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A GENERAL FRAMEWORK FOR PELLET REACTOR MODELING: APPLICATION TO P-RECOVERY

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Abstract. Emphasis in recent years has been focused on improving processes which lead to enhanced phosphate recovery. This paper studies the precipitation features of calcium phosphate in a fluidized bed reactor in a concentration range between 4 et 50mg/L and establishes the conditions for optimum phosphate removal efficiency. For this purpose, two models are coupled for predicting the pellet reactor efficiency. First, a thermodynamical model is used for predicting calcium phosphate precipitation vs. initial conditions (pH, [P], [Ca], T..). The second one is a reactor network model. Its parameters are identified by an optimization procedure based on Simulated Annealing (SA) and Quadratic Programming (QP). The efficiency is computed by coupling a simple agglomeration model with a combination of elementary systems representing basic ideal flow patterns (perfect mixed flow, plug flow,...). More precisely, the superstructure represents the hydrodynamical conditions in the fluidized bed. The observed results show that a simple combination of ideal flow patterns is involved in pellet reactor modeling, which seems interesting for a future control. The experimental prototype used for validation purpose is first described. Then, the thermochemical model is presented for calcium phosphate precipitation. The third part is devoted to the reactor network-oriented model. The approach presented is finally validated with experimental runs.

INTRODUCTION

The need to limit phosphate emission in the environment has diverted the attention in recent years to processes which lead to the recovery of phosphate. The P-discharge in aqueous natural environment leads to an excessive development of algae and, generally to a pH increase, thus corresponding to eutrophication. Consequently, the phosphorus reduction in rivers is considered as a key factor of the fight against pollution. The principal legislative tool in Europe for fighting against eutrophication is the EC Urban Waste Water Treatment Directive (271/91/EEC). The precipitation of phosphate salts is a way of P-recovery in effluents with a low concentration in inorganic phosphorus. In the last years, several works were devoted to calcium phosphate precipitation in the so-called pellet reactor (Seckler, 1994) (Hirasawa I. and Toya Y, 1990).

The purpose of the study presented in this paper is to develop a methodology based on modeling for optimization of the pellet reactor efficiency. The experimental prototype used for validation purpose is first described. Then, the thermochemical model is presented for the calcium phosphate precipitation. The third part is devoted to the reactor network-oriented model. The approach is finally validated with experimental runs.

PROCESS DESCRIPTION

The process is based on calcium phosphate precipitation obtained by mixing a phosphate solution with calcium ions and a base. More precisely, it involves a fluidized bed of sand continuously fed with aqueous solutions (see Figure 1.). Calcium phosphate precipitates upon

the surface of sand grains. At the same time, small particles, i.e., “fines”, leave the bed with the remaining phosphate not recovered in the reactor. A layer of fines which has agglomerated is observed at the upper zone of the fluidized bed. Both total and dissolved concentrations of phosphorus, pH and the temperature were measured at the outlet stream. The temperature is kept constant during the experimental run.

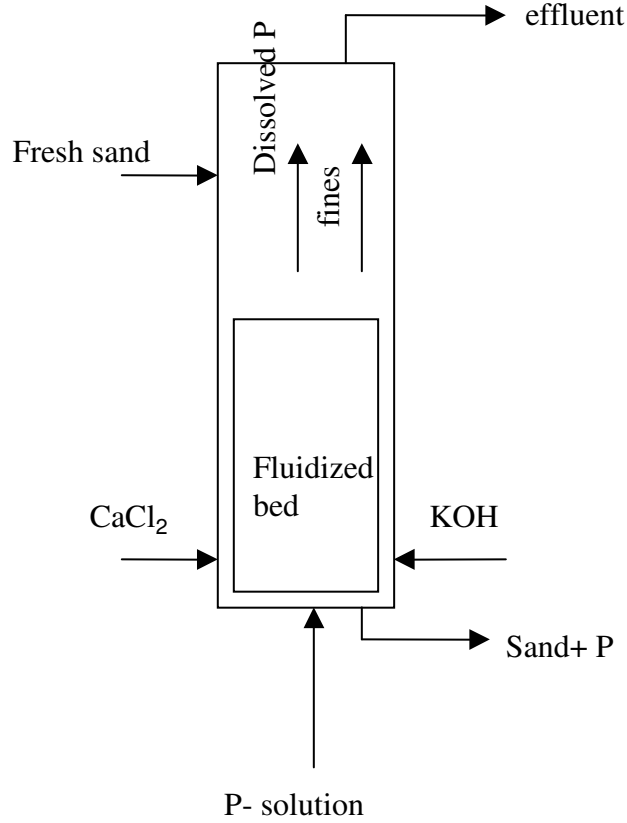


Figure 1. Schematic representation of the pellet reactor

In order to measure the dissolved P concentrations, the upper outlet stream was filtered immediately over a 0.45 μm filter and analyzed. Another sample was pre-treated with HCl in order to dissolve any suspended solid and the total phosphorus amount was measured. The phosphate removal efficiency (η) of the reactor and the conversion of phosphate from the liquid to the solid phase (X) are respectively defined as:

$$\eta = \frac{w_{p,in} - w_{p,tot}}{w_{p,in}} \quad (1)$$

$$X = \frac{w_{p,in} - w_{p,sol}}{w_{p,in}} \quad (2)$$

where $w_{p,in}$ represents the flowrate of the phosphorus component at reactor inlet, $w_{p,tot}$ gives the total flowrate of phosphorus both as dissolved and as fines at reactor outlet and $w_{p,sol}$ is the flowrate of dissolved P at the reactor top outlet. If η_{agg} is the agglomeration rate, that is, the ratio between fines in the bed and in the outlet stream, the following relation can be deduced:

$$\eta = \eta_{agg} X \quad (3)$$

The phosphate covered grains are removed from the bottom of the bed and replaced intermittently by fresh sand grains. In most studies reported in the literature (Morse et al., 1998), the phosphate removal efficiency of a single pass reactor, even at industrial scale, has an order of magnitude of only 50%. Let us recall that the pellet reactor efficiency depends not only on pH but also on the hydrodynamical conditions (Montastruc et al., 2002a). Moreover, the conversion rate depends on calcium and phosphate ion concentrations, as well as on supersaturation, ionic strength, temperature, ion types, pH but also on time (solid-solid transformation) as noted in the literature (Baronne and Nancollas, 1977), (Van Kemenade and de Bruyn, 1987).

MODELING PRINCIPLES

Two models are successively used to compute the reactor efficiency. At first level (see Figure 2), a thermochemical model determines the quantity of phosphate both in the liquid and solid phases vs. pH value, temperature and calcium concentration. A second modeling step could involve an agglomeration model which requires, as classical parameters, (Mullin, 1993) the density value of the precipitated calcium phosphates and fine diameter. Moreover, the agglomeration rate depends on the hydrodynamical conditions, particularly the eddy sizes. These values are difficult to obtain and require a lot of assumptions which are difficult to verify practically. Consequently, another alternative is proposed in this paper to tackle the problem. The two-stage methodology is detailed in what follows (see Figure 2.).

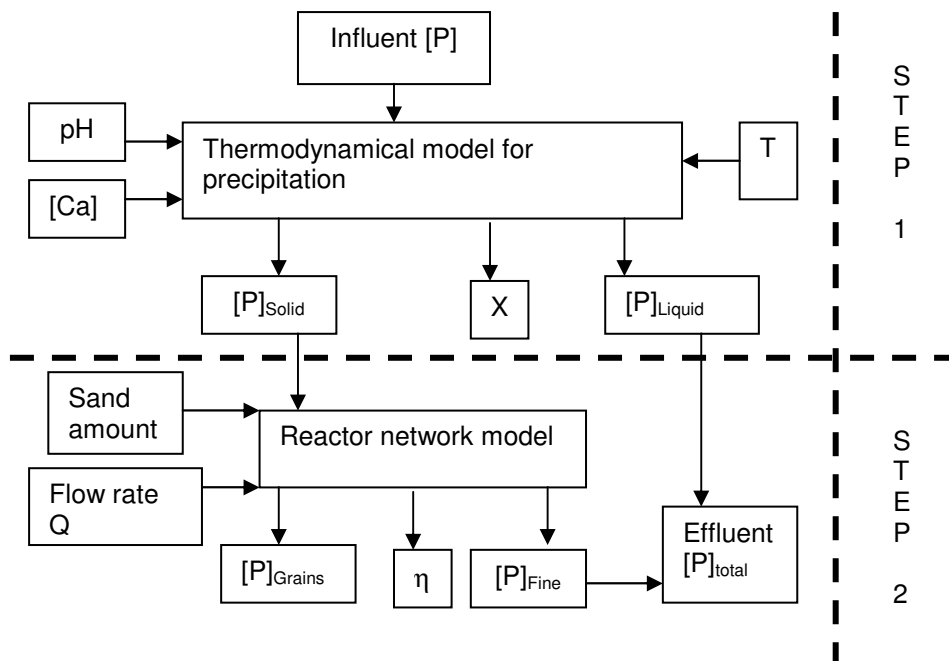


Figure 2. Principles of pellet reactor modeling

1. Thermodynamical model

The objective is to propose a mathematical model for the computation of the conversion for the system $\text{Ca-PO}_4\text{-H}_2\text{O}$. To model the evolution of phosphate conversion rate as a function of pH with respect to the different calcium phosphate species precipitation, the mass and electroneutrality conservation balances as well as the supersaturation were taken into account. Only the final stage of the calcium phosphate precipitation is considered. Note also

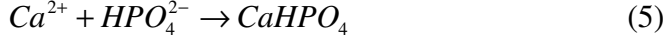
that solid-solid transformations are not taken into account. The assumed situations here are based on non dissolution of the less stable phase.

The precipitation of ACP can be written as follows:



The model inputs are the concentrations of calcium, phosphate and KOH.

The model is then used to determine if precipitation of DCPD is possible in these new conditions according to the following reaction:



For this purpose, the phosphate mass balances and the electroneutrality equation for DCPD precipitation are solved.

It means that if DCPD supersaturation is greater than zero, precipitation of DCPD is likely to occur. The model outputs are the conversions of both ACP and DCPD, the concentrations of the different ions and pH.

The concentrations of ions and complexes are determined from chemical equilibrium relations (see table 1)(Montastruc et al., 2002b).

Table 1. Equilibrium constants for the system $Ca-PO_4-H_2O$, $K_i = \frac{(A_i)(B_i)}{(AB_i)}$

K_i	A_i	B_i	AB_i	K_i value
K_1	H^+	$H_2PO_4^-$	H_3PO_4	$7.1285 \cdot 10^{-3}$
K_2	H^+	HPO_4^-	$H_2PO_4^-$	$6.2373 \cdot 10^{-8}$
K_3	H^+	PO_4^-	HPO_4^-	$453.942 \cdot 10^{-15}$
K_4	Ca^{2+}	$H_2PO_4^-$	$CaH_2PO_4^+$	$3.908 \cdot 10^{-2}$
K_5	Ca^{2+}	HPO_4^-	$CaHPO_4$	$1.8239 \cdot 10^{-3}$
K_6	Ca^{2+}	PO_4^-	$CaPO_4^-$	$347.536 \cdot 10^{-9}$
K_7	Ca^{2+}	OH^-	$CaOH^+$	$5.8884 \cdot 10^{-2}$
K_w	H^+	OH^-	H_2O	$1.004 \cdot 10^{-14}$

Consequently, the system to be solved for ACP precipitation contains 12 non-linear equations with 12 variables, i.e. concentrations of the aqueous species (11) and conversion. This set of equations was solved by a Newton-Raphson method. The system of equations was solved for various initial KOH concentrations in order to analyze the influence of pH on conversion. Since calcium is fed in the form of calcium chloride, the chloride concentration was taken equal to 2 $[Ca^{2+}]$. The activity coefficient of each species is given by the classical Debye-Huckel model. A preliminary study was performed to determine the influence of equilibrium constants and activity model on the equilibrium (Montastruc et al., 2002b). The main result was that the activity model had no influence but the sensitivity of the equilibrium constant was very important.

2. Reactor network model

The second step of the proposed methodology involves the computation of the pellet reactor efficiency. This phase has been achieved by the identification of the pellet reactor as a reactor network involving a combination of elementary systems representing basic ideal flow patterns (perfect mixed flows, plug flows,...)(see Figure 3). The combination of elementary systems representing basic ideal flow patterns is described by a superstructure (Floquet et al., 1989). It contains 4 perfect mixed flows arranged in series, 2 plug flows, 1 by-pass, 2 dead volumes (without reaction) and 1 recycling flow and represents the different flow arrangement (integer variables) that is likely to take place in the fluidized bed. Let us recall that more than four

series of perfect mixed flows produce the same effect as a plug flow.

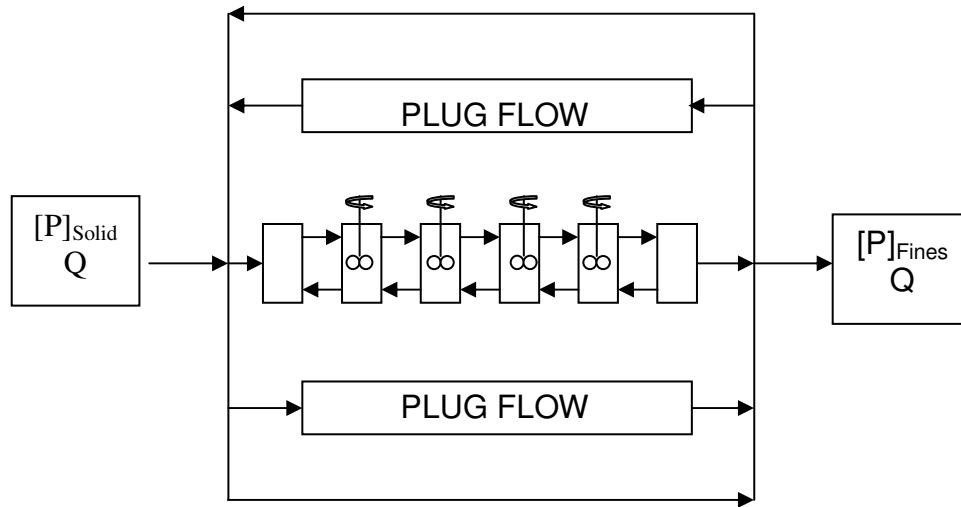


Figure 3. Superstructure detail

The precipitation phenomenon is described as an agglomeration of fines particles on large grains, which is represented by Smoluchowski's equation (Mullin, 1993).

$$\frac{dN_i}{dt} = -kN_iN_j \quad (i=\text{fines}, j=\text{grains}) \quad (6)$$

which can easily be written in an equivalent form as follows:

$$\frac{dC_i}{dt} = -KC_iN_j \quad (7)$$

N_k is the particle concentration either fines or grains (m^{-3}) and C_k is the corresponding concentration (mg/m^3). K and k represent kinetic constants ($\text{m}^{-3} \cdot \text{s}^{-1}$).

$$N_j = \frac{1 - \varepsilon}{\frac{4}{3}\pi r_j^3} \quad (8)$$

The bed porosity ε is calculated with a modified Kozeny-Carman equation (van Dijk and Wilms, 1991):

$$\frac{\varepsilon^3}{1 - \varepsilon} = 130 \left(\frac{v_{\text{sup}}^{1.2} \nu^{0.8}}{g(2r_j)^{1.8}} \right) \left(\frac{\rho_l}{\rho_s - \rho_l} \right), \quad (9)$$

where r_j is the grain radius, v_{sup} the superficial velocity (m/s), ν the kinematic viscosity (m^2/s) and ρ the density (kg/m^3).

The continuous variables are the "kinetic" constant (K), the flowrate (5) and the reactor volumes (8). In fact, the superstructure represents the hydrodynamical conditions in the fluidized bed. The "kinetic" constant is obtained for each combination generated by the Simulated Annealing algorithm. This kinetic constants depends only on the precipitation temperature and not on flowrate and sand amount. A summary of the global methodology for computing the efficiency is presented in figure 2.

At the upper level of the procedure, the scheduling of the basic structures is first optimized by S.A. (Kirkpatrick et al., 1983). The dynamic management of the different constraints

generated by the structures induced by the stochastic simulated annealing algorithm is then solved by a Quadratic Programming algorithm (QP) (QP package from the IMSL library). At the lower level, the set of parameters is identified for a given structure by QP. The J objective function for QP is to minimize the square distance between the experimental and the computed points.

$$J = \text{Min} \left[\left(\eta_{\text{agg}_{\text{exp}}} - \eta_{\text{agg}_{\text{mod}}} \right)^2 \right] \quad (10)$$

EXPERIMENTAL POINTS AND VALIDATION

1. Phosphate conversion

Experimental points have been used to validate the approach (Figure 4). They correspond to an initial phosphorus concentration of 50mg/L, a Ca/P molar ratio equal to 3 and a temperature equal to 20°C. The simulation fitting was carried out by adjusting the solubility constant values of both mineral species (ACP and DCPD).

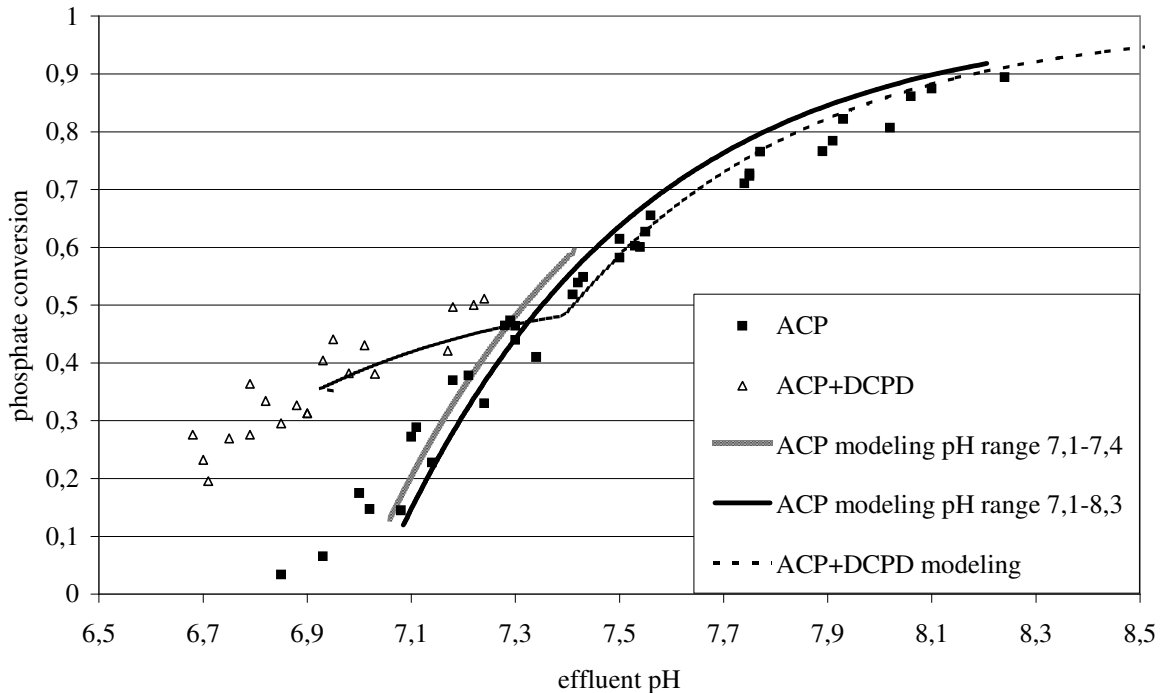


Figure 4. Phosphate conversion vs. to effluent pH

The pKs value for ACP which corresponds to the best fitting of the experimental results is equal to 25.297 for pH values higher than 7.4. This pKs value has the same order of magnitude than the average one reported in the literature (Montastruc et al., 2002b). The pKs value for DCPD is fixed to 6.346 when considering the zone for pH lower than 7.4, thus implying precipitation of ACP and also DCPD, in order to adjust the model with the experimental points (Figure 4). For pH values lower than 7.4, only ACP is assumed to precipitate. This case is probably due to the fact that the CaP particles were not agglomerated around the sand grains (clean sand) and no DCPD precipitation was observed: the pKs has been taken equal to 25.476. In this part, the only adjusted parameters are the ACP and DCPD pKs value. The equilibrium is very sensitive to the pKs value (Montastruc et al., 2002c).

2. Phosphate efficiency

The agglomeration rate represented by a first order equation has also been identified with experimental runs (see Figure 5.). The experimental rate has been determined for each flow rate by minimization of the square distance for each point between the experimental efficiency and the computed efficiency (see the relation 3).

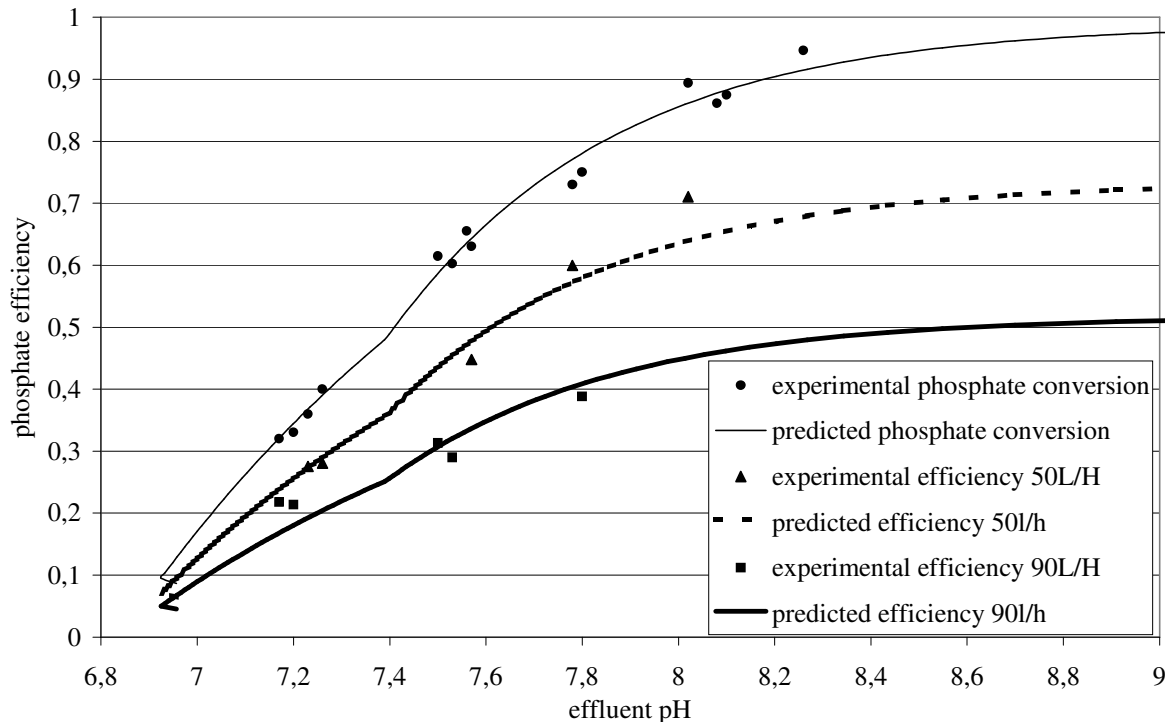


Figure 5. Phosphate efficiency vs. to effluent pH

The adjusted parameters are the kinetic constants and the reactor combination (Montastruc et al., 2003). The reactor combination obtained for modeling the efficiency for two values of total flowrate of the solution to be treated (50 and 90L/H) is very simple and contains two series of perfect mixed flows with a parallel plug flow. The Simulated Annealing searches the simplest combination for efficiency modeling covering the explored flowrate range.

DISCUSSION AND CONCLUSIONS

A two-stage methodology was proposed in this paper for pellet reactor modeling used for P-recovery by calcium phosphate precipitation case. Table 2 summarizes the input and optimization variables adopted in the presented methodology. The first model is a thermodynamical one while the second representing the hydrodynamical in the fluidized bed. It is important to notice that the conditions parameters of second model are the outlet values of the thermochemical one. This study improves the understanding of the precipitation of two calcium phosphates in either neutral or basic environment from a thermodynamical viewpoint. It gives for high pH values a domain in which only ACP precipitation is likely to occur and for neutral pH values a zone in which conditions of precipitation of ACP and DCPD are likely to take place.

Table 2. Input, optimization variables and results for the two stage methodology

Stage	1	2
Input parameters	[ions], T	Sand amount Flow rate, $[P]_{\text{solid}}$
Optimization variables	pKs ACP pKs DCPD	K Superstructure
Results	pH $[P]_{\text{solid}}$	η

Moreover, a hybrid optimization technique combining a Simulated Annealing and a Quadratic Programming method has been developed for identification of a reactor network which represents the pellet reactor for P-recovery, viewed as a mixed integer programming problem. Two levels are involved: at the upper level, the SA generated different combinations and at the lower level, the set of parameters is identified by a QP method. The observed results show that for the two values of the total flowrate of the solution to be treated, a simple combination of ideal flow patterns is found, which seems interesting for the future control of the process.

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