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On the Influence of Chemical Methods of Activation of Layered Silicates on Their Properties

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Abstract. The effect on the adsorption and structural properties of layered silicates of various crystal chemical structures during activation with a solution of sulfuric acid and sodium carbonate is investigated. The effectiveness of the use of acid activation and pretreatment with sodium carbonate to improve the adsorption characteristics of aluminosilicate raw materials is shown on the example of bentonite with a montmorillonite content of less than 70%. The results of the research showed that the activation of bentonite from the deposit of the Republic of Tatarstan with a solution of sulfuric acid and sodium carbonate contributes to the transformation of its adsorption and structural properties, in particular, an increase in the adsorption index in relation to methylene blue and cation exchange capacity by 25 and 40%, respectively. During acid treatment, the H-form of montmorillonite is formed due to ion exchange, and when treated with sodium salt, the Na-form is formed.

INTRODUCTION

Natural polymineral raw materials containing mainly layered silicates are bentonites and bentonite-like clays. Bentonites mainly contain montmorillonite (MMT) $M_{x/n}{}^{n+}[Al_{4-x}Mg_x](Si_8)O_{20}(OH)_4$ and hydrosludes with an admixture of quartz and feldspar. The mineral composition of bentonites has ensured their widespread use in various industries, in particular for the production of drilling fluids, adsorbents, composite materials and molding mixtures, and others [1-3]. In montmorillonite, a hydrargillite alumina-oxygen layer (alumina-oxygen octahedra) connects two silica-oxygen layers. A three-layer package with a thickness of 9.4 nanometers ends with a "grid" of negatively charged oxygen ions. In the tetrahedral layer of montmorillonite, up to 15% Si^{4+} is replaced Al^{3+}, and in octahedra Al^{3+} replaced by Mg^{2+}, Fe^{2+} and others [4]. Substitution of cations in tetrahedral and octahedral positions of montmorillonite forms a negative charge of the layer of about 0.2-0.5 EV [5]. Substitution of cations in tetrahedral and octahedral positions of montmorillonite forms a negative charge of the layer about 0.2-0.5 The negative charge is compensated by interlayer exchange cations Na^+, Ca^{2+}, Mg^{2+} etc. usually in a hydrated form, which in turn provides high adsorption activity on the inner and outer surfaces of the crystal [5], the ability to exchange ions, swelling and self-dispersion with the formation of incomplete structural elements – playtlets. The types of active centers of montmorillonite for which adsorption is possible are shown in Figure 1 [6].
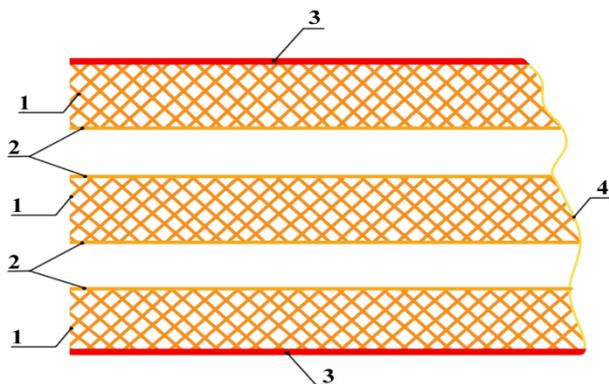
Figure 1. Adsorption centers of montmorillonite: 1 – elementary layer; 2 – surface of individual layers (3rd kind surface); 3 - basal surface (2nd kind surface); 4 – cleavage surface (1st kind surface).

The surfaces of individual layers with a negative charge (2) are responsible for the presence of the bulk of exchange cations. Oxygen ions and hydroxyl groups are located on the basal surfaces (3). There are uncompensated bonds on the cleavage surfaces (4), as well as atoms and groups Si, A1, O, Mg, OH – centers of adsorption of cations and anions.

Chemical methods of bentonite activation, such as treatment with inorganic acids, alkalis, planning, reduction of Fe(III), modification by nanoparticles of naturally related oxides, significantly affect the layered structure of layered silicates [7-10]. This was the reason for a wide range of studies of fine fractions of bentonites from various deposits, mainly containing from 70% montmorillonite (the Tenth Khutor, Zyryanskoye, Dash-Salakhlinskoye and Dinosaur deposits in Russia) and the effects of their modifications [2, 11]. For example, the pillarization of bentonite with polyhydroxocations of iron (III), aluminum and zirconium (IV) by the "co-deposition" method leads to an increase in the adsorption capacity of the sorbents obtained with respect to copper (II) and nickel (II) cations up to 22 mg/g with a specific surface area of 60-180 m^2/g and a predominance of pores of 1.5-4.0 nanometers (60-70%) [12], treatment of Tagansky bentonite 13M HNO_3 (90 °C, 5 hours, bentonite: acid ratio - 1:6) leads to an increase in the specific surface area according to BET from 110 to 280 m^2/g and the pore volume from 0.11 to 0.3 cm^3/g (micropores from 0.03 to 0.1 cm^3/g) [13]. In another study, activation of 20% H_2SO_4 bentonite within an hour allowed to increase the total exchange capacity from 0.64 to 0.98 µEq/L and the maximum adsorption volume from 0.12 to 0.16 cm^3/g [14]. At the same time, the influence of chemical influences on bentonite deposits with a montmorillonite content of less than 70% in the mineral composition has not been sufficiently studied, which can serve as a basis for developing the base of aluminosilicate raw materials and expanding the range of products obtained on their basis.

The purpose of the work is to study the effect of acid activation and treatment with sodium salts on the adsorption properties of bentonite from the Nurlat deposit of the Republic of Tatarstan.

MATERIALS AND METHODS OF RESEARCH

The basic composition was alkaline-earth Ca, Mg-bentonite of the Nurlat deposit, Republic of Tatarstan [SiO_2 – 56.4%, Al_2O_3 – 20.0%, Fe_2O_3 – 7%, FeO – 1.13%, CaO – 1.61%, MgO – 2.78%, (K_2O+Na_2O) – 2.0%, other losses during the calcination – 9.08%]. According to the data of X-ray analysis, the studied bentonite contains the following minerals: Ca-montmorillonite (c = 15.05 Å), muscovite, chlorite, kaolinite, zeolite clinoptylotite, albite and quartz. The average particle diameter (d_{cp}) of bentonite is 46 microns with a predominance of the dusty fraction 5-40 microns [1].

The adsorption index (A, mg/g) and the cation exchange capacity (CEC) were determined by the method of adsorption of the cationic dye methylene blue (MB) according to the State Standard 21283-93. MB belongs to the cationic dyes with the formula $C_{16}H_{18}ClN_3S$, thiazine group, and molecule size 17.0Å × 7.6Å × 3.25Å. Dilute sulfuric acid with a concentration of 5 mol/dm^3 was used for acid treatment. The treatment was carried out as follows. The dried averaged bentonite suspension weighing 0.3 g was placed in a conical flask with a volume of 250 cm^3, 25 cm^3 of distilled water was poured and boiled for 3 minutes. The flask with the suspension was cooled under a stream of cold water, H_2SO_4 was dosed with different volumes and shaken. Then the contents of the flask were

titrated with a solution of methylene blue to determine the adsorption index. Activation with sodium carbonate was carried out by a wet method, in which a paste of the composition (bentonite + water + soda) is prepared – drying – grinding – activated bentonite with precipitation $CaCO_3$ и $MgCO_3$.

RESULTS AND DISCUSSION

The treatment of the investigated bentonite with sulfuric acid at a concentration of 5 mol/dm^3 results in a 25% increase in its adsorption capacity for methylene blue from 98.3 to 124.1 mg/g (fig. 2, Table 1), which is related to the increase in the proportion of active centers in the crystals of the bentonite minerals - montmorillonite, muscovite, and chlorite, as well as kaolinite, which has surfaces with surface hydroxyl groups. The minerals in bentonite form several types of surface salt-like compounds with methylene blue: on different surfaces where they are active with respect to the dye, and at sites of disrupted bonds – on the edges, corners, and fractures of the crystals.

The transformations of the structure of smectites under the influence of solutions of inorganic acids are described in detail in works [5, 7, 8, 13]. In general, acid treatment promotes the partial replacement of interlayer cations Ca^{2+} and Mg^{2+} with hydrogen ions from the acid. Prolonged treatment of bentonite with acid for more than an hour and at a temperature of 60 °C leads to intensive leaching of cations from octahedral positions and partial penetration of leached octahedral cations into the interlayer space. These transformations result in partial protonation of OH groups, disruption of octahedral layers, and transformation of the interaction between tetrahedral and octahedral layers, which reduces the layer charge and changes the interaction between adjacent layers, as well as promotes the amorphization of tetrahedral layers with the formation of amorphous silica (fig. 3) [5, 7, 13]. The decrease in layer charge should lead to a decrease in cation exchange capacity, which is not observed in these studies. This is primarily due to the absence of prolonged thermochemical acid treatment, during which structural cations are not released from the crystalline lattice of layered minerals at active sites where MB molecules are adsorbed in various quantitative ratios. Secondly, the presence of impurities such as feldspar (albite – 15%) makes it difficult to completely remove Ca^{2+} and Mg^{2+} ions from the bentonite samples. In addition, sulfuric acid easily oxidizes organic components present in bentonite, which is often used during their purification.
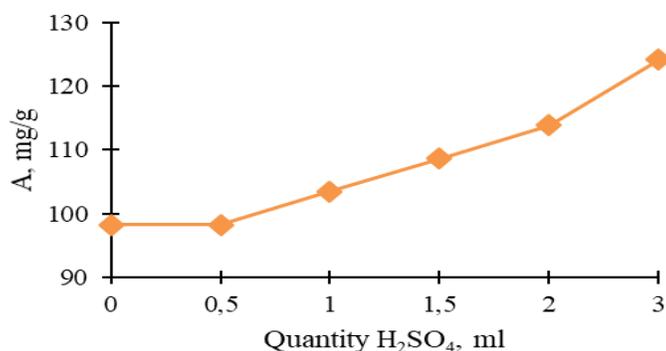

Figure 2. Dependence of bentonite adsorption in relation to methylene blue on concentration H_2SO_4.

The parameters of acid treatment of bentonite clays, such as the nature and concentration of the acid, temperature and activation time, and the ratio of bentonite to acid solution from different deposits are individual and depend mainly on the chemical composition and further application of the activated samples. At the same time, the duration of acid treatment has a determining value for the formation of adsorption properties and the composition of the surface layer, therefore, samples with treatment less than an hour were obtained in the work, which provides an increase in the adsorption capacity and exchange capacity while preserving the crystalline lattice of smectites. Acid activation with current technological parameters is considered insufficiently economically effective since it is limited by high acid consumption (3 ml of acid per 0.3 g of bentonite powder) and the subsequent labor-intensive process of washing off its excess, depending on the intended purpose. Modified bentonites with acid can be used as catalysts for removing heavy metals, radionuclides, and for oil processing, as well as in modeling the barrier properties of designed storage facilities for radioactive and industrial waste, especially in the case of handling liquid radioactive waste [8, 10, 15].
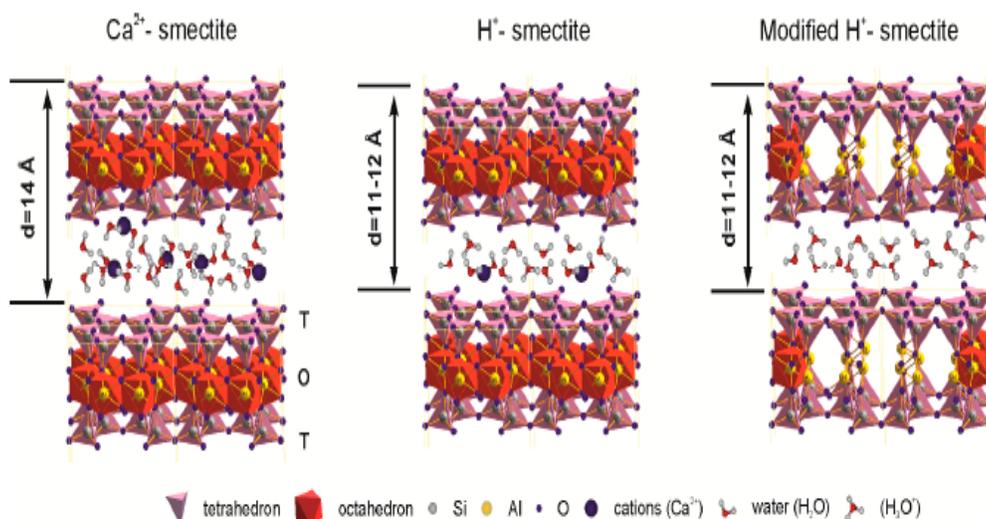
Figure 3. Schematic representation of the structural changes of montmorillonite during treatment with solutions of inorganic acids [5].

Treating a 3% suspension of bentonite by mixing it with Na_2CO_3 leads to an increase in adsorption capacity towards organic dyes by 35-40% (Table 1). In this activation method, the reaction Ca, Mg-bentonite + Na_2CO_3 = Na-bentonite + Ca^{2+}, Mg^{2+} in a solution with pH = 9 is carried out. When the alkaline environment is formed, the end surfaces of the clay particles are charged negatively due to the amphoteric properties of the lateral edge of the octahedral lattice surface. As a result, in the ion exchange complex, Ca^{2+} (0.106 nm) and Mg^{2+} (0.078 nm) ions are replaced by Na^+ ions (0.098 nm), which disrupts the electron neutrality of the system, since another Na^+ cation is required to maintain it, but it is difficult for it to localize in the initially occupied Ca^{2+} area. Therefore, the positive compensating charge of the exchange complex is redistributed, causing a change in the interaction of electrostatic nature between the layers and increasing the degree of hydration, which ultimately leads to an increase in swelling, colloidal properties and adsorption capacity of the bentonite. Na_2CO_3-modified bentonites are used to obtain drilling fluids, lithium casting mixtures, and composite materials.

Table 1. MB adsorption index and cation exchange capacity (CEC) of bentonite.

No. of sample	Bentonite composition	A [mg/g]	CEC [mg-eq.]
1	Basic composition (Ca-Bent)	98.3	30.7
2	H-Bent	124.1	38.7
3	Na-Bent	137.2	42.8

CONCLUSION

This work presents results that allow to establish the effectiveness of pre-treatment of aluminosilicates using the example of alkaline earth bentonite RT in terms of improving their structural and adsorption properties. The results of the research showed that the activation of bentonite from the Republic of Tatarstan deposit with a solution of sulfuric acid and sodium carbonate contributes to the transformation of its adsorption-structural properties, in particular, an increase in the adsorption index by MB and cation exchange capacity by 25 and 40%, respectively. In the process of acid treatment, the hydrogen form of MMT is formed due to ion exchange. These transformations are the result of changes in the ion-exchange complex of layered silicates, an increase in the adsorption centers or their energy. Activation with sodium carbonate is preferable to activation with sulfuric acid, since it increases the adsorption properties to a greater extent by converting montmorillonite into Na-form with significantly lower reagent consumption.

ACKNOWLEDGMENTS

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