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THE EFFECTS OF OPERATING PARAMETERS ON NITROGEN ISOTOPES
SEPARATION BY DISPLACEMENT BAND CHROMATOGRAPHY

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ABSTRACT

The separation of nitrogen isotopes by displacement band chromatography was studied under various operating conditions, using columns packed with sulfonated polystyrene-divinyl benzene, cation exchange resins. Average resin size was varied from 10 to 113 μm , operating temperature from 23 to 70°C, displacing solution concentration from 0.3 to 0.9 N, and superficial velocity from 1.0 to 2.0 cm/min. The maximum separative power for nitrogen isotopes was directly proportional to stage velocity (band velocity/height equivalent to a theoretical stage). The effects of operating parameters on the separative power were therefore evaluated in terms of stage velocity. The results indicate that operating temperature and resin particle size have greater effects on the maximum separative power than do displacing solution concentration and flow rate.

INTRODUCTION

Various isotopes have been successfully enriched and separated by displacement band chromatography (DBC) on a laboratory-scale (1,2,3). DBC is a process in which a band of feed-containing mixed species or isotopes is moved for segregation through a column

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packed with an ion exchange resin. The DBC system is relatively compact, resulting from a very small HETP (height equivalent to a theoretical plate) of the resin column and in-situ refluxes at the band boundaries. The compactness of the system makes this process quite attractive for separating isotopes, since a large number of stages and extensive reflux units are typically required for such processes. In addition, the operational simplicity and flexibility associated with this process present a good opportunity for scaling-up and commercializing production of isotopes.

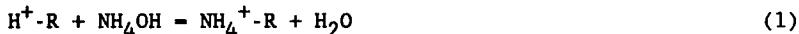
In order to characterize the DBC system and predict its isotopic distribution capability, a few mathematical models and correlations have been developed (2,4). However, reported information on the separative power for such a system appears to be limited for use in process evaluation (5). This paper, therefore, reviews recent experimental data on DBC nitrogen isotope separation and develops a correlation for the separative power as a function of operating parameters.

THEORY

Chemistry

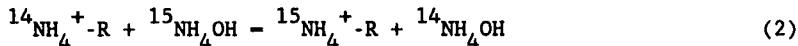
In the separation of nitrogen isotopes by DBC, an ammonium band is formed and the nitrogen isotopes are distributed within it. The work scheme of DBC is analogous to a conventional distillation system, where the boundaries of the moving band of ammonium ions perform like the reflux and reboiler of a distillation column. Thus, as in a reflux unit, ammonium ions are released from the resin by a sodium hydroxide displacing solution and converted to ammonium hydroxide for downward flow in the liquid phase (Figure 1). This exchange occurs at the rear boundary of the band. Similarly, as in a reboiler, the ammonium hydroxide solution is converted to ammonium ions at the front boundary of the band. These ions are retained in the resin phase as if forming an upward flux relative to the downward moving band, as shown in Figure 1. The counter-current flow of the solution and ions is thus developed as the band moves down the resin column, resulting in the separation of nitrogen isotopes. The following are the major reactions that occur at different parts of the moving band:

At the front boundary of the band



where $\cdot R$ denotes resin phase

Within the band



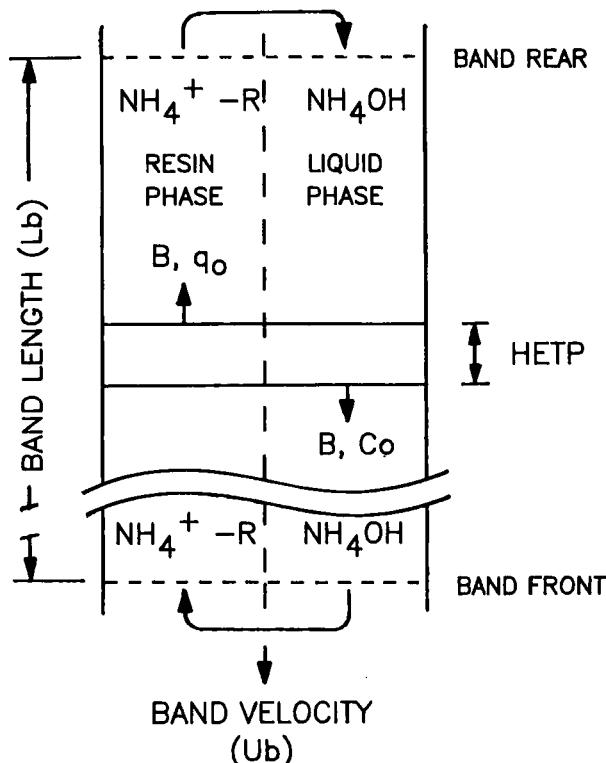
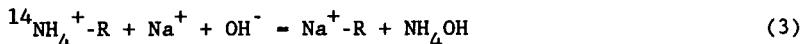


Fig. 1. Displacement band chromatographic system for nitrogen isotope separation. B is interstage mass transfer rate, q_0 and C_0 are nitrogen concentrations in resin phase and liquid phase, respectively.

At the rear boundary of the band



Separative Power

The commonly used term to characterize isotopic separation cascades for evaluation is the maximum separative power (6). This term defines the maximum attainable production rate of a desired isotope per unit volume of a cascade. For nitrogen DBC systems this quantity can be calculated by solving the following equation of continuity as an initial step (7).

$$\mu \frac{\partial x}{\partial t} = B \frac{\partial^2 x}{\partial s^2} - \epsilon B \frac{\partial}{\partial s} [x(1-x)] \quad (4)$$

where x = mole fraction of N-15
 μ = average nitrogen holdup per stage, g
 t = breakthrough time, s
 s = stage number
 B = interstage mass flow rate, $q_o u_b A$, g/s
 where q_o = resin phase nitrogen concentration
 (or resin capacity) per unit of bed
 volume, g/cm³
 u_b = band velocity, cm/s
 A = column cross-sectional area, cm²
 ϵ = separation factor, 0.0257

The assumption of Equation (4) is based on a transient binary system with no feed and product removal features. By numerically solving the equation (4) with the experimental conditions, a simulated concentration profile for N-15 may be determined.

In this computation the number of stages, n , is assumed and confirmed by fitting the simulated profile to the corresponding experimental profile. Then the HETP value

$$HETP = L_b/n \quad (5)$$

can be calculated with the experimentally measured band length, L_b .

The maximum separative power is defined as

$$\delta U_m = B \epsilon^2 / 4 \quad (6)$$

or the maximum separative power per unit volume,

$$\delta U_{mv} = (B \epsilon^2 / 4) / (HETP \cdot A) \quad (7)$$

Substitution of $B = q_o u_b A$ into equation (7) gives

$$\delta U_{mv} = (\epsilon^2 q_o / 4) (u_b / HETP) \quad (8)$$

Equation (8) indicates that the maximum separative power per unit volume is proportional to the stage velocity, $u_b / HETP$ of the band, which is the number of stages that the band passes through per unit time.

The band velocity is generally known through the mass balance equation,

$$u_b = C_o u_s / (q_o + fC_o) \quad (9)$$

where C_o = liquid phase nitrogen concentrations, g/cm^3
 u_s = superficial velocity, cm/s
 f = void fraction

or directly from experimental observation. All the separative powers reported in this paper were calculated using equation (8) with computed HETP and experimentally observed u_b .

As a special case, one could consider a steady-state equilibrium operation of DBC. For such an operation an expression for the total number of stages commonly known as Fenske equation,

$$n = \ln(R_r/R_f) / \ln\alpha$$

where $R_r = x/(1-x)$ at band rear
 $R_f = x/(1-x)$ at band front
 $\alpha = 1 + \epsilon$

may be applied in calculating $\text{HETP} = L_b/n$.

Thus, the maximum separative power per unit volume can be calculated with experimentally measurable information;

$$\delta U_{\text{mvs}} = (\epsilon^2 q_o / 4) \{ (u_b / L_b) [\ln(R_r/R_f) / \ln\alpha] \} \quad (11)$$

The band length in Equation (11) may also be determined by using the mass balance equation:

$$L_b = C_o Q_b / [(q_o + fC_o) A] \quad (12)$$

where Q_b = feed volume, cm^3

In our previous report (7), the maximum separative power per unit volume in terms of average concentration, c and stage residence time, T_r was estimated by

$$\delta U_{\text{mv}} = \epsilon^2 \bar{c} / (8T_r) \quad (13)$$

where \bar{c} = average nitrogen concentration within stage, $q_o + fC_o$, g/cm^3
 T_r = stage residence time, s

Equation (13) was derived by substituting $B = \mu/2T_r$ and $\mu = \bar{c}$ (HETP•A) into Equation (7). However, c was erroneously estimated by using an inaccurate averaging formula which resulted in lower separative powers than actual by a factor of about three.

EXPERIMENTAL

The separation of nitrogen isotopes was carried out in columns packed with sulfonated polystyrene-divinyl benzene polymer resins. The columns consisted of a glass tube, 6.3 mm i.d. and 33 cm long, and were fitted with two adjustable length bed supports. A water jacket permitted removal of the heat of reaction and maintained a constant temperature for each resin column. The loading and feeding of the feed and displacing solutions to the column was achieved by operating a 10-port, 2-position switching valve. Deionized water was used as a carrier liquid to drive the feed and displacing solution through the system while a metering pump regulated the flow rate. The column effluent was monitored by a conductivity meter to locate the band. Samples of the band were then collected on a fraction collector for mass-spectrometer analysis. A more detailed account of the experimental system and procedure was reported elsewhere (7). The experimental system was operated at varied conditions.

The operating parameters controlled for this study were the operating temperature and average resin particle size, which ranged from 23 to 70°C and 10 to 113 micrometers; as well as the displacing solution concentration and superficial velocity, which varied from 0.3 to 0.9 N and 1.0 to 2.0 cm/min, respectively (Table 1).

Table 1. Operating parameters and their settings for experimental runs.

Run No.	Resin size μm	Temperature °C	Concentration N	Flow rate mL/min
13	10	23	0.6	0.623**
17*	10	23	0.6	0.467
18	10	23	0.3**	0.467
19	10	23	0.6	0.312**
21	10	50**	0.6	0.467
22	10	70**	0.6	0.467
24	57**	23	0.6	0.467
25	113**	23	0.6	0.467
27	10	23	0.9**	0.467

*represents standard run.

**represent variations from the standard.

A 1.5 N HCl solution was used to prepare the resin for a first run as well as to regenerate the resin after each run. During regeneration, H^+ ions of the HCl replaced the Na^+ ions remaining on the resin from the NaOH displacing solution. Once the pH (e.g., 0.01) of the resin column effluent indicated that the

regeneration was completed, excess HCl still remaining in the resin column was removed with a deionized water flush. During this flushing, the 5 mL feed loop attached to the switching valve was filled with 0.5 N NH_4OH containing 50% N-15 isotope and the 30 mL displacing solution loop was filled with 0.6 N NaOH. When the switching valve was turned to the feeding position, the carrier water pushed the NaOH displacing solution which in turn pushed the NH_4OH feed. Thus, the NH_4OH , which defined the front boundary of the band, reached the resin column first, followed by the NaOH displacing solution which defined the rear boundary, and finally by the carrier water (See Figure 1). As the front of the band emerged from the column the fraction collector was activated to collect NH_4OH samples that were subsequently converted to dry N_2 gas for isotopic analysis by mass spectrometry.

RESULTS

Separative Power

The maximum separative powers calculated from the experimental data are shown plotted in Figure 2. The result provides striking confirmation of the linear dependency of the maximum separative

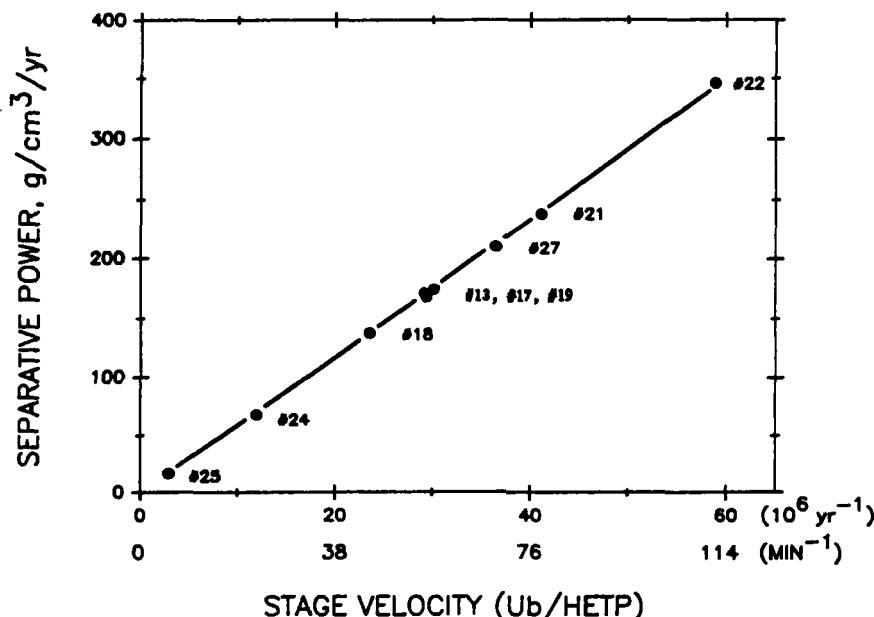


Figure 2. Maximum separative power for N-15 isotope as a function of stage velocity. The data points represent experimental runs as indicated by their numbers.

power on stage velocity for the systems with constant separation factor (ϵ) and resin capacity (q_0), as predicted by Equation (8). Furthermore, it reveals that slight variation of separation factor due to temperature and pressure changes and some differences in resin capacity for different resin types, as exhibited in varied systems, have little effect on the linear relationship of the maximum separative power on the stage velocity. It appears that the effect of these varied constants on the maximum separative power is relatively small and even that effect is partially cancelled out by the opposing effect of the stage velocity which is functionally interdependent with these constants. The fitting, by a single straight line, of all the data points representing a variety of test conditions, confirms this point. Within the ranges of operating parameters studied, this finding implies, the maximum separative power can be considered not only linearly dependent on the stage velocity but also independent on the term, $(\epsilon^2 q_0/4)$ of Equation (8). This relationship, therefore, suggests that the stage velocity can effectively represent the process variables involved in the determination of the maximum separative power and may be used as a design variable for the design and operation of nitrogen DBC processes.

Stage Velocity

The stage velocity (u_b/HETP) is a term that can be defined as the number of stages passed by the band per unit of time. However, it is implicit and indirect in specifying a DBC process. It is, therefore, desirable to understand its relative dependence on process conditions.

Figure 3 illustrates such relationships. Resin size, operating temperature, displacing solution concentration and superficial velocity are the four operating parameters tested for their effects on this design variable (u_b/HETP). As shown in the figure, resin size and operating temperature have significant effects on HETP, with virtually no effect on the band velocity as indicated by Equation (9). Two vertical line segments, connecting triangles (Run #'s 25, 24 and 17) and circles (Run #'s 17, 21, and 22) shown in the figure depict this trend. The decrease of average resin size from 113 to 10 micrometers resulted in the increase of stage velocity from 3.0 to 29.4 yr^{-1} (Figure 4), which corresponds to the increase of the maximum separative power from 16.4 to $168.0 \text{ g/cm}^3/\text{yr}$ (Figure 2). Similarly, the increase of operating temperature from 23 to 70°C increased the stage velocity from 29.4 yr^{-1} to 58.9 yr^{-1} , raising the maximum separative power from 168.0 to $346.1 \text{ g/cm}^3/\text{yr}$. On the other hand displacing solution concentration (or liquid phase feed concentration) and superficial velocity affected both band velocity and HETP to nearly the same extent as shown in Figure 3. As a result their net effects on the stage velocity were small; the effect of superficial velocity was inappreciable and that of displacing solution concentration minor within this study limits. Figure 4 shows that the stage velocity increased from 23.6 yr^{-1} to 36.5 yr^{-1} , increasing the maximum

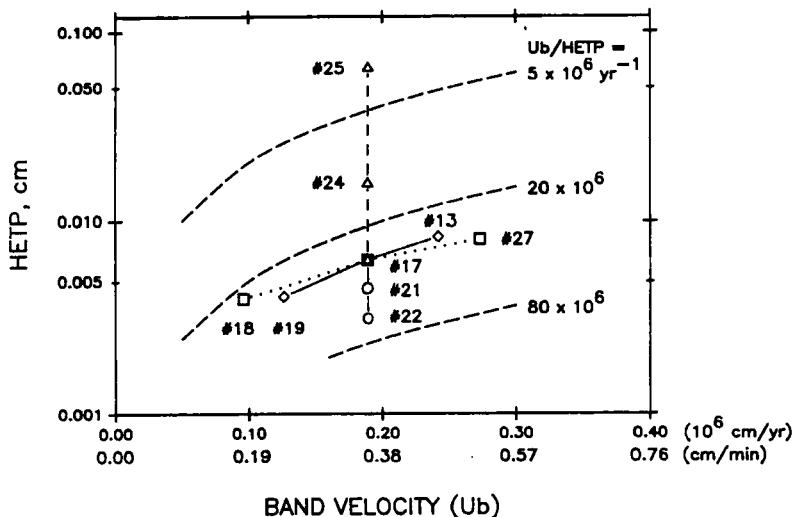


Figure 3. Effects of operating parameters on band velocity, HETP, and stage velocity (u_b /HETP). The triangles represent the runs for different resin sizes; circles for temperatures; squares for concentrations; and diamonds for superficial velocities.

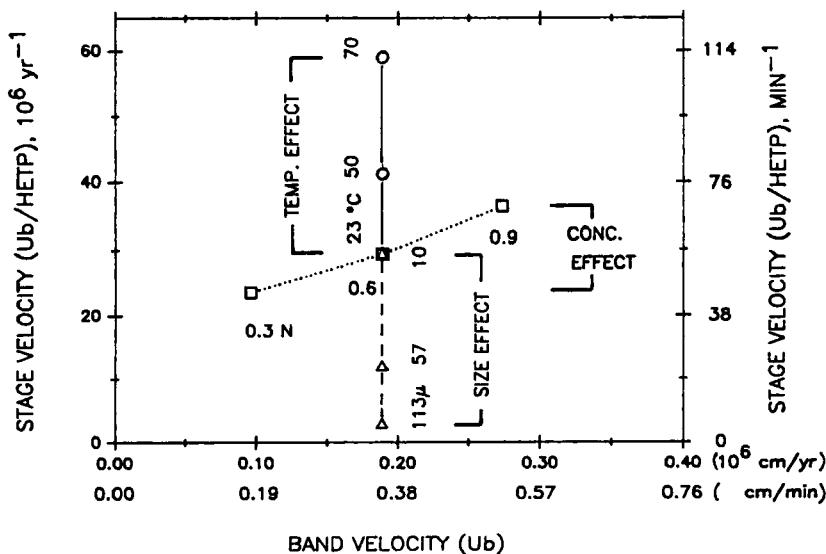


Figure 4. Effects of resin size, operating temperature, and displacing solution concentration on stage velocity, expressed as a function of band velocity. The corresponding run numbers can be found in Figure 3 or Table 1.

separative power from 137.4 to 209.9 g/cm³/yr, as the displacing solution concentration increased from 0.3 to 0.9 N.

CONCLUSION

The maximum separative power for a nitrogen isotope can be expressed as a linear function of stage velocity in displacement band chromatography. It is, therefore, feasible to use the stage velocity as a design variable for such isotopic separation processes, when its correlations to operating parameters are known. The experimental results show that the stage velocity (and thus the maximum separative power) increases with smaller size resin, increased operating temperature, and increased displacing solution (or liquid phase feed) concentration. The increase of the maximum separative power by a factor of up to 10 is achievable by using a smaller size resin, a factor of 2 by increasing the operating temperature and a factor of 1.5 by increasing the displacing solution concentration, within the variable ranges studied in this work.

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