

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Continuous Isotope Separation in Systems with Solid Phase. II. Separation of Nitrogen Isotopes with Use of Ion-Exchange Resin

Alexey V. Kruglov^a; Boris M. Andreev^b; Ygor E. Pojidaev^b

^a DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA, USA ^b PHYSICO-CHEMICAL DEPARTMENT, MENDELEYEV UNIVERSITY OF CHEMICAL ENGINEERING OF RUSSIA, MOSCOW, RUSSIA

To cite this Article Kruglov, Alexey V. , Andreev, Boris M. and Pojidaev, Ygor E.(1996) 'Continuous Isotope Separation in Systems with Solid Phase. II. Separation of Nitrogen Isotopes with Use of Ion-Exchange Resin', Separation Science and Technology, 31: 4, 471 — 490

To link to this Article: DOI: 10.1080/01496399608002211

URL: <http://dx.doi.org/10.1080/01496399608002211>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Continuous Isotope Separation in Systems with Solid Phase. II. Separation of Nitrogen Isotopes with Use of Ion-Exchange Resin

ALEXEY V. KRUGLOV*

DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA 55455, USA

BORIS M. ANDREEV and YGOR E. POJIDAEV

PHYSICO-CHEMICAL DEPARTMENT
MENDELEYEV UNIVERSITY OF CHEMICAL ENGINEERING OF RUSSIA
MOSCOW 125190, RUSSIA

ABSTRACT

This work deals with the separation of nitrogen isotopes by chemical exchange between ammonia in an aqueous solution and a cation-exchange resin in the NH_4^+ form. Using this system, a continuous process in a simulated moving bed (SMB) is developed. Two operations, the column under total reflux and a continuous feed operation, have been studied. In the latter, the product enriched in heavy nitrogen ^{15}N was removed from the unit. The operating conditions (2.1–30.5 cm/s superficial liquid velocity, 0.7 mm average resin granules size, and 0.98 N solution of a displacement agent) were close to those used in industrial applications. By studying the separation of nitrogen isotopes, it was shown that displacement ion-exchange chromatography in a practically standard liquid-phase SMB unit provides the opportunity for the flexible production of a number of isotopes of light elements. We found that flow converting is robust, and the operation and control are simple. It appears that the process design proposed in this work may also be applied for efficiently separating substances other than isotopic mixtures whenever a proper displacement band chromatographic system with nondispersive ends of the band is found.

* To whom correspondence should be addressed.

INTRODUCTION

Isotope fractionation has been one of the most interesting subjects in separation science, and the importance of isotopic separation is increasing due to the wide use of isotopes in energy and life science applications. A large number of stable isotopes and isotope-related materials is available today. For instance, Oak Ridge National Laboratory is responsible for isotope enrichment and the distribution of approximately 225 nongaseous stable isotopes from 50 multi-isotopic elements (1). Both traditional methods, such as electromagnetic isotope separation, and state-of-the-art techniques, such as plasma and molecular laser isotope separations, are being developed to achieve special isotopic chemical and physical requirements.

While most stable isotopes are produced in relatively small quantities, a few are used in large quantities and have dedicated enrichment processes to meet their volume needs. This group primarily includes heavy isotopes of hydrogen, nitrogen, carbon, and oxygen. In practice, fractionation of these isotopes is carried out by counter-current processes in vapor-liquid or gas-liquid systems. The world production of these materials (except for deuterium) lies in the range of 10^1 – 10^2 kg/year (2–4). In all cases the heavy isotope is much less abundant in the nature. Thus, the natural abundance of ^{15}N is 0.365 at.%, ^{18}O 0.204 at.%, and ^{13}C 1.11 at.%, whereas commodity chemicals commonly contain 90–99.9 at.% of the corresponding isotopic forms.

Mixtures of isotopes are characterized by a very small difference in the physicochemical properties of distinct isotopic species. If two phases are in equilibrium, one of the isotopes is distributed more abundantly in one of the phases with respect to the other. The applicability of a specific system for separating isotopes may be characterized by the equilibrium separation factor α , defined as

$$\alpha = [y(1 - y)]/[x(1 - x)] \quad (1)$$

with y being the atomic fraction of the isotope of interest in the enriched phase and x being the atomic fraction of this isotope in the phase which is exhausted with this species. For most systems suitable for separating isotopes of the light elements, the values of α are in the 1.01 to 1.05 range. Bearing in mind the low natural abundance of the isotopes of interest, it is clear that hundreds of theoretical separation stages must be applied to obtain the desired enrichment factors. A considerable chemical processing industry is required to achieve this on a commercial scale. Distillation, chemical exchange, and thermal diffusion have proved to be among the most satisfactory techniques for separating isotopes of the light elements (3–5).

Heavy nitrogen, ^{15}N , is a very valuable commercial product for which there is presently a growing demand in many research and industry applications. The primary use of the ^{15}N isotope is as a chemical tracer in the study of various agricultural, ecological, and physiological processes (6, 7). For example, the efficacy of nitrogen-containing fertilizers can be readily determined by measuring the degree of plant uptake of a fertilizer labeled with the relatively rare ^{15}N isotope.

Currently the production of ^{15}N is by cryogenic distillation of NO (8, 9). Isotopic separation by this technique uses the principle that the rate of condensation and evaporation of NO gases differ slightly among the various isotopic components of this gas. Cryogenic distillation requires a substantial capital investment, and separation columns are typically tens of meters in height (10). The equipment is highly complex, and the process control must be very robust to avoid the formation of solid N_2O_4 in the column because of its close boiling and freezing points at the operating pressure (1 atm).

The other technique brought into industrial operation employs a chemical isotopic exchange between NO and HNO_3 (11). Sulfur dioxide is consumed by chemical refluxing for the purpose of converting nitric acid into NO at one of the column ends, and the dilute sulfuric acid formed is a by-product in this process. This process results in an increased ecological hazard and a large volume of waste.

It is known that high values of the equilibrium separation factors for isotopes of many light elements, and for nitrogen isotopes in particular (12, 13), are also observed in systems with a solid phase. These systems have some very interesting applications with exchanging resins. In fact, various isotopes have been successfully enriched and separated on a laboratory scale by displacement band chromatography (14–16). This is a process in which a band of feed-containing mixed species of isotopes is moved for segregation through a column packed with an ion-exchange resin (17). Nitrogen isotopes were separated using this technique by Spedding et al. (12), who were the first to study the chemical exchange in a system consisting of an aqueous solution of ammonia and a cation-exchange resin in the NH_4^+ form. This system was adopted in our study, and so its chemistry along with the separating principles will be discussed in detail in the next section.

As was pointed out above, in order to multiply a small single separation effect and to carry out separation continuously, a countercurrent process has to be used. Referring to systems with a solid phase, the moving-bed operation encounters many problems because of the difficulties associated with actual solids movement (attrition, cumbersome solids handling system for recycling, nonuniformity of solid flow, etc.).

The solids problems may be avoided by using a simulated moving-bed technique (SMB) (18) instead of the moving-bed operation. This technology has recently emerged as a very efficient technique for handling some separations in the chemical, food, and pharmaceutical industries (19). In SMB units the solid beds are fixed and their continuous movement is simulated by a discrete movement obtained by shifting the feed and withdrawal points at discrete times along the column axis in the same direction as the fluid flows.

In this context it is worthy to note that during the last few years the SMB principle has been intensively investigated to separate racemic mixtures of enantiomers (20). This problem is very similar to isotope separation because it also deals with binary mixtures characterized by very small separation factors.

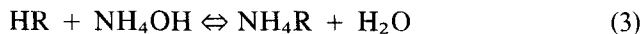
In a previous paper (21) we studied the gas-phase separation of isotopes of the light elements with the use of solid adsorbents. This work applies simulated moving-bed technology for liquid-phase continuous isotope separation by displacement band chromatography. We report the results of the separation of nitrogen isotopes by chemical exchange in the system formed by an aqueous ammonia solution and a strong acid ion-exchange resin in the NH_4^+ form.

SEPARATION PRINCIPLES

If an aqueous solution of ammonium hydroxide is placed in contact with a suitable exchanging resin, the following exchange reaction occurs:



the result of which, under equilibrium conditions, is that the heavy nitrogen, by means of the ammonium ion, is distributed more abundantly in the solid phase, which is the resin. Spedding et al. (12), at ambient temperature and using Dowex 50X12 resin, found the value $K = 1.0257 \pm 0.0002$ for the equilibrium constant in this equation, which in this case is equivalent to the elementary separation factor α . In order to multiply the elementary effect for separating ^{15}N , they arranged the Dowex 50X12 resin in a column and first treated it by passing a dilute acid through the column until the bed was completely saturated with H^+ , and the resin was then washed with water. At the top of the column, a quantity of solution of NH_4OH was then added until a band of ammonia was formed (see Fig. 1). The lower end of this band was quite clear, thanks to the reaction



occurring in that region, whose equilibrium constant is $\sim 10^9$. Once a band

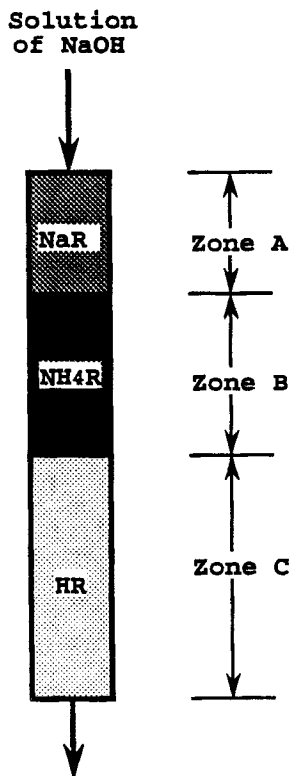
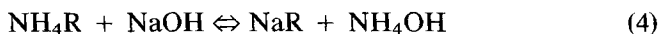


FIG. 1 Diagram of the batch displacement band chromatographic process for separating nitrogen isotopes with the use of a cation-exchange resin.

of the desired length had been formed, it was moved from the top of the column to the bottom by feeding the head of the column with an eluant solution of NaOH. At this point, the following reaction takes place:



which, having an equilibrium constant of about 10^5 , in turn guarantees a very clear rear end to the band. The band of adsorbed ammonia thus shifts downward, still between two clear limits, and it is in equilibrium with a solution of NH_4OH along its entire length. As the band gradually drops, the ^{15}N tends to accumulate toward the rear end and the ^{14}N toward the front end. It was concluded (12) that chemical exchange with resins is a

separation method mainly suited for producing, in laboratory quantities, isotopes of elements that are not too heavy.

Recently, Park et al. (22) studied this process under various operating conditions, using columns packed with sulfonated polystyrene-divinylbenzene cation-exchange resins. The average resin size was from 10 to 113 μm , the operating temperature from 23 to 70°C, the displacing solution concentration from 0.3 to 0.9 N, and the superficial velocity from 1.0 to 2.0 cm/min. The maximum separative power for nitrogen isotopes was directly proportional to the stage velocity (band velocity/height equivalent to a theoretical stage). Their results indicate that separation is more efficient with a smaller size resin, an increased operating temperature, and an increased displacing solution concentration.

SMB PROCESS FOR SEPARATION OF ISOTOPES BY DISPLACEMENT BAND CHROMATOGRAPHY

The displacement band chromatographic system outlined above was utilized to achieve a continuous separation, and this section describes the simulated moving-bed process developed in our work.

A schematic representation of a generic countercurrent column under total reflux, i.e., when neither feed nor products are introduced or withdrawn, is given in Fig. 2(a). It consists of a countercurrent contactor (separation zone) and two flow converting units. In the case of distillation, for instance, the flow converting units are the condenser and reboiler. In isotope fractionation the flow converting units are designated for transferring isotopes to be separated from one phase to the other. Figure 2(b) shows the equivalent SMB process for nitrogen isotope separation in the system involved. Each box in this scheme represents a fixed-bed section packed with resin. The resin in the separation zone is in the NH_4^+ form, and the aqueous solution of ammonia is in the liquid phase.

A solution of NaOH is continuously fed to the bottom of the lower flow converting unit, where Reaction (3) occurs. As a result, the $\text{Na}^+/\text{NH}_4^+$ ion-exchange front moves upward. The addition of each equivalent of NaOH to the lower flow converting unit shifts an equivalent of NH_4^+ into solution in the ion-exchange front region. The consequence is adsorption of an equal quantity of NH_4^+ in the upper flow converting unit, where Reaction (2) takes place. The two ion-exchange fronts thus advance along the SMB column with equal velocities. Periodically, when these two fronts pass a distance equal to the length of a single section, a switch of flows is made. Accordingly, each fixed-bed section moves one position downward, giving rise to a countercurrent movement between the liquid and solid phases. The resin leaving the lower flow converting unit is in the

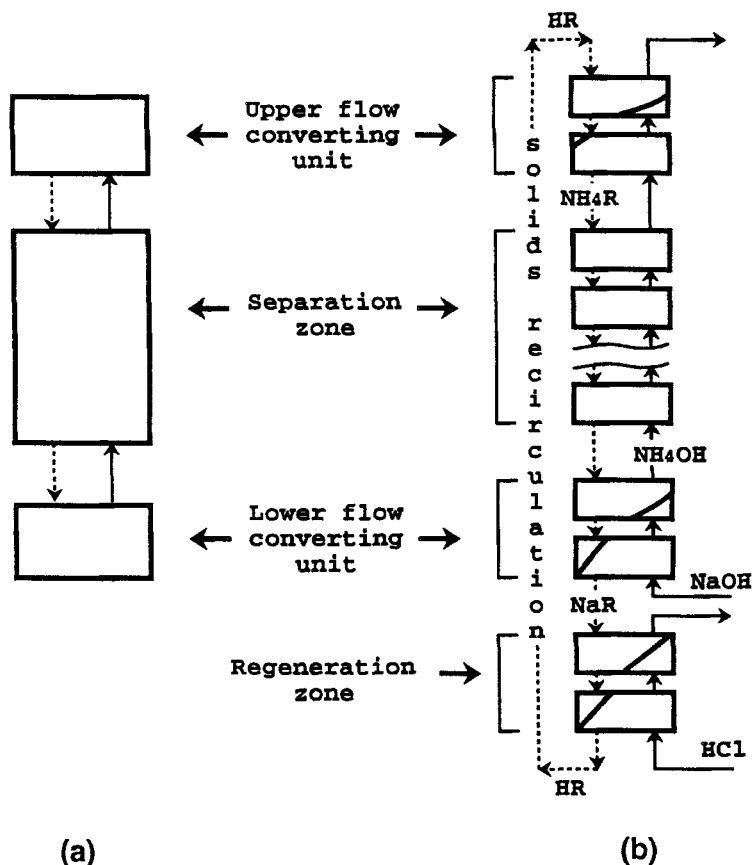


FIG. 2 Schematic representation of a countercurrent separation column under total reflux (a) and the equivalent SMB process for nitrogen isotope separation with the use of an ion-exchange resin (b).

Na^+ form. It is then converted to the H^+ form in the regeneration zone by a hydrochloric acid solution (see Fig. 2).

By means of the periodic switching of flows, the solids recirculates in the column, so the resin moves from the regeneration zone to the upper flow converting unit where it adsorbs NH_4^+ ions in accordance with Reaction (2). Due to this countercurrent operation, the heavy nitrogen, being distributed more abundantly in the resin phase, is concentrated at the bottom of the column. In turn, the light isotope ^{14}N , being less strongly adsorbed, is concentrated in the top of the column.

EXPERIMENTAL SECTION

A schematic diagram of the experimental setup is presented in Fig. 3. The simulated moving bed consisted of 12 uniform sections packed with the strong acid cation exchanger KU1x8. Some properties of the resin are given in Table 1. Each section was 10 mm in diameter and 50 mm in height. Two sections constituted the upper flow converting unit. There were three sections in the lower flow converting unit. Five fixed beds formed the separation zone where the chemical isotope exchange between NH_4OH and NH_4R occurred. Finally, two sections were in the regeneration zone (see Fig. 2), to which a solution of hydrochloric acid was fed to convert the resin to the H^+ form:



All sections were placed in a thermostat bath and maintained at a temperature of 298 K. Configuration of the simulated moving bed along with the values of the operating parameters used in the experiments are summarized in Table 2.

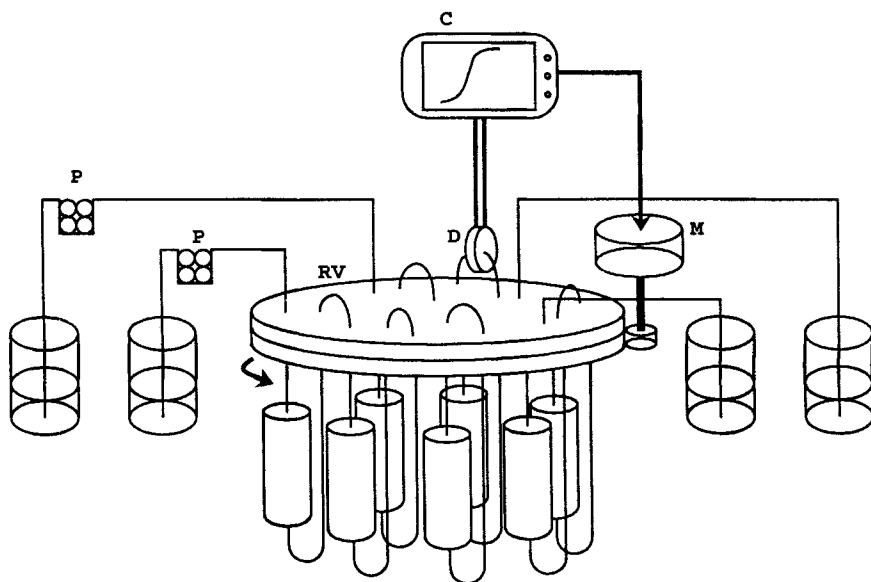


FIG. 3 Schematic diagram of the experimental setup. RV = rotary valve; P = peristaltic pumps; D = conductivity detector; M = step motor; C = computer.

TABLE 1
Physicochemical Properties of Dry Resin KU2×8

Skeleton	Styrene-divinylbenzene
Structure	Macroreticular
Functional groups	SO ₃ H
Crosslinking degree	8%
Average particle size	0.7 mm
Swelling in water	85%
Internal porosity	0.34
Concentration of acid sites	4.31 meq/g dry resin

To operate flow switching in the simulated moving-bed system, a specially designed multichannel disk rotary valve has been built. Details of the construction may be found elsewhere (21). All the fixed-bed sections were connected to the turning part of the valve, whereas the communications between them along with the external streams were connected to the stationary part of the valve (see Fig. 3). Countercurrency between the solid and gas phases was achieved by periodically rotating the moving part of the valve (together with the sections) in the direction opposite to that of the fluid flow. The liquid flows in the apparatus were maintained with peristaltic pumps.

Prior to the experiments the resin in all 12 sections was converted to the H⁺ form by feeding a 0.35 N solution of hydrochloric acid to the

TABLE 2
Configuration of the Simulated Moving Bed for Nitrogen
Isotope Separation

Number of sections:	
In the upper flow converting unit	2
In the separation zone	5
In the lower flow converting unit	3
In the regeneration zone	2
Single fixed-bed section:	
Height	5 cm
Diameter	1 cm
Operating temperature	298 K
Liquid flow rate	0.56–8.14 mL/min
Displacement agent	NaOH (0.98 N)
Regeneration agent	HCl (0.35 N)

unit. Then five sections were saturated with 0.98 N aqueous solution of ammonium hydroxide to form the separation zone. When the first flow switch occurred, the lowest section in the separation zone moved down to the lower flow converting unit. By applying the NaOH solution to the unit, the ion-exchange front $\text{Na}^+/\text{NH}_4^+$ was advancing up and finally broke through the fixed bed. This was registered by a conductivity detector placed in between the lower flow converting unit and the separation zone. The signal was passed over to the computer which was interfaced with a step motor, which executed the next flow switch in the system (Fig. 3). In this way the $\text{Na}^+/\text{NH}_4^+$ ion-exchange front was shifted back to the lower flow converting unit, and so on. Simultaneously, in the upper flow converting unit the development of the NH_4^+/H^+ ion exchange front took place in a basically identical manner. The separation experiments were performed until a steady-state isotope concentration profile along the unit was formed. The heavy isotope ^{15}N was concentrated in the lower part of the separation zone, and the light isotope ^{14}N was concentrated in the upper part.

The connections between the sections on the stationary part of the rotary valve were provided with special microports so that the liquid could be sampled from each port for analysis in order to determine the distribution of isotopes along the column.

The Reagent-grade purity NaOH, NH_4OH , and HCl solutions were used for the experiments. Solutions of the desired concentrations were prepared by mixing the initial chemicals with distilled water. Analysis of nitrogen isotopes was done with an isotopic mass-spectrometer MI-1101.

RESULTS AND DISCUSSION

It was pointed out earlier that because of the low values of α for isotopic mixtures, very effective flow refluxing is necessary to obtain good separation. Specifically in our case it is important that all nitrogen is completely transferred from solids to liquid in the lower flow converting unit, likewise all nitrogen should be quantitatively adsorbed by resin in the upper flow converting unit. To verify this we studied the cyclic development of the ion-exchange fronts in the SMB unit by measuring concentrations of sodium and ammonium ions in between fixed-bed sections. Figure 4 shows the Na^+ and NH_4^+ ion concentration profiles in both flow converting units just before and just after two successive flow switches. It can be seen that within the switching time interval the development of ion-exchange fronts in both ends of the SMB column occurs in a "constant pattern" regime, i.e., without dispersion in time. This confirms the system works satisfactorily, and all the nitrogen can be recycled without loss within the separation zone.

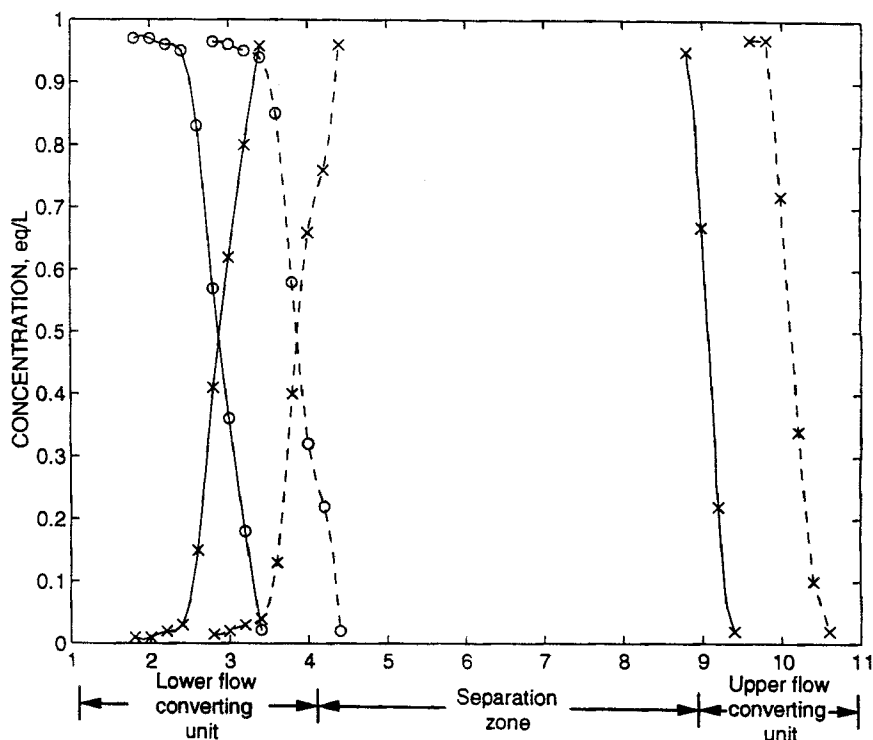


FIG. 4 Na^+ (O) and NH_4^+ (X) ion concentration profiles in the lower and upper flow converting units at cyclic steady-state just after switching flows (solid curves) and just before switching flows (dashed curves).

The experiments on nitrogen isotope separation under total reflux were carried out using natural abundance ammonia (0.365 at.% of ^{15}N). The flow rate of liquid was varied from 0.56 to 8.10 mL/min. The corresponding superficial velocity values lie in the 2.1–30.5 cm/min range that is typical for industrial applications. Figure 5 shows the average ^{15}N concentration profiles in the separation zone of the SMB after cyclic steady-state is reached.

On the basis of the steady-state isotope concentration profiles, the overall separation factor K was calculated:

$$K = \frac{x_l/(1 - x_l)}{x_u/(1 - x_u)} \quad (6)$$

where x_l and x_u are the atomic fractions of ^{15}N isotope measured in the

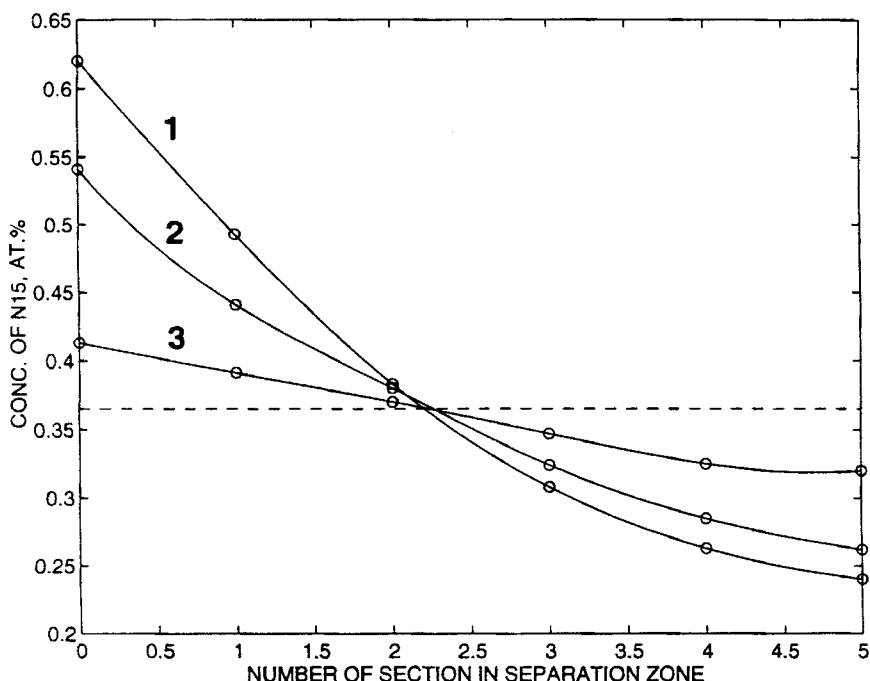


FIG. 5 Average ^{15}N concentration profiles in the SMB column under total reflux at steady-state. 1: $\nu = 0.714$ cm/min; 2: $\nu = 5.51$ cm/min; 3: $\nu = 10.37$ cm/min.

lower and the upper ends of the separation zone, respectively. In our case $x_1, x_u \ll 1$, so we can use $K = x_1/x_u$. The height equivalent to a theoretical plate (HETP) was then computed (4):

$$\text{HETP} = L \frac{\ln \alpha}{\ln K} \quad (7)$$

It was found that HETP grows in a linear fashion with the liquid flow rate, and Fig. 4 shows the effect of the superficial velocity on HETP.

The dependence of HETP upon the operating parameters for a counter-current adsorber was derived by Ruthven (23). By considering a linear adsorption isotherm, the axially dispersed plug flow model, and the linear rate expression, the following expression for HETP was obtained:

$$\text{HETP} = L(\text{Pe}^{-1} + \text{St}^{-1}) \ln \gamma / (\gamma - 1) \quad (8)$$

where γ is the ratio of the sorbate flow in the solid and fluid phases, L is

the length of the separation zone, and Pe and St are the Péclet and Stanton numbers. For separation under total reflux, $\gamma = 1$, so Eq. (8) takes simple form

$$HETP = L(Pe^{-1} + St^{-1}) \quad (9)$$

Two parameters, the axial diffusivity D_L and the overall mass transfer coefficient k_v , have to be known to apply Eq. (9). These values were determined from pulse experiments (24). The measurements were done directly in the SMB unit so that the 12 sections, connected in series, were used as a single fixed-bed column. For the overall mass transfer coefficient, the value $k_v = 8.3 \times 10^{-3} \text{ s}^{-1}$ was obtained. Assuming that the mass transfer is limited by diffusion of NH_4OH in the macroreticular resin granule pores, and using the correlation for k_v obtained by Glueckauf and Coates (25):

$$k_v = 15D_{\text{eff}}/R^2 \quad (10)$$

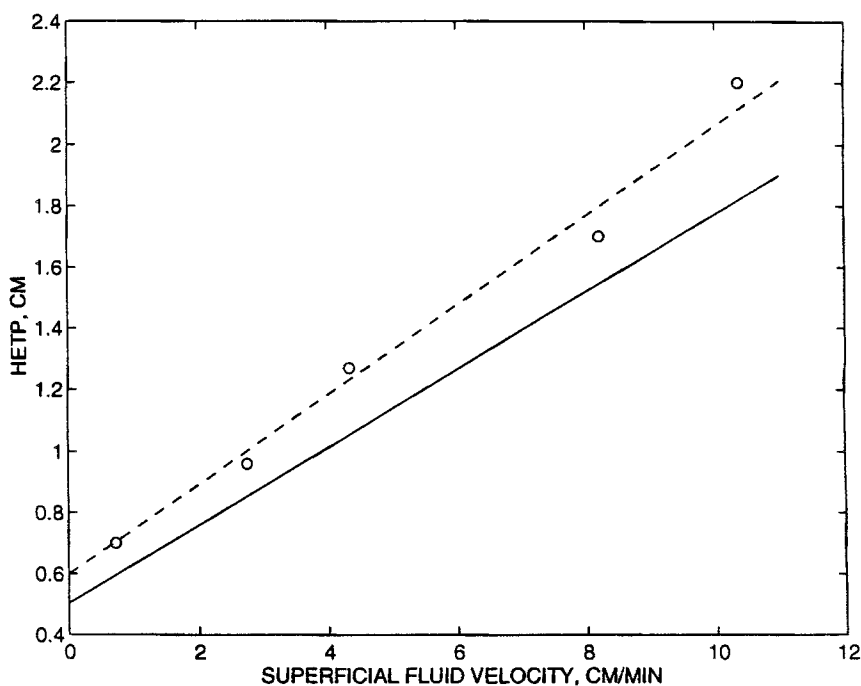


FIG. 6 Effect of the superficial fluid velocity on HETP.

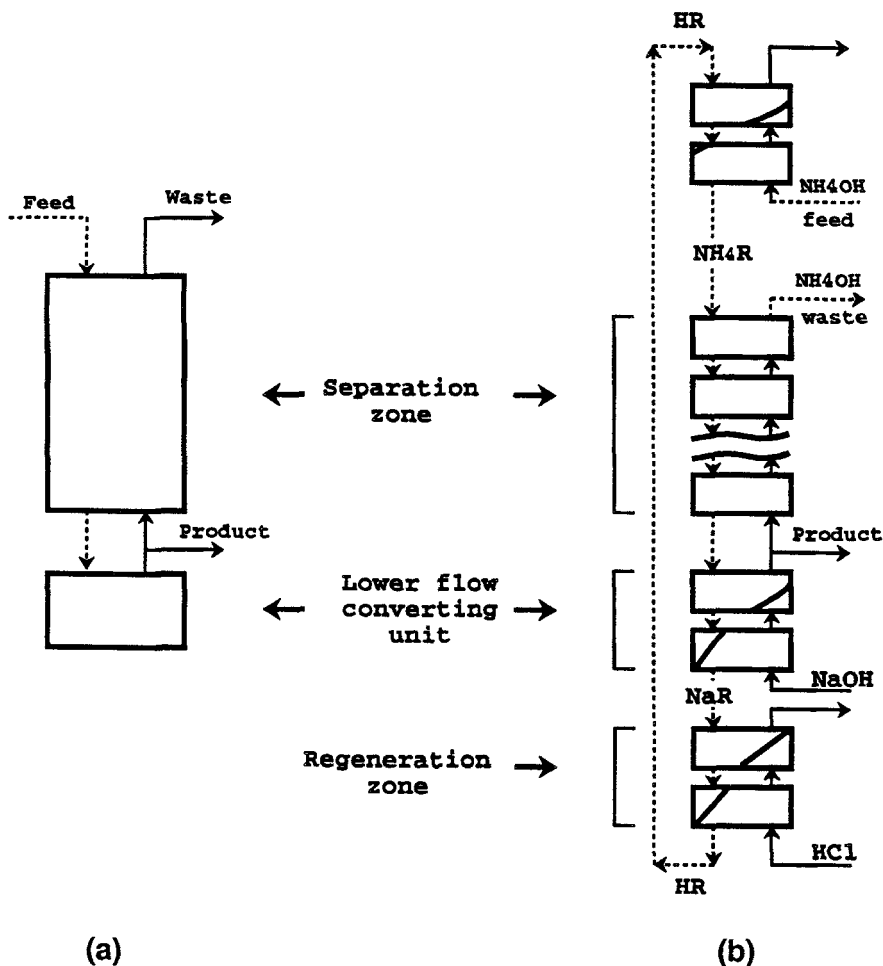


FIG. 7 Schematic representation of a continuous feed process concentrating only one component of the mixture (a) and the equivalent SMB process for concentrating heavy nitrogen ^{15}N (b).

with $D_{\text{eff}} = (\epsilon'/\gamma')D_m$ a reasonable value of 2.1 was obtained for the resin granule tortuosity factor.

The axial dispersion coefficient was determined by fitting the following expression to the experimental data (26):

$$\epsilon\text{Pe} = 0.2 + \lambda\text{Re}^{0.48} \quad (11)$$

The parameter λ was found to be equal to 0.42 instead of 0.011, the value known from the literature (26). The higher overall axial diffusivity observed in our system was probably due to the end effects in the sections and dispersion in the connecting tubes, as compared against a single fixed bed of the same length.

The prediction obtained by Eq. (8) (solid line in Fig. 6) appears to be quite satisfactory. The deviation from the experimental data can be attributed to the relatively low number of fixed-bed sections in the separation zone.

In addition to the experiments under total reflux, which are necessary to estimate the system separative efficiency, we also attempted a continuous feed operation. For this a process for concentrating only the heavy nitrogen, ^{15}N , has been adopted. The schematic of a generic countercurrent process, having as its purpose the concentration of only one component of the mixture, along with the corresponding scheme of the SMB

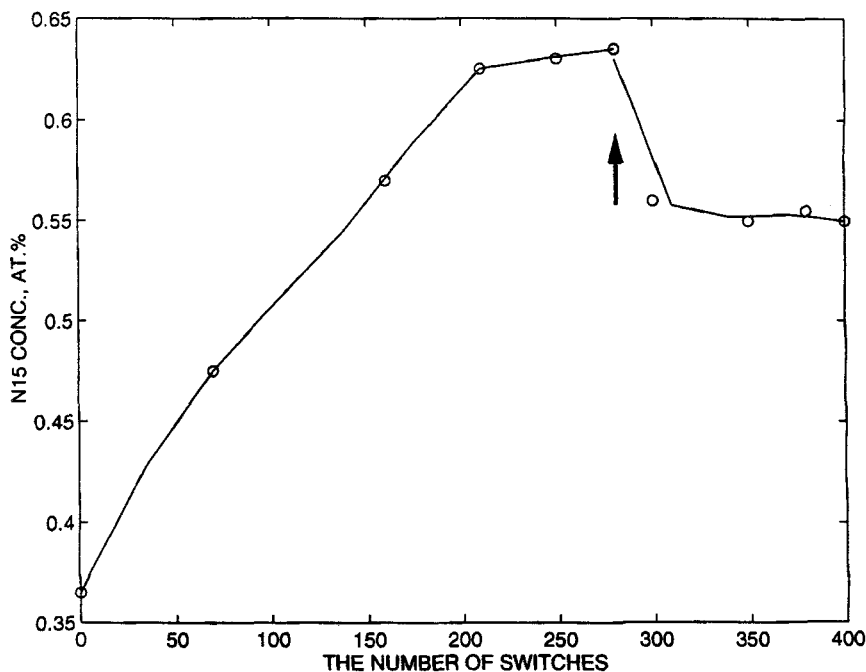


FIG. 8 ^{15}N concentration in the bottom of the separation zone during start-up in the continuous feeding experiment. Arrow indicates the time when product began being removed.

column are presented in Fig. 7. The feed to the SMB column in this case is basically composed of solids: the natural abundance ammonia solution (0.365 at.% of ^{15}N) is applied to the first section in the upper flow converting unit so that the resin in it becomes saturated with nitrogen of approximately the same isotope composition. When the flows are switched, this section "feeds" the column, joining the separation zone. The flow of liquid leaving the separation zone is exhausted with the heavy isotope (waste). The product, enriched in ^{15}N , is removed from the bottom. This is the so-called "transit" scheme: the feed and waste streams are of the same chemical composition (aqueous ammonia solution) but differ in the concentrations of nitrogen isotopes.

Figure 8 shows the concentration of ^{15}N in the bottom of the separation zone during start-up for the experiment with continuous feeding. Note that the unit reaches cyclic steady-state only after approximately 280 switches. We see that attaining a cyclic steady-state with this process

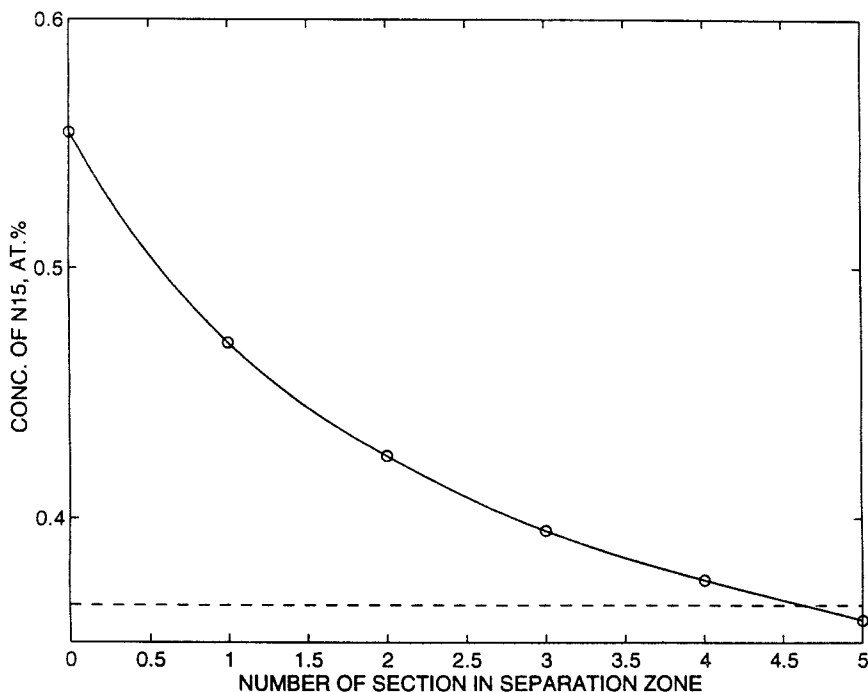


FIG. 9 Average ^{15}N concentration profile in the SMB column at steady-state for the continuous feeding experiment.

takes a very long time. Because of the low initial concentration of heavy nitrogen in the feed stream, a large volume of the feed material has to be processed during start-up to accumulate ^{15}N in the unit.

After 290 switches (indicated by an arrow in Fig. 8) we started to remove the product. That was done with a low flow rate piston pump. The flow rate of the product was 0.014 mL/min, which is only 0.51% in terms of the flow rate in the separation zone. Due to this operation, the enrichment attained in the unit dropped by approximately 30%. It is worth pointing out that the transient from the first to the second stationary regime occurred much faster than the transient following the start-up of the unit.

At the end of the experiment the liquid phase from the sections was analyzed, and Fig. 9 shows the ^{15}N concentration profile along the separation zone of the SMB. The results of the continuous feeding experiment show that the operation is robust and the process is simple to control.

CONCLUDING REMARKS

A continuous liquid phase process for separating nitrogen isotopes by displacement band chromatography in a simulated moving bed is developed and investigated. Two operations, the column under total reflux and a continuous feed operation with product enriched in ^{15}N , were studied.

Based on the results obtained, we conclude that a liquid-phase SMB process for separating isotopes with the use of ion-exchange displacement band chromatography has some advantages if compared with the traditional fractionation processes in vapor-liquid or gas-liquid systems. They are as follows.

1. The separating system is very compact because of a very small HETP (compared with those typical for gas-liquid countercurrent contactors).
2. The chemical refluxing occurs virtually in-situ: these are basically two narrow ion-exchange fronts adjoining the separation zone. As a result, there is no hold-up in the flow converting units. This is a very nice feature of our process because in traditional techniques such as distillation, the start-up procedure, carried out under total reflux, takes a rather long time, substantially because of hold-up in the condenser and reboiler.
3. The arrangement of the SMB system as a series of fixed beds instead of as a single vertical column also makes this process quite attractive for application, since a large column height and, therefore, tall buildings are typically required for such processes. Another advantage of

subdividing the column into a series of "compartments" is that in case of shutdown or a halt in operation, isotopic profiles may be "conserved" inside the SMB, and a new long-time start-up without actual processing can be avoided. That is impossible for the case of gas-liquid contactors.

By studying nitrogen isotope separation it was shown that displacement ion-exchange chromatography in a practically standard liquid-phase SMB unit provides the opportunity for the flexible production of a whole number of isotopes of the light elements. We found that operation and control of such unit are simple, and flow converting is robust.

Analysis of the literature shows that ion-exchange band chromatography as an application for isotopic separation has been the recent focus of many investigations. Thus, isotopes of calcium (27), strontium (28), lithium (29), potassium, rubidium, and magnesium (30), tin (31), boron (32), and some others were separated using conventional fixed-bed columns packed with ion-exchanging materials. It is noteworthy that isotopes of metals are much more difficult to separate, for these elements commonly do not have gaseous or volatile compounds, and so traditional isotope separation techniques cannot be applied here.

It appears that our proposed process design may also be applied for separating substances other than isotopic mixtures, whenever the proper displacement band chromatographic system with nondispersive ends of the band is found.

ACKNOWLEDGMENT

The financial support of the Russian Department of Energy is gratefully acknowledged.

SYMBOLS

D_L	axial diffusivity (cm^2/s)
D_{eff}	$= (\epsilon'/\gamma')D_m$, effective pore diffusivity (cm^2/s)
D_m	molecular diffusivity (cm^2/s)
HETP	height equivalent to a theoretical plate (cm)
k_v	overall mass transfer coefficient (s^{-1})
K	$= [x_1/(1 - x_1)]/[x_u/(1 - x_u)]$, overall separation factor
Pe	$= \nu L/D_L$, Péclet number
St	$= k_v L/\nu$, Stanton number
T	temperature (K)
L	length of the separation zone (cm)

x	atom fraction of heavy nitrogen in the solid phase
y	atom fraction of heavy nitrogen in the liquid phase

Greek Letters

α	$= [x/(1 - x)]/[y/(1 - y)]$, equilibrium separation factor
ϵ'	internal porosity of the resin granule
γ	ratio of the sorbate flow in the solid and fluid phases
γ'	tortuosity factor
ν	liquid velocity (cm/min)

Subscripts

l, u	lower and upper ends of the countercurrent separation column
--------	--

REFERENCES

1. J. G. Tracy and W. S. Aaron, *Nucl. Instrum. Methods Phys. Res.*, A334, 45 (1993).
2. *Stable Isotopes Sales*, Mound Facility Customer and Shipment Summaries, Miamisburg, OH, 1990.
3. *ORNL Isotopes Facilities Shutdown Program Plan*, Oak Ridge, TN, 1990.
4. B. M. Andreev, J. D. Zelvensky, and S. G. Katalnikov, *Physico-Chemical Methods for Stable Isotope Separation*, Energoatomisdat, Moscow, 1982.
5. I. Dostrovsky and M. Epstein, in *Stable Isotopes* (H.-L. Schmidt, H. Forstel, and K. Heinzinger, Eds.), Elsevier, Amsterdam, 1982.
6. R. Knowles and T. H. Blackburn, *Nitrogen Isotope Techniques*, Academic Press, San Diego, 1993.
7. P. W. Rundel, J. R. Ehleringer, and K. A. Nagy, *Stable Isotopes in Ecological Research*, Springer-Verlag, New York, 1989.
8. V. Avona and H. Spicer, *Am. Lab.*, p. 106 (April 1987).
9. N. A. Matwiyoff, in *Isotope and Radiation Techniques in Soil Physics and Irrigation Studies*, IAEA, Vienna, 1974.
10. D. E. Armstrong, B. B. Inteer, T. R. Mills, and J. G. Montoga, in *Stable Isotopes: Proceedings of the Third International Conference* (E. R. Klein and P. D. Klein, Eds.), Academic Press, New York, 1979.
11. E. Crell, in *Stable Isotopes in the Life Sciences, Proceedings of the Technical Committee Meeting*, IAEA, Vienna, 1977.
12. F. H. Spedding, J. E. Powell, and H. J. Svec, *J. Am. Chem. Soc.*, 77, 6125 (1955).
13. N. Tanaka, A. Yamaguchi, and M. Araki, *Ibid.*, 107, 7781 (1985).
14. S. Fujine, *Sep. Sci. Technol.*, 17, 1049 (1982).
15. M. Aida, Y. Fujii, and M. Okamoto, *Ibid.*, 21, 643 (1986).
16. W. K. Park and E. D. Michaels, *Proceedings of the International Symposium on Isotope Separation and Chemical Exchange for Uranium Enrichment*, Tokyo, Japan, October–November 1990.
17. H. London, *Separation of Isotopes*, Newnes, London, 1961.
18. D. B. Broughton and S. A. Gembicki, in *Fundamentals of Adsorption* (A. L. Myers and G. Belfort, Eds.), Engineering Foundation, New York, 1984.
19. D. M. Ruthven and C. B. Ching, *Chem. Eng. Sci.*, 44, 1011 (1989).

20. S. C. Stinson, *Chem. Eng. News*, p. 38 (September 1994).
21. B. M. Andreev, A. V. Kruglov, and Y. L. Selivanenlo, *Sep. Sci. Technol.*, **30**, 3211 (1995).
22. W. K. Park, E. D. Michaels, and C. P. Carroll, *Ibid.*, **25**, 1909 (1990).
23. D. M. Ruthven, *Can. J. Chem. Eng.*, **61**, 881 (1983).
24. O. Levenspiel, *Chemical Reaction Engineering*, Wiley, New York, 1962.
25. E. Glueckauf and J. L. Coates, *J. Chem. Soc.*, p. 1308 (1947).
26. J. B. Butt, *Reaction Kinetics and Reaction Design*, Prentice-Hall, Engelwood Cliffs, NJ, 1980.
27. T. Oi, N. Morioka, H. Ogino, H. Kakihana, and M. Hosoe, *Sep. Sci. Technol.*, **28**, 1971 (1993).
28. T. Oi, H. Ogino, M. Hosoe, and H. Kakihana, *Ibid.*, **27**, 631 (1992).
29. T. Oi, A. Kondoh, and E. Ohno, *J. Phys. Sci.*, **48**, 811 (1993).
30. T. Oi and H. Kakihana, *Proceedings of the International Symposium on Isotope Separation and Chemical Exchange for Uranium Enrichment*, Tokyo, Japan, October–November 1990.
31. A. K. Najjar, M. F. Orayth, and S. I. Nikitenko, *Polyhedron*, **12**, 791 (1993).
32. H. Huang, C.-C. Hsiang, S.-C. Lee, and G. Ting, *Proceedings of the International Symposium on Isotope Separation and Chemical Exchange for Uranium Enrichment*, Tokyo, Japan, October–November 1990.

Received by editor May 30, 1995