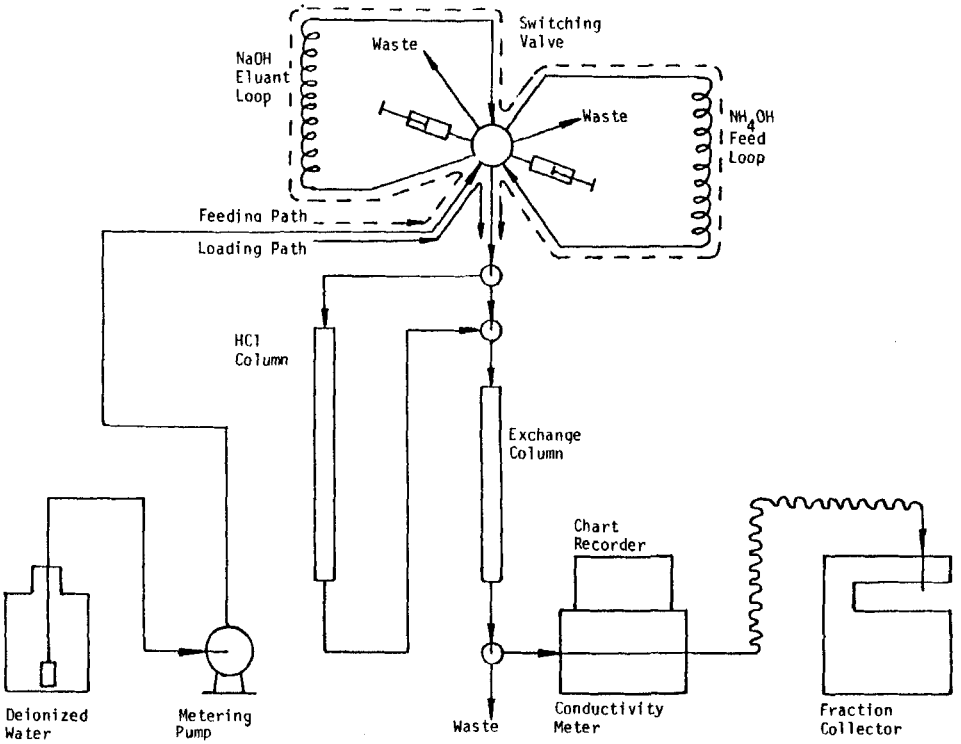

Fig. 2. Schematic diagram of nitrogen isotopes separation system

system, a NH_4OH solution containing about 50% ^{15}N isotope was processed along the resin. A NaOH solution was used as the eluant. Table 1, lists the test variables and their ranges used in the experiment. The superficial velocity, regulated by a microprocessor-controlled metering pump, was typically set at 2.0 cm/min. However, other rates were also tried. The pressure ranged from 60 to 553 psia, depending on the flow rate and the resin characteristics. Water jacket cooling was employed to remove the heat of reaction and maintain the column temperature at 23°C. The resin column was a glass tubing, 6.3 mm i.d. and 33 cm long, fitted with two adjustable length bed supports, except for Run Number 1 which was 6.6 mm i.d. and 33 cm long. Retaining frits and distributors held the resin in place.

Table 1. Variables and Their Ranges

Variables	Ranges
Resin Size	7 - 150 micrometers*
Resin Crosslinkage	8, 12, 14, 16%
Feed Concentration	0.25 - 0.75 N NH_4OH
^{15}N in Feed	47 - 51%
Eluant Concentration	0.3 - 0.9 N NaOH
Eluant/Feed Concentration Ratio	1.0, 1.2
Flow Rate	0.31 - 0.76 mL/min
Superficial Velocity	1.0 - 2.2 cm/min
Temperature	23°C
Pressure	60 - 553 psia
Bed Height	20.7 - 23 cm
Column ID	0.63, 0.66 cm
Bed Volume	6.5 - 7.9 cm^3
Void Fraction	0.18 - 0.40
Resin Capacity	2.34 - 2.60 meq/mL

*150 micrometers = 100 mesh

A 1.5 N HCl solution was used to regenerate the resin on the exchange column after each run (Figure 2). Na^+ ions left on the resin are replaced by H^+ ions during regeneration; as carrier water pushes the HCl solution onto the exchange column. Once regeneration is complete (pH indicates endpoint), a water flush removes excess HCl solution.

Figure 2 shows the actual flows for loading the loops and feeding the exchange column. A 10-port, 2-position switching valve is set up at the heart of the flow system to enable the loading and feeding schemes shown. During loading, the NH_4OH feed loop (typically 5 mL @ 0.5 N) and NaOH eluant loop (typically 30 mL @ 0.6 N) are filled while water is flushing the exchange column. When the valve switches to feeding, carrier water pushes the NaOH eluant, which in turn pushes the NH_4OH feed. Thus, the exchange column sees NH_4OH feed first, then a slug of NaOH eluant, and finally the carrier water (Figure 1).

The conductivity of the column effluent was used to monitor an actual exchange run (Figure 3). Roughly five minutes after starting the feed, H^+ ions (displaced from the resin by NH_4^+ ions) were indicated by a slight increase in conductivity. A large in-

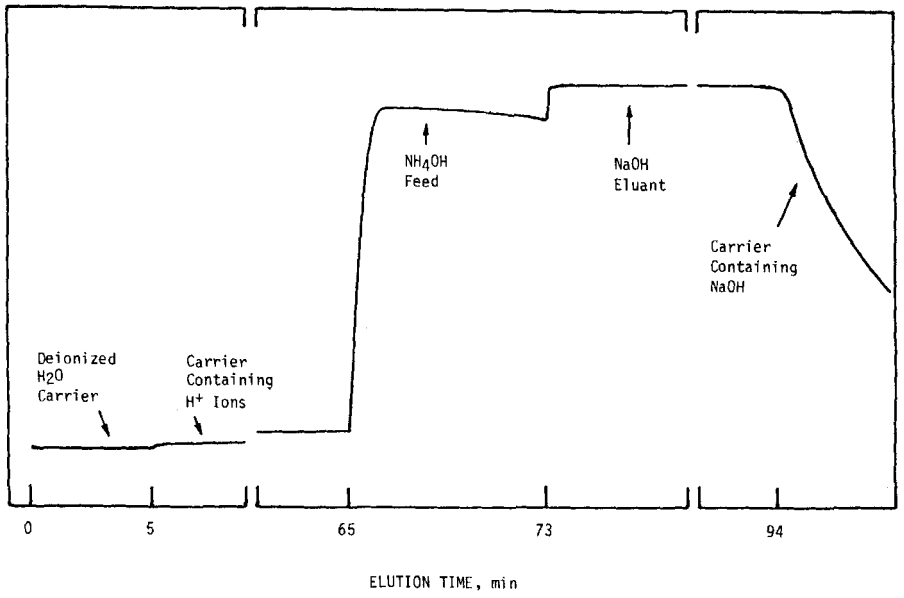

Fig. 3. Liquid phase chromatogram

crease in conductivity (at approximately one hour) indicated the appearance of the ammonium band. A final step change in conductivity showed the breakthrough of NaOH eluant. When NH_4^+ ions were detected, a fraction collector was activated to collect samples for isotopic enrichment vs. distance along the band length.

The NH_4OH liquid samples collected were converted to dry N_2 gas for isotopic analysis. Several proven methods for the conversion (4,5) were combined and adapted to a batch type preparation scheme. In this scheme the NH_4OH sample was first converted to NH_4Cl using excess (0.5 - 1 mL) 1.5 N HCl solution, and evaporated to dryness under a stream of He gas. The dried NH_4Cl was later reacted with 1-2 mL of NaOBr solution under vacuum to give N_2 gas. The N_2 generated was transferred to a N_2 gas container for subsequent isotopic analysis on a mass spectrometer (MS). Figure 4 shows components of the nitrogen sample preparation system.

The ion currents at m/e = 28, m/e = 29 and m/e = 30 were measured for each gas sample on the MS. These numbers were used

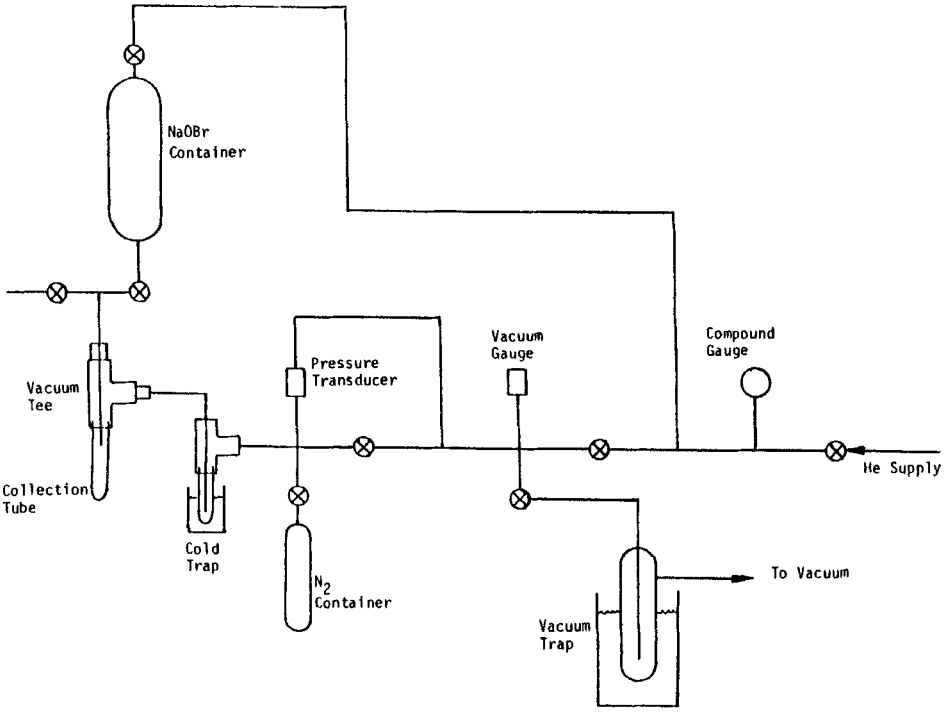

Fig. 4. Schematic diagram of nitrogen sample preparation apparatus

for the corresponding concentration terms of the equation,

$$\text{Atom \% } {}^{15}N = [1/2({}^{14}N{}^{15}N) + ({}^{15}N_2)] / [({}^{14}N_2) + ({}^{14}N{}^{15}N) + ({}^{15}N_2)] \quad (4)$$

to calculate the ^{15}N concentration.

DATA ANALYSIS

Application of the principle of conservation of mass to the transient, displacement band, chemical exchange process without

feed or product withdrawal results in the following equation describing the distribution of isotopes within the band (6):

$$\mu \frac{\partial x}{\partial t} = B \frac{\partial^2 x}{\partial s^2} - \epsilon B \frac{\partial}{\partial s} [x (1 - x)] \quad (5)$$

where $x(s,t)$ = mole fraction of ^{15}N
μ = inventory per stage, g
ϵ = α - 1, separation factor, 0.0257
B = interstage mass flow rate, g/s
s = stage number
t = time, s

Note that this equation is only valid when ϵ is small and the cascade can be considered to be a continuum in the number of stages, s.

Equation (5) can be solved numerically (7) to describe the evolution of the isotopic profile in the displacement band. When the interstage flow rate,

$$B = q_o U_b A \quad (6)$$

where q_o = resin capacity per unit of bed volume, g/cm^3
U_b = band velocity, cm/s
A = column cross-sectional area, cm^2

and the total holdup in the band are determined from the conditions of the experiment, only the number of stages remains as an unknown parameter. The number of stages in the band may be determined by fitting the experimentally measured isotopic profile to profiles computed from Equation (5). Figure 5 shows a typical result obtained by this procedure.

The important parameters derived from the experiments are the stage residence time, T_r,

$$T_r = \mu/2q_o U_b A \quad (7)$$

and the height equivalent to a theoretical plate, HETP,

$$HETP = L_b/n \quad (8)$$

where L_b = band length, cm
n = number of equilibrium stages

The performance of any chemical exchange separation process is completely characterized by the separative power per unit volume,

$$\delta U = \epsilon^2 \bar{c}/8T_r \quad (9)$$

where $\bar{c} = 2q_o c_o/(q_o+c_o)$
c_o = aqueous ammonia concentration, g/cm^3

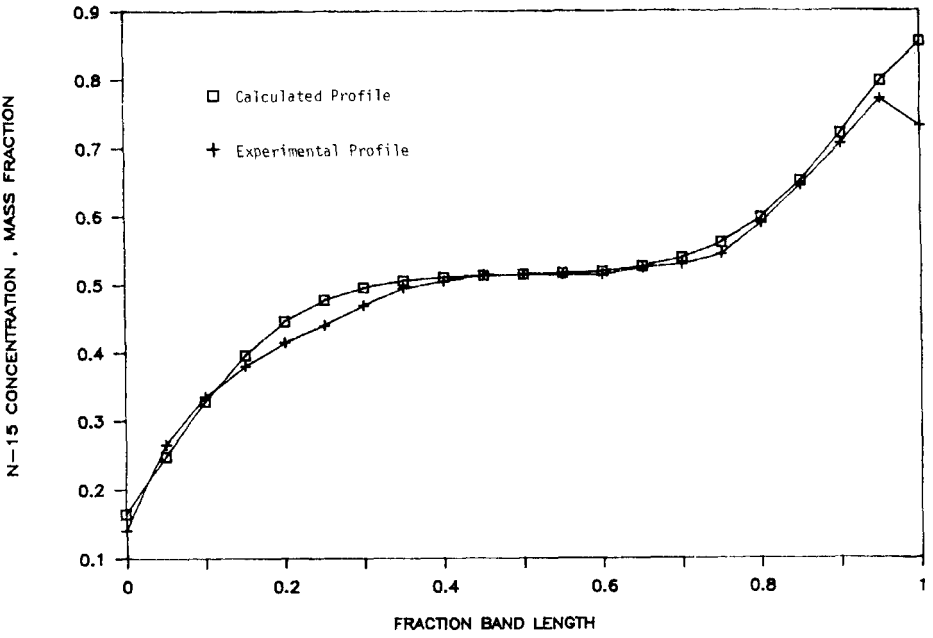

Fig. 5. Comparison of calculated and experimental concentration profiles for ^{15}N isotope (Run Number 17)

This parameter combines both the separative characteristics of the process and the throughput capacity of the process. The size of plant required to perform a given isotope separation is inversely proportional to δU. The results of our experimental work have, for this reason, been expressed in terms of separative power per unit volume.

RESULTS

Effects of Resin Characteristics

In this study the resin size and degree of crosslinking were chosen as the key resin characteristics which would affect isotopic separation as measured by separative power, HETP, and ^{15}N concentration profile. The 100/200 mesh (75-150 m) Dowex 50W-X12

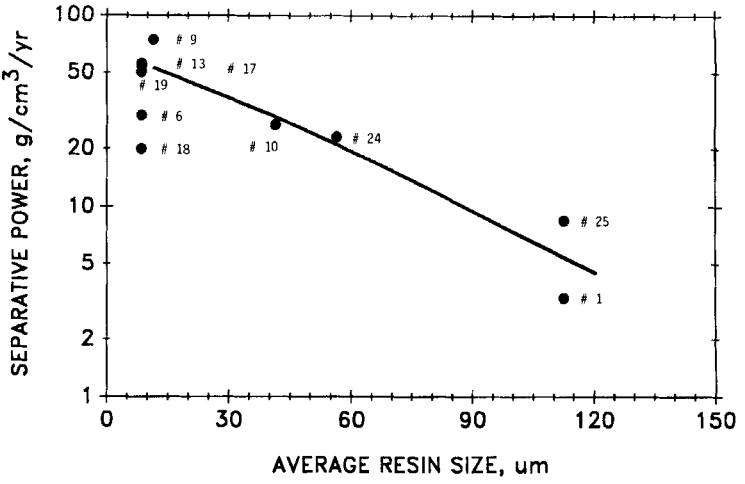

Fig. 6. Effects of resin size on separative power.

resin which was used by Spedding et. al served as the reference resin in determining the effects of other resins.

Generally, separative power, as defined by Equation (9), increased as resin size decreased, as shown in Figure 6, although some data showed scatter, probably from differences in operating parameters and other resin characteristics. Run Numbers 1 (Dowex 50W-X12) and 13 (Benson BC-X12) show an increase in the separative power by a factor of 17 for a factor of 13 decrease in resin size (Table 2). Thus, the extent of isotope separation can be greatly enhanced with smaller resins. This is attributed to the exchange rate being controlled by resin phase diffusion, in which smaller resins enable NH_4^+ ions to inter-diffuse faster. Aminex A-9 resin, used for Run Number 9, showed an even greater effect on separative power and HETP, clearly indicating it as the best performing resin among the resins tested. However, its high purchase price limited its use.

Because smaller resins increased both column pressure buildup and bed compression, the superficial velocity and bed height were limited, for later runs, to 2.0 cm/min and 22 cm, respectively. At these conditions, the pressure buildup remained below the limit for the glass columns used.

The degree of crosslinking in polymer resins was another important factor that controlled the hydration capacity, gel phase

TABLE 2: DETAILS OF SELECTED CHROMATOGRAPHIC RUNS

RUN #	RESIN NAME	RESIN TYPE	RESIN SIZE, μ	RESIN DRY WEIGHT, g	BED HEIGHT, cm	N-15 IN FEED, %	NH_4OH CONC, N	NaOH CONC, N
1	DOWEX *	50W-X12	100-200 MESH	3.22	23.0	47.4	0.5	0.6
6	BENSON	BC-X16	7-10	3.65	21.4	47.4	0.5	0.6
9	AMINEX	A-9	11.5	3.16	21.4	47.4	0.5	0.6
10	DOWEX	50W-X12	<400 MESH	3.25	20.7	47.4	0.5	0.6
13	BENSON	BC-X12	7-10	3.04	21.3	47.4	0.5	0.6
17	BENSON	BC-X12	7-10	3.04	22.0	51.0	0.5	0.6
18	BENSON	BC-X12	7-10	3.04	22.0	51.0	0.25	0.3
19	BENSON	BC-X12	7-10	3.04	22.0	51.0	0.5	0.6
24	AG	50W-X12	200-400 MESH	3.12	22.0	51.0	0.5	0.6
25	AG	50W-X12	100-200 MESH	3.57	22.0	49.0	0.5	0.6

RUN #	TEMPERATURE, °C	PRESSURE, psia	FLOW RATE, mL/min	BAND LENGTH, cm	BAND VELOCITY, cm/min	SEPARATIVE POWER, $g/cm^3/yr$	HETP, cm	N-15 RANGE, %
1	23	60	0.760	2.2	0.51	3.27	0.071	35-54
6	23	155	0.692	2.5	0.47	29.8	0.016	24-72
9	23	300	0.623	2.5	0.46	74.4	0.0054	13-83
10	23	101	0.623	2.4	0.44	26.7	0.015	26-72
13	23	553	0.623	2.6	0.46	55.8	0.0074	22-78
17	23	495	0.467	2.6	0.35	53.9	0.0056	14-80
18	23	515	0.467	2.8	0.18	20.0	0.0045	13-89
19	23	415	0.312	2.6	0.24	50.4	0.0042	11-85
24	23	325	0.467	2.7	0.36	23.0	0.0173	32-72
25	23	235	0.467	2.75	0.36	8.5	0.047	37-59

* REFERENCE RESIN

porosity and rigidity of the resins; these factors directly affect both resin bed strength and the rate of isotopic ion exchange. When crosslinkage decreased from 16 to 12%, at a fixed flow rate and eluant concentration, the Benson resin showed: 1) increased pressure buildup (from 155 to 553 psia); 2) increased bed compression (from 0.7 to 1.5 cm); and 3) increased separative power (from 29.8 to 55.8 $g/cm^3/yr$). To balance separative power and pressure buildup at a given flow rate, an optimum crosslinking resin needed to be chosen. At 2.0 cm/min, 12% was near optimal for most runs, which provided high separative power within a safe pressure limit, hence subsequent runs were performed with the 12% crosslinked Benson resin.

Effects of Operating Parameters

The major operating parameters varied for this study were flow rate and NaOH concentration (which controlled the aqueous NH_4OH concentration within the band). Their operational ranges are shown in Tables 1 and 2.

The effects of superficial velocity on the process and isotopic separation were chiefly obtained from Run Numbers 17 and 19. These runs were made using the same resin column pre-conditioned at the same bed height. As expected, the pressure drop, bed shrinkage and band velocity were all reduced as the superficial velocity was lowered. The band length, however, was not affected. As shown in Table 2, the range of the ^{15}N isotope distribution was expanded farther and HETP was decreased by 25% as a result of the lower (33%) superficial velocity. This trend was confirmed in other similar runs including Run Number 13. Figure 7 shows the linear change of HETP with respect to band velocity for Run Numbers 13, 17 and 19.

The effects of eluant concentration on the process can be seen by comparing two runs, Numbers 17 and 18. The ranges of ^{15}N isotope distribution for these runs reveal a greater total enrichment for the lower eluant concentration run (Table 2). The resultant HETP was 20% smaller for the 50% lower eluant concentration. Similar concentration effects were observed with two other runs made at 0.5 N and 0.9 N eluant concentrations.

An effort was made to compare the relative magnitudes of the influences exerted by reducing the eluant concentration and the superficial velocity (Run Numbers 18 and 19). A common factor that controls HETP appears to be band velocity, which is a function of concentration and superficial velocity. Figure 7 shows a generally decreasing pattern of HETP for decreasing band velocity. Since separative power is proportional to band velocity (U_b) and inversely proportional to HETP as expected from Equations (7) and (8), the ratio, U_b/HETP, can be used as a guiding parameter in determining the relative effects of eluant concentration and superficial velocity on the separative power.

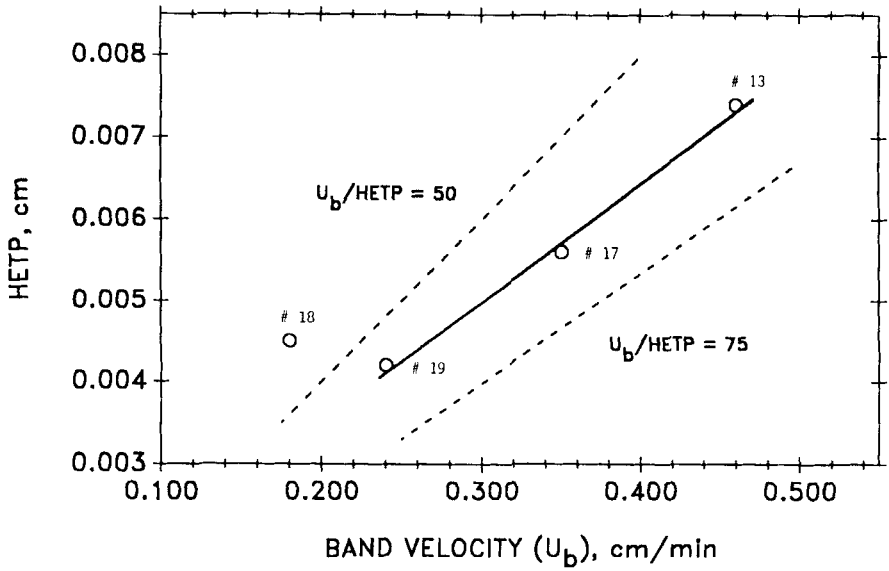

Fig. 7. Effects of band velocity on HETP

Figure 7 indicates that the decrease of superficial velocity (Run Number 19 relative to Run Number 17) had little effect on separative power, while the decrease of eluant concentration (Run Number 18) lowered separative power. The dotted lines representing U_b/HETP at 50 and 75 signify the upper category of the separative power achieved for most runs.

CONCLUSION AND DISCUSSION

The use of smaller size resins greatly enhances the extent of nitrogen isotope separation, increases separative power and decreases HETP. By selecting an optimum degree of crosslinking for these resins, an enhanced isotope separation can be achieved within reasonable process conditions. The HETP can further be decreased by lowering the superficial velocity and/or eluant concentration. However, this may reduce the separative power also. The band velocity, which is a function of superficial velocity and concentration may be used as a process variable in controlling HETP. Furthermore, the ratio, band velocity/HETP, may be adjusted in optimizing the process conditions for a desired separation. Based on the large separative power associated with the small resins, the size of resin column required to perform a given isotope separation

may be greatly reduced using small resins with an optimum crosslinkage. The column size requirement may also be reduced to a certain extent by increasing the eluant concentration. However, the superficial velocity appears to have insignificant impact on the column sizing while having much influence on the process conditions within the range studied.

The liquid holdup is very small in both the resin bed and the internal refluxes when compared to liquid-liquid contacting processes; thus less transient time is required for system equilibrium. Control over the process appears to be easier than in liquid-liquid processes, although a scaled-up system would require automation for multi-columns.

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