1. Introduction

Industrial activity in the exploration, enrichment of natural raw materials (ore, coal, etc.) and its further processing (obtaining coke, cast iron, steel, nonferrous metals, etc.) are accompanied by the formation of significant amounts of technogenic waste, including that in the form of slimes, which are discarded into the slime collectors. The accumulation of waste leads to an increase in the ecological risk of polluting the adjacent territories and underground waters.

At the same time, a solid phase of the slimes of chemical, metallurgical, mining, coal industries is frequently a valuable mineral raw material, while it is expedient to use a liquid phase in the closed system of circulating water supply of enterprises instead of clean water.

As a whole, slime waters of the majority of enterprises in chemical sector are heterogeneous systems with a polydisperse composition of the solid phase of different nature and are inhomogeneous multicomponent mechanical mixtures with complex granulometric composition. For slimes and silts from many production facilities (for example, coal preparation plants), characteristic is the high (to 90 %) content of finely dispersed (less than 40 µm) fractions of solid phase, which makes their purification technologically complicated and economically inadvisable.

Under contemporary conditions, enormous attention is paid to the improvement of existing technologies and devising new effective methods for the water purification, to the implementation of resource-saving low-waste technologies, modernization of existing methods and designs of water-purifying devices. Such solutions make it possible to save material and natural resources, as well as utilize valuable components of slime wastes.

It was revealed by the results of industrial tests on the purification of polydisperse slime waters of different origin that the effectiveness of cleaning depends on granulometric composition of the solid phase in the slime, its initial concentration, conditions for conducting the flocculation. All the above-stated leads to the need for establishing the best (optimum) conditions for flocculation and thickening of the solid phase of polydisperse slimes depending on the factors that influence the strength of floccules.

In connection with this, a relevant scientific-practical task is the intensification of processes of cleaning the polydisperse slimes of industrial enterprises.

2. Literature analysis and problem statement

The existing water-slime circuits of the processing enterprises, described in the literary sources [1–4], imply two stages of cleaning the generated slimes. The first stage, as a rule, includes a primary clarification (thickening) of slime in the sumps or slime collectors. Following it, the dehydration of thickened slime is conducted with the aid of centrifuges or filtering equipment [5]. This makes it possible to close the water rotation cycle of enterprises and to direct purified water to meet the needs of an enterprise.

The application of one or another process of dehydration depends mainly on the hydraulic coarseness and the granulometric composition of slime, as well as the expediency of using the solid phase as a commodity product [6]. The world prac-
The phenomenon of aggregation of the solid phase of highly dispersed suspensions with the application of flocculants is widely used for the dehydration of sediments in the filtering or centrifuging equipment [10]. Thus, for instance, article [11] notes the high efficiency of ionogenic (cationic and anionogenic) flocculants for cleaning the coal slime in comparison with the nonionogenic one that requires considerable consumption. Authors of paper [12] recommend, for cleaning the slimes of coal preparation, using anionogenic flocculant and they established the dependence of its consumption on the concentration of solid phase and pH value. The adsorption activity of polymeric flocculant is also influenced by other factors, for example, the mineralization of liquid phase [13]. A variety of factors that affect the process of flocculation leads to an increase in its dosage, instead of optimizing the process itself, for example, the stages of adsorption of polymer at the surface of the particles and the development of aggregation.

As a result of destruction of those already formed floc
cules, contemporary water and slime circuits carry out the aggregation of finely dispersed fractions of the solid phase before each apparatus for pre-flocculation, which leads to essential expenditures. Therefore, solving the problems on the scientifically substantiated choice of methods for the intensification of separation of inhomogeneous polydisperse suspensions and maximally effective use of a flocculant is important. One of such methods is the selection of the best parameters for realization of the process of floccules formation at the minimum consumption of expensive chemical reagents.

In addition, researchers have not formed a unified approach about the regimes of flocculation and the indicators, which are used for the evaluation of effectiveness of this process.

Thus, detecting the patterns governing the floccules formation in polydisperse slimes will make it possible to intensify the process of cleaning slime and to minimize consumption of expensive flocculant.

### 3. Aim and tasks of research

The aim of present work is to examine the ways for the intensification of dehydration of polydisperse suspensions in the process of their flocculation, as well as to explore the factors that influence the development of aggregation, resistant to mechanical actions.

To achieve the set aim, the following tasks were to be solved:
- to study influence of the concentration of solid phase and disperse composition of slime on the effectiveness of floccules formation;
- to examine dependence of floccules deposition velocity on the disperse composition;
- to propose a criterion of effectiveness of the process of development of aggregation, resistant to mechanical actions;
- to examine the structure of floccules under different regimes of deposition and the possibilities of directed change in their strength toward mechanical actions.

### 4. Materials and the methods of research into the process of flocculation of polydisperse coal slime

#### 4. 1. Preparation of model slimes with the controlled parameters

A research into the flocculation of polydisperse slimes was conducted on the model slimes with the controlled parameters of concentration and disperse phase, synthesized in the following way. The real slime, taken from one of the acting coal preparation plants, was passed through the sieves, size 40, 60, 80 and 100 µm, while large fractions were separated. Slime with the fraction below 40 µm was thickened by settling and then diluted by clarified liquid to the concentrations from 10 to 100 g/dm³, necessary for defining effect of the concentration of solid phase on the process of flocculation.

For the subsequent sets of experiments on the study of effect of disperse composition, we synthesized slime with the content of solid phase from 10 to 100 g/dm³ and the addition of medium grade, size 40–100 µm, in the amount from 5 to 30 %.

A fraction larger than 100 µm was not of interest for further studies. Density of the solid phase of slime was 1.7 kg/dm³.

#### 4. 2. Procedure for conducting studies of the process of flocculation of polydisperse slimes

The measurement of kinetics of the floccules deposition under regime of free (unconstrained) settling was conduct
ed in the laboratory measuring cylinder, diameter 50 mm, height 500 mm.

Before the actual experiment, the type of flocculant and its concentration were selected. For the slime of this produc
tion, we used nonionogenic and anion-active flocculants in the calculation of 200 g/t.

The calculated amount of diluted solution with mass fraction of flocculant at 0.1 % was added into the upper layer of measuring cylinder by two portions. At first, nonionogenic flocculant (the stage of adsorption at the surface of solid phase) – 20 % of the total amount of flocculants, then the remaining 80 % of anionogenic (the stage of floccules formation). After the introduction of each portion of flocculant, the contents of cylinder were stirred by its tenfold slow
tilting. With the aid of a stopwatch, we measured the time interval, during which the interface of two phases covers the distance between two rings, marked on the cylinder. This path comprised 0.4 the height of cylinder, which corresponds to the zone of free sedimentation of particles. Then, according to the obtained experimental data, we calculated the rate of floccules deposition ($V_\text{p}$, mm/s).

For evaluating the quality of flocculation of slimes (mechanical strength of aggregates), the following technological test is used. Upon completion of the floccules deposition and the measurement of their rate of deposition, we repeatedly stirred the sample by a mixer at the velocity at the tip of the blade approximately of 2 m/s for 40 seconds in a rectangular tank 12×7 cm. Then we poured the contents into the measuring cylinder and determined the rate of deposition of the weighed particles in the sample ($V_\text{p}$, mm/s).

This mechanical action imitated the motion of the flocculated slime from the unit for thickening (sump) to the unit of dehydration (centrifuge or pressure filter). Residual rate of deposition after mechanical action characterizes dimensions of aggregates, therefore, the strength of floccules and their sedimentation activity.

At the stages of introduction of the first portion of flocculant and determining the settling velocity of the floccules before and after mechanical action, we took samples of slime, which were studied under the microscope.

5. Results of examining the process of flocculation of polydisperse slimes

By the results of the conducted experimental research, we calculated the rate of deposition of floccules as the ratio of 0.4, the height of the clarified layer (free deposition), to the time it took for the floccules to cover this path. The primary results of experiment were the points in the coordinates “time of floccules deposition – concentration of solid phase in the slime”. Each point was the averaged value of the results of three-to-four experiments. Relative deviation in experimental data from the mean value (ratio of the value of deposition velocity in particular experiment to the mean value of several experiments, conducted in the same point) did not exceed 9.4 %.

Results of research into the rate of deposition of floccules on the concentration of solid phase in the slime and the content of average fraction in the interval 0–30 % (value of lines in the graph) are given in Fig. 1. It is evident from the graphs that with the increase in the concentration of solid phase, the effectiveness of flocculation falls and optimum for the deposition of floccules in the field of gravitational forces is in interval 20–30 g/dm$^3$ at the identical concentration of flocculant.

At the same time, with an increase in the content of medium fraction (40–100 µm) of the solid phase in slime from 10–30 %, the speed of clarification of slime substantially increases. The formation of large agglomerates with sufficiently good deposition velocity (exceeding 10 mm/s) is observed, which is confirmed by the photographs of floccules, represented in Fig. 2.

With an increase in the concentration exceeding 60 g/dm$^3$, instead of the stable aggregates, floccules of diffuse form are formed, Fig. 3, a, b, which acquires clear outlines with an increase in the concentration of medium class, Fig. 3, c, d.

There is practical interest in the rate of deposition of the flocculated slime after its exposure to mechanical action...
from the mixer. Dependences of this speed on the content of medium class (40–100 µm) of the solid phase and the concentrations are represented in Fig. 4. The graphs demonstrate that the residual velocity falls with an increase in the concentration, while the optimum is displaced into the region of concentrations 10–30 g/dm³.

An increase in the content of medium class in the slime contributes to the retention of speed (strength of aggregates) at higher concentrations, which, similar to the speed without mechanical action, are limited by the concentration of 60 g/dm³. As can be seen from Fig. 4, the content of the medium class also influences the strength of the formed aggregates, with an increase in the share of which in the slime, the retention of size and strength of the floccules is observed (consequently, residual rate of deposition).

At the concentration of particles the size larger than 40 µm above 10 %, an increase in the deposition velocity of the floccules is observed even after mechanical action with sufficiently good speed (above 3 mm/s at the concentrations of solid phase to 30 g/l). Clear outlines of floccules are observed (Fig. 5, c–b) and the liquid phase after their settling remains transparent.

### 6. Discussion of results of examining the flocculation of polydisperse slimes

According to the concepts on the process of flocculation, the development of aggregation by the ortho-kinetic mechanism occurs in two stages: the adsorption of polymer at the surface of the particle and then the formation of bridges between the particles. At low concentrations of the solid phase, flocculate is distributed evenly in the volume of disperse medium and it is adsorbed well at the surface of the solid particles. An increase in the concentration of solid phase obviously leads to the non-uniform distribution of polymer at the surface of the particles, whose convergence contributes to the start of the second stage – the aggregation of particles. This leads to the formation of unstable bonds and, accordingly, unstable floccules that are destroyed under mechanical influences. At the same time, at the low concentrations, there are more macromolecules of polymer per unit of area of the interphase (per each particle), which increases the strength of the particles bond in the structure of aggregate.

As studies revealed, important role in the process of forming the aggregates, resistant to mechanical influence, is also played by the structure of the formed floccules, which depends on the presence of medium grade (particles, larger in size). Obviously, due to the larger surface, such particles adsorb more macromolecules of polymer, as well as more effectively capture smaller particles, coming out as floccules formers. Due to the larger mass and adsorption surface, the fraction larger than 40 µm aggregates small particles with the formation of stronger bonds than when combining small (size less than 40 µm) particles between one another. Photographs, taken at the first stage of flocculation (the introduction of nonionogenic polymer), represented in Fig. 6, display that at identical concentration of the solid phase in the presence of medium grade, clearly expressed nuclei of future aggregates are formed (Fig. 6, b–d). In the absence of medium grade – a cluster of small clots of the solid phase (Fig. 6, a).

Furthermore, the less the particles are, the more difficult it is for them to overcome repulsive forces (“wedging pressure”) and to approach each at a sufficiently close distance (commensurate to their radius), necessary for the aggregation. Since the energy, necessary for overcoming the potential barrier, is proportional to the mass of the particle, then the larger particles more effectively concentrate small ones at their surface, approaching them and capturing them.

Analyzing results of experimental studies, it is possible to argue that the sufficiently convenient qualitative indicator of strength of the formed floccules is the residual rate of their deposition following a mechanical action, which, in turn, corresponds to the size of floccules and strength of the bond between particles. An alignment with the conditions for the optimum ratio of the concentration and the disperse composition of slime at the stage of development of aggregation (flocculation of slimes) makes it possible to obtain sufficiently durable floccules, resistant to mechanical actions,
and to eliminate the need for the pre-flocculation of slime before the dehydrating equipment (centrifuges or pressure filters), that is, to save reagents.

**Fig. 6.** Photographs of the formed nuclei of flocules after the introduction of the first dose of flocculant at concentration 30 g/l and the content of medium fraction in slime, %: a – 0, b – 15, c – 20, d – 30

Results of industrial tests demonstrated that a sufficiently high efficiency of the removal of solid phase in the centrifuges at the level of 90–98 % is achieved at the values of flocules deposition rate (thickened before the centrifuge of coal slime) equal to $V_2 > 2$ mm/s. This magnitude shows sufficiently high strength of flocules and makes it possible to carry out effective thickening of slime in the centrifuge without adding a new portion of flocculant with the minimum entrainment of solid phase.

When examining the intersection region of the obtained experimental curves (Fig. 4) with the value of flocculation effectiveness $V_2 = 2$ mm/s, obtained under industrial conditions, it is possible to build a dependence of the influence of medium grade and concentration on the strength of flocules, which corresponds to the minimum consumption of flocculant (Fig. 7).

Thus, using this dependence, it is possible to sufficiently accurately predict effectiveness of the flocculation of the coal slime (when satisfying all other conditions of obtaining laboratory data). By knowing the concentration and screen composition of slime, it is possible to control the process of flocculation and formation of durable flocules by bringing the concentration (dilution of slime) or the content of medium grade (by additional introduction of solid phase, for example, micro-sand) to the desired value in the curve.

**Fig. 7.** Dependence of residual strength of flocules after mechanical action on the content of medium grade and the concentration of solid phase in slime

### 7. Conclusions

Conducted studies allow us to formulate the following conclusions:
- research into the influence of concentration of the solid phase on the effectiveness of flocules formation revealed that the best settling velocity of flocules (their dimension) is observed in the range of 10–30 g/dm$^3$ and, at an increase in the concentration, decreases because of the insufficient adsorption of polymer at the surface of solid particles;
- study of dependence of the settling velocity of flocules on the disperse composition demonstrated that the settling velocity and the strength of aggregates toward mechanical action grows with an increase in the share of content of grade above 40 µm, starting at 10 % and higher;
- residual speed after mechanical action, which is proportional to the size of flocules and must not be less than 2 mm/s may serve a criterion of effectiveness of the process of development of aggregation, resistant to mechanical actions;
- by creating optimum conditions for the adsorption of polymer, for example, by changing the concentration of solid phase and the content of medium grade (particles 40–100 µm) at the stage of flocules formation, it is possible to control the process and to form sufficiently durable flocules at the minimum consumption of flocculant.

### References