Article

Recycling prospects for saponite-containing water at diamond processing plants in Arkhangelsk region, Russia

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Abstract: The analysis of methods of cleaning and processing of saponite-bearing technogenic waters of diamond mining enterprises of the Arkhangelsk region is carried out. The perspective of the electrochemical separation method for extracting saponite from man-caused waters, providing a targeted change in its structural-texture, physico-chemical and mechanical properties, is shown. The possible directions of realization of saponite and products of its modification in various branches of industry are considered.

Keywords: saponite-containing waters, diamond processing plants, cryogenic treatment, electrochemical separation, saponite product applications.

1. Introduction

Developing of Lomonosov deposit in the Archangelsk diamond province, currently including 10 kimberlite pipes, to the depth allowing for quarry operations will require extracting of about 300 mln t of diamond-bearing ore and barren rock [1, 2]. The rock of the deposit pipes is almost entirely displaced by clay minerals, predominantly saponite, amounting to 90% in the vent facies [1].

Saponite, belonging to smectite group minerals, is characterized by high physico-chemical activity and low density in aqueous media owing to its tendency to hydrate. When in an aqueous medium, saponite disperses forming a suspension, which creates difficulties both in operating of tailing dumps and managing the closed water circulation at processing plants.

In this regard, search activity, justification and effective process development techniques for treatment and reprocessing saponite-containing man-caused waters from the diamond processing plants have become the challenging objectives. They are determined by the necessity of developing a qualitative water circulating system. All that will ensure both the advanced diamond recovery and environmental mitigation, including byproduct manufacturing of target-oriented saponite-containing marketable products, which are characterized by a vast scope of application in various industrial fields.

2. Structure and properties of saponite

These properties are valued by the industry are described in detail in numerous textbooks, reference books and professional papers. The mineral saponite with the formula according to IMA list [3] $(Ca,Na)_{0.3}(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2{\cdot}4H_2O$ is one of the most common members of the smectite group along with montmorillonite and nontronite [4].

Saponite like any smectite has the unique physical and chemical properties which are of scientific interest: high cation exchange capacity, swelling and rheological properties, hydration and dehydration, high plasticity, bonding capacity and their ability to react with inorganic and organic reagents [5]. These properties are the results of:

-the layered nature of the crystal structure with the presence of weakly bound cations;

-wide range of chemical composition variations;

-extremely small particle size and flat form and the correspondingly large specific surface area.

2.1. Crystal structure

The basic structure of smectite group minerals has been defined (well known) and illustrated in many publications, one representation of which is given in Figure. Smectites are three-layer minerals. This three-layer package has two silica tetrahedral sheets joined to a central octahedral sheet. That is the basis for classifying the smectite structures as 2:1 phyllosilicates. Due to substitutions in the tetrahedral or the octahedral sheet, or to the existence of vacancies in the octahedral sheetthe surface of the three-layer package has a negative charge which creates a charge imbalance.

According to the Nomenclature Committee of AIPEA [6] the layer charge of smectites varies from 0.2 to 0.6 electrons per half unit cell (e/h.u.c.). The layer charge is balanced by the interlayer cations Na, Ca, K, Mg, Fe, which are weakly bounding и exchangeable. The interlayer space contains water molecules. The number of molecules is not constant and can increase depending on the grade of interlayer cation, causing swelling of mineral particle. The interlayer space also contains water molecules in varying quantities which may increase depending on the interlayer cation kind and cause the layers to distend and the mineral particles to swell. Indeed it has been shown that layer charge is related to the colloidal properties of smectites such as swelling; charge heterogeneity, which includes both charge magnitude and charge localization is also related to these properties [7].

Saponite belongs to the trioctahedral series of minerals of the smectite group. Notwithstanding both the wide occurrence of saponite in nature and extensive previous study, the saponite structure has not been determined yet. The authors are of the opinion that the reason for it the absence of material applicable for single-crystal investigations.

2.2. Chemical composition and properties

The chemical composition of naturally occurring saponite is highly variable due to common Fe^{2+}, Fe^{3+} and Al^{3+} substitutions for Mg^{2+} in the octahedral sheet, which are accompanied by partial Al^{3+} and Fe^{3+} substitutions for Si^{4+} in the tetrahedral sheet [8, 9]. Thus, saponite from the Arkhangelsk kimberlite province contains 5.09% Al_2O_3, 3.14% Fe_2O_3 and 2.56% FeO [10], their crystal-chemical formulae, calculated on 22 charges, is the following: $(Ca_{0.1},Na_{0.1},K_{0.1})0.3(Mg_{2.6},Fe^{2+}_{0.1},Fe^{3+}_{0.2})2.9(Si_{3.6},Al_{0.4})_4O_{10}(OH)\ 2.8H_2O$.

Saponite is different from the other smectites as part of the negative tetrahedral charge is balanced by substitution of octahedral Mg^{2+} by trivalent cations, Al^{3+} or Fe^{3+}, i.e. the octahedral sheet can to bears a positive charge. However, the tetrahedral charge, due to substitution of Si4+ by Al^{3+} is much greater and outbalances any possible positive octahedral charge [11].

The mineral's properties are drastically affected by substitutions, their quantity and cation kind. Moreover, the iron present in the mineral as an isomorphous impurity may vary its oxidation degree in response to certain conditions, which leads to changing of the mineral's properties.

Fairly often, the composition of natural saponite is heterogeneous and, similar to the rest of smektites and other layered silicates, may contain fragments of other layered silicates, up to forming of mixed-layer structures. Saponite is commonly found in association with montmorillonite or talc [12-14]. According to the authors of [14], mixed-layered aggregates of this type have a greater surface area of up to 283 m²/g, and a high concentration of mesopores comparable with quality sorbents.

In order to obtain a chemically and phase-wise homogeneous composition, saponite is synthesized to make controllable its properties, primarily the surface charge distribution [15-17]. One of the recent examples is the use of synthetic saponites as hydro processing catalyst components in refining gas described in a patent by Chevron Corp [18]. The growing interest in synthesis methods in the past decade has been generated by competitive advantages of synthetic saponite, i.e. its mesoporosity, controllable acidic and basic properties and stability [19, 20].

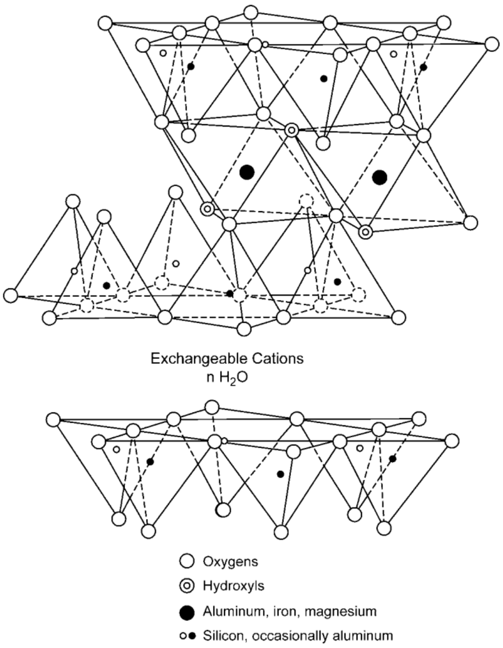

Figure. Diagrammatic sketch of the structure of smectites [21]

Being weakly bonded with the structure packages, the interlayer cations Na, Ca, K, Mg can be easily removed from it, or substituted for other cations, without destroying the three-layer package.

Traditionally, the cations are removed via acid treatment. Researching in the area of acidic modification of saponite is also provoked by the possibility of altering the coordination of O-layer cations to the extent of obtaining an individual silicate layer with a super-high surface area [22-25].

In the case of trioctahedral saponite, the conditions required for almost complete removal of the octahedral layer with resulting surface increase of up to 300 m²/g and microporosity are rather mild [26].

There is no evidence of studies of the sorption mechanism on natural saponite, but some results have been reported on the sorption of saponite-containing products [27, 28].

Regarding the thermal properties, the Arkhangelsk saponite is close to smektite [10]. Differences can be observed in the area of the second endothermic effect, which is attributable to occupancy of the octahedral layer.

The unique property of smektite crystals consisting in increasing or decreasing of the number of water molecules between its layers from 0 to 4 layers/ , causing the basal distance to increase from 10 to 22 Å, has been widely researched [29 et al.]. Swelling occurs in polar organic solvents as well. The layer charge effect produced on swelling has been fairly well researched [7]. But no studies on saponite swelling have been reported yet.

Studies of smektite-water suspensions represent a by far greater challenge. Smektites form fine crystals usually of the size 0.5 µm. When in small concentrations, the suspensions possess Newtonian properties created by hydrodynamic forces, whereas at increasing concentrations the inter-particle interactions trigger non-Newtonian behavior. The variety of interactions caused by electrostatic and electrokinetic characteristics is of great current interest (see, for instance, [5]).

Saponite is the least studied among the smektites although it is known that in aqueous suspensions it also demonstrates high, and ambiguous, electrokinetic potential values [30].

3. Techniques of recycled water clarification at the processing plants and receiving thickened saponite product

The methods currently used to accelerate the precipitation of saponite particles and sediment compacting include reagent and cryogenic treatment, bubbling with carbon dioxide, and exposing to acoustic, electric and magnetic fields [1, 31-34].

The authors of [31, 32] have proposed carbonizing to accelerate clearing of the slurry tailings and circulating water at the processing plant of the Lomonosov GOK (PP LGOK), Severalmaz JSC. The method incorporates interaction of pure carbon dioxide with saponite-containing water yielding carbonic acid further interacting with calcium and magnesium compounds, contained in saponite, and forming water-soluble hydrocarbonates $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$. According to the authors, transferring of calcium and magnesium ions to solution promotes the destruction of the colloid structure with evolution of pure water.

Pilot testing of the technology of carbonization of saponite-containing slurry and circulating water of the PP LGOK has demonstrated the possibility of obtaining clarified water containing less than 0.5 mg/dm^{3}of solids. However, the initial solid content in the experiments did not exceed 110 g/dm^3 and it achieved 158 g/dm^3 in the thickened slurry after a 4-day settling [31, 32], whereas natural settling of dumped water samples with initial solid contents of 50-100 g/dm^3 takes 7 and more days for the slurry to separate under the action of gravity to a clarified part with a solid content of less than 5 g/dm^3 and a precipitate containing up to 200 g/dm^3 of solids [7, 8].

In 2013, S.A. Bakharev conducted a commercial testing of a plant of complex acoustic impact on circulating water (CAIP-CW) at the PP LGOK; the geometric size of the pond was 307×37×3.7 m [33]. Prior to commercial testing, the circulating water was highly turbid both in the lower horizon of the pond, i.e. the settling area, and at the outlet of discharge pipes. In the middle horizon (0.4 м), the slime particles concentration was about 3.31 g/dm^3; in the upper horizon (0.2 м) it was 1.26 g/dm^3. During the commercial testing of CAIP-CW the turbidity of circulating water diminished considerably compared to gravity clarification: the slime particles concentrations in the middle and upper horizons became, respectively, 0.32 g/dm^3, and 0.16 g/dm^3.

The results of acoustic thickening of saponite-containing precipitate at CAIP-CW are of practical importance because saponite in this case can be extracted and recycled. Using the reagent-free (acoustic) thickening of the saponite-containing precipitate, S.A. Bakharev discovered that the concentration of particles in the precipitate can be increased from 89 to 743-790 g/dm^3. The precipitate structure reminded that of modeling clay.

However, the report [33] does not describe the experimental conditions of saponite-containing precipitate thickening. Moreover, the high values of the solid-phase contents in the resulting saponite-containing products of 743-790 g/dm^3 (at a power consumption of 0.5 Wt/m^3 of the slurry) are uncharacteristic of the hygroscopic saponite, which may signify high quartz, dolomite and other mineral contents in the samples. Unfortunately, the author does not disclose the results of mineralogical analyses of the precipitates. The data on sieve composition of the initial and obtained products, presented by the author [33], also look questionable due to the small size of pure saponite (less than 7 μm) and, which is worse, of the obtained precipitates because at a content of 400 g/dm^3 of the highly hygroscopic saponite, the suspension becomes viscous and non-flowing. Therefore, the sieve analysis of precipitates with saponite contents of 743-790 g/dm^3 might have been possible only after repeat diluting it with water and vigorous stirring, which must have resulted in destroying of the floccules that are supposed to be formed by S.A. Bakharev.

The experiments of the authors of [1, 34] have proved the effectiveness of unconventional techniques, including the cryogenic treatment, in clarification of circulating water at the diamond-treatment plants. Cryogenic treatment incorporates freezing and defrosting of a saponite suspension, which destroys the diffusion layer of the particles, preventing the converging of the particles and forming a precipitate, thus initiating the saponite sediment genesis. The essential factor in this case is the frosting-defrosting regime. At a slow rate, allowing for draining of the separating moisture, the precipitate is the densest; the density of precipitate carcass achieves 0.74 g/dm^3 exceeding that of initial suspension more than 4 fold. Besides, the resulting precipitate, as believed by the author of work [1], acquires the ability to further diagenetic alterations because increasing of gravity loads promotes the growth of the number and area of contacts between the particles strengthening the precipitate structure.

The efficiency of the reagent method for thickening of saponite precipitate was experimentally tested by F.S. Karpenko [1] using 18 various flocculants, inorganic coagulating agents $AlCl_3$ and Al_2SO_4, and also the effect of electric and magnetic fields on the process of precipitating and thickening of the forming saponite precipitate. It was shown that using reagents permits to increase the precipitation rate several hundred-fold failing, however, to increase the precipitate density or diminish its porosity so that it is practically indistinguishable from the precipitate formed under natural conditions. What is more, the precipitate in the experiments is unstable; if stirred, it forms a water suspension. It should be remembered that the consumptions of flocculants and coagulating agents are considerable (up to 180 g/t and up to 150 g/t, respectively). The most effective reagents proved to be anionic flocculants of the series Praestol No2540 and Magnafloc 156, ensuring for a saponite suspension the precipitation rate of 30 cm/h and the maximum carcass density of 0.24 g/cm^3.

Settling and thickening of the saponite precipitate were not affected by either the electric or magnetic fields [1].

All this raises doubts regarding the effectiveness of reagent treatment, bubbling with carbon dioxide or acoustic impact at high contents (over 50-100 g/dm^3) of fine slimes. It should be also noted that neither of the aforementioned methods allows for targeted alteration of the precipitate mineral composition.

For recovering of saponite from process water of diamond plants, the authors of [35-39] have developed and tested a reagent-free electrochemical method and equipment for its implementation – electrochemical separators. The apparatus realize the process of electrophoretic extraction of the saponite-containing product at the anode and osmic evolution of water at the cathode. The obtained concentrate (electrochemically modified saponite) is characterized by high concentrations of the solid phase (up to 620 g in 1 dm^3 of suspension) and high contents (more than 74.5%) of saponite and montmorillonite at low quartz and dolomite contents (less than 12% and 5%, respectively) compared to the initial saponite-containing product (60-68%, 14-20%, and 6-10%, respectively). The product is suitable for the production of quality building materials and sorbents owing to its chemical composition of modified saponite-containing product (SiO_2, Al_2O_3, CaO, Fe_2O_3, FeO, TiO_2, Na_2O, K_2O, SO_3 etc. as the main components), denser packing, high content of smectite group minerals, and the presence of exchange cations [40].

It is evident that the most effective techniques of producing and thickening of saponite precipitate are cryogenic treatment and electrochemical separation. However, the former can be applied only in winter and has the drawback of the likelihood of repeat dispersing of defrosted saponite-containing product by melting water.

4. Range of saponite product applications

Saponite has been actively researched in recent years [41-93] as a valuable product with unique properties and a wide range of application including the chemical, food and consumer goods industries, agriculture, medicine and pharmacology, foundry practices, metallurgy, and construction.

4.1. Application of saponite in agriculture

Much of the research has been devoted to utilizing of saponite in agriculture, livestock husbandry, and veterinary as an active or suspending agent and mineral additive to fodder [41-47].

The authors of [43, 44, 47] have developed a compound for pre-sowing treatment of winter wheat incorporating the raxil pesticide – a 2 % wettable powder and saponite, i.e. saponite-based thixotropic water suspensions for plant protection, and a method of improving the agrochemical performance of ammonium saltpeter whereby saponite as a mineral adsorbent is added in 2% per mass of the ready product.

Inventions [45, 46] present the processes of manufacture of cattle fodder admixed with saponite, and also a KANIR-3 amide-concentration mineral additive based on grain offal and carbamide admixed with saponite, potato starch and sodium sulfate.

The standards listed in works [41, 42] establish the general technical requirements to the quality of saponite flour as an integral-action ameliorant – a magnesium-containing fertilizer produced from saponite clay with high magnesium contents (up to 12%) [41], and also to the quality of saponite-containing polymineral preparations used as additives to broiler-chicks fodder [42].

4.2. Application of saponite in cosmetic industry

Recent years have seen introducing saponite in manufacture of cosmetics, as ingredient of cosmetics and preparations, and in manufacture of hygiene, deterging, and bleaching materials [48-56].

In works [48, 49] there have been proposed powder cosmetic composites containing powdered clay minerals (talc, kaolin, saponite, mica, etc.), treated by fluorine, and an almost water-free oily component. The share of the clay minerals in the cosmetic product varies between 0.5 to 50%.

The authors of [50-54] have developed the following preparations: facial cosmetics containing an ultraviolet adsorbent containing 0.001-0.005% mol per 10 g of clay mineral, such as saponite; a cosmetic composition for skin and hair based on water-soluble derivatives of chitin, clay minerals and intercalated clay; cosmetic deodorants containing up to 40 wt% of clay minerals (saponite, montmorillonite, beidellite, kaolin, etc.). These cosmetic hair, scalp and/or skin detergents (shampoos and shower gels) contain up to 50% of detergents (surface-active materials), 0.001 to 5% of insoluble conditioning agents and up to 15% of clay [54].

The authors of [55, 56] have developed a water-softening reagent for household washing and dishwashing machines based on fine-crystal zeolite (50-70 %), clay minerals (2-10 %) such as saponite, montmorillonite and hectorite, a sodium salt of (co) polymeric carboxylic acid (5-15 %), sodium sulfate (1-10 %), an organic surface-active material (0-3 %), and water. A method for the production of a bleaching agent consisting of a bleaching activator and an inorganic bonding substance (montmorillonite, saponite or hectorite with an ion-exchange capacity of 50-100 mg-eq/100 g) has also been proposed.

4.3. Application of saponite in pharmaceutics industry

Works [57-59] demonstrate the possibility medicine-related applications of saponite including the preparation of drugs and medications (tocopherol antioxidant – vitamin E), clay compounds, including the IB-group metals (Au, Ag, Cu), pharmaceutical composites as solutions containing chitosan and nano-size clay acting as an active ingredient raising the oxygen barrier, and dispersed antimicrobial nano-particles from a clay mineral.

The authors of [57] have proposed a method for manufacturing of α-tocopherol used as antisterile vitamins, anticholesterol agents boosting the blood flow, antioxidants, etc. Tocopherol derivatives can be commercially manufactured using saponite, bentonite or montmorillonite as catalysts in which the mobile cations are displaced for one of the following metals: scandium, yttrium, aluminum, iron, tin, copper, titanium, zinc, nickel, gallium, or zirconium.

Work [58] describes a method for the production of a clay mineral containing an IB-group metal (Au, Ag, Cu) intercalated in it due to the contact of a clay aqueous dispersion (0.5-6.0%) with a cation-exchange resin stoichiometrically associated with an IB-group metal ion. The method provides substitution of over 30% of exchange cations in the clay mineral for an IB-group metal. The clay material containing Ag, for instance, is used as a basic component or thickener for coating materials with antifungal properties.

The authors of work [59] have proposed a method for the production of antimicrobial nano-size clay inhibiting the growth and proliferation of microorganisms by displacing the interlayer cations of the clay by an alkylamine. Clay of this kind can prevent the detriment from microorganisms such as malignant bacteria and fungi. Preparation of the antimicrobial nano-size clay includes the following stages: dispersing of a clay nano-particle (the clay can be montmorillonite, saponite, hectorite, etc.) in organic acid solutions, obtained by adding an organic solvent (ethanol, methanol, isopropyl alcohol, acetone, dimethylformamide, dimethylsulfoxide, or N-methylpyrrolidone), to a solution containing distilled water and chlorohydric acid; adding of alkylamine; filtering and drying of the obtained product.

4.4. Application of saponite in various technology processes

Saponite is known [60-73] to be used in various technological processes either per se or an ingredient of sorbents, catalysts, carrying agents, thickeners and pigments, either in natural or activated form.

The author of [60] presents a survey of research on the heavy metal adsorption by clay materials, with a focus on findings of the past decade (2006-2016). The work describes the structure, classification and chemical composition of different clay minerals and analysis of their adsorption behavior. The survey has confirmed that both natural and modified forms of clay minerals are effective in water treatment from heavy metal ions. Nonetheless, it is pointed out that research on modification and synthesis of new clay materials and their application in adsorbing of dissimilar pollutants from the environment is still of current interest.

The authors of [61] have demonstrated the possibility of removing Cu(II) from aqueous solutions by using natural and acid-activated clays. They have researched the adsorption isotherms, the process kinetics and thermodynamics. The interaction of Cu(II) ions with clays and their acid-activated species has been studied in an equilibrium batch process. The experiments were conducted by varying pH, interaction time, Cu(II) ions concentrations, clay quantities and temperatures. The clays had a satisfactory adsorption ability of Langmuir monolayer of 9.2-10.1mg/g; the acid-activated clays – 31.8-32.3 mg/g. The interactions were endothermic and brought about increasing of entropy and decreasing of the Gibbs energy.

Compared to untreated clay minerals, the acid-activated ones acquire greater adsorption capacity due to increased surface and pore volume. The removing is affected by pH, and the quantity of adsorbed matter increases with pH growth until the ions begin to precipitate as insoluble hydroxides at pH higher than 6.0. Adsorption the Cu(II) ions is very rapid at the onset of the adsorbed substance-adsorbent interaction. The process kinetics is highly complicated and, although the authors have applied different kinetic models, they failed to draw a definite conclusion about the rate process mechanisms. It is highly probable, however, that the adsorption follows the second-order process. The validity of Langmuir isotherm regarding the Cu(II)-clay interactions suggests that the Cu(II) ions are largely retained at the clay surface owing to chemical reactions.

Work [62] demonstrates the efficiency of mechanically and chemically activated saponite in removing of Cu and Ni ions from aqueous solutions. The mechanical and chemical activation of saponite was achieved by high-energy grinding in a planetary ball mill. The mechanical stresses emerging during the high-energy grinding have considerably altered the saponite structure and created an active Mg-OH surface with a high acid neutralization. The Cu^{2+} ion as $Cu(OH)_2$ was removed by activated saponite more effectively than Ni^{2+}. As a result of mechanical activation, the sorption capacity of saponite in relation to Cu^{2+} ions increased from 33.2 mg/g to 287 mg/g, whereas for Ni^{2+}ions it increased from 46.0 mg/g to 124 mg/g. It has been established that the adsorbed metal ions form insoluble hydroxides on saponite surface and are therefore inaccessible for further ion exchange. The formation of insoluble $Cu(OH)_2$ has been confirmed by XRD and SEM analysis and the formation of $Ni(OH)_2$ – by SEM analysis. This research has illustrated the feasibility of modifying smectites in order to produce sorbents effective in the treatment of process water containing heavy-metal ions.

As discovered by V.G. Minenko et al., the saponite-containing product, obtained by electrochemical separation of process water, is characterized by high sorption capacity in relation to nickel and copper ions (40 and 90 mg/g, respectively). After roasting at 750 °C, these values increase to 189 and 224 mg/g, respectively. The metal-containing phases were diagnosed and the metals' sorption mechanism was validated using the XRD and SEM with EDS. The product thermally activated at 750 °C ensures cleaning of the nickel and copper ions from solution to the fishery water requirements, according to MAC (0.01 and 0.001 mg/dm^3) at the initial concentrations in solution of 50 and 250 mg/dm^3 [63].

Patent [64] proposes a method for ion adsorption of six-valent chromium on natural ferro-saponite. The methods of adsorption and subsequent reduction of six-valent chromium, aimed at total removal of chromium from water, incorporate the interaction of 0.04 M solutions of potassium dichromate with natural ferro-saponite clays at temperatures ranging between 50 to 200 °C during 1 to 3.0 hours.

Work [65] demonstrates the feasibility of application of the saponite-based sorption technique in purification of water contaminated with uranium (over 90%). It has been shown that equilibrium in the U (VI) – saponite system establishes in the course of 8 hours. The saponite – pH relationship has a clear maximum at pH 5-7. The isotherm of U (VI) sorption on saponite is described by the Langmuir empirical equation. The sorption process is shown to be affected by complexing reagents (ethylenediaminetetraacetic acid – EDTA, carbonate ions and fulvic acids).

The authors [66] presents the results of quantitative determination and comparison of reactive properties of bentonite clays FEBEX and MX-80 and saponite in forming barriers and europium immobilization (hydrothermal treatment was performed using $Eu(NO_3)_3$ (^{151}Eu and ^{153}Eu, with 52.2% ^{153}Eu) and radioactive ^{152}Eu for quantitative assessment of the reactions). Saponite was found to make a better barrier than bentonite. The results have shown that at 200 °C $\leq T \leq$ 350 °C, the europium immobilization with saponite, FEBEX and MX-80 will be completed after 8.5 months while at 80°C$\leq T \leq$ 200°C, it will take several years. The reaction rate is not affected by the clay type, but the immobilizing ability of bentonite is lower than that of saponite.

The authors of [67] have proposed a technology yielding a composite and the composite-based catalyst. The composite consists of laminated clay homogeneously dispersed in an inorganic oxide matrix. The clay is dispersion is arranged so the clay layers are completely surrounded by the inorganic oxide matrix. The inorganic oxide was selected from a group consisting of Al_2O_3, TiO_2, SiO_2, ZrO_2, P_2O_5 and their mixtures. The clay share amounts to 5 to 80 wt % of the composite. The clays used in the composite were saponite, montmorillonite, etc. The composite can be applied as catalyst in alkylation or hydrogen cracking.

The invention described in work [68] represents a method for the production of glycerol polymers with a saponite catalyst. In broader terms, the invention belongs to methods of polymerization of raw materials, including glycerol and its derivatives, but the proposed method incorporates heating of the raw material in the presence of at least one magnesium saponite clay catalyst in the "H form" to the temperature of condensation polymerization for a time sufficient to obtain glycerol polymers or its derivatives. Saponite catalyst in the "H form" is obtained by substituting the Na^+ ions in the ion-exchange process for H^+ and NH_4^+ ions.

The authors of [69] have proposed an aqueous composite diminishing surface friction. The composite contains a solid lubricant and a modified, or a synthetic, clay mineral. The clay minerals used as thickeners are smectite clays such as saponite, montmorillonite, hectorite etc. The share of the solid lubricant is usually 1 wt% of the aqueous composite, more rarely 3 to 40 %. The clay mineral is modified by preliminarily mixing it with a water-soluble organic polymer in water followed by spray drying of the mixture. If necessary, the resulting dried mixture is ground to the size of 1 to 20 μm. The content of water-soluble polymer in such a mixture is 0.1 to 40 wt%.

Invention [70] proposes a method for the production of a granular adsorbent featuring a high hardness, water-resistance and good adsorbing efficiency by mixing a certain quantity of layered silicate mineral with an alkali metal hydroxide, which is followed by pelletizing and calcination. The granular adsorbent is obtained by mixing 0.1 to 300 weight parts of a layered silicate mineral with 100 weight parts of an alkali metal hydroxide, which is followed by pelletizing and calcinng.

The alkali metal hydroxide in this case is represented by magnesium, calcium, etc. hydroxides. The mineral layered silicate is a natural mineral such as saponite, montmorillonite, beidellite, kaolinite, bentonite, etc. If needed, inorganic fibers, a pigment or an antibacterial agent can be added. The recommended adsorbent size is 0.5 to 10 mm.

The authors of work [71] propose an effective composition for removing the metal dusting/ based on a composite containing a substrate, an organic ion or a metal-binding agent. The substrate contains saponite, montmorillonite, natural zeolite, synthetic zeolite, polymer resin, lignite, kaolinite or a combination thereof. The organic ion includes quaternary amines, imidazolium salts, phosphonium salts, tetra alkyl ammonium, bis-(hydrogenated tallow)-dimethyl-ammonium chloride, bis-(hydrogenated tallow)-benzyl-methyl-ammonium chloride, 4,5-dihydro-1-methyl-2-nortallow-alkyl-1-(2-tallow-amidoethyl)-imidazolium methyl sulfate, 1-ethyl-4,5-dihydro-3-(2-hydroxyethil)-2-(8-heptadecenyl); -imidazolium ethyl sulfate, or combinations thereof. The metal-binding agent comprises mercaptan, carboxylic acid, chelating agents, amines, esters, carboxylic acids, alcohols, ethers, aldehydes, ketones, alkenes, mercaptans, thiols, tert-dodecanethiol, nonanethiol, octanethiol, n-stearic acid, palmitic acid, or combinations thereof.

4.5. Application of saponite for producing nano-composites, textile and paper

It is known [72-84] that saponite is applied in manufacture of polymeric and polymer-ceramic composites, nano-composites, textile and paper.

The authors of [72] have synthesized the nano-composites wherein the layers of anionic clay are intercalated between the layers of cationic clay, which is achieved by mixing an aqueous colloid dispersion of laminated layers of copper hydroxide, or α-cobalt hydroxide, with an aqueous colloid dispersion of saponite. The behavior of nano-composites, resembling a chlorite mineral with metal hydroxide layers, intercalated between saponite layers, and the initial layered solid substances was different during the thermal decomposition. In the case of chlorite-like nano-composites, it produced the nano-composites with metal oxide nano-particles (CuO/Co_3O_4) uniformly distributed throughout the saponite matrix. The size of oxide nano-particles in the nano-composite can be varied by changing such decomposition parameters as temperature and duration.

The authors of [73] have proposed and researched the nano-composites consisting of quaternary fulvic acid (QFA) and saponite. The fulvic acid (FA) was produced from sodium humate and nitric acid and further synthesized into QFA. The QFA-intercalated saponite (QFA-saponite) was prepared by using ultrasonic radiation. In order to improve the thermal and mechanical characteristics of polylactic acid (PLA), the QFA-saponite/PLA nano-composites were obtained from QFA-saponite and PLA via the solution intercalation. Furthermore, the anti-bacterial properties QFA-saponite/PLA nano-composites have been investigated. The QFA-saponite/PLA nano-composites exhibited better thermal and mechanical properties compared to pure PLA owing to the nanomeric dispersion of QFA-saponite in the PLA matrix. The optimal thermal and mechanical properties of QFA-saponite/PLA nano-composites were observed at a QFA-saponite content of 1wt %. Moreover, the QFA-saponite/PLA nano-complexes were found to have a high bacteriostatic activity against bacteria.

The authors of [74] have proposed a technique yielding a nano-composite material from a composite incorporating a synthetic thermoplastic polymer (polyopheline) in amounts of 5 to 90 wt %; of 5 to 80 % of a filler as nano-particles obtained from natural or synthetic phyllosilicates or laminated silicate clay (saponite, montmorillonite, etc.); and 5 to 50% of a deflocculating agent obtained using controlled free-radical polymerization.

Work [75] also proposes a method for producing polyolephynic nano-composites by stirring in a melt at 120-290 °C a mixture of polyophylline, a filler (1 to 15% in terms of polyolephyne) represented by a laminated silicate clay (saponite, montmorillonite, etc.), a laminated hydroxycarbonate or phyllosilicate and a non-ionogenic surface-active material (0.1 to 7.5% in terms of polyolephyne mass). The non-ionogenic surface-active material is a block- or a graft-copolymer having hydrophilic (ethylene oxide block) and hydrophobic (polyolephyne, fluorocarbon, siloxane or low-molecular methacrylate) segments. The surface-active non-ionogenic materials can be sorbitan ester, dimethylsiloxane-ethylenoxide copolymer block, or poly(methylmetalkrylate)-poly(oxoethylen) copolymer block.

The nano-composite materials can be additionally admixed [74, 75] with phenol antioxidants, light stabilizers, solvents, pigments, coloring and plasticizing agents, admixtures enhancing the impact resistance, thixotropic agents, acid acceptors and/or metal deactivators.

These nano-composite materials can be applied in manufacture of foam plastic, fibers, various building, hygienic, packing, insulating and textile materials, strand or molded articles, storage basins, footware, printing forms, image carriers and circuit boards, optic and magnetic materials, furniture, playthings, sports and household items, etc.

The authors of [76] have proposed a composite material obtained at the temperature of 190-220 °C based on thermoplastic (80.0-99.5 %) and a filler (0.5-20 %). The filler is a laminated silicate (saponite, montmorillonite, palygorskite, kaolin, bentonite, etc.) modified by QAS (a quaternary ammonium salt) at a silicate to QAS ratio of (2÷200):1. This material is used in manufacture of technical parts such as friction bearings.

Invention [77] proposes a method for the production of porous particles of a composite material in which one of the components is aluminum oxide and the other is water-swellable clay (saponite, montmorillonite, etc.) homogeneously dispersed in the aluminum oxide component. The average pore diameter of the composite material is 1 to 150 μm. Roasting of the porous particles at 537.8 °C for 2 hours provides a surface area of about 200 m^2/g; the average pore diameter in terms of nitrogen is 60 to 400 Å; the average pore volume in terms of nitrogen of 0.5 to 2.0 cm^3/g.

The authors of [78] have proposed a technique of producing a polymeric nano-composite based on clay with dispersed olefin and polyolefin resin. The nano-composite is characterized by high stretching and thermal resistance, without detriment to transparency. The method incorporates immersing of the catalyst and co-catalyst into the clay, immersing of olefin into the clay and polymerization thereof. The clay is represented by montmorillonite, hectorite, saponite, vermiculate, etc. The catalyst of olefin polymerization represents an organic complex bonded with a metal selected from among Zr, Ti, Ni and Pd; the co-catalyst represents one of the alumoorganic compounds such as $(C_2H_5)_3Al$, $(C_2H_5)_2AlCl$, $(C_2H_5)AlCl_2$, $(t\text{-}C_4H_9)_3Al$ and $(iso\text{-}C_4H_9)_3Al$.

Invention [79] proposes a method for the production of a composite clay material with improved properties incorporating treating of the clays with an agent containing 10-80 mol % of hydroxoorganic onium ions and polymers of vinyl alcohols. The organic onium ions for this experiment were obtained from an acrylic oligomer with an average molecular mass of 1000-15000. The preferred kinds of clay materials are laminated clay minerals such as saponite, montmorillonite, etc.

Invention [80] proposes a technique of producing a nano-composite based on polymeric clay (montmorillonite, saponite, bentonite, hectorite, etc.) subsequently modified with an agent including two or more hydroxyl groups, silanol or alkyldiisocyanate with carbon atom values of 2-10.

The authors of work [81] propose a method yielding stable suspensions of a biomass containing inorganic particles. There have been developed liquid suspensions containing a suspending medium, fine biomass particles and small particles of inorganic material. The inorganic material with the particle size a 3 mm to 50 μm (saponite, alumina, transition metals hydroxides, sepiolite, etc.) stabilize the suspension making it possible to avoid sludging during the pipeline or cistern transportation. The suspension is used in biofuel manufacture. The biomass contains polymeric materials such as cellulose and lignocellulose. The liquid suspension medium may also contain either water or alcohol, or carbonic acid. The production process of the biomass suspension is accelerated by varying the temperature, pH value, evaporation of liquid suspension medium, or via their combination.

The authors of [82] have demonstrated the feasibility of a microwave synthesis of mesoporous acidic saponites characterized by a specific area of 603 m^2/g and the size of lamina crystallites of about 4 nm by applying a quaternary ammonium salt, surface-active substances or a polymer as a matrix, and also have investigated the effect of pH, temperature and H_2O/Si molecular ratio on the process. Required acidity was obtained by roasting the NH_4 form.

Work [83] proposes a method for the production and application of laminated phyillosilicate particles (silicate clay particles) with controllable sizes. This invention refers to methods of producing of laminated phyllosilicate particles such as saponite, montmorillonite, kaolinite, bentonite, etc., either with or without, surface modification; with particle sizes of 0.05 to 15 μm. Powders of this type are added to plastic or ceramic matrixes. Preliminary grinding to the size of 5-100 μm is performed using either dry or wet techniques in flushing mills. This is followed by monitored solvent extraction of the particles sized 0.05 to 15 μm. Extraction is either dry, in dynamic classifiers, or wet using centrifuges. It is recommended that the surface of phyllosilicate particles should be modified using acrylic biologically active materials and also acetate, alcohol solutions or silver, copper, iron, nickel or cobalt salts.

The authors of [84] have proposed a method for the production of fire-proof paper incorporated in fire-resistant film laminate and used in heat- and acoustic-insulating systems in civil aviation and other areas. The fire-proof paper, applied in manufacture of fire-proof films, contains inorganic biodegradable fibers, organic reinforcing fibers, organic and inorganic fibers or a filler, and, although not necessarily, refractory ceramic fibers. The inorganic binding or filling agent is represented by clay (saponite, bentonite, montmorillonite, etc.) and also ground inorganic or ceramic fibers, molten silicon oxide, etc.

4.6. Application of saponite for producing building materials

In recent years, much research has been aimed at utilization of saponite-containing waste of kimberlite ore concentration in manufacture of building materials including binding agents, plasters, ceramics, and other products.

For instance, works [2, 85, 86] propose a method for pelletizing of iron-ore concentrates and producing high-quality building materials.

In works [87-89] it is proposed to utilize clays with saponite composition as binding agents in manufacture of autoclave silicate materials.

The authors of [90] have prepared a method for the production of building plaster by utilizing natural minerals, including clays. Compared to conventional cement mixtures, the resulting mixture is characterized by low fissuring, good acoustic absorption, and better adhesion and initial strengths.

Work [91] proposes a method for controlling the water-cement ratio in hardening concrete mixture by adding a fine saponite-containing product made from kimberlite ore concentration waste. The addition of a 7% saponite-containing material provided an almost two-fold increase in the concrete strength and improving of the frost-resistance brand to F150.

It has been proved that the thickened saponite-containing material can be recovered as ceramic bricks [92]. The maximum compressive strength of the samples was 13 MPa. The same authors obtained a cement clinker of the 250 brand (75 % of lime and 25 % of thickened saponite-containing product) for the production of Portland cement.

The modified saponite-containing product has been used to produce high-brand ceramic bricks with a compressive strength, within the sintering temperature range, of 800-1000°C of 61.3±2.8 – 80.9±3.6 MPa, a bending strength of 11.9±1.7 – 26.7±2.1 MPa, a density of 1.9±0.1 -2.2±0.2 g/cm^3, water absorption 13.6±0.4 – 11.0±0.3%, and fire shrinkage 1.15±0.22 % - 3.2±0.3% [30, 93].

It also seems attractive to continue researching the possibility of involving the saponite-containing concentrates in pellets manufacture and using the electrochemically obtained concentrates as drilling water component due to the small size (less than 7 μm) of quartz particles in the concentrate.

5. Conclusion

Consequently, on the basis of the analyzed capacity, techniques of producing and saponite-containing waste recycling, which develop during processing and enrichment of the M.V.

Lomonosov kimberlite deposit, with allowance for their structure and mineral composition investigation, we have come to the conclusion that the cryogenic treatment and electrochemical separation are the most advanced techniques for the recycled water treatment at the processing plants.

The electrochemical separation promotes manufacture of modified saponite-containing products, which are characterized by the elevated level of minerals belonging to smectite group, decrease of mineral particles size, more compact structure and larger specific surface. All of these characteristics presuppose wide possibilities for further manufacturing high-quality ceramic materials and heavy-metal sorbents.

Thus, the research reported in works [28, 30, 63, 93] focused on the physical-technical, and sorption properties of electrochemically modified saponite-containing products to estimate the feasibility of converting them to high-quality ceramic items and heavy-metal sorbents. Having examined the structure and mineral composition of electrochemically modified saponite – a waste of circulating water from diamond-bearing kimberlite concentration, the authors were the first to scientifically and experimentally validate some effective methods affording to manufacture high-quality ceramic materials with improved physical-mechanical and decorative properties and heavy-metal sorbents characterized by high cation-exchange capacity.

Additionally, the following directions can be considered to be advanced:

-applying of modified saponite-containing products for pelletizing;

-manufacturing of drilling fluids (clay mud) due to low size of quartz crystal particles (less than 7 μm) in the concentrate;

-manufacturing of various compound materials (plastic foams, plastics, building, hygienic, packing, sealing and fabric materials, molded articles, vessels, footwear, furniture, toys, sporting and kitchen facilities, other goods).

References

1. Karpenko, F.S., Saponite-containing precipitation accumulation conditions and thickening in tailing ponds of Lomonosov diamond deposit, Cand. geol.-min. sci. dissertation, Moscow: 2009. (In Russian)
2. Bezborodov, S.M., Verzhak, V.V., Verzhak, D.V., Garanin, V.K., Garanin, K.V., Zuev, V.M., Kudryavtseva, G.P., Pylaev, N.F. Way of recycling diamond industry wastes. RU Patent 2206534, 20.06.2003. Bull. No6 .
3. The official IMA-CNMNC List of Mineral Updated list of IMA-approved minerals (March 2018)
4. https://www.mindat.org/min-11119.html
5. Odom, I.E. Smectite clay minerals: properties and uses. *Philosophical Transactions of the Royal Society A*, **1984**, 311, 391-409.
6. Guggenheim, S., Adams, J.M., Bain, D.C., Bergaya, F., Brigatti, M.F., Drits, V.A., Formoso, M.L.L., Gala´n, E., Kogure, T., Stanjek, H. Summary of recommendations of nomenclature committees relevant to clay mineralogy: Report of the Association Internationale pour l'Etude des Argiles (AIPEA) Nomenclature Committee for 2006. *Clay Minerals*, **2006**, 41, 863-877.
7. Laird, D.A. Influence of layer charge on swelling of smectites. *Applied Clay Science*, **2006**, 34, 74-87.
8. Decarreau, A., Bonnin, D. Synthesis and crystallogenesis at low temperature of Fe(III)-smectites by evolution of coprecipitated gels: Experiments in partially reducing conditions. Clay Minerals, **1986**, 21, 861-877.
9. Jasmund, K., Lagaly, G. *Tonminerale und Tone. Struktur, Eigenschaften, Anwendung und Einsatz in Industrie und Umwelt.* Steinkopff Verlag: Darmstadt., 1993; p. 490.
10. Ogorodova, L.P., Kiseleva, I.A., Mel'chakova, L.V., Vigasina, M.F., Krupskaya, V.V., Sud'in, V.V. Calorimetric determination of the enthalpy of formation of natural saponite. *Geochemistry International*, **2015**, 53, 7, 617-623.
11. Christidis, G.E. The concept of layer charge of smectites and its implications for important smectite-water properties. *EMU Notes in mineralogy*, **2011**, 11, Chapter 6, 239-260.
12. Alietti, A., Mejsner, J. Structure of a talc/saponite mixed-layer mineral. *Clays Clay Miner*, **1980**, 28, 388-390.

13. Eberl, D.D., Jones, G., Khoury, H.N. Mixed-layer kerolite/stevensite from the Amargosa Desert, Nevada. *Clays Clay Miner*, **1982**, 57, 115-133.
14. Steudel, A., Friedrich, F., Schuhmann, R., Ruf, F., Sohling, U., Emmerich K. Characterization of a fine-grained interstratification of turbostratic talc and saponite. *Minerals*, 2017, 7, 5; doi:10.3390/min7010005
15. Breukelaar, J., van Santen, R.A., De Winter, A.W. Synthetic saponite-derivatives, a method for preparing such saponites and their use in catalytic (hydro) conversions. US Patent 5089458. 18.02.1992.
16. Farmer, V.C., McHardy, W.J., Elsass, F., Robert M. hk-ordering in aluminous nontronite and saponite synthesized near 90ºC: Effects of synthesis conditions on nontronite composition and ordering. *Clays and Clay Minerals*, 1994, 42, 180-186.
17. Grauby, O., Petit, S., Decarreau A., Baronnet, A. The nontronite-saponite series: An experimental approach. *European Journal of Mineralogy*, 1994, 6, 99-112.
18. Kuperman, A.E., Maesen, T., Dykstra, D., Uckung, I.J. Magnesium aluminosilicate clays-synthesis and catalysis, US Patent 20100087313, 08.04.2010.
19. Tkachenko O.P., Kustov, L.M., Kapustin, G.I., Mishina, I.V., Kuperman, A. Synthesis and acid-base properties of Mg-saponite. *Mendeleev Communications*, **2017**, 27(4), 407-409.
20. Baldermann, A., Dohrmann, R., Kaufhold, S., Nickel, C. The Fe-Mg-saponite solid solution series – a hydrothermal synthesis study. *Clay Minerals*, **2014**, 49, 391-415.
21. Murray, H.H. Applied clay mineralogy. Occurrences, processing and application of kaolins, bentonites, palygorskite-sepiolite, and common clays. Elsevier B.V.: UK, 2007. p. 188.
22. Krupskaya, V.V., Zakusin, S.V., Tyupina, E.A., Dorzhieva, O.V., Zhukhlistov, A.P., Belousov, P.E., Timofeeva, M.N. Experimental study of montmorillonite structure and transformation of its properties under treatment with inorganic acid solutions. *Minerals*, **2017**, 7, 49; doi: 10.3390/min7040049
23. Komadel, P. Structure and chemical characteristics of modified clays. In Natural Microporous Materials in Environmental Technology; Misealides, P., Macasek, F., Pinnavaia, T.J., Colella, C., Eds.; Kluwer: Alphen aan den Rijn, The Netherlands, 1999; pp. 3-18.
24. Tkac, I., Komadel, P., Muller, D. Acid-treated montmorillonites – a study by 29Si and 27Al MAS NMR. *Clay Minerals*, **1994**, 29, 11-19.
25. Kumar, P.,; Jasra, R.V., Bhat, T.S.G. Evolution of Porosity and Surface Acidity in Montmorillonite Clay on Acid Activation. *Ind. Eng. Chem. Res*., **1995**, 34, 1440-1448.
26. Vicente, M.A., Suarez Barrios, M., Lopez Gonzalez, J.D., Banares Munoz, M.A. Characterization, surface area, and porosity analyses of the solids obtained by acid leaching of a saponite. *Langmuir*, **1996**, 12, 566-572.
27. Morozova, M.V., Frolova, M.A., Makhova, T.A. Sorption-desorption properties of saponite-containing material. *Journal of Physics: Conf. Series*, 929, **2017**, 012111; doi :10.1088/1742-6596/929/1/0121 11
28. Minenko, V.G., Samusev, A.L., Selivanova, E.A., Bajurova, Ju.L., Silikova, A.R., Makarov, D.V. Study of copper ions sorption with electrochemically modified saponite. In Proceedings of Mineralogy of technogenesis – 2017. Institute of Mineralogy, Ural Branch of RAS: Miass, Russia, 2017; pp.190-199. (In Russian)
29. Norrish, K. The swelling of montmorrilonite. *Discussions of the Faraday Society*, **1954**, 18, 120-134.
30. Chanturiya, V., Minenko, V., Suvorova, O., Pletneva, V., Makarov, D. Electrochemical modification of saponite for manufacture of ceramic building materials. *Applied Clay Science*, **2017**, *135*, 199-205.
31. Asonchik, K.M., Utin, A.V., Kovkova, T.M., Kostrov A.M. Tailings slurry carbonization plant pilot-scale testing at the Lomonosovsky mining and concentration complex. *Obogashchenie Rud (Mineral Processing)*, **2016**, *1(361)*, 47-53.
32. Utin, A.V. Method of thickening saponite suspension. RU Patent 2448052, 20.04.2012. Bull. No11.
33. Bakharev, S.A. The return water acoustical treatment at a diamonds recovery plant tailings storage facility cell. *Obogashchenie Rud (Mineral Processing)*, **2014**, *6*, 3-7.
34. Dvoychenkova, G.P., Minenko, V.G., Kaplin, A.I., Kobelev, D.A., Bychkova, G.M. Experimental substantiation of the use of non-standard methods for recycled water clarification at the processing plants AK ALROSA. In Proceedings of International Conference " The Plaksin's Readings — 2007". Kola Science Centre of RAS: Apatity, Russia, 2007; pp. 332-336. (In Russian)
35. Chanturiya, V.A., Minenko, V.G., Timofeev, A.S., Dvoychenkova, G.P., Samofalov, Yu.L. Electrochemical method of the extraction of montmorillonite group minerals from the tailing dump waters. *Gornyi Zhurnal (Mining Journal)*, **2012**, *12*, 83-87.

36. Chanturiya, V.A., Minenko, V.G., Samusev, A.L., Timofeev, A.S., Ostrovskaya, G.Kh. Electrochemical separation of OAO «Severalmaz» facilities saponite-containing tailings pulp. *Obogashchenie Rud (Mineral Processing)*, **2014**, 1, 49-52.
37. Minenko,V.G. Justification and design of electrochemical recovery of saponite from recycled water. *Journal of Mining Science*, **2014**, *50*, 595-600.
38. Chanturiya, V.A., Minenko, V.G., Samusev, A.L., Dvoychenkova, G.P., Kur'janov, M.B., Timofeev, A.S. Method of deslimation of circulating saponite-containing waters and device its implementation. RU Patent 2529220, 27.09.2014. Bull. No27.
39. Chanturiya, V.A., Trofimova, E.A., Bogachev, V.I., Minenko, V.G., Dvoychenkova, G.P., Kur'janov, M.B., Timofeev, A.S. Method of extraction of saponite-containing substances from return water and device for its implementation. RU Patent 2535048, 10.12.2014. Bull. No34.
40. Osipov, V.I., Sokolov, V.N. Clays and their properties. Composition, structure and formation of properties. GEOS: Moscow, Russia, 2013; p. 576. (In Russian)
41. National standard of Ukraine DSTU 7110:2009. Saponite meal. Ameliorant of the combined action. General specifications.
42. National standard of Ukraine DSTU 4906:2008. Food for animals. Polimineral substances based saponitis and glauconitis for broiler chickens. Specifications.
43. Derecha, O.A., Klyuchevich M.M. Composition for presowing treatment of winter wheat seeds. UA Patent 54892, 17.03.2003. Bull. No3.
44. Frisch, G., Maier, T. Thixotropic aqueous plant protection agent suspensions. CA Patent 2158711, 22.03.1996.
45. Kulik, M.F., Velichko, I.N., Ovsienko, A.I., Khimich, V.V., Gricyk V.E., Vasilenko S.V., Gerasimchuk A.P. Method of obtaining food for pigs. SU Patent 1748780, 23.07.1992. Bull. No27.
46. Karunskyi, O.Y., Nikil'bursky, M.I., Riznichuk, I.F. Amidoconcentrate mineral additive kanir-3. UA Patent 48445, 15.08.2002. Bull. No8.
47. Roik, M.,V., Hurskyi, D.S., Barshtein, L.A., Heiko, V.D., Musich, V.I., Metalidi, V.S., Zaryshniak, A.S., Boiko, V.S., Cherednychok, I.I., Yanov, V.P. Method for improving the agrochemical properties of ammonium nitrate. UA Patent 46004, 15.05.2002. Bull. No5.
48. Tomoko, S., Kanemaru, T., Matsuzaki, F., Yanaki, T. Powdery composition. Patent EP 1402875, 31.03.2004.
49. Tokubo, K., Yamaguchi, M., Suzuki, J., Yoshioka, T., Kanda, F., Fukuda, M., Ikeda, T., Kawaura, T., Yagita, Y. Spherical clay mineral powder, process for production thereof and composition containing the same. US Patent 5165915, 24.11.1992.
50. Takuo, S., Kenji, S. Ultraviolet absorbent composition and cosmetic containing the same. JP Patent 60081124, 09.05.1985.
51. Takeshi, Y., Tomiyuki, N. Composition for skin and hair. JP Patent 63275507, 14.11.1988.
52. Herve, D., Jocelyne, B., Maguy, J., Lucia, L.A. Procede d'exfoliation d'argiles intercalees. FR Patent 2882997, 15.09.2006. Bull. No06/37.
53. Klein, W., Kaden, W., Röckl, M. Desodorierende kosmetische Mittel (Deodorizing cosmetic products). DE Patent 4009347, 26.09.1991.
54. Decoster, S., Beauquey, B., Cotteret, J. Composition cosmetiques detergents et utilisation (Cosmetic detergent composition and utilization). FR Patent 2722091, 12.01.1996. Bull. No96/02.
55. Upadek, Horst; Schwadtke, Karl; Seiter, Wolfgang; Pioch, Lothar. Granulares, phosphatfreies Wasserenthartungsmittel (Granular, phosphate-free water softener). DE Patent 3931871, 04.04.1991.
56. Hoeghst, A.G. Granulierte Blaichaktivatoren und ihre Herstellung (Granulated bleach activators and their preparation). DE Patent 4439039, 09.05.1996.
57. Matsui, M., Yamamoto, H. Process for the preparation of tocopherol derivatives and catalyst. US Patent 5536852, 16.07.1996.
58. Koga, S., Sugiyama, H., Suzuki, K. Preparation of clay mineral containing metal. JP Patent 02116611, 01.05.1990.
59. Hong, S.I.; Park, H.W., Cho, Y.J., Rhim, J.W. Antimicrobial nano-particle clay and manufacturing method thereof. Patent KR 20080075813, 19.08.2008.
60. KashifUddin, M. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade // *Chemical Engineering Journal*, **2017**, *308*, 438-462.

61. Bhattacharyya, K.G., Gupta, S.S. Removal of Cu(II) by natural and acid-activated clays: an insight of adsorption isotherm, kinetic and thermodynamics. Desalination, **2011**, *272*, 66-75.
62. Petra, L., Billik, P., Melichová, Z., Komadel, P. Mechanochemically activated saponite as materials for Cu^{2+} and Ni^{2+} removal from aqueous solutions. *Applied Clay Science*, **2017**, *143*, 22-28.
63. Minenko, V.G., Makarov, D.V., Samusev, A.L., Suvorova, O.V., Selivanova, E.A. New efficient techniques of saponite recovery from process water of diamond treatment plants yielding high-quality marketable products. In Abstracts of the XXIX International Mineral Processing Congress, 17-21 September, **2018**, Moscow, Russia, 187-188.
64. Parthasarathy, G., Sreedhar, B., Boyapati, M.C. Method for adsorption and reduction of hexavalent chromium by using ferrous-saponite. US Patent 2006016757, 26.01.2006.
65. Pshinko, G.N., Kobets, S.A., Bogolepov, A.A., Goncharuk, V.V. Treatment of waters containing uranium with saponite clay. *Journal of Water Chemistry and Technology*, **2010**, *32*, 10-16.
66. Villa-Alfagemea, M., Hurtado, S., Castro, M., Mrabet, S., Orta, M., Pazosc, M., Alba, M. Quantification and comparison of the reaction properties of FEBEX and MX-80 clays with saponite: Europium immobilisers under subcritical conditions. *Applied Clay Science*, **2014**, *101*, 10-15.
67. Holmgren, J.S., Schoonover, M.W., Gembicki, S.A., Kocal, J.A. Catalysts containing homogeneous layered clay/inorganic oxide. Patent EP 0568741, 10.11.1993. Bull. No93/45.
68. Kraft, A. Method for preparing polymers of glycerol with a saponite catalyst. US Patent 20030105274, 05.06.2003.
69. Nozoe, T., Tsuji, Y., Black-Wood, W., Kojima, K., Ozaki, M., Hori, S. Friction reducing coatings. Patent WO 2011082137, 27.10.2010.
70. Ota, S., Kurosaki, K. Production of granular adsorbent. Patent JP 10137581, 26.05.1998.
71. Angeles-Boza, A.M., Landis, C.R., Shumway, W.W. Composition and method for removing metal contaminants. US Patent 2012261609, 18.10.2012.
72. Nityashree, N., Gautam, U.K., Rajamathi, M. Synthesis and thermal decomposition of metal hydroxide intercalated saponite. *Applied Clay Science*, **2014**, *87*, 163-169.
73. Wang, W., Zhen, W., Bian, S., Xi, X. Structure and properties of quaternary fulvic acid–intercalated saponite/poly (lactic acid) nanocomposites. *Applied Clay Science*, **2015**, *109-110*, 136-142.
74. Moad, G., Sajmon, D.F., Din, K.M., Li, G., Mejjadann, R.T.A., Vermter, K., Pfehndner, R. Dispersants in nanocomposites. RU Patent 2404208, 20.11.2010. Bull. No32.
75. Moad, G., Sajmon, D.F., Din, K.M., Li, G., Mejjadann, R.T.A., Pfehndner, R., Vermter, K., Shnajder, A. Method of preparing polyolefin nanocomposites. RU Patent 2360933, 10.07.2009. Bull. No9.
76. Burmistr, M.V., Sukhyi, K.M., Ovcharov, V.I.A composition material. Patent UA 77823, 15.01.2007. Bull. No1.
77. Ljuss'er, R.Z., Plesha, S., Vehar, C.S., Uiterbi, G.D. Hydrothermally stable high-porous composite materials of the type alumina/swelled clay and methods for preparation and use thereof. RU Patent 2264254, 20.11.2005. Bull. No32.
78. Jin, Y.H., Kim, J.A., Kim, J.G., Kwak, S.J., Park, H.J., Park, M. Preparation method of clay-dispersed olefin-based polymer nanocomposite. Patent KR 20030025308, 29.03.2003.
79. Usuki, A., Hiruta, O., Okada, A. Composite clay material. Patent JP 10158459, 16.06.1998.
80. Hwang, S.Y., ImSeung, S. Modified clay, a treating method thereof, clay-polymer nanocomposite and a manufacturing method thereof. Patent KR 20100068823, 24.06.2010.
81. O'Connor, P., Daamen, S. Stable suspensions of biomass comprising inorganic particulates. Patent WO 2008020046, 21.02.2008.
82. Gebretsadik, F., Mance, D., Baldus, M., Salagre, P., Cesteros, Y. Microwave synthesis of delaminated acid saponites using quaternary ammonium salt or polymer as template. Study of pH influence. *Applied Clay Science*, **2015**, *114*, 20-30.
83. Lagaron, C. Method for obtaining laminar phyllosilicate particles having controlled size and products obtained using said method. Patent WO 2011101508, 25.08.2011.
84. Garvi Chad E. Fire-proof film laminate. RU Patent 2448841, 27.04.2012. Bull. No12.
85. Apollonov, V.N., Verzhak, V.V., Garanin, K.V., Garanin, V.K., Kudrjavtzeva, G.P., Shlykov, V.G. Saponite from the Lomonosov diamond deposit. *Izvestiya VUZov. Geologiya i Razvedka*, **2003**, *3*, 20-37. (In Russian).
86. Posukhova, T.V., Dorofeev, S.A., Garanin, K.V., Siaoin, Gao. Diamond industry wastes: mineral composition and recycling. *Moscow University Geology Bulletin*, **2013**, 68, *2*, 96-107.

87. Volodchenko, A.N. Cementing based magnesial clays for autoclave silicate material. In Proceedings of the International Conference: Scientific researches and their practical application. Modern state and ways of development '2012, 3(30), 38-42.

88. Volodchenko, A.N., Zhukov, R.V., Lesovik, V.S. Silicate-based materials overburden Arkhangelsk diamond province-ray. *University News. North-Caucasian region. Technical Sciences Series*, **2006**, *3*, 67-70. (In Russian).

89. Volodchenko, A.N. Effect of mechanical activation of lime-saponite binding on the properties of silicate materials autoclave. *Bulletin of BSTU named after V.G. Shukhov*, **2011**, *3*, 12-16. (In Russian).

90. Kim Dae Hee. Manufacturing method of construction plastering mortar using natural minerals. Patent KR 20020026897, 12.04.2012.

91. Morozova, M.V., Ayzenstadt, A.M., Makhova, T.A. The use of saponite-containing material for producing frost-resistant concretes. *Industrial and civil construction*, **2015**, *1*, 28-31. (In Russian).

92. Oblitcov, A.Y., Rogalev, V.A. Prospective ways of diamondiferous rock enrichment wastes utilization at M.V. Lomonosov diamond deposit. *Proceedings of the Mining Institute*, **2012**, *195*, 163-167. (In Russian).

93. Chanturiya, V.A., Minenko, V.G., Samusev, A.L., Masloboev, V.A., Makarov, D.V., Suvorova, O.V. Method of manufacturing wall products and tiles. RU Patent 2640437, 09.01.2018. Bull. No1.