DOI: 10.6060/ivkkt.20226509.6634

УДК: 541.18.042.2:678.745

ФЛОКУЛЯЦИЯ ДИСПЕРСНЫХ СИСТЕМ ПОЛИФУНКЦИОНАЛЬНЫМИ ПОЛИМЕР-НЕОРГАНИЧЕСКИМИ ГИБРИДАМИ

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Разработка новых высокоэффективных многофункциональных флокулянтов актуальна для селективного разделения глиняных суспензий. Наиболее подходящими среди них являются полимер-неорганические гибриды, обладающие превосходной производительностью по сравнению с неорганическими коагулянтами и синтетическими полимерами. Синтез полимер-неорганических гибридов осуществлен в две стадии. На первой стадии конденсацией хлорида алюминия и карбоната аммония при температуре $t = 70$ °C, $pH = 3–4$ и интенсивном перемешивании был получен золь $Al(OH)_3$. На второй стадии $Al(OH)_3$ смешивали с водными растворами полимеров при комнатной температуре. По изменению температуры плавления гибридных образцов установлено наличие взаимодействий между катионом Al^{3+} и карбоксилатными группами анализируемых сополимеров акриламида. Проведен сравнительный анализ эффективности ряда систем, содержащих водорастворимые анионные сополимеры акриламида и полифункциональные полимер-неорганические гибриды на их основе. На количественном уровне проанализировано влияние концентрации и строения полимерных флокулянтов на механизм флокуляции и уплотнения осадков, определены их константы уплотнения. Более высокие значения констант уплотнения отмечены в системах с добавками гибридных образцов, что обусловлено участием их макромолекул в формировании флокул на первой стадии процесса осаждения, а на стадии уплотнения осадков выявлена их деформация и уплотнение при сохранении рыхлой структуры с образованием объемных флокул. Рассмотрены факторы, определяющие оптимальный режим флокуляции глиняных дисперсных систем полимер-неорганическими гибридами в водных средах. Показана перспективность использования новых флокулирующих систем в процессах фильтрации, флотации, а также интенсификации очистки сточных вод от дисперсных примесей.

Ключевые слова: флокулянт, анионные сополимеры акриламида, полимер-неорганические гибриды, суспензия глины

FLOCCULATION OF DISPERSE SYSTEMS BY POLYFUNCTIONAL POLYMER-INORGANIC HYBRIDS

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Development of novel high-capacity multifunctional flocculants is a promising solution to selective separation of clay suspensions. Among such flocculants, polymer-inorganic hybrids are the most attractive for their excellent performance as compared with inorganic coagulants or synthetic polymers. Synthesis of polymer-inorganic hybrids was carried out in two stages. At the first stage, $Al(OH)_3$ sol was obtained by condensation of aluminum chloride and ammonium carbonate in the following conditions: t = 70 °C, pH = 3-4, intensive stirring. In the second stage, $Al(OH)_3$ was mixed with aqueous solutions of polymers at room temperature. By changing the melting temperature of hybrid samples, the presence of interactions between the Al^{3+} cation and the carboxylate groups of the analyzed acrylamide copolymers were established. This paper reports synthesis and comparative efficiency analysis of systems that contain water-soluble anionic copolymers of acrylamide and respective polyfunctional polymer-inorganic hybrids. We performed a quantitative characterization of concentration and structural effects of polymer flocculants on the flocculation mechanism and sludge thickening. Sludge thickening constants were determined. Higher values of thickening constants were noted in systems with additives of hybrid samples, due to the participation of their macromolecules in the formation of floccules at the first stage of the sediment process, and at the stage of thickening of sediments, their deformation and compaction were revealed while maintaining a loose structure with the formation of bulk floccules. We considered the factors allowing to optimize flocculation of clay dispersions by polymer-inorganic hybrids in aqueous media. These novel flocculants were shown to have a good potential for applications in filtration or flotation processes as well as for wastewater treatment for removal of disperse impurities.

Key words: flocculant, anionic copolymers of acrylamide, polymer-inorganic hybrids, clay suspensions

Для цитирования:

Проскурина В.Е., Кашина Е.С., Рахматуллина А.П. Флокуляция дисперсных систем полифункциональными полимер-неорганическими гибридами. *Изв. вузов. Химия и хим. технология*. 2022. Т. 65. Вып. 9. С. 39−46. DOI: 10.6060/ivkkt.20226509.6634.

For citation:

Proskurina V.E., Kashina E.S., Rakhmatullina A.P. Flocculation of disperse systems by polyfunctional polymer-inorganic hybrids. *ChemChemTech* [*Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*]. 2022. V. 65. N 9. P. 39−46. DOI: 10.6060/ivkkt.20226509.6634.

INTRODUCTION

Development of efficient technologies for controlling stability of disperse systems (DS) is an urgent problem for various industrial processes that require intensive and selective separation of solid and liquid phases: flocculation, filtration, sedimentation, and sludge separation and drying [1, 2]. Among multiple real disperse systems, the following ones were characterized in detail in this respect: thiokol dispersion, manganite suspension, fluorite suspension, mineral suspensions of corundum [3-5], and waste waters from various industrial processes [6-8]. Along with acrylamide (AA) copolymers, efficient flocculants are represented by additives of polymer-inorganic hybrids that contain ionogenic water-soluble synthetic polyacrylamide flocculants and sols of metal hydroxides [9]. An organic component of such a hybrid is an AA copolymer with high molecular weight and adsorption capacity. Its inorganic component is represented by $Al(OH)_3$. These components make such hybrids efficient systems allowing to control coagulation and flocculation in multicomponent disperse systems. As compared with individual coagulants and flocculants, such hybrids offer a suitable alternative for performing sedimentation of suspensions and sols [10-11]. Our previous papers [12-14] characterize major aspects of flocculation processes involving cationic polymer-inorganic hybrids and TiO_2 as a model disperse system and performed in the free (unhindered) settling mode. Today, it is of particular importance to evaluate flocculation kinetics of real DS such as a clay dispersion. The behavior of real disperse systems demonstrates considerable differences from their models during hindered settling of disperse phase in the presence of polymer flocculants. Therefore, this work aims at synthesis and of four flocculants that differ in the nature of their polymer component, its molecular weight, and the concentration of ionogenic groups and comparing efficiency of these flocculants in sedimentation of clay suspensions in free and hindered modes.

EXPERIMENTAL

In this work, we used a real disperse system represented by a kaolinite ($Al_{14}[Si_4O_{10}](OH)_8$) and kaolinite-hydromicaceous ($Al_2O_3\cdot 2SiO_2\cdot 2H_2O$) composite with the average radius of particles $\overline{R} = 21\cdot 10^{-6}$ m. According to the data of granulometric analysis, it was obtained the composition of suspension. This system is slightly polydisperse ($R_{min} = 7\cdot 10^{-6}$ m, $R_{max} = 60\cdot 10^{-6}$ m).

The research focused on water-soluble polymer flocculants such as anionic copolymer AA Accofloc (A1) (Japan) with the viscosity-average molecular weight ($\overline{M}\eta$) = 4.27·106 (Fig. 1), β = 18.0 mol %. We also studied a superabsorbent “Aquasin” (A2) (Russia, Technical Requirements 2219-017-74584703-2011), $\overline{M}\eta$ = 0.016·106, β = 57.7 mol.%.

We used the CB-1 sedimentometer to characterize sedimentation of the disperse phase particles (C_{DP} = 0.8%) in the real disperse system in the free settling mode.

In the preliminary experiments, we studied hindered settling of particles in a real disperse system and analyzed dispersed phase concentrations in the range of 2-12%. It was found that C_{DP} = 8% provides the most convenient and reliable control over sedimentation in the hindered settling mode. At C_{DF} < 8%, a blurred interface was observed, while C_{DF} > 8% reduced the working volume of cylinders (the volume of clarified liquid). Flocculation and sludge thickening were tracked by a changing position of the interface between the clarified liquid and the turbid suspension in the measuring cylinder with the working volume of 2000 cm^3. Pre-calculated volumes of dilute polymer solutions with the concentrations of 0.1%, 1% were introduced into the upper layer of the supernatant liquid. The content of the cylinders was then thoroughly mixed.

Viscosity-average molecular weight of polymer solutions was measured by Ostwald viscometer with the capillary diameter $0.54\cdot 10^{-3}$ m. The correction for the kinetic energy of the liquid flow did not exceed 1.5%. Therefore, it was not considered for calculating the viscosity numbers η_{rel}/C (Fig. 1).

Average sizes of particles and electrokinetic potentials of their surfaces were determined on Zetasizer Nano-ZS dynamic light scattering and zeta potential analyzer. Zeta potentials of particles in aqueous disperse systems were determined by electrophoretic light scattering with the M3PALS technology (Malvern Instruments Ltd).

Thermal analysis of samples was performed on DSC 1 STAReSystem differential scanning calorimeter by Mettler Toledo (USA) up to 300 °C with the heating rate of 3 °C/min and the weight of samples from 1 to 5 mg. The samples were dried in a drying oven at t = 80 °C to their constant weight. The resulting dry crystals were studied by differential scanning calorimetry (DSC).

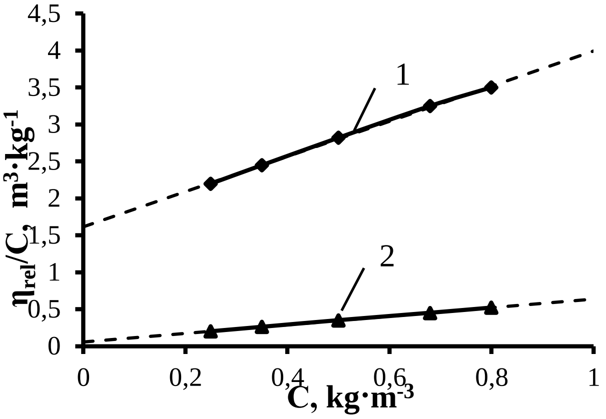


Fig. 1. Concentration dependences of viscosity numbers η_{rel}/C (solvent: 0.5 M KBr) plotted for anionic flocculants: 1 – A1; 2 – A2
Рис. 1. Концентрационная зависимость чисел вязкости $\eta_{уд}/C$ (растворитель – 0,5 M KBr) для анионных флокулянтов: 1 – A1; 2 – A2

RESULTS AND DISCUSSION

The first stage of research focused on synthesis of polymer-inorganic hybrids and finding optimal synthesis conditions. Sols were synthesized by the following condensation reaction: $2AlCl_3 + 3(NH_4)_2CO_3 + + 3H_2O \rightarrow 2Al(OH)_3\downarrow + 6NH_4Cl + 3CO_2$ ($AlCl_3$ is the stabilizer). The reaction was carried out in the following conditions: t = 70 °C, pH = 3–4, intensive mixing. In the experiments, we used the sol of $Al(OH)_3$ with the molar ration of components $(NH_4)_2CO_3$: $AlCl_3$ = 1:1.5; this sol is characterized by a steady size of its particles ($d(Al(OH)_3)$ = 300 nm) as well as stable optical properties, and pH. The forming $Al(OH)_3$ sol is charged positively (ξ = +20 mV). $Al(OH)_3$ sols synthesized with at other rations of their initial components undergo decomposition within 24 h: changes in optical properties and pH are followed by formation of amorphous precipitates, which then crystallizes [15]. To synthesize polymer-inorganic hybrids, we selected a common available method: mixing aqueous solutions of components, which produce a hybrid, at the pre-set ratio of components and room temperature.

Thermal analysis of forming floccules was performed to detect possible interactions between Al^{3+} cations and carboxylate groups of analyzed AA copolymers by changing melting temperature of hybrid samples. Differential scanning calorimetry (DSC) data (Fig. 2) demonstrate that our hybrid system with the “Aquasin” superabsorbent and $Al(OH)_3$ sol (HA2) has a higher melting temperature as compared with a similar polymer-inorganic hybrid Accofloc (HA1) indicating formation of stronger coordination bonds in the first complex.

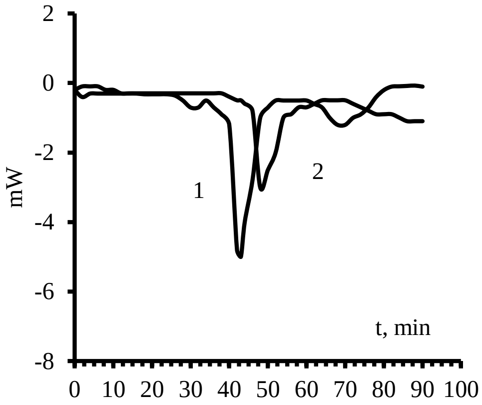


Fig. 2. DSC characterization of hybrid flocculating systems: 1- HA1 and 2 - HA2

Рис. 2. Данные ДСК для гибридных флокулирующих систем: ГА1; ГА2

As we can see in Fig. 4, the hybrids do not decompose in the temperature range of 40-300 °C. The following melting heats were found for the hybrids: HA1 $\Delta H = -22.2$ kJ/mol, HA2 $\Delta H = -49.9$ kJ/mol confirming that stronger bonds form in the HA2 hybrid.

At the next stage of research, we analyzed the influence of acrylamide copolymers on sedimentation of a real DS in aqueous medium. According to the sedimentation analysis, small amounts of the A1 copolymer ($C = 0.05 \cdot 10^{-4}$ %) lead to a substantial acceleration of clay sedimentation. A different flocculation behavior was observed for the A2 (co)polymer that may be caused by differences in molecular weights (M) and ionogenic group concentrations (β) of these polymers. To estimate flocculating parameters of the analyzed (co)polymers, we calculated flocculating effects D and flocculating activities λ [16]:

$$D = \frac{\bar{u}_i}{\bar{u}_0} - 1, \qquad (1)$$

$$\lambda = \left[\frac{\bar{u}_i}{\bar{u}_0} - 1\right] \cdot \frac{1}{C} = \frac{D}{C}, \qquad (2)$$

where $\bar{u}_0$ и $\bar{u}_i$ are average rates of clay suspension sedimentation for $Q = 0.4$ in the presence and absence of a polymer flocculent with the concentration C, respectively.

Flocculation of a real DS was performed by systems with different concentrations of polymers (Table 1). We can see that the anionic sample A1 demonstrates higher flocculating activity than the sample A2. Comparison of the date in table 1 indicates a distinct dependence of a flocculating activity on the molecular weight of the AA copolymer. According to Fig. 5, clay systems are charged negatively ($\xi = -16.1$ mV) so as AA copolymer macromolecules. In the studied systems, therefore, a bridge flocculation (not neutralization) is a prevailing process. To explain distinct differences in flocculating activities λ of anionic samples, we should consider specific details of the respective flocculation mechanism. Adsorption of macromolecules on surfaces of DF particles is known to be the first stage of flocculation, which mostly determines an entire flocculation process [17]. According to the concepts developed by Flory, macromolecular coils do not overlap at low polymer concentrations, so the density of segments is uniform at all the points of solution and can be adequately described by a mean-field theory [17].

Table 1

Dependences of the flocculating activity λ on the concentration of copolymers C in the free and hindered settling modes

Таблица 1. **Зависимость флокулирующей активности λ от концентрации сополимеров C в режимах свободного и стесненного оседания**

Polymer	Settling modes	$C \times 10^3$, kg/m^3				
		0.05	0.55	2.05	6.5	19.2
A1	free	2.83	2.32	5.54	2.87	1.91
A2		0.22	0.04	0.11	0.05	0.02
		$C \times 10^3$, kg/m^3				
		0.2	2.2	8.2	25.5	72.5
A1	hindered	1.12	1.54	1.21	2.14	3.09
A2		3.08	8.11	32.25	40.17	55.26

In systems with a “good” solvent, macromolecular coils undergo intensive swelling and overlapping. In turn, it results in density fluctuations of polymer segments. Adsorption of anionic AA (co)polymers is carried out by not only localized adsorption centers (mostly represented by charged ions and functional groups) but also by non-localized adsorption centers on surfaces of DF particles [18]. It is confirmed by particularly high degree of adsorption of nonionogenic polyacrylamide (PAA) in the real DS: over 95% of PAA macromolecules undergo irreversible adsorption on surfaces of DF particles.

Analyzing flocculation processes, we should consider that even for minimal values $C = 0.05 \cdot 10^{-4}$ %, hundreds or thousands of macromolecules N_m adsorb on the surface of a single DF particle. Increase in the flocculant concentration leads to a proportional growth in the number of adsorbed macromolecules (Table 2). The calculations are performed for the concentration of the DF particles C_{DF} = 0.8 %.

One of the most important parameters, which influence sedimentation, is the concentration of dispersed phase (C_{DF}). In the mode of free (unhindered) settling without flocculants, dispersed phase particles do not interact and the sedimentation rate is constant: u ≅ const (at low concentrations $C_{DF} < 0.8$ %). In the hindered settling mode, interactions between dispersed phase particles cannot be neglected. Therefore, u = f(C_{DF}) for $C_{DF} > 0.8$ %. Nonconstant C_{DF} values of systems with [C_p] = const change automatically the [C_p]/C_{DF} ratio.

Table 2

The ratio of the number of polymer macromolecules to the number of clay particles at the lowest and highest concentrations of the polymer additive

***Таблица 2.* Соотношение количества макромолекул флокулянтов и частиц глины при минимальной и максимальной концентрации полимерной добавки**

Polymer	*β*, mol%	*C* × 10^4, %	Number of macromolecules N_M	Number of particles N_P	(N_M/N_P) × 10^{-6}
A1	18.0	0.05	$7.05 \cdot 10^{11}$	$160.7 \cdot 10^6$	0.0044
		19.2	$2.71 \cdot 10^{14}$		1.68
A2	57.7	0.05	$1.88 \cdot 10^{14}$		1.17
		19.2	$7.22 \cdot 10^{16}$		449.7

Note: where Np is the number of dispersed phase particles in the clay suspension;
Nm is the number of anionic copolymer macromolecules per the number of clay particles in suspension
Примечание: где Np - количество частиц дисперсной фазы в глинистой суспензии;
Nm - количество макромолекул анионного сополимера на количество частиц глины в суспензии

The C_{DF} parameter influences such macroscopic parameters as adsorption, flocculating effect, and flocculating activity of polymers [13]. In the free settling mode, the largest values of the parameter D were found for the HA1 sample (Table 3). The optimal concentration of the hybrid system HA1 was found to be C = $2.05 \cdot 10^{-4}$ %. Comparing the D parameter of the hybrid samples HA1 and HA2 in the hindered settling mode revealed that the polymer-inorganic hybrid HA2 is an order of magnitude more efficient than the hybrid HA1 (Table 3). According to date, the hybrid sample HA2 demonstrates poor flocculating performance, so its parameters will be minimal at the stage of sludge thickening.

Table 3

Flocculation effect and electrokinetic potentials of systems with various polymer additives

***Таблица 3.* Данные флокулирующих эффектов и электрокинетических потенциалов систем в зависимости от концентрации полимерной добавки**

Hybrid system	Settling modes	C·10^3, kg/m^3	D	ξ, mV
HA1	free	0.05	2.76	
		0.55	2.31	
		2.05	5.28	
		6.5	2.61	
		19.2	1.72	
	hindered	0.2	0.98	-15.2
		2.2	0.37	-12.0
		8.2	1.36	-10.5
		25.5	2.17	-8.8
		72.5	3.25	-5.4
HA2	free	0.05	0.19	
		0.55	0.01	
		2.05	0.08	
		6.5	0.02	
		19.2	0.01	
	hindered	0.2	2.13	-16.4
		2.2	7.28	-18.0
		8.2	30.02	-20.1
		25.5	36.51	-22.2
		72.5	51.17	-24.5

The concentration effect of the hybrid systems HA1 and HA2 on flocculation of a clay suspension was estimated from the electrokinetic potential data (Table 3). Table 3 illustrates a considerable reduction of the ξ-potential with the increase of the HA2 concentration. According to the DSC data, interactions between the ionogenic groups of the “Aquasin” superabsorbent and positively charged Al^{3+} ions in the HA2 hybrid system correlate with the ξ-potential values. Because of negatively charged clay particles (ξ = –16.1 mV) and high content of ionogenic groups in polymer chains a (β = 57.7 mol.%), the HA2 hybrid system intensifies formation of floccules, increases their average size, and enhances the flocculating effect D.

To evaluate mean square sizes of macromolecules $\left(\overline{R^2}\right)^{0.5}$, the Flory equation can be used [18]: $[\eta] \cdot M = \Phi\left(\overline{R^2}\right)^{1.5}$, where [η] is the limiting viscosity number, Φ is the Flory constant ($2.6 \cdot 10^{21}$). By using viscosity numbers $\left(\frac{\eta_{rel}}{C}\right)$ instead of [η] for very low concentrations of hybrid polymer-inorganic flocculating systems ($C \sim 0.2 \cdot 10^{-6}$ g/cm^3), we can show that the mean square sizes of the hybrid systems

$\left(\overline{R^2}\right)^{0.5}_{HA1} = 2.46\cdot10^{-12}$ and $\left(\overline{R^2}\right)^{0.5}_{HA2} = 0.162\cdot10^{-16}$ exceed $1\cdot10^{-7}$ m [17]. Considering high thermodynamic and kinetic flexibility of acrylamide fragments [18, 19], A1 and A2 macroions in water can be described as highly swelled and elongated coils.

From theoretical and practical points of view, it is interesting to analyze clay flocculation data obtained in the presence of hybrid systems at higher values Q > 0.6 corresponding to the sludge thickening stage. We processed the kinetic data in the $\ln[Q_{max} - Q(t)] = f(t)$ coordinates obtained in the presence of anionic samples at the final sedimentation stage. These data allowed to calculate the sludge thickening constants γ from the slopes of the plot lines (Fig. 3) [20].

The minimal value V_{sl} and density ρ_{sl} of sludge was calculated by the following equations:

$$V_{sl} = (1 - Q_{max})V_0, \tag{3}$$

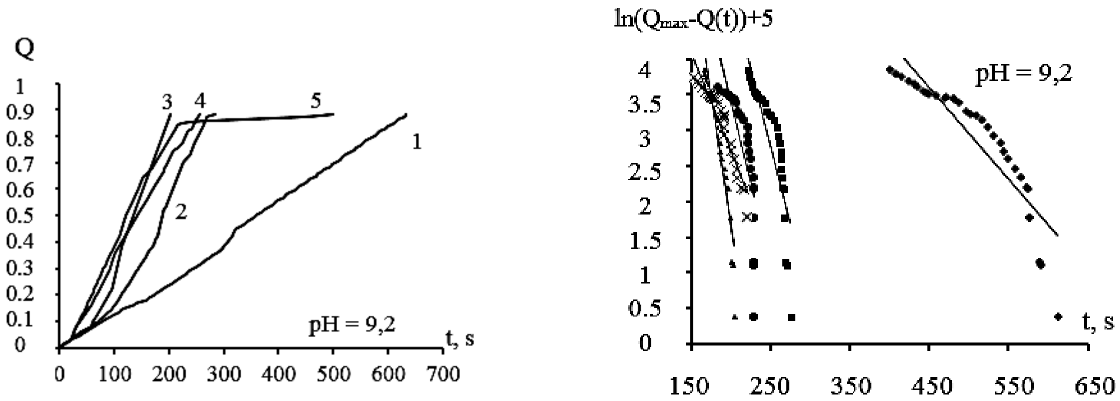
where V_0 is the work volume of suspension in the cylinder and

$$\rho_{sl} = \frac{m + \left(V_{sl} - \dfrac{m}{\rho}\right)\cdot\rho_0}{V_{sl}}, \tag{4}$$

where ρ_0 is the density of water, ρ is the density of DF particles, and m is the weight of a powder sample.

Table 4 reveals a certain correlation between the λ, γ, and ρ_{sl} parameters. The higher is the flocculating activity λ, the higher are the thickening constants γ and lower are the sludge densities ρ_{sl}.

As opposed to the HA2 hybrid behavior, higher values of γ and lower sludge densities in the systems with added AA copolymers (Table 4) are related to participation of A2 copolymer macromolecules and the HA2 hybrid sample and formation of floccules at the first stage of the process. Thus, deformation and thickening of floccules occur at the final stage of the process (sludge thickening). In the range of values Q ~ Q_{max}, less dense structures form inside local volumes of the real DS particles with adsorbed macromolecules of flocculating systems and thus produce bulky floccules.



a b

Fig. 3. Flocculation (a) and sludge thickening (b) curves in the coordinates Q(t) (1-5) and ln $[Q_{max} — Q(t)]=f(t)$ (1-5) – without flocculating additives (1); (2, 3) – C_{DF} = 0.8 %; (4, 5) – C_{DF} = 8 %: 2, 4 – A1; 3, 5 – A2

Рис. 3. Кривые по флокуляции (а) и уплотнению осадков (б) глины в координатах Q(t) (1-5) и ln $[Q_{max} — Q(t)]=f(t)$ (1-5) – без добавок флокулянтов (1); (2, 3) – $C_{ДФ}$ = 0,8 %; (4, 5) – $C_{ДФ}$ = 8 %: 2, 4 – A1; 3, 5 – A2

Table 4

Concentration dependence of the sludge density ratio ρ_{sl}/ρ^0_{sl} (ρ^0_{sl} is the sludge density without the polymer additives)

Таблица 4. Концентрационная зависимость отношения плотностей осадков $\rho_{ос}/\rho^0_{ос}$ ($\rho^0_{ос}$ – плотность осадка в отсутствие полимерной добавки)

Flocculating systems		*C* × 10³, kg/m³			
		0.2	2.2	8.2	25.5
A2	ρ_{sl}/ρ^0_{sl}	0.99	0.93	0.86	0.89
	$\gamma\times10^3$, s^{-1}	42	50	43	25
HA2	ρ_{sl}/ρ^0_{sl}	0.98	0.96	0.96	0.94
	$\gamma\times10^3$, s^{-1}	8	10	33	30

CONCLUSIONS

In this work, we considered the influence of a dispersed phase concentration on sedimentation of a clay suspension by anionic polymer-inorganic hybrids, which differ in molecular weight and concentration of ionogenic groups. We synthesized polymer-inorganic hybrids that include a composition of the anionic acrylamide copolymer Accofloc and $Al(OH)_3$ sol (HA1) or the superabsorbent "Aquasin" and the $Al(OH)_3$ sol (HA2). In the free settling mode, the commercial flocculant (HA1) demonstrated the strongest flocculation effect. In the hindered settling mode, the flocculation efficiency of the HA2 hybrid is an order of magnitude higher than that of its HA1 counterpart, so its parameters will be minimal at the stage of sludge thickening. Higher concentrations of polymer-inorganic hybrids HA2 in the hindered settling mode were shown to substantially increase the thickening constant due to formation of floccules at the first stage of sedimentation. Thus, we proposed optimal flocculation modes for clay dispersions by polyfunctional polymer-inorganic hybrids in aqueous media both for free and hindered settling.

The work was carried out using the equipment of the Center for Collective Use "Nanotechnologies and Nanomaterials" of KNRTU.

The authors declare the absence a conflict of interest warranting disclosure in this article.

Работа выполнена с использованием оборудования ЦКП «Нанотехнологии и наноматериалы» ФГБОУ ВО «КНИТУ».

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

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Поступила в редакцию 07.04.2022
Принята к опубликованию 23.06.2022

Received 07.04.2022
Accepted 23.06.2022