J Math Chem (2014) 52:115–131
DOI 10.1007/s10910-013-0248-2

ORIGINAL PAPER

Modeling the (^{15}N) isotope separation column

Eva-Henrietta Dulf · **Cristina I. Muresan** ·
Mihaela L. Unguresan

Received: 1 May 2013 / Accepted: 16 August 2013 / Published online: 28 August 2013

Abstract The chemical processes developed in the ^{15}N-isotope separation plant are very complex and many details are not yet known in totality. Accurate models for such isotope separation plants offer an invaluable insight towards optimizing the production and establishing an adequate control action. A model of such an isotope plant is presented in the paper. The results are validated by simulation, based on a lot of experiments. The model is then used to evaluate and establish the necessary conditions for a maximum production for an existing pilot plant. For protection purposes, the experimental data used in this paper have been scaled.

Keywords Isotope separation column · Mathematical modeling · Nitrogen separation

1 Introduction

In scientific research or industrial applications, the stable isotopes O (oxygen), N (nitrogen), C (carbon), etc are widely used [1–5]. In natural conditions, the ratio of concentration of the nitrogen ^{14}N/^{15}N is: 99.635/0.365 (%). In specific applications a greater "abundance" of the isotope (^{15}N) is required, if possible up to 99.9 (%).

E.-H. Dulf · C. I. Muresan (✉)
Department of Automatic Control, Technical University of Cluj-Napoca,
Memorandumului Street, No. 28, Cluj-Napoca, Romania
e-mail: cristina.pop@aut.utcluj.ro

E.-H. Dulf
e-mail: Eva.Dulf@aut.utcluj.ro

M. L. Unguresan
Department of Chemistry, Technical University of Cluj-Napoca,
Memorandumului Street, No. 28, Cluj-Napoca, Romania

More methods to separate the (^{15}N) isotope are known, both on a laboratory scale and on large scale production. The present paper studies the method invented by Spindel and Taylor about 1955 [6–8], which is based on the “chemical exchange” [9] between liquid phase of nitric acid and gaseous phase of monoxide and dioxide of nitrogen [10]:

$$\begin{cases} N^{15}O + HN^{14}O_3 \rightleftarrows N^{14}O + HN^{15}O_3 \\ N^{15}O_2 + HN^{14}O_3 \rightleftarrows N^{14}O + HN^{15}O_3 \end{cases} \tag{1}$$

The paper presents a Babkov model of the nitrogen separation process based on chemical exchange. The model is validated based on experimental data and further used to compute the required settings for maximum production for a pilot plant built at the National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania (http://www.itim-cj.ro/en/index.php).

The paper is structured as follows. The first section presents the Babkov model of nitrogen separation columns, with and without extraction. The equations necessary to evaluate the production potential of such columns are further presented, followed by some subsections that validate through experimental data the steady state and transient regime model derived previously. The next section presents the application example: a pilot plant nitrogen isotope separation column. The model presented in the previous section is used here to compute the production potential of this pilot plant. The authors show that under some given conditions a maximum production may be achieved.

2 The Babkov model of the column

A mathematical model for the isotope separation column has been proposed by Babkov [11], being validated for the separation of (^{15}N) through chemical exchange during the experiments performed by Monse and Spindel [12] or by Pompidor [13,14]. The model presented in this paper is derived based on Babkov approach and validated using experimental data.

The isotope separation coefficient $\propto$ in steady state conditions for the kth plate:

$$\alpha = \frac{\frac{\bar{x}_k}{1-\bar{x}_k}}{\frac{(N^{15})G_k}{1-(N^{15})G_k}}, \tag{2}$$

with $\left(^{15}N\right) G_k = \frac{\bar{x}_k}{\alpha - \bar{x}_k(\alpha - 1)}$, where x_k is the ^{15}N isotope concentration in the liquid phase on column plate k, $\bar{x}_k$ is the maximum ^{15}N isotope concentration in the liquid phase on column plate k obtained at steady state and total reflux, $\left(^{15}N\right) G_k$ is the ^{15}N isotope concentration in the gaseous phase coming out of plate k.

Throughout the paper the following notations will be used: S_p—the isotope enriching defined by $S_p = \frac{x_p}{x_0}$, $\overline{S}_p$—the isotope enriching defined by $\overline{S}_p = \frac{\bar{x}_p}{\bar{x}_0}$, $\overline{S}_E$—the enriching corresponding to an extraction E, p—the number of theoretical plates in the

Table 1 Validation of Eq. (5)

P (atom/h)	$\overline{S}_p = \alpha^p$	$\overline{S}_p = \frac{\overline{x}_p}{\overline{x}_0}$	$\overline{x}_p = \alpha^p x_0$	$\overline{x}_p$
	Eq. (5)	Eq. (4)	Eq. (5)	Eq. (4)
10	1.63	1.63	0.0060	0.0060
20	2.65	2.64	0.0098	0.0098
30	4.32	4.27	0.0160	0.0158
40	7.04	6.89	0.0260	0.0255
50	11.5	11.0	0.0424	0.0408
60	18.7	17.5	0.0691	0.0649
70	30.4	27.4	0.1126	0.1015
80	49.6	42.0	0.1834	0.1554
90	80.7	62.3	0.2987	0.2307
100	131.5	88.7	0.4866	0.3281

column, L—the feed flow into the column, X—volumetric feed flow into the column, V_0—the number of isotope atoms in the liquid phase of concentration x_p hold up in the plant outside the separation column.

The equilibrium condition in steady state on the kth plate is given by:

$$L \cdot \overline{x}_{k-1} = L \cdot \left({}^{15}N\right) G_k = L \cdot \frac{\overline{x}_k}{\alpha - \overline{x}_k(\alpha - 1)}. \tag{3}$$

Considering that $\left({}^{15}N\right) G_k = \overline{x}_{k-1}$ [11], the following relation is obtained:

$$\overline{x}_k = \frac{\alpha\, \overline{x}_{k-1}}{1 + (\alpha - 1)\, \overline{x}_{k-1}}. \tag{4}$$

For a reduced ^{15}N concentration, the denominator of (4) may be approximated as $1 + (\alpha - 1)\overline{x}_{k-1} \cong 1$, and (4) is reduced to $\overline{x}_k = \alpha\, \overline{x}_{k-1}$, leading:

$$\overline{x}_1 = \alpha\, x_0 \quad \text{and} \quad \overline{x}_k = \alpha^k x_0. \tag{5}$$

The concentration x_p is thus computed using Eqs. (4) and (5). To validate this first mathematical modeling step, the values obtained for x_p are compared with the experimental data [11] given in Table 1.

The comparative results in Table 1 show that the valid region for Eq. (5) is limited to ^{15}N concentrations below 6 %.

Further assumptions are considered in the modeling phase, such as [11]: the isotope separation coefficient is $\alpha = 1.055$, throughout the entire column length, the gaseous nitrogen hold-up is negligible compared to the liquid hold-up, the nitrogen atoms hold-up on plate H_0 is the same on all plates of the column, the relative concentration $R_k = \frac{x_k}{1-x_k}$ remains the same on all plates.

For concentrations $x_k \ll 1$ and $R_k \approx x_k$, the following relation holds:

$$\frac{x_1 - x_0}{\overline{x}_1 - x_0} = \frac{x_k - x_0}{\overline{x}_k - x_0} = \frac{x_p - x_0}{\overline{x}_p - x_0}. \tag{6}$$

Equation (2) holds also during transient regime:

$$\left({}^{15}N\right) G_k = \frac{x_k}{\alpha - x_k(\alpha - 1)}. \tag{7}$$

In what follows the assumption that the relative concentration remains the same on all plates is modified, considering that Eq. (6) holds for all values of x_0.

The equilibrium relation for ^{15}N as shown in Fig. 1 is written as:

$$L \cdot dt \cdot x_0 - L \cdot dt \cdot \frac{x_1}{\alpha - x_1(\alpha - 1)} = H_0 dx_1 + \cdots + H_0 dx_k + \cdots + H_0 dx_p + V_0 dx_p. \tag{8}$$

For a column with total reflux the term:

$$P_0 = L \cdot x_0 - L \frac{x_1}{\alpha - x_1(\alpha - 1)}, \tag{9}$$

represents the ^{15}N quantity retained in the column on a time unit, namely the total reflux "production". The ^{15}N accumulated in a time unit dt is given by:

$$dM = H_0 dx_1 + \cdots + H_0 dx_k + \cdots + H_0 dx_p + V_0 dx_p. \tag{10}$$

Considering also that the relative concentration remains the same on all plates, the ^{15}N quantity may be expressed as a function of a sole parameter. Using:

$$\frac{x_k - x_0}{\overline{x}_k - x_0} = \frac{x_1 - x_0}{\overline{x}_1 - x_0}, \tag{11}$$

the following relation is obtained:

$$dx_i = \frac{x_k - x_0}{\overline{x}_k - x_0} dx_1 = K_1 dx_1, \tag{12}$$

and the sum dM in (10) may be written as:

$$dM = \sum_{i=1}^{p} \left(H_0 K_i + V_0 K_p\right) dx_i = U_1 dx_1. \tag{13}$$

The term U_1 may be explicitly computed only for small concentrations of ^{15}N, otherwise only a numeric approach may be performed.

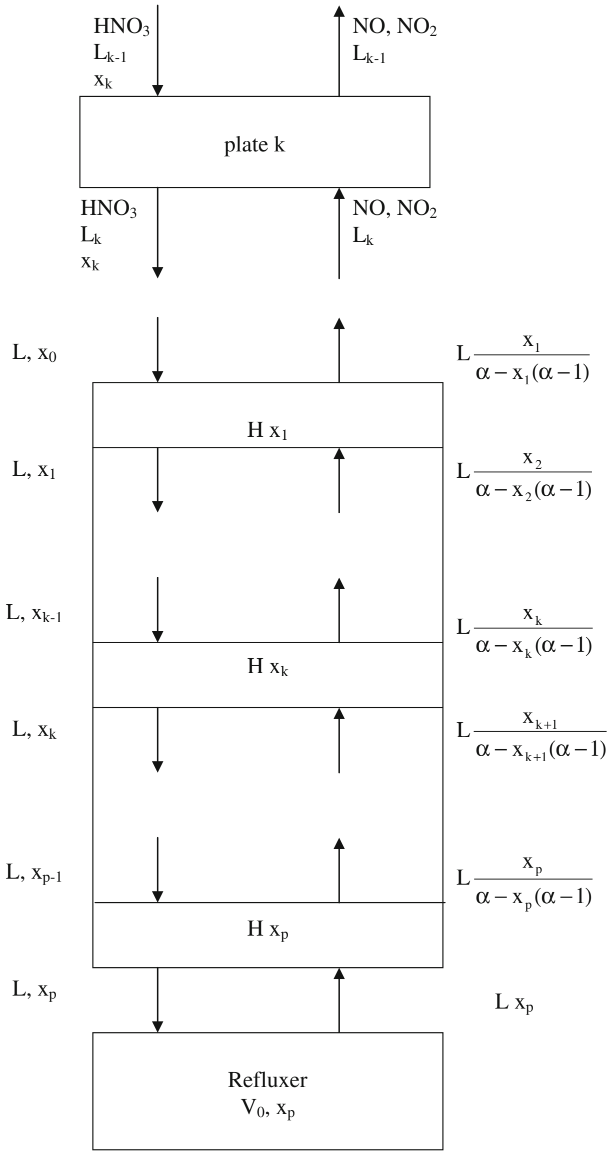

Fig. 1 Flows and concentration on the ^{15}N column, without extraction

Since the column is fed with nitric acid of a natural concentration of $^{15}x_0 = 0,365\,\%$, then we have the following $\alpha - x_1(\alpha - 1) \approx \alpha$ and $\bar{x}_1 = \alpha\, x_0.\bar{x}_1$. Thus, Eq. (8) may be rewritten as:

$$\left(Lx_0 - \frac{x_1 L}{\alpha}\right) dt = \left(H_0 \sum_{i=1}^{p} K_i + V_0 K_p\right) dx_1 = U_1 dx_1 \text{ or}$$

$$d\left[\log\left(Lx_0-\frac{x_1L}{\alpha}\right)\right]=-\frac{L}{U_1\,\alpha}dt. \tag{14}$$

The initial conditions $x_i = x_0$ at t = 0 lead to the following equation:

$$x_1 = x_0\left[\alpha-(\alpha-1)\exp\left(-\frac{L}{U_1\,\alpha}t\right)\right]. \tag{15}$$

Relation (6) leads to:

$$\frac{x_1}{x_0}=1+\left(\frac{x_p}{x_0}-1\right)\cdot\frac{\overline{x}_1-x_0}{\overline{x}_p-x_0}.$$

Taking into account that $x_1 = \alpha$ and $S_p = \frac{x_p}{x_0}$, the following relation is obtained:

$$S_p-1=(\overline{S}_p-1)\left[1-\exp\left(-\frac{t}{T}\right)\right], \tag{16}$$

where $T = \frac{U_1\,\alpha}{L}$ is the time constant for column start-up at total reflux. Using the approximation for small ^{15}N concentrations, leads to:

$$\begin{aligned}
x_i &= \alpha^i\cdot x_0\\
K_i &= \frac{\alpha^i-1}{\alpha-1}\\
U_1 &= H_0\sum_{i=1}^{p}\left(K_i+V_0K_p\right)=H_0\left(\frac{\alpha-1}{\alpha-1}+\frac{\alpha^2-1}{\alpha-1}+\ldots+\frac{\alpha^i-1}{\alpha-1}+\ldots+\frac{\alpha^p-1}{\alpha-1}\right.\\
&\quad\left.+V_0\frac{\alpha^p-1}{\alpha-1}\right)=\frac{1}{\alpha-1}\cdot H_0(\alpha+\alpha^2+\cdots+\alpha^i+\cdots+\alpha^p-p)+V_0\frac{\alpha^p-1}{\alpha-1}.
\end{aligned}$$

Considering also that:

$$(1+\alpha+\alpha^2+\ldots+\alpha^i+\cdots+\alpha^p)=\frac{1-\alpha^{p+1}}{1-\alpha},$$

the relations for U_1 and T may be written as:

$$U_1=\frac{1}{\alpha-1}\cdot\left[(\alpha^p-1)\left(H_0\frac{\alpha}{\alpha-1}+V_0\right)-p\cdot H_0\right] \tag{17}$$

$$T=\frac{\alpha}{(\alpha-1)\,L}\cdot\left[(\alpha^p-1)\left(H_0\frac{\alpha}{\alpha-1}+V_0\right)-p\cdot H_0\right]. \tag{18}$$

with T being equal to K(α) established by Pompidor [13].

From a control engineering point of view, the isotope separation column behaves as a first order system having the initial values $S_p = 1$ at t = 0 and asymptote $S_p = \overline{S}_p$ for $t = \infty$, with the time constant $T = \frac{U_1\,\alpha}{L}$.

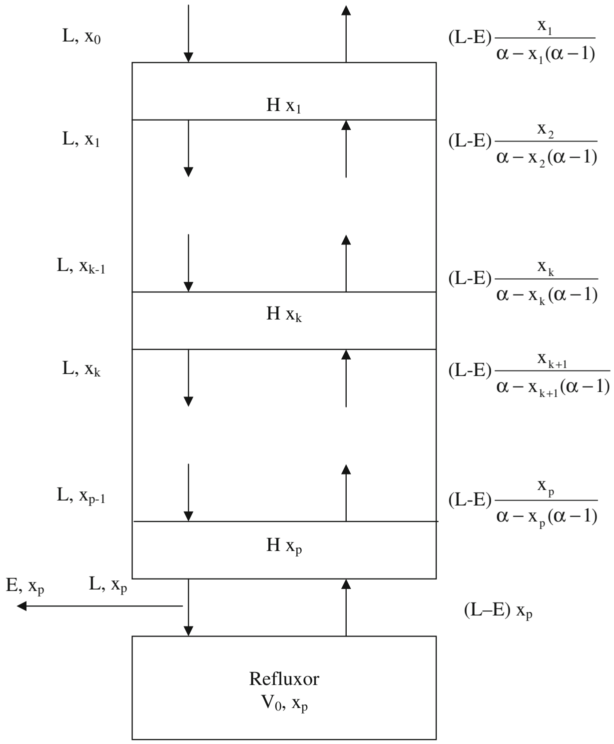

Fig. 2 Flows and concentration on the ^{15}N column, with constant extraction

2.1 Mathematical model for column start-up with extraction

In what follows, the assumption of Babkov for steady state relations is considered to hold for a column operating under constant extraction E (^{15}N atom/h).

The equilibrium relation for ^{15}N, based on Fig. 2, is given by:

$$\left[Lx_0 - (L-E)\frac{x_1}{\alpha - x_1(\alpha-1)} - E\,x_p\right]dt = U_1 dx_1. \tag{19}$$

Using the following equations:

$$\alpha - x_1(\alpha-1) \approx \alpha$$
$$x_p = x_0 + (x_1 - x_0)\frac{\overline{x}_p - x_0}{\overline{x}_1 - x_0} = x_0 + (x_1 - x_0)\frac{\overline{S}_p - 1}{\alpha - 1},$$

leads to:

$$(B' - Ax_1)dt = T\,dx_1, \tag{20}$$

in which $A = 1+\frac{E}{L}[\frac{\alpha}{\alpha-1}(\overline{S}_p-1)-1]$, $B' = \{\alpha+\frac{E}{L}[\frac{\alpha}{\alpha-1}(\overline{S}_p-1)-\alpha]\}x_0$, $T = \frac{U_1\alpha}{L}$ and

$$dt = -\frac{T}{A}\, d\log\left(B' - Ax_1\right). \tag{21}$$

Initial conditions refer to: the enrichment $\overline{S}_p$ at the bottom of the column is attained at $t=0$, corresponding to $x = \overline{x}_1$,while the extraction E is constant starting at $t = 0_+$.

Integrating Eq. (21) leads to:

$$T = -\frac{T}{A}\log\frac{B' - Ax_1}{B' - A\overline{x}_1}, \tag{22}$$

or $\exp\left(-\frac{t}{T}A\right) = \frac{\frac{B'}{Ax_0}-\frac{x_1}{x_0}}{\frac{B'}{Ax_0}-\frac{\overline{x}_1}{x_0}}$.

From (6) the following set of relations is obtained:

$$\begin{aligned} x_1 &= x_0 + \left(x_p - x_0\right)\frac{\overline{x}_1 - x_0}{\overline{x}_p - x_0} \\ \frac{x_1}{x_0} &= S_1 = 1 + \left(S_p - 1\right)\frac{\alpha - 1}{\overline{S}_p - 1} \\ \frac{\overline{x}_1}{x_0} &= \overline{S}_1 = 1 + (\overline{S}_p - 1)\frac{\alpha - 1}{\overline{S}_p - 1}. \end{aligned}$$

Replacing $\frac{x_1}{x_0}$ and $\frac{\overline{x}_1}{x_0}$ in the exponential equation given above leads to:

$$\exp\left(-\frac{t}{T}A\right) = \frac{\frac{B'}{Ax_0} - 1 - \left(S_p - 1\right)\frac{\alpha-1}{\overline{S}_p-1}}{\frac{B'}{Ax_0} - 1 - \left(\overline{S}_p - 1\right)\frac{\alpha-1}{\overline{S}_p-1}} = \frac{F\left(\overline{S}_p - 1\right) - \left(S_p - 1\right)}{F\left(\overline{S}_p - 1\right) - \left(\overline{S}_p - 1\right)}, \tag{23}$$

with

$$F = \left(\frac{B'}{Ax_0} - 1\right)\frac{1}{\alpha - 1} = \frac{1 - \frac{E}{L}}{1 + \frac{E}{L}\left[\frac{\alpha}{\alpha-1}\left(\overline{S}_p - 1\right) - 1\right]}. \tag{24}$$

Rearranging (23) yields:

$$\begin{aligned} \left(S_p - 1\right) &= (\overline{S}_p - 1) + \left[F(\overline{S}_p - 1) - (\overline{S}_p - 1)\right]\left[1 - \exp\left(-\frac{t}{T}A\right)\right] \\ &= (\overline{S}_p - 1) + \left[(S_E - 1) - (\overline{S}_p - 1)\right]\left[1 - \exp\left(-\frac{t}{T}A\right)\right]. \end{aligned} \tag{25}$$

For $t=0$, $S_p = \overline{S}_p$, while for $t = \infty$, $S_p \to 1 + F(\overline{S}_p - 1) = \overline{S}_E$. Therefore, $\overline{S}_E$ is the value obtained under constant extraction E.

From a control engineering perspective, the enrichment has a first order system dynamics with an initial value of $\overline{S}_p$, asymptote $\overline{S}_E$, and a time constant $T_S = \frac{T}{A}$, with (T_S) less than (T) since (A) is greater than unity.

The relation:

$$\overline{S}_E = 1 + F(\overline{S}_p - 1) = 1 + \frac{1 - \frac{E}{L}}{1 + \frac{E}{L}\left[\frac{\alpha}{\alpha - 1}\left(\overline{S}_p - 1\right) - 1\right]} \cdot (\overline{S}_p - 1), \tag{26}$$

allows for computation of the steady state enrichment with an extraction E, knowing only the value $\overline{S}_p$ at total reflux.

From (26), we have that:

$$E = L \cdot \frac{\overline{S}_p - \overline{S}_E}{\frac{\alpha}{\alpha - 1}\left(\overline{S}_p - 1\right)\left(\overline{S}_E - 1\right) + \left(\overline{S}_p - \overline{S}_E\right)}, \tag{27}$$

or:

$$\begin{aligned} \frac{\alpha}{\alpha - 1} &= \frac{\left(1 + \frac{E}{L}\right)\left(\overline{S}_p - \overline{S}_E\right)}{\frac{E}{L}\left(\overline{S}_p - 1\right)\left(\overline{S}_E - 1\right)} = C \\ \alpha &= \frac{C}{C - 1}. \end{aligned} \tag{28}$$

Relation (27) allows for the computation of E knowing only the values of $\overline{S}_p$ and $\overline{S}_E$. Relation (28) allows for the computation of α, especially in experiments where the values E, L, $\overline{S}_p$ and $\overline{S}_E$ have already been measured.

2.2 Productive potential of separation columns: with and without extraction

Using Eq. (9), for $E = 0$, the total reflux production may be computed as:

$$P_0 = L \cdot x_0 - L\frac{x_1}{\alpha},$$

and further, using (3), we obtain:

$$x_1 = \frac{\alpha - 1}{\overline{S}_p - 1}\left(x_p - x_0\right) + x_0,$$

yelding:

$$\begin{aligned} P_0 &= L\,x_0 - \frac{L}{\alpha}\frac{\alpha - 1}{\overline{S}_p - 1}x_p + \frac{L}{\alpha}\frac{\alpha - 1}{\overline{S}_p - 1}x_0 - \frac{L}{\alpha}x_0 \\ P_0 &= L\,x_0\frac{\alpha - 1}{\alpha} \cdot \frac{\overline{S}_p - S_p}{\overline{S}_p - 1}. \end{aligned} \tag{29}$$

P_0 is a liniar function of S_p, passing through the points $P_0 = 0$, $S_p = \overline{S}_p$ (plate value) and $P_0 = L\,x_0\frac{\alpha-1}{\alpha}$, $S_p = 1$ (maximum P_0 value, obtained at the begining of the experiment).

The column production in steady state ($E \neq 0$) has the expression:

$$P_S = E \cdot \overline{x}_E = E \cdot \overline{S}_E \cdot x_0.$$

While P_0 represents the (^{15}N) quantity retained during a time slot on a total reflux column during its start-up, P_S represents the (^{15}N) quanitity extracted during a time slot from a column operating at steady state conditions. P_S may be directly computed using Eq. (26):

$$P_S = \overline{S}_E \cdot E \cdot x_0 = \left[1 + \frac{1-\frac{E}{L}}{1+\frac{E}{L}\left[\frac{\alpha}{\alpha-1}\left(\overline{S}_p - 1\right) - 1\right]} \cdot \left(\overline{S}_p - 1\right)\right] \cdot E \cdot x_0 \quad (30)$$

or using Eq. (27):

$$P_S = \overline{S}_E \cdot x_0 \cdot L \cdot \frac{\overline{S}_p - \overline{S}_E}{\frac{\alpha}{\alpha-1}\left(\overline{S}_p - 1\right)\left(\overline{S}_E - 1\right) + \left(\overline{S}_p - \overline{S}_E\right)}. \quad (31)$$

The representative curve of P_S as a function of $\overline{S}_E$ is a hiperbola branch with the limits in the points: $P_S \to 0$ for $\overline{S}_E \to \overline{S}_p$, $P_S \to Lx_0$ for $\overline{S}_E \to 1$.

2.3 Validation of the $\overline{S}_E$ and P_S equations for a column operating in steady state conditions and continuous extraction

Equations (26), (27) and (30) have been verified using the experimental data provided by [15]. The columns have a height of 3 and 4 meters respectively, with 57 % nitric acid feed flows in the range of 3–4 l/h. The nitrogen "quantity" extracted, E, is expressed as: $E = V \cdot a$, where V is the volumetric flow and a is the ^{15}N concentration in the extracted product. The main results obtained for $\overline{S}_E$, $\frac{E}{L}$ and P_S are presented in Figs. 3 and 4.

Experimental relations (26), (27) and (30) are verified with a maximum error of 3–5 %. The figures above—Figs. 3 and 4 show that the experimental data is closely approximated by the mathematical model derived.

2.4 Validation of the mathematical model in transient regime

The transient regime equation corresponds to a first order system, with the most important parameter of the dynamic model represented by the time constant $T = \frac{U_1\alpha}{L}$ and the time constant associated with the column operating under extraction $T_S = \frac{T}{A} = \frac{U_1\alpha}{LA}$.

The validation of the time constants are done using the same experiments of [14]. The initial experimental data are given in Table 2 [14].

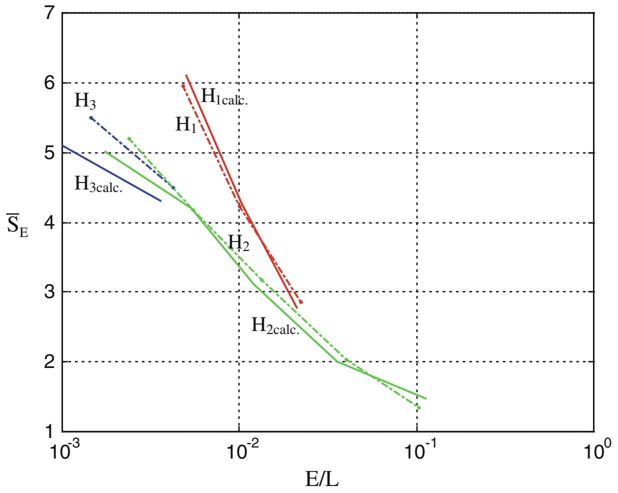

Fig. 3 Results for $\overline{S}_E$ and E/L in steady state with withdraw

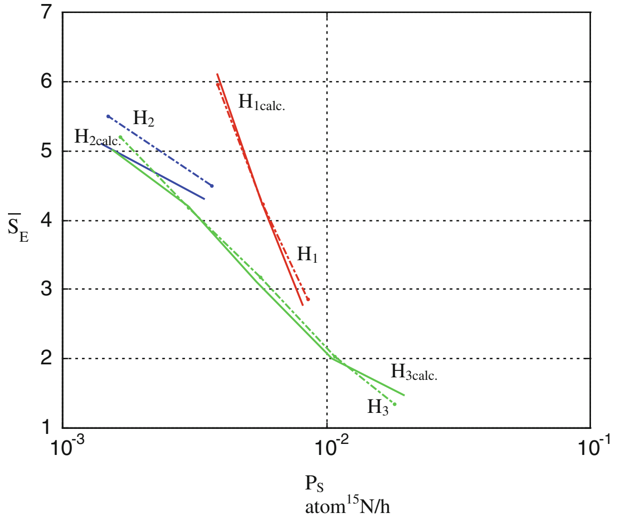

Fig. 4 Results for $\overline{S}_E$ and P_S in steady state with withdraw

The points on the curve $S_P = f(t)$ are computed based on the following data: t_1—the abundancy of the starting plate, t_2—the abundancy of the final plate, T or T_S—the time constants (hours), G—the final response fraction and h_0—the start hour of the experiment. Next, the authors compute:

$$G = \left(1 - e^{-Z}\right)$$

$$Z = \frac{t}{T}$$

Table 2 Initial experimental data

Experiment	H_1			H_3				
Plate concentration: $t \cdot 10^4$	428			228				
Time constant: $T = \frac{U_1 \cdot \alpha}{L}$	14.9			5.3				
$\frac{E}{L}$	0.00478	0.00989	0.022	0.00236	0.00542	0.0133	0.04	0.1024
A	2.01	3.12	5.70	1.24	1.55	2.40	5.10	11.4
$T_S = \frac{T}{A}$	7.41	4.76	2.61	4.24	3.42	2.21	1.04	0.46
Extraction plate: $t_E \cdot 10^4$	220	160	107	193	156	118	74	50
Start hour of the extraction h_0	0–23	52–58	81	43.3	60	76	93.3	105

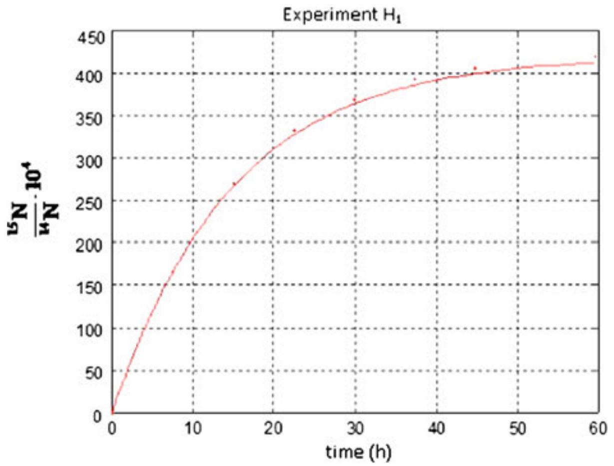

Fig. 5 Model validation in transient regime using experiment H_1

$$h = Z \cdot T$$
$$h = h_0 + \Delta h$$
$$\Delta t = G\,(t_1 - t_2)$$
$$t = t_1 - \Delta t.$$

The calculated curves are presented in Figs. 5 and 6, containing also the corresponding experimental data. The mathematical model described does not take into account the effect of the chemical reaction on the chemical exchange. Due to this, the greatest accuracy of the model was obtained for a reflux gas in equillibrium with the nitric acid in the feed flow. The time constant may serve to predict the column start up with a sufficient accuracy. The required time to reach 98 % enrichment in the final value will be approximately $4T_S$.

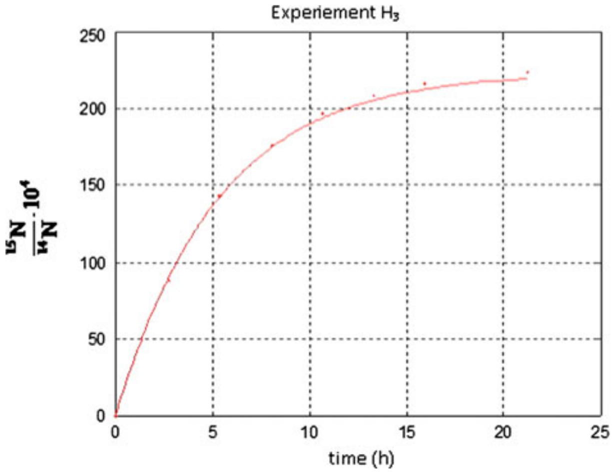

Fig. 6 Model validation in transient regime using experiment H_3

3 Results and discussions: model application to a pilot plant (^{15}N) isotope separation column

The mathematical model derived was further applied to a nitrogen isotope separation process based on NO–HNO_3 exchange, fed with nitirc acid 57 % at 20 °C and a total reduction of the reflux gas.

The simplified scheme of (^{15}N) isotope separation column [1,16,17], of 5 m length and 4 cm diamater, is depicted in Fig. 7 with: N, n—the mole fraction of ^{15}N in liquid and gaseous phase [−]; L, G—specific flow of ^{15}N in the recycled streams in $[\text{moles} \cdot s^{-1} \cdot m^{-2}]$; H_l, H_g—the holdup in $[\text{moles} \cdot m^{-3}]$; T—rate of transfer of ^{15}N-isotope in $[\text{moles} \cdot s^{-1} \cdot m^{-3}]$; K—the transfer rate coefficient $[\text{moles} \cdot s^{-1} \cdot m^{-3}]$; α—the separation factor [−], with $T = -k\,[N\,(1 - n) - \alpha\, n\,(1 - N)]$ $[\text{moles} \cdot s^{-1} \cdot m^{-3}]$.

The enrichment process is governed by the equations [18]:

$$\begin{aligned} H_l \frac{\partial N}{\partial t} + L \frac{\partial N}{\partial z} &= +T \\ H_g \frac{\partial n}{\partial t} + G \frac{\partial n}{\partial z} &= -T. \end{aligned} \tag{32}$$

The isotope exchange is achieved in column, endowed with a special packing [1]. The withdrawal (P) enriched in (^{15}N) isotope is possible at the bottom side of the column. The column is fed with constant nitric acid flow (F), with a natural concentration (0.3654 %) of (^{15}N). In the bottom refluxer (R_1) [19], using sulphur dioxide, the (NO) and (NO_2) are “generated” according to the chemical reaction:

$$\begin{cases} 2HNO_3 + 3SO_2 + 2H_2O = 3H_2SO_4 + 2NO \\ 2HNO_3 + SO_2 \quad = H_2SO_4 + 2NO_2 \end{cases} \tag{33}$$

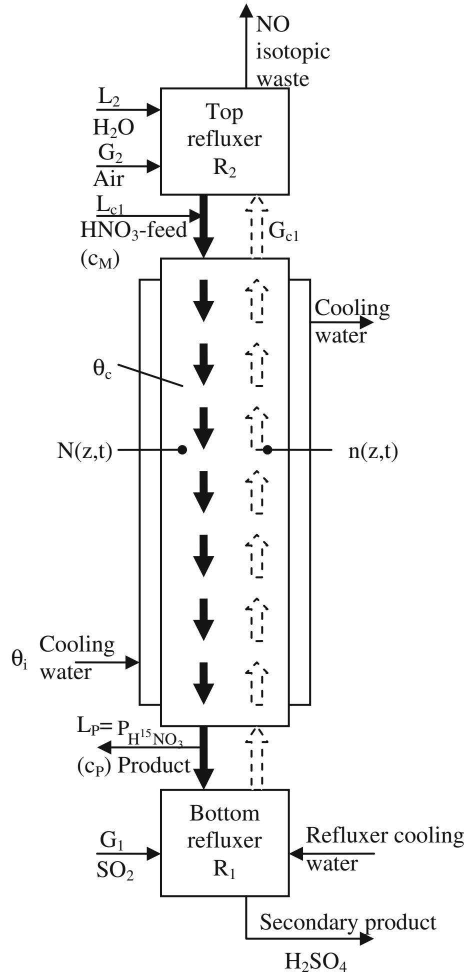

Fig. 7 Simplified arrangement of the ^{15}N-isotope separation plant

The top refluxer (R_2), Fig. 7, provides the reverse phase transformation:

$$\begin{cases} 3NO_2 + H_2O = 2HNO_3 + NO \\ NO + 1/2O_2 = NO_2 \end{cases} \tag{34}$$

while the nitric acid flow is enriched in (^{15}N) isotope.

Based on Eq. (29), different productions according to different feeding streams have been computed. The results, given in Table 3, show that there is a feeding stream that leads to a maximum production for a given enriching. This is due to the fact that a diminishing in the feed flow L causes an increment in the enrichment $\overline{S}_p$.

At column start up, by modifying the feed flow the production can be made maximum and therefore the column start up is in an accelerated fashion. To compute the feed flow variations required for such a start up, a relation between $\overline{S}_p$ and L has to be

Table 3 Total reflux production

Experiment	Feed flow × (l/h)	Molar feed flow L (mol/h)	$\overline{S}_p = \alpha^p$	$P_0 = L\frac{\alpha-1}{\alpha} \cdot x_0 \left[\text{atom}^{15}\text{N/h}\right] \cdot 10^3$
H_1	3.0	24.8	11.35	6.54
H_3	3.0	44.5	5.98	6.54
B_3	2.0	37.1	17.30	4.36
B_2	2.9	51.9	12.20	6.32
B_5	3.6	37.1	6.97	7.84

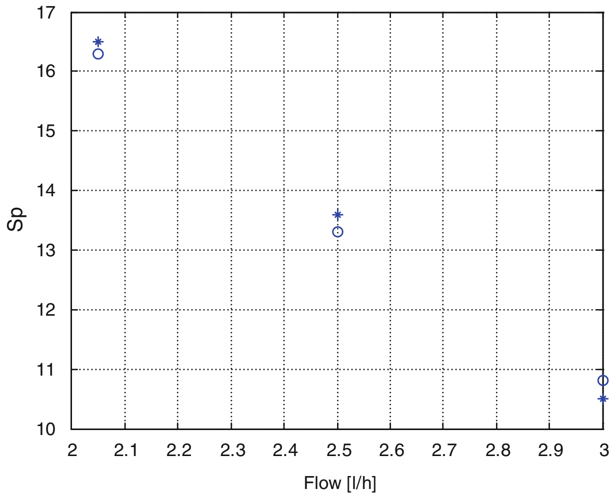

Fig. 8 $\overline{S}_p$ values

derived. Such relation may be given in a logarithmic form:

$$\overline{S}_p = A + B \log \frac{C}{x},$$

with A = 1.3, C = 6 and B varies as a function of the column height.

The following relation holds:

$$\overline{S}_p = 1, 3 + R\,K \log \frac{6}{X}, \tag{35}$$

with X the nitric acid flow (l/h), while RK is a function of the column height. The relation (35) is valid since the $\overline{S}_p = f(X)$ curve has no discontinuities.

Figure 8 presents the $\overline{S}_p$ values corresponding to a 5 m column and for different values of X as given in the B_2, B_3 and B_5 experiments of Koehret [20]. A medium value for RK was computed.

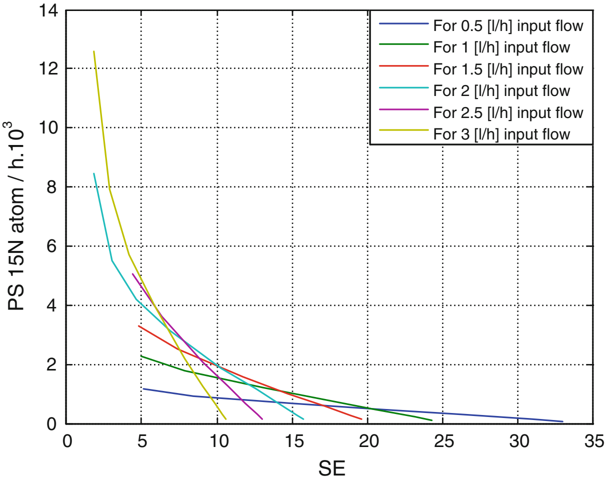

Fig. 9 Computed P_S values

P_S values computed as a function of S_E in Eqs. (26) and (30) with $\frac{E}{L}$ as an intermediate parameter, for different values of the feed flow, are given in Fig. 9. The results show that there is a certain feed flow X that ensures a maximum production for a fixed ^{15}N concentration—S_E. Therefore, a maximum production may be achieved.

4 Conclusions

Accurate models offer the possibility for studying different phenomena and possibilities for optimization of the processes. The enrichment attained may be evaluated using the dynamic models, while the steady state offers extremely useful information for deriving the column operating parameters.

The Babkov model presented in this paper has been firstly validated using various sets of experimental data collected from different nitrogen separation columns. Then, the model has been used to determine the optimum feed flow in order to achieve a maximum production for an existing pilot plant. The results in this paper may be used to increase the production potential of the pilot plant.

References

1. D. Axente, M. Abrudean, A. Baldea, Isotope Separation ^{15}N, ^{18}O, ^{10}B, ^{13}C by isotopic exchange, (in Romanian), (Casa Cartii de Stiinta, Cluj-Napoca, 1994)
2. A. Kohzu, T. Miyajima, I. Tayasu, C. Yoshimizu, F. Hyodo, K. Matsui, T. Nakano, E. Wada, N. Fujita, T. Nagata, Environ. Sci. Technol. **42**, 7837 (2008)
3. A. Montanez, C. Abreu, P. Gill, G. Hardarson, M. Sicardi, Biol. Fertil. Soils **45**, 253 (2009)
4. P. Sarr, M. Khouma, M. Sene, A. Guisse, A. Badlane, T. Yamakawa, Soil. Sci. Plant. Nutr. **54**, 142 (2008)
5. C. Bosshard, P. Sorensen, E. Frossard, D. Dubois, P. Mader, S. Nanzer, A. Oberson, Nutr. Cycl. Agroecosyst. **83**, 271 (2009)
6. W. Spindel, T.I. Taylor, J. Chem. Phys. **23**, 981 (1955)

7. W. Spindel, T.I. Taylor, J. Chem. Phys. **24**, 626 (1956)
8. L.N. Kauder, T.I. Taylor, W. Spindel, J. Chem. Phys. **41**, 232 (1959)
9. T. Ishida, Y. Ono, J. Nucl. Sci. Technol. **43**, 391 (2006)
10. X.C. Ding, T. Kaneshiki, M. Arima, M. Nomura, T. Suzuki, Y. Fujii, Prog. Nucl. Energ. **50**, 504 (2008)
11. S.I. Babkov, N.M. Zavoronkov, G.N. Cernych, L.V. Strelcov, Kernenergie **5**, 219 (1962)
12. E.U. Monse, W. Spindel, L.N. Kauder, T.I. Taylor, J. Chem. Phys. **32**, 1557 (1962)
13. G. Pompidor, G. Etude, des périodes transitoires de mise en regime des colonnes de separation isotopique (PhD Thesis, Toulouse, 1967)
14. J. Mahenc, G. Pompidor, Chim. et Ind. Génie chimique **99**, 1137 (1968)
15. G. Guernier, Action de la témperature et étude de l' influence de soutirages sur les performances d' une colonne d' enrichissemnt isotopique (PhD Thesis, Toulouse, 1969)
16. E.H. Dulf, Cl. Festila, About the Mathematical Modeling and Simulation of the (^{15}N) Isotope Separation Column, Proceedings of the 15th International Conference CSCS-15, Bucharest, Romania (2005)
17. E.H. Dulf, Cl. Festila, (^{15}N) Isotope separation column: simplified model for control and simulation, in *Proceedings of SINTES 12 The International Symposium on System Theory, Automation, Robotics, Computers, Informatics, Electronics and Instrumentation, Craiova, Romania* (2005)
18. K. Cohen, The theory of isotope separation as applied to the large-scale production of U^{235}. (McGraw-Hill Book, New York, 1951)
19. D. Axente, M. Abrudean, A. Baldea, J. Radioanal. Nucl. Chem. **207**, 163 (1996)
20. B. Koehret, Etude sistematique de l" influence des parametres hidrodinamique et geometrigue sur les performances des colonnes de separation isotopique. (PhD Thesis, Touluse, 1969)