Modeling and Simulation of the Ammonia Synthesis Column

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Abstract: - The paper presents the possibilities of simulation of steady and dynamic regimes for ammonia synthesis columns. We present the possibilities of study of the dynamic regimes for automatic control of the temperature in catalyst layers and propose an advanced control structure using the fresh gas flows between catalyst layers as commands. We also present the possibilities of optimization of the column steady states to obtain a higher conversion factor using the control of gas flows between the catalyst layers. This optimization algorithm is part of the main advanced control program for the synthesis column.

Key-Words: - Advanced control system, modeling, simulation, ammonia plant synthesis

INTRODUCTION

Ammonia synthesis is the first stage in the manufacturing of nitrous chemical products (fertilizers, plastics, explosives, etc.). The direct synthesis process, from basic gases (hydrogen and nitrogen) needs a theoretical and experimental study of the synthesis installation, in order to determine the optimum working regimes. This is determined by:

1. The direct synthesis reaction $N_2 + H_2 = NH_3$ is a reversible exothermic reaction which must take place at equilibrium to get a maximum conversion rate.
2. The conversion rate depends of a series of technological factors, the most important being: temperature (the temperature increase leads to ammonia decomposition, thus leading to conversion rate decrease), catalyst activity (which is decreasing in time because of catalyst exhausting) and pressure. The maximum ammonia concentration that can be obtained is between 14% and 22% and depends of the pressure and the temperature.
3. The synthesis columns are built with fixed catalyst layer and there is no possibility to control the temperature inside the catalyst layer. To compensate this inconvenience, the columns are built with multiple catalyst layers (Kellog process), offering the possibility of introduction of cold gas between the layers in order to reduce the temperature and ammonia concentration at the input into the next layer, thus increasing the quantity of produced ammonia and the conversion rate.
4. The catalyst is spent non-uniform, starting with the first layer. Controlling the injection flows on each layer leads to efficient use of the catalyst, increasing the conversion rate on ending layers while the beginning layers are exhausted, thus increasing the quantity of produced ammonia and the conversion rate.
5. The real catalyst activity can be different from the manufacturer specifications. Using optimizing software based on real process measurements, the real catalyst activity value can be determined and further used for control.

Therefore, his paper tries to solve the following problems:
- The development of simplified models and programs for the column working regimes:
- The modeling of the steady states considering the variations of the concentration and temperature along the catalyst layers (the variation against the spatial coordinate).
- The development of optimization procedures for the steady states, using as optimization criteria the maximum final conversion rate, and the calculation of optimum cold gas flows to be injected between layers.
- The modeling of the dynamic regimes considering the catalyst layers as a lumped parameter system and developing real time control software for the control of temperatures and cooling flows.
- The development of fault detection and correction algorithms (actuator blocking, malfunctioning of temperature sensors) and control algorithms in fault conditions for the column during the repair periods.

COLUMN MODELING AND SIMULATION IN DYNAMIC REGIME

One of industrial procedures to obtain ammonia (NH3) from components, nitrogen (N2) and hydrogen (H2) takes place at medium pressure (p=150 bar) in a multi-layer synthesis column (usually four layers). The column structure is presented in figure 1.
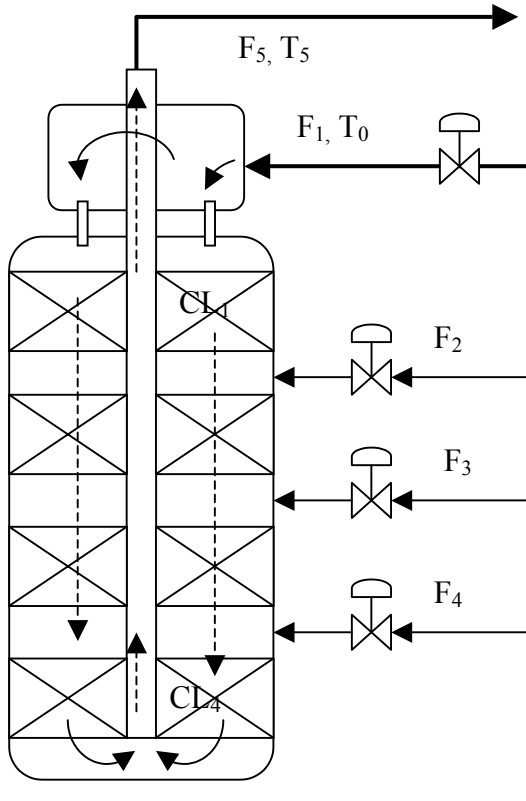

Fig. 1. Synthesis column

The main feed of the synthesis column consist of flow F1, at a temperature T0 of 290-300 degree Celsius, that is preheated to 400 degree Celsius in the heat exchanger located at the column entrance. The synthesis reaction that takes place in the catalyst layers is highly exothermic. Thus, through flows F2, F3, and F4 introduced between catalyst layers at a temperature T0, we get the following:
-direct gas cooling between catalyst layers in order to maintain the optimum reaction parameters in the new layer;
-reduction of the ammonia concentration in the gas mixture (H_2, N_2, CH_4, NH_3) below the equilibrium value, in order to allow the ammonia production increase per production unit.

Ammonia is the primary feedstock for the nitrogenous fertilizer industry. Many of ammonia technology companies (for ex. Kellogg Brown & Root, Romanian Chemical Industry) develop strong research activities in the direction of engineering, construction, training, control, operating and maintenance services.

This paper try to develop a control strategy for realize a maximum conversion of reactants can be obtained, for given status and functional parameters at the reactor entrance and for fixed geometry of catalyst systems. During operation perturbing factors can appear, which necessitate the use of advanced control structures and appropriate control algorithms.

From the analysis of the technological flow, we can obtain the block diagram of the ammonia synthesis column that is shown in figure 2.

In order to obtain a simpler dynamic model for the synthesis column, the column was decomposed in eight functional blocks. For each block we can write the mass balance equations for nitrogen and hydrogen and the thermal balance equation for the gas mix. We are taking into consideration the reaction speeds that depend of the working temperature and pressure in each layer zone. The coefficients appearing in the equations can be determined partly using the relations from literature and partly from measurements in the real installations. Finally, after coefficient correction and model validation, we obtain the following model for the synthesis column:

a) Heat Exchanger:

$$\frac{dT_{a1}}{dt} = \frac{F_j}{1000}(c_{p0}T_0 - c_a T_{a1}) + 5.0392(T_4 - T_{a1})$$

(1)

b) Catalyst layer j

$$\frac{dx_{aj}}{dt} = \frac{F_j}{1000}c_j(x_{a0} - x_{aj}) + \frac{F_{Rj}}{1000}c_j(x_{a0} - x_{aj}) + c_{Rj}K_{Tj}(T_j)V_{Rj}(x_{aj},x_{bj})$$

(2)

$$\frac{dx_{bj}}{dt} = \frac{F_j}{1000}c_j(x_{b0} - x_{bj}) + \frac{F_{Rj}}{1000}c_j(x_{b0} - x_{bj}) + c_{Rj}K_{Tj}(T_j)V_{Rj}(x_{aj},x_{bj})$$

(3)

$$\frac{dT_j}{dt} = \frac{F_j}{1000}(c_{aj}T_{aj} - c_{pj}T_j) - H_{Rj}K_{Tj}(T_j)V_{Rj}(x_{aj},x_{bj})$$

(4)
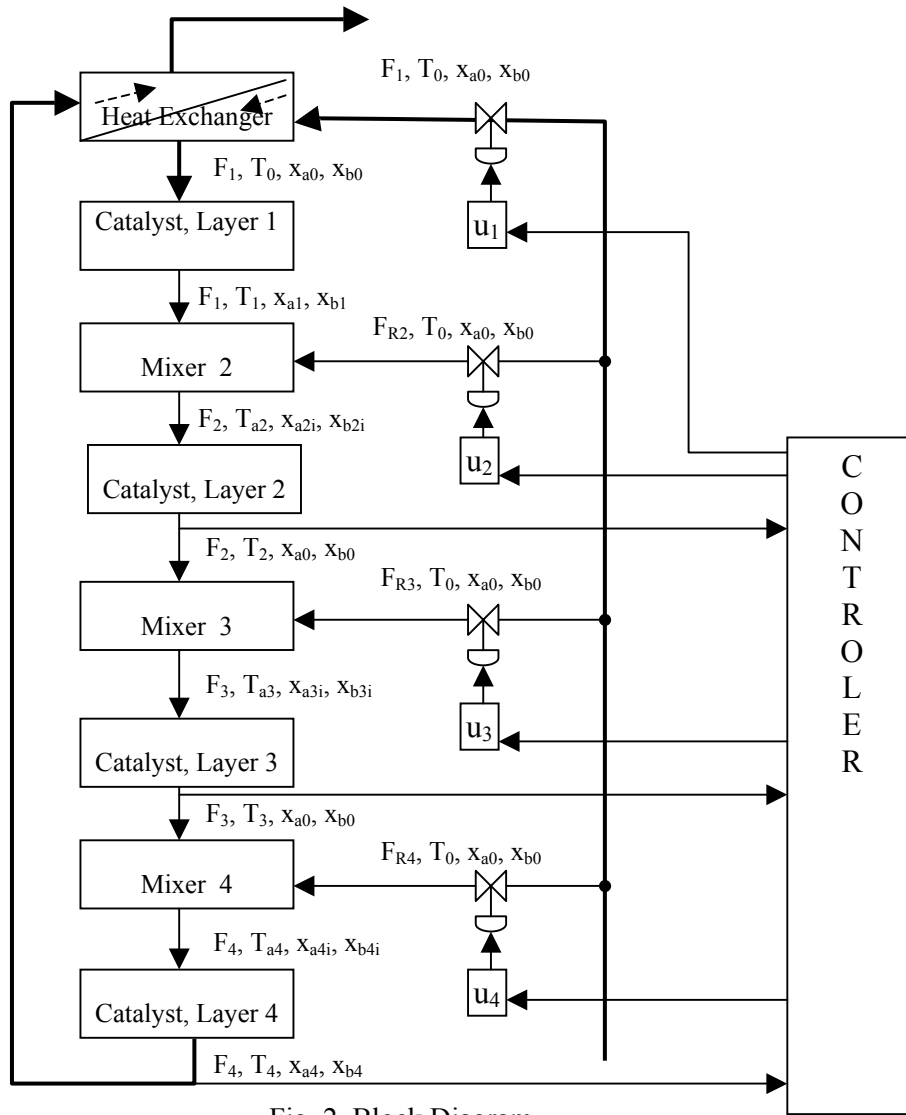
Fig. 2. Block Diagram

c) Mixer j

$$\frac{dT_{aj}}{dt} = \frac{F_{j-1}}{1000}(c_{pj-1}T_{pj-1} - c_{pj}T_j) + \\ + \frac{F_{Rj}}{1000}(c_{p0}T_0 - c_{pj}T_j) \tag{5}$$

$$V_{Rj} = 0,9x_{aj}\left[\frac{x_{bj}^3}{(0.60648 - x_{aj} - x_{bj})^2}\right]^{0,521} - \\ \left[\frac{(0.60648 - x_{aj} - x_{bj})^2}{x_{bj}^3}\right]^{0,479} \tag{6}$$

$$K_{Tj} = \exp\left(27.751 - \frac{25107.7}{T_j}\right) \tag{7}$$

were:

- $j = \overline{1,4}$ $F_{R1}=0$, $F_1 = 18860$ Kmol/h, $F_j = F_{j-1} + F_{Rj}$;
- c_j, c_{p0}, c_{p1}, c_{pj} are thermal and mass coefficients,
- T_j (j=1…4) are temperatures in the catalyst layer j

- T_{aj} (j=1…4) are temperatures at the output of the mixer j
- x_{aj}, x_{bj} are the concentrations of the nitrogen and hydrogen on the layer j

$F_2=F_1+F_{R2}$; $F_3=F_1+F_{R1}+F_{R2}$; $F_4=F_1+F_{R1}+F_{R2}+F_{R3}$;

The coefficient values are presented in Annex, table 1. The mathematical model of the synthesis column given by equations (1-7) was implemented in Matlab in order to study the column operation in dynamic regime, to determine the sensitivity of the commands u_1-u_4 (see fig. 2) reported to column parameters and the allowed ranges for commands and to determine the temperature ranges in the column for temperature sensors design.

Because of the high cost of the gas concentration sensors, temperature sensors mounted inside the catalyst layers and mixing areas are used to provide feedback for the control algorithms.

OPTIMIZATION PROCEDURES FOR THE MAXIMUM FINAL CONVERSION RATE

In order to obtain maximum conversion rate of nitrogen and hydrogen into ammonia, we must determine the optimum cooling flows between the catalyst layers and working temperatures in the column. Advanced control algorithms determine these parameters periodically or on demand, using an optimization algorithm.

The optimization algorithm is based on following hypotheses:

-The equivalent reactor for each layer is considered adiabatic;

-The catalytic reactions are taking place in quasi-homogenous layers;

-The gas cooling is considered instantaneous compared with the mass and heat transfer inside the catalyst layer;

-The gas flow through the catalyst layer can be approximated by a traveling model;

-Pressure losses on catalyst layers are negligible;

In steady state, for each catalyst layer we can define the mathematical model of the process:

a) Conversion rate

$$\frac{dx_{aj}}{dz} = \frac{S}{F_{MN0}} V_{Raj} \qquad (8)$$

b) Heat accumulation inside the gas mix and catalyst

$$\frac{dT_j}{dz} = -\frac{S}{F_M c_p}(-\Delta H_{Ra})V_{Raj} \qquad (9)$$

where: x_{Ai} = conversion rate on layer j, T_j = temperature on layer j, F_{mn0} =nitrogen molar flow at the reactor entrance, c_p = molar specific heat of the synthesis gas, V_{Raj} = reaction speed, DH_{Ra}=reaction enthalpy (depends on T).

The reaction speed can be represented as a function of catalyst used and reactants (NH3, N2, H2) concentrations in real and equilibrium conditions (Tempkin-Pijev model).

$$V_{Raj} = \frac{K_{tj}(T)}{\sqrt{p}}\left[\frac{y_{NH_3}^{*2}}{y_{H_2}^{*3} y_{N_2}^{*}} \frac{y_{H_2}^{1.5} y_{N_2}}{y_{NH_3}} - \frac{y_{NH_3}}{y_{H_2}^{1.5}} \right] \qquad (10)$$

Equilibrium concentrations and constants can be represented as a function of equilibrium conversion rate x_c and fugacity coefficients for N_2, H_2 and NH_3. Eventually we obtain an algebraic equation that gives us the equilibrium conversion rate:

$$a_2 x_e^2 - 2a_1 x_e + a_0 = 0 \qquad (11)$$

The real solutions of the equation represent the maximum possible value for the conversion rate. At the entrance in the new catalyst layer we determine the conversion rate:

$$x_j = \frac{x_{ej-1}F_{10}}{F_{10} + \sum_{i=}^{j} F_{Ri}} \qquad (12)$$

and temperature

$$T_j = \frac{F_m c_{pm} T_{ej-1} + F_{Ra}c_{pj}T_1}{(F_m + F_{Ra})c_p} \qquad (13)$$

Relations (8-13) can be integrated using initial conditions x=0 and $T_{i0}=T_1$ and we can obtain the optimum flow Fi and temperatures at the entrance of each layer: F_{R2}=3000Kmol/h, F_{R3}=1900 Kmol/h, F_{R4}=600 Kmol/h, T_2=717 K, T_3=734 K, T_4=753 K and the final conversion is $X_A = 0.221$.

In figure 3 is presented the dependence between the conversion rate and temperature for each layer.

ADVANCED CONTROL OF SYNTHESIS COLUMNS IN FAULT CONDITIONS

In figure 2 is presented the block diagram of the advanced control system for the synthesis column. The system provides the temperature and cooling flow control, based on optimum values provided by the optimization block.

This strategy uses the flows F1 to F4 to get a maximum conversion rate and a maximum production for normal working conditions. Also, these flows can be used in the case of a temporary fault of the main feed (actuator fault for the flow F1) or in the case of catalyst exhaustion for the first or second layer.

For advanced control, the conventional control of the ammonia synthesis column at the Kellogg ammonia plant from Craiova was replaced with numeric control (DCS and PLS), using a hierarchical distributed control structure. Beside the standard software, new software was developed to monitor and optimize the synthesis process.

The program structure for advanced control of the synthesis column is presented in figure 4.

Periodically, during operation, the optimal procedure is called to compute the optimal flows F1 to F4 and optimal temperatures at the entrance and exit of every layer, using the current data from the process (temperatures, pressures, gas composition).
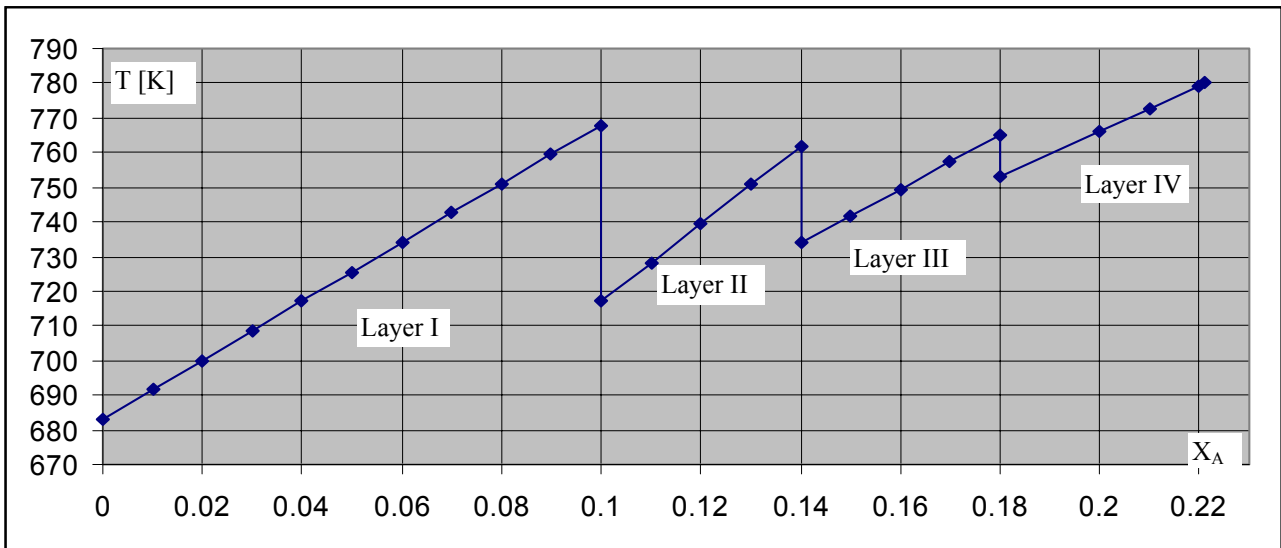
Fig. 3. Evolution of conversion rate and temperature for each layer

For the first stage, we ran a computer simulation of the system, using mathematical models, based on termochemical kinetics and data for the actual catalyst used in the process. The results were very closed to the real data obtained from the process. In fig. 3 is represented the diagram of the temperatures and concentrations for each catalyst layer. The program allowed the simulation of different fault conditions as actuators blocking and allowed the
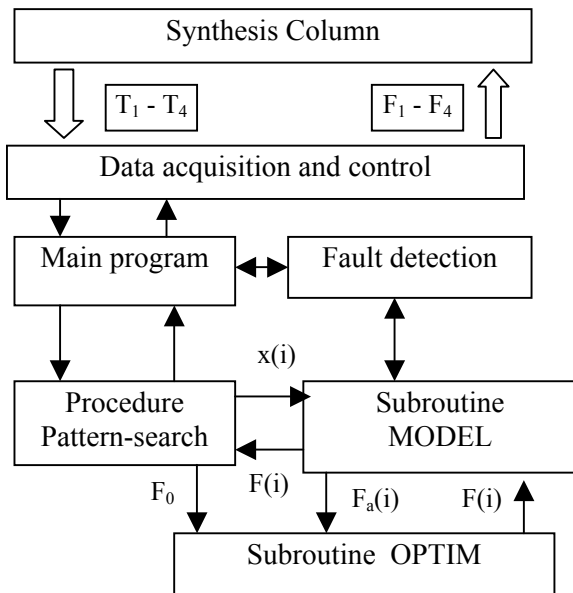

Fig. 4. Control structure

development of control strategies for the synthesis column using the other available flows. The conversion rate can be maintained, in certain conditions, close to the normal but the ammonia production decreases with 25%.

The operating logs for some ammonia column from the ammonia plants have revealed a series of faults that can appear in the equipment or in the control structure:

-Blocking or hysteresis operation of actuators for layer flows F_1, F_2, F_3 and F_4.

-Improper preheated synthesis gas or improper pressure control in the compressor zone that can lead to important changes in hot gas temperature T_i or flow F_i.

-Changes of the heat transfer coefficients caused by build up inside or outside the superheater's pipes and coils.

It is necessary to highlight the action channels for these possible faults and the measurable outputs of the process that are directly and faster modified by these perturbations. Using the equations (1 - 5) we can develop the block diagram presented in figure 5. We can define the pairs that represent the direct channels fault-perturbed output: (F_2-T_2, F_3-T_3) and remains available the pair (T_i-T_1) even T_i can also modify simultaneously T_2 and T_3. The perturbations in synthesis system (T_i and F_i) can also modify T_1. Accordingly we can define the error vector DE as a matrix function of fault vector DE.

$$DE = \begin{bmatrix} T_{2p} - T_{2m} \\ T_{3p} - T_{3m} \\ T_{1p} - T_{1m} \end{bmatrix} = F\left(\begin{bmatrix} F_2 \\ F_3 \\ T_i \end{bmatrix} \right) \qquad (14)$$

Applying the analytical method principles presented [5, 6] we will obtain the block diagram, presented in fig. 5, that was verified throw simulation.
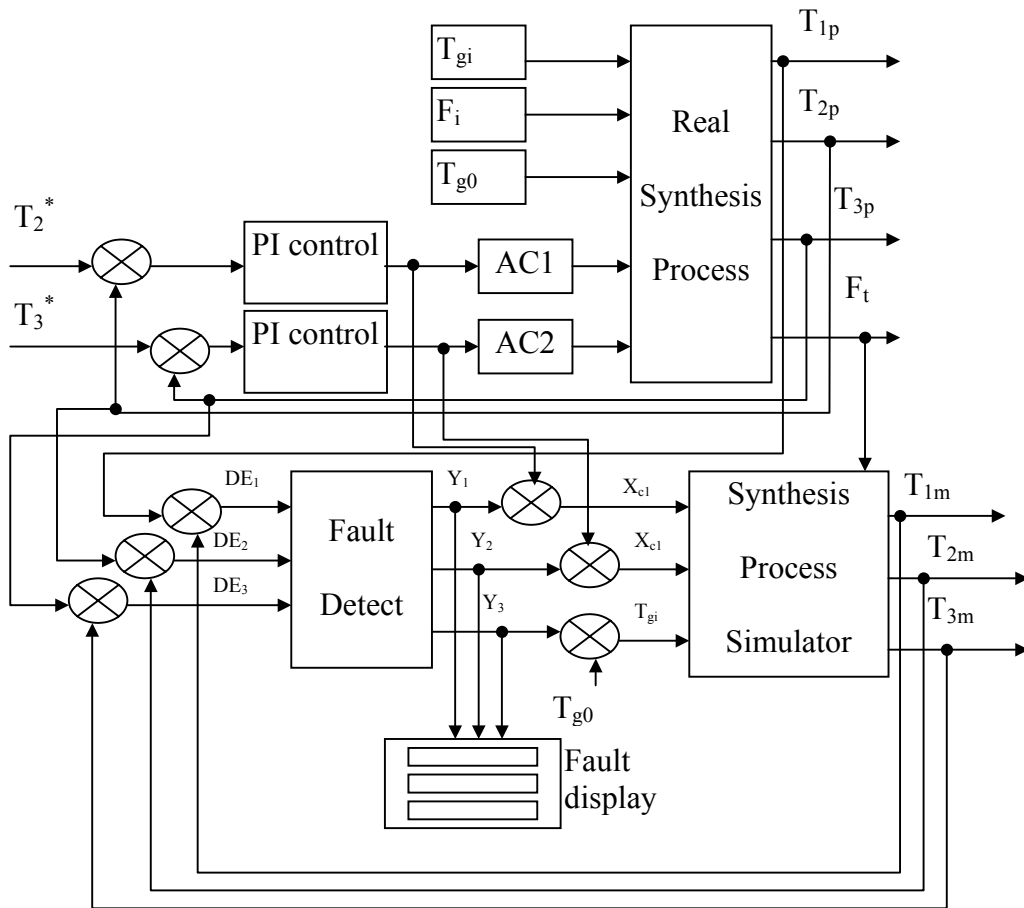
Fig.5. Simulation block diagram

CONCLUSIONS

The program allows the operators from the control room to permanently evaluate the working conditions and compare them with the optimal values.

- It allows the permanent control of process parameters.

- It allows the simple adaptation to the real optimal working conditions.

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ANNEX

Table 1. Equation constants

Const	Layer I	Layer II	Layer III	Layer IV
c_i	5.504	3.4673	2.01	0.5225
c_{Ri}	1	0.514	0.635	0.12793
c_{ai}	5.4763	3.40831	1.992	0.5225
c_{pi}	5.5048	3.4621	2.01	0.5225
c_{p0}	0.2133	0.21229	0.11239	0.11229