ABSTRACT

of dissertation for the degree of Doctor of Philosophy (PhD)
in the specialty 6D072400 – Technological machines and equipment

Kazenova Aikerim Ongarbekovna

Development of models and methods of stabilization of fractions distribution upplied to thermodynamically unstable dispersed systems in chemical apparatuses

Actuality of the research issue. Technological processes in which physicochemical transformations are accompanied by processes of aggregation of the disperse phase often form the basis of the technological cycle in the chemical, pharmaceutical, metallurgical, and other industries. However, despite a considerable amount of work, many problems in this area remain poorly studied, and the widespread models of the processes of aggregation and clustering of disperse phases in complex physicochemical systems have a number of drawbacks that reduce their practical value.

The analysis shows that the most significant drawbacks of the known models (Smoluchowski and Becker-Döring equations) are due to insufficient consideration of the fact that dynamic cluster structures interacting in systems change their characteristics over time. It is especially important to take these phenomena into account in nanosystems, where the speed of technological processes is high and the requirements for uniformity of the fractional composition of the obtained disperse systems are also great. At the same time, the resources for effective control over fast processes are very limited. Therefore, it is especially important to correctly calculate and select the optimal values of the defining control parameters.

There is a need in new theoretical approaches that allow to take into account the kinetics of aggregation processes at different time hierarchies under conditions of mixed kinetics, when the influence of both diffusion parameters and the parameters of the internal kinetics of aggregation is comparable, i.e. the dependence of the aggregation activity of clusters of the disperse phase on the lifetime of the clusters, as well as their fine internal structure.

The subject of the research is aggregation processes of disperse clusters in disperse systems and hydrodynamics of dense dispersions.

The objective of the work is to carry out a critical analysis of modern approaches to describing the processes of aggregation of disperse systems in chemical apparatuses and on this basis to propose new, physically justified models that allow taking into account the phenomena of transformation of the structure of clusters over time, as well as develop methods of kinetic and hydrodynamic calculation that are applicable in the optimal design of production processes for stabilized disperse systems with high uniformity of fractional composition.

In accordance with the objective, the following **tasks** were solved: **-** a critical analysis of aggregation models from the perspective of taking into account the

internal structure of clusters, transformations of their structure at various characteristic times under conditions of different concentrations of disperse media; - development of mathematical models to take into account the influence of the factors noted above on the kinetics of aggregation processes and the fractional composition of dispersion; - carrying out experimental studies to verify the adequacy of the proposed models and study the effect of the dispersion residence time and control parameters in the working volume of the apparatus on the fractional composition; - development of methods for calculating operating parameters to ensure a stable fractional composition of dispersions; - creation of models for the formation of dense dispersions of homogeneous fractional composition and their flow in the nodes of the apparatus of the technological scheme; - development of mathematical models and methods for calculating the processes of unloading and transportation of dispersions, taking into account the dissipation of energy in the working volume.

Scientific novelty of the research:

- the task of describing the aggregation activity of disperse phase clusters was physically justified and set, not only depending on their order and diffusion kinetics, but also taking into account the transformation of the cluster structure and their residence time in the working volume of the apparatus;

- it was shown that, in contrast to the known models for taking into account the residence time of reaction mixtures and the degree of mixing in reactors, in the case of cluster aggregation, the problem of transformation of the internal structure of particles can have a significant effect on the aggregation activity;

- models of the cluster aggregation in the dense polydisperse systems were developed that take into account the noted factors of the internal structure and age of the clusters;

- as a result of the experiments, the influence of the time of the aggregation process on the distribution function of the fractional composition of the dispersion was confirmed, and the dependences for calculating the distribution function taking into account the time factor were obtained;

- models were developed for calculating the time of deposition of coagulated disperse mixtures and model for calculating control parameters for controlling the process of unloading and transportation of dense dispersions.

Theoretical significance of the research lies in the creation of the scientifically based model of the cluster aggregation in the disperse systems taking into account the time transformation of their structure, as well as the model of the flow of the dense disperse system taking into account the volumetric energy dissipation.

Practical value. The methodology was developed for assessing the control parameters of the aggregation process in order to ensure stable fractional composition; the methodology was proposed for calculating energy costs for transportation and unloading of the disperse systems with non-Newtonian rheology; the methodology was proposed for calculating the control parameters for optimizing the regime of impulse transportation and unloading. The results obtained were implemented in the form of the methodology for calculating the unloading and transportation of sediments and slags in KazNIIHimproekt LLP, as well as in the educational process at M. Auezov South Kazakhstan State University.

Publications by the research theme. On the theme of the dissertation, 12 scientific works were published, including 3 articles in the journals recommended by the Committee for Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, 3 articles in the publication included in SCOPUS international database for scientific journals and having a percentile of CiteScore above 25, according to the requirements of the Ministry of Education and Science of the Republic of Kazakhstan and 6 articles in proceedings of international conferences. The content of the articles covers the main content of the dissertation.

Introduction gives assessment of the current state of the scientific problem being solved, the basis and initial data for the development of the theme, the rationale for the need for research work, information on the planned scientific and technical level of development and metrological support of the dissertation, the actuality and novelty of the theme, the relationship of this work with other scientific research works, the objective, object and subject, tasks of the research, methodological base, provisions to be defended, practical value and testing the practical results.

The first section of the work considers literature review of the problems of describing and modeling the processes of aggregation in the disperse systems from the point of view of the fractional composition formation kinetics, as well as the practical significance of aspects related to these issues. Based on the analysis, the research tasks were formulated.

The second section of the work considers development of new mathematical models of irreversible aggregation of the disperse systems. The aggregation model was developed that takes into account the transformation of the cluster structure of the disperse phase, conceptual prerequisites were formulated for deriving the modified kinetic equation with allowance for relaxation times, corresponding modified integral and differential equation was obtained:

$$\frac{dC_I}{dt} = \frac{1}{2}\sum_{J=1}^{I-1}\int_0^t\int_0^t N_{J,I-J}C_J(t_1)C_{I-J}(t_2)dt_1dt_2 - \sum_{J=1}^{\infty}\int_0^t\int_0^t N_{I,J}C_I(t_1)C_J(t_2)dt_1dt_2 \qquad (2.1)$$

Theoretical aspects of the scaling of speed nuclei in the Smoluchowski aggregation equation were described: the role of internal transformations of the internal structure of clusters and the change in their aggregation activity due to the history of formation. In accordance with this concept, it was proposed to represent the kinetic model of aggregation in the form of a system of two kinetic equations, where the aggregation nuclei were written as the product of internal and external factors described by the internal and external kinetic equations, respectively.

$$N_{I,J} = N_{I,J}^{(in)} \cdot N_{I,J}^{(out)} \qquad (2.2)$$

The first factor describes the effect of transformation of the cluster structure over time, the second describes the change in time of the cluster concentrations of different orders.

The special factor of stabilization of the fractional composition $\tilde{W}$ was introduced and the approach to its calculation based on the physical characteristics of the disperse medium was substantiated:

$$\tilde{W} = \frac{C_{2i}}{C_i} = \frac{(3/2)^{\beta}}{1+(zi)^{\beta}} \tag{2.3}$$

where to calculate the parameters z and β by the tabular values of the physicochemical characteristics of the medium the corresponding relations were proposed in the dissertation.

The developed models allow to describe the dynamic processes in the disperse systems with complex structural transformations of the aggregated clusters of the disperse phase.

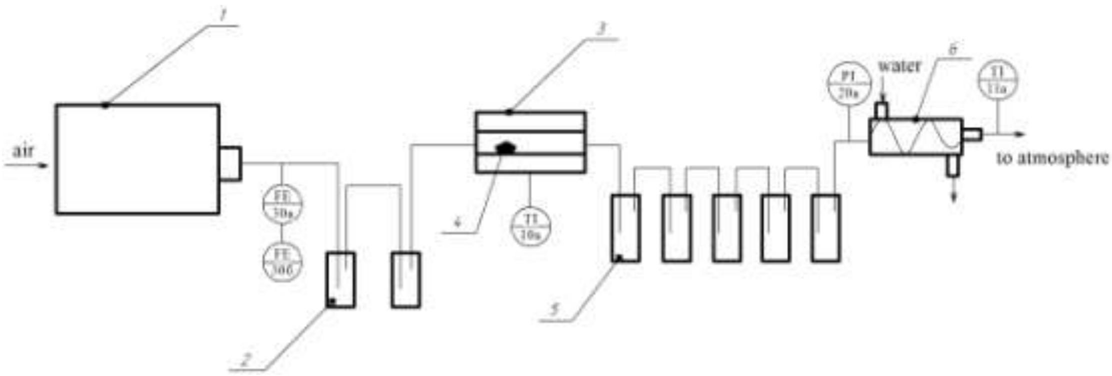
The third section of the work considers experimental studies of the regimes of the formation of dispersions with a given narrow fractional composition in desublimation processes. The object of the research was the process of desublimation of vapors of silicon dioxide SiO_2.

The main objective of the experimental studies was to study the variations in the fractional composition of the dispersion at various time stages of the desublimation process.

The research facility contained two main nodes. The first node is the node for producing oversaturated silicon dioxide vapor. The technological process at this stage was based on the well-known method of enrichment of high-silicon phosphorites of Karatau and was tested earlier in various experiments on desublimation. The second node is the node of the vapor desublimation in the system of successive Drexel flasks.

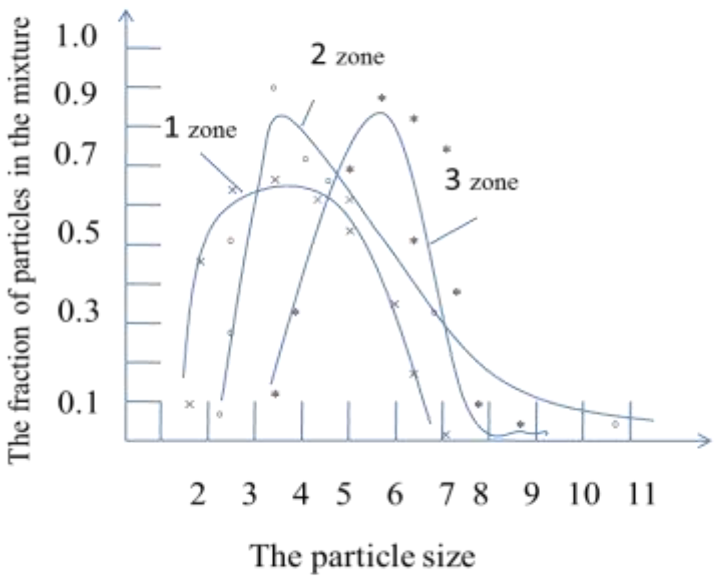
A total of 33 sublimates were made and analyzed based on five prepared samples. In each case, the particle size distribution function was determined by counting the number of particles in the microphotography field by applying a grid with a step of 2 μm. JSM-6490LV scanning electron microscope (SEM) was used as equipment for carrying out electron microscopic studies of the desublimate.

The facility diagram is shown in Figure 1.



1 – compressor, 2 – drying node, 3 – electric furnace, 4 – sublimated sample, 5 – desublimation and recovery system, 6 – heat exchanger
Figure 1 – Scheme of the experimental facility

Figure 2 presents some results of statistical processing of the experimental results.



× 1 zone – average period of passage of the 1st and 2nd flasks of Drexel;
◦ 2 zone – average period of passage of the 3rd and 4th flasks of Drexel;
∗ 3 zone – period of passage of the 5th flask of Drexel.

Figure 2 – Density distribution of the dispersion cluster size of the desublimate in microns in different time zones at a temperature at the inlet of the flask system 450ºC

The results of the experimental studies confirmed the theoretical conclusion that there is a stage of rapid formation of primary nucleates and a subsequent stage of slow diffusion-controlled growth of aggregates. With a large initial oversaturation, when a large number of embryos (monomers) of the disperse phase is quickly formed in a unit volume of the apparatus, the contribution of many-particle collisions is especially large. Then there is a sharp decrease in oversaturation and the aggregation process begins to be limited by diffusion resistance in the gas phase. This leads to a sharp decrease in the intensity of aggregation and the result is a dispersion of a fairly uniform fractional composition.

Based on the experimental studies, empirical dependences were obtained for calculating the curve of the distribution density of clusters by size and sphericity coefficients in the following form:

$$f(i,T) = A\exp(-C_1 iT/T_*) - B\exp(-C_2 iT/T^*) \qquad (3.1)$$

The coefficients of formula (3.1) for the time zones: for the 1st zone $A=1.52$; $B=0.62$; $C_1=0.54$; $C_2=0.74$; for the 2nd zone $A=2.38$; $B=0.80$; $C_1=0.66$; $C_2=0.62$; for the 3rd zone $A=2.60$; $B=0.72$; $C_1=0.81$; $C_2=0.52$; T_* - characteristic time for the zones.

The fourth section of the work considers development of the models and description of modes of overload and transportation of the disperse systems; theoretically describes the phenomenon of precipitation formation and modes of overload and transportation of the disperse systems in the nodes of technological apparatuses. A model of gravitational sedimentation of bidisperse suspension in the conditions of mutual aggregation of particles of various fractions; a model for calculating flow parameters of dense polydisperse suspensions, a model for controlling the disperse material overload were developed. As a result of the simulation, the methods were proposed for constructing a curve of the sediment accumulation from various dispersion fractions and a curve of the concentration change of the initial clusters. The approach to the problem of describing the flow of dense suspensions and sediments was developed, which allows to calculate the flow speed of dense suspensions near a solid wall and the speed of outflow from the reservoir.

$$V_f = -\gamma(H_0 - H) + \sqrt{\gamma^2(H_0 - H)^2 + 2gH} \qquad (4.1)$$

The new model demonstrates good qualitative agreement with the experimental observations, but requires a more detailed analysis of the array of experimental data in order to clarify a number of control parameters applied to specific physicochemical systems.

Conclusion gives brief conclusions on the results of the dissertation research, assessment of completeness of solutions to the tasks, recommendations and initial data on the specific use of the results, assessment of the technical and economic efficiency of implementation and level of work performed in comparison with the best achievements in this field.

Notations: C_I - volume concentrations of the *I* order clusters in the disperse phase, 1/m^3; g – gravitational acceleration, m/s^2; H – height of the disperse medium layer in the reservoir, m; $N_{I,J}$ - the aggregation nuclei of cluster of the orders *I, J*, m^3/s; *t* – time, s; V_f - outflow speed, m/s; γ - outflow coefficient, 1/s.