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

Valentine A. Chanturiya 1, Vladimir G. Minenko 1, Dmitriy V. Makarov 2*, Olga V. Suvorova 3, Ekaterina A. Selivanova 4

1 Institute of Comprehensive Exploitation of Mineral Resources of the Russian Academy of Sciences, Kryukovsky Tupik, 4, Moscow, 111020, Russia
2 Institute of North Industrial Ecology Problems, Kola Science Centre of the Russian Academy of Sciences, Fersman St., 14a, Apatity, 184209, Russia
3 I.V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Kola Science Centre of the Russian Academy of Sciences, Fersman St., 26a, Apatity, 184209, Russia
4 Geological Institute, Kola Science Centre of the Russian Academy of Sciences, Apatity, Fersman St., 14, 184209, Russia
* Correspondence: mdv_2008@mail.ru, makarov@inep.ksc.ru; Tel.: +7-81555-79-3-37

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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] \((\text{Ca,Na})_0.3(\text{Mg,Fe})_3(\text{Si,Al})_6\text{O}_{10}(\text{OH})_2\cdot 4\text{H}_2\text{O}\) 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 sheet the surface of the three-layer package has a negative charge which creates a charge imbalance.

According to the Nomenclature Committee of AIPRA [6] the layer charge of smectites varies from 0.2 to 0.6 electrons per half unit cell \((\text{e/h.u.c.})\). The layer charge is balanced by the interlayer cations Na, Ca, K, Mg, Fe, which are weakly binding \(\text{m}\) 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 $\text{Fe}^{2+}$, $\text{Fe}^{3+}$ and $\text{Al}^{3+}$ substitutions for $\text{Mg}^{2+}$ in the octahedral sheet, which are accompanied by partial $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ substitutions for $\text{Si}^{4+}$ in the tetrahedral sheet [8, 9]. Thus, saponite from the Arkhangelsk kimberlite province contains 5.09% $\text{Al}_2\text{O}_3$, 3.14% $\text{Fe}_2\text{O}_3$ and 2.56% $\text{FeO}$ [10], their crystal-chemical formulae, calculated on 22 charges, is the following:

\[
(\text{Ca}_{0.3}, \text{Na}_{0.1}, \text{K}_{0.1})_0.3(\text{Mg}_{2.9}, \text{Fe}^{2+}_{0.3}, \text{Fe}^{3+}_{0.2})_3(\text{Si}_{3.6}, \text{Al}_{0.4})_6\text{O}_{10}(\text{OH})_2\cdot 4\text{H}_2\text{O}.
\]

Saponite is different from the other smectites as part of the negative tetrahedral charge is balanced by substitution of octahedral $\text{Mg}^{2+}$ by trivalent cations, $\text{Al}^{3+}$ or $\text{Fe}^{3+}$, i.e. the octahedral sheet can to bears a positive charge. However, the tetrahedral charge, due to substitution of $\text{Si}^{4+}$ by $\text{Al}^{3+}$ 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 smectites 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 m$^2$/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].

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 m$^2$/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/Å, 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. Smekites 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 smectites 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(HCO₃)₂ and Ca(HCO₃)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/dm³ of solids. However, the initial solid content in the experiments did not exceed 110 g/dm³ and it achieved 158 g/dm³ 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/dm³ 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/dm³ and a precipitate containing up to 200 g/dm³ 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 m), the slime particles concentration was about 3.31 g/dm³; in the upper horizon (0.2 m) it was 1.26 g/dm³. 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/dm³, and 0.16 g/dm³.

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/dm³. 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/dm³ (at a power consumption of 0.5 Wt/m³ 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/dm³ 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/dm³ 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 frostung-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$_2$SO$_4$, 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$_2$O$_3$, CaO, FeO$_x$, FeO, TiO$_2$,
Na$_2$O, K$_2$O, S$O_3$ 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 as 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 smectities 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/dm³) at the initial concentrations in solution of 50 and 250 mg/dm³ [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 of [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(NO₃)₃ (¹⁵¹Eu and ¹⁵⁵Eu, with 52.2% ¹⁵³Eu) and radioactive ¹³²Eu for quantitative assessment of the reactions). Saponite was found to make a better barrier than bentonite. The results have shown that at 200 °C ≤ T ≤ 350 °C, the europium immobilization with saponite, FEBEX and MX-80 will be completed after 8.5 months while at 80°C≤T ≤ 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 Al₂O₃, TiO₂, SiO₂, ZrO₂, P₂O₅ 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 NH₄⁺ 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 calcination.
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 lignite, and 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-butyl-dihydroxyethyl-1-(2-tallow-amidoethyl)-imidazolium methyl sulfate, 1-ethyl-4,5-dihydro-3-(2-hydroxyethyl)-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/CeO₂) 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 (polyphylene) as a matrix 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 polyphylene, a filler (1 to 15% in terms of polyphlene) represented by a laminated silicate clay (saponite, montmorillonite, etc.), a laminated hydroxy-carbonate or phyllosilicate and a non-ionogenic surface-active material (0.1 to 7.5% in terms of polyphylene mass). The non-ionogenic surface-active material is a block- or a graft-copolymer having hydrophilic (ethylene oxide block) and hydrophobic (polyolephyn, 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(oxyethylen) 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, footwear, 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 m²/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 cm³/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 aluomoorganic
compounds such as (C₅H₅)₅Al, (C₅H₅)₅AlCl, (C₅H₅)₅AlCl₂, (t-C₅H₅)₅Al and (iso-C₅H₅)₅Al.

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
hydroxooorganon ionium ions and polymers of vinyl alcohols. The organic ionium 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 alkylisocyanate 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 m²/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 H₂O/Si molecular ratio on the process. Required acidity was obtained by roasting the NH₄ form.

Work [83] proposes a method for the production and application of laminated phyllosilicate particles (silicate clay particles) with controllable sizes. This invention refers to methods of producing 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/cm³, 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 \( \mu \text{m} \)) 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).

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