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IMPROVEMENT OF WATER RECYCLING SYSTEMS FOR WATER MINING ENTERPRISES

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Abstract

This work considered the method of deposition of saponite-containing slurry, which is a diamond tailings. It is shown that the application of magnesium chloride as an electrolyte solution significantly increases the rate of sedimentation of solid-containing saponite suspensions. Sedimentation rate, defined particle size and zeta potential values of the investigated suspensions were calculated. A scheme for clarification of saponite-containing suspension, which provides the subsequent use of clarified water, was proposed.

Key words: *saponite-containing suspension, electrokinetic (zeta) potential, electrolytic coagulation, the degree of clarification*.

1. INTRODUCTION

The object of this research is waste from processing of diamond factory (deposit named after M.V. Lomonosov), located 100 km from the city of Arkhangelsk. The development of this field is produced over the last ten years and, despite numerous studies on this topic, has not yet solved the problem of waste disposal, namely saponite-containing suspension, which is due to the nature of the chemical structure, has a very low rate of sedimentation. Significant amounts of the resulting suspension (up to 500 m^3/h) and not solved problem with clarification are predetermine the increase of the volume of tailings and could have a negative impact on the environment, because uncontrolled dike break fencing can lead to irreversible consequences.

2. EXPERIMENTAL PART

In the present work the influence of the doubly charged electrolyte solution, added to the saponite-containing solution, on the deposition rate of solid particle suspensions, on the zeta potential and particle size were shown. Also proposed flow chart of clarifying wastes and use of clarified water for water recycling.

Preliminary studies was showed that the addition to the original slurry singly charged electrolytes (sodium chloride, hydrochloric acid, sodium hydroxide, sodium sulfate) were not significantly increase the rate of deposition of the solid phase of the suspension. However, the use of these substances in vivo is impractical from an environmental point of view. Therefore, the search of a suitable electrolyte was continued.

The solution of magnesium chloride was chosen as an electrolyte. It is known that the substance (magnesium chloride or mineral “bischofite”) is non-toxic, widely used in national economy (as a fertilizer, in medicine, as an anti-icing agent) and is very accessible. In addition, aqueous solutions of salts are not affected by the process of hydrolysis and, therefore, the

calculated concentration of counter ion (Mg^{2+}), entered into the system does not require taking into account losses on the secondary reaction of the particles occurring chemical transformation.

At the first stage of the research by measuring the dynamics of the solution turbidity [1] when added different amounts of $MgCl_2$ to a system its optimal concentration was determined. Its addition is a violation of sedimentation-diffusion equilibrium in the reaction medium. One of the methods of determining the optimal concentration of the electrolyte, causing a violation of sedimentation-diffusion equilibrium in the colloid system is calculated from the experimental data of changes in turbidity of the suspension with the use of optical methods of analysis [2].

Optical characteristics were recorded during the experiments at a wavelength of λ=520 nm. The temperature of the solution in all experiments was kept constant 20±1^{0}C.

In all experiments, we used the following procedure for preparation of the colloid solution: initial saponite-containing suspension was diluted with distilled water at a ratio of 1/500(empirically established that with such dilution factor - transmittance values is in the range 0.2 -1); preparing a solution of $MgCl_2$ with concentration 1 mol/L; to the 50 ml of the diluted suspension was added 0.25 ml of solution $MgCl_2$ with concentration 1 mol/L for the preparation of concentration 0.005 mol/L. Solution was thoroughly mixed by bubbling air for 30 seconds, installed in the spectrophotometer cuvette and fixed value of the transmittance (T) in time.

For the solution of $MgCl_2$ with concentration in the test suspension of 0.005, 0.010, 0.015, 0.020 mol /L we repeated experience. In addition, in parallel we measured the optical characteristics of the initial suspension (blank experiment). The graph of the functional dependence T = f (τ), constructed from experimental data from a series of experiments with the addition of solution of $MgCl_2$ with different concentrations, shown in Fig.1. According to the character shown in Fig. 1 can be concluded that the addition of a salt $MgCl_2$ to the suspension of saponite significantly increases the rate of sedimentation of particles from solid phase. The effective time of the electrolyte activity in all series of the experiment is 80-90 min (in addition of singly charged ions H^+ and Na^+ this option is 120, and 150 min, respectively).

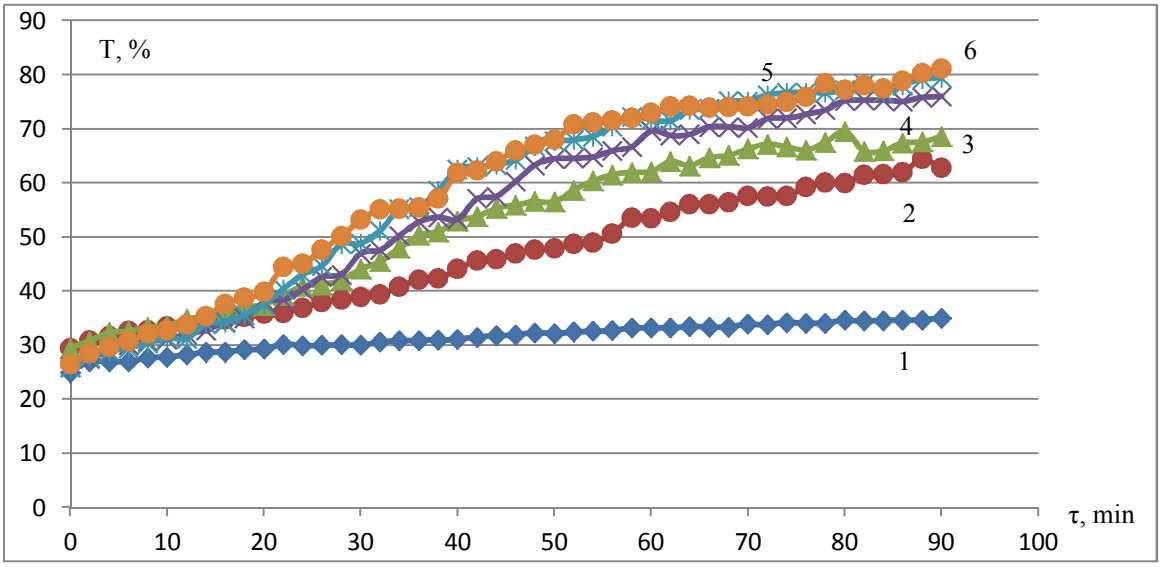

Fig.1. Change of transmittance T (%) of the suspension in time (τ) with the addition of $MgCl_2$ concentration in the reaction mixture (mol/L): 1 – blank experiment, 2 – $2,5\times10^{-3}$; 3 – $5,0\times10^{-3}$; 4 – $1,0\times10^{-2}$; 5 – $1,5\times10^{-2}$; 6 – $2,0\times10^{-2}$.

Fig. 2 shows the transmittance (T) of the suspension depending on the concentration of $MgCl_2$ solution when exposed reaction mixture is 80 min. The dates, presented in Fig. 2, suggest that the optimum concentration of electrolyte is in the suspension of 0.015 mol/L, therefore for the subsequent experiments used this concentration.

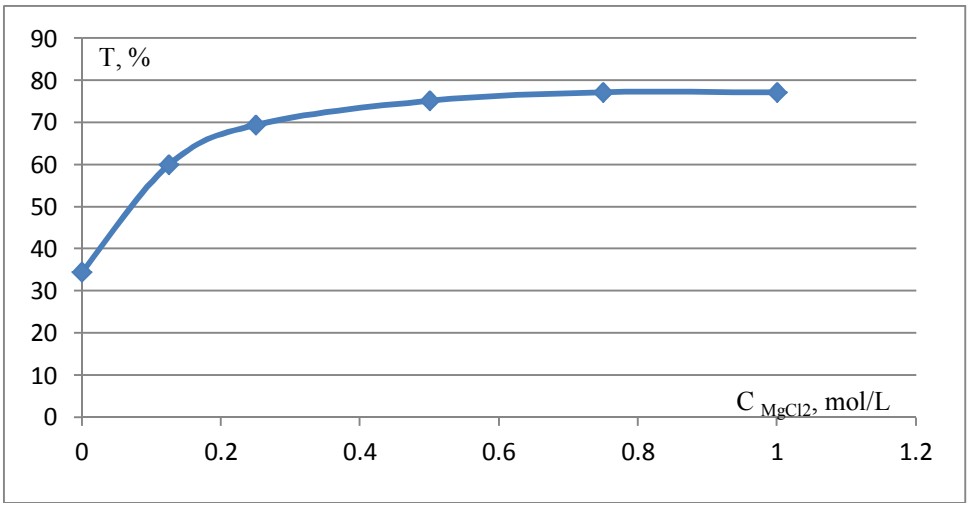

Fig.2. Change of transmittance (T %) of the suspension in depending on the concentration of the solution $MgCl_2$ (C) during exposure of the reaction mixture 80 min.

The degree of clarification of the suspension (T_0) was calculated by the formula (1), and the results of calculations are presented in Fig. 3 as a function $T_0 = f(\tau)$:

$$T_0=(T_\tau-T_1)/(T_{max}-T_1)\cdot 100\%, \qquad (1)$$

where T_τ - the value of the transmission for a suspension of the exposure time τ,%; T_1 - the value of the transmission at the initial time, %; T_{max} - the maximum possible value of light transmission coefficient (T_{max} = 1). The data presented in Fig. 3 show that in 90 min of the experiment the degree of clarification of the suspension is 75% at a concentration of 0.015 electrolyte. (In comparison with the results for H^+ - 67% for Na^+ - 48%).

The experimental data allowed to calculate the rate of clarification of the suspension ($V=dT/d\tau$). For this purpose, the approximation of dependences obtained (Fig. 3) by various mathematical functions was carried. This operation showed that the most adequate experimental data and in this case is described by a polynomial of degree four:

$$T_0=a_1\cdot\tau^4+ a_2\cdot\tau^3+ a_3\cdot\tau^2+ a_4\cdot\tau+b \qquad (2)$$

Table 1 shows the values of the coefficients of the equation for the tests with the optimal concentration of the electrolyte.

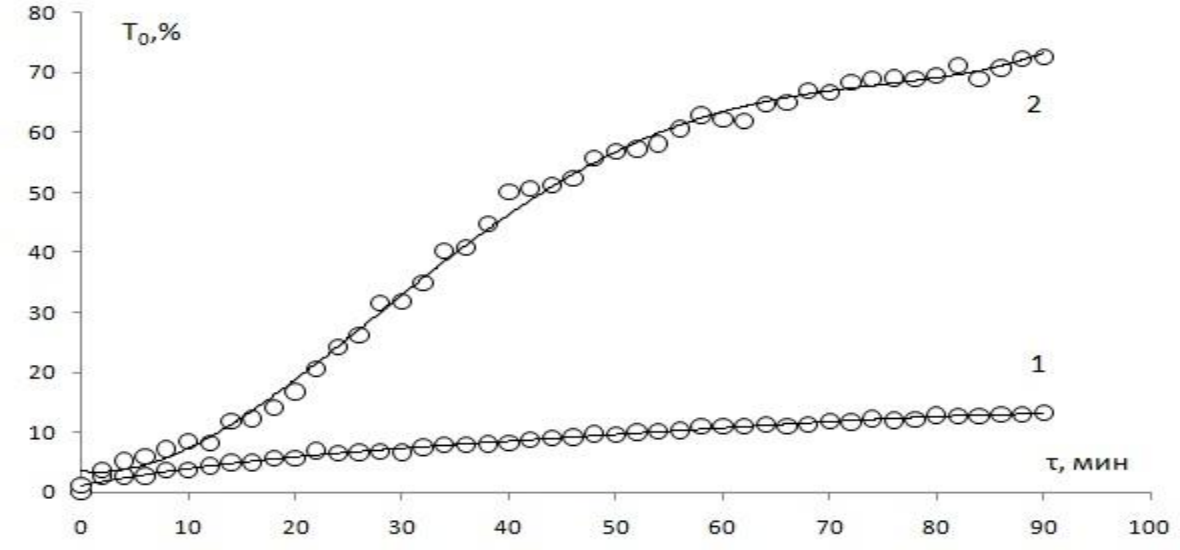

Fig. 3. The value of the degree of clarification, depending on the exposure time of the reaction mixture: 1 - by adding a solution $MgCl_2$ (concentration 0.015 mol / L) 2 – blank test.

Table 1. The values of the coefficients of the equation (2).

Concentration of the electrolyte, mol/L	Coefficients				
	a_1	a_2	a_3	a_4	b
0,015	6×10^{-6}	-12×10^{-4}	$68{,}9\times10^{-3}$	$-19{,}9\times10^{-2}$	3,49

The derivative to time of equation (2) is the current speed of the process of clarification of the suspension.

Graphs of dependences shown in Fig. 4 show that the maximum rate of clarification of the suspension with the addition of the electrolyte has a value of 1.31 min^{-1}, which is achieved within 30 min after addition of $MgCl_2$ with concentration 0.015 mol /L.

By the time interval of 90 min the rate of clarification of the suspension is practically zero, which indicates the completion of the sedimentation of particles under these conditions. It should be noted that the results of calculating the current rate of spontaneous clarification of the suspension showed almost increase in this parameter, its maximum by 90 min of the experiment (1.05 min^{-1}).

In parallel, has been defined particle size (diameter, D) and the value of ζ-potential (examples of protocols, see Fig. 5 and 6) by clarification of the suspension by the methods of measuring the dynamic and electrophoretic light scattering analyzer on the submicron particle size and zeta potential DelsaNano.

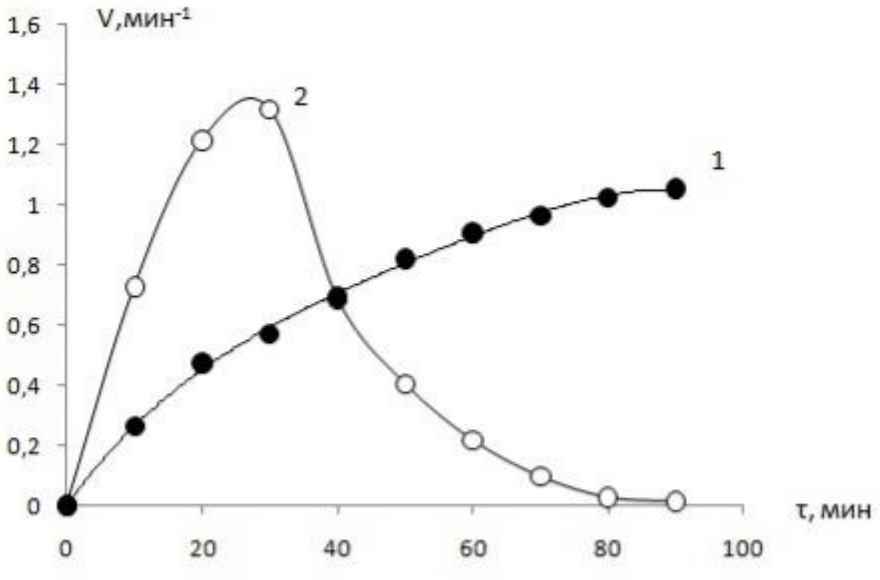

Fig. 4. Changing of the rate of sedimentation in time by adding a solution $MgCl_2$: 1 – blank test, and 2 - by adding a solution $MgCl_2$ (concentration of 0.015 mol/L).

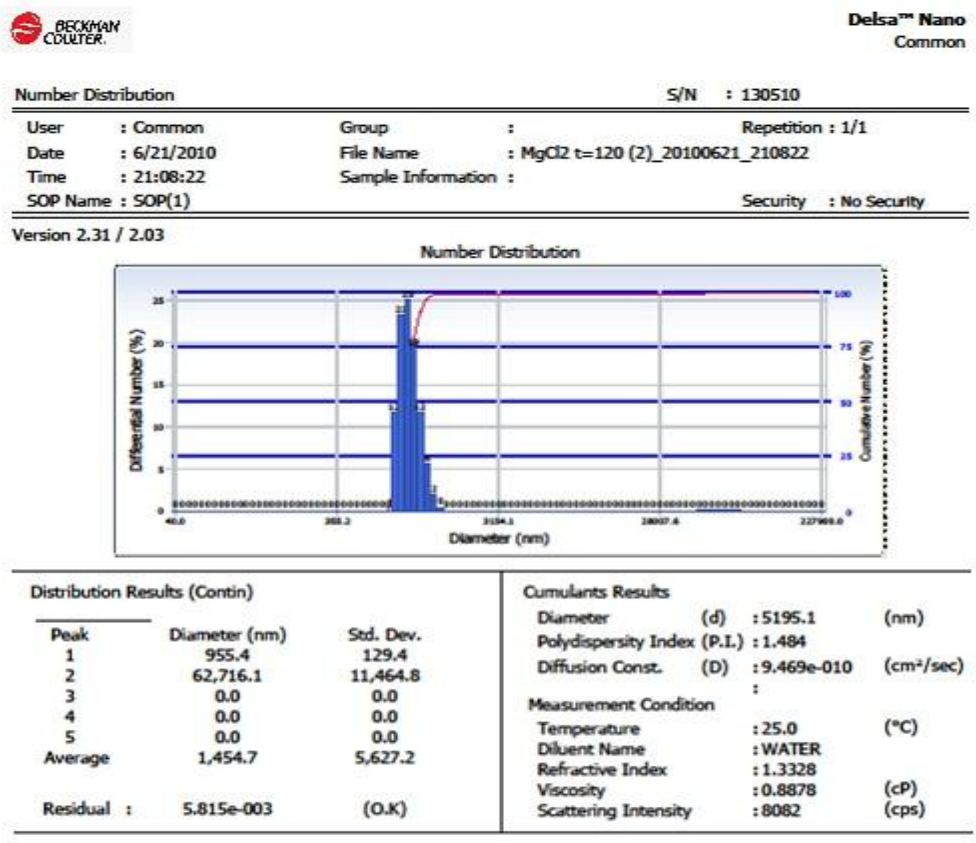

Fig. 5. An example of protocol for determining the particle size on analyzer DelsaNano .

The experimental results were presented in Table 2.

The experimental results presented in Fig. 4 and in Table 2, by our opinion, have a good agreement. Thus, the absolute value of ζ-potential of particles in dispersed phase of the suspension has a value less than 35 mV. For most of zols it is a critical value of the potential, that is, if $\zeta > |35|$ mV, coagulation was observed. Coagulation in colloidal systems occurs much earlier than the zol reaches to the isoelectric state (ζ-potential is zero) and is the faster, the lower the value of the zeta-potential [1, 3].

In our case, saponite-containing particles having a surface charge of the ζ = -20mV, are able to spontaneously enlargement by overcoming the electrostatic barrier due to the forces of mutual attraction. However, the process proceeds with a low rate. Adding an electrolyte causes a sharp decrease in the surface charge of particles. The particles reach almost isoelectric state ζ = - (7 ÷ 10) mV, which causes a significant increase in the size of the first 30 minutes and as a consequence, a significant acceleration of the clarification of the suspension.

Index of polydispersity of the initial suspension increased after the addition of an electrolyte in it, which may indicate the presence of a large system capable to sedimentation, formations, and not large-sized particles, which are characterized by slow sedimentation. Attention to the fact that due to the presence of the maximum particle size at 30 min. By our view, this can be explained by a significant decrease in partial concentration of the solution, which in turn leads to a reduction of contacts between particles, leading to their enlargement.

Table 2. The values of ζ-potential and particle size of suspensions

Concentration of the electrolyte, mol/L	Time of exposure, min	ζ-potential, mV	D, nm	Index of polydispersity
0	0	-20,62	2300±100	0,891
	30	(-16,78)÷(-19,27)		0,750
	60			0,690
	90		2500	0,653
	120		2700	0,611
0,015	0	-20,35	2700	0,641
	30	(-6,71)÷(-10,36)	5200	1,484
	60		3600	0,985
	90		3600	0,928
	120		3700	0,991

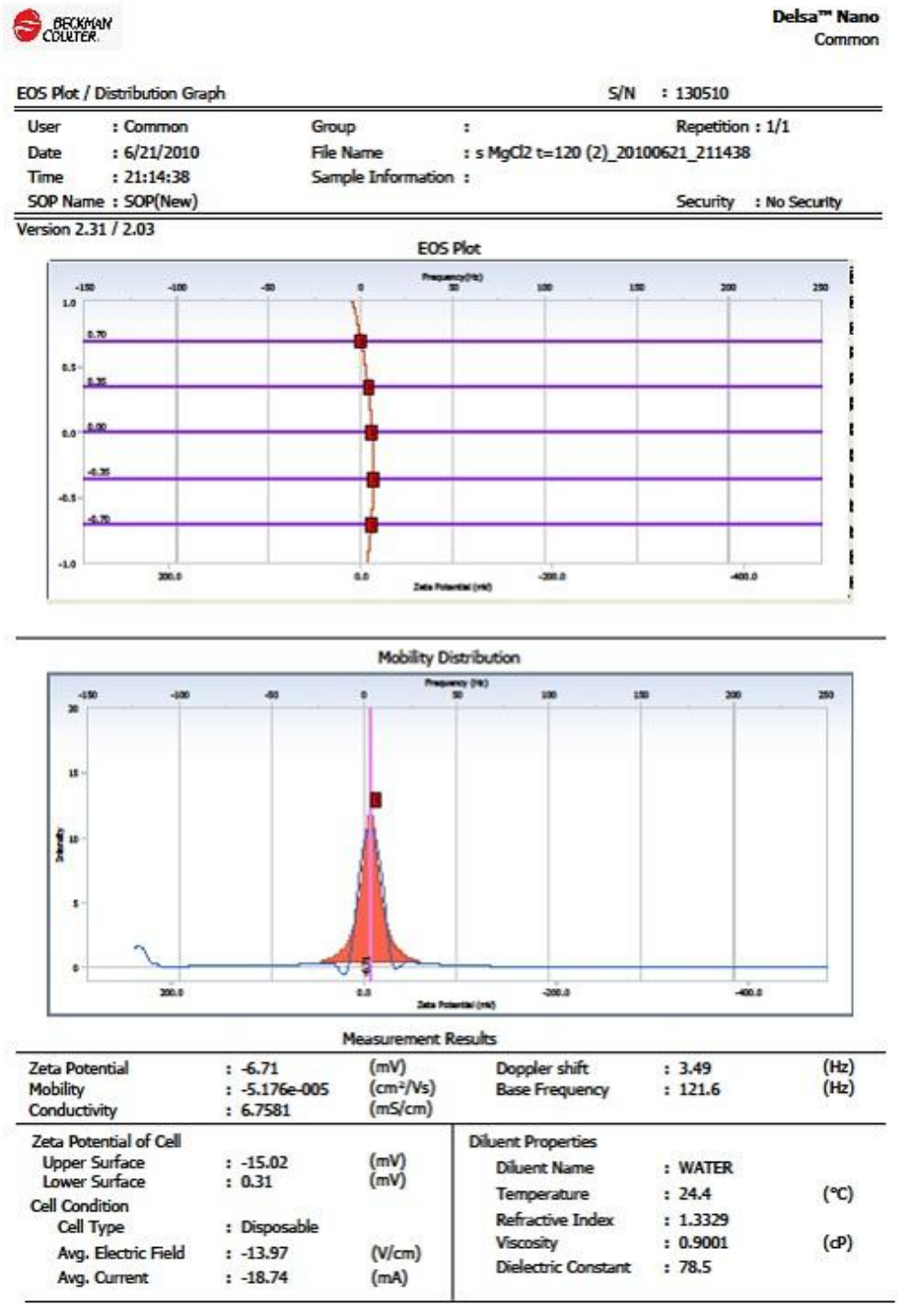

Fig. 6. An example of protocol for determining the ζ-potential on analyzer DelsaNano .

The experimental data allowed to calculate the true rate of sedimentation of particles(U) in studied suspensions. Thus, based on the classical theory of the provisions of sedimentation stability of colloidal systems [1, 3], and considering that the suspension with sufficiently large particles are kinetically unstable formations can be written

$$f = V(d - d_0)g\,, \qquad (3)$$

where f - the force of gravity, acting on the particle; V - volume of the particle; g - acceleration of gravity; d and d_0 - density of saponite -containing clay particles and water (0,998 × 10^3 kg/m^3) [2].

The density of the matter of the dispersed phase was determined after a preliminary separation, drying and grinding in the planetary ball mill Retsch PM100 to the size of 1 micron by standard method [4]. Since the density of saponite-containing solids phase was 2,555 ×10^3 kg/m^3.

Force f is constant and under they influence the particle moves in a dispersion medium as constant acceleration. Simultaneously with the force of gravity acting on the particle strength the viscous resistance of the medium f^1:

$$f^1 = 3\pi D\eta U\,, \qquad (4)$$

where D - diameter of the particle; η - viscosity of the dispersion medium (1,005 × 10^{-3}Pa.s [5,6]); U-sedimentation velocity of the particle. When $f = f^1$ particle starts moving at a constant maximum speed that can be calculated using the following equation:

$$U = \frac{V(d-d_0)g}{3\pi D\eta}\,, \qquad (5)$$

considering that $V = \frac{4}{3}\pi r^3$ (r - radius of the particle), the equation (5) takes the following form:

$$U = \frac{2D^2(d-d_0)g}{27\eta}\,. \qquad (6)$$

According to equation (6) the real rate of sedimentation of particles of saponite-containing suspension in the case-load of experience and expertise with the addition of electrolyte was calculated. Thus, the spontaneous deposition of particles of the solid phase is characterized by a nearly constant rate, equal to 2,12 ÷ 2,95 cm/h. With the introduction of the slurry concentration of $MgCl_2$ 1,5 × 10^{-2} mol/l, sedimentation rate of particles increases to 10.91 cm/h.

The addition of magnesium chloride solution to the saponite-containing suspension significantly increases the rate of sedimentation in a dilute condition for the original pulp was shown.

It should be noted that the clarified water in the use of additives have the transmission coefficient close to unity (0.97), and in settling time of 70-90 minutes for the initial slurry volume, sediment is about half of the total and about 50% of the clarified water, which can used for water recycling, or for other needs of the factory.

In order to optimize the process of the adding of electrolyte and the time of intervals obtained by the action of the coagulant, a model plant for gradual clarification of pulp, which is presented in Figure 7, was proposed.

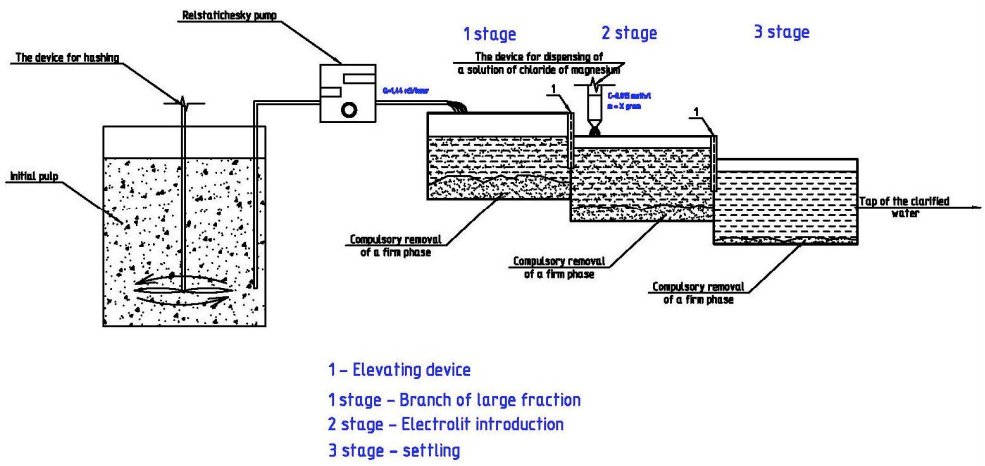

Fig. 7. A model plant for gradual clarification of pulp.

3. CONCLUSIONS

The possibility of using as the electrolyte-coagulant the magnesium chloride for clarification of saponite-containing suspensions was shown.

Deposition rate of solid particles of the suspension, the values of zeta potential and particle size were calculated.

A scheme for pulp bleaching with magnesium chloride was proposed.

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