

Досліджено вплив концентрації твердої фази бурових стічних вод на змінення швидкості осідання твердої фази при агрегатоутворенні під час фізико-хімічного методу очистки води з використанням флокулянтів та коагулянтів. Це важливо, тому що зміна концентрації твердої фази у стічній воді є неконтрольованим процесом під час реагентної очистки та суттєво впливає на механізм агрегатоутворення та кінетику осідання твердої фази.

Дослідження проводилися на модельній стічній воді, виготовленій шляхом розбавлення відпрацьованого бурового розчину водопровідною водою. Було встановлено, що застосування флокулянтів без коагулянтів не ефективно і не призводить до агрегатоутворення. Встановлено, що оптимальною дозою коагулянту сульфату алюмінію для порушення стійкості дисперсної системи буровий стічної води є 65 міліграм/г, а збільшення дозування коагулянта не впливає на швидкість осадження пластівців. Серед флокулянтів найбільшу активність проявляє аніонний флокулянт А-19. При згущуванні шлему спостерігається руйнування флокул і за 9 хвилин швидкість осадження флокул знижується вдвічі. Збільшення концентрації флокулянта з 0,8 міліграм/г до 1,6 міліграм/г приводить до збільшення швидкості осадження твердої фази в 2–2,5 разів.

Показано, що концентрація твердої фази впливає на швидкість осадження флокул, оптимальні умови агрегатоутворення спостерігаються за концентрації 4–6 г/л. Механічні дії на агрегати призводять до руйнування флокул залежно від концентрації твердої фази. Встановлено, що зміни в дисперсній системі можна спостерігати за зміною водневого показника, який змінюється залежно від концентрації твердої фази в буровій стічній воді. Зростання концентрації твердої фази з 1 до 10 г/л призводить до зміни рН від 7,2 до 8,3, після введення коагулянта спостерігається зниження рН, а подальше руйнування агрегатів приводить до збільшення водневого показника.

Одержані в результаті досліджень дані і запропонована методика можуть бути використані для підбору оптимальних дозувань реагентів при очищенні бурових стічних вод.

Ключові слова: коагуляція, флокуляція, очищення бурових стічних вод, агрегатоутворення, міцність флокул, швидкість осідання

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REVEALING PATTERNS IN THE AGGREGATION AND DEPOSITION KINETICS OF THE SOLID PHASE IN DRILLING WASTEWATER

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1. Introduction

Energy independence of any country requires increasing amounts of oil and gas production. This task can be solved at intensive development of oil and gas industry, and, consequently, by drilling and operation of more wells.

A drilling process is accompanied by drilling waste, such as drilling wastewater (DWW), used drilling fluid, and drill cuttings. Drilling wastes can contain impurities and heavy metals in dangerous concentrations [1], as well as adversely affect components of the biosphere, hydrosphere, and lithosphere [2]. The main objective of drilling is the construction of productive wells with the lowest possible environmental impact.

A possibility of negative impact of drilling wastewater on the environment largely depends on the quantity and toxicological characteristics of pollutants, which are

used for preparing drilling mud. There is also a danger of emissions of hydrocarbons and radioactive elements at the surface, as well as heavy metals. For example, paper [3] estimated wastewater pollutants from three plants discharging wastewater from the natural gas development in Pennsylvania. It was found that barium, strontium, bromides, chlorides, benzene, the total dissolved salts and suspended solids, exceeded the norm.

When sludge pits are practically utilized, liquid wastes evaporate from a pit mirror; abundant atmospheric precipitation can lead to the overflows of chemically hazardous drilling wastewater and the used drilling mud through the edges of the pit. In case of emergency, a hydro-insulating film, which lays at the bottom of the pit, is torn, the result being the penetration of contaminants into soil that entails the migration of chemical elements and soil mineralization over large areas. That leads to disruption of ecological balance

and, in many cases, to the degradation of flora and fauna at a given area, as well as increases the risk of contamination of water and food with heavy metals that are dangerous for human health [4].

A technique to dump wastes into open sludge pits, in practice at present, cannot fundamentally solve the problem of disposal of liquid drilling waste because pits remain to be a source of negative influence even over long periods after drilling ends. The issue on a possibility to dispose of and recycle liquid waste, specifically DWW, has not been fully resolved up to now and thus requires additional research in this area. The physical-chemical composition of DWW varies widely and depends on the amount of washing fluid, as well as the share of drilling mud and chemicals that penetrated the water. At the same time, for practical drilling, it is promising to purify DWW for reuse at a rig as technical water. Reuse of the treated DWW would make it possible to reduce fresh water consumption, as well as significantly decrease the amount of liquid waste discharged into sludge pits.

According to [5], almost half of the total volume of waste during drilling accounts for drilling wastewater (48 %), 33 % – used drilling mud, the remaining 19 % – a solution for testing and removed rock. Drilling wastewater consists of liquid wastes resulting from various technological operations when drilling a well: partial dumping of used drilling fluid, cleaning of grids at vibratory sieves, cooling of pumps' rods, equipment and production sites washing.

Chemical composition of drilling wastewater at various rigs differs depending on the composition of used drilling fluid, the geological and climatic conditions of well location, and the depth of drilling.

The drilled-out particles of clay rocks, while rising to the surface, merge with the drilling mud filtrate and swell. The mineralogical composition of drill cuttings is determined by the lithological composition of drilled rocks; it can change when a well deepens. The chemical composition of drill cuttings depends on its mineral composition and the properties of a drilling mud. Drilling wastewater has high mobility and can accumulate contaminants. The base of drilling wastewater is the used drilling mud that contains up to 15 % of organic compounds (petroleum products, chemical reagents) and up to 37 % of a weighting agent [6].

Essential components of any clay drilling mud are the clay powders: bentonite (main clay mineral is montmorillonite), palygorskite (main clay mineral is attapulgite). Clay is used as a stabilizer of drilling mud and a viscosity regulator. When drilling a well and disclosing the deposits with abnormally high layer pressure, drilling mud must be made heavier; this involves weighting agents: barite (anhydrous barium sulphate) and hematite. A regulator of the mud pH, used to achieve the required parameters, is caustic soda (NaOH). Surface-active substances (SAS) are also part of drilling muds. In order to degas drilling mud, defoaming reagents are used, and when it is required to maintain drilling mud density, reagents-stabilizers are applied (a carbon alkaline reagent, carboxymethylcellulose, hydrolyzed polyacrylamide, etc.), reagents-thinners (ferrochrome lignosulfonate, lignoxin, etc.). In addition, the formulations include such substances as lime, sodium bicarbonate, different types of salts, heat stabilizers, emulsifiers, lubricants, corrosion inhibitors, biocides, etc.

Drilling waste treatment methods include recycling, removal, decontamination, and disposal of wastes. The

treatment types of liquid drilling waste are conditionally divided into mechanical, physical, chemical, biological, and combined [7]; those methods that are commonly applied at present are analyzed in more detail in [8].

The first stage of DWW treatment involves mechanical methods (cleaning at screens, settling in sand traps, centrifugation), which make it possible to capture only the large fractions of rock that pollute DWW. Next, there is the task on cleaning the water from finely dispersed particles in soak clay that form a stable dispersed system.

To accelerate the process of deposition of suspended particles in disperse systems, coagulants are used, and to intensify the process of deposition of these particles – flocculants [9]. Coagulants disrupt the stability of a disperse system and lead to the aggregation of fine fractions into flakes. A coagulant that is used for DWW treatment is aluminum sulphate $Al_2(SO_4)_3$ while polymers based on polyacrylamide (PAA) are used as flocculants. The primary effect of polyacrylamide is to contribute to increasing the size of flakes at coagulation [10].

A complex chemical composition, which depends both on a drilling technology in a given area and the geological structure of underlying gas reservoirs, as well as the presence of a thin fraction of soak clay in wastewater, complicate the processes of its treatment. Therefore, in each case, at each well, it is necessary, depending on the conditions for wastewater formation, to explore a possibility to treat DWW, as well as adjust reagent consumption.

Thus, it is an important scientific and practical task to undertake a research and devise a procedure for treating the actual drilling wastewater, which would be applicable at wastewater treatment plants.

2. Literature review and problem statement

The choice and efficiency of a method for treating drilling wastewater from suspended substances depends on the concentration of the solid phase, conditions for the course of the process, and the concentrations of reagents.

Paper [11] studied the treatment of drilling wastewater from a system of the sulphonated drilling mud at the Shengli oil field, East China. The wastewater was deeply cleaned using a combined chemical coagulation process at a dosage of 18 g/l at pH=7, as well as by adding cationic polyacrylamide in the amount of 8 mg/l. The wastewater then underwent centrifugal separation and catalytic ozone oxidation over 40 minutes. However, the high-quality centrifugal separation requires the formation of stable strong floccules. Otherwise, under the action of centrifugal forces, the finely dispersed fraction would again pollute the wastewater. These issues are not addressed in this publication. In addition, paper [11] lacks any information on the treatment efficiency at different concentrations of pollutants in the water.

Study [12] addresses the optimization of treatment parameters when dewatering bentonite drilling mud through a combination of flocculation with lime in a range from 0 up to 10 g/l and subsequent electric filtration. Application of direct current made it possible to effectively dehydrate the sludge at an optimal amount of lime (0.3 g/l), which was significantly lower than those typically used during simple filtration (10 g/l). However, a given method requires considerable expenses on reagents and electric filtration.

An analysis of the aggregation of dispersed particles, described in work [13], reveals that the deposition rate of floccules depends on the concentration of the suspended particles and their dispersion. It is shown that the best conditions for the formation of large and strong floccules in coal sludge are achieved at a concentration of 10–30 g/l and in the presence of a large phase the size over 40 μm in the amount exceeding 20 %. That indicates that during parameters optimization and selection of reagent dosing it is necessary to take into consideration the concentration of the solid phase in wastewater. The concentration of the solid phase in DWW is not constant for each drilling rig and may vary depending on the amount of washing water, which requires additional research.

Paper [14] examined the influence of cationic and anionic polyelectrolytes, as well as regimes and intensity of suspension agitation on the kinetics of formation, destruction of bentonite aggregates and a kaolin particle in a flow-through system. It was found that there are various dependences of flocculation on a dose of the added polyelectrolytes for diluted and concentrated suspensions. This is explained by the varying degree to which the flocculants are adsorbed at the surface of particles approaching the equilibrium state at different concentrations of dispersed phases.

At the same time, the issues on selecting the optimal concentration of a coagulant and flocculant are not fully described in the scientific literature. The effects of such factors as the temperature, pH level, as well as the rate of agitation, which affect the course of the process of coagulation and flocculation of actual drilling wastewater, also remain insufficiently examined. Additional research is also needed into the strength of the formed aggregates to mechanical influences, as well as conditions for maintaining the strength of floccules at transportation and subsequent dewatering of waste water.

The process of coagulation typically involves different hydrodynamic conditions. Publications [15] investigated the effectiveness of coagulation over a wide range of shear stresses. The applied model solution of suspended solids at surface waters was the synthetic suspension of bentonite in tap water. It was found that the flakes formed by iron chloride cannot grow at a medium shear stress, for instance, 1.5 Pa. On the contrary, polyelectrolytes lead to large dense flakes, resistant to a shear stress. It is shown that the destruction of floccules turns out to be irreversible regardless of the coagulant and experimental conditions. This suggests that studying the aggregation must consider the hydrodynamic conditions for the coagulation of impurities, as well as the conditions to maintain floccules strength during dehydrating. A research into floccule strength using an example of coal sludge [16] has shown that maintaining the size of the formed aggregates can be achieved by adjusting the concentration of a solid phase in wastewater, its disperse composition, duration of sludge thickening, the ratio and dosage of flocculants.

It was established in [17] that water-yielding capacity of floccules and the maximum shear stress are maximal over an interval of polymer concentration in the range of 0.15–0.2 mg/g, at which the density of floccules increases by 1.4–1.6 times. However, the paper did not consider the impact of other factors, such as the solid phase concentration and pH.

Study [18] notes that the coagulation process is affected by pH of the medium, process duration and the temperature of the medium.

Publications [14, 15] describe patterns in the aggregation of bentonite clay, although the authors failed to consider the aggregation and sedimentation of actual DWW, with their peculiarities and differences from clay solutions.

In drilling wastewater, the concentration of the solid phase varies from a few grams to 10 g/l [5], and suspended particles are typically represented mainly by a fraction to 10–20 μm [19]. Furthermore, the base of many drilling fluids is bentonite clay, susceptible to self-dispersion and highly hydrophilic at that [20].

An analysis of the scientific literature revealed [5, 11, 19] that a low concentration of the solid phase, the special properties of soak clay, as well as the complex chemical composition of DWW, do not make it possible to recommend certain parameters for sewage treatment and the dosage of reagents. That leads to the fact that the development of a treatment method for each drilling rig requires experimental studies involving actual fluids. In addition, the composition of DWW may differ depending on the stage (depth) of drilling, and, therefore, the pre-selected reagents may fail at a change in the composition of wastewater. Typically, at wastewater treatment plants, the concentration of the solid phase can vary up to 10 g/l, and, consequently, control over the process and maintaining the required treatment efficiency can be easily achieved by changing the dosing of reagents. Thus, an unresolved aspect of the task to treat DWW is still finding the optimal conditions and concentrations of reagents to disrupt the stability of a disperse system and the aggregation of actual drained water. It is also a relevant task to devise a procedure for operational adjustment of reagents dosage directly at the sewage treatment plants.

3. The aim and objectives of the study

The aim of this study was to determine patterns in the aggregation and sedimentation of drilling wastewater depending on the concentration of the solid phase and a dosing of reagents.

To achieve the set aim, the following tasks have been solved:

- to investigate the effect of dosage of reagents on the kinetics of DWW solid phase deposition;
- to identify patterns in the aggregation and sedimentation of the solid phase at a combination of coagulant with flocculants depending on the concentration of the solid phase in wastewater.

4. Procedure for experimental research into the aggregation and kinetics of DWW solid phase deposition

4. 1. Materials and methods to study the properties of DWW

Experimental study was performed using the model solutions of drilling wastewater at a concentration of 1–10 g/l, which were prepared by diluting a batch of the actual used drilling mud with water. A solid phase concentration interval corresponds to the concentration of standard DWW, described for example, in [5]. The used drilling mud based on bentonite clay, treated with polymers, of density $1,230 \pm 30 \text{ kg/m}^3$, was taken from one of the acting drilling rigs at drilling at depths of 220–2,400 m. To achieve the required concentration of the wastewater, we preliminary determined

a moisture content of the drilling mud by drying it at a temperature of 100 ± 5 °C to a constant weight. The laboratory scale TVE-0,21-0,001-a (Ukraine) (Fig. 1, *a*) was used to weigh the batch of sludge; taking into consideration a moisture content of 73 %, we diluted it with water to the concentration required for this study.

We examined the time of agitation and the impact of mechanical influence on the aggregate sludge by using the laboratory pneumatic agitator (Fig. 1, *b*) with a controlled number of revolutions, as well as the magnetic stirrer MM-5 (Fig. 1, *c*).

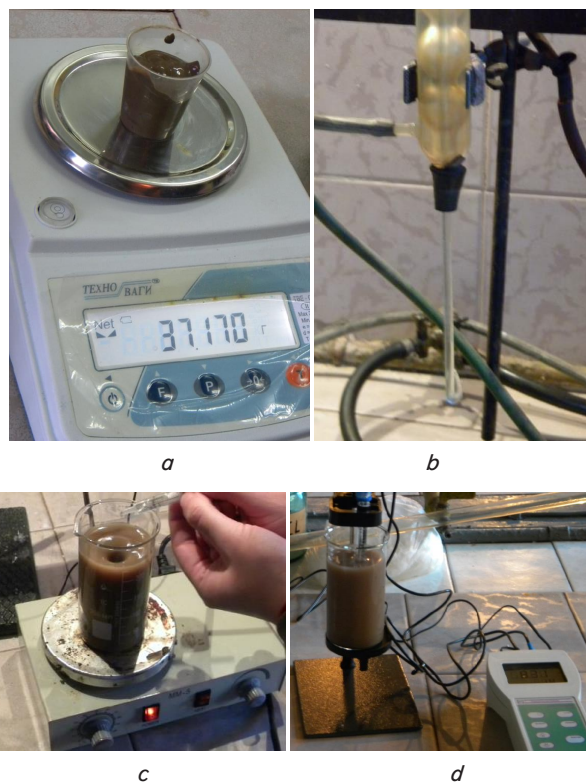


Fig. 1. Laboratory equipment to study the aggregation of drilling wastewater: *a* – laboratory scale; *b* – agitator; *c* – magnetic stirrer; *d* – pH-meter

The activity rate of hydrogen ions pH in the samples of drilling wastewater was determined at the pH-meter pH-150 MI (Russia).

To explore the process of aggregation and to acquire microphotographs, we applied the digital USB microscope with a magnification of up to 1,600 Digital Microscope (China).

4. 2. Procedure for studying the deposition rate of DWW aggregates

We studied the drilling wastewater aggregation in the following sequence. The first stage involved the selection of optimal doses of reagents: coagulant and flocculant. To this end, we added to the measuring cylinders, with a capacity of 500 ml and 50 mm in diameter, containing the drilling slurry of a certain concentration, different dosage of coagulants and flocculants, and measured the deposition rate of the solid phase. The coagulants used were a 10 % solution of aluminum sulphate $Al_2(SO_4)_3$. A flocculant was selected among the anionic flocculants of grade A-19, A-3, A-25; we also tested the flocculant of cationic type K-7 made by

“Ecoflok”. For the experiments, we prepared a concentrated 0.5 % solution of the flocculant, which was diluted to a working concentration of 0.05 %.

We measured the kinetics of floccules deposition after the introduction of the flocculant under a free (unconstrained) deposition mode in the laboratory measuring cylinders with a volume of 500 ml, 50 mm in diameter, according to the procedure described in more detail in [21], with the following clarifications. We introduced, by using a syringe, to a sample of the wastewater with a certain concentration, first, the coagulant, then we stirred the cylinder by 10-time shaking upside down for about 10 seconds until the formation of small flakes. Next, we injected the required amount of the flocculant and repeated the agitation of the wastewater over 10 seconds. The duration of flake formation and of the floccule formation following the introduction of the reagents was found experimentally, via the visual observation of the behavior of aggregates at stirring. Following the formation of floccules, we used a stopwatch to measure the time over which the phase boundary travels the path, which was half the size of the cylinder. This path was accepted based on the condition for free deposition of wastewater with a solid phase concentration less than 10 g/l (we visually observed the limited deposition and a deposition rate drop in the lower third of the cylinder). Based on the acquired experimental data, we calculated the aggregate deposition velocity (V , mm/s) as the ratio of the path traveled by the phase boundary to the time of free deposition in line with (1):

$$V = \frac{0,5H}{t_i}, \quad (1)$$

where H is the height of the cylinder, mm; t_i is the time for free sedimentation of aggregates and the clarification of the cylinder by $0,5 \cdot H$, s.

For each sample of the wastewater, depending on the concentration of the solid phase, we calculated a reagent solution dosage (ml) based on its consumption (in milligrams) per unit mass of the solid phase (in grams). Thus, the amount of the introduced solution of reagents corresponded to a certain concentration of the solid phase in the amount of wastewater. That relates to that the process of aggregation depends on the surface of the solid phase: coagulation – on a change in the charge at the surface of particles, flocculation – on adsorption of the polymer at the surface of particles and creation of polymeric bridges. The surface of the solid phase in a finely dispersed mixture is proportional to its concentration, which is why it is more meaningful to build dependences based not on the volume of wastewater, but per unit mass of the solid phase in water. Therefore, a working reagent solution (a 10 % solution of coagulant and a 0.05 % solution of flocculant) during experiments was dosed in the amount proportional to an increase in the concentration of the solid phase.

In the course of work, we selected samples of the formed aggregates and examined them under a microscope.

The temperature of all samples of the wastewater was maintained constant at 14–15 °C.

4. 3. Procedure for processing experimental results

The response function used in the experiments was the velocity of sludge aggregates deposition. The chosen independent variables affecting the response function were the dosage of reagents (flocculant), the concentration of DWW

solid phase, and the duration of mechanical impact on aggregates that results in their destruction.

In the course of regression analysis, we set the task on finding a functional dependence of the response mathematical expectation $M(Y)$ on the values for specified factors X : $M(Y)=f(X1, X2, \dots, Xn)$.

The results of experiments were mathematically treated using the software package Statistica 7.0, intended for statistical processing of data from experimental research. The data obtained were treated by establishing a dependence of the response on independent variables, mapping them in a graphical form and constructing, based on this, regression models for the assigned parameters.

Initial results from experiments were plotted in the diagrams in the following coordinates: the time of floccules sedimentation – a solid phase concentration in sludge. Each point at these diagrams was the averaged value for the results from three to five experiments. Relative deviation of experimental data from the mean value fluctuated in the range of 0.05–0.2 mm/s, but not greater than 5 % of the average value.

5. Results of studying the deposition kinetics of a solid phase in the drilling wastewater under a combined effect of coagulant and flocculant

The result of analyzing the samples of the used drilling mud has established that about 95 % of the samples were represented by a fraction less than 10 μm . The model solutions of wastewater, prepared based on a given drilling mud, were the finely dispersed stable systems of brown coloration. Settling the wastewater of concentrations 1–10 g/l without adding the reagents that make it possible to disrupt stability of the system, produced no results. After 6 hours of sedimentation, there was a barely notable sludge with a height of approximately 1.5 mm at the bottom of the graduated cylinder. As a result of sedimentation over the next 24 hours, the layer of the sludge grew to 12 mm, without significant changes in coloration, color, and turbidity of wastewater. This suggests that the deposition of solid finely dispersed particles in soak clay requires the use of the chemical enhancement of a deposition process – to apply reagents.

At the first stage, we studied a possibility for depositing a finely dispersed phase using an $\text{Al}_2(\text{SO}_4)_3$ coagulant. To this end, we added to four measuring cylinders with wastewater containing a solid phase in the amount of 5 g/l a different amount of coagulant: 65, 100, 130, and 200 mg/g, respectively. Results of changes in the deposition kinetics for the height of the cylinder (the total height of the layer of wastewater in the cylinder was 130 mm, which corresponded to a 250 ml sample) are shown in Fig. 2. It has been shown that at a dosage of aluminum sulphate of 65 mg/g there occurs the deposition of flakes. Further increasing the concentration of a coagulant does not significantly speed up the process, which is comparable to the accuracy of the experiment. One can argue that the concentration of a coagulant in the amount of 65 mg/g is optimal, so in further experiments we used aluminum sulfate in this dosage. For the further enlargement of formed aggregates, it is appropriate to search for effective flocculants, capable of aggregating the flakes formed by a coagulant.

In order to select the type of a flocculant and to examine its capability to form stable floccules, the next stage involved

studying the influence of flocculants on sedimentation of the solid phase in the process of thickening sludge. It was found that for DWW the introduction of flocculants to the sample without any pre-treatment by a coagulant prevents the separation of sludge into phases and the aggregation does not occur. In the course of the study, we tested three different anionic flocculants and one cationic; flocculants were injected in the amount of 0.8 mg/g after introducing the coagulant in the amount of 65 mg/g to wastewater with a solid phase content of 7 g/l. Every 3 minutes, we stirred the settling sludge anew by a one-time rollover of the graduated cylinder and registered a deposition rate. The result of the study (Fig. 3) has established that only two anionic flocculants demonstrate active aggregation (A-19 and A-3), while the anionic A-25 and cationic K-7 flocculants almost do not form floccules. In addition, the anionic flocculant A-19 forms stronger floccules that have a somewhat faster deposition rate.

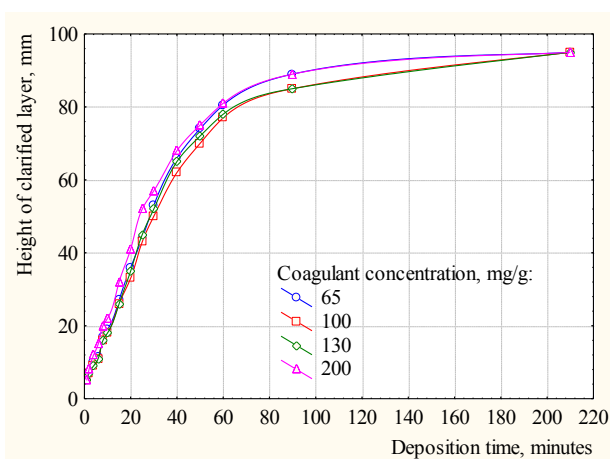


Fig. 2. Dependence of clarification duration of the drilling wastewater with a solid phase concentration of 5 g/l on an aluminum sulfate dosage

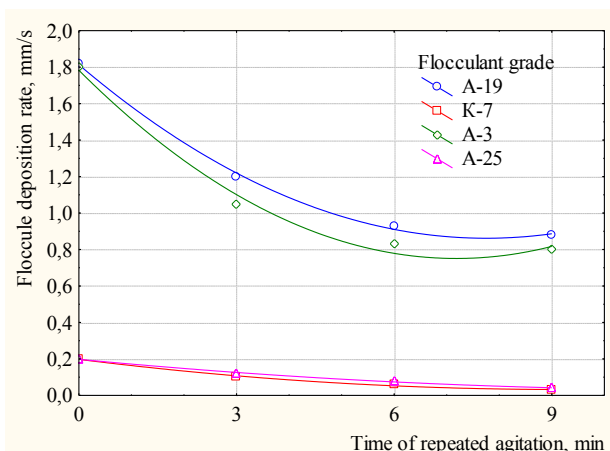


Fig. 3. Dependence of floccule sedimentation rate on thickening duration for the examined grades of flocculants

Following the selection of the dosage of a coagulant and the grade of a flocculant, one should have an idea about the dependence of floccule sedimentation rate on the concentration of DWW solid phase and the flocculant consumption. Results from this study are given in Table 1 and shown in Fig. 4.

Table 1

Averaged results from studying the sedimentation rate of floccules dependent on a flocculant dosage (at a constant dose of coagulant of 65 mg/g)

Flocculant consumption, mg/g	Floccule deposition rate (mm/s) following the introduction of reagents at a solid phase concentration, g/l						
	1	2,5	4	5	6	7,5	10
0.8	1.1	2.2	3.6	4.1	2.9	1.8	0.5
1.2	2	3.5	6.1	7.3	5.7	3.85	2.6
1.6	3	6.7	8.2	9.8	7.4	6.15	3.72

Increasing a flocculant dosage significantly increases the deposition rate and can become a technique to control the process of treatment. It was established that the extremely low (1–2.5 g/l) and high (7.5–10 g/l) concentrations of the solid phase deteriorate the conditions for the formation of large aggregates of floccules.

As a result of processing and smoothing data from Fig. 4, we derived a regression equation, which makes it possible to calculate a deposition rate of floccules depending on the consumption and concentration of a flocculant

$$V = -5,8007 + 1,9604 \cdot C + 5,6793 \cdot Q - 0,1923 \cdot C^2 + 0,0884 \cdot Q \cdot C - 0,4152 \cdot Q^2, \quad (1)$$

where C is the concentration of solid phase in wastewater, g/l; Q is the flocculant dosage, mg/g.

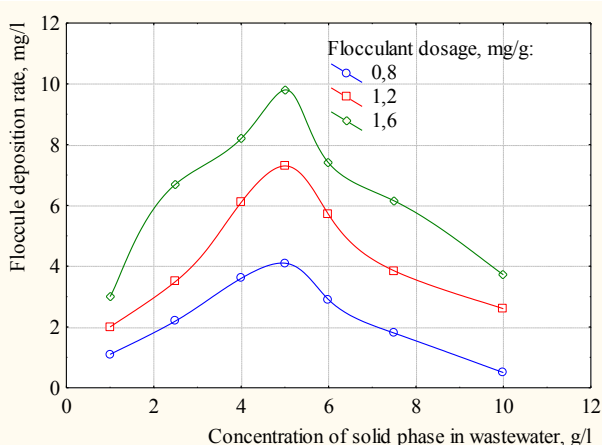


Fig. 4. Dependence of floccules sedimentation rate on flocculant dosage (at a constant dose of coagulant 65 mg/g)

At the next stage, we investigated the strength of the formed floccules exposed to mechanical influence. Such a research is crucial to understand the way the size of the floccules and their deposition rate change during transportation and agitation in different devices. Results of our study are given in Table 2 and shown in Fig. 5.

The result of processing experimental data is the derived regression equation that takes into consideration the dependence of residual floccule sedimentation rate on the time of their destruction, and the concentration of the solid phase:

$$V = 1,4694 + 0,5922 \cdot C - 0,0981 \cdot t - 0,0645 \cdot C^2, \quad (2)$$

where t is the duration of the stirrer's influence, s.

Table 2

Averaged results from studying the sedimentation rate of floccules dependent on the duration of mechanical influence (at constant doses of coagulant of 65 mg/g and flocculant of 0.8 mg/g)

Duration of mechanical influence, s	Deposition rate of floccules (mm/s) following the introduction of reagents at a concentration of solid phase, g/l						
	1	2,5	4	5	6	7,5	10
0	1.1	2.2	3.6	4.1	2.9	1.8	0.5
20	0.75	1.2	1.4	1.6	1.2	0.3	0.17
40	0.45	0.9	0.93	0.9	0.7	0.19	0.1

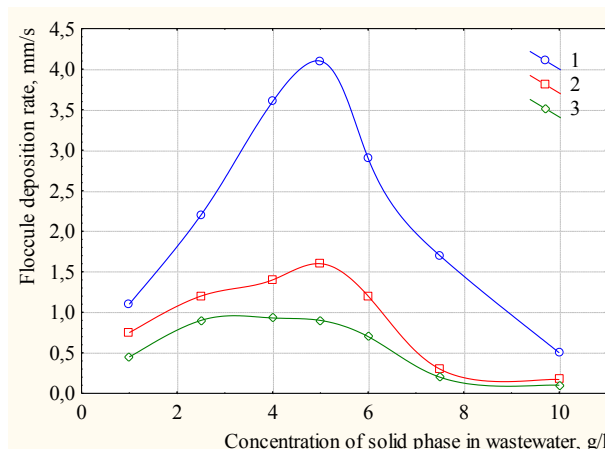


Fig. 5. Dependence of floccule sedimentation rate on the duration of mechanical influence (rotation speed of the mixer is 90 rpm; speed at the end of the blade is approximately 0.5–1 m/s) at a constant dose of coagulant of 65 mg/g and flocculant of 0.8 mg/g: 1 – without mechanical influence; 2 – influence by the stirrer over 20 seconds; 3 – influence by the stirrer over 40 seconds

Of interest is the data on determining the pH of DWW and the dependence of a hydrogen indicator on the concentration of solid phase in the process of aggregation and destruction of aggregates; measurement results are given in Table 3 and shown in Fig. 6.

Table 3

Dependence of change in hydrogen indicator (pH) on the concentration of solid phase in the process of aggregation and destruction of aggregates

Experiment stage	Value for a hydrogen indicator (pH) at a solid phase concentration, g/l						
	1	2,5	4	5	6	7,5	10
Prior to reagent introduction	7.8	8.03	8.16	8.26	8.27	8.28	8.3
Following the introduction of coagulant in the amount of 65 mg/g	6.8	6.8	6.8	6.8	6.75	6.7	6.6
Following the introduction of flocculant in the amount of 0.8 mg/g	7.0	7.2	7.21	7.14	7.16	7.15	7.05
Following the mechanical influence on floccules over 20 s	7.05	7.25	7.32	7.28	7.27	7.26	7.17
Following the mechanical influence on floccules over 40 s	7.17	7.3	7.4	7.3	7.3	7.31	7.28

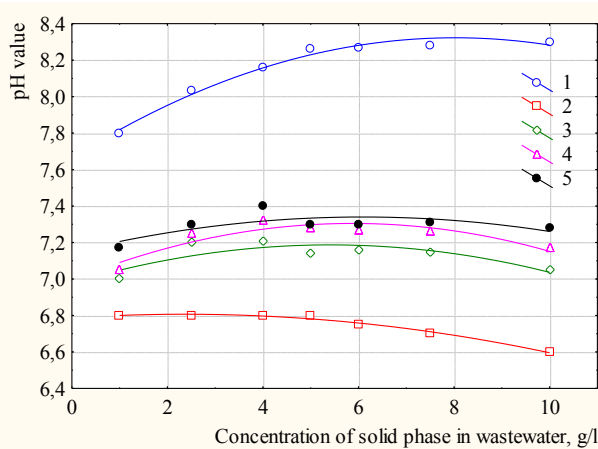


Fig. 6. Dependence of change in hydrogen indicator on the concentration of solid phase in the process of flocculation (at a constant dose of coagulant of 65 mg/g and flocculant of 0.8 mg/g): 1 – drilling wastewater without adding reagents; 2 – DWW following the introduction of coagulant; 3 – without mechanical influence; 4 – effect of stirrer over 20 seconds; 5 – effect of stirrer over 40 seconds

The diagram shows that the pH value prior to the introduction of reagents, after the introduction of each reagent, and after mechanical influences, changes depending on the concentration of the solid phase. An analysis of data along Curve 1 allows us to derive a regression equation that makes it possible to determine the DWW pH depending on concentration or to calculate a solid phase concentration depending on the pH value:

$$pH = 7,6646 + 0,1642 \cdot C - 0,0102 \cdot C^2 \quad (3)$$

There are also certain regularities in the increase of pH at the destruction of sludge aggregates and a transition of the solid phase and the negative charges absorbed at them to the liquid phase.

6. Discussion of results of studying the patterns in aggregation and kinetics of the DWW solid phase deposition

Our study into the influence of a coagulant dosage on deposition rate of the solid phase in drilling wastewater (Fig. 2) has shown that increasing a dose over 65 mg/g slightly alters the kinetics of deposition. This relates to that the effect of aluminum sulphate implies the destabilization of a dispersed system. After the formation of small flakes, it is not expedient to increase a dose of coagulant; it does not significantly affect the sedimentation rate change. This suggests that the formed flakes must be enlarged by other methods, such as flocculation.

An analysis of data from Fig. 3 allows us to recommend, as the best flocculant for this type of DWW, the anionic flocculant A-19. It was also found that over time, at sludge thickening, a floccule deposition rate is somewhat reduced (according to Fig. 3, over 9 minutes the deposition rate decreased by almost 2 times). This is explained by the fact that, as the sludge thickens, there occurs the destruction of the formed aggregates in the process of water loss and in the contact between floccules. Therefore, when designing

wastewater treatment facilities, one must take this fact into consideration, and it is desirable to prevent the excessive thickening of floccules at settlement plants before their dehydration.

A mechanism of aggregate formation at DWW treatment can be described by the following classic scheme and by microphotographs (Fig. 7). At the first stage, when introducing a coagulant to the finely dispersed system (Fig. 7, a), the charge is removed from the surface of clay particles – they stick into finely dispersed flakes (Fig. 7, b). The introduction of the flocculant causes the formation of aggregates by clumping the formed flakes and their enlargement (Fig. 7, c). Mechanical impact on floccules destroys their structure; loose structures and fine particles form, returning into a liquid phase (Fig. 7, d).

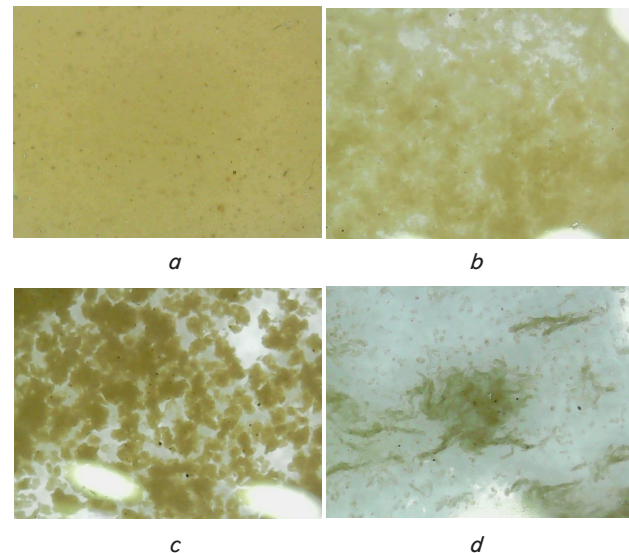


Fig. 7. Photographs of aggregation at DWW treatment: a – disperse system prior to reagent introduction; b – flake formation at coagulation; c – floccule formation; d – destruction of aggregates under mechanical influence

A study illustrated in Fig. 4 has shown that for DWW not only the dosage of a flocculant is of paramount importance, but the concentration of solid phase in DWW. Even though the dosage of all reagents is calculated per unit of the solid phase, there is a dependence of sedimentation rate on the concentration of the solid phase with an optimum at 5 ± 1 g/l. This is explained by that at lower and high concentrations there form small and loose (less dense) floccules. At low concentrations, the aggregates are dispersed throughout a fluid volume and cannot be enlarged qualitatively. At high concentrations, flocculation occurs slightly faster due to a contact with the solid phase in the volume and, hence, the flocculant does not mix well enough with the particles of the solid phase, it is adsorbed unevenly at the surface of particles. The results of our study make it possible to recommend maintaining the optimal concentration at DWW treatment by regulating the supply of water to wash sludge directly at DWW source or by diluting the concentrated wastewater to optimum concentration. That would make it possible to significantly, based on Fig. 4, save a costly flocculant.

The derived equation (1) is of practical interest and enables the calculation of not only the expected deposition rate of floccules depending on the concentration of the solid phase and consumption of the flocculant, but the

selection of a flocculant dosage depending on a value for the required deposition rate, necessary for the operation of settling facilities.

An analysis of change in deposition rate under mechanical influence (Fig. 5) allows us to argue that the sludge deposition rate after destruction depends on the concentration of sludge to a greater degree – the higher the sludge concentration, the less the floccule strength. For example, the mechanical influence on sludge with a concentration exceeding 7 g/l of solid leads to a reduction in floccule sedimentation rate by more than 10 times. At concentrations less than 7 g/l, an observed decrease in speed under the same influence is only by 2–4 times. The dependence (2) derived as a result of experimental data processing makes it possible to predict a change in the residual floccule sedimentation rate over time depending on the concentration of the solid phase. By using this equation, one can also select conditions (for instance, time) for the transportation of treated water for subsequent dehydration. These data agree well with earlier studies undertaken for coal sludge [13, 16, 21].

Results from studying a change in hydrogen indicator (Fig. 6) demonstrate the presence of correlation between a change in pH and the presence of a solid phase in DWW supplied for treatment or at one of the stages in treatment. Such patterns are of practical interest and show that it is possible to control the process using the pH-metry, at least to determine the concentration of a solid phase in WW fed to treatment in line with equation 3.

The advantage of our study is that the procedure, described in the paper, can be easily enough applied directly at sewage treatment plants to determine the dependences described in relation to the specificity of DWW from a particular drilling rig. Application of the described procedure would make it possible to rapidly determine optimal dosages of reagents subject to changes in the composition of DWW.

The downside of the performed research is that we considered only one sample of the drilling wastewater from one of the stages in drilling. A given study does not take into consideration a possibility to alter the chemical and fractional composition of DWW solid phase throughout the entire process of drilling; therefore, it is not complete. At the same time, the results obtained are applicable to determine the flow rate of reagents for drilling wastewater with a con-

centration of up to 10 g/l when using drilling mud based on bentonite clay.

Promising avenues for further research are to undertake an additional research into the optimization of aggregation process and maintaining the mechanical strength of formed aggregates during transportation and dewatering of sludge.

7. Conclusions

1. As a result of research into the influence of dosing of reagents on deposition kinetics of the solid phase in drilling wastewater, it was established that the introduction of flocculants without coagulants does not lead to aggregation while an increase in the coagulant dosage has no effect on the settling velocity of flakes from the solid phase. It has been established that for a given sample of DWW a sufficient dosage of aluminum sulfate coagulant in order to disrupt stability of a dispersed system is 65 mg/g. Among flocculants, the most active is the anionic flocculant A-19. At sludge thickening, there occurs the destruction of floccules; over 9 minutes the floccule deposition rate reduces two-fold. An increase in the concentration of a flocculant from 0.8 mg/g to 1.6 mg/g leads to a higher deposition rate of the solid phase, by 2–2.5 times.

2. It was established that depending on the concentration of the solid phase in wastewater there are changes in the conditions for aggregation and sedimentation of the solid phase in a combination of coagulant and flocculant. It has been established that the concentration of the solid phase affects the floccule deposition rate; the optimum conditions for aggregation are observed at a concentration of 4–6 g/l. Mechanical influences exert the same destroying effect on aggregates depending on the concentration of the solid phase – increasing the concentration of sludge above 7 g/l leads to a more significant reduction in the deposition rate of destroyed floccules. It was established that changes in a dispersed system can be observed based on a change in hydrogen indicator. Thus, with an increase in the concentration of DWW solid phase from 1 to 10 g/l, pH changes from 7.2 to 8.3. Following the introduction of the coagulant and, consequently, a decrease in pH, the subsequent destruction of aggregates leads to a natural increase in hydrogen indicator.

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