DOI: 10.6060/ivkkt.20226501.6447

УДК: 666.5:576.1

ИССЛЕДОВАНИЕ ВЛИЯНИЯ СЕРНОКИСЛЫХ СОЛЕЙ НА ПРОЦЕСС ОТСТАИВАНИЯ ГЛИНИСТОЙ СУСПЕНЗИИ

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Предприятие ПАО «Севералмаз» занимается разработкой алмазного месторождения вблизи природоохранной зоны, следовательно, требует обеспечения эффективной и безопасной технологии добычи полезных ископаемых. Для разработки и внедрения данной технологии были отобраны пробы оборотной и карьерной воды на предприятии и подвержены рентгенофазовому, рентгенофлуорисцентному и гранулометрическому анализу. На основании результатов этих анализов были подобраны и разработаны коагулянты, способные превратить огромную массу пустой породы, производимой предприятием, во вторичный продукт. Применение сульфатов щелочных металлов для разделения глинистых тонкодисперсных частиц, представленных преимущественно сапонитом, является довольно перспективным. Измерены скорость осаждения и изменение кислотности суспензии, а также произведено сравнение с традиционными коагулянтами. Осадки, обработанные сульфатами щелочных металлов, подвергли рентгенофазовому и рентгенофлуорисцентному анализу, а также предположили возможный механизм процесса уплотнения частиц. Сапонит -глинистый минерал монтморилонитовой группы, содержащий большое количество магния, обладающий сорбционными свойствами. Получаемые в ходе разработки минеральные глинистые осадки являются перспективным сырьем для целого ряда вторичных продуктов. Частицы сапонита, вследствие их геометрических и физико-химических характеристик, образуют крайне устойчивую к седиментации суспензию. Применение сульфатов щелочных металлов оказывается существенно эффективнее, чем применение традиционных промышленных коагулянтов, а применение кальцийсодержащих шламов в качестве утяжелителей позволяет интенсифицировать процесс. Получаемые осадки содержат достаточное количество калия и магния для создания на основе сапонитового осадка минерального калий-магниевого удобрения, высушенная глина может служить основой для морозостойкого бетона.

Ключевые слова: алмаз, сапонит, коагуляция, сернокислый натрий, сернокислый калий, скорость осаждения

Для цитирования:
Зубкова О.С., Алексеев А.И., Сизяков В.М., Полянский А.С. Исследование влияния сернокислых солей на процесс отстаивания глинистой суспензии. *Изв. вузов. Химия и хим. технология*. 2022. Т. 65. Вып. 1. С. 44–49

For citation:
Zubkova O.S., Alekseev A.I., Sizyakov V.M., Polyansky A.S. Research of sulfuric acid salts influence on sedimentation process of a clay suspension. *ChemChemTech* [*Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*]. 2022. V. 65. N 1. P. 44–49

RESEARCH OF SULFURIC ACID SALTS INFLUENCE ON SEDIMENTATION PROCESS OF A CLAY SUSPENSION

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PCSJ "Severalmaz" is a diamond mining enterprise near nature reserve areas. Ttherefore, it requires the provision of effective and safe mining technology. For the development and implementation of this technology, samples of recycled and quarry water were taken at the enterprise and subjected to X-ray phase, X-ray fluorescence, and granulometric analysis. Based on the results of these analyses, coagulants were selected and developed that can turn a huge mass of waste rock produced by the enterprise into a secondary product. The use of alkali metal sulfates for the separation of clay fine particles, represented mainly by saponite, is quite promising. The deposition rate and changes in the acidity of suspension were measured and compared with traditional coagulants. Precipitate treated with alkali metal sulfates was investigated by X-ray phase and X-ray fluorescence analysis, and a possible mechanism of the sediment compression was suggested. Saponite is a clay mineral of the montmorillonite group that contains a large amount of magnesium and has sorption properties. The mineral clay sediments obtained during the mining process are promising raw materials for a number of secondary products. Saponite particles, due to geometric and physico-chemical characteristics, form an extremely resistant to sedimentation suspension. Application of alkali metal sulfates is significantly more effective than traditional industrial coagulants, and additional treatment of calcium-containing slurries as weighting agents allows to intensify the process. The resulting sediments contain a sufficient amount of potassium and magnesium to create a mineral potassium-magnesium fertilizer based on saponite sediment, also dried clay can serve as the basis for frost-resistant concrete.

Key words: diamond, saponite, coagulation, sodium sulfate, potassium sulfate, precipitation rate

INTRODUCTION

The development of closed production cycle enterprises is a major concern of modern industry and especially it is significant for mineral resources mining, which causes strong environmental contamination, technogenic catastrophes [1-3]. The Lomonosov diamond deposit is the main source of diamonds in the North of the European part of Russia. The mining process is carried out in difficult natural conditions, with poor regional infrastructure. This makes the water purification problem significant and requires a complex solution of all problems with maximum possible benefit and less possible environmental influence.

The main related minerals in diamond mining are light clay fine minerals: dolomite, kaolinite, saponite, serpentine, which make up about half the mass of the entire extracted ore [4]. Most of those clay particles do not settle under gravity influence and form a stable suspension in the entire volume of cycle water. Applied water treatment technology is insufficient. The suspended particles concentration in the tailings pond increases annually and reduces the quality of cycle water, which leads to premature overflow of the tailings pond, and increases the risk of a technogenic disaster. A complex and efficient solution to those problems is required for industrial application with water purification facility and waste rock recycling technology to negate all environmental damage of diamond mining [4-6].

The efficiency of quarry water treatment for the industry is determined by the rate of suspension sedimentation or by the amount of purified liquid. For well-condensed sediments, the liquid content is characterized by the ratio L:S (liquid: solid) is equal to 1:2. However, for saponite suspension, this ratio is equal to 8:1. One of the methods for breaking the stability of the suspension is the addition of electrolytes. Electrolytes decrease the surface potential of suspended particles and enhance subsequent sedimentation of the suspension. Therefore, the use of strong salts as coagulants is a promising solution to a problem [7].

Chemical composition of suspension was investigated and coagulant with weighting additive based on its properties and structure was chosen to obtain the maximum amount of purified water, as well as solid product with prospective properties for its secondary application [8]. A weighting additive that enhances sedimentation rate was found and tested, and methods of minimizing environmental damage from the facility were considered.

METHODS

Samples of recycled water were taken from water-reducing wells that supply the processing plant with water from the tailings pond.

The granulometric composition of suspended minerals was obtained using the Horiba LA-950 laser express particle size distribution analyzer.

The mineral and chemical composition of the particles and the resulting sediment were analyzed using an XRD-7000 X-ray diffractometer [9], and the results were analyzed using an integrated database [10], tables by Feklichev [11] and Micheev [12].

Cycle water samples with a suspension content of 40 g/l were selected in 1-liter graduated cylinders. The pH value of the sample water was measured and equal to 8.61. Different amount of coagulant (1, 3, 5 g) was added in 3 cylinders with stirring, then the saponite suspension settled under static conditions. The deposition process lasted for 8 h, and the height of the purified liquid was measured at 30 min intervals. A similar experiment was performed with the introduction of calcium-containing weighting additives, which were added at first 30 min after the coagulant application.

The deposition rate of an untreated clay mineral, taking into account the laminar flow regime of the liquid, is calculated with sufficient accuracy using the Stokes formula (1):

$$w_{\text{ос}} = k\frac{d^2(\rho-\rho_{\text{c}})g}{18\mu_{\text{c}}} \quad (1)$$

The optimal value of the deposition rate is calculated using formula (2):

$$v_0 = \frac{H_1}{t_{кр}} \quad (2)$$

The average deposition rate is calculated using formula (3):

$$v_i = \frac{H_i}{t_i} \quad (3)$$

RESULTS AND DISCUSSION

The main efficiency index, as mentioned above, is the deposition rate of suspended particles. For an untreated suspension, the velocity is calculated by equation (1), and for plate particles (k = 0.32), it is $5.81 \cdot 10^{-17}$ m/s, which indicates the existence of a stable suspension, which is not affected by natural precipitation under gravity force [14, 15].

The concentration of montmorillonite group particles in the tailings pond varies from 40 g/l at the surface to more than 200 g/l at a depth near 2 m. The cycling water taken for enrichment contains from 1 g/l to 270 g/l of mineral particles. More than 50% of the suspended particles have a size of less than 2 µm, which refers to the fine fraction of the mineral. The chemical composition of suspended particles in recycled water is shown in Table 1, and the X-ray spectrum of suspended particles is shown in Fig. 1. The suspended mineral particles of the cycle water contain a sufficient amount of magnesium according to its chemical composition shown in Table 2 for application as a raw material for magnesium-potassium fertilizer.

Table 1

Chemical composition of cycle water samples in terms of oxides

***Таблица 1.* Химический состав проб взвесей оборотной воды в пересчете на оксиды**

Sample	Concentration, mass.%							
	SiO_2	MgO	Fe_2O_3	Al_2O_3	CaO	K_2O	Na_2O	Other
Suspended particles of cycle water	53.9	26.25	7.3	5.59	2.56	1.59	1.23	1.58

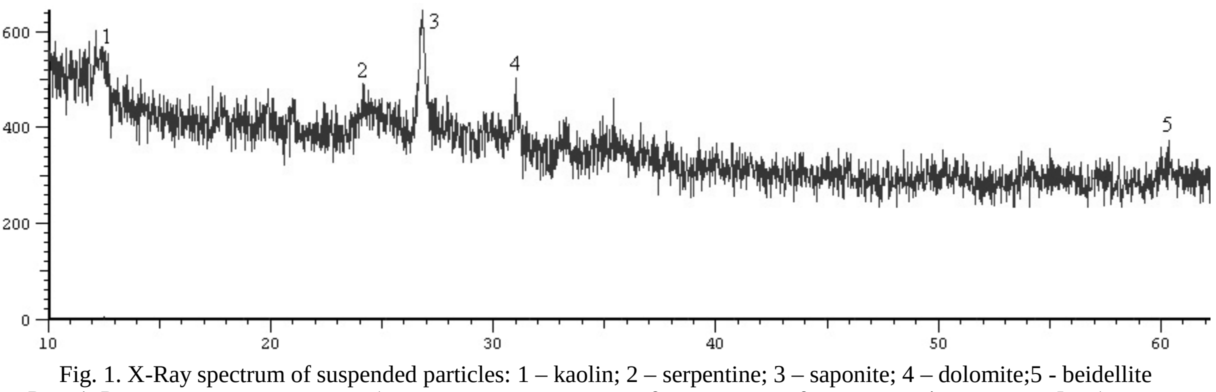

Fig. 1. X-Ray spectrum of suspended particles: 1 – kaolin; 2 – serpentine; 3 – saponite; 4 – dolomite;5 - beidellite

Рис. 1. Рентгенограмма взвесей оборотной воды: 1 –каолин; 2 –серпентин; 3 –сапонит; 4 –доломит; 5 – бейделит

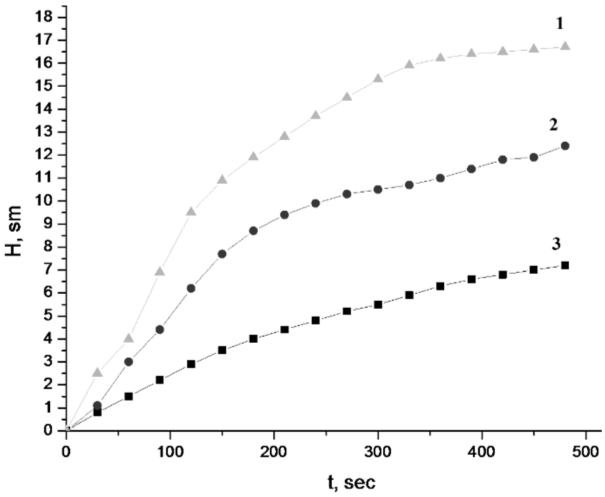

Fig. 2. Height of purified liquid during an experiment. 1– K_2SO_4; 2 – Na_2SO_4; 3 –$CaSO_4$

Рис. 2. Высота столба осветленной жидкости во время эксперимента. 1– K_2SO_4; 2 – Na_2SO_4; 3 – $CaSO_4$

A salt formed by strong acid and base, used as coagulant has a complex effect on the saponite mineral. Due to the complete dissociation and the higher electrical and chemical activity of alkali metals, these compounds probably cause the substitution of magnesium and calcium ions for potassium and sodium in the DL (Double Layer) of micelles formed by the mineral. This substitution reduces EDL (Electric Double Layer) of formed micelles, which leads to a release of connected water and the mineral salts formed by electrolytes as presented in Fig. 2. This provides a much greater water output, relative to other types of coagulants. The formation of poorly soluble calcium sulfate also contributes to the agglomeration centers' formation and thus enhances sedimentation. Particle connection by insoluble sulfates reduces the factor of waste rock dust storms. The deposition rates for the use of potassium and sodium sulfate, as well as the pH of purified water, are shown in Table 3 and Fig. 3.

Table 2

Chemical composition of sediment after coagulant treatment in terms of oxides

***Таблица 2.* Химический состав осадка после обработки коагулянтами в пересчете на оксиды**

Settled sample	Composition, mass.%								
	SiO_2	Al_2O_3	Fe_2O_3	SO_3	**K_2O**	**MgO**	CaO	NaO	Other
K_2SO_4	35.9	3.4	6.6	15.0	**18.0**	**17.1**	1.6	1.0	2.4
Na_2SO_4	36.1	4.4	8.7	14.8	2.4	**18.3**	1.7	16.9	13.6

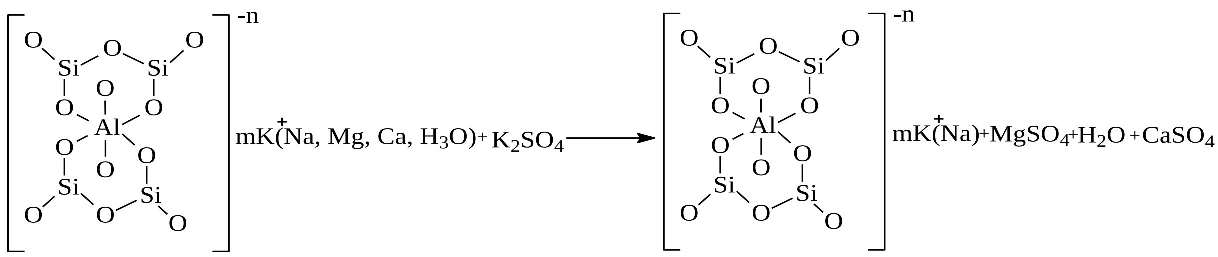

Fig. 3. Mechanism of water release at potassium sulfate treatment

Рис. 3. Механизм высвобождения воды при обработке сернокислым калием

Table 3

Presipitation rates and acidity of purified water at coagulant treatment

***Таблица 3.* Скорости осаждения, кислотность воды при обработке коагулянтами**

Coagulant 3g/l	Avg. settlement rate		Optimalsettlement rate		pH	
	With additive, sm/min	w/o additive, sm/min	With additive, sm/min	w/o additive, sm/min	With additive	w/o additive
K_2SO_4	0.057	0.041	0.061	0.042	9.15	8.87
Na_2SO_4	0.039	0.028	0.038	0.28	9.48	9.06

CONCLUSION

Investigation of suspended saponite particles precipitation process efficiency enhancement from recycled water has been carried out. The mineral composition of the initial suspension and the resulting sediment was studied using X-ray methods. The granulometric composition of suspensions is typical for fine suspensions and these particles are resistant to sedimentation. To increase the efficiency of purification according to the composition of mineral particles, potassium and sodium sulfates were selected as coagulants and calcium aluminocarbonates as weighting additives for sedimentation studies of suspended particles by the described method. The amount of obtained pure water by sulfates treatment increased by 200% compared to standard coagulants [14, 15], also there is no such strong pH shift (table 3) [15].

Further studies of the electrochemical mechanism of suspension destabilization and, in particular, changes in the surface potential, as well as changes in the sediment composition, allow us to determine the most efficient method of precipitation of the solid particles from cycle and quarry water of the Lomonosov processing plant and form a promising recyclable condensed product, as well as purified cycle water with the required characteristics for the ore processing. Application of strong electrolytes also requires the establishment of closed water cycling for future nature conservation in the mining area or further complex purification, due to the accumulation of sulfates in the recycled water during sulfate treatment and the discrepancy in the content of other chemical elements.

Treatment of water with potassium sulfate at the Lomonosov processing plant has several prospects. The accumulation of sulfates in water within a closed water cycle may reduce the consumption of coagulant for cleaning, also it may increase the efficiency of the purification process, and waste rock dumps of calcium-containing minerals from nearby enterprises could be used as weighting additives sources [4,7], but these statements require further investigation for commercial evaluation. The resulting sediment has a sufficient amount of magnesium and potassium in its structure, which makes saponite a promising raw material for the production of fertilizers for recovering lands fertility (Table 2) [4,8, 16, 17, 18]. Dry saponite and kaoline clays can also be applied as construction material or sorbent [7, 16, 19, 20].

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

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

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Поступила в редакцию 19.05.2021
Принята к опубликованию 19.11.2021

Received 19.05.2021
Accepted 19.11.2021