

# <sup>15</sup>N ISOTOPE SEPARATION COLUMN: SIMPLIFIED MODEL FOR CONTROL AND SIMULATION

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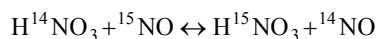
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**Abstract:** The chemical processes developed in the <sup>15</sup>N-isotope separation plant are very complex and many details are not yet known in totality. The authors are concerned with the problem of developing effective and readily implemental techniques for modelling and control of the isotope separation plant. In the present paper are selected the main variables. The main connections between input and output variables and between input variables and the parameters are presented in equation which the enrichment process is governed by. Based on a lot of experiments, the results are validated by simulation.

**Keywords:** <sup>15</sup>N-isotope separation column, lumped parameter models, simulation.

## 1. INTRODUCTION

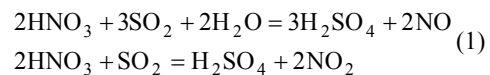
The general aim of control system is to keep the controlled plant at a desired level, reducing the effects of the external disturbances. If the „controlled plant” is a column for the <sup>15</sup>N-isotope separation using the principle of the „chemical exchange” (Axente, 1994), in accord to the reaction:



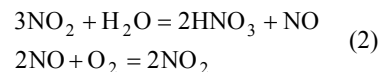
there will be always a slightly greater proportion (concentration) of the <sup>15</sup>N isotope in the nitric acid than in the nitric oxide (with a ratio about 1.055). The oxide and the acid are contacted in a counter current arrangement in a vertical packed separation column, so that a “horizontal” transport of the <sup>15</sup>N-isotop in the direction of the acid will arise. In order to increase this “enrichment” process, the nitric acid feeding on the top side of the column (and flowing to the bottom of the column) is converted in oxides of nitrogen, which is a gas ascending in the column. In the top of the column, in reaction with water, the oxides are partially re-converted in nitric acid, which flows to the base of the column and so, there will be

a natural tendency for the <sup>15</sup>N-isotope to concentrate at the bottom end of the column.

The conversion acid → oxides is effected in the bottom refluxer, following the reactions of the nitric acid with sulfur dioxide (with a very small loss of material):



The sulfur acid is a secondary product, used in industry. In the top-refluxer, the gaseous mixture of nitric oxide and nitrogen dioxide, with air and water, produces nitric acid:



The output of the separation plant is the isotopic product in its qualitative (concentration) and quantitative (amount) properties of the product. The main inputs are: *the amount (flow rates)* of the substances and of the compounds supplying the plant and *the energy* exchanged by the plant.

The quality of the isotopic product is analyzed using a dedicated mass-spectrometer, but a closed-loop, including the spectrometer, leads to a very complex theoretical analysis and it is difficult and ineffective to implement. (Kaucsar, 2001). Therefore multiple local control loops must be applied for each “important” variable. Of course, between these variables there are complex interdependences.

To operate the separation plant according to the design performance, it is necessary to maintain the temperatures, flows, etc. “near” their design values in order to ensure that material not accumulate in (flooding) or drain out of any part of the plant. It is also useful to analyze the effects of the fluctuation of the variables from the average in order to avoid the difficulty of the transport of material from stage to stage or the mixing of material of different concentration from different stages and the diminution of the separating power of the plant.

## 2. EVOLUTION OF THE SEPARATION PROCESS IN THE CASCADE

In the column are contacted a liquid phase: nitric acid and a gas: oxides of nitrogen. The phase in which  $^{15}\text{N}$ -isotopic enrichment is desired (acid) will be marked by capital letters and the other phase, by small letters (Axente, 1994; Cohen, 1951). The direction of the enriched phase is taken as positive and the length along the column will be measured in this direction. On define (Cohen, 1951):

$N, n$  – the mole fraction of  $^{15}\text{N}$  in liquid and gas phase [ - ];

$L, G$  – specific flow of  $^{15}\text{N}$  in the recycled streams in [ $\text{moles}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ ];

$H_l, H_g$  – the holdup in [ $\text{moles}\cdot\text{m}^{-3}$ ];

$T$  – rate of transfer of  $^{15}\text{N}$ -isotope in [ $\text{moles}\cdot\text{s}^{-1}\cdot\text{m}^{-3}$ ];

$K$  – the transfer rate coefficient [ $\text{moles}\cdot\text{s}^{-1}\cdot\text{m}^{-3}$ ];

$\alpha$  – the separation factor [ - ],

with

$$T = -k[N(1-n) - \alpha n(1-N)] \quad (3)$$

[ $\text{moles}\cdot\text{s}^{-1}\cdot\text{m}^{-3}$ ].

The enrichment process is governed by the equations (Cohen, 1951):

$$\begin{aligned} H_l \frac{\partial N}{\partial t} + L \frac{\partial N}{\partial z} &= +T \\ H_g \frac{\partial n}{\partial t} + G \frac{\partial n}{\partial z} &= -T \end{aligned} \quad (4)$$

The steady-state is achieved when all the parameters are constant. In this state, for the main variables, the following assumptions are valid:

- the flow-rate and the concentration of the column feeding nitric acid are constant;
- the temperature in the column is constant;

- the product rate flow is small;
- the ratio of the water/acid rate flow ( $r_{w/a}$ ) is constant (in the top refluxer  $R_2$ );
- the height ( $h_i$ ) of the exothermal chemical reaction (Kaucsar, 2001) (in the bottom refluxer  $R_1$ ) is maintained at a given “optimal” level;
- the flow rate of the sulfur dioxide is constant.

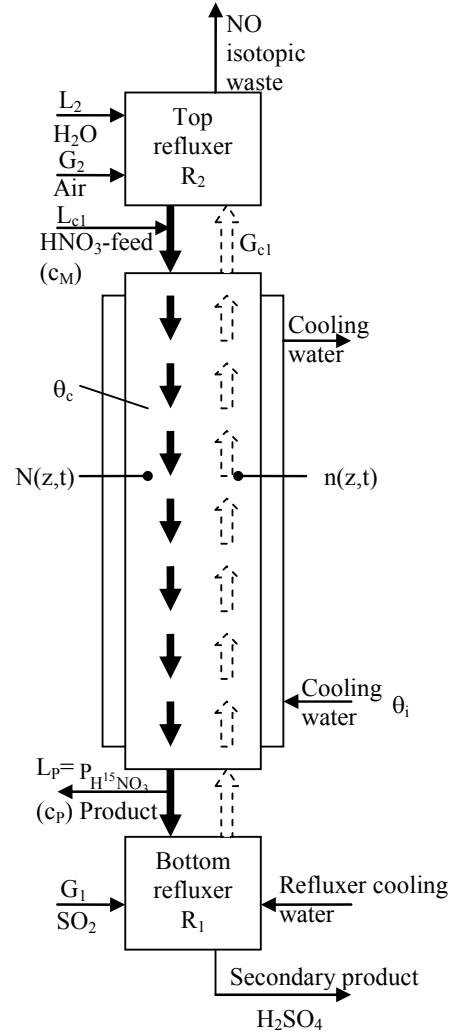


Figure 1. Simplified arrangement of the  $^{15}\text{N}$ -isotope separation plant

Based on the data related in literature (Axente, 2001), the authors are searching for the main connections between input and output variables and between input variables and the parameters in equation (4).

The main input variables, given in figure 1, are:

- rate-flow ( $L_{c1}$ ) of the nitric acid with the mole ratio ( $c_M$ );
- rate-flow ( $L_{c2}$ ) of the water, or the ratio

$$r_{w/a} = \frac{L_{c2}}{L_{c1}} \quad (5)$$

- temperature of the cooling water ( $\theta_i$ );
- rate-flow of the sulfur dioxide ( $G_1$ );
- rate-flow of the end-product (P) with the mole-fraction ( $c_p$ ).

The “direct” output variables are:

- the middle temperatures in the column ( $\theta_c$ );
- the “position” of the reaction zone in the bottom-refluxer ( $h_h$ );
- the evolution of the mole-fractions (N, n) of  $^{15}\text{N}$  in recycled streams (liquid and gas).

The “indirect” outputs are the values of the parameters:

- ( $\alpha$ ) = separation factor
- and ( $k$ ) = transfer rate coefficient.

### 2.1. The thermal systems

In controlling the  $^{15}\text{N}$  isotope separation process, the temperature ( $\theta_c$ ) of the separation column is one important variable. Thus, the temperature ( $\theta_c$ ) must be maintained at a constant level using a classical “jacket” system (Papadache, 1971).

In a simplified analysis, the temperature is controlled by the temperature ( $\theta_i$ ) of the cooling (in some cases heating) water, but it is also influenced by the temperature in the bottom refluxer ( $R_1$ ), temperature dependent on the flow-rate of the sulfur dioxide ( $G_1$ ). The external temperature ( $\theta_{ext}$ ) acts as a disturbance.

If ( $T_{\theta_j}$ ), ( $T_{\theta_c}$ ) are the time-constants of the material in jacket respectively in column (Papadache, 1971), the thermal behavior of the column is described by the equation:

$$\begin{aligned} \theta_c(s) \cong & \frac{K_{\theta 1} \cdot e^{-s\tau_{m1}}}{(T_{\theta c} s + 1)(T_{\theta j} s + 1)} \cdot \theta_i(s) + \\ & + \frac{K_{\theta g} \cdot e^{-s\tau_{mg}}}{(T_{\theta c} s + 1)} \cdot G_1(s) - \frac{K_{\theta d}}{(T_{\theta d} s + 1)} \cdot \Delta\theta_{ext}(s) \end{aligned} \quad (6)$$

The values of the parameters in equation (6) can be calculated using both analytical and experimental identification (Papadache, 1971).

In the bottom refluxer ( $R_1$ ), the exothermal chemical reaction is developed in a certain zone, which must be maintained at a given “optimal” height. This is localized by measuring the temperature gradient along the refluxer (Kaucsar, 2001; Axente, 2001). The height of the “thermal zone” ( $h_h$ ) is a function of the nitric acid and water flow, but the most effective factor is the sulfur dioxide rate flow ( $G_1$ ).

For the transfer function

$$H_{\theta 2}(s) = \frac{h_h(s)}{G_1(s)} \quad (7)$$

the authors propose the “general equation for thermal processes” (Papadache, 1971):

$$H_{\theta 2}(s) \cong \frac{K_{\theta 2} \cdot e^{-s\tau_{mR}}}{T_{\theta R} s + 1} \quad (8)$$

### 2.2. The evolution of the main parameters

The significant parameters in the  $^{15}\text{N}$ -isotope separation analysis are the separation factor ( $\alpha$ ) and the transfer rate coefficient ( $k$ ).

The detailed analysis is very complex. The authors simplified the problem with a linear approximation for an operating point ( $\alpha = \alpha_N = \text{rated value}$ ).

Based on the data from (Axente, 2001), the “observed values” of ( $\alpha$ ) are given for different temperature ( $\theta_c$ ) in the column and for different mole-fractions of the nitric acid (6.9M – 11.8M). The linear approximation proposed by authors, in the steady-state is:

$$\alpha(\theta_c, c_M) = \alpha_N + k_{\theta}(\theta_c - \theta_c^*) + k_c(c_M - c_M^*) \quad (9)$$

where ( $\theta_c^*$ ) and ( $c_M^*$ ) are the set-points (references) for temperature and mole-fraction. The previous equation can be written as:

$$\Delta\alpha(\theta_c, c_M) = \alpha_N + k_{\theta} \cdot \Delta\theta_c + k_c \cdot \Delta c_M \quad (9')$$

The particular values ( $\alpha_N$ ,  $k_{\theta}$ ,  $k_c$ ) are calculated using (Axente, 1994).

In accord to equation (1), the chemical reaction between nitric acid and sulfur dioxide (refluxer  $R_1$ ) generate nitric oxide (NO) and nitrogen dioxide. The ratio between oxide and dioxide concentrations in the gaseous mixture depends on the water flow-rate in the refluxer. The increase of nitric oxide concentration leads to the increase of the (overall single stage) separation factor ( $\alpha$ ) (Axente, 2001), while the nitrogen dioxide concentration diminution under a certain value (Axente, 2001) diminishes the chemical exchange rate (T) in the separation column. Based on the experimental data from (Axente, 2001), results a smaller variation of the separation factor ( $\alpha$ ) as function of the water-acid rate flow ratio ( $r_{w/a}$ ). More significant is the change of the exchange rate (T), or, in particular, of the coefficient ( $k$ ) of the transfer rate. Also, the authors propose the linear approximation like:

$$k = k_N^* \left[ 1 + \beta_k (r_{w/o} - r_{w/o}^*) \right]$$

or

$$\Delta k = k_N^* (1 + \beta_k \cdot \Delta r_{w/o}) \quad (10)$$

The particular values for ( $k_N^*$ ;  $\beta_k$ ;  $r_{w/o}^*$ ) were calculated using (Axente, 1994; Axente, 2001).

Following the previous equations, the transfer matrix of the *simplified* separation plant is:

$$\begin{aligned} \begin{matrix} \theta_c \\ h_h \\ \Delta\alpha \\ \Delta k \end{matrix} &= \begin{vmatrix} \frac{K_{\theta 1} \cdot e^{-s\tau_{m1}}}{(T_{\theta c} s + 1)(T_{\theta j} s + 1)} & \frac{K_{\theta g} \cdot e^{-s\tau_{mg}}}{T_{\theta c} s + 1} & 0 & 0 \\ 0 & \frac{K_{\theta 2} \cdot e^{-s\tau_{m2}}}{T_{\theta R} s + 1} & 0 & 0 \\ \frac{k_{\theta} \cdot K_{\theta 1} \cdot e^{-s\tau_{m1}}}{(T_{\theta c} s + 1)(T_{\theta j} s + 1)} & 0 & \frac{k_c}{T_{\alpha} s + 1} & 0 \\ 0 & 0 & 0 & \frac{\beta_k}{T_{\beta} s + 1} \end{vmatrix} \\ \begin{matrix} \theta_i \\ G_1 \\ \Delta c_M \\ \Delta r_{w/a} \end{matrix} &+ \begin{vmatrix} -K_{\theta d} e^{-s\tau_{md}} \\ T_{\theta d} s + 1 \\ 0 \\ 0 \\ 0 \end{vmatrix} \cdot \begin{vmatrix} d \\ 0 \\ 0 \\ 0 \end{vmatrix} \end{aligned} \quad (11)$$

Now, with the parameter given by the equations (9), (10), the authors analyzed the evolution of the  $^{15}\text{N}$ -isotope enrichment in the nitric acid.

### 3. SIMULATION RESULTS

Using the previous equations and the results reported in (Dulf, 2005), a great number of simulation were possible, for realistic or hypothetic situations. From these, a number of four experiences are presented in the following. The first two consider the time evolution and the enrichment ( $N_z/N_0$ ) is considered on the bottom (based) of the column. Figure 2 gives the evolution of the enrichment ratio for a change of the column (average) temperature from 25°C ( $\alpha=1.055$ ; time from 0 to 5 days) up to 25.8°C ( $\alpha=1.054$ ; time from 5 to 14 days). It is very important to note the relative small influence of the temperature on the enrichment process (of course, in a small domain). Figure 3 gives the evolution of the enrichment process if the concentration of the feeding nitric acid changes from value 10M ( $\alpha=1.055$ ; time from 0 to 5 days) up to 15.5M ( $\alpha=1.0438$ ; time from 5 to 14 days). Figure 4 gives a hypothetic variation of the  $^{15}\text{N}$ -isotope enrichment if the temperature on the first 10 plates would be 25°C and the temperature on the rest (11-40) would be 25.8°C. Finally, the figure 5 gives the evolution of the  $^{15}\text{N}$ -isotope enrichment (neglecting the time constants) if the concentration of the nitric acid would be 10M on the first 20 plates and the concentration would be 15.5M on the rest (21-40).

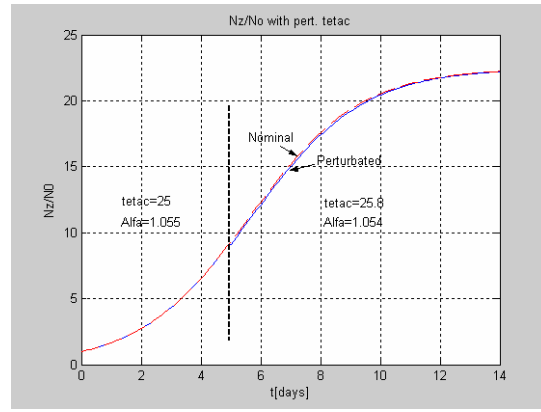


Figure 2. Simulation results: change in  $\theta_c$

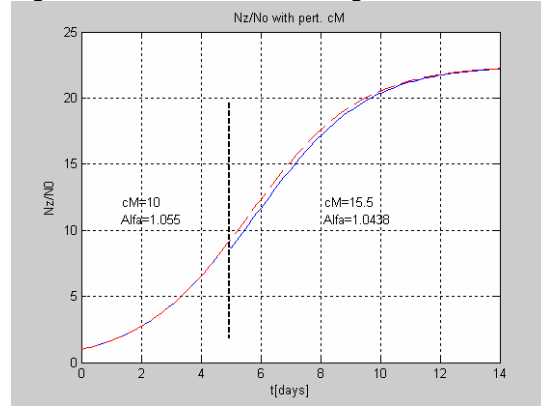


Figure 3. Simulation results: change in  $c_M$

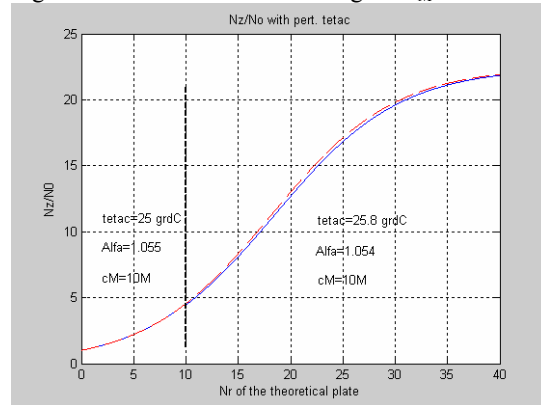


Figure 4. Simulation results: change in  $\theta_c$

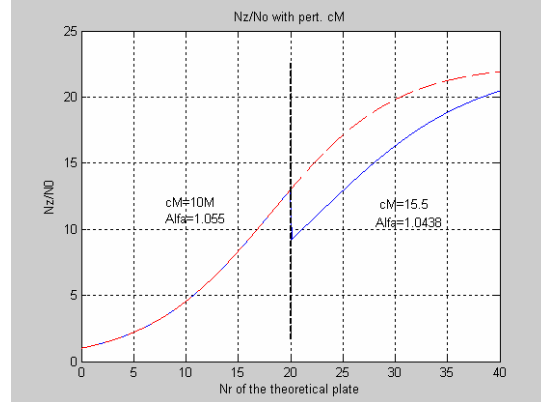


Figure 3. Simulation results: change in  $c_M$

#### 4. CONCLUSIONS

The isotope separation plant is complex equipment, nonlinear, with variable parameters and with very large equivalent time constant (of the order of days). The linear simplified mathematical model is, in opinion of authors, the single way to implement an effective control system. The validation of the simplified mathematical model is based: on the exact equations (Cohen, 1951) and on the experimental data (Axente, 1994; Dulf, 2005). The obtained mathematical model will be used in predictive-robust control of the plant.

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