ASSOCIATION POUR LE DÉVELOPPEMENT DE L'ENSEIGNEMENT ET DE LA RECHERCHE EN SYSTÉMATIQUE APPLIQUÉE

MELISSA

Memorandum of Understanding
ECT/FG/MMM/97.012

ESTEC/Contract N° 12924/98/NL/MV
of 10 July 1998

TECHNICAL NOTE : 44.2

Numerical simplification of the dynamic model of the nitrifying compartment for the elaboration of a nitrite estimator

Version : 0
Draft

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April 1998

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Document Change Log

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0	0	April 1999	Draft

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1. INTRODUCTION

Versus the TN 35.2, the following modifications have been done in the present note :

- Taking into account the dissociation of CO_2 and NH_3.
- Elimination of an approximation which consisted in considering that the values of the inputs of each tank i of the column at a given moment n are equal to the outputs of the tank i-1 at the previous moment n-1. This approximation was not disturbing the mass conservation of atom N (as it was checked in TN 35.2) but made unbalanced the transformation of atom C (which was discovered after the issue of TN 35.2).
- The column is represented under the concise form of a classical state system :

$$\begin{cases} \dot{X} = A \,.\, X + B \,.\, U \\ Y = C \,.\, X + D \,.\, U \end{cases}$$

2. NOTATION

For each substrate of the problem and for each tank of the column :

a : molar concentration in the gas phase

b : molar concentration in the liquid phase of the molecular form

b' : molar concentration in the liquid of all the ionic forms

c : molar concentration at the thermodynamic equilibrium

d_G : molar concentration in the incoming gas flow

d_L : molar concentration in the incoming liquid flow of the molecular form

$d_L^{'}$: molar concentration in the incoming liquid flow of all the ionic forms

q_G : gas flow rate (1/h)

q_L : liquid flow rate (1/h)

r : mean volumetric production or consumption rate (mol/1/h)

K : volumetric transfer coefficient in liquid phase (notation K_{La} in TN 27.1)

k_p : partition coefficient of gas-liquid equilibrium

With this notation, each variable is considered as a vector whose components are the corresponding values of the substrates. For example, a is the vector of the molar concentrations of the substrates (O_2, CO_2 and NH_3)in the gas phase. All these concentrations are in mol/1.

For each part of the column (A or tank n of B or C) the volumes are :

V_G : volume of gas (beads not included, for part B)

V_L : volume of liquid (beads not included, for part B)

The derivative of the function y versus a variable t is written $\frac{dy}{dt}$ or $\dot{y}$.

3. SIMPLIFIED SYSTEM OF EQUATIONS FOR ANY TANK OF THE COLUMN

3.1. Bi-phases substrates

Considering any part of the column (part A or C or any tank of B) :

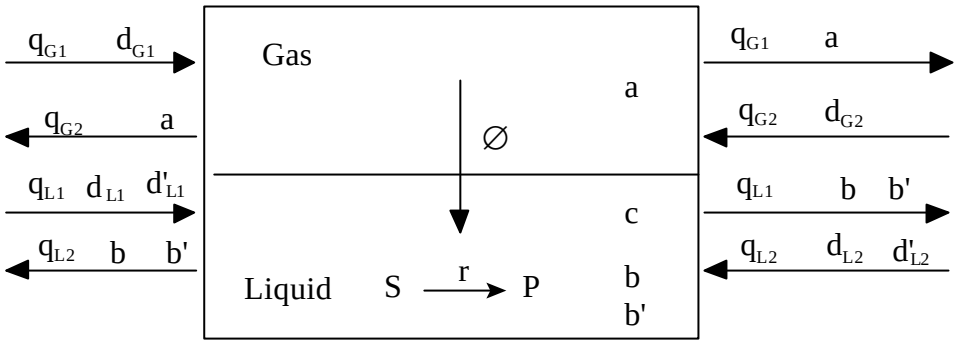

Figure 1 : Concentrations and mass fluxes of any part of the column

In this figure 1, S and P mean Substrate and Product and the indices 1 and 2 are :

1 : for flow from left to right hand side ;
2 : for flow from right to left hand side.

In the liquid phase, the concentration of a molecular form, x, and the one of its ionic form x' are linked by the relation.

$$x' = k \cdot x$$

with

$$k = \frac{K_{a1}}{[H^+]} \cdot \left(1 + \frac{K_{a2}}{[H^+]}\right) \quad \text{for } CO_2 \text{ solvated}$$

$$k = \frac{K_b \cdot [H^+]}{k_e} \quad \text{for } NH_3 \text{ solvated}$$

$$k = 0 \quad \text{for the other compounds}$$

Assuming that the temperature and the pH are constant and that the thermodynamic equilibrium is reached for these dissociation reactions along the column at any moment, the 3 following relations are deduced :

$$\begin{cases} b' = k.b \\ d'_{L1} = k \,.\, d_{L1} \\ d'_{L2} = k \,.\, d_{L2} \end{cases}$$

The behaviour of any tank is described by the 4 following equations.

With the assumptions of perfect gases, the gas-liquid equilibrium is written (justification in Annex 1) :

$$a = \alpha \,.\, c \qquad \text{with :} \quad \alpha = \frac{k_p}{n_o \cdot V_M} \tag{1}$$

n_o = 55.56 (number of mols in a litre of water)
V_M = 24.86 (molar volume under 1 atmosphere and 303 K)

The mass flux, $\varnothing$, from gas to liquid is :

$$\varnothing = K\,(c - b) \tag{2}$$

The mass conservation in the gas is :

$$V_G \,.\, \frac{da}{dt} = -\varnothing . V_L + q_{G1}(d_{G1} - a) + q_{G2}(d_{G2} - a) \tag{3}$$

The mass conservation in the liquid is :

$$V_L \,.\, \frac{db}{dt} = (r + \varnothing) \,.\, \frac{V_L}{1+k} + q_{L1}(d_{L1} - b) + q_{L2}(d_{L2} - b) \tag{4}$$

So, given the following new input variables q_G, q_L, d_G and d_L :

$$q_G = q_{G1} + q_{G2}$$

$$q_L = q_{L1} + q_{L2}$$

$$q_G \,.\, d_G = q_{G1} \,.\, d_{G1} + q_{G2} \,.\, d_{G2}$$

$$q_L \,.\, d_L = q_{L1} \,.\, d_{L1} + q_{L2} \,.\, d_{G2}$$

The previous system of equations becomes a system of 4 equations with 4 unknowns (a, b, c and $\varnothing$) :

$$a = \alpha \cdot c \tag{5}$$

$$\varnothing = K\,(c-b) \tag{6}$$

$$V_G \cdot \frac{da}{dt} = -\varnothing \cdot V_L + q_G\,(d_G - a) \tag{7}$$

$$V_L \cdot \frac{db}{dt} = (r + \varnothing)\,\frac{V_L}{1+k} + q_L\,(d_L - b) \tag{8}$$

Using Laplace transforms and cancelling small time constants lead to a relation between the inputs of the problem r, d_G, d_L and the outputs a and b (details in Annex 2) :

$$\frac{db}{dt} = \frac{1}{\tau_1}\,(-b + G_1 \cdot d_L + G_2 \cdot d_G + G_3 \cdot r) \tag{9}$$

$$a = \alpha_4 \cdot b + \alpha_5 \cdot d_G \tag{10}$$

3.2. Mono-phase substrates

For the substrates only present in liquid phase (NO_2^- , NO_3^- , $HPO_4^=$ and $SO_4^=$), the derivative of the concentration is :

$$\frac{db}{dt} = \frac{1}{\tau_L}\,(-b + \tau_L \cdot r + d_L) \tag{11}$$

with $\tau_L = \dfrac{V_L}{q_L}$

4. MODEL OF THE NITRIFYING COMPARTMENT

4.1. Recall

For each compound and for each tank of the column, the equations are :

for the biphase compounds :

$$\left| \begin{array}{l} \dot{b} = -\frac{1}{\tau_1} . b + \frac{G_2}{\tau_1} . d_G + \frac{G_1}{\tau_1} . d_L + \frac{G_3}{\tau_1} . r \\ a = \alpha_4 . b + \alpha_5 . d_G \end{array} \right.$$

for the monophase compounds :

$$\dot{b} = -\frac{1}{\tau_L} . b + \frac{1}{\tau_L} . d_L + r$$

The constants G_1, G_2, G_3, α_4, α_5 and τ_1 are defined in Annex 2.

The constant τ_L is defined in paragraph 3.2.

Notations :

Subsequently, the system of equations is put under matrix and vector form.

1. The notation M = diag (V) means
   M is a square matrix with the elements of the vector V on the main diagonal (all the other elements of M are null).
2. When M is a matrix, M' means the transpose of M.

4.2. State equations of each tank

Each tank i of the nitrifying compartment is described by the following state system :

$$\left| \begin{array}{l} \dot{X}_i = A_i . X_i + B_i . U_i + E_i . R_i \\ Y_i = C_i . X_i + D_i . U_i \end{array} \right. \qquad (12)$$

The indices 1, 2, 3 are related to the compounds O_2, CO_2 and NH_3
4 to 7 are related to the compounds NO_2^- , NO_3^- , $HPO_4^=$, $SO_4^=$.

The matrices and vectors of (12) are defined hereafter.

$$X_i = [b_{1i}, b_{2i}, b_{3i}, b_{4i} \ldots b_{7i}]'$$

$$U_i = [d_{G1i}, d_{G2i}, d_{G3i}, d_{L1i}, d_{L2i}, d_{L3i}, d_{L4i} \ldots d_{L7i}]'$$

$$R_i = [r_{1i}, r_{2i} \ldots r_{7i}]'$$

N.B. : The vectors X_i, U_i and R_i are column vectors.

- $A_i = \text{diag}(V)$

with :

$$V = \left[-\frac{1}{\tau_{11i}}, -\frac{1}{\tau_{12i}}, -\frac{1}{\tau_{13i}}, -\frac{1}{\tau_{L4i}}, \ldots, -\frac{1}{\tau_{L7i}} \right]$$

- $$B_i = \begin{bmatrix} \text{diag}(V_1) & \text{diag}(V_2) & 0_{34} \\ 0_{43} & 0_{43} & \text{diag}(V_3) \end{bmatrix}$$

0_{mn} : null matrix with dimension : m rows
n columns

with :

$$V_1 = \left[\frac{G_{21i}}{\tau_{11i}}, \frac{G_{22i}}{\tau_{12i}}, \frac{G_{23i}}{\tau_{13i}} \right]$$

$$V_2 = \left[\frac{G_{11i}}{\tau_{11i}}, \frac{G_{12i}}{\tau_{12i}}, \frac{G_{13i}}{\tau_{13i}} \right]$$

$$V_3 = \left[\frac{1}{\tau_{L4i}}, \ldots, \frac{1}{\tau_{L7i}} \right]$$

- $C_i = \begin{bmatrix} diag(V) & 0_{34} \\ I_3 & 0_{34} \\ 0_{43} & I_4 \end{bmatrix}$

with :

$V = [\alpha_{41i}, \alpha_{42i}, \alpha_{43i}]$

I_n = identity matrix with dimension n

- $D_i = diag(V)$

with :

$V = [\alpha_{51i}, \alpha_{52i}, \alpha_{53i}, 0, 0, 0, 0, 0, 0, 0]$

- $E_i = diag(V)$

with :

$$V = \left[\frac{G_{31i}}{\tau_{11i}} , \frac{G_{32i}}{\tau_{12i}} , \frac{G_{33i}}{\tau_{13i}} , 1 , 1 , 1 , 1 \right]$$

The matrix A_i is a square matrix with dimension $N_G + N_L$. The matrices D_i and E_i are square matrices with dimension $2 . N_G + N_L$.

N_G = number of bi- phases compounds
N_L = number of monophase compounds
$N_G = 3$
$N_L = 4$

4.3. State equations of the nitrifying compartment

The compartment is divided into $N_B + 2$ tanks (1 tank for part A, N_B tanks for part B, 1 tank for part C) put in series.

Figure 2 shows the scheme of column with 3 tanks (when $N_B = 1$). Each box of this scheme represents the state system of the corresponding tank.

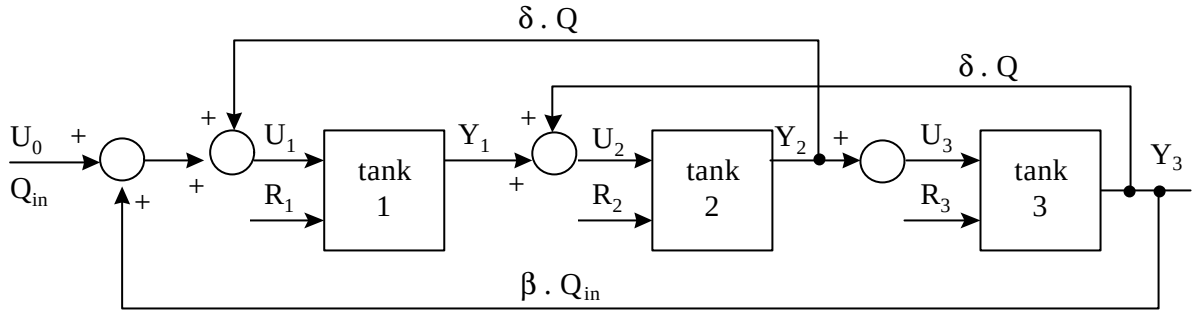

Figure 2 : Scheme of a nitrifying column with 3 tanks (N_B = 1)

Q_{in} is the incoming flow rate of gas or liquid.

- β is the ratio of the recirculating flow versus Q_{in} :

  $\beta = R_G$ for the gas (R_G and R_L are notations of TN 27.1)
  $\beta = R_L$ for the liquid

- δ is the back flow ratio :

  δ = f' for the gas (f and f' are notations of TN 27.1)
  δ = f for the liquid
  $Q = (1+\beta) . Q_{in}$

In order to calculate the unknowns :

$\dot{X}_1 \dots \dot{X}_i \dots \dot{X}_n$ with $n = N_B + 2$

$Y_1 \dots Y_i \dots Y_n$

the following system has to be solved (equations 1.1 to n.3).

Tank 1 (part A of the column) :

$$\dot{X}_1 = A_1 . X_1 + B_1 . U_1 + E_1 . R_1 \quad (1.1)$$

$$Y_1 = C_1 . X_1 + D_1 . U_1 \quad (1.2)$$

$$Q_{in}(U_0 + \beta . Y_n + \delta(1+\beta) . Y_2) = Q_{in}(1+\delta) . (1+\beta) . U_1 \quad (1.3)$$

Tank i ($2 \leq i \leq N_B + 1$) :

$$\dot{X}_i = A_i \,.\, X_i + B_i \,.\, U_i + E_i \,.\, R_i \qquad \text{(i.1)}$$

$$Y_i = C_i \,.\, X_i + D_i \,.\, U_i \qquad \text{(i.2)}$$

$$Q(1+\delta) \,.\, Y_{i-1} + Q \,.\, \delta \,.\, Y_{i+1} = Q(1+2\delta) \,.\, U_i \qquad \text{(i.3)}$$

Tank n = N_B+2 (part C of the column) :

$$\dot{X}_n = A_n \,.\, X_n + B_n \,.\, U_n + E_n \,.\, R_n \qquad \text{(n.1)}$$

$$Y_n = C_n \,.\, X_n + D_n \,.\, U_n \qquad \text{(n.2)}$$

$$Y_{n-1} = U_n \qquad \text{(n.3)}$$

These equations (1.1) to (n.3) can be parted into 3 groups :

group 1 : equations (1.1) ... (i.1) ... (n.1)
group 2 : equations (1.2) ... (i.2) ... (n.2)
group 3 : equations (1.3) ... (i.3) ... (n.3)

Given the following matrices A, B, C, D, E, G, H and vectors X, U, Y, R, F.

$$X = \begin{bmatrix} X_1 \\ \vdots \\ X_i \\ \vdots \\ X_n \end{bmatrix} \quad U = \begin{bmatrix} U_1 \\ \vdots \\ U_i \\ \vdots \\ U_n \end{bmatrix} \quad Y = \begin{bmatrix} Y_1 \\ \vdots \\ Y_i \\ \vdots \\ Y_n \end{bmatrix} \quad R = \begin{bmatrix} R_1 \\ \vdots \\ R_i \\ \vdots \\ R_n \end{bmatrix} \quad F = \begin{bmatrix} U_0 \\ 0 \\ \vdots \\ \vdots \\ 0 \end{bmatrix}$$

$$A = \begin{pmatrix} A_1 & & \mathbf{0} \\ & \ddots & \\ & A_i & \\ & & \ddots \\ \mathbf{0} & & A_n \end{pmatrix} \quad B = \begin{pmatrix} B_1 & & \mathbf{0} \\ & \ddots & \\ & B_i & \\ & & \ddots \\ \mathbf{0} & & B_n \end{pmatrix} \quad C = \begin{pmatrix} C_1 & & \mathbf{0} \\ & \ddots & \\ & C_i & \\ & & \ddots \\ \mathbf{0} & & C_n \end{pmatrix}$$

$$D = \begin{pmatrix} D_1 & & \mathbf{0} \\ & \ddots & \\ & D_i & \ddots \\ \mathbf{0} & & D_n \end{pmatrix} \qquad E = \begin{pmatrix} E_1 & & \mathbf{0} \\ & \ddots & \\ & E_i & \ddots \\ \mathbf{0} & & E_n \end{pmatrix}$$

G =

1	**2**	**i-1**	**i**	**i+1**	**n-1**	**n**	
	$-\delta(I_{10}+\beta)$					$-\beta$	**1**
$-(I_{10}+\delta)$		$-\delta$					**2**
	$-(I_{10}+\delta)$		$-\delta$				**i-1**
		$-(I_{10}+\delta)$		$-\delta$			**i**
			$-(I_{10}+\delta)$		$-\delta$		**i+1**
				$-(I_{10}+\delta)$		$-\delta$	**n-1**
					$-I_{10}$		**n**

H =

1	**2**	**i-1**	**i**	**i+1**	**n-1**	**n**	
$(I_{10}+\delta)(I_{10}+\beta)$							**1**
	$I_{10}+2\delta$						**2**
		$I_{10}+2\delta$					**i-1**
			$I_{10}+2\delta$				**i**
				$I_{10}+2\delta$			**i+1**
					$I_{10}+2\delta$		**n-1**
						I_{10}	**n**

I_{10} is the identity matrix with dimension 2 . N_G + N_L = 10. The matrices D, E, G and H are square matrices with dimension (2 N_G + N_L) . (N_B + 2).

The matrix A is a square matrix with dimension (N_G + N_L) . (N_B + 2).

N.B. : For example, in the standard nitrifying compartment : N_B = 5, so the dimension of A is 49.

The previous system (equations (1.1) to (n.3)) becomes :

$$\left|\begin{array}{l} \dot{X} = A \,.\, X + B \,.\, U + E \,.\, R \\ Y = C \,.\, X + D \,.\, U \\ G \,.\, Y + H \,.\, U = F \end{array}\right.$$

with the unknowns $\dot{X}$, U et Y.

By cancelling the unknown U, the following system is obtained :

$$\left|\begin{array}{l} \dot{X} = A \,.\, X + B \,.\, (G \,.\, D + H)^{-1} \,.\, (F - G \,.\, C \,.\, X) + E \,.\, R \\ Y = C \,.\, X + D \,.\, (G \,.\, D + H)^{-1} \,.\, (F - G \,.\, C \,.\, X) \end{array}\right. \qquad (13)$$

Expression of R matrix of consumption/production rates :

Given :

$$Y_{X1} = \begin{pmatrix} -5.4269 & -6.5106 \\ -1 & -1 \\ -4..5341 & -0.1994 \\ 4.3347 & -15.1714 \\ 0 & 15.1714 \\ -0.0089 & -0.0089 \\ -0.0035 & -0.0035 \end{pmatrix} \quad \text{and} \quad Y_{m1} = \begin{pmatrix} -1.5 & -0.5 \\ 0 & 0 \\ -1 & 0 \\ 1 & -1 \\ 0 & 1 \\ 0 & 0 \\ 0 & 0 \end{pmatrix}$$

These matrices Y_{x1} and Y_{m1} are composed of the stoechiometric coefficients of the growth and maintenance reactions for N_s and N_b, according to TN 27.1 of LGCB.

Given μ_m and m the matrices of maximum growth and maximum maintenance.

$$\mu_m = \begin{pmatrix} 5.7 \,.\, 10^{-2} & 0 \\ 0 & 3.6 \,.\, 10^{-2} \end{pmatrix} \quad \text{and} \quad m = \begin{pmatrix} 3.38 \,.\, 10^{-3} & 0 \\ 0 & 7.92 \,.\, 10^{-3} \end{pmatrix}$$

Given $Klim_i$ the matrix of limiting consumption of substrates for the tank i :

$$Klim_i = \begin{pmatrix} a_1 & 0 \\ 0 & a_2 \end{pmatrix}$$

with $a_1 = 0$ if $[O_2\, L]_i = 0$ or $[NH_3\, L]_i = 0$

$a_2 = 0$ if $[O_2\ L]_i = 0$ or $[NO_2^-]_i = 0$

N.B. : it could be assumed that $[O_2\ L] > 0$ (O_2 in excess in each tank), which would avoid using a sensor for the measurement of O_2.

Given $r_{\mu i}$ the matrix of limiting growth.

$$r_{\mu i} = \begin{pmatrix} a_1 & 0 \\ 0 & a_2 \end{pmatrix}$$

with :

$$a_1 = \frac{[O_2\ L]_i}{K_{sNs1} + [O_2\ L]_i} \cdot \frac{[NH_3\ L]_i}{K_{sNs2} + [NH_3\ L]_i}$$

$$a_2 = \frac{[O_2\ L]_i}{K_{sNb1} + [O_2\ L]_i} \cdot \frac{[NO_2^-]_i}{K_{sNb2} + [NO_2^-]_i}$$

The global growth rate, R_{gi} , and maintenance rate, R_{mi}, are, for each tank i :

$$R_{gi} = r_{\mu i} \cdot \mu_m \cdot C_{Xi}$$

$$R_{mi} = Klim_i \cdot m \cdot C_{Xi}$$

with the column vector of concentrations of active biomass N_s and N_b :

$$C_{Xi} = \begin{bmatrix} [X_{Ns}]_i \\ [X_{Nb}]_i \end{bmatrix}$$

The matrix of consumption/production rates is :

$$R_i = Y_{X12} \cdot R_{gi} + Y_{m12} \cdot R_{mi}$$

otherwise :

$$R_i = J_i \cdot C_{Xi}$$

with :

$$J_i = Y_{X12} \,.\, r_{\mu i} \,.\, \mu_m + Y_{m12} \,.\, Klim_i \,.\, m$$

Given :

$$J = \begin{pmatrix} J_1 & & \mathbf{0} \\ & \ddots & \\ & J_i & \\ & & \ddots \\ \mathbf{0} & & J_n \end{pmatrix}$$

$$C_X = \begin{bmatrix} C_{X1} \\ \vdots \\ C_{Xi} \\ \vdots \\ C_{Xn} \end{bmatrix} \qquad R = \begin{bmatrix} R_1 \\ \vdots \\ R_i \\ \vdots \\ R_n \end{bmatrix}$$

$$\Rightarrow \quad R = J \,.\, C_X \tag{14}$$

State system of the column

The equations (13) and (14) lead to the state system of the column :

$$\left| \begin{array}{l} \dot{X} = A_e \,.\, X + B_e \,.\, U_0 + E \,.\, J \,.\, C_x \\ Y = C_e \,.\, X + D_e \,.\, U_0 \end{array} \right. \tag{15}$$

with :

$$A_e = A - B(G \,.\, D + H)^{-1} \,.\, GC$$
$$C_e = C - D\,(G \,.\, D + H)^{-1} \,.\, GC$$
$$B_e = \text{10 first columns of } B(G \,.\, D + H)^{-1}$$
$$D_e = \text{10 first columns of } D(G \,.\, D + H)^{-1}$$

Recall :

1) 10 is the dimension of the vector U_0

2) U_0 is the concentrations of the compounds in the incoming gas and liquid flows :

$$U_0 = \begin{bmatrix} [O_2]_G \\ [CO_2]_G \\ [NH_3]_G \\ [O_2]_L \\ [CO_2]_L \\ [NH_3]_L \\ \left[NO_2^-\right] \\ \left[NO_3^-\right] \\ \left[HPO_4^=\right] \\ \left[SO_4^=\right] \end{bmatrix}$$

5. SIMULATION

5.1. Configuration of the simulation

The configuration of the simulation are those of TN 27.2 (L. Poughon, Laboratoire de Génie Chimique Biologique) :

- standard configuration described p.12 and 13 ;
- number of equivalent tanks in the fixed bed : 5
- stoïchiometries p.3 ;
- dissociation constant of CO_2/HCO_3^- p.2 ;
- limiting substrates defined p.4 ;
- no inhibitory substrate ;
- no limitation due to liquid/biofilm transfer
- transfer coefficient $K_{La} = [51 \quad 51 \quad 500] \quad h^{-1}$
  for O_2 CO_2 NH_3
- partition coefficient $k_p = [45990 \quad 1853.1 \quad 11.349]$
  for O_2 CO_2 NH_3 (non ionic form)

The compounds involved in the simulation are :

- O_2 G(Gas phase) and L(Liquid phase)
- CO_2 G and L
- NH_3 G and L
- HCO_3^-
- NO_2^-
- NO_3^-
- $HPO_4^{=}$
- $SO_4^{=}$
- X_N_s (biomass Nitrosomonas, active and global (active + decay))
- X_N_b (biomass Nitrobacter, active and global (active + decay))

5.2. Results

Figures 3 to 6 are composed of 8 graphs whose the last one (below right hand side) is common to all the figures of a same simulation and shows the average active biomass concentration in the fixed bed (part B of the column). The 7 other graphs are connected to tank 1 (of the fixed bed) in the figures 3 and 5, and to tank 5 (the last one of the fixed bed) in the figures 4 and 6.

The figures 5 and 6 are abscise zooms of figures 3 and 4, respectively.

The composition of the gas phase (G notation) is given in molar fraction (mf), the composition of the liquid phase (L notation) is given in mol/l or g/l (for biomass).

Tank 1 of fixed bed :

During the 40 first hours approximately, the growth of biomass Ns is exponential while the concentrations of substrates HCO_3^-, O_2 and NH_3 are decreasing more or less exponentially.

At about time t = 40 h, the NH_3 concentration (1 mmol/l) becomes limiting : the growth of biomass bends, so that the consumption rate of HCO_3^- is decreasing (CO_2 concentration reaches its minimum). On the contrary, NO_2^- concentration is maximum (1 mmol/l).

After that point, the consumption of NO_2^- by N_b is greater than its production by N_s.

The O_2 concentration goes on decreasing slowly (until 0.15 mmol/l at the end of the simulation). The NH_3-L and NO_2^- concentrations are nearly stabilised at 0.3 mmol/l. During the last 150 h, NH_3-G decreases slowly from 1 to 0.5 10^{-5} molar fraction.
After 200 h, the biomasses N_s and N_b are still growing.
All the NH3 is not transformed in nitrate : a part of NH3 is consumed by N_s and a part of NO_2^- is consumed by N_b .

Tank 5 of fixed bed :

The 40 first hours are quite similar to those of thank 1.
Beyond that time, the NH3 concentration becomes low (0.1 mmol/l). The growth rate of global biomass becomes null and the active biomass disappears progressively. As O_2 is less and less consumed by biomass, its concentration in the liquid phase comes close to its thermodynamic limit : 0.23 mmole/l.

After its maximum at 1 mmol/l, NO_2^- concentration is getting low (0.02 mmol/l).

As for Ns, the biomass Nb is getting null (0.01 g/l) at the end.

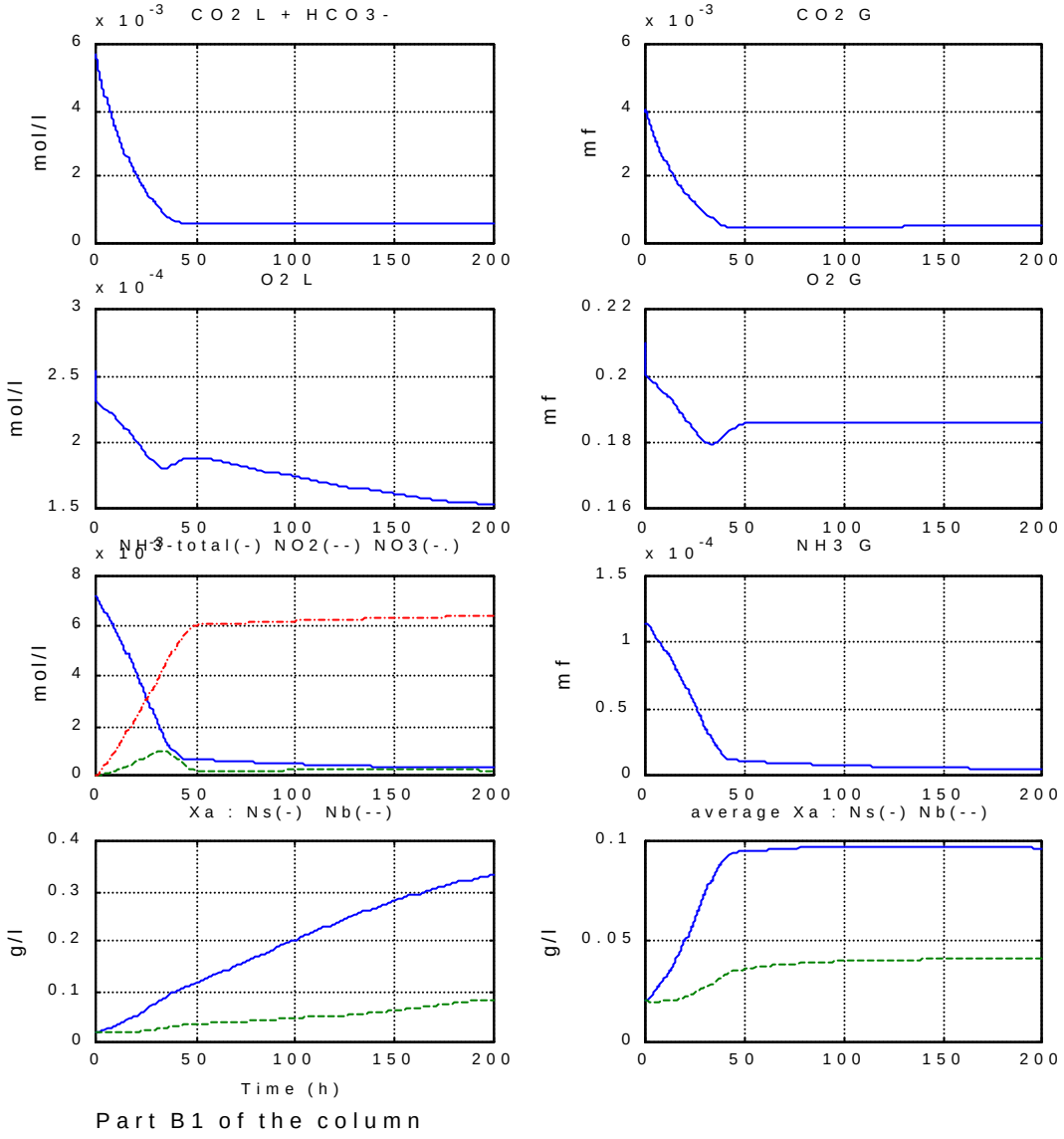

Figure 3 : Input cst : O2 CO2 NH3 G & L; Growth of biomass

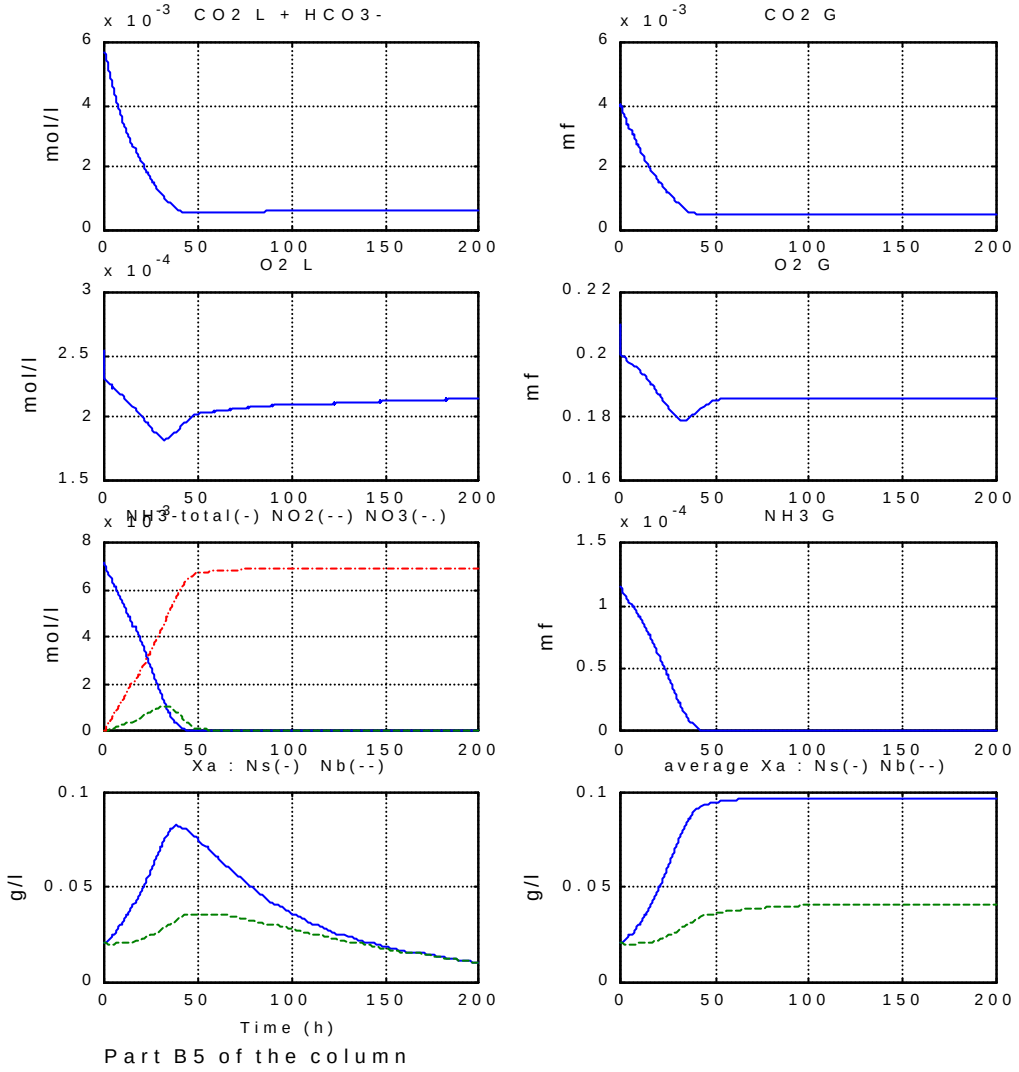

Figure 4 : Input cst : O2 CO2 NH3 G & L; Growth of biomass

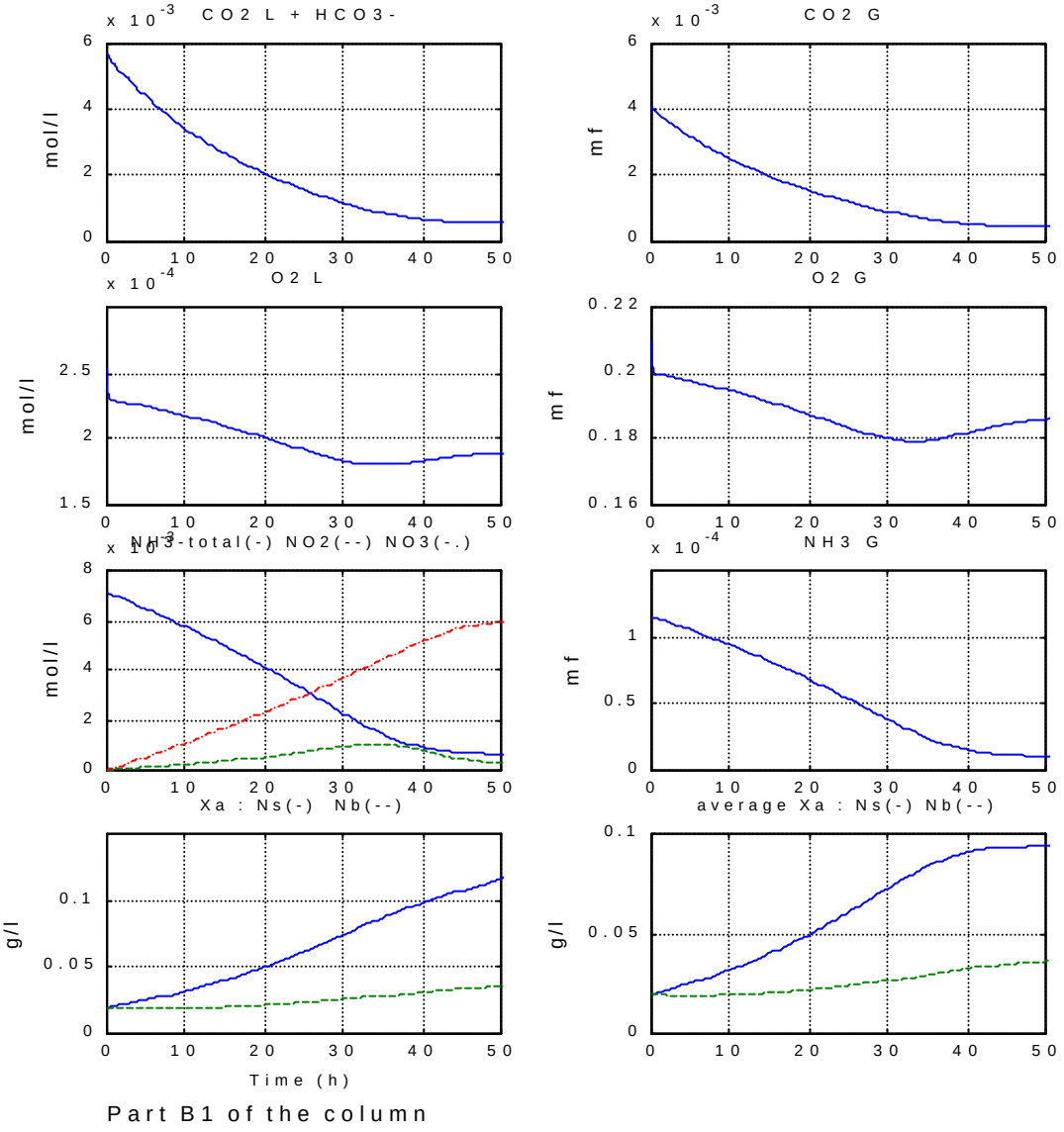

Figure 5 : Zoom on the 50 first hours of figure 3

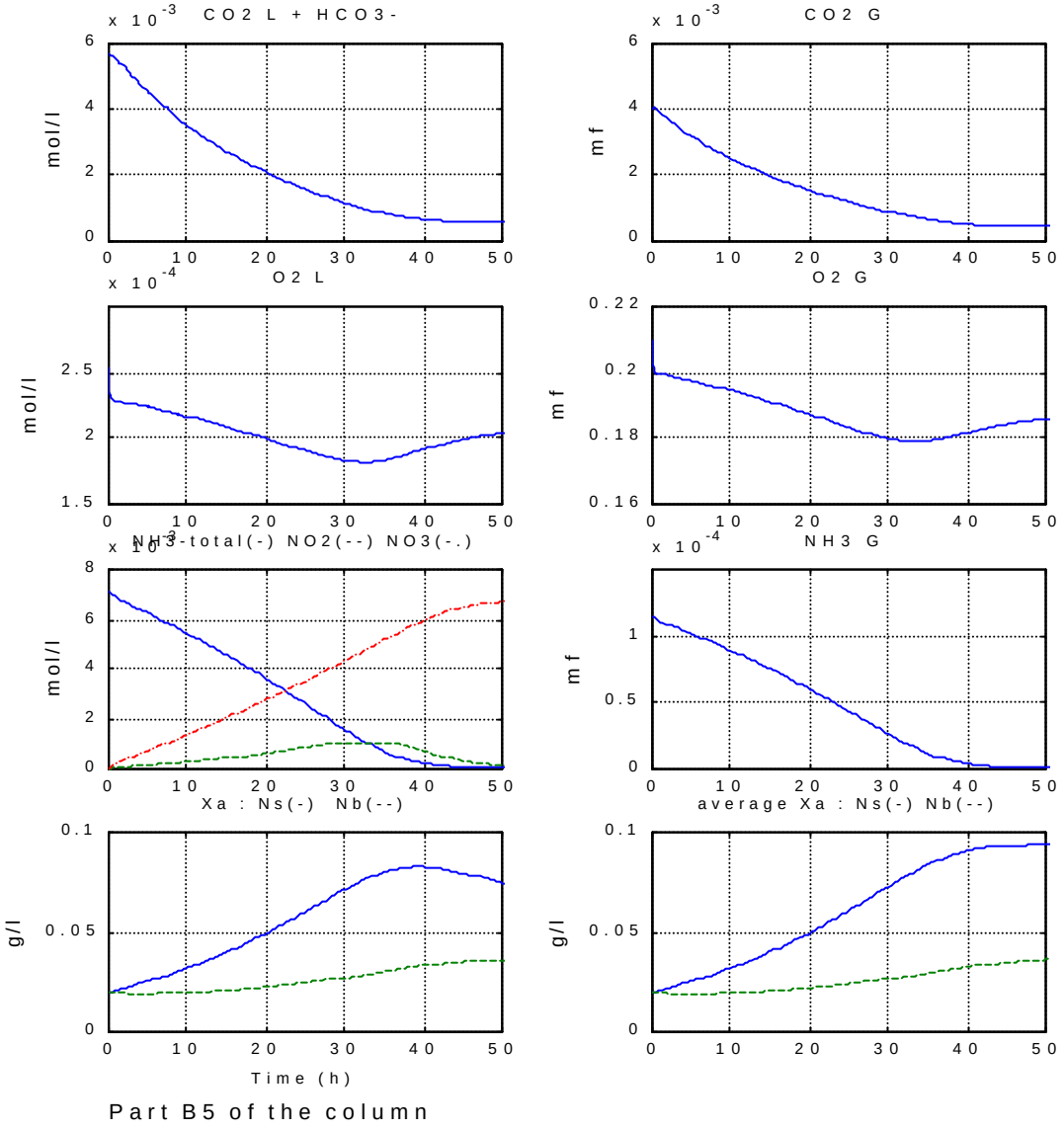

Figure 6 : Zoom on the 50 first hours of figure 4

6. CHECKING THE MASS BALANCE

The mass balance is checked for the atoms C, N, S and P (figure 7). At the beginning of the simulation, the mass of atom C is not exactly balanced (error of 1 %) but the balance is good after the transient. The mass of the other atoms is well balanced : error smaller than 0.01 % .

In TN 35.2 it was assumed that the values of the inputs of each tank i of the column at a given moment n are equal to the outputs of the tank i-1 at the previous moment n-1. It is checked now that this approximation was not disturbing the mass conservation of atom N but made unbalanced the transformation of atom C . This approximation is cancelled in the present simulator.

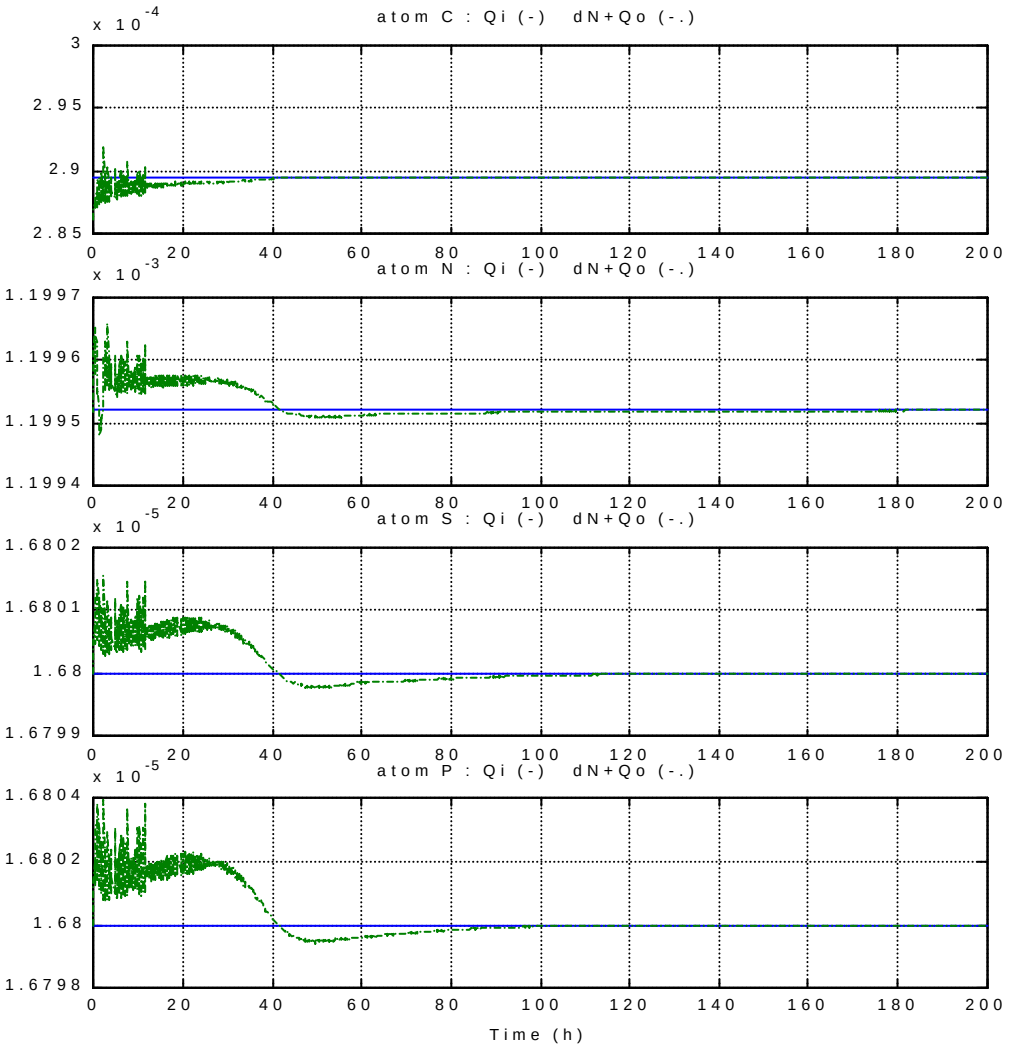

Figure 7 : Checking the mass balance of the column

7. CHECKING THE APPROXIMATION OF THE GAS/LIQUID EQUILIBRIUM

In order to estimate the error that is done when the non linear law of gas/liquid equilibrium is replaced by the linear relation (1), one need only to compare for each compound i the partition coefficient k_i to the ratio :

$$z_i = \frac{y_i}{x_i}$$

with :

$$y_i = \frac{a_i}{\sum a_i}$$

$$x_i = \frac{c_i}{\sum c_i}$$

where : a_i is the molar concentration in the gas phase

c_i is the molar concentration in the liquid phase at thermodynamic equilibrium

Now $z_i = \frac{a_i}{c_i} \cdot \frac{\sum c_i}{\sum a_i}$

and $a_i = \alpha_i \cdot c_i$ with $\alpha_i = \frac{k_i}{n_{lo} \cdot V_M}$ (notations of Annexe 1)

therefore

$$z_i = \frac{k_i}{n_{lo} \cdot V_M} \cdot \frac{\sum c_i}{\sum a_i}$$

With the legitimate approximation $\sum c_i = n_{lo}$

$$z_i = \gamma \cdot k_i \quad \text{where} \quad \gamma = \frac{1}{V_M \cdot \sum a_i}$$

γ is independent of compound i and depends on the sum of all the concentrations whose variation is low.

The figure 8 shows that the mean value of γ is about 3.5 %, which means that the right partition coefficient k_i is overestimated of this quantity. In order to compensate this overestimation, the right value of k_i could be reduced of 3.5 % in the simulations.

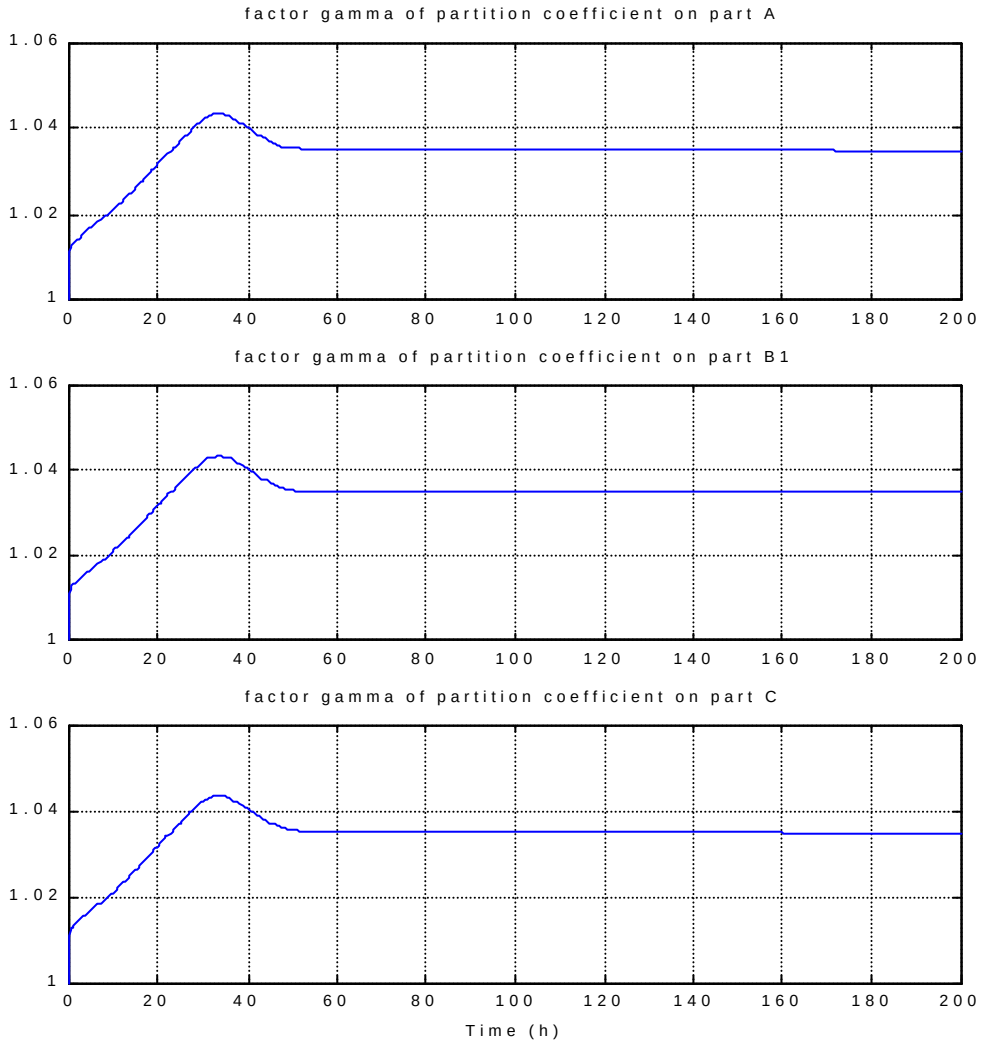

Figure 8 : checking the value of g

8. CONCLUSION

The concise form of the state system of the nitrifying column (15) will be used in order to estimate the biomass and the nitrite concentrations.

REFERENCES

POUGHON L. "Review of models and basis of a dynamic structured model of the nitrifying compartment". ESTEC contract PRF 151739, February 1996, TN 27.1.

POUGHON L. "Description of the nitrifying column model and first simulations". ESTEC contract PRF 151739, May 1996, TN27.2

LECLERCQ J.J. "Numerical simplification of the dynamic model of the nitrifying compartment". CONTRACT ESTEC n° 161 399, may 1998, TN 35.2.

ANNEX 1

APPROXIMATE RELATION FOR GAS/LIQUID EQUILIBRIUM

The gas/liquid equilibrium of each compound i is characterised by the partition coefficient k_i :

$$k_i = \frac{y_i}{x_i}$$

where y_i = molar fraction of compound i in gas phase
x_i = molar fraction of compound i in liquid phase

Here, the compounds involved are O_2 CO_2 NH_3 H_20 and N_2.

Given :
- V_g volume of gas (in l)
- V_l volume of liquid (in l)
- n_{gi} number of mol of compound i in gas phase
- n_{li} number of mol of compound i in liquid phase
- V_M molar volume at pressure and temperature of the column
- a_i molar concentration of compound i in gas phase
- c_i molar concentration of compound i in liquid phase at thermodynamic equilibrium

Assumptions :

1. The total number of mols in liquid is the number of mols of water :

$$\sum_i n_{li} = n_{l0} \cdot V_l \quad \text{with} \quad n_{l0} = \frac{1000}{18} = 55.56 \text{ mol / l}$$

2. The gas are perfect :

$$\sum_i n_{gi} = \frac{V_g}{V_M}$$

Molar fraction and concentration are related by :

$$y_i = \frac{n_{gi} \cdot V_M}{V_g} = a_i \cdot V_M$$

$$x_i = \frac{n_{li}}{n_{l0} \cdot V_1} = \frac{c_i}{n_{l0}}$$

$$\Rightarrow a_i = \alpha_i \cdot c_i \quad \text{with} \quad \alpha_i = \frac{k_i}{n_{l0} \cdot V_M}$$

This last relation is the equation (1) of the system of the bi-phases substrates.

ANNEX 2

SIMPLIFICATION OF THE EQUATIONS SYSTEM OF THE BI-PHASES SUBSTRATES

The starting point of the resolution is the following set of equations (relations (5) to (8) of paragraph 3).

$$a = \alpha \cdot c$$

$$\phi = K(c - b)$$

$$V_L \cdot \frac{db}{dt} = (r + \phi) \cdot \frac{V_L}{1 + k} + q_L \cdot d_L - q_L \cdot b$$

$$V_G \cdot \frac{da}{dt} = -\phi \cdot V_L + q_G \cdot d_G - q_G \cdot a$$

Cancellation of c and ϕ gives :

$$\frac{(K \cdot V_L}{1 + k} + q_L) b + V_L \cdot \frac{db}{dt} = \frac{K \cdot V_L}{\alpha (1 + k)} \cdot a + \frac{V_L}{1 + k} \cdot r + q_L \cdot d_L$$

$$\left(\frac{K \cdot V_L}{\alpha} + q_G \right) a + V_G \cdot \frac{da}{dt} = K \cdot V_L \cdot b + q_G \cdot d_G$$

Using the Laplace transforms :

$$(1 + \theta_1 p) \cdot b = \alpha_1 \cdot a + \alpha_2 \cdot r + \alpha_3 \cdot d_L \qquad \text{(A2.1)}$$

$$(1 + \theta_2 p) \cdot a = \alpha_4 \cdot b + \alpha_5 \cdot d_G \qquad \text{(A2.2)}$$

with :

$$\theta_1 = \frac{V_L}{\frac{K \cdot V_L}{1 + k} + q_L}$$

$$\theta_2 = \frac{V_G}{\frac{K \,.\, V_L}{\alpha} + q_G}$$

$$\alpha_1 = \frac{K \,.\, V_L}{\alpha(K \,.\, V_L + (1 + k) \,.\, q_L)}$$

$$\alpha_2 = \frac{V_L}{K \,.\, V_L + (1 + k) \,.\, q_L}$$

$$\alpha_3 = \frac{(1+k) \,.\, q_L}{K \,.\, V_L + (1 + k) \,.\, q_L}$$

$$\alpha_4 = \frac{K \,.\, V_L}{\frac{K \,.\, V_L}{\alpha} + q_G}$$

$$\alpha_5 = \frac{q_G}{\frac{K \,.\, V_L}{\alpha} + q_G}$$

p : the Laplace variable

Although the notations have not been changed with the Laplace transformation, the functions a, b, r, d_L and d_G are now functions of the Laplace variable p. (Before the transformation, they were functions of time).

Cancellation of a in (A2.1) and (A2.2) :

$$a = \frac{\alpha_4}{1 + \theta_2 \, p} \, b + \frac{\alpha_5}{1 + \theta_2 \, p} \,.\, d_G \qquad \text{(A2.3)}$$

gives :

$$(1 - \alpha_1 \, \alpha_4)(1 + \beta_1 \, p + \beta_2 \, p^2) \,.\, b = \alpha_2(1 + \theta_2 \, p) \,.\, r + \alpha_1 \, \alpha_5 \, d_G + \alpha_3 (1 + \theta_2 \, p) \,.\, d_L \qquad \text{(A2.4)}$$

with :

$$\beta_1 = \frac{\theta_1 + \theta_2}{1 - \alpha_1 \,.\, \alpha_4}$$

$$\beta_2 = \frac{\theta_1 \cdot \theta_2}{1 - \alpha_1 \cdot \alpha_4}$$

Study of $y = 1 + \beta_1 p + \beta_2 p^2$:

Given :

$$y = \beta_2 \left(p^2 + \frac{\beta_1}{\beta_2} p + \frac{1}{\beta_2} \right)$$

Given p_1 and p_2 the roots of $p^2 + \frac{\beta_1}{\beta_2} p + \frac{1}{\beta_2}$.

$$\Rightarrow \quad \left| \begin{array}{l} y = \beta_2 (p - p_1)(p - p_2) \\ \text{and } p_1 \cdot p_2 = \dfrac{1}{\beta_2} \end{array} \right.$$

Given $\tau_1 = -\frac{1}{p_1}$ et $\tau_2 = -\frac{1}{p_2}$ such as $\tau_1 > \tau_2$.

The expression of y becomes :

$$y = \frac{\beta_2}{p_1 \cdot p_2} \cdot (1 + \tau_1 p)(1 + \tau_2 p)$$

$$\Rightarrow \quad y = (1 + \tau_1 p)(1 + \tau_2 p) \qquad \text{(A2.5)}$$

So (A2.4) becomes :

$$(1 - \alpha_1 \alpha_4)(1 + \tau_1 p)(1 + \tau_2 p) \cdot b = \alpha_2 (1 + \theta_2 p) \cdot r + \alpha_1 \alpha_5 d_G + \alpha_3 (1 + \theta_2 p) \cdot d_L \qquad \text{(A2.6)}$$

For the compounds O_2, CO_2 and NH_3 and for $1 \leq N_B \leq 50$, the two following approximations can be done :

$$1 + \tau_2 p = 1 + \theta_2 p \qquad \text{(figure A2.1 shows that } \frac{\theta_2}{\tau_2} \simeq 1)$$

$(1 + \tau_1 p)(1 + \tau_2 p) = 1 + \tau_1 p$ (figure A2.2 shows that τ_2 is negligible versus τ_1)

The relation (A2.6) becomes :

$$b = \frac{G_1}{1 + \tau_1 p} . d_L + \frac{G_2}{1 + \tau_1 p} . d_G + \frac{G_3}{1 + \tau_1 p} . r \qquad (A2.7)$$

with :

$$G_1 = \frac{\alpha_3}{1 - \alpha_1 . \alpha_4}$$

$$G_2 = \frac{\alpha_1 . \alpha_5}{1 - \alpha_1 . \alpha_4}$$

$$G_3 = \frac{\alpha_2}{1 - \alpha_1 . \alpha_4}$$

In the same way (A2.3) gives :

$$a = \alpha_4 . b + \alpha_5 . d_G \qquad (A2.8)$$

The relations (A2.7) and (A2.8), binding the inputs r, d_G and d_L, of the one part, and the outputs, a and b, of the other part, are first order transfers with the time constant τ_1.

The inverse Laplace transforms allow to express the expressions of a and b :

$$\frac{db}{dt} = \frac{1}{\tau_1} \left(- b + G_1 . d_L + G_2 . d_G + G_3 . r \right) \qquad (A2.9)$$

$$a = \alpha_4 . b + \alpha_5 . d_G \qquad (A2.10)$$

Although the notations have not been changed with the Laplace transformation, the functions a, b, r, d_L and d_G are functions of time again, as they were before resolution through Laplace transforms.

The relations (A2.9) and (A2.10) are the relations (9) and (10) given in paragraph 3.

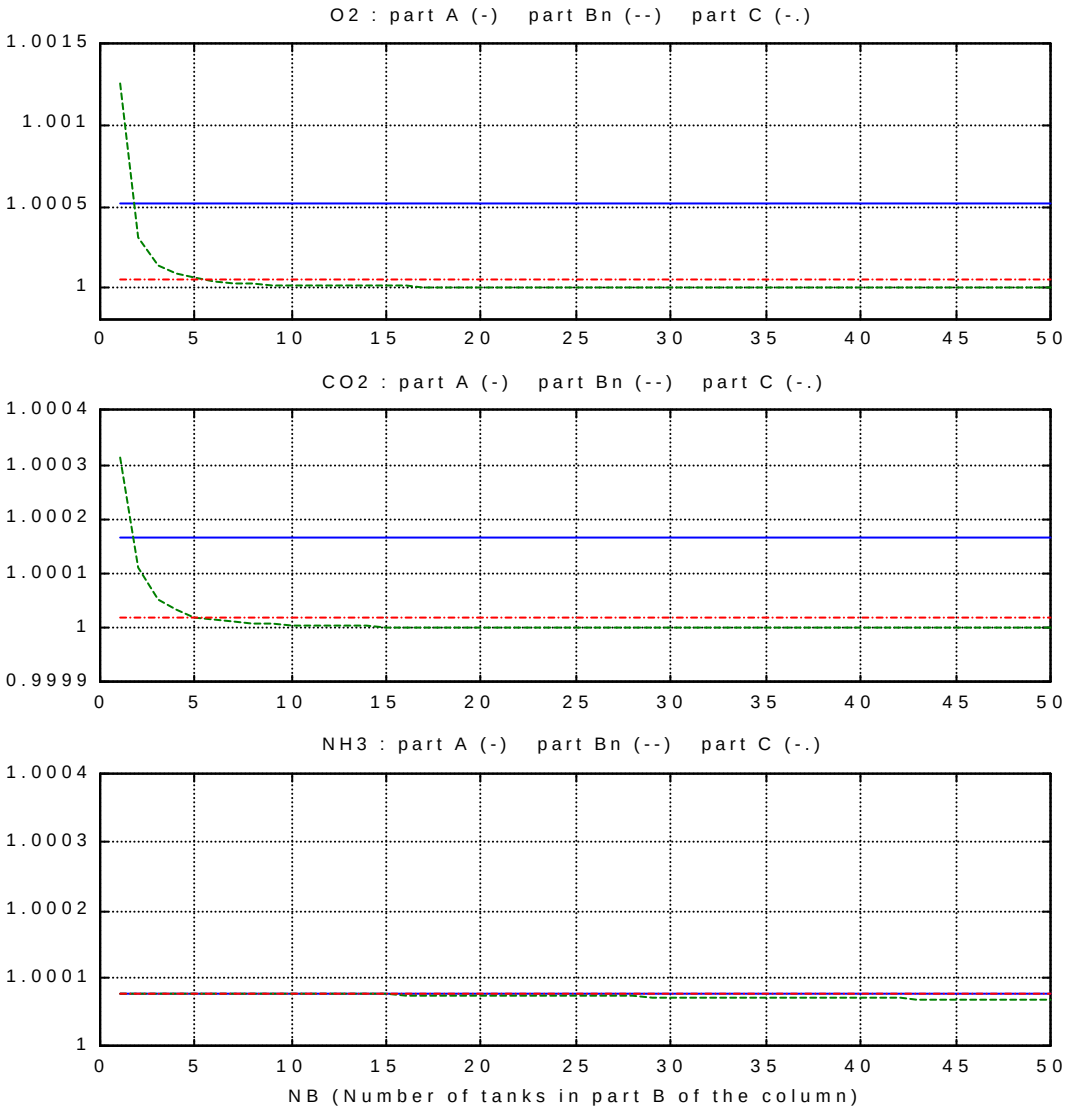

Figure A2.1 : Time constants ratio $\frac{\theta_2}{\tau_2}$

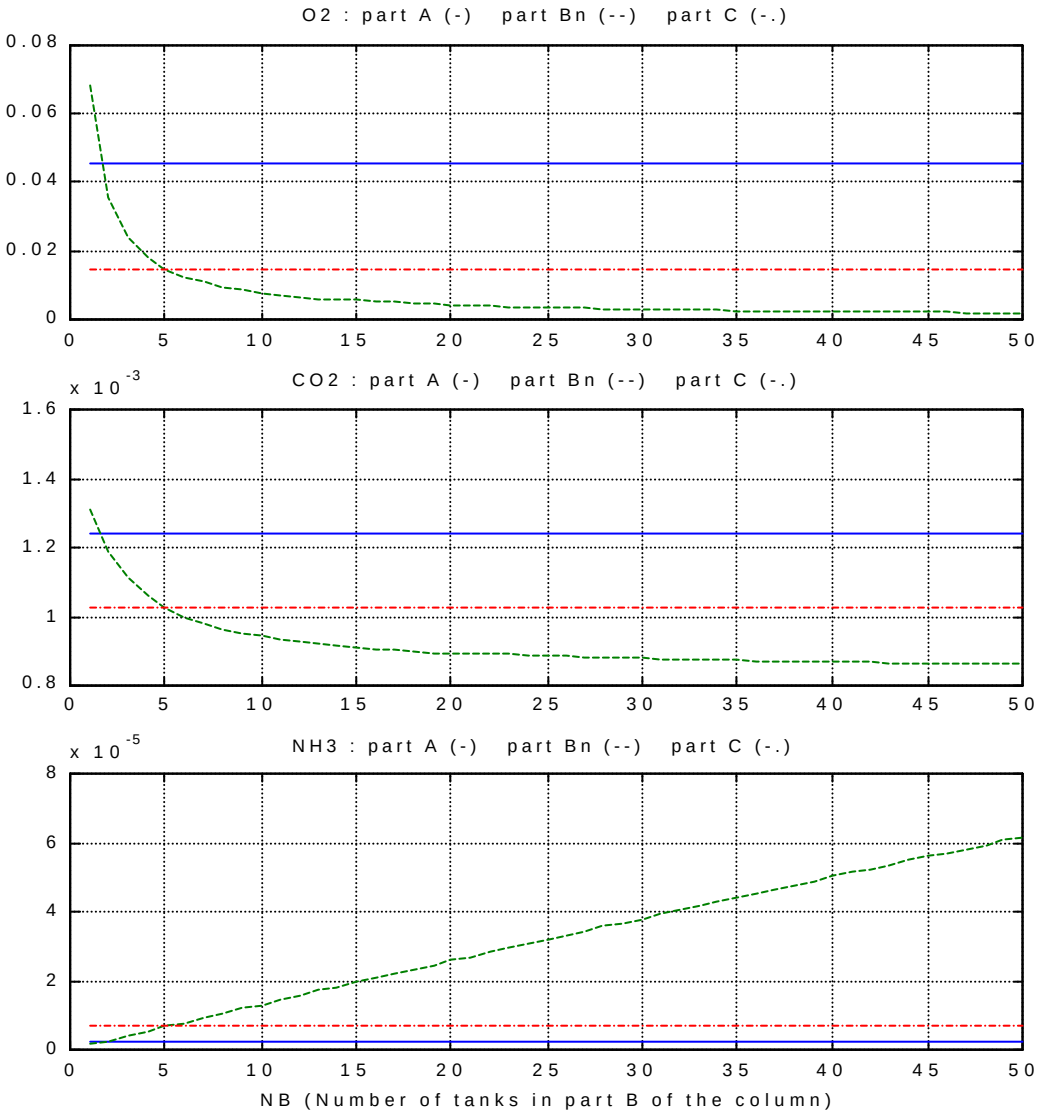

Figure A2.2 : Time constants ratio $\frac{\tau_2}{\tau_1}$

ANNEX 3

```
%*************************************************************
%       Nitrifying column                                    *
%       Version 2.0     April 1999                           *
%                                                            *
%       State system according to TN 44.2                    *
%          . dissociation of CO2 and NH3                     *
%          . column = linear combination of tanks            *
%                                                            *
%       i_sim.m   Initialisation of the simulation           *
%                                                            *
%*************************************************************

 clear all

global NL NG NS NB NX NO
global Ae Be Ce De E
global Gin RG fG Fin RL fL
global KCO2
global NO
global iO2 iNH3 iNO2 iSub iSubO iXNs iXNb iXag
global KlNs KlNb mumax maint Yx Yx1 Ym1

arret = 0;
% Simulation parameters
        tdeb=0;
        tmin=1e-8;
        tmax=.2;
        prec=1e-6;
        tfin=300;
        nbptx=ceil(1.2*tfin/tmin);
        nbptx = 100000;

% Simulation horizon
        dt = .05;        % simulation period of the inputs
        T = [0:dt:tfin]';
        [m,n] = size(T);

% type of test
% ------------
typtst = 5;     titre = 'Impulse response of the column; No biomass; NO2-';
typtst = 7;     titre = 'Input step:NO3-; No biomass; Checking mass balance';
typtst = 9;     titre = 'Input step:NH3 G; No biomass; Checking mass balance';
typtst = 6;     titre = 'Input cst:O2 CO2 NH3 G and L; Growth of biomass';
                %At starting : G/L thermodynamical equilibrium inside the column
                %Incoming G : O2 CO2; incoming L : NH3 HPO4 SO4
typtst = 3;     titre = 'Input cst:O2 CO2 NH3 G and L; Checking the steady state';
typtst = 11;     titre = 'Input step:O2 CO2 NH3 G and L at thermo. equi.; No biomass;
Checking mass balance';
typtst = 8;     titre = 'Input step:NO2-; No biomass; Checking mass balance';
typtst = 12;    titre = 'Input step:CO2 Gas; No biomass; Checking mass balance';
typtst = 1;       titre = 'Input step:O2 CO2 Gas, NH3 L; No biomass; Checking mass
balance';
typtst = 2;     titre = 'Input cst:O2 CO2 NH3 G and L; X0=0';
typtst = 4;     titre = 'Step response of the column with input of SO4 = 10^-4 mol/l';
typtst = 10;    titre = 'Input step:O2 CO2 NH3 G and L; Growth of biomass';
                %At starting : G/L thermodynamical equilibrium inside the column
                %Incoming G : O2 CO2; incoming L : NH3 HPO4 SO4
                %Difference with typtst=6 : no step at starting

% general parameters
% ------------------
```

```
        NL = 4;         % number of mono-phase substrates in the liquid phase
        NG = 3;         % number of bi-phases substrates (in the L and G phases)
        NS = 2;         % number of strains of bacteria (Ns and Nb)
        NX = NG+NL+2*NS;% nb of coef of state vector Xi for any tank
        NO = NX+NG;     % nb of outputs for any tank

% Column parameters
%------------------
        NB = 5;         % number of stirred tanks in part B (fixed bed)
        VA = 1.48;      % volume of part A (l)
        VB = 6.17;      % volume of part B (l)
        VC = 0.45;      % volume of part C (l)
        epsL = .33;     % volume ratio of liquid
        epsG = .04;     % volume ratio of gas

        VnB = VB / NB;  % volume of an equivalent stirred tank
        epsT = epsG + epsL;

        Gin = .03*60;     % incoming gas volumic rate (l/h)
        Fin = .0028*60;   % incoming liq volumic rate (l/h)
        RG = 1*99.0;       % recycling ratio of gas
        RL = 1*6.42;       % recycling ratio of liquid
       %RL = 45/2.8;       % recycling ratio of liquid
        fG = 0;            % ratio of backward flow in a tank (gas phase)
        fL = 0;            % ratio of backward flow in a tank (liquid phase)

% kinetic parameters
% ------------------
        Nls = 4;                        % nb of limiting substrates
        Nis = 2;                        % nb of inhibitory substrates

        %          Ns          Nb
        mumax = [5.7e-2 ;   3.6e-2];    % max specific growth rate (1/h)
        maint = [3.38e-3;   7.92e-3];   % maintenance coeffcient (1/h*(mol/gbio))

        KlNs0 = [5.05e-6           ;    % limiting substrate : O2   (mol/l)
                 6.625e-5         ];    % limiting substrate : NH3  (mol/l)
                %1e-10             ;    % no limitation with HCO3-

        KlNb0 = [           1.7e-5 ;    % limiting substrate : O2   (mol/l)
                            3.6e-4];    % limiting substrate : NO2- (mol/l)
                %           1e-10  ;    % no limitation with HCO3-

        In =    [1e30       1e30   ;    % inhibitory substrate : NO2- (mol/l)
                 1e30       1e30]  ;    % inhibitory substrate : NO3- (mol/l)

                                        % inverse of yield of biosynthesis :
                                        % (mol substr./mol biomass)
        Yx1  =  [-5.4269   -6.5106 ;    % O2
                  -1        -1      ;    % HCO3-
                  -4.5341   -0.1994 ;    % NH3
                  4.3347    -15.1714;    % NO2-
                  0          15.1714;    % NO3-
                  -0.0089   -0.0089 ;    % HPO4--
                  -0.0035   -0.0035];    % SO4--
                % 4.3099    -0.0248 ;    % H+   (unused for simplification)
                % 1          1     ];    % HO-  (unused for simplification)

                                        % inverse of yield of maintenance :
                                        % (mol substr./mol maintenance substr.)
        Ym1  =  [-1.5      -0.5    ;    % O2
```

```
                0          0      ;    % HCO3-
                -1         0      ;    % NH3
                1         -1      ;    % NO2-
                0          1      ;    % NO3-
                0          0      ;    % HPO4--
                0          0     ];    % SO4--

        % change of unit of Yx1 :
        Matom = [12;   1;      16;    14;   32;  31]; %C H O N S P atomik mass
        Scomp = [1     1.6147 .3906 .1994 .0035 .0089]; % stoechio composition
        M_nitri = Scomp*Matom;
        Yx1 = Yx1 / M_nitri; % (mol substrate / g biomass)


        Yx(1,1) = 1/Yx1(3,1);   % yield for (global) growth of Ns (g X/mol NH3)
        Yx(2,1) = 1/Yx1(4,2);   % yield for (global) growth of Nb (g X/mol NO2-)

% gas/liquid transfer parameters
% ------------------------------
        KLa = 1*[51; 51; 500];    % O2 CO2 NH3   (1/h)

% partition coefficients
% ----------------------
        kpartN = [4.599e4; 1853.1; 11.349  ];   % O2 CO2 NH3 (T=303K,non ionic form)
                                                % computed from TN35.1,ADERSA

% dissociation coefficient (for CO2)
% ----------------------------------
        Ka = 4.627e-7;          % at T=303K, from TN 35.1,ADERSA
        KCO2 = Ka / 1e-8;       % [HCO3-] = KCO2 * [CO2]solvated

% dissociation coefficient (for NH3)
% ----------------------------------
        Kb = 1.6916e-5;         % basicity cst at T=303K, from TN 35.1,ADERSA
        Ke = 1.4376e-14;        % ionic product at T=303K, from TN 35.1,ADERSA
        KNH3 = Kb * 1e-8 / Ke;  % [NH4+] = KNH3 * [NH3]solvated

% dissociation coefficient (for H3PO4)
% ------------------------------------
        Ka = 6.166e-8;          % (at T=298K, from TN 27.2,LGCB)
        xx = 1e-8/Ka;   KPO4 = 1+xx;       %[PO4]total = f([HPO4=])

% dissociation vector for the biphase substrates
% ----------------------------------------------
        Kdis = [0; KCO2; KNH3]; % O2  CO2  NH3

% Initialization of constants
%----------------------------
    KlNs = (KlNs0 * ones(1,NB+2))';
    KlNb = (KlNb0 * ones(1,NB+2))';

% initial concentrations in the column
% ------------------------------------
  %1. Gas phase :
        fm_O2_0  = .21;         % O2  (molar fraction)
        fm_CO2_0 = .004;        % CO2 (molar fraction)
        fm_H2O_0 = 4.129e-2;    % H2O (molar fraction)
        C_NH3_t = 7.14e-3;      % NH3 (molar concentration of N total in liquid phase)
    if (typtst == 1 | typtst == 11 | typtst == 12)
        fm_O2_0  = 0;           % O2  (molar fraction)
        fm_CO2_0 = 0;           % CO2 (molar fraction)
```

```
        C_NH3_t = 0;            % NH3 (molar concentration of N total in liquid phase)
    elseif typtst == 2
    elseif typtst == 3
    elseif (typtst == 4 | typtst == 5)
        fm_O2_0  = 0;           % O2  (molar fraction)
        fm_CO2_0 = 0;           % CO2 (molar fraction)
        fm_H2O_0 = 0;           % H2O (molar fraction)
        C_NH3_t = 0;            % NH3 (molar concentration of N total in liquid phase)
    elseif typtst == 6
    elseif (typtst == 7 | typtst == 8 | typtst == 9)
        fm_O2_0  = 0;           % O2  (molar fraction)
        fm_CO2_0 = 0;           % CO2 (molar fraction)
        C_NH3_t = 0;            % NH3 (molar concentration of N total in liquid phase)
    end
    fm_NH3_0 = C_NH3_t/(1+KNH3)*kpartN(3)/55.56;      % NH3 (molar fraction)
    fm_N2_0 = 1 - fm_O2_0 - fm_CO2_0 - fm_NH3_0 - fm_H2O_0;    % N2
    % conc. in gas phase (perfect gases at T=303 K and P=1 atm)
    VM = 22.4 * 303 / 273;  % molar volume (l/mol)
    CN2 = fm_N2_0 / VM;         % mol/l
    CH2O = fm_H2O_0 / VM;       % mol/l
  %2. Liquid phase :
        C_O2_0   = fm_O2_0 / kpartN(1) * 55.56;       % mol/l
        C_CO2_0  = fm_CO2_0/kpartN(2)*55.56;          % mol/l (CO2 solvated)
        C_NH3_0  = C_NH3_t/(1+KNH3);                  % mol/l (NH3 solvated)
        C_NO2_0  = 0;                                 % mol/l
        C_NO3_0  = 0;                                 % mol/l
        C_PO4_0  = 1e-4;                              % mol/l (HPO4--)
        C_SO4_0  = 1e-4;                              % mol/l (SO4--)
        C_XNs_0  = 0;                                 % g/l
        C_XNb_0  = 0;                                 % g/l
    if (typtst == 1 | typtst == 4 | typtst == 5 | typtst == 11 | typtst == 12)
        C_PO4_0  = 0;                                 % mol/l (HPO4--)
        C_SO4_0  = 0;                                 % mol/l (SO4--)
    elseif (typtst == 6 | typtst == 10)
        C_XNs_0  = 2e-2;                              % g/l
        C_XNb_0  = 2e-2;                              % g/l
    elseif (typtst == 7 | typtst == 8 | typtst == 9)
        C_PO4_0  = 0;                                 % mol/l (HPO4--)
        C_SO4_0  = 0;                                 % mol/l (SO4--)
    end

%Temporal input :
%----------------
    CG0 = [fm_O2_0; fm_CO2_0; fm_NH3_0] / VM;        % mol/l
    CL0 = [C_O2_0; C_CO2_0; C_NH3_0; C_NO2_0; C_NO3_0; C_PO4_0; C_SO4_0];
    CX0 = [C_XNs_0; C_XNb_0; C_XNs_0; C_XNb_0];

    if typtst == 1
        CG = [.21; .004; 0]/VM;
        CL = [0; 0; 7.14e-3/(1+KNH3); 0; 0; 0; 0];
    elseif typtst == 2
        CG = CG0;
        CL = [1; 1; 1; 0; 0; 0; 0] .* CL0;
    elseif typtst == 3
        CG = CG0;
        CL = CL0;
    elseif (typtst == 4)
        CG = CG0;
        CL = [0; 0; 0; 0; 0; 0; 1e-4];
    elseif (typtst == 5)
        CG = CG0;
```

```
        CL = [0; 0; 0; 0; 0; 0; 0];
    elseif (typtst == 6 | typtst == 10)
        CG = [1; 1; 0] .* CG0;
        CL = [0; 0; 1; 1; 1; 1; 1] .* CL0;
    elseif typtst == 7
        CG = CG0;
        CL = [0; 0; 0; 0; 1; 0; 0];
    elseif typtst == 8
        CG = CG0;
        CL = [0; 0; 0; 1; 0; 0; 0];
    elseif typtst == 9
        CG = [0; 0; 1];
        CL = [0; 0; 0; 0; 0; 0; 0];
    elseif typtst == 11
        fm_NH3 = 7.14e-3/(1+KNH3)*kpartN(3)/55.56;      % NH3 (molar fraction)
        CG = [.21; .004; fm_NH3]/VM;
        CL = [CG./kpartN*55.56; 0; 0; 0; 0]; % G and L at thermo. equi.
    elseif typtst == 12
        CG = [0; .004; 0]/VM;
        CL = [0; 0; 0; 0; 0; 0; 0];
    end

    dG = ones(size(T))*CG';     % incoming gas [O2,CO2,NH3] conc (mol/l)
    dL = ones(size(T))*CL';       % incoming  liq [O2,CO2,NH3,NO2,NO3,HPO4,SO4]  conc
(mol/l)
    if (typtst ~= 4 & typtst ~= 10)
      t0 = .05;
      ind = find(T<=t0);
      dG(ind,:) = ones(size(ind)) * CG0';
      dL(ind,:) = ones(size(ind)) * CL0';
    end

% Computation of the state system of the nitrifying compartment
%-------------------------------------------------------------
    alpha = kpartN / 55.56 / VM;
    [Ae,Be,Ce,De,E] = statesys(NG, NL, NB, Gin, Fin, RG, RL, fG, fL, ...
                               VA, VnB, VC, epsL, epsG, epsT, ...
                               alpha, Kdis, KLa);

    % saving in order to use the following values in the estimators
    save p_estim NG NL NB Gin Fin RG RL fG fL ...
                 VA VnB VC epsL epsG epsT ...
                 alpha Kdis KLa ...
                 mumax maint Yx1 Ym1 NO NS KlNs KlNb VM

% Initialization of the state vector
%-----------------------------------
        X0 = CL0;
        for ii = 1:NB+1
          X0 = [X0; CL0];
        end
        X0 = [X0; 0; 0; 0; 0];
        for ii = 1:NB
          X0 = [X0; CX0];
        end
        X0 = [X0; 0; 0; 0; 0];

        if typtst == 2
          X0 = 0*X0;
       %elseif typtst == 4 % computation of Impulse Response with SO4
       %  X0(10) = 1/VA/epsL*epsT;
```

```
        elseif typtst == 5 % computation of Impulse Response with NO2
          X0(7) = 1/VA/epsL*epsT;
        end

% Initialization of vector of indices
%-------------------------------------
    iO2  = 1:NG+NL:(NB+1)*(NG+NL)+1; % indices of O2 L in the state vector
    iNH3 = 3:NG+NL:(NB+1)*(NG+NL)+3; % indices of NH3 L in the state vector
    iNO2 = 4:NG+NL:(NB+1)*(NG+NL)+4; % indices of NO2- in the state vector
    iSub = 1:(NG+NL)*(NB+2);         % ind. of subs. in state vector
    iSubO= 1:(2*NG+NL)*(NB+2);       % ind. of subs. in output vector
    iXNs = 1 : 2*NS : 2*NS*(NB+1) + 1;
    iXNs = iXNs + (NG+NL)*(NB+2); % ind. of act. biomass Ns in the state vector
    iXNb = iXNs + 1;              % ind. of act. biomass Nb in the state vector
    iXag = (NG+NL)*(NB+2) + 1 :(NG+NL+2*NS)*(NB+2); % ind. of active and global

        if 0   % printing the following values in a file
         %diary res1
          NB
          ch = '     A       Bn        C'
          VG_c
          VL_c
          tauL_c
          ch = '     O2      CO2       NH3'
          K=KLa'
          k=kpartN'
          Ka = Kdis'
          tau1_A = tau1_c(1,:)
          tau2_A = tau2_c(1,:)
          tau2_tau1_A = tau2_tau1_c(1,:)
          tau1_Bn = tau1_c(2,:)
          tau2_Bn = tau2_c(2,:)
          tau2_tau1_Bn = tau2_tau1_c(2,:)
          tau1_C = tau1_c(3,:)
          tau2_C = tau2_c(3,:)
          tau2_tau1_C = tau2_tau1_c(3,:)
          teta2_A = teta2_c(1,:)
          teta2_tau1_A = teta2_tau1_c(1,:)
          teta2_Bn = teta2_c(2,:)
          teta2_tau1_Bn = teta2_tau1_c(2,:)
          teta2_C = teta2_c(3,:)
          teta2_tau1_C = teta2_tau1_c(3,:)
         %diary off
        end

        % Checking the mass balance
        % 1. Matrices of the stoechio. comp. of the right hand side compounds
        %      C       N       S       P
        MYa = [0       0       0       0       ;        % O2
               1       0       0       0       ;        % CO2
               0       1       0       0      ];        % NH3

        %      C       N       S       P
        MYb = [0       0       0       0       ;        % O2
               1       0       0       0       ;        % CO2
               0       1       0       0       ;        % NH3
               0       1       0       0       ;        % NO2
               0       1       0       0       ;        % NO3
               0       0       0       1       ;        % HPO4
               0       0       1       0      ];        % SO4
```

```
        %      C       N       S       P
        MYx = [1       .1994   .0035   .0089   ;        % biomass Ns
               1       .1994   .0035   .0089  ];        % biomass Nb

        % 2. matrices of volume of tanks
        Vg = [ VA*epsG/epsT;
               VnB*epsG*ones(NB,1);
               VC*epsG/epsT];
        Vl = [ VA*epsL/epsT;
               VnB*epsL*ones(NB,1);
               VC*epsL/epsT];


if arret
% break
end
disp(' *** End of initialization ***')
```

```
%************************************************************
%       Nitrifying column                                   *
%       Version 2.0     April 1999                          *
%                                                           *
%       State system according to TN 44.2                   *
%                                                           *
%       column.m : Computation of the derivative vector     *
%                                and output vector          *
%                                                           *
%************************************************************

  function [sys,x0]=column(tn,x,u,flag,X0)

% COLUMN        S-Function for simulation of the nitrifying column
%
% Synopsis
%       [sys,x0]=column(tn,x,u,flag,X0)
%
% Parameters
%       X0      initial state vector
%
% State vector x
%       Length of the state vector : NX * (NB + 2)
%         with : NX = NG + NL + 2*NS
%                NG = number of bi-phases substrates (present in Gas and Liquid)
%                NL = number of mono-phase substrates (present in Liquid only)
%                NS = number of strains (Nitrosomonas and Nitrobacter)
%                NB = number of equivalent tanks in part B of the column
%                NE = NG + NL
%                NU = NE * (NB + 2)
%       The state vector is composed of the concentrations of the compounds
%       of the column in liquid phase only.
%       Indices of the compounds in the state vector :
%         For a tank i (i between 1 and NB+2)
%         Indice                          Compound
%         (i-1)*NE + 1                    O2    in Liquid phase
%         (i-1)*NE + 2                    CO2   in Liquid phase
%         (i-1)*NE + NG                   NH3   in Liquid phase
%         (i-1)*NE + NG + 1               NO2
%         (i-1)*NE + NG + 2               NO3
%         (i-1)*NE + NG + 3               HPO4
%         (i-1)*NE + NG + NL              SO4
%         NU + 2*(i-1)*NS + 1             Xv_Ns  active Nitrosomonas biomass
%         NU + 2*(i-1)*NS + NS            Xv_Nb  active Nitrobacter biomass
%         NU + 2*(i-1)*NS + NS + 1        Xt_Ns  global Nitrosomonas biomass
%         NU + 2*(i-1)*NS + NS + NS       Xt_Nb  global Nitrobacter biomass
% Inputs
%       The input vector is composed of the concentrations of the compounds
```

```
%       of the incoming liquid and gas flows.
%       Indices of the compounds in the inputs vector :
%         Indice     Compound
%         1          O2    in the incoming gas flow (flow rate : Gin)
%         2          CO2   in the incoming gas flow (flow rate : Gin)
%         3          NH3   in the incoming gas flow (flow rate : Gin)
%         NG + 1     O2    in the incoming liquid flow (flow rate : Fin)
%         NG + 2     CO2   in the incoming liquid flow (flow rate : Fin)
%         NG + 3     NH3   in the incoming liquid flow (flow rate : Fin)
%         2*NG + 1   NO2   in the incoming liquid flow (flow rate : Fin)
%         2*NG + 2   NO3   in the incoming liquid flow (flow rate : Fin)
%         2*NG + 3   HPO4  in the incoming liquid flow (flow rate : Fin)
%         2*NG + 4   SO4   in the incoming liquid flow (flow rate : Fin)
%
% Outputs
%       The state vector is composed of the concentrations of the compounds
%       of the column in gas and liquid phases.
%       Indices of the compounds in the state vector :
%         For a tank i (i between 1 and NB+2)
%         Indice                          Compound
%         (i-1)*NE + 1                    O2    in Gas phase
%         (i-1)*NE + 2                    CO2   in Gas phase
%         (i-1)*NE + 3                    NH3   in Gas phase
%         (i-1)*NE + NG + 1               O2    in Liquid phase
%         (i-1)*NE + NG + 2               CO2   in Liquid phase
%         (i-1)*NE + NG + 3               NH3   in Liquid phase
%         (i-1)*NE + 2*NG + 1             NO2
%         (i-1)*NE + 2*NG + 2             NO3
%         (i-1)*NE + 2*NG + 3             HPO4
%         (i-1)*NE + 2*NG + 4             SO4
%         NU + 2*(i-1)*NS + 1             Xa_Ns  active Nitrosomonas biomass
%         NU + 2*(i-1)*NS + 2             Xa_Nb  active Nitrobacter biomass
%         NU + 2*(i-1)*NS + NS + 1        Xg_Ns  global Nitrosomonas biomass
%         NU + 2*(i-1)*NS + NS + 2        Xg_Nb  global Nitrobacter biomass
%

global NL NG NS NB NX NO
global Ae Be Ce De E
global iO2 iNH3 iNO2 iSub iSubO iXNs iXNb iXag
global KlNs KlNb mumax maint Yx Yx1 Ym1

%> Sizes array and Initial conditions ----------------------------------------
if flag==0,
   NI = 2*NG+NL;
   sys = [
        NX*(NB+2)   % continuous states
        0           % discrete states
        NO*(NB+2)   % outputs
        NI          % inputs
        0           % discontinuous ...
        0           % direct feedthrough
        ];
   x0 = [X0];


%> Continuous state (computation of derivatives) -----------------------------
elseif abs(flag)==1,
  % The concentrations cannot be negative
    ind = find(x<0);
    x(ind) = zeros(size(ind));
```

```
  % Computation of the matrix J (notation of TN 44.2)
  %--------------------------------------------------
    [mui,mai,rmu] = irate(x,iO2,iNH3,iNO2,KlNs,KlNb,mumax,maint);
    dim = NG+NL;
    J = zeros(dim*(NB+2),NS*(NB+2));
    ind1 = 1:dim;
    ind2 = 1:NS;
    for ii = 1:NB+2
      Ji = Yx1*diag(mui(:,ii)) + Ym1*diag(mai(:,ii));
      J(ind1,ind2) = Ji;
      ind1 = ind1 + dim;
      ind2 = ind2 + NS;
    end

  % Computation of growth rate of active and global biomass
  %--------------------------------------------------------
    mua = mui + diag(maint.*Yx) * (1-rmu); % specific growth rate of active bio.
    Cx = [x(iXNs)'; x(iXNb)'];  % concentration of active biomass Ns and Nb
    rX = mua .* Cx;  % growth rate of active biomass Ns and Nb
    rg = mui .* Cx;  % growth rate of global (active + decay) biomass Ns and Nb

  % Computation of the derivative of the state vector
  %--------------------------------------------------
    % subtrates :
    Cx = reshape(Cx,NS*(NB+2),1);
    sys(iSub) = Ae*x(iSub) + Be*u + E*J*Cx;

    % active and global biomass :
    sys(iXag) = reshape([rX; rg],2*NS*(NB+2),1);

%> Outputs ------------------------------------------------------------------
elseif flag==3,
  % The concentrations cannot be negative
    ind = find(x<0);
    x(ind) = zeros(size(ind));

  % Computation of the output vector
  %---------------------------------
    % subtrates :
    sys(iSubO) = Ce * x(iSub) + De * u;

    % active and global biomass :
    ind = (NG+NL)*(NB+2) + 1 :(NG+NL+2*NS)*(NB+2);
    sys(ind + NG*(NB+2)) = x(ind);

%> ------------------------------------------------------------------------
else
   sys = [];
end
```

```
%*********************************************************************
%       Nitrifying column and Estimators                             *
%       Version 2.0     April 1999                                   *
%                                                                    *
%       State system according to TN 44.2                            *
%                                                                    *
%                                                                    *
%       irate.m : instantaneous rate of production of substrates     *
%                                                                    *
%*********************************************************************

function [mui,mai,rmu] = irate(x,iO2,iNH3,iNO2,KlNs,KlNb,mumax,maint)

% x   : state vector
% mui : limited specific growth rate of active biomass Ns or Nb for each tank
% mai : limited specific maintenance rate of active bio. Ns or Nb for each tank



  % Computation of rmu = mu/mumax :
  x1 = x(iO2).*x(iNH3);
  x2 = x(iO2).*x(iNO2);
  a1 = x1 ./ (KlNs(:,1) + x(iO2)) ./ (KlNs(:,2) + x(iNH3));
  a2 = x2 ./ (KlNb(:,1) + x(iO2)) ./ (KlNb(:,2) + x(iNO2));
  rmu = [a1, a2]';

  % Computation of the limited specific global growth rate 'mui'
  mui = diag(mumax) * rmu;

  % Computation of the limited specific maintenance rate 'mai'
  Klim = [x1' > 0; x2' > 0];
  mai = diag(maint) * Klim;
```

```
%*****************************************************************
%       Nitrifying column and Estimators                         *
%       Version 2.0     April 1999                               *
%                                                                *
%       State system according to TN 44.2                        *
%          . dissociation of CO2 and NH3                         *
%          . column = linear combination of tanks                *
%                                                                *
%       statesys.m : Computation of the state system of the column *
%                                                                *
%*****************************************************************

function [Ae,Be,Ce,De,E] = statesys(NG, NL, NB, Gin, Fin, RG, RL, fG, fL, ...
                                    VA, VnB, VC, epsL, epsG, epsT, ...
                                    alpha, Kdis, KLa)


for ii = 1:3  % for the differents parts of the column
  if ii == 1        % Part A of the column
    VL = VA*epsL/epsT;    % volume of liquid
    VG = VA*epsG/epsT;    % volume of gas
    qL = Fin * (1+RL) * (1+fL);
    qG = Gin * (1+RG) * (1+fG);
  elseif ii == 2    % Tank n of the part B of the column
    VL = VnB*epsL;        % volume of liquid
    VG = VnB*epsG;        % volume of gas
    qL = Fin * (1+RL) * (1+2*fL);
    qG = Gin * (1+RG) * (1+2*fG);
  elseif ii == 3    % Part C of the column
    VL = VC*epsL/epsT;    % volume of liquid
    VG = VC*epsG/epsT;    % volume of gas
```

```
  qL = Fin * (1+RL) * (1+fL);
  qG = Gin * (1+RG) * (1+fG);
end

tauL1 = qL/VL * ones(NL,1);                    % inverse of tauL
if NG == 0    % case of the nitrite estimator
  As = -tauL1;
  Bs = tauL1;
  Cs = 1;
  Ds = 0;
  Es = 1;
else          % case of the column and biomass estimator
  % Computation of teta1 teta2 beta1 beta2
  den1 = VL*KLa + qL*(1+Kdis);
  den2 = VL*(KLa ./ alpha) + qG;
  teta1 = VL * (1+Kdis) ./ den1;
  teta2 = VG ./ den2;
  alpha1 = VL * KLa ./ alpha ./ den1;
  alpha2 = VL ./ den1;
  alpha3 = qL * (1+Kdis) ./ den1;
  alpha4 = VL * (KLa ./ den2);
  alpha5 = qG ./ den2;
  den3 = 1 - alpha1 .* alpha4;
  beta1 = (teta1 + teta2) ./ den3;
  beta2 = (teta1 .* teta2) ./ den3;

  xx = zeros(2,NG);
  for jj = 1:NG
    % for column    : jj = [1 2 3] --> O2  CO2  NH3
    % for estimator : jj = [1]     -->          NH3
    xx(:,jj) = roots([1 beta1(jj)/beta2(jj) 1/beta2(jj)]);
    taux(:,jj) = -1 ./ xx(:,jj);  % time const. of bi-phasis compound jj
  end
  if ~all((taux(1,:) ./ taux(2,:)) < .07)
    message = 'The approximation of first order is not justified.';
    message = [message ' Loop : ' num2str(ii)]
    tau2_tau1 = taux(1,:) ./ taux(2,:)
    arret = 1;
  end
  tau = taux(2,:)';

  if ~all((teta2 ./ tau) < .07)
    message = 'The approximation of first order is not justified.';
    message = [message ' Loop : ' num2str(ii)]
    teta2_tau1 = (teta2 ./ tau)'
    arret = 1;
  end
  G1 = alpha3 ./ den3;                          % Gain of b/dL
  G2 = alpha1 .* alpha5 ./ den3;                % Gain of b/dG
  G3 = alpha2 ./ den3;                          % Gain of b/r
  Gp1 = alpha4 .* G1;                           % Gain of a/dL
  Gp2 = alpha4 .* G2 + alpha5;                  % Gain of a/dG
  Gp3 = alpha4 .* G3;                           % Gain of a/r
  As = [
        -diag(1./tau), zeros(NG,NL);
        zeros(NL,NG),  -diag(tauL1)];
  Bs = [
        diag(G2./tau), diag(G1./tau), zeros(NG,NL);
        zeros(NL,NG),  zeros(NL,NG),  diag(tauL1) ];
  Cs = [
        diag(alpha4),  zeros(NG,NL);
```

```
          eye(NG),       zeros(NG,NL);
          zeros(NL,NG),  eye(NL)     ];

    Ds =  diag([alpha5; zeros(NG + NL,1)]);

    Es =  diag([G3./tau; ones(NL,1)]);
  end

% 1. matrices for each tank of the column
%----------------------------------------
  if ii == 1        % Part A of the column
    AA2 = As;      BA2 = Bs;
    CA2 = Cs;      DA2 = Ds;      EA2 = Es;
  elseif ii == 2    % Tank n of the part B of the column
    AB2 = As;      BB2 = Bs;
    CB2 = Cs;      DB2 = Ds;      EB2 = Es;
  elseif ii == 3    % Part C of the column
    AC2 = As;      BC2 = Bs;
    CC2 = Cs;      DC2 = Ds;      EC2 = Es;
  end
end

% 2. Matrices of the equivalent state system
%-------------------------------------------
  dim1 = NG+NL;
  dim2 = 2*NG+NL;
  A = zeros(dim1*(NB+2));
  B = zeros(dim1*(NB+2), dim2*(NB+2));
  C = zeros(dim2*(NB+2), dim1*(NB+2));
  D = zeros(dim2*(NB+2));
  E = zeros(dim1*(NB+2));
  ind1 = 1:dim1;
  ind2 = 1:dim2;
  A(ind1,ind1) = AA2;
  B(ind1,ind2) = BA2;
  C(ind2,ind1) = CA2;
  D(ind2,ind2) = DA2;
  E(ind1,ind1) = EA2;
  for ii = 2:NB+1
    ind1 = ind1 + dim1;
    ind2 = ind2 + dim2;
    A(ind1,ind1) = AB2;
    B(ind1,ind2) = BB2;
    C(ind2,ind1) = CB2;
    D(ind2,ind2) = DB2;
    E(ind1,ind1) = EB2;
  end
  ind1 = ind1 + dim1;
  ind2 = ind2 + dim2;
  A(ind1,ind1) = AC2;
  B(ind1,ind2) = BC2;
  C(ind2,ind1) = CC2;
  D(ind2,ind2) = DC2;
  E(ind1,ind1) = EC2;

  v1 = -[fG*ones(1,NG),fL*ones(1,NG+NL)];
  v2 = -[(1+fG)*ones(1,NG),(1+fL)*ones(1,NG+NL)];
  v3 = -[fG*(1+RG)*ones(1,NG),fL*(1+RL)*ones(1,NG+NL)];
  v4 = v2;
  for ii = 2:NB+1
    v3 = [v3, v1];
```

```
    v4 = [v4, v2];
  end
  G = diag(v3,(2*NG+NL)) + diag(v4,-(2*NG+NL));
  v1 = -[RG*ones(1,NG),RL*ones(1,NG+NL)];
  G(1:(2*NG+NL),(2*NG+NL)*(NB+1)+1:(2*NG+NL)*(NB+2)) = diag(v1);
  G((2*NG+NL)*(NB+1)+1:(2*NG+NL)*(NB+2),(2*NG+NL)*NB+1:(2*NG+NL)*(NB+1))      =      -
eye((2*NG+NL));

  v1 = [(1+2*fG)*ones(1,NG),(1+2*fL)*ones(1,NG+NL)];
  v2 = [(1+fG)*(1+RG)*ones(1,NG),(1+fL)*(1+RL)*ones(1,NG+NL)];
  for ii = 2:NB+1
    v2 = [v2, v1];
  end
  v2 = [v2, ones(1,(2*NG+NL))];
  H = diag(v2);

  Z1 = G*D + H;
  Z2 = (Z1'\B')'; % more precise than B/Z1 (accord. to Matlab doc)
  Z3 = (Z1'\D')'; % more precise than D/Z1 (accord. to Matlab doc)
  Z4 = G*C;
  Ae = A - Z2*Z4;
  Ce = C - Z3*Z4;
  Be = Z2(:,1:2*NG+NL);
  De = Z3(:,1:2*NG+NL);
```