

## **Mathematical modelling of reaction kinetics applied for industrial dihydrate method of P<sub>2</sub>O<sub>5</sub> production**

I.V. Soboleva, E.M. Koltsova

Department of Cybernetics of Chemical Engineering, Mendeleev Chemical-  
Technological University of Russia (MUCTR)  
Miusskaya sq. 9, Moscow, Russia, 125047

Tel. 007(095) 9786589, Fax (095) 2004204, E-mail: isoboleva@freemail.ru

### **Abstract**

Kinetics of calcium sulfate crystallization during the process of phosphoric acid extraction was studied in this work. Mechanisms of calcium sulfate crystal nucleation and growth were found out. Continuous original method of cyclic sulfuric acid feed was developed for the industrial phosphoric acid production by dihydrate method resulted in significant increasing of production yield.

**Keywords:** modelling, phosphoric acid, dihydrate method

### **1. Introduction**

Acidic methods of phosphorus-containing ores treatment are the main for phosphoric fertilizers obtaining. More than 60 % of phosphorus containing fertilizers all over the world is produced on the basis of extraction phosphoric acid, the main methods of its production being dihydrate method.

The process of phosphoric acid extraction is a concurrent process including both natural phosphates dissolution in sulfuric acid solutions and crystallization of calcium sulfate modifications (calcium sulfate dihydrate or calcium sulfate hemihydrate) depending on dihydrate, hemihydrate or dihydrate - hemihydrate methods carried out under different temperatures conditions.

Main purpose of this paper was to investigate experimentally and by means of mathematical modelling kinetics of main processes occurring during dihydrate method of phosphoric acid extraction, namely: kinetics of phosphates dissolution, of passivation film formation on phosphates grains, of calcium sulphate dihydrate nucleation and growth in solution; to find out optimal conditions for industrial dihydrate process and, on the basis of experimental and computer investigations of kinetics, to propose a new method of extraction phosphoric acid production by a dihydrate method, consisting in organisation of cyclic sulphuric acid feed.

### **2. Objectives and techniques of mathematical modelling of reaction kinetics applied for dihydrate method of phosphoric acid extraction**

Laboratory and industrial experimental accumulated materials allowed us to carry out analysis of phosphates dissolution and calcium sulphate crystallisation elementary acts and to define a type of processes rate dependencies on their moving forces. For the calcium sulphate crystallisation description the mechanism of a homogeneous nucleation and crystals' growth in the kinetic area is accepted. Scheme of the processes interaction, described by the mathematical model, is shown in the fig. 1.

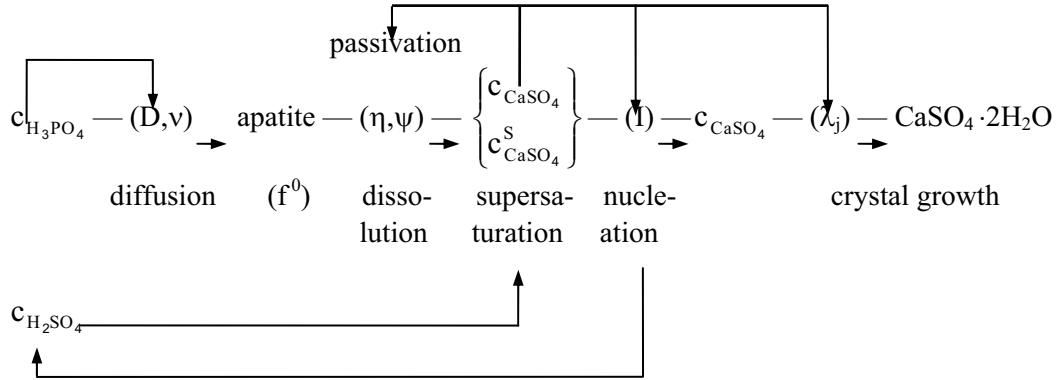


Figure 1. Scheme of physical-chemical phenomena interaction in the combined mathematical model of phosphates dissolution and calcium sulphate crystallisation processes.

Moving forces type of phosphates dissolution and crystallisation processes are based on the equation of universal mass transfer moving force, including enthalpy component, velocity component of non-equilibrium phases and on differences in chemical potentials of dissolved substance in the flow core and near the phases' interface surface.

Formatting alongside with a phosphoric acid calcium sulfate dihydrate has a shape of stretched parallelepiped. Therefore when modeling calcium sulfate dihydrate production we should consider growth of two facets.

Taking into account that both processes (phosphorite dissolution and calcium sulphate crystallization) are described within the framework of ideal mixing isothermal reactor models the following equations for velocities of the main processes were developed:

for phosphorite particles dissolution rate  $\eta$  and passivation filming rate  $\psi$ :

$$\eta = \frac{K_2}{\rho_a} \left( \frac{\varepsilon D^4}{\nu l^2} \right)^{1/6} \frac{c_{H_3PO_4} e^{-K_1 h}}{\rho_\sigma}; \quad \psi = R(a + bl)^q (c_{CaSO_4} - c_{CaSO_4}^S); \quad (1)$$

for calcium sulphate nucleation rate  $I$ , for average rate of calcium sulphate crystal growth  $\lambda_j$  on linear parameters  $L_j$ :

$$I = K_3 \left( \frac{c_{CaSO_4} - c_{CaSO_4}^S}{c_{CaSO_4}^S} \right)^n; \quad \lambda_j = K_{j+3} \left( \frac{c_{CaSO_4} - c_{CaSO_4}^S}{c_{CaSO_4}^S} \right)^{m_j}, \quad (2)$$

where  $\rho_a$  and  $\rho_\sigma$  - the densities of apatite and passivation films with the thickness  $h$ ;  $D$  - molecular diffusion factor,  $\varepsilon=dl/dt$  - a linear rate of phosphate particle sizes transformations at the dissolution;  $e$  - specific capacity on mixing;  $l$  - size of phosphate particles ;  $h$  - a thickness of sulfuric film on phosphate surfaces;  $n$  - viscosity;  $v$  - rate of dissolving,  $C_{CaSO_4}$  and  $C_{CaSO_4}^S$  - actual and equilibrium concentrations of  $CaSO_4 \cdot 2H_2O$  in phosphoric acid solutions, accordingly.  $K$ ,  $R$ ,  $a$ ,  $b$ ,  $q$  - constants.

For the description of sulphate calcium mass crystallisation and polydispersed phosphorite dissolution the equations for the particles' size distribution functions were used. The particles ensemble evolution of phosphorite was examined in two-dimensional phase space with co-ordinates:  $l$  - size of phosphorite non-dissolved grain,  $h$  - thickness of the passivation film. For the crystallisation process two characteristic linear sizes of crystal  $L1$  and  $L2$  were selected as phase space co-ordinates. For description of dissolution process experimental data, received by the method of radioactive isotopes on laboratory installation were used.

The mathematical model of extraction phosphoric acid production under the periodic conditions for dihydrate process was developed on the basis of mentioned above equations. As result of mathematical modelling the dissolution rate of polydispersed composition phosphorite, the rate of nucleation and the crystal growth rate were calculated, kinetic constants were found

For modeling mass crystallization of calcium sulfate dehydrate, zero moment  $\mu_0$  and first two moments  $\mu_{11}$  and  $\mu_{22}$  of distribution function density on size for calcium sulfate crystals. Moreover, average size of  $j$ -th galley of crystal is:

$$\langle l \rangle_j = \mu_{1j} / \mu_0, \quad j=1,2 \dots$$

For industrial continuous process of phosphoric acid extraction the rectangular ten-sectional reactor with the working capacity of  $740 \text{ m}^3$  was chosen as the most widely spread type of reactors used in phosphoric acid production. Taking into consideration a number of assumptions, this type of reactor can be described as the model consisting of five units of ideal mixing with the following process flow diagram:

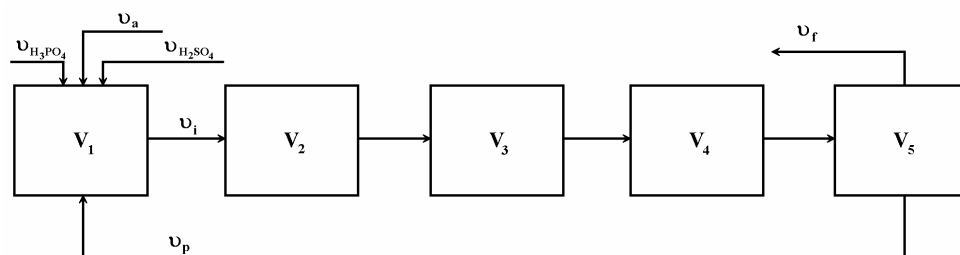


Fig. 2 Process flow diagram for continuous industrial process integration

where  $v_{H_2SO_4}$ ,  $v_{H_3PO_4}$  - volume flow rates of the sulphuric and phosphoric acids;  
 $v_a$ ,  $v_f$ ,  $v_p$  - volume flow rates of apatite, pulp on stage of filtration and circulation;

$V_{1-5}$  - capacities of units, corresponding to the capacity of two adjacent sections of simulated reactor;  $U_i$  - pulp flow into  $i$  unit of reactor model that is equal to the amount of loaded reagents.

According to the flow scheme mentioned above the equations for balances of apatite particles and dihydrate calcium sulphate crystals for  $i$  unit of reactor model are

:

$$\begin{aligned} \frac{\partial f^{(i)}}{\partial t} - \eta \frac{\partial f^{(i)}}{\partial l} + \psi \frac{\partial f^{(i)}}{\partial h} = & U_1 \frac{U_p}{V_1} f^{(5)} + U_2 \frac{U_i}{V_i} f^{(i-1)} - U_5 \frac{U_i}{V_i} f^{(i)} - U_3 \frac{U_f}{V_i} f^{(5)} - \\ & - U_3 \frac{U_p}{V_i} f^{(5)} + U_6 \frac{U_a}{V_i} f^0 \end{aligned} \quad (3)$$

$$\frac{d\mu_0^{(i)}}{dt} = I^{(i)} + U_1 \frac{U_p}{V_1} \mu_0^{(5)} + U_2 \frac{U_i}{V_i} \mu_0^{(i-1)} + U_5 \frac{U_i}{V_i} \mu_0^{(i)} + U_3 \frac{U_f}{V_5} \mu_0^{(5)} + U_3 \frac{U_p}{V_i} \mu_0^{(5)} \quad (4)$$

For each component of liquid phase the similar material balance equations were developed.

So the equation for sulphuric acid concentration has of the form of:

$$\begin{aligned} \rho_1 \frac{dc_{H_2SO_4}}{dt} = & -\rho_{CaSO_4} P [\lambda_1^{(i)} \mu_{1,2}^{(i)} + \lambda_2^{(i)} \mu_{1,1}^{(i)}] \frac{M_{H_2SO_4}}{M_{CaSO_4}} - c_{H_2SO_4}^{(i)} \frac{d\rho_1^{(i)}}{dt} + U_1 \frac{U_p}{V_i} \rho_1^{(5)} c_{H_2SO_4}^{(5)} + \\ & + U_2 \frac{U_i}{V_i} \rho_1^{(i-1)} c_{H_2SO_4}^{(i-1)} - U_5 \frac{U_i}{V_i} \rho_1^{(i)} c_{H_2SO_4}^{(i)} - U_3 \frac{U_f}{V_5} \rho_1^{(5)} c_{H_2SO_4}^{(5)} - U_3 \frac{U_p}{V_5} \rho_1^{(5)} c_{H_2SO_4}^{(5)} + \\ & + U_1 \frac{U_{H_2SO_4}}{V_1} \rho_{H_2SO_4} c_{H_2SO_4} \end{aligned} \quad (5)$$

Equation for phosphoric acid concentration:

$$\begin{aligned} \rho_1^{(i)} \frac{dc_{H_3PO_4}}{dt} = & 3J_1^{(i)} \rho_a \frac{M_{H_3PO_4}}{M_a} - c_{H_3PO_4}^{(i)} \frac{d\rho_1^{(i)}}{dt} + U_1 \frac{U_p}{V_i} \rho_1^{(5)} c_{H_3PO_4}^{(5)} + U_2 \frac{U_i}{V_i} \rho_1^{(i-1)} c_{H_3PO_4}^{(i-1)} - \\ & - U_5 \frac{U_i}{V_i} \rho_1^{(i)} c_{H_3PO_4}^{(i)} - U_3 \frac{U_f}{V_5} \rho_1^{(5)} c_{H_3PO_4}^{(5)} - U_3 \frac{U_p}{V_5} \rho_1^{(5)} c_{H_3PO_4}^{(5)} + U_1 \frac{U_{H_3PO_4}}{V_1} \rho_{H_3PO_4} c_{H_3PO_4} \end{aligned} \quad (6)$$

Equation for calcium sulphate concentration in liquid phase:

$$\begin{aligned}
\rho_1^{(i)} \frac{dc_{\text{CaSO}_4}}{dt} = & 5J_1^{(i)} \rho_a \frac{M_{\text{CaSO}_4}}{M_a} - c_{\text{CaSO}_4}^{(i)} \frac{d\rho_1^{(i)}}{dt} - \rho_{\text{CaSO}_4} J_2^{(i)} - \rho_{\text{CaSO}_4} P [\lambda_1^{(i)} \mu_{1,2}^{(i)} + \lambda_2^{(i)} \mu_{1,1}^{(i)}] + \\
& + U_1 \frac{U_p}{V_1} \rho_1^{(5)} c_{\text{CaSO}_4}^{(5)} - U_2 \frac{U_i}{V_i} \rho_1^{(i-1)} c_{\text{CaSO}_4}^{(i-1)} - U_5 \frac{U_i}{V_i} \rho_1^{(i)} c_{\text{CaSO}_4}^{(i)} - U_5 \frac{U_f}{V_i} \rho_1^{(5)} c_{\text{CaSO}_4}^{(5)} - \\
& - U_5 \frac{U_p}{V_i} \rho_1^{(5)} c_{\text{CaSO}_4}^{(5)} \tag{7}
\end{aligned}$$

where  $M$  - a molecular weight of component,  $I_1 = \int_0^H \int_{l_0}^{l_1} f \lambda \partial(r+b) / \partial l \partial h$ ,  $I_2 = \int_0^H \int_{l_0}^{l_1} f \Psi \partial b / \partial l \partial h$  - rates of nucleation,  $L$ ,  $l_0$  - maximum and minimum sizes of phosphate particles,  $H$  - a maximum size of thickness of sulfuric film;  $r$  - a volume of phosphate particles;  $b$  - a volume of a sulfuric film.

Equations System (1)-(7) presents itself a mathematical model base, describing main physical – chemical processes, which take place in industrial apparatus.

For determination of crystallisation process kinetic parameters the series of experiments on industrial installation was carried out. When processing the experiments results the following function type was used as unbalanced criterion:

$$\begin{aligned}
F = \sum_{k=1}^n \left\{ \left( \frac{c_{k\text{CaSO}_4}^t - c_{k\text{CaSO}_4}^e}{c_{k\text{CaSO}_4}^e} \right)^2 + \left( \frac{c_{k\text{H}_2\text{SO}_4}^t - c_{k\text{H}_2\text{SO}_4}^e}{c_{k\text{H}_2\text{SO}_4}^e} \right)^2 + \left( \frac{c_{k\text{H}_3\text{PO}_4}^t - c_{k\text{H}_3\text{PO}_4}^e}{c_{k\text{H}_3\text{PO}_4}^e} \right)^2 + \right. \\
\left. + \left( \frac{\rho_k^t - \rho_k^e}{\rho_k^e} \right)^2 + \left( \frac{L_{1k}^t - L_{1k}^e}{L_{1k}^e} \right)^2 + \left( \frac{L_{2k}^t - L_{2k}^e}{L_{2k}^e} \right)^2 \right\} \tag{8}
\end{aligned}$$

### 3. Results and conclusions.

As result of mathematical modelling the dissolution rate of polydispersed composition apatite, the rate of nucleation and the crystal growth rate for each unit of reactor were calculated. It was shown that in the industrial reactor all the processes practically are over in the fifth-sixth sections (in the third unit of the model) and approximately 65% of reactor working capacity provides the theoretical capacity. That's why it was set the problem of developing such extraction phosphoric acid production method which will provide the full occupation of reactor working capacity in order to increase the productivity and to rise  $\text{P}_2\text{O}_5$  extraction factor. It will result in saving of raw materials and power conservation.

We developed the phosphoric acid production method in the non-steady-state technological conditions. As a control parameter when realising these conditions the sulphuric acid flow rate in the reactor was chosen. In the fig. 3 the curves of sulphuric acid concentration constrained oscillation and extraction degrees for the non-steady-state sulphate conditions are shown. As can be seen from the figure the concerned method of process organisation allows us to create two sulphate levels, corresponding to the optimum conditions of dissolution and crystallisation processes during the stay time

in the reactor zone. By means of mathematical model the optimal values of amplitude and frequencies of sulphuric acid flow rate periodic oscillation were obtained. The industrial tests of developed technological conditions were carried out and they have confirmed efficiency of the developed extraction phosphoric acid production method.

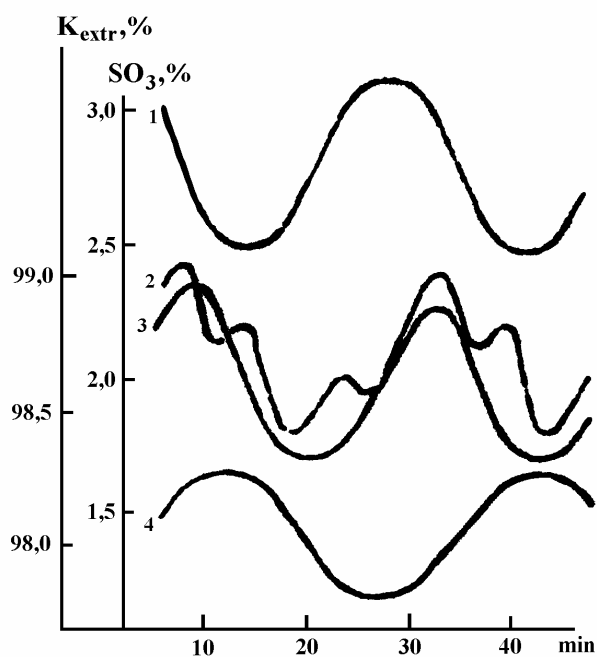


Figure 3. Alterations of the process characteristics under the non-steady-state conditions. 1 -  $SO_3$  in 1-st unit (calculation), 2 -  $SO_3$  in 2-nd unit (calculation), 3 -  $SO_3$  in 3-d unit of reactor (experiment), 4 - the extraction coefficient in 2-nd unit of the model

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