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Peculiarities of Designing Periodic Chemical Apparatuses with Formation of New Insoluble Phases

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The paper deals with the methodology for modeling chemical apparatuses characterized by the formation of insoluble dispersed phases in the working volume. Modification of the Smoluchowski's equation for aggregation process in systems with chemical sources of insoluble phases has been submitted. The approach to calculating the time of stay of reagents in the periodic reactor characterized by formation and sedimentation of an insoluble phase in the working zone of the apparatus has been carried out.

1. Introduction

Processes of chemical technologies are accompanied frequently by formation of a new solid dispersed phase. It can be in cases of phase transition, such as crystallization or desublimation, or it can be formation of insoluble substances during chemical reactions. Methods for calculating apparatuses in which the process is accompanied by phase transitions of "liquid-solid" or "vapour-solid" types are developed more or less in detail (Sontag, Strenge, 1970). However methods for calculating and designing the processes in chemical reactors distinguishing by formation of insoluble products of chemical reactions in working zones of the apparatuses are developed to a less degree. At the same time, it is possible to call a lot of directions in the modern science dealing with processes and apparatuses of chemical technologies in which the problems of calculating the kinetic and dynamical characteristics of reactors with formation of a solid phase in a working zone are relevant.

1. Creation of sorbents, catalysts and molecular grids with given structure.
2. Creation of methods for calculating and optimal engineering of technological processes dealing with a method of chemical sedimentation.
3. Elaboration of polymeric films for molecular covering the products of chemical mechanical engineering and the electro-technical industry.

The situation with calculation of these processes becomes complicated by the fact that chemical reactions, physical processes and purely hydrodynamic processes occur in volume of one apparatus.

So, the area of researches in this work is limited to working out methods of calculation and designing of processes and chemical apparatuses in which there exist formation and aggregation of insoluble products. We consider the periodic reactors for which the main point is calculation of the effective time of reagents finding into the work zone. The list of references contains only key works regarding our theme.

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2. System Analysis and Theoretical Details

In conformity with the offered approach the work volume of the apparatus is divided into three zones: a kinetic zone in which there is a transition of formed insoluble substances into a solid phase, i.e. nucleation; a zone of aggregation of primary particles limited by diffusion, and the third zone of the constrained sedimentation and deposit consolidation. Certainly, such division is conventional. However, the primary nucleation is the first stage of aggregation process absolutely. During this process microscopic amorphous particles or partially crystalline particles-monomers are generated (Stechemesser, 2005).

Let us consider the first order reaction occurring in a solution under the conventional scheme $A \to B$, and describe also the primary nucleation kinetics by means of the delay of formation of an insoluble phase C relatively to the time of reagent formation B for the certain nucleation period. Then

$$\left.\frac{dC}{dt}\right|_n = \frac{A_0}{\tau_c}\exp\left(-\frac{t-\tau_n}{\tau_c}\right), \tag{1}$$

where A_0 is the initial concentration of the reagent A, t is the current time, τ_c is the characteristic time of the chemical reaction, τ_n is the characteristic time of the nucleation, C is the concentration of the insoluble product.

The analysis of known data allows asserting that as a result of primary nucleation there are mainly monomers of an insoluble phase (Stechemesser, 2005). Then Smoluchowski's equation expanded by the chemical source looks as follows (Wattis, 2006).

$$\frac{dC_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} N_{j,i-j}C_j(t)C_{i-j}(t) - \sum_{j=1}^{\infty} N_{i,j}C_i(t)C_j(t), \tag{2}$$

$$\frac{dC_1}{dt} = -\sum_{j=1}^{\infty} N_{1,j}C_1(t)C_j(t) + \chi\frac{A_0}{\tau_c}\exp\left(-\frac{t-\tau_n}{\tau_c}\right), \tag{3}$$

where factor χ considers the monomer mass, and C_i is the concentration of i-mer.

In our work the equation for calculating the total concentration $M_0 = \sum_{i=1}^{\infty} C_i$ of clusters of an insoluble phase has been received by means of the method of generating functions (Wattis, 2006):

$$\frac{dM_0}{dt} = -\frac{1}{2}M_0^2 + \frac{A_0\exp(\tau_n/\tau_c)}{\tau_c}\exp\left(-\frac{t}{\tau_c}\right), \tag{4}$$

The analytical solution of equation (4) expressed by Bessel functions can be easily received.
Figures 1, 2 depict some results of the numerical experiments and theoretical researches.

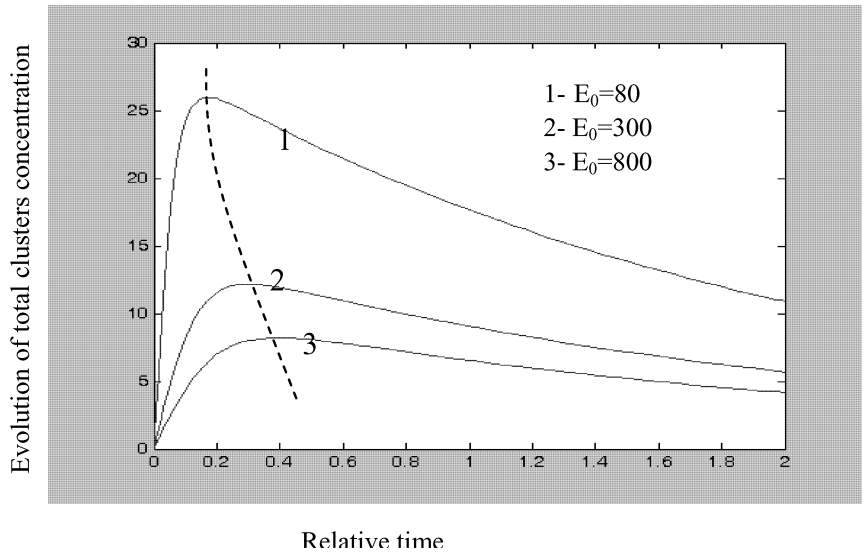

Figure 1. Total concentration of clusters in the system with first-order reaction

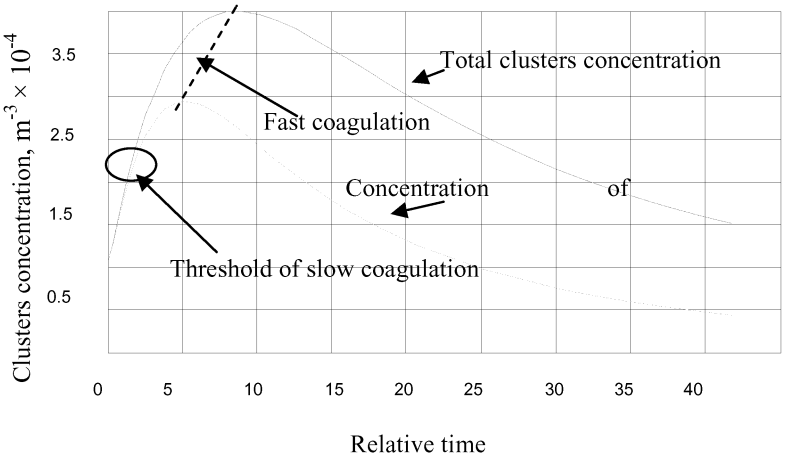

Figure 2. Stages of aggregation

As a result of numerical experiments the following relations for the dependence of a maximum of the total concentration of clusters in the system with first order reaction on the parameter has been obtained.

$$(t/\tau)_{\max} = 0{,}437 E_0^{-0{,}286}, \tag{5}$$

$$E_0 = \frac{A_0 \exp(\tau_n/\tau_c)}{\tau_c} \tag{6}$$

The greatest interest, from the point of view of the process kinetics in the reactor, represents comparison between the rate of evolution of total clusters concentration and concentration of the clusters, formed as a result of primary nucleation of the reaction product (Brener et al., 2009). The moment when speed of aggregation of monomers starts to prevail over speed of primary nucleation is clearly observed from the Figure 2. It is a so-called threshold of slow coagulation. Other important phenomenon is the time shift between the maximums of the concentration of monomers and the maximums of total concentration of clusters. This shift diagnoses the second stage of aggregation that is the so-called fast aggregation.

3. Periodic Reactor Modelling

This section deals with the methods for modelling periodic chemical reactors in the case when an insoluble dispersed phase is being formed in a working zone. Following problems are thus solved:
1. Distribution of concentration of a dispersed solid phase over height of the periodic reactor with mixing has been described.
2. The procedure for calculating the time of reagents stay into the reactor with allowing for the formation and sedimentation of solid phase has been developed.
The general model reads (Fadda et al., 2009)

$$D_{ef}\frac{\partial^2 C}{\partial z^2} - (W - V)\frac{\partial C}{\partial z} + I_{chem} = \frac{\partial C}{\partial t}, \tag{7}$$

where I_{chem} - intensity of a chemical source depending on a reaction order, W is the speed of sedimentation, V is the fluid speed, D_{eff} is the effective diffusion coefficient, z is the longitudinal coordinate.
The rate of sedimentation taking into account the evolution of average size of solid particles in consequence of aggregation reads:

$$W = \zeta a^2 \left(1 - \exp\left(-\frac{t}{\tau}\right)\right)^2 \tag{8}$$

Formation of suspension in the periodic reactor with a mixer has been considered in approach of isotropic turbulence. The solution of the equation of diffusion for the reactor of periodic type in case of a reaction of the first order with rate coefficient k looks as follows

$$C_{sol} = -\frac{D_{ef} C_l^0 \exp(-kt)}{W} + C_{sol}(0)\exp\left(\frac{W\ z}{D_{ef}}\right) \tag{9}$$

The concentration of solid phase averaged over height of the reactor reads

$$\overline{C}_{sol} = \frac{D_{efC_{sol}(0)}}{W\ H}(\exp(W_{sol} H / D_{ef}) - 1) - \frac{D_{ef} C_l^0}{W}\exp(-kt)\,, \tag{10}$$

where H is the reactor height.
The stage of the end of chemical transformations and achievement of demanded conversion in the periodic reactor with mixing is characterized by an exit on the curve of stable distribution of suspension density over height of the apparatus (see Figure 3).

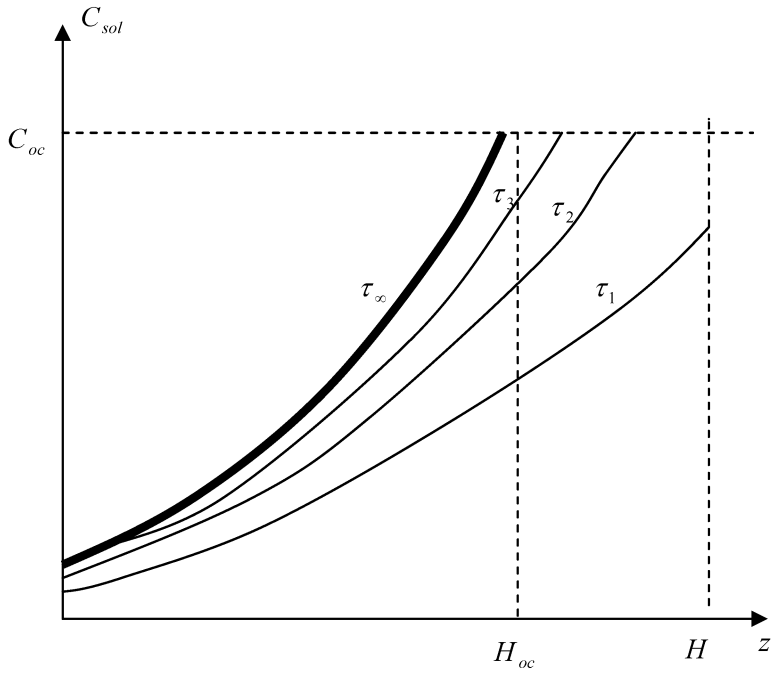

Figure 3. Plots of exit to stable curve of the density of suspension: $\tau_1 < \tau_2 < \tau_3 < \tau_\infty$

After the end of the first period of sedimentation in the periodic reactor still there are dregs of the first fraction in a zone of height

$$H_1 = (W_2 - W_1)T_2 \tag{11}$$

where W_1, W_2 are the sedimentation velocities of small (index 1) and big (index 2) fractions; T_2 is the time of complete sedimentation of the big fraction.

In this zone the gradient of density of the first fraction will be observed. This gradient can be calculated from the following reasons.
Inasmuch as $\rho_1(t) = \rho_{10} - \rho_3(t)$, for the time delay of sedimentation between fronts of different fractions it is possible to write.

$$t = \frac{z}{W_2 - W_1} \tag{12}$$

Then we obtain the expression for calculating the density of small fraction in the zone between sedimentation fronts:

$$\rho_1(z) = \rho_{10} - \rho_3(z/(W_2 - W_1)) \tag{13}$$

where ρ_3 is the density of the aggregate fraction.
Thus, the presented model allows counting almost all basic characteristics of process of sedimentation of suspension accompanied by the aggregation of fractions.

4. Conclusion

1. The model of aggregation of a disperse phase in systems with chemical reactions which is based on the Smoluchowski's equation for binary coagulation is submitted.
2. Regularities of process of aggregation in systems with a chemical source of monomers of an insoluble phase are studied, and presence of two critical concentrations in the course of coagulation of an insoluble phase in the reacting systems caused by achievement of a threshold of coagulation for primary monomers and the end of the active stage of chemical reactions in the periodic reactor is confirmed.
3. The mathematical model of periodic chemical reactors with mixing devices for calculating and optimizing processes with formation of an insoluble phase in the working zone has been carried out.

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