9. Bolto, B. Organic polyelectrolytes in water treatment [Text] / B. Bolto, J. Gregory // Water Research. – 2007. – Vol. 41, No. 11. – P. 2301–2324. doi:10.1016/j.watres.2007.03.012
10. Heller, H. Anionic Polyacrylamide Polymers Effect on Rheological Behavior of Sodium-Montmorillonite Suspensions [Text] / H. Heller, R. Keren // Soil Science Society of America Journal. – 2002. – Vol. 66, No. 1. – P. 19. doi:10.2136/sssaj2002.0019
11. Wang, W.-D. Experimental study on slime water flocculation sediment based on the montmorillonite hydration expansion inhibition [Text] / W.-D. Wang, H.-F. Wang, J.-T. Sun, Y. Sun // Journal of Coal Science and Engineering (China). – 2013. – Vol. 19, No. 3. – P. 530–534. doi:10.1007/s12404-013-0414-y
12. Lopez-Maldonado, E. A. Improving the Efficiency of a Coagulation-Flocculation Wastewater Treatment of the Semiconductor Industry through Zeta Potential Measurements [Text] / E. A. Lopez-Maldonado, M. T. Oropeza-Guzman, A. Ochoa-Teran // Journal of Chemistry. – 2014. – Vol. 2014. – P. 1–10. doi:10.1155/2014/969720
13. Petzold, G. Higher efficiency in the flocculation of clay suspensions by using combinations of oppositely charged polyelectrolytes [Text] / G. Petzold, M. Mende, K. Lunkwitz, S. Schwarz, H.-M. Buchhammer // Colloids and Surfaces A: Physicochemical and Engineering Aspects. – 2003. – Vol. 218, No. 1–3. – P. 47–57. doi:10.1016/s0927-7757(02)00584-8
14. Shkop, A. Exploring the ways to intensify the dewatering process of polydisperse suspensions [Text] / A. Shkop, M. Tseitlin, O. Shestopalov // Eastern-European Journal of Enterprise Technologies. – 2016. – Vol. 6, No. 10 (84). – P. 35–40. doi:10.15587/1729-4061.2016.86085
15. Shkop, A. Study of the strength of flocculated structures of polydispersed coal suspensions [Text] / A. Shkop, M. Tseitlin, O. Shestopalov, V. Raiko // Eastern-European Journal of Enterprise Technologies. – 2017. – Vol. 1, No. 10 (85). – P. 20–26. doi:10.15587/1729-4061.2017.91031
16. Konduri, M. K. R. Influence of pH and ionic strength on flocculation of clay suspensions with cationic xylan copolymer [Text] / M. K. R. Konduri, P. Fatehi // Colloids and Surfaces A: Physicochemical and Engineering Aspects. – 2017. – Vol. 530. – P. 20–32. doi:10.1016/j.colsurfa.2017.07.045

ИССЛЕДОВАНИЕ ЭФФЕКТИВНОСТИ ОЧИСТКИ МЕЛКОДИСПЕРСНОГО ШЛАМА ВОДООБОРОТНОГО ЦИКЛА МЕТАЛЛУРГИЧЕСКОГО ПРЕДПРИЯТИЯ

Исследованы особенности очистки шламов водооборотного цикла металлургического производства. Выявлено, что поступление взвешенных веществ в шламовые воды происходит периодически и неравномерно. Установлено, что шламы газоочисток металлургического предприятия содержат до 93 % мелкодисперсной фракции твердой фазы класса менее 20 мкм. Рекомендовано применение лабораторных тестов качества шлама и эффективности флокуляции. В ходе промышленных испытаний установлена возможность очистки шлама с эффективностью до 99 % флокуляционно-центробежным способом с применением методики лабораторных тестов.

Ключевые слова: газоочистка металлургического предприятия, мелкодисперсные шламы, шламы газоочистки, модуль очистки.

Shkop Andrii, *PhD, Director, LTD «Scientific and Technical Center «Ecomash», Kharkiv, Ukraine, e-mail: shkop_ecomass@ukr.net, ORCID: https://orcid.org/0000-0002-1974-0290*

Briankin Oleksandr, *Postgraduate Student, Department of Chemical Technique and Industrial Ecology, National Technical University «Kharkiv Polytechnic Institute», Ukraine, e-mail: bryankin@i.ua, ORCID: https://orcid.org/0000-0002-7897-4417*

Shestopalov Oleksii, *PhD, Associate Professor, Department of Chemical Technique and Industrial Ecology, National Technical University «Kharkiv Polytechnic Institute», Ukraine, e-mail: shestopalov.it@khpi.edu.ua, ORCID: https://orcid.org/0000-0001-6268-8638*

Ponomareva Natalya, *PhD, Associate Professor, Department of Integrated Technologies, Processes and Devices, National Technical University «Kharkiv Polytechnic Institute», Ukraine, ORCID: https://orcid.org/0000-0001-8931-5882*

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Shkop A., Briankin O., Shestopalov O., Ponomareva N.

INVESTIGATION OF FLOCCULATION EFFICIENCY IN TREATMENT OF WET GAS TREATMENT SLIME OF FERROALLOYS PRODUCTION

Досліджені склад і особливості флокуляції шламів водооборотного циклу виробництва феросплавів. Виявлено, що хімічний склад і концентрація твердої фази шламів змінюється в часі. Встановлено, що особливості змішення шламів з флокулянтом грають важливу роль у флокулоутворенні. Для очищення шламів рекомендовано вводити флокулянт двома порціями 35–40 % і 60–65 % відповідно з часом змішення до 30 секунд першої дози і близько 10 секунд другої.

Ключові слова: *флокуляція шламів, дрібнодисперсні шлами, шлами газоочищення, модуль очищення, виробництва феросплавів.*

1. Introduction

Metallurgical production is accompanied by the formation of a huge amount of industrial waste (IW), reaching 30 % of the output of steel. About 80 % of them are slag, about 20 % of dust and slime of gas treatment [1]. Today Ukrainian enterprises discharge over 2 billion m^3/year of untreated and insufficiently treated sewage into water bodies, which leads to a deterioration of the ecological condition of water bodies and the surrounding natural environment as a whole. The most dangerous is the waste water of metallurgical enterprises containing

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heavy metals toxic to biota. The volume of sewage discharged by the enterprises of ferrous and non-ferrous metallurgy and machine-building enterprises of Ukraine reaches 500 million m^3/year.

Existing circulating water supply systems operate with a purge, which is about 10 % of the circulating water flow in the systems. The main reason for the purging and discharge of undertreated sewage into external slime collectors is the low efficiency of water rotation cycle treatment facilities.

The use of wastewater and slime for gas treatment of smelters in the water cycle system of enterprises due to the high content of chemical compounds in unacceptable by existing standards for concentrations requires considerable expenditure for their treatment.

Therefore, an increase in the efficiency of water treatment of water-rotation cycles of metallurgical enterprises is topical.

2. The object of research and its technological audit

The object of research is the process of wastewater treatment from suspended solids produced as a result of wet gas treatment of the off-gases of the shop for ferroalloys production of one of the metallurgical enterprises. The current scheme of recycling water supply of gas treatment is shown in Fig. 1.

The combustion products of smelters (1), (2) from the upper part of the arch are subjected to wet gas treatment, and from under the arch space are sent to wet gas scrubbers. The composition of blast furnace gases depends on the charge in the furnaces, which includes: iron-containing briquettes, quartzites, lime, wood chips, coke, «ДО» coal, electrode mass. After wet dust collection of flue gases, slime waters with an average temperature of ≈ +50°...+70 °C are formed.

From the shops, the slime waters of the wet gas scrubbing are transported by gravity through inclined pipelines Ду 700 mm to the distribution tank (3).

In the drain pipe of the ferrosilicon production shop, the filtrate pipelines are embedded. The maximum flow of slime water into the radial thickener (4) at the time of the technological audit is 850 m^3/h.

The temperature of the slime water, measured in the pipelines near the distribution tank, is shown in Table 1.

In appearance:

- slime waters of the ferromanganese alloys production shop, a solid orange-brown liquid;
- ferrosilicon production shop – gray-green liquid with separately floating aggregates of black color;
- mixtures – a gray liquid with visible aggregates of black color up to 1.5 mm in size.

At the bottom of the pipeline, a layer of about 200 mm in height is found from deposits of various colors, shapes and sizes. The size of individual conglomerates varies from 0.5 to 80 mm in cross section. The color of most of the elements is black, there are conglomerates of white and greenish color.

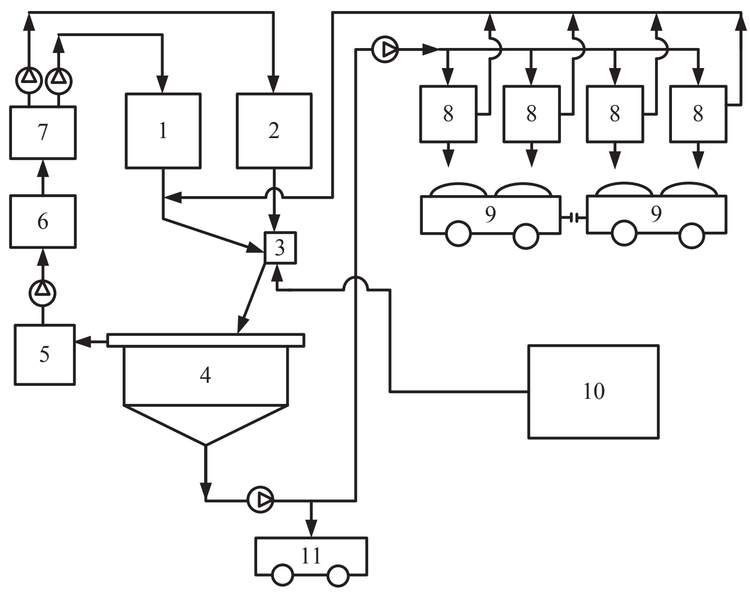

Fig. 1. The existing water-slime scheme for the ferroalloys production:
1, 2 – smelting shops producing ferromanganese alloys and ferrosilicon; 3 – mixing tank; 4 – radial thickener; 5 – hot clarified water collector; 6 – cooling tower; 7 – chilled water collector; 8 – filter-press; 9 – railway wagons; 10 – flocculant preparation station; 11 – railway tank wagons

Table 1

The temperature of slime waters of ferroalloys shops

Slime waters	Air temperature, °C	Slime temperature in the case of operating cooling tower, °C	Slime temperature in the case of non-operating cooling tower, °C
Ferromanganese alloys shop	7–15	42–44	52–55
Ferrosilicon production shop		53–55	62–65

Before entering the radial thickener, the slime from both shops is mixed in a distribution tank. At the mixing point of the flows, a cationic flocculant solution with a concentration of 0.025–0.05 % is introduced. Further, the flow of slime water along an inclined pipeline enters the charging device of a radial thickener.

The flocculant solution is prepared in a stand-alone building in 2 tanks with a volume of 12–13 m^3. At the same time, one tank is consumable, while in the second one a new flocculant solution is being prepared. A solution of flocculant with an initial concentration of 0.05 % workers is prepared 2 times a day (1 time per shift). Mixing of the flocculant solution takes place by bubbling with air for 12 hours.

Clarified water (draining of the radial thickener) flows into the collector (5) to the inlet of the «hot group» pumps, which pump the clarified water for cooling to the cooling tower (6). After the cooling tower, clarified water enters the collector (7) at the inlet of the «cold group» pumps supplying the pulp to the wet gas scrubbers.

The radial thickener is made in the form of a cylindrical bowl with a conical bottom. The volume of the radial thickener is 1500 m^3. The flow of slime water and the withdrawal of the clarified product are carried out continuously. Pumping of the condensed product from the radial thickener is performed in a batch mode: according to the operation cycle of chamber filter presses.

The content of suspended solids in clarified water ranges from 25 mg/l to 1.5 g/l. On separate days the content of suspended solids in clarified water reached 22 g/l. Samples of thickened slime and clarified pulp are shown in Fig. 2.

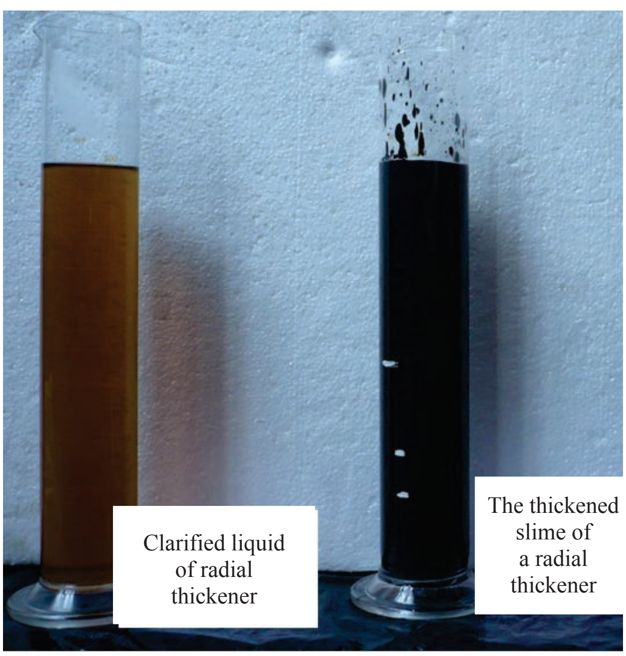

Fig. 2. Samples of clarified water and thickened slime of a radial thickener

According to the laboratory analysis, the content of suspended solids in clarified water, shown in Fig. 2, is 66 mg/l, in the thickened product – 111.5 g/l.

The thickened product with solids content of 95 g/l is a flowing liquid, and with a solids content of 111.5 g/l is a paste-like product.

The thickened slime is supplied by a centrifugal pump to the filter-press dewatering unit (8). The dewatered product of filter presses is unloaded into dumpcars (9). The wagons carry solid waste to the landfill in the amount of 18 tons/day.

The filtrate is piped into the slime water pipeline of the ferrosilicon production department and further to the radial thickener according to the scheme (Fig. 1).

Due to the partial replacement of coke for coals of the «ДО» brand in the charge of smelting shop of ferrosilicon production resulted in an increase in the concentration of suspended solids in slime waters. The site for slime treatment can't cope with increased load. Therefore, the excess part of the slime of the radial thickener is taken out by the tanks (11) to the landfill of liquid wastes in an amount up to 34 tons/day.

One of the most problematic areas in this process is insufficient slime treatment from suspended solids, which leads to a significant contamination of clarified water and the need for additional dilution of the slime (make-up) with clean tap water, as well as the costly removal of slime in liquid form. This is due to the fact that the slime flocculation at the inlet to the radial thickener does not occur with proper efficiency, despite the supply of a flocculant solution. Based on the results of the study of the current system for the preparation and dosing of flocculant, it is established that the dosing of the flocculant is made at one point of the slime water pipe, without adjusting the flocculant dose when the slime concentration and chemical composition change.

Laboratory and pilot-design studies are conducted to study the methods for selecting, blending and dosing flocculants with the purpose of developing an effective technology for treatment of slime waters and testing high-performance equipment for slime dewatering.

3. The aim and objectives of research

The aim of research is identification of flocculation peculiarities of gas treatment slime of ferroalloys production.

To achieve this aim it is necessary

1. To conduct laboratory studies of the composition and properties of real wet gas treatment slime of ferroalloys production.

2. To investigate the effect of the introduction and mixing of flocculants on the efficiency of aggregation and sedimentation of the solid phase of slimes.

3. To conduct industrial tests for slime treatment and determine the efficiency of the dewatering equipment, depending on the features of the flocculant and slime feed.

4. Research of existing solutions of the problem

The conditions for the gas treatment wastewater formation are influenced and largely determine the chemical composition and physico-chemical properties of wastewater. These properties are formed depending on the features of the technology of metallurgical production, the raw materials used and the temperature for melting, the type of charge and other factors. Change in the properties of water polluted in the production cycle leads to a decrease in the efficiency of treatment facilities used in the reverse scheme.

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The classical scheme of slime treatment is their clarification in radial thickeners and other settling facilities. To increase the sedimentation rate of suspended solids, various methods of chemical intensification of the agglomeration process of the particles are used, for example, using flocculants and coagulants, and the thickened slime is sent to dewatering by filtration.

In addition, many enterprises do not pay attention to the effectiveness of mixing the flocculant and the features of its adsorption processes on the solids particles and aggregation.

Recently, polymeric flocculants for the treatment of industrial wastewater have been increasingly used [2]. Compared to coagulation, organic polymers are used in smaller doses, do not carry an additional ion load and are of lower cost [3, 4].

In the modern literature, the possibilities of intensifying the slime flocculation process by combining and sequentially introducing non-ionic, anionic or cationic flocculants are described [5, 6].

Recently, new reagents for particle aggregation have been developed that combine the hybrid properties of inorganic coagulants and flocculants on an organic basis [7, 8].

Granulometric composition of slimes plays a major role in the processes of their capture, dehydration and further use. The question of the relationship of water to the solids determines the initial moisture and water-release capacity of the sediment and allows to determine the feasibility of using specific methods for its preparation and dehydration.

The peculiarity of the structure of water molecules possessing a dipole moment, hydrogen bonds, the originality of the structure, requires careful study of the behavior of slime water in existing technological processes. Thin liquid films on the surface of the solids pores and in the capillaries have anomalous properties that differ from the properties of the liquid in the volume. The density of charges on the solids boundary decreases upon transition to a liquid. This fall can be considered as a function of the position of the slip boundary between a solid and a liquid, which is characterized by the electrokinetic ξ-potential of the solids and leads to a change in the pH of the medium [9, 10].

Thus, treatment of dispersed slime, especially with the use of reagents to intensify the processes of solids deposition, is multifactorial and not fully understood. The complexity of taking into account the change in the set of parameters on which the flocculation efficiency depends, leads to a decrease in the efficiency of the treatment plant and the need for additional studies.

5. Methods of research

5.1. Method of laboratory studies of wet gas treatment slimes. Laboratory studies of slime waters are carried out for:

– measurements of the kinetics of solids sedimentation as a function of the dispersed composition;
– chemical analysis and determination of the hydrogen index of slime waters;
– selection of flocculants for treatment and dehydration of slime in a centrifuge;
– investigation of the influence of mixing features of flocculant and slime waters solution on the flocculation efficiency;
– development of technological tests for an operative analysis of flocculation quality and the content of suspended particles in clarified water.

Studies are carried out on the actual slimes of ferroalloys production shops.

The determination of suspended particles and salts in slime waters is carried out in accordance with GOST 6687.8-87 and OST 34-70-953.13-90. The pH is measured using pX-150МИ device (Russia).

The measurement of sedimentation kinetics is carried out in a laboratory measuring cylinder with a diameter of 50 mm, without the use of chemical reagents (flocculants) in the field of gravity.

In the laboratory study of the flocculation process of slime waters, cationic flocculants PC-5045, ТФК-18 and ТФК-7 are used. Flocculant solutions are prepared at a concentration of 0.05 % and dosed into a graduated cylinder with a syringe.

To prepare 500 ml of 0.5 % solution, 500 ml of tap water and 0.5 g of flocculant powder are taken. The flocculant powder is poured into the water by continuously mixing with a magnetic stirrer. After 2 hours of mixing, 100 ml of the prepared flocculant solution is mixed with 900 ml of tap water and 1 l of a 0.05 % flocculant solution is prepared.

In determining the sedimentation kinetics, the position of the interface between the phases «suspended matter – clarified water» is measured in time with an interval of 15 seconds. In each interval, the deposition rate is calculated. In this case, the position of the phase separation boundary is determined, at which the velocity began to decrease, i. e., when the sedimentation of suspended solids in the liquid passed into the sediment seal at the bottom of the cylinder. The position of this boundary is taken to calculate the averaged sedimentation rate.

The sedimentation rate is calculated as the ratio of the distance over which the interface between the phases shifted to the time interval spent for this displacement.

The content of suspended solids in the compacted sediment is calculated from the ratio of the volumes of clarified liquid and sediment. At the same time, the total content of suspended substances in the sample is known and it is assumed that all the suspended substances have precipitated.

In order to determine the optimum flocculation regime, the following methods of mixing the flocculant solution with slime water are conducted:

– feeding of flocculant with one-time and hydrostatic mixing (operating scheme at the given enterprise);
– feeding the flocculant with one-time and hydrodynamic mixing in a mixer for 15 seconds;
– feeding the flocculant in equal doses after 10 seconds, with hydrostatic mixing;
– feeding the flocculant in equal doses, but after the first dosing, hydrodynamic mixing in a mixer for 15 seconds, after the second dosing, hydrostatic mixing for 10 seconds.

When flocculation is carried out, the sedimentation rate of the slime floccules is determined before and after mechanical influences according to the method of laboratory tests described in [11, 12].

5.2. Method of industrial tests. Industrial tests for treatment and dehydration of slimes were carried out on a modernized [10] ОГШ-type centrifuge of the «ECOMASH» STC (Kharkiv, Ukraine). During the tests, various methods of feeding and mixing of flocculants and regimes selected in the course of laboratory studies were investigated.

Method No. 1. Investigation of the possibility of slime treatment of the ferrosilicon production shop, taken before the radial thickener, with the supply of flocculants to two points «into the flow» followed by treatment and dehydration of the slime in a centrifugal unit. The tests were carried out according to the technological scheme shown in Fig. 3.

According to the scheme, the slime from the ferrosilicon production shop (2) is taken directly into the mixing tank and pumped into the measuring tank (7) just prior to feeding. From the tank, the slime waters through the mixer (11) are fed to the centrifugal unit for dehydration (8). A solution of flocculant is fed into the flow of slime waters moving through the mixer at two points (12) and the corresponding samples are taken.

Method No. 2. Investigation of the possibility of slime treatment taken before the radial thickener, with the supply of flocculants to one point «under the stirrer». The tests were carried out according to the technological scheme shown in Fig. 4.

According to the scheme, the slime from the ferrosilicon production shop (2) is taken directly to the mixing tank and the pump is fed into a tank with a stirrer (11). A solution of the flocculant is fed into the same tank. Slime waters mixed with flocculant are transported into the flow-measuring tank (7) with the closed bottom drain (simulated sedimentation tank). In the flow-measuring tank there is a separation of slime waters. Clarified product is transported through the drainage connection of the tank. Sedimentary suspended solids accumulate at the bottom of the tank. After filling the tank with thickened slime, the supply of feed and flocculant is stopped, and the thickened slime is transferred to the centrifugal unit for dehydration (8).

Method No. 3. Investigation of the possibility of slime mixture treatment: thickened slime of a radial thickener and slimes of the ferrosilicon production shop with cationic flocculant feed into one point «under the stirrer».

The investigations were carried out according to the scheme (Fig. 4) with the following changes: slime from the ferrosilicon production shop (2) is taken directly into the mixing tank and pumped into a tank with a stirrer (11) just prior to feeding. The thickened slime of the radial thickener (5) is supplied to the storage tank by a pump. From the storage tank of the pump, thickened slimes are fed into a tank with a stirrer (11). A flocculant solution is fed into the same tank. The flow rates of slime water from the workshop and thickened slime of the radial thickener are adjusted by manual latches to obtain the required concentration of suspended solids. Slime waters mixed with flocculant by gravity enter the flow-measuring tank (7) (without draining from the measuring and flow-measuring tank), and then for dehydration into a centrifugal unit (8).

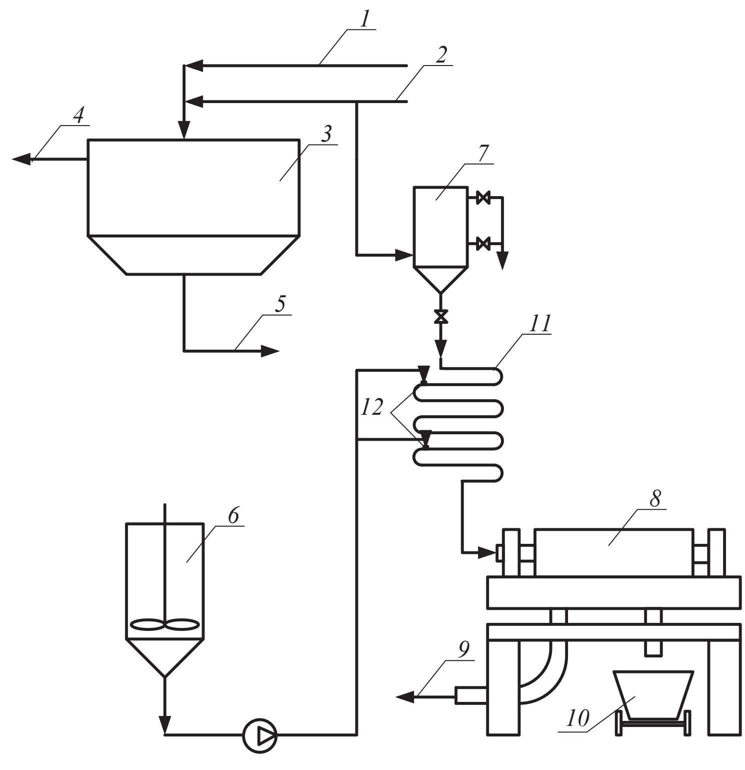

Fig. 3. Technological scheme of slime treatment with the supply of flocculants in two points «in the flow» and dehydration in a centrifugal unit: 1 – slime pipeline of ferromanganese alloys production shop; 2 – slime pipeline of ferrosilicon production shop; 3 – radial thickener, 4 – clarified water removal; 5 – thickened slime removal; 6 – flocculant preparation station; 7 – flow-measuring tank; 8 – centrifugal unit; 9 – centrifuge centrate removal; 10 – wheelbarrow for discharge of the centrifuge sediment; 11 – coil for hydrostatic mixing of flocculants; 12 – points of flocculant injection

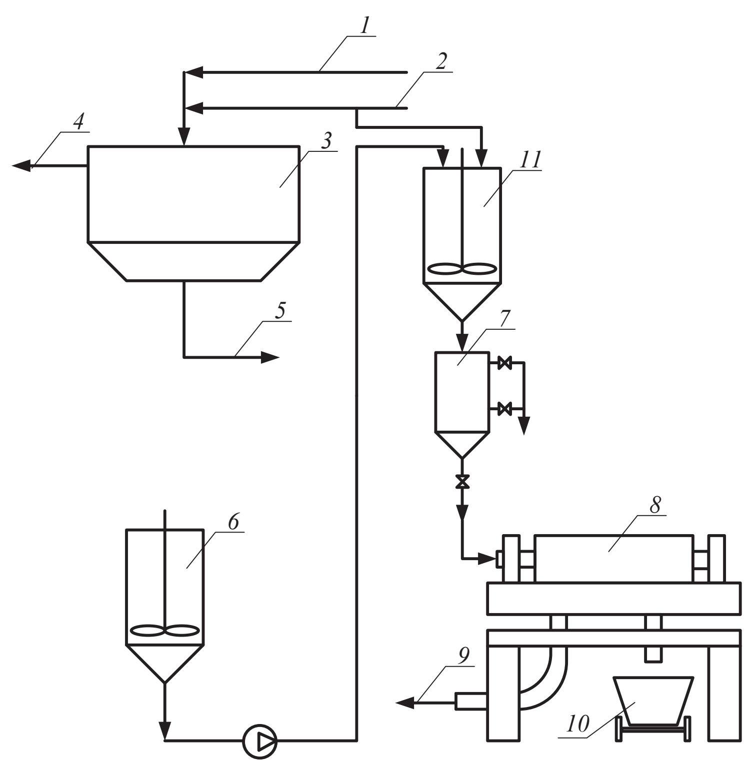

Fig. 4. Technological scheme of slime treatment with the supply of flocculants in one point «under the stirrer»: 1–10 – the same as in the description of Fig. 3; 11 – tank with a stirrer

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6. Research results

6.1. Results of laboratory study of slime samples of ferroalloy plant. To measure the sedimentation kinetics of suspended particles, a sample of slime water at the inlet to a radial thickener with a suspended matter content of 2 g/l is taken.

At the bottom of a measuring cylinder with a volume of 500 ml, as sediments precipitated, an increase in the thickness of the sediment is observed, which practically stopped after 20 minutes.

The results of measurements of sedimentation kinetics are given in Table 2.

In addition, a laboratory test of slime samples from the ferrosilicon production shop (directly at the outlet from the shop – Sample No. 1), in front of the radial thickener (before mixing of slime water – Sample No. 2). The results of sedimentation kinetics of the samples are given in Table 3.

Comparison of the sedimentation rate of suspended solids in samples 1, 2 near the shop and in the pipeline from the shop near the radial thickener is shown in Fig. 5, a comparison of the dispersed composition in Table 3.

Table 2

Kinetics of solids sedimentation of radial thickener feed

Time, minutes	Height of the clarified layer, mm	Speed of particle falling mm/sec	Particle size (calculated), mm	Temperature, °C	Sediment weight, g/l	Content of suspended particles in the clarified phase, g/l
1,5	235	2.611	0.07	60	1.2	0.8
2	230	1.917	0.05	59		
3	228	1.267	0.045	58		
5	227	0.757	0.035	57	1.6	0.4
10	229	0.382	0.03	55		
15	229	0.254	0.015	53		
20	230	0.192	0.015	51		
30	230.5	0.128	0.013	48		
45	230.5	0.085	0.01	46	1.75	0.25
60	231	0.064	0.005	44		
90	231	0.043	0.004	42		
150	231.5	0.026	0.003	40		
180	232	0.021	0.002	38		
360	232	0.011	0.001	30		

Table 3

Granulometric composition and concentration of solids of slime samples

Place of sampling	Class yield, μm				Solids concentration, g/l
	<20	20…40	60…40	>60	
Feeding of the radial thickener	16	20	60	4	2.0
Slime at the outlet of the ferrosilicon production shop (Sample No. 1)	11.1	6.7	82.2		2.21
Slime of slime water mixing (Sample No. 2)	15	25	60	0	1.4

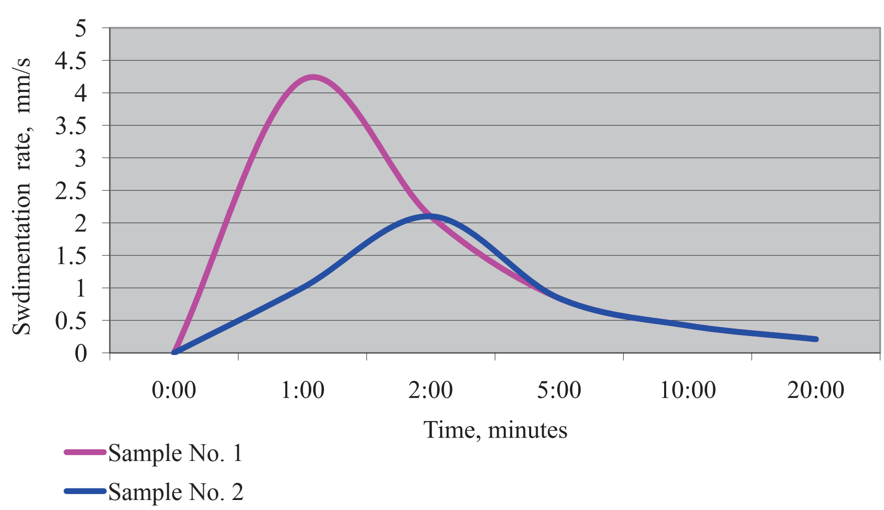

Fig. 5. Graph of comparison of the sedimentation rate of suspended solids: Sample No. 1 – slime taken directly from the ferrosilicon production shop; Sample No. 2 – slime taken in the pipeline before feeding into the radial thickener

Analysis of Tables 2, 3 and Fig. 5 indicates the presence of a larger proportion of coarsely dispersed particles with a size greater than 40 μm in sample No. 1 than in sample No. 2.

The results of the analysis of wet gas treatment slime for the content of suspended solids and salts selected at different time intervals (the interval between sampling of each sample of 2–4 weeks) are presented in Table 4.

Table 4

The content of suspended particles and salts in samples of slime water

Sampling number	Content of suspended particles in sample, g/l	Content of sail in sample, g/l	pH
1	2.9	14.3	8.4
2	2.6	24.3	10.13
3	8.4	23	10
4	3.8	17.4	9
5	4.6	21.4	10.1
6	7.25	18.6	10.16
7	3.4	26.4	8.2

Chemical analysis of clarified water samples of a radial thickener, which are selected at intervals of approximately 1 month, is shown in Table 5.

Table 5

Chemical analysis of clarified waters of a radial thickener

Controlled parameter of slime composition, mg/dm^3	Values of slime parameters		
	Sample No. 1	Sample No. 2	Sample No. 3
Suspended particles	637	1060	580
pH	10.1	10.16	10.13
Iron	0.55	0.2	0.8
Zinc	0.5	0.45	0.1
Calcium	18	12	120
Manganese	<0.01	0.002	0.01
Magnesium	41	<5	80
Silicon	30	69	275
Chlorides	205	147	2100
Sulphates	1574	4320	5680
Carbonates	2800	8050	8400
Phenol	2.05	18	34.5
Potassium	6100	5890	4800

The results of laboratory studies on the selection of flocculants are presented in Table 6.

Table 6

Selection of the type of flocculant

Solids concentration, g/l	Slime temperature, °C	pH	The amount and type of flocculant injected into the sample			Sedimentation rate of floccules, mm/s	Sedimentation rate of floccules after mechanical action, mm/s
			PC-5045 (0.05 %) ml	ТФК-18 (0.05 %) ml	ТФК-7 (0.05 %) ml		
1.5	20	8.15	1	–	–	3.5	
			1.6	–	–	4.6	2.6
2.5			2	–	–	3	1.9
			2.6	–	–	3.5	2.3
3.5			3	–	–	2.7	1.5
			4.2	–	–	3.1	1.8
4.5			5	–	–	3.2	1.7
1.5	50	8.34	1.6	–	–	6.17	4.6
2.5			1	–	–	4.4	2.9
3.5			2	–	–	4	2.75
4.5			3	–	–	2.3	1.5
			3.6	–	–	2.3	1.5
1.5	20	8.16	–	3	–	3.3	2.4
			–	5	–	4.5	3.3
2.5			–	5	–	3.14	2.3
			–	7	–	3.4	2.7
3.5			–	8	–	2.8	2.2
			–	10	–	2.9	2.5
4.5			–	10	–	2.18	1.8
			–	12	–	2.18	1.8
1.5	50	8.37	–	5	–	3.14	2.7
2.5			–	5	–	3.7	3.0
			–	7	–	3.7	2.95
3.5			–	10	–	4.2	1.6
4.5			–	12	–	2.3	2
1.5	20	8.3	–	–	1	5	3
2.5			–	–	1	4.18	2.5
3.5			–	–	1.2	3.8	2.38
4.5			–	–	1.3	2.18	2.2
			–	–	1.5	2.7	1.7
1.5	50	8.45	–	–	1	4.7	2.1
2.5			–	–	1	3.8	1.5
3.5			–	–	1.6	3.4	1.9
4.5			–	–	2.8	2.75	1

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Analysis of Table 6 shows the high efficiency of flocculants PC-5045 and ТФК-7. There is also an increase in the quality of flocculation with increasing temperature and a decrease in the sedimentation rate of floccules as the solids concentration in the slime increases.

The results of determining the optimal flocculation regime depending on the methods of mixing the solution of the flocculant ТФК-7with slime waters are shown in Fig. 6 (the specific consumption of the flocculant in all the experiments is 375 g/t, the slime temperature is 50 °C).

In Fig. 6:

Test No. 1 – feeding of flocculant with one-time and hydrostatic mixing (operating scheme at the given enterprise).

Test No. 2 – feeding the flocculant with one-time and hydrodynamic mixing in a mixer for 15 seconds.

Test No. 3 – feeding the flocculant in equal doses after 10 seconds, with hydrostatic mixing.

Test No. 4 – feeding the flocculant in equal doses, but after the first dosing, hydrodynamic mixing in a mixer for 15 seconds, after the second dosing, hydrostatic mixing for 10 seconds.

The clarified phase after determining the sedimentation rate of the floccules in the first and second versions contain no more than 0.25 g/l, in the other – from 0.25 to 0.5 g/l. After determining the sedimentation rate of floccules after mechanical action, the content of suspended particles in clarified water is in all cases up to 0.3...0.4 g/l.

In the next step, the dependence of the flocculant consumption on the solids concentration in the range of 2–20 g/l is determined. Flocculation is carried out in two points with hydrostatic mixing, with dosages of 50/50 at the first and second points. Test flocculant used in laboratory studies – ТФК-7 (0.05 %). Fig. 7 shows the results of experiments with a specific consumption of flocculants corresponding to the sedimentation rate of floccules – 5 mm/s.

The increase in the specific consumption of flocculant with a growth in concentration above 6–10 g/l is explained by the onset of cramped sedimentation, thereby increasing the specific consumption of the flocculant.

The results of the determination of the mixing time and the ratio of the flocculants at the first and second flocculation points (injection of the first and second flocculant portions) are shown in Fig. 8.

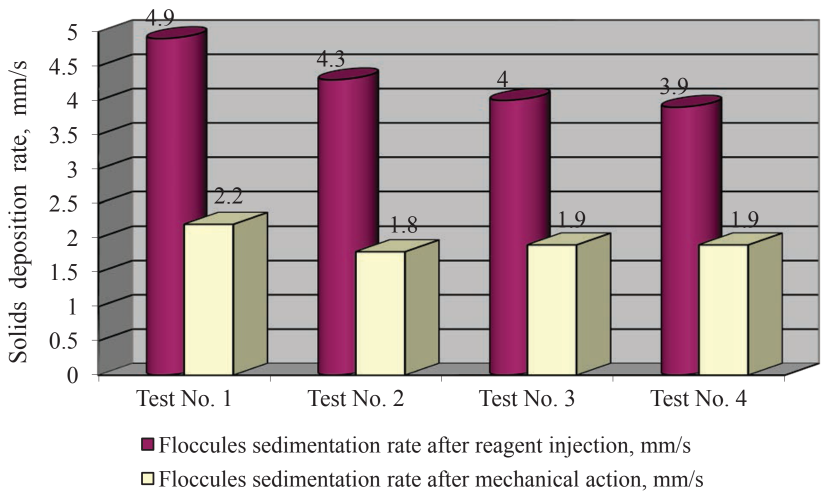


Fig. 6. Results of mixing of flocculants with slimes

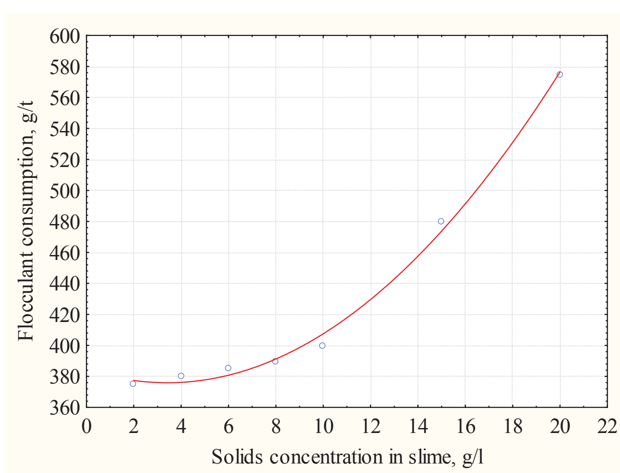
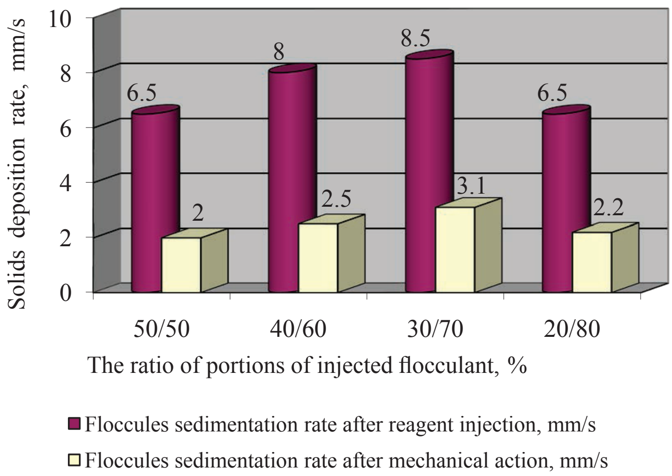
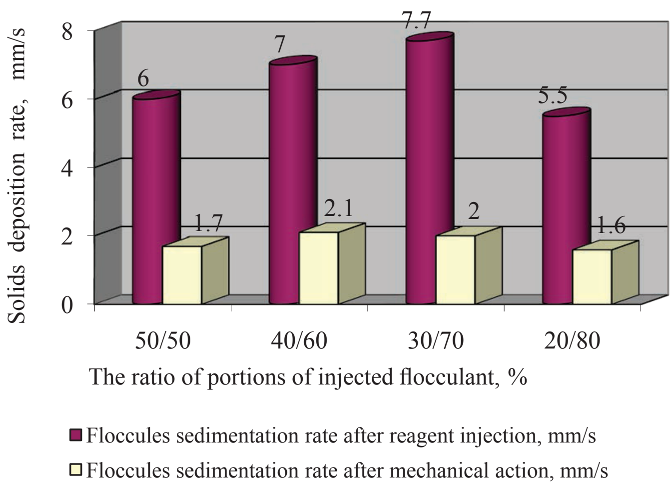


Fig. 7. Dependence of flocculant consumption on the solids concentration



a



b

Fig. 8. Influence of the mixing time and the ratio of injection of flocculants to the aggregate formation: *a* – mixing at the first point of 20 s; *b* – mixing at the first point of 60 s

Mixing at the first point is carried out using a 4-blade helical stirrer with a mixing mode of 730 rpm and a time of 20 and 60 seconds (Fig. 8, *a*, *b*). With the injection of the second portion of the flocculant, hydrostatic mixing (10–15 s) is carried out, with various dosages (% of the total volume) of the flocculant. Specific consumption of flocculant is 650 g/t.

Additional laboratory samples of slime waters are mixed with a solution of the flocculant ТФК–7 at t = 45–65 °C.

Flocculant is injected in two doses (fractional flocculation), the first portion – 35 % of the dosage, the second – 65 % of the dosage. After the first dosing point in studies No. 1–4 (Table 7), mixing is performed by turning the measuring cylinder for 20–30 seconds, in studies with the No. 5–6 turns over within 60 seconds. After the second dosing point, mixing occurs for 10–20 seconds. The results are shown in Table 7.

After determination of the sedimentation rate, the content of suspended solids in the clarified product is: in sample 1 – 0.3 g/l, in sample 2 – 0.3–0.4 g/l, and in sample 3 – 0.35–0.45 g/l.

Table 7

Repeated flocculation studies

No.	Solids concentration, g/l	t, °C	Flocculant consumption, g/l	Floccules sedimentation rate, mm/s	Floccules sedimentation rate after mechanical action, mm/s	Slime source
1	2.25	65	625	8.2	3.3	Sample 1
2		45	250	4.2	2.2	
3	1.4	50	417	3.8	2.3	Sample 2
4	0.75	50	714	4.5	2	Mixture of samples No. 1 and No. 2
5		45	500	3.5	2.1	
6		55	571	3.6	1.9	

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6.2. Results of industrial test of slime treatment efficiency. The results of industrial studies of the methods 1–3 described in paragraph 5.2, of the mixing of the flocculant with the slime are presented in Table 8.

Table 8

The results of industrial tests of the mixing of the flocculant with the slime

Type of the flocculant	Technological parameters			
	Flocculant consumption, g/t	Treatment capacity, m^3/h	Solids concentration in the feed of the centrifuge, g/l	Solids concentration in the purified water, g/l
Method No. 1				
ТФК-18	2204	5.2	3.927	0.163
ТФК-7	1742	6.6	3.914	0.67
ТФК-7	895	3.27	3.074	0.758
PC5045	843	3.27	3.263	0.581
Method No. 2				
ТФК-18	2540	4.5	12.022	4.138
PC5045	1470	6.3	34.419	1.214
Method No. 3				
ТФК-7	1236	6.3	19.257	4.006
PC5045	1939	6	12.891	1.069

Analysis of Table 8 shows that the treatment of slime waters of the ferrosilicon shop with flocculation at two points in the «flow» is most acceptable. This method provides effective treatment of slime water up to the value required for gas treatment ≤0.35 g/l using ОГШ-type continuous sedimentation centrifugal units. Also, a rather high efficiency of 0.581–0.758 g/l of flocculants PC5045 and ТФК-7 at a minimum 850–900 g/t of their consumption is observed.

6.3. Discussion of research results. Analysis of the dispersed composition and sedimentation rate in the field of gravitational forces shows that the wastewater from the ferrosilicon production workshop has:

– a large proportion of large particles (up to 82 % larger than 40 μm);

– a large proportion of finely dispersed (up to 40 % in size less than 40 μm) before the thickener. The change in the dispersed composition of particles in the slime during transportation is explained by the fact that in the process of transportation of gas treatment slimes from the shops to the radial thickener (Fig. 1) gravity particles of class 40–100 μm in the pipe are deposited in a gravity flow. This, on the one hand, leads to clogging of the pipelines, on the other hand, worsens the kinetics of sedimentation of suspended particles at the inlet to the radial thickener. Sedimentation of fine-grained slime by the flocculation method is complicated when the share of the fraction exceeds 40 μm and requires a higher expenditure, since the larger particles act as centers of aggregation. Dependences of the sedimentation rate of particles on the fraction greater than 40 μm are described in more detail in [11, 12].

As a result of the chemical analysis (Table 4), it is established that the slime waters of wet gas treatment have an alkaline medium pH 8.5–10.5 and contain up to 26 g/l of salts accumulated during the circulation. Also, water clarified in a radial thickener contains a changing chemical composition with a complex ionic situation (Table 5). Fluctuations in the salinity and alkalinity of water lead to a change in the kinetics of adsorption and bridging of the flocculant, which is not taken into account in the practice of the treatment plants of many enterprises. A detailed examination of the regularities of the influence of these parameters on aggregation requires additional studies and is practically not described in the modern literature.

The results of studies of the flocculation process on samples of gas treatment slimes (Tables 6, 7 and Fig. 6–8) show that for quality slime flocculation it is necessary:

– more effective flocculation is observed when the slime temperature increases (Tables 6, 7), which is explained by the intensification of diffusion processes;

– when the concentration of suspended solids is increased, in slime waters more than 6 g/l, dilution with clarified water from the thickener must be provided before flocculation to avoid disruption of its operation due to a reduction in the sedimentation rate of aggregates due to constrained sedimentation;

– it is necessary to dosing the flocculant solution with a concentration of 0.05 % fractional, in two points (two portions). At the first point, it is necessary to maintain the flocculant consumption of 35–40 % of the required dose and to hydrodynamically mixfor 20–30 seconds. At the second point, dose the remainder of the flocculant from the required dose with hydrostatic mixing for 10 seconds.

Industrial tests confirm the rationality of injection of flocculant in two portions. The most effective treatment of slime waters of the workshop is observed when using flocculants of Aquatop-type PC-5045 and ТФК-7, the temperature of slime water above 50 °C and the dispersed slime composition with the yield of a class fraction of more than 40 μm in excess of 80 %. That is, for effective treatment it is necessary to take the slime intake directly at the outlet from the ferrosilicon production shop.

At the same time, increased consumption of flocculant, relative to laboratory studies, may be associated with a change in the chemical (salt) composition of the slime. The identification of flocculation features in the presence of various salts requires additional studies.

7. SWOT analysis of research results

Strengths. As a result of the experiment, it is found that effective flocculation, and, consequently, treatment of the gas treatment slimes of metallurgical enterprises is possible only when the main factors affecting aggregation are taken into account. Such factors are the solids concentration and its dispersed composition, the method of sampling and mixing of slime with flocculants, and the slime temperature. Using the most optimal conditions for flocculation, treatment and dewatering of slime will reduce the cost of expensive chemical reagents, prevent water losses in the water circulation system and reduce the volumes and costs of slime removal.

Weaknesses. To determine the possibility of optimizing the flocculation process of chemical-complex slimes, additional studies of factors affecting aggregation and the stability of disperse systems are necessary.

Opportunities. The next stage of the research will be the investigation of the influence of the chemical composition of the slime on the flocculation and the selection of reagents for slime treatment by physicochemical methods. This will make it possible to control the process of flocculation, and, consequently, the treatment efficiency within a wider range of factors.

Threats. Accounting for more factors when treatment of slimes and wastewater of enterprises complicates the process of carrying out technological operations. And also requires additional efforts (changes in process parameters, for example, dilution), equipment such as classifying tanks, additional mixers and tanks, or changes in the structure of the water cycle.

8. Conclusions

1. Laboratory studies of the composition and properties of real wet gas treatment slime produced by ferroalloys show a high content of dissolved salts up to 26 g/l, a changing chemical composition and pH, and a high proportion (about 40 %) of finely divided solids of less than 40 μm in size.

2. It is found that mixing of the flocculant with the slime is expediently carried out in two portions. And in the first portion, maintain the flocculant consumption of 35–40 % of the required dose and hydrodynamically mix for 20–30 seconds, and in the second portion add the remainder of the flocculant with hydrostatic mixing for 10 seconds. The most effective treatment of slime waters produced by ferroalloys occurs when using flocculants of Aquatop-type PC-5045, ТФК-7, temperature above 50 °C.

3. The experimental design work has established the possibilities for effective treatment of wet gas treatment waters to the required standards (≤0.35 g/l) with the use of ОГШ-type sedimentary centrifugal units in a continuous mode according to the scheme for injection of the flocculant in two portions in different slime mixing regimes.

References

1. Kovalenko, A. About gas purification sludges of domain and steel-smelting manufactures [Text] / A. Kovalenko // Eastern-European Journal of Enterprise Technologies. – 2012. – Vol. 2, No. 12 (56). – P. 4–8. – Available at: \www/URL: http://journals.uran.ua/eejet/article/view/3919/3587
2. Bolto, B. Organic polyelectrolytes in water treatment [Text] / B. Bolto, J. Gregory // Water Research. – 2007. – Vol. 41, No. 11. – P. 2301–2324. doi:10.1016/j.watres.2007.03.012
3. Ghimici, L. Application of polyelectrolytes in phase separation processes [Text] / L. Ghimici, I. A. Dinu, E. S. Dragan // New Trends in Ionic (Co) Polymers and Hybrids. – NY, USA: Nova Science, Hauppauge, 2007. – P. 31–64.
4. Zeng, D. Application of a chitosan flocculant to water treatment [Text] / D. Zeng, J. Wu, J. F. Kennedy // Carbohydrate Polymers. – 2008. – Vol. 71, No. 1. – P. 135–139. doi:10.1016/j.carbpol.2007.07.039
5. Schwarz, S. Influence of humic acid on the flocculation of clay [Text] / S. Schwarz, G. Petzold, U. Geissler, N. Smolka // Colloid & Polymer Science. – 2004. – Vol. 282, No. 7. – P. 670–676. doi:10.1007/s00396-003-0989-8
6. Mende, M. Destabilization of model silica dispersions by polyelectrolyte complex particles with different charge excess, hydrophobicity, and particle size [Text] / M. Mende, S. Schwarz, G. Petzold, W. Jaeger // Journal of Applied Polymer Science. – 2006. – Vol. 103, No. 6. – P. 3776–3784. doi:10.1002/app.25573
7. Tzoupanos, N. D. Preparation, characterisation and application of novel composite coagulants for surface water treatment [Text] / N. D. Tzoupanos, A. I. Zouboulis // Water Research. – 2011. – Vol. 45, No. 12. – P. 3614–3626. doi:10.1016/j.watres.2011.04.009
8. Lee, K. E. Flocculation of kaolin in water using novel calcium chloride-polyacrylamide (CaCl2-PAM) hybrid polymer [Text] / K. E. Lee, T. T. Teng, N. Morad, B. T. Poh, Y. F. Hong // Separation and Purification Technology. – 2010. – Vol. 75, No. 3. – P. 346–351. doi:10.1016/j.seppur.2010.09.003
9. Lopez-Maldonado, E. A. Improving the Efficiency of a Coagulation-Flocculation Wastewater Treatment of the Semiconductor Industry through Zeta Potential Measurements [Text] / E. A. Lopez-Maldonado, M. T. Oropeza-Guzman, A. Ochoa-Teran // Journal of Chemistry. – 2014. – Vol. 2014. – P. 1–10. doi:10.1155/2014/969720
10. Shkop, A. Research of ways to reduce mechanical influence on floccules in a centrifuge [Text] / A. Shkop, M. Tseitlin, O. Shestopalov, V. Raiko // Technology Audit and Production Reserves. – 2017. – Vol. 1, No. 3 (33). – P. 39–45. doi:10.15587/2312-8372.2017.93690
11. Shkop, A. Exploring the ways to intensify the dewatering process of polydisperse suspensions [Text] / A. Shkop, M. Tseitlin, O. Shestopalov // Eastern-European Journal of Enterprise Technologies. – 2016. – Vol. 6, No. 10 (84). – P. 35–40. doi:10.15587/1729-4061.2016.86085
12. Shkop, A. Study of the strength of flocculated structures of polydispersed coal suspensions [Text] / A. Shkop, M. Tseitlin, O. Shestopalov, V. Raiko // Eastern-European Journal of Enterprise Technologies. – 2017. – Vol. 1, No. 10 (85). – P. 20–26. doi:10.15587/1729-4061.2017.91031

ИССЛЕДОВАНИЕ ЭФФЕКТИВНОСТИ ФЛОКУЛЯЦИИ ПРИ ОЧИСТКЕ ШЛАМОВ МОКРОЙ ГАЗООЧИСТКИ ПРОИЗВОДСТВА ФЕРРОСПЛАВОВ

Исследованы состав и особенности флокуляции шламов водооборотного цикла производства ферросплавов. Выявлено, что химический состав и концентрация твердой фазы шламов изменяется во времени. Для очистки шламов рекомендовано вводить флокулянт двумя порциями 35–40 % и 60–65 % соответственно с временем смешения до 30 секунд первой дозы и около 10 секунд второй.

Ключевые слова: флокуляция шламов, мелкодисперсные шламы, шламы газоочистки, модуль очистки, производства ферросплавов.

Shkop Andrii, *PhD, Director, LTD «Scientific and Technical Center «Ecomash», Kharkiv, Ukraine, e-mail: shkop_ecomass@ukr.net, ORCID: https://orcid.org/0000-0002-1974-0290*

Briankin Oleksandr, *Postgraduate Student, Department of Chemical Technique and Industrial Ecology, National Technical University «Kharkiv Polytechnic Institute», Ukraine, e-mail: bryankin@i.ua, ORCID: https://orcid.org/0000-0002-7897-4417*

Shestopalov Oleksii, *PhD, Associate Professor, Department of Chemical Technique and Industrial Ecology, National Technical University «Kharkiv Polytechnic Institute», Ukraine, e-mail: shestopalov.it@khpi.edu.ua, ORCID: https://orcid.org/0000-0001-6268-8638*

Ponomareva Natalya, *PhD, Associate Professor, Department of Integrated Technologies, Processes and Devices, National Technical University «Kharkiv Polytechnic Institute», Ukraine, ORCID: https://orcid.org/0000-0001-8931-5882*