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To cite this article: A E Buntin *et al* 2022 *IOP Conf. Ser.: Earth Environ. Sci.* **990** 012041

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Features of the chemical composition and structure of bentonites in Tatarstan

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Abstract. The article studies the chemical, mineralogical, granulometric composition and type of chemical bond, as well as meso- and macrostructure of bentonite of the Nurlat deposit of the Republic of Tatarstan. By laser diffraction, the average particle size in the studied bentonite was found to be dominated by fractions of particles with a size of less than 10 μm (31.18%) and 10-40 μm (36.99%). The average particle size of bentonite was 45.67 μm . According to X-ray analysis, bentonite is mineralogically represented by montmorillonite with an interplane distance of 15.0 \AA (001), muscovite, chlorite, kaolinite, clinoptilolite, albite and quartz. The microstructure of bentonite is formed mainly by large anisometric flattened microaggregates and volumetric isometric aggregates up to 70 μm . The average pore size was 0.23 μm , porosity was 39.2%. The microstructural model was cellular with elements of a spongy structure.

1. Introduction

Natural aluminosilicate materials, which include bentonite clays, are in great demand in many industries: as a binding agent in metallurgy for pelletizing iron ore concentrate or molding mixtures for foundry production (GOST 28177-89); in the preparation of drilling fluids for drilling wells (GOST 25795-83); in the production of adsorbents and waterproofing material of engineering safety barriers for the disposal of radioactive waste [1-3] The estimated reserves of bentonite in the world are more than 10 billion tons, in Russia – 335 million tons. The annual production of bentonite is constantly increasing. Over a nine-year period, the total increase in bentonite reserves in Russia amounted to 95 million tons. Significant reserves in category A+B+C₁ fall on the Biklyanskoye, Berezovskoye and Nurlatskoye fields of the Republic of Tatarstan (44.6 million tons). The quality of bentonites in the explored categories is low. The main part of the developed deposits in Russia is represented by sedimentary bentonite of alkaline earth type, consisting of 60-70% montmorillonite (MT), as well as deposits formed by bentonite-like aluminosilicate raw materials [1-3]. Bentonites of Republic of Tatarstan are characterized by relatively average indicators of plasticity and adsorption, low swelling and colloidal.

All over the world, the development of the raw material base of aluminosilicate raw materials leads to the improvement and emergence of new, commercially promising technologies for the production of bentonite products, taking into account the geology and individual qualitative characteristics of natural materials of each deposit. In turn, the effective development of these technologies requires a comprehensive analysis of the composition and structure of aluminosilicate raw materials, which determine the quality of the final products and the prospects for application.



The aim of the work is to study the composition and structure of bentonite of the Nurlat deposit of the Republic of Tatarstan.

2. Materials and methods

Studies of particle size distribution were carried out by laser diffraction using the Horiba LA-950V2 laser particle size analyzer in accordance with ISO 13320:2009.

The phase composition was analyzed by X-ray method using a Rigaku smartLAB diffractometer. Shooting mode: angle interval from 3° to 65°, scanning step 0.02, exposure 1 second at a point. The MT content was determined by the first diagnostic reflex corresponding to the interplane distance (hkl): 12.0-15.0 Å (001).

Infrared absorption spectra of bentonite were obtained using an IR Fourier spectrometer Frontier (Perkin Elmer) with the console of disturbed total internal reflection DTIR. Shooting modes: scanning range 4000-500 cm⁻¹, resolution 4 cm⁻¹. The samples were prepared in the form of compressed KBr tablets, which were used at natural humidity.

The calculations of chemical bonds «element-oxygen» components (C_C – covalent character, C_M – metallic character, C_I – ionic character) were carried out according to the method described in [4-5].

The microstructure of the samples was determined by scanning electron microscopy using a LEO-1430 VP microscope (Carl Zeiss, Germany). The samples, prior ground into powder, were glued onto aluminum plates, coated with gold by cathode sputtering in argon medium and viewed in high vacuum mode.

3. Results and discussion

Chemical and mineral composition. In the tables 1 and 2 the data on chemical and mineral composition of the studied aluminosilicate raw materials is given. According to Tables 1 and 2, the composition of bentonite is dominated by oxides of silicon, aluminum and iron. The SiO₂/Al₂O₃ ratio for bentonite is 2.6. According to X-ray phase analysis mineralogically, bentonite is represented by MT, muscovite, chlorite, kaolinite, zeolite (clinoptilolite), albite and quartz (figure 1). Of these, layered (two-dimensional) silicates include montmorillonite, muscovite and chlorite with three-layer packages, kaolinite with a two-layer package. Frame (three-dimensional) silicates include albite and zeolite. As a result, the studied bentonite is characterized by a polymineral composition with a predominance of layered silicates (figure 2). MT is determined by a diagnostic reflex (figure 1) corresponding to the interplane distance (hkl): 15.0 Å (001), which indicates the predominance of Ca²⁺ and Mg²⁺ ions in the ion exchange complex. In accordance with GOST 9169-75, the analyzed raw materials belong to refractory (refractory more than 1350°C), semi-acidic, with a high content of coloring oxides, natural aluminosilicates.

Table 1. Chemical composition of Nurlat bentonite.

Composition	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃ /FeO	CaO	MgO	K ₂ O+Na ₂ O	Olc
Mass content [%]	56.4	20.0	–	7.0/1.13	1.61	2.78	2.0	9.08

Table 2. Mineral composition of bentonite according to X-ray analysis.

Raw materials	Phase composition	Content, [%] by weight
Bentonite	Chlorite	22
	Muscovite	22
	Feldspars (albite)	15
	Montmorillonite	13
	Quartz	13
	Kaolinite	9
	Zeolite (Clinoptilolite)	6

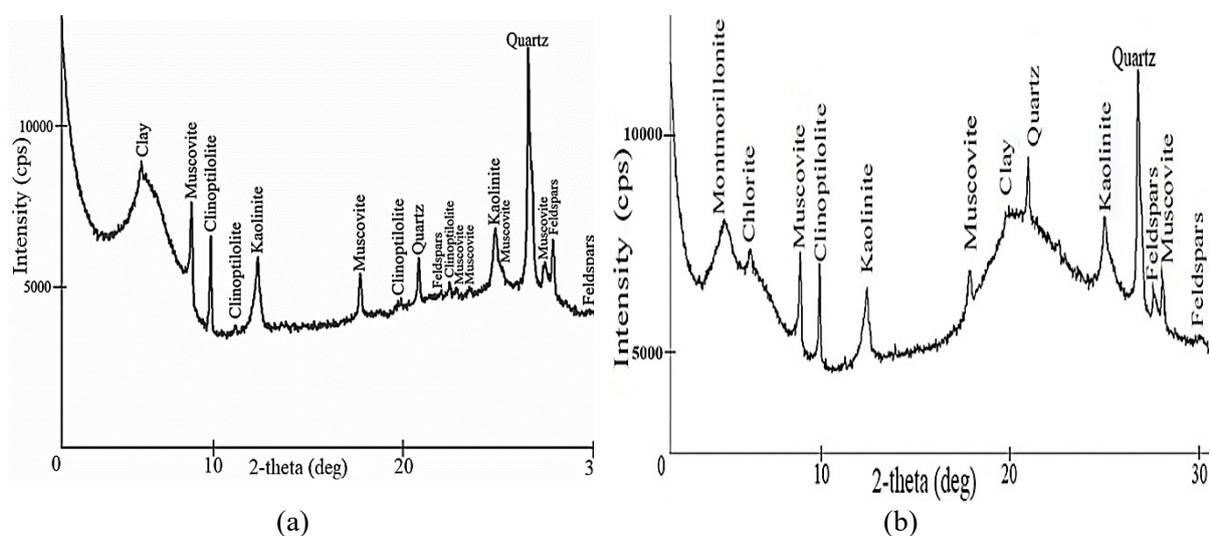


Figure 1. Diffractograms of oriented (a) and glycerin-saturated bentonite specimens (b).

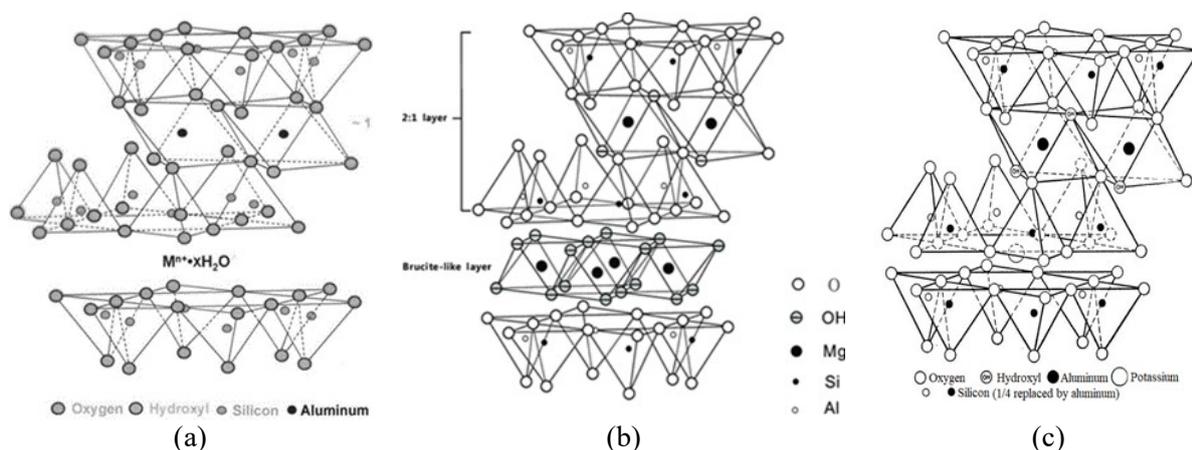


Figure 2. Structures of the main layered silicates of bentonite: MT (a), chlorite (b) and muscovite (c) [6, 7].

Features of chemical bonding of the elements that make up the main structural framework of bentonites. In order to comprehensively assess the structure of bentonite and effect on its properties, additional consideration is needed for the features of heteronuclear chemical bonds of the elements that form them. According to modern concepts [4, 5], they are characterized by a mixed character, i.e. the bond is considered as an overlay on its covalent component of metallic and ionic components. The calculated data on the parameters of the element-oxygen chemical bond in aluminosilicates are shown in table 3. It follows from Table 3 that chemical bonds in aluminosilicates of the main aluminum- and silicon-oxygen compounds (with the exception of Al–O(H) and Si–O(H)) have a metallic-ionic-covalent character with the predominance of the latter component and sufficiently high energy. It is the predominant covalent nature of bonds in aluminosilicates that determines their three-dimensional polymer structure, with an increased (due to the high ionic energy of the E–O bond) melting point, hydrophilicity and low reactivity. In addition, a higher proportion of ionic character (C_i), rather than C_m , in these bonds (25.9% and 30.2%, respectively) determines their high polarity and, as a consequence, the possibility of electrostatic interactions during the formation of associates and aggregates that are based on them.

Table 3. Calculated parameters of chemical bonding in aluminosilicates.

Chemical bond	C _C [%]	C _M [%]	C _I [%]	Bond length [Å]	Bond energy [kJ/mol]
Al–O	46.7	23.1	30.2	1.75	437
Al–O(H)	49.0	35.6	15.4	–	–
Si–O	51.7	22.4	25.9	1.62-1.7	473
Si–O(H)	54.4	35.1	10.5	1.62-1.7	–
H–O	54.5	22.0	23.5	0.97	460

Granulometric composition. The average size of bentonite particles and their distribution are shown in Table 4. As follows from table 4, fractions of particles with a size of less than 10 microns (31.18%) and 10-40 microns (36.99%) dominate in bentonite. The average particle size is 45.67 microns. In terms of dispersion, the raw materials under study should be classified as coarse, due to the low content of clay particles with sizes less than 1 and 10 microns.

Table 4. Size distribution of bentonite particles.

Fraction [μm]	1-5	5-10	10-40	40-63	63-80	80-100	100-150	150-200	200-300	≥300	Avg. size
Particle content [%]	12.59	18.59	36.99	7.73	4.48	4.27	7.36	4.38	3.26	0.35	45.67

Infrared spectroscopy. Figure 3 shows the spectrum of Nurlat bentonite. The entire set of absorption bands characteristic of silicate structures is observed in the infrared spectrum of bentonite. There are two main areas. In the first region of 4000-3000 cm⁻¹ there are bands of valence vibrations (change in bond lengths) of structural OH-groups associated with octahedral cations, as well as water molecules associated through hydrogen bonds. The absorption bands characteristic of the silicate structure are located in the second region of 1400-400 cm⁻¹.

The absorption peak at 3620.91 cm⁻¹, according to the authors [8], is the result of the superposition of individual absorption bands corresponding to the valence vibrations of AlOHAl and AlOHMg, as well as the vibrations of MgOHFe, AlOHFe, FeOHFe, etc.

The absorption band of low intensity with a peak at 1636.62 cm⁻¹ corresponds to the deformation vibrations of water molecules [9]. The increase in its intensity is associated with an increase in the number of adsorbed water molecules in the interlayer space of montmorillonite and the energy of hydrogen bonds.

The absorption band of the highest intensity in the region of 995.81 cm⁻¹ corresponds to the valence vibrations of the Si–O–Si bond in the crystal lattice of minerals of the montmorillonite group (tetrahedra of the silicon-oxygen framework). The presence of this absorption band, shifted towards lower frequencies from most valence Si–O bands, is due to the substitution of Si⁴⁺ in the tetrahedral position by trivalent cations [10].

The absorption peak at 912.13 cm⁻¹ corresponds to deformation vibrations of the non-bridged Al–Al–O–H bond [2], which is longer, weaker than the Si–O bond. Its intensity is extremely sensitive to the entry of divalent ions into octahedral positions, noticeably falling with increasing degree of substitution. The absorption peaks at 796.34 cm⁻¹ and 778.66 cm⁻¹ correspond to the deformation vibrations of α-SiO₂ [11].

The band with a frequency of 693.34 cm⁻¹ refers to deformation vibrations of the Si–O–Si bridge bond [12]. The absorption peak at 518.72 cm⁻¹ corresponds to deformation fluctuations of Al–(O–Si) bonds, which according to [13] are the most sensitive region to the presence of Al³⁺ in the octahedral layer.

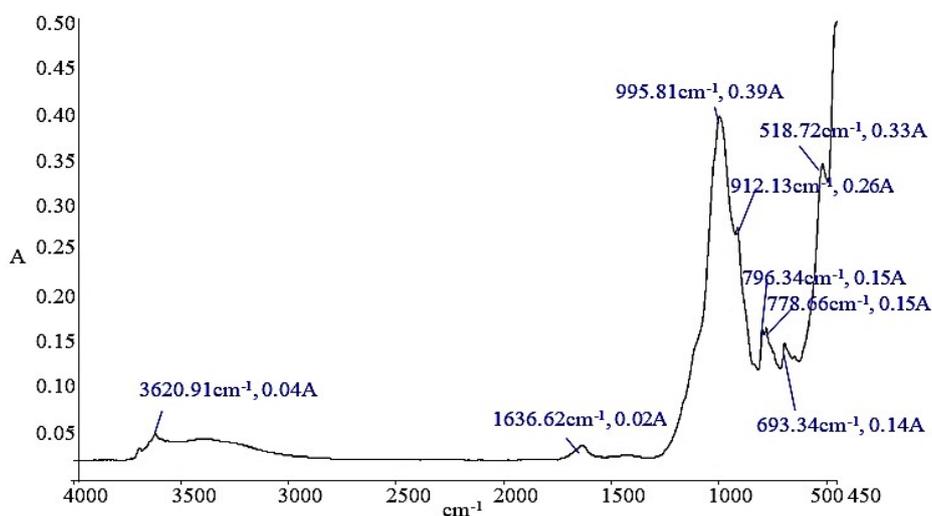


Figure 3. IR absorption spectrum of bentonite.

Differential thermal analysis. On the thermogram of bentonite, two main endothermic peaks are distinguished. The first peak at 86°C corresponds to the removal of mechanical water and, unlike the thermogram of pure montmorillonite (the maximum peak temperature of 170°C) is shifted towards lower temperatures characteristic of the kaolinite phase. The peak at 497.2°C indicates the removal of chemical water (crystallization and constitutional). Removal of chemical water destroys the crystal structure and leads to irreversible dehydration processes. Residual mass at 1199.5°C is 81.47%.

Electron microscopy. It follows from the electronic photographs in figure 4 that bentonite is characterized by a different aggregated microstructure. The following structural elements are distinguished: ultramicroaggregates composed of primary aluminosilicate particles, microaggregates (1-10 μm), aggregates (10-100 μm) with a chaotic or poorly oriented arrangement, as well as grains, microcrystals of salts and ore minerals. The most common are anisometric microaggregates and volumetric isometric aggregates, in which ultramicroaggregates (0.1 to ~ 2 μm) having a lamellar, leaf-shaped form contact in the basis-basis, basis-chip type [14]. The particles of montmorillonite have the form of elongated, slightly curved plates, scales and form sufficiently large and dense microaggregates of various configurations.

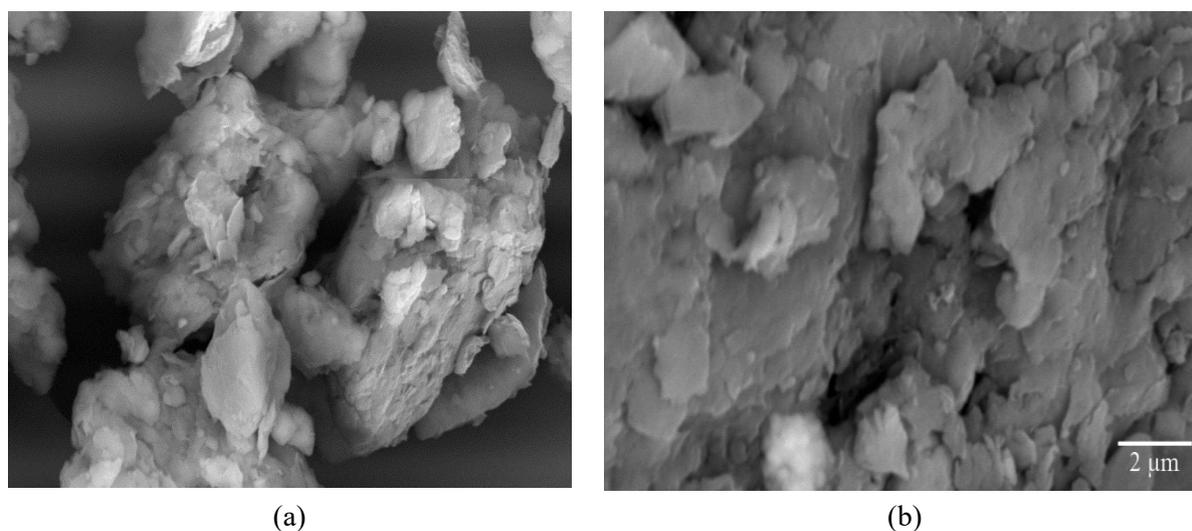


Figure 4. Photos of bentonite microstructure.

The microstructure of bentonite is formed mainly by large anisometric flattened microaggregates ranging in size from 3 to 10 μm with a predominance of lamellar and flake-like forms and volumetric isometric aggregates (up to 70 μm). The pore space is mainly represented by intermicroaggregate with a diameter of up to 5 μm , interultramicroaggregate with a width of up to 1 micron, interparticle anisometric and slit-like micropores, the width of the latter is 0.2 μm . The average pore size determined by electron micrography is 0.23 μm , porosity is 39.2%. Based on the analysis of electronic photographs of structures, the microstructure model of the studied bentonite according to the classification presented in [14] should be attributed to cellular with elements of a spongy structure.

4. Conclusion

The article studies the granulometric, mineralogical, chemical composition and structure of bentonite of the Nurlat deposit of the Republic of Tatarstan. The obtained data, taking into account the predominant content of layered silicates in the composition of the studied bentonite, provides the possibility of its use after modification to obtain inexpensive natural adsorbents. Tatarstan bentonite is also suitable for use as a component of molding mixtures in foundry production, a binding agent in metallurgy for pelletizing iron ore concentrate and expanded clay.

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