Modeling Aggregation of Insoluble Phase in Reactors

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Abstract—In the paper we submit the modification of kinetic Smoluchowski equation for binary aggregation applying to systems with chemical reactions of first and second orders in which the main product is insoluble. The goal of this work is to create theoretical foundation and engineering procedures for calculating the chemical apparatuses in the conditions of joint course of chemical reactions and processes of aggregation of insoluble dispersed phases which are formed in working zones of the reactor.

Keywords—Binary aggregation, Clusters, Chemical reactions, Insoluble phases.

I. INTRODUCTION

IN many cases processes of chemical technologies are accompanied by formation of the new solid disperse phase. It can be phase transition, as in cases of crystallization or desublimation, or it can be formation of low soluble substances during chemical reactions [1]-[12].

As a whole it is possible to allocate a lot of directions of a 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 polydisperse solid phase in a working zone are relevant.

1. Production of nano-dispersed powders of oxides of precious metals for constructional and functional bioceramics.
2. Creation of sorbents, catalysts and molecular grids with given structure.
3. Creation of methods for calculating and optimal engineering of technological processes dealing with the method of chemical sedimentation.
4. Elaboration of polymeric films for molecular covering of products of chemical mechanical engineering and electro technical industry.
5. Elaboration of ways of producing nano-disperse rheological additives for suspensions with given characteristics.

Methods for calculating apparatuses in which there are phase transitions of types "liquid-solid" or "vapor-solid" are developed more or less in detail [12]-[14].

However engineering methods of calculation and designing of processes in chemical reactors with formation of low soluble products of chemical reaction in working zones of the apparatuses are developed to a lesser degree [15], [16].

The area of researches in this work is limited to working out methods for calculating and designing processes and chemical apparatuses in which there exist formation and aggregation of suspensions of low soluble products of chemical reactions.

Therefore, the goal is to create theoretical foundation and engineering procedures for calculating the chemical apparatuses in the conditions of joint course of chemical reactions and processes of aggregation of an insoluble dispersed phase formed in working zones of the reactor.

II. MATHEMATICAL MODEL

The primary nucleation is the first stage of aggregation process. During this process microscopic amorphous particles or partially crystalline particles-monomers have been generated in a solution.

Let us consider the first order reaction occurring in a solution under the conventional scheme $A \rightarrow B$ with the rate constant k. Further we will use capital Roman letters for denoting reactants and their concentrations. Then the concentration of a product of reaction reads:

$$B = A_0 \left(1 - \exp\left(-\frac{t}{\tau_c} \right) \right) \quad (1)$$

where A_0 is the initial concentration of reactant A.

$$\tau_c = 1/k . \quad (2)$$

Further we consider primary nucleation of the product of reaction B with formation of clusters of an insoluble phase: $B \rightarrow C$.

The primary nucleation kinetics will be described by means of time of delay of the insoluble phase C formation relatively the time of the reaction product formation during the certain period of nucleation τ_n.

The time that is imperative for reaching the equilibrium concentration of the product B in solution will not be taken into account. This approach is acceptable, probably, for low soluble substances.

Then

$$\left. \frac{dC}{dt} \right|_n = \frac{dB}{dt} = \frac{A_0}{\tau_c} \exp\left(-\frac{t - \tau_n}{\tau_c} \right) \quad (3)$$

The analysis of known data allows asserting that as a result of primary nucleation there are mainly monomers of the insoluble phase. Then Smoluchowski equation expanded by the chemical source looks as follows [6], [7], [15], [16].

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$$\frac{dC_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} N_{j,i-j} C_j(t) C_{i-j}(t) - \sum_{j=1}^{\infty} N_{i,j} C_i(t) C_j(t) \tag{4}$$

$$\frac{dC_1}{dt} = -\sum_{j=1}^{\infty} N_{1,j} C_1(t) C_j(t) + \chi \frac{A_0}{\tau_c} \exp\left(-\frac{t-\tau_n}{\tau_c}\right) \tag{5}$$

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

Let us introduce a generating function of the type [15]:

$$\tilde{C}(t,z) = \sum_{i=1}^{\infty} C_i(t) \exp(-iz) \tag{6}$$

In the case of constant aggregation cores $N_{i,j} = \eta_{ag} = const$ the kinetic equation in the terms of generating function reads

$$\frac{\partial \tilde{C}}{\partial t} = \frac{1}{2}\tilde{C}(t,z) - \tilde{C}(t,0)\tilde{C}(t,z) + \chi \frac{A_0}{\tau_c} \exp\left(-\frac{t-\tau_n}{\tau_c} - z\right). \tag{7}$$

The method of generating functions can be effectively used for deriving the equation for the total concentration of clusters of insoluble phase:

$$M_0 = \sum_{i=1}^{\infty} C_i. \tag{8}$$

Then the sought-for equation follows from (7) under $z = 0$ reads

$$\frac{dM_0}{dt} = -\frac{1}{2}M_0^2 + \frac{A_0 \exp(\tau_n/\tau_c)}{\tau_c}\exp\left(-\frac{t}{\tau_c}\right). \tag{9}$$

Let us introduce parameters which are convenient for analytical decision of (9).

$$\exp\left(-\frac{t}{\tau_c}\right) = s, \tag{10}$$

$$E_0 = \frac{A_0 \exp(\tau_n/\tau_c)}{\tau_c}. \tag{11}$$

After minimal rearrangements (9) will look as follows

$$\frac{dM_0}{ds} = \frac{\tau_c}{2s}M_0^2 - E_0 \tag{12}$$

The following substitution is suitable to solving the obtained Riccati equation

$$U = \exp\left(-\int \frac{\tau_c}{2s}\right) M_0 ds \tag{13}$$

As a result we get

$$s\frac{d^2U}{ds^2} + \frac{dU}{ds} - \frac{\tau_c}{2}A_0 U = 0 \tag{14}$$

The analytical decision of the given equation expressed by Bessel's functions I_0 and K_0 reads:

$$U = U_1 I_0\left(\sqrt{2A_0\tau_c s}\right) + U_2 K_0\left(\sqrt{2A_0\tau_c s}\right) \tag{15}$$

Finally we obtain the sought-for solution in the form

$$M_0 = -\frac{2s}{\tau_c}\frac{dU/ds}{U} \tag{16}$$

Let us consider now the second order reaction occurring in a solution under the conventional scheme $A + B \rightarrow C$.

The solution for the concentration of reaction product C reads

$$\tilde{N} = \frac{A_0 B_0 (1 - \exp(k_2(A_0 - B_0)t))}{B - A\exp(k_2(A_0 - B_0)t)}. \tag{17}$$

At the singular case, i.e. when $A_0 = B_0$ the above relation transforms to

$$C = \frac{A_0^2 k_2 t}{(1 + A_0 k_2 t)} \tag{18}$$

The Smoluchowski equation for aggregation kinetics of the monomers of insoluble product $\tilde{N}_1$ now reads

$$\frac{dC_1}{dt} = -\sum_{j=1}^{\infty} N_{1,j} C_1(t) C_j(t) + \Phi_1(t) \tag{19}$$

$$\Phi_1(t) = \frac{A_0 B_0 (1 - \exp((A_0 - B_0)(t - \tau_n)/\tau_c))}{B_0 - A_0 \exp((A_0 - B_0)(t - \tau_n)/\tau_c)} \tag{20}$$

where

$$\tau_c = 1/k_2. \tag{21}$$

In this case the method of generating functions is also applicable. And after the analogous transformations we get the following equation for the total concentrations of insoluble clusters.

$$\frac{dM_0}{dt} = -\frac{1}{2}M_0^2 + \frac{A_0 B_0 (1 - E_0 \exp((A_0 - B_0)t/\tau_c))}{B_0 - A_0 E_0 \exp((A_0 - B_0)t/\tau_c)} \tag{22}$$

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$$E_0 = \exp\left(-\left(A_0 - B_0\right)\frac{\tau_n}{\tau_c}\right). \qquad (23)$$

The obtained equation can be also solved with the help of Bessel's functions. However, we do not give here the appropriate expression as it has an unwieldy form.

III. Numerical Experiment

Fig. 1 depicts some results of calculating the evolution of the total concentration of solid clusters of different orders in the system with the first-order chemical reaction, and Fig. 2 depicts the mentioned evolution in the system with the second-order reaction.

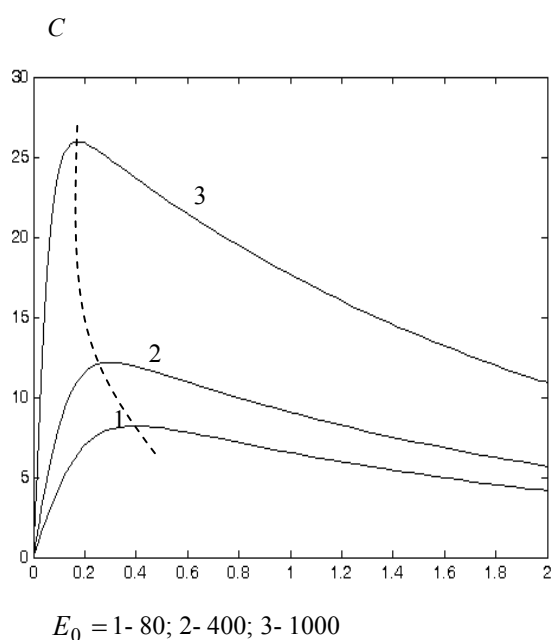$E_0 = 1\text{-}80;\ 2\text{-}400;\ 3\text{-}1000$

Fig. 1 The evolution of the total concentration of solid clusters in the system with the first-order reaction at small-time

The numerical experiments did not show a principal difference in qualitative behavior of the time-dependences of the total clusters concentration in the cases of first or second-order reactions. The differences observed reduce to quantitative peculiarities.

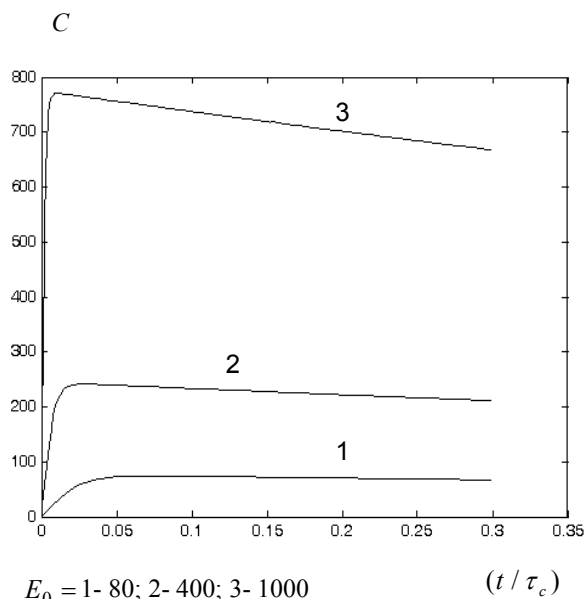$E_0 = 1\text{-}80;\ 2\text{-}400;\ 3\text{-}1000$ $\qquad (t/\tau_c)$

Fig. 2 The evolution of the total concentration of solid clusters in the system with the second-order reaction at small-time

As a result of numerical experiments we obtain the following approximations for describing the time when the maximum of total clusters concentration can be observed in the systems with the first (24) and the second-order (25) reactions.

$$(t/\tau_c)_{max} = 0,437 E_0^{-0,286}. \qquad (24)$$

$$(t/\tau_c)_{max} = 0,348 E_0^{-0,346}. \qquad (25)$$

The form of relations (24), (25) shows that the parameter E_0 can be used as control parameter for engineering calculations.

IV. Discussion and Conclusion

However, 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.

The moment when the speed of aggregation of monomers starts to prevail over the speed of primary nucleation is clearly observed from the Fig. 3. It is a so-called threshold of slow aggregation.

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.

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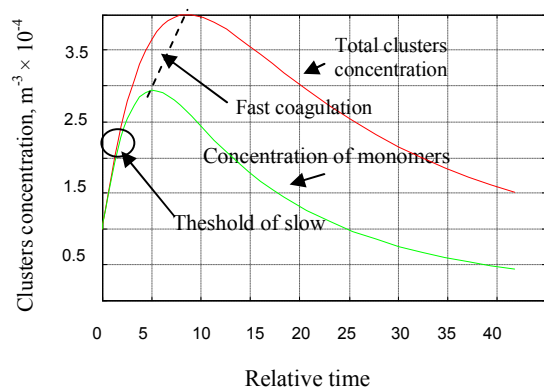International Journal of Chemical and Molecular Engineering
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Fig. 3 The time evolution of cluster concentration of different orders

Aggregation is characterized by fast increase in the concentration of monomers in the initial time, and then the total concentration of clusters of higher orders begins to dominate. The extremes of concentration of higher orders clusters are clearly displaced over time.

At any given time there is a certain average order of clusters. From this it follows that for the batch reactor for which the main characteristic time is the duration of the reaction [17], [18], it is necessary to know the average order of clusters, besides the total concentration of clusters of insoluble phase, since the average cluster size determines the time of solid phase deposition.

In really the situation with calculation becomes complicated by the fact that chemical reactions, physical processes and purely hydrodynamic processes occur in volume of one apparatus [18]. However, the systematic approach allows to make decomposition of this difficult problem and to offer mathematical models for its various stages.

Certainly, such division is conventional. However, it can be explained by that most intensive chemical transformations are carried out in the field of not constrained movement of streams of phases, i.e. in the field of the maximum effective factors of diffusion.

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