COMPLEX PROCESSING OF SAPONITE WASTE OF A DIAMOND-MINING ENTERPRISE

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ABSTRACT. The article is devoted to the problem of enrichment of saponite diamond-bearing ore and the problem of utilisation of the enrichment waste. The characteristics of the deposit and the shortcomings of the existing diamond mining method are given, a review of the literature on this issue is made. The material balance of production is shown in the article, the mineralogical composition of the saponite effluent is given and the main tasks for creating a closed water circulation system are put forward on the basis of material balance. The proposed scheme is constructed as follows: extraction of ore → ore enrichment → production of concentrate → waste while enrichment of ore → pure water produced by diluting and thickening the waste with calcium aluminosilicate reagent → obtaining calcium aluminosilicate reagent from condensed waste. The article describes the mineral composition of saponite pulp after the process of enrichment of diamond-bearing ore investigated by X-ray fluorescent method. Research is presented on the deposition of saponite pulp with different reagents (aluminium sulphate, oxychloride, polyacrylamide flocculant) compared with calcium aluminosilicate. The scheme of the closed water circulation of the processing plant and utilisation of the condensed product is presented taking into account the chemical composition.

Keywords: diamond ore, saponite, closed cycle of water circulation

КОМПЛЕКСНА ОБРАБОТКА НА САПОНИТНИ ОТПАДЪЦИ В ПРЕДПРИЯТИЕ ЗА ДОБИВ НА ДИАМАНТИ

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РЕЗЮМЕ. Статията е посветена на проблема за обогатяването на сапонитната диамантоносна руда и проблема с оползотворяването на отпадъците от обогатяването. Дадени са характеристиките на находището и недостатъците на съществуващия метод за добив на диаманти, направен е преглед на литературата по този въпрос. В статията е показан материалният баланс на производството, даден е минералният състав на сапонитните отпадъчни води и са изведени основните задачи за създаване на затворена циркулационна система въз основа на материалния баланс. Предложената схема е изградена по следния начин: извличане на руда → обогатяване на руда → производство на концентрат → отпадъци при обогатяване на руда → чиста вода, получена чрез разреждане и сгъстяване на отпадъците с калциев алумосиликатен реагент → получаване на калциев алумосиликатен реагент от кондензирани отпадъци. В статията се описва минералният състав на сапонитната пулпа след обогатяването на диамантносната руда, изследван чрез рентгенов флуоресцентен метод. Представени са изследвания за отлагането на сапонитна пулпа с различни реагенти (алуминиев сулфат, оксихлорид, полиакриламиден флокулант) в сравнение с калциевия алумосиликат. Представена е схемата на затворената циркулация на водата в преработвателното предприятие и използването на кондензирания продукт, като се взема предвид химичният състав.

Ключови думи: диамантена руда, сапонит, затворен цикъл на циркулация на водата

Introduction

The assessment of the ecological status and well-being of natural systems and their effective protection and appropriate use are among the major problems of social and economic importance.

The diamond deposit named after M. V. Lomonosov is the main object in the development of the diamond mining industry in the European North of Russia. Its development will be accompanied by a violation of the lithological base of the landscape, changes in the hydrological characteristics of the watercourses in the area of the deposit, and impacts on groundwater. In general, the main factors affecting the components of the environment are as follows (Groshev, 2003):

- Dust emissions from open mine workings that pollute the atmospheric air and form anthropogenic anomalies that are contrasting and really significant (Groshev V.A. 2003.);

- Deflation and erosion of tailing dumps of concentrating factories, which form intensive scattering streams in water systems and relatively local technogenic areas in soils (Groshev, 2003);

- Drainage from underground mine workings and quarries, which form intensive and extended scattering streams in water systems (Groshev, 2003);

- Effluents from processing plants after treatment facilities, polluting water systems (Groshev, 2003).

It is very important to note here that, in view of the existing problems in the environment, most countries in the world are moving to a completely different principle of handling resources and generated waste, including from mining.

This is the 3R principle:

- reduce is the reduction of waste generation;
- reuse is reutilisation;
- recycle is processing.

Due to increased attention to the scarcity of natural resources and the problem of waste pollution over the past few years, interest in the cyclical economy has grown significantly.

The Russian enterprise PJSC “Severalmaz“ has one of the main important unresolved environmental problems and this is the absence of highly efficient closed water that reduces the efficiency of diamond-bearing ore enrichment process.

Literature review

At the deposit named after M. V. Lomonosov, the kimberlites are mainly with a predominance of saponite in their composition (more than 70%), the deposit is located in the central part of the White Sea-Kuloi plateau in the bend of the Zolotitsa River, which flows into the White Sea.

The deposit is represented by six kimberlite pipes: “Pomorskaya“,“Arkhangelskaya“,“Karpinsky-1“,“Karpinsky-2“, “Pionerskaya“ and “Lomonosov“.

The technology of ore dressing created by Russian specialists at enrichment plants is at the level of world standards, and exceeds the world level by individual technical processes and equipment.

At the same time, the main lack of enrichment in diamond mining in the Arkhangelsk diamond province (ADP) is the lack of understanding of the material costs to eliminate the shortcomings of the existing method of enrichment and disposal of waste at PJSC “Severalmaz”. According to the material balance, in order to obtain 0.42 g of diamonds from the pipes Arkhangelsk and Karpinsky-1, 4 tons of ore need to be processed and this drawback is the rationale for the need for environmental thoroughness of this issue.

In 2002, Vaganov, Golubev and Minorin created a methodical guide to assess the forecast resources of diamonds, precious, and non-ferrous metals. The manual examines the methodological basis and techniques for identifying promising areas and estimating the forecasted diamond resources. The classifications of the main types of diamond deposits are performed and given in the paper. In addition, geological and industrial quantitative models of diamond deposits are described, the characteristics of which can be used to calculate the material balance of industrial facilities (Vaganov et al., 2002).

According to their data, to date, 97% of the mined diamonds in Russia come from the indigenous deposits, and they account for the bulk of the balance reserves (94.7%).

Increase in production at the diamond deposit named after M.V. Lomonosov entails a number of problems, one of which is the utilisation of a large volume of tailings of clay rock. The fact is that a distinctive feature of this diamond deposit is the high content of di- and trioctahedral clay minerals of the smectite group in the kimberlite rock, which is characteristic of the rocks of the alkaline-ultrabasic composition of the Arkhangelsk diamondiferous province. This phenomenon is called claying of kimberlites (Oblitsov, Rogalyov, 2012).

In the course of technological processes using water at the concentrator, waste (sludge) with a large concentration of clay particles (mainly saponite mineral) is formed.

A significant increase in tailing volumes, associated with increased water content of smectites, leads to an increase in the size of the tailing dump, which manifests itself both in the dam's build-up and in the occupation of new areas. During the first two years of operation (from 2005 to 2007) impounding was carried out in the tailings pond of the first stage with a mark of the pier of the pioneer dam of 116 m. In December 2007, the second stage of the dam with a mark of the crest of 120 m was put into operation, providing the work of the tailing dump in 2011. The annual volume of ore processing in 2009 amounted to 1050 thousand tons. The design density of the particles for calculating the volume of stacked tailings is assumed to be 2.7 g/cm^3. In parallel to the development of the field, the volume of tailings to be stored increases, and the required capacity for filling the tailing pond accordingly grows. It seems natural that at such volumes of tailings it is necessary to search for ways of utilising their most interesting part, the smectite-containing rock (Oblitsov, Rogalyov, 2012).

According to the material balance, the main drawback of the existing method of dressing saponite ores in the Arkhangelsk region is that practically the entire volume of crushed ore must be passed through the separation aquatic tailing system when processing large volumes of the rock mass.

The further development of deposits will lead to a significant increase in the volume of pulp (water + saponite) in sludge reservoirs. Due to the high dispersity and the developed diffuse layer, the saponite particles are highly resistant to water.

In addition, the presence of microaggregates of clay minerals along with sand grains, which determine their physical and mechanical properties, and the presence of saponite in the sediment deposits, negatively affect the stability of tailing dams (Oblitsov, Rogalyov, 2012).

The disadvantages of thickening saponite-containing suspension by means ofhigh-compression thickeners are: high capital costs, high consumption of reagents, high power consumption and a number of other shortcomings. The use of domestic and foreign coagulants and flocculants to precipitate suspensions has not yet yielded an effective result because of their high ion exchange capacity, and the facts about re-stabilisation of the suspension after addition of coagulants have been revealed.

Alekseev was engaged in the processing of aluminosilicate raw materials, ion exchange in a clay suspension, and complex processing of apatite-nepheline ores on the basis of closed technological schemes.

Dmitrenko investigated the effect of saponite treatment with hydrochloric acid on its acid-base and sorption properties.

Pashkevich developed a method for sludge processing - a method for increasing tailing dumps.

Tutygin studied the influence of the nature of the electrolyte onthe process of coagulation of subunit-containing clay minerals.

Sizyakov was engaged in the modernisation of the technology of complex processing of Kola nepheline concentrates at the Pikalevo alumina refinery plant.

Nevzorov investigated the properties of tail sediments in the enrichment of kimberlite ore.

However, the work of the above-mentioned authors does not touch upon the calculation of the effective rate of deposition of saponite and its compaction in the sludge accumulator of the diamond mining concentrator.

In order to achieve the set goals, it is necessary to develop and implement a set of measures in the full processing of saponite-bearing diamond wastes, as well as to encourage buyers to purchase building materials and other products made from man-made raw materials, including from waste (utilisation) or reclamation of disturbed lands in quarries.

Methods and materials

Lomonosov Processing Plantmaterial balance calculation

The Lomonosov Ore Mining and Processing Plant is the No. 1 processing plant with a processing capacity of 4 million tons of ore per year, which provides annual production of about 2.2 million carats of diamonds.

1 carat of diamond weighs 0.2 grams 2,200,000, 0.2 = 440.000 g diamonds = 440 kg of diamonds.

Processing 1 million tons of ore per year, 440 kg of diamonds can be obtained.

1. In 2016, 2012.7 thousand carats we reproduced, 402,540 grams = 402.54 kg.

2. The content of diamonds in the ores and sands in the Arkhangelsk and Karpinsky tubes is 2.1 car/ton or 0.2 · 2.1 = 0.42 g/t.

3. Calculation of processed ore for 2016 402,540 g: 0.42 g/ton of ore = 958428.57 t/year.

4. Calculation of the percentage of diamonds in the parent ore

5. 1 ton of ore contains 0.42 g of diamonds, that is 1,000,000 g of ore contain 0.42 g of diamonds, which is:

(0.42 · 100): 1000000 = 42: 1000000 = 0.000042%

Thus, 99.000058% is the saponite mineral0.000042% is the diamond mineral.

According to the data of the material balance, the main drawback of the existing method of saponite ore dressing is that when processing large volumes of rock mass, practically the entire volume of crushed ore (from 1 ton of ore 0.42-1.2 grams of diamond is extracted) is stored in tailing dumps consisting mainly of saponite mineral.

The mineralogical and crystal chemical characteristics of saponite create large technological obstacles for solving the problem of organising a closed water scheme at the processing enterprise of PJSC “Severalmaz”.

It is known that water can be in three different states in nature: gaseous, liquid or solid.

As an example in Figure 1, the simplest state diagram of water dioxide describes the properties that determine the performance of the water-saponite diamond ore (crystalline solid) process cycle.

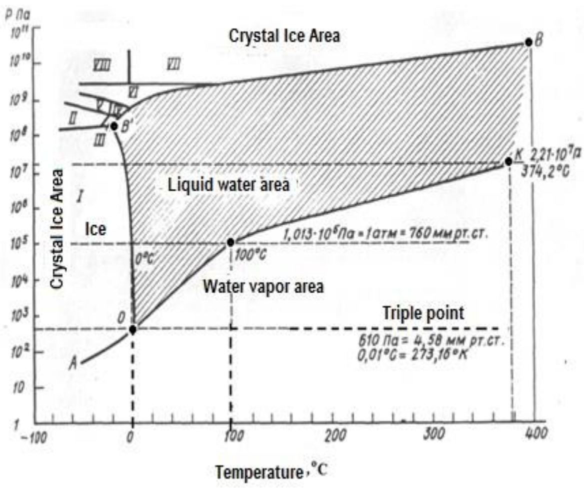

Fig. 1. Single component system - water

The combination of substances or bodies is meant by the physico-chemical system of water (Figure 1) used in the technology of processing diamond ores that are in interaction and separated from the external environment by real or imaginary boundaries.

In this case, water is used as the main technological reagent, which is repeatedly used in the water circulation system in the circulating system. The chemical-technological process of grinding the diamond-saponite ore is carried out in aqueous solutions; therefore, it is advisable to start the study of the equilibrium processes with an analysis of the water state diagram (Fig. 1).

The operating time of the processing plant is presented in Figure 2 by months in 2017. The graph was built depending on the time of four different climatic conditions: winter – spring – summer – autumn with the use of a one-component water chart presented in Figure 1 and the temperature climate conditions corresponding to the Arkhangelsk region for the entire period of 2017. The graph shows that from April to October, for the concentrator, the plant is in a liquid state and with a lower content of suspended substances, and from November to April, everything below the zero line is the formation of ice on the tailings and the natural thickening of liquid water, slurry, into the pulp with a high content of suspended substances.

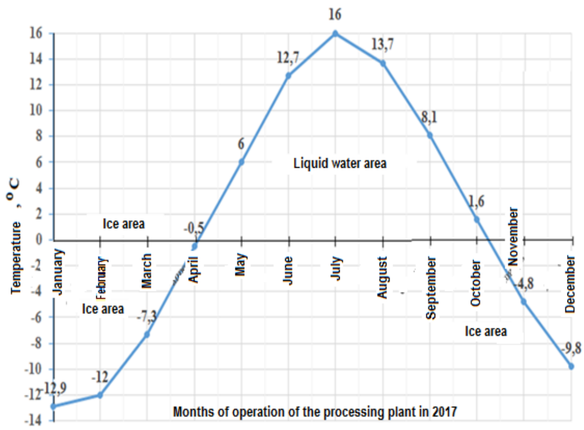

Fig. 2. Influence of climatic parameters on the implementation of the technological process of the concentration plant

These shortcomings can lead to a decrease in the extraction of diamonds in technological processes of heavy medium and X-ray luminescent operations, and to the need of searching of clean water consumption and improvement of the environmental safety of the enterprise.

Research is needed on the mineral and granulometric composition of the pulp after the enrichment of ore at the tailings and the water after the tailings when the water enters the enrichment (circulating water).

Study of the mineral composition of the pulp after the enrichment process

The clay mineral saponiteforms a finely dispersed clay suspension with a concentration of saponite in the circulating water of 5 ... 200 g/d^3, colloidal particles with a particle size of 1...3 microns. The deposition of the clay mineral saponite ends after 1.5 years without treatment with cohulants and flocculants.

Because of the properties of the saponite mineral, which has the characteristic not only to «swell», but also to disperse and stabilise, forming a non-precipitating fine-grained gel-like structure bonded with Ca and Mg ions (~20%), the tailings sites allocated by the project increase (Feklichev, 1989).

The pure mineral sapponite-stevensite has the mineralogical structural formula $Na_xMg_3(Al_xSi_{4-x}O_{10})(OH_2)\cdot 4H_2O$, a monoclinic syngony, density of 2 g/cm^3, Mohs hardness 2 (refined data: density 2,3-2,5 g/cm^3, Mohs hardness 2.5) (Churkina, Lopatin, 2017).

The physical and chemical characteristics of the liquid phase of the samples under study are almost identical and characterised by slightly alkaline pH values, low oxidation-reduction potential, and a small amount of mineralisation.

According to the “Severalmaz” company, it is not difficult to obtain the required quality discharge (500 mg/l), but it is impossible to obtain a thickened product with a density of 70% by weight on thickeners.

The increased content of clay particles in the circulating water to enrich the ore leads to scaling the scheme or attracting additional water from other circulating water for pro sources.

The soil composition is heterogeneous and varies in the depth of occurrence. In the upper layers of its composition there is a mixture of sandy loam (up to 30%), saponite (up to 60%), and vermiculite (up to 10%). With the development in depth in the ground, the content of saponite increases (up to 90%) and, accordingly, the content of sand loam (up to 5%) and vermiculite (up to 5%) decreases.

The mineral composition is shown in Figure 3 and Table 1.

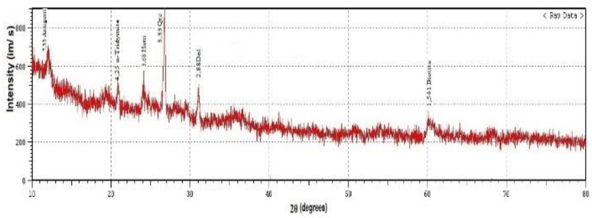

Fig. 3. The mineral composition of the pulp after the enrichment process

The mineral composition is mainly represented by heavy minerals (the density of the mineral is higher than the density of quartz and is considered a heavy fraction) such as hematite, dolomite, biotite, quartz, antigorite, and tridymite (Feklichev, 1989).

Table 1. *Oxide composition*

Number	Oxide	Content, mass%
1	SiO_2	55.9
2	Al_2O_3	4.01
3	MgO	17.45
4	Fe_2O_3	13.12
5	CaO	4.42
6	K_2O	2.09
7	TiO_2	0.92
8	MnO	0.23
9	Na_2O	0.54
10	P_2O_5	0.63

The chemical composition of the sample shows that quartz-containing, iron-containing and magnesium-containing substances, which are distributed over the entire surface of the tailing pond, are the ones that mainly enter the environment.

Investigation of granulometry of saponite suspension

According to the technological scheme, the system of recycled water supply is organised as follows: concentrating plant - tailing dump - concentrating mill. Reserved water after the tailings is fed to the grinding mill, then fed to the classifiers. An express universal laser particle size distribution analyser Horiba LA-950 was used to study the granulometric composition of suspensions, which makes it possible to determine the granulometric composition of the discharge from the classifiers after the saponite ore dressing process (Fig. 4).

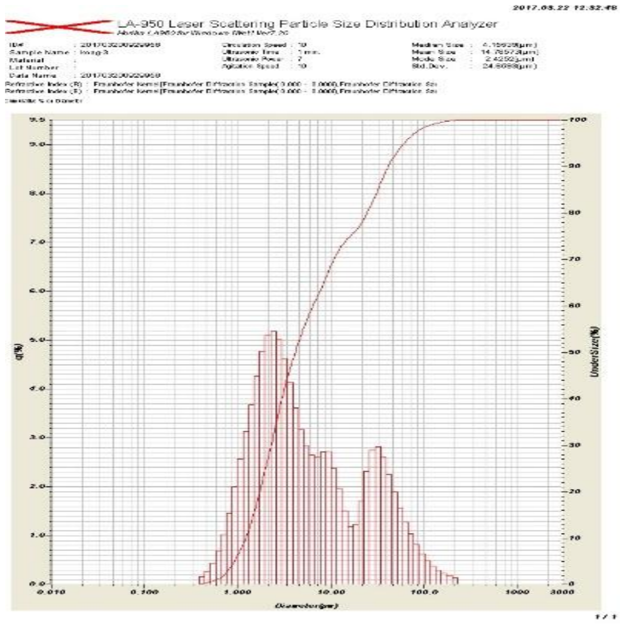

Fig. 4. Granulometric composition of the discharge from the classifier

According to the results of the study, it was found out that the minimum particle size of saponite ore is 0.011 μm in this case, the deposition rate decreases sharply and the Brownian displacement increases. Saponite ore particles are highly dispersed and practically do not precipitate, but due to the Brownian motion they move in any direction.

Let's calculate the deposition rate for a given particle size by the formula:

$$w_{pr} = \frac{d^2(\rho-\rho_d)\cdot g}{18\mu_d} \quad (1)$$

The deposition rate for such a particle size is $1.02 \cdot 10^{-14}$, this suggests that the saponite pulp is also a colloidal solution and the particles do not settle under the action of gravity. In laboratory conditions, the precipitation of saponite ore without the addition of coagulants and flocculants is about 1 mm per day or about 0.4 m per year.

Synthesis of inorganic precipitant

To effectively deposit with the St. Petersburg Mining University, a calcium aluminosilicate (CAS) reagent was developed.

The synthesis of the calcium aluminosilicate reagent is carried out in accordance with the diagram of CaO-Al_2O_3-SiO_2(Figure 5) and temperature fields of crystallisation of tricalcium silicate and tricalcium aluminate (Alekseev, Alekseev, 2007).

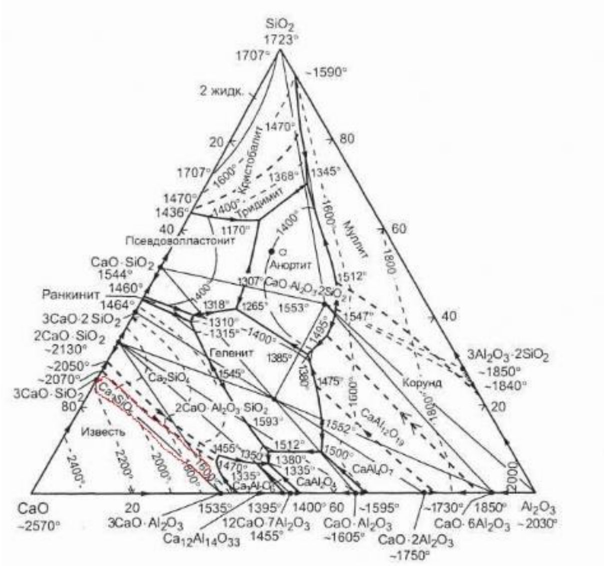

Fig. 5. Diagram of the system state

Taking into account this circumstance, a method of obtaining an active sorbent in the process of wastewater treatment by the decomposition of the initial silicate reagent is proposed.

This property of calcium silicates is associated with the structural features of crystalline compounds. Synthesis of calcium silicates of a given composition depending on the initial ratio of CaO: SiO_2 in the charge is recommended in the following temperature ranges:

$$xCaO + ySiO_2 \xrightarrow{773\text{–}1372\ K} 2CaO{\cdot}SiO_2 \xrightarrow{1273\text{–}1473\ K}$$
$$3CaO{\cdot}2SiO_2 \xrightarrow{1373\text{–}1573\ K} CaO{\cdot}SiO_2 \xrightarrow{>1523\ K} 2CaO{\cdot}SiO_2$$

This composition of the obtained calcium aluminium silicate inorganic coagulant is determined by the initial chemical composition of the raw mix, which varies with different contents of the main minerals of tricalcium silicate, dicalcium silicate, tricalcium aluminate, and quaternary alumoferrite (Alekseev, 1982).

The composition of the composite coagulant is a granulated mixture of self-separating slag based on calcium and magnesium silicates and hydroaluminosilicates from a number of clays and hydromica mica, and is thermally treated in the 850-900 °C temperature range.

The process of purification of recycled water with the content of clay saponite material is as follows:

$$Ca_2SiO_4 + 2H_2O = 2Ca^{2+}_{aq} + H_2SiO^{2-}_{4,\,aq} + 2OH^-_{aq}$$

When contacting calcium silicates with water, the primary act is its chemical interaction with the formation of ions in the solution.

Calcium hydrosilicate has in its structure hydroxyl groups, capable of cationic and anionic ion exchange (Alekseev, 1985).

The substitution reaction OH- group into cations in an alkaline medium is composed of successive stages:

adsorption: $Si\text{-}OH + Me\,(OH)^{(x-1)+} = Si\text{-}OH|HO\,Me^{(x-1)+}$;

condensation: $Si\text{-}O\text{-}Ca + An^- = Si\text{-}O\text{-}CaAn$.

Since charged particles of the dispersed phase are present in the saponite suspension, the addition of calcium aluminium silicate inorganic coagulant is effective. The use of coagulants with increased basicity will help ensure the production of large aggregates with a high deposition rate and large flakes.

The destruction of the double electron layer of the colloidal saponite particle is achieved due to the chemical activity of the inorganic coagulant.

Experiments were carried out on the deposition of suspended solids in the circulating water with a content of 30-40 g/litre with aluminium sulphate, oxychloride, polyacrylamide flocculant and developed coagulant (Fig. 6).

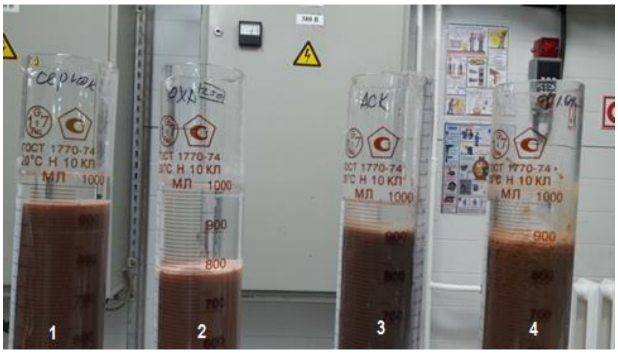

Fig. 6. The results on the deposition of saponite pulp, solid content 25-30 g/l after 60 minutes

Experiments show that compared to traditional coagulants, calcium aluminosilicate reagent thickens saponite pulp and purifies water to enrich the ore.

The results on the removal of suspended solids are presented in Table 2.

Table 2. *The results of experiments on the thickening and purification of recycled water*

Number	Coagulant	Clean water level, cm
1	7% solution of aluminium sulphate	3
2	9% aluminium oxychloride solution	11
3	Calcium Aluminosilicate Reagent	3
4	Flocculant	7

The chemical composition of the condensed part allows the creation of waste-free production according to the diagram CaO-Al_2O_3-SiO_2 and obtaining a coagulant for sedimentation and thickening in the territory of the mining and processing plant. (Table 3).

Table 3. *The chemical composition of the condensed product*

Number	Oxide	Content, mass%
1	SiO_2	28.86
2	Al_2O_3	6.47
3	MgO	3.83
4	Fe_2O_3	5.8
5	CaO	52.89
6	K_2O	0.44
7	TiO_2	0.44
8	Na_2O	0.26
9	P_2O_5	0.07

The hazard class of sediment is 4 after the thickening process with aluminum sulphate, oxychloride, polyacrylamide flocculant. Substances in the sediment after coagulation lead to certain violations of the ecological system, but it is able to recover in about 3 years.

Conclusion

Based on there search, the following conclusions can be drawn:

1. Deposition of the saponite suspension due to its density is impossible without prior dilution.

2. Prior to using traditional coagulants for precipitation (aluminum sulphate), the chemical composition of saponite ore has been studied throughout the process cycle, and their size is taken into account when depositing suspended particles.

3. Based on the granulometric and chemical composition of the ore, and the suspension, a coagulant with specified physical and chemical properties was synthesised.

4. Due to the astringent properties of the synthesised inorganic mineral precipitator, the load on the walls of the dam reduces, which prevents it from further destruction and leads to a decrease in the areas occupied by the tailing dump.

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