*Article*

# Experimental Study of Montmorillonite Structure and Transformation of its Properties under the Treatment of Inorganic Acid Solutions

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**Abstract:** The paper discusses the mechanism of montmorillonite structure alteration and bentonites properties modification (on the example of samples from clay deposit Taganka, Kazakhstan) due to the thermochemical treatment (treatment with inorganic acid solutions at different temperatures, concentrations and reaction times). With the use of the suit of methods certain processes were distinguished: transformation of montmorillonite structure, which appears in the leaching of interlayer and octahedral cations, protonation of the interlayer and OH groups at octahedral sheets. Changes in the structure of the 2:1 layer of montmorillonite and its interlayer result in significant changes in the properties – reduction of cation exchange capacity and an increase of specific surface area. The results of the work showed that bentonite clays retain a significant portion of its adsorption properties even after the long term and intense thermochemical treatment (6M HNO3, 60°C, 108 hours)

**Keywords:** engineering barriers; bentonite clays; thermochemical treatments; montmorillonite; structure modification; adsorption properties

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## 1. Introduction

Clay minerals are widely used in various industries, including nuclear power and particularly radioactive waste management as the component of barrier systems for wastes disposal. These systems are used for radioactive waste depositories of different activity and intended to provide storage safety for several hundreds or thousands years due to the high adsorption capacity and low water permeability [1-3].

The main component of the engineered barriers is bentonite, which contains 70-95% of montmorillonite, a dioctahedral specie of the smectite mineral group. Montmorillonite is a 2:1 type hydrous aluminosilicate with the octahedral sheet "sandwiched" between two tetrahedral sheets. Cation substitution in tetrahedral and mostly in octahedral sites provides negative layer charge about 0.2-0.5eV. Layer charge is counterbalanced by interlayer cations ($Na^+$, $Ca^{2+}$, $Mg^{2+}$, etc.) and water molecules [4-8] that provides adsorption sites on the inner and outer surface of the crystal. These particularities of montmorillonite structure determine specific properties of bentonite clays, especially high adsorption capacity towards heavy metals, such as cesium, plutonium and others which are commonly found in radioactive wastes.

However, in response to the long term usage of bentonite clays in engineered barrier systems, they can be affected by aggressive fluids, decreasing barriers insulating properties. The aim of this

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study was to evaluate the mechanism of montmorillonite transformation under the treatment with acid solutions and its influence on bentonite properties.

## 2. Materials and Methods

Fine bentonite <1 μm fractions separated from bentonites from Mukhortala (Buriatia, sample Mt-M) and Taganskoye (Kazakhstan, sample named Mt-T) deposits were used for this study. Montmorillonite content is 70% for Mt-T sample and 97% for Mt-M sample. Impurities in Mt-M sample were presented by 20-30% of opal C/A, which could not be removed with the sedimentation technique, and quartz (about 2-3%) in Mt-T sample.

The experiments were carried out with HCl solutions (0.125M, 0.25M, 0.5M, 1M, 3M) at room temperature for 7 days (Mt-T1 и Mt-M samples) and with 1M $HNO_3$ solutions (Mt-T2 sample) at 50°C for 12, 36, 50 and 108 hours. Montmorillonite samples from Taganskoye deposit, used in the experiment, have quite different composition and were named Mt-T1 for the experiment with HCl acid and Mt-T2 for the experiment with $HNO_3$ acid.

Initial and modified samples were analyzed with a suit of methods. X-ray diffraction patterns were obtained with Rigaku X-ray diffractometer Ultima-IV, acquired under the funding of Moscow State University Development Program (Cu-Kα radiaton, semiconductor 1D detector D/Tex-Ultra, scan range 3-65°2θ, scan speed 5°/min, step – 0.02°2θ). Partially oriented specimens were prepared by pressing powder in a sample holder.

Excessive pressure and surface leveling leads to partial orientation of the montmorillonite particles in the sample plane. We did not succeed to prepare samples with a good degree of particle orientation from drops of aqueous suspensions because some samples were significantly modified after the treatment so that they could not form thin films onto a glass surface. The results were analyzed according [4, 5, 9].

IR absorption spectra were obtained using Bruker FTIR spectrometer Vertex 80v equipped by DTGS detector and KBr-splitter. Recordings were performed under vacuum evacuation in the wavelength range 4000-400 $cm^{-1}$, with a resolution of 4 $cm^{-1}$. Samples were prepared as pressed KBr-tablets which firstly were measured at a room humidity and then after heating for 24 hours at 150°C. Processing of the results was performed using OPUS 7.0 software, the baseline correction is performed automatically by Concave Rubberband.

Natural montmorillonites (MM-M, MM-T1, MM-T2), as well as some samples after treatment, were selected by the results of X-ray diffraction studies (MM-M – 3.0M HCl; MM-T1 – 0.25 and 0.5M HCl; 12 and 108 hours) for the further investigation by high-resolution transmission electron microscopy (HRTEM) using JEM-2100 with an attachment for X-ray energy dispersive analysis of X-Max.

Specific surface area of samples eavaluation was carried out using the Analyzer Quadrasorb SI/Kr. Adsorption was performed at the liquid nitrogen temperature (77.35 K). Nitrogen with a purity of 99.999% served as an adsorbate. Helium grade 6.0 (99.9999%) was used for the volume calibration of the measuring cells. Calculation was carried out by the BET multiple-point isotherm in the range of P/Ps from 0.05 to 0.30. Samples were pre-dried under vacuum at 100°C.

Cation exchange capacity was determined by triethylenetetramine copper complex $[Cu(Trien)]^{2+}$ adsorption method [10].

## 3. Results and Discussions

### *Transformation of the montmorillonite structure under acid treatment.*

Considerable crystal-chemical transformations, in particular, changes of montmorillonite micromorphology and adsorption characteristics were detected under the treatment with hydrochloric and nitric acid solutions. A variety of processes modifying structure and properties of montmorillonite particles were observed during the treatment with inorganic acid solutions: dissolution of carbonates and feldspar, destruction of the most defective phyllosilicate phases (e.g., nanosized smectites), removal of cations from the interlayer spacing, substitution of interlayer

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cations with oxonium ion, leaching of the octahedral cations, and finally the complete destruction of the structure.

Studied montmorillonite samples are characterized by the heterogenous composition of the interlayer cations $Ca^{2+}$ and $Mg^{2+}$ for the MM-M sample (d001 = 15.3Å), and $Ca^{2+}$, $Mg^{2+}$and $Na^{+}$ (d001 = 13.7Å and d001 = 13.9Å, respectively) for Mt-T1 and Mt-T2 samples [11]. The presence of $Na^{+}$ cations in the exchangeable cations composition in Mt-T samples is determined by complicated shape of the (001) profile with a peak maximum at 13.7Å (Fig. 1, Tab. 1). Also, this fact was confirmed by the EDX data (Tab. 2), and described in previous studies of the bentonites from Taganskoye deposit [12, 13].

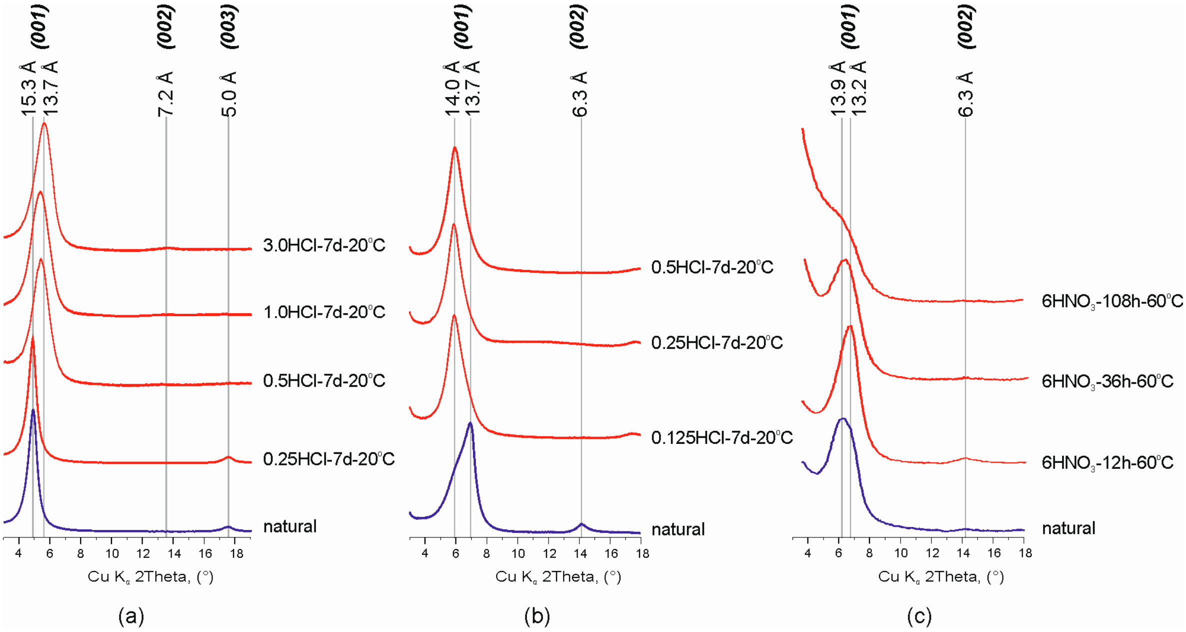


**Figure 1.** Fragments of the X-ray diffraction patterns of natural and treated montmorillonites: (a) MM-M; (**b**), (**c**) - MM-T. 3.0HCl, $7HNO_3$ – type of acid and concentration, 7d (days), 12h (hours) – time of treatment, 20°C, 90°C – temperature of treatment.

Treatment of Mt-M sample with hydrochloric acid solution with various concentrations leads to partial protonation of interlayer, which is observed by a decrease of d00l values and changes of basal reflections series from d001 = 15.3Å, d003 = 5.0Å, d005 = 3.0Å to d001 = 13.7Å. d002 = 7.2Å, d003 = 4.8Å, d004 = 3.6Å (Fig. 1). Such changes in XRD patterns occur due to the leaching of the interlayer cations ($Ca^{2+}$ and $Mg^{2+}$) and partial protonation of interlayer space, i.e. substitution of interlayer cations with oxonium ion [14, 15]. However many authors noted that protonation of Ca-Mg montmorillonite is much faster than Na-forms [12].

Profile alignment of basal reflections (001) and displacement of maximum 13.7Å to 14.0Å was observed after treatment of MM-T1 sample with hydrochloric solution. Complex profile shape of (001) reflection indicates the presence of two possible montmorillonite phases with different interlayer in the sample. This was also found by other researchers of Taganskoye montmorillonite deposit [12]. Since any other impurities except quartz were not found in this sample, the described change in the XRD patterns can be attributed to the partial destruction (dissolution) of the most defective and probably nano-scale particles of Na-montmorillonite.

Treatment of Mt-T sample with 1M $HNO_3$ solution for 12 hours leads to a displacement of the (001) reflex from 13.9Å to 13.2Å with an increase of its intensity. This fact is explained by the dissolution of the defective part of the montmorillonite and enhancement of the interlayer ordering by partial leaching of $Ca^{2+}$ and $Mg^{2+}$ cations. Further treatment of the sample with nitric acid solution reduces the layer stacking ordering degree and disintegrates 2:1 layer structure of montmorillonite. In XRD patterns, the described process is manifested by a decrease in the peaks intensities and broadening of the basal reflections until the complete disappearance except (001) reflection.

Displacement of the (001) reflection back to 13.9Å after the 36 and 108 hours of treatment can be explained by the octahedral cations leaching and their appearance in the interlayer space of montmorillonite.

**Table 1.** Changes of the structural parameters, textural and adsorption characteristics of montmorillonites due to acid activation

| **Sample** | **Treatment** | | | **Interlayer space** d001(Å) | **Particle thickness,** nm h(00l) (CSR) | **Number of layers,** N | **Specific surface area,** SBET (m2/g) | **Total pore value,** VΣ (sm$^3$/g) | **Cation exchange capacity,** CEC (mg*eq/100g) |
|---|---|---|---|---|---|---|---|---|---|
| | acid | T, °C | time | | | | | | |
| Mukhortala (MM) | - | | | 15.3 | 10.7 | 7 | 77 | 0.211 | 46 |
| | 0.25 HCl | 20°C | 7 d | 15.3 | 12.2 | 8 | 79 | 0.219 | 43 |
| | 0.5 HCl | 20°C | 7 d | 14.0 | 7.0 | 5 | 92 | 0.243 | - |
| | 1.0 HCl | 20°C | 7 d | 14.0 | 5.6 | 4 | 95 | 0.256 | 49 |
| | 3.0 HCl | 20°C | 7 d | 13.7 | 5.5 | 4 | 101 | 0.328 | 64 |
| Taganskoe (MM-T1) | - | | | 13.7 | 9.6 | 7 | 42 | 0.074 | |
| | 0.125 HCl | 20°C | 7 d | 14.0 | 7.0 | 5 | 45 | 0.084 | 65 |
| | 0.25 HCl | 20°C | 7 d | 14.0 | 7.0 | 5 | 50 | 0.095 | 64 |
| | 0.5 HCl | 20°C | 7 d | 14.0 | 5.6 | 4 | 51 | 0.083 | 70 |
| Taganskoe (MM-T2) | - | | | 13.7 | 8.2 | 6 | 67 | 0.085 | 86 |
| | 1 HNO3 | 60°C | 12 h | 14.0 | 7.0 | 5 | 110 | 0.114 | 58 |
| | 1 HNO3 | 60°C | 36 h | 14.0 | 7.0 | 5 | 191 | 0.192 | 56 |
| | 1 HNO3 | 60°C | 102 h | 13.8 | 5.5 | 4 | 301 | 0.353 | 40 |

0.25 HCl, 1 HNO3 – concentration in molls, 7 d – 7 days, 12h – 12 hours

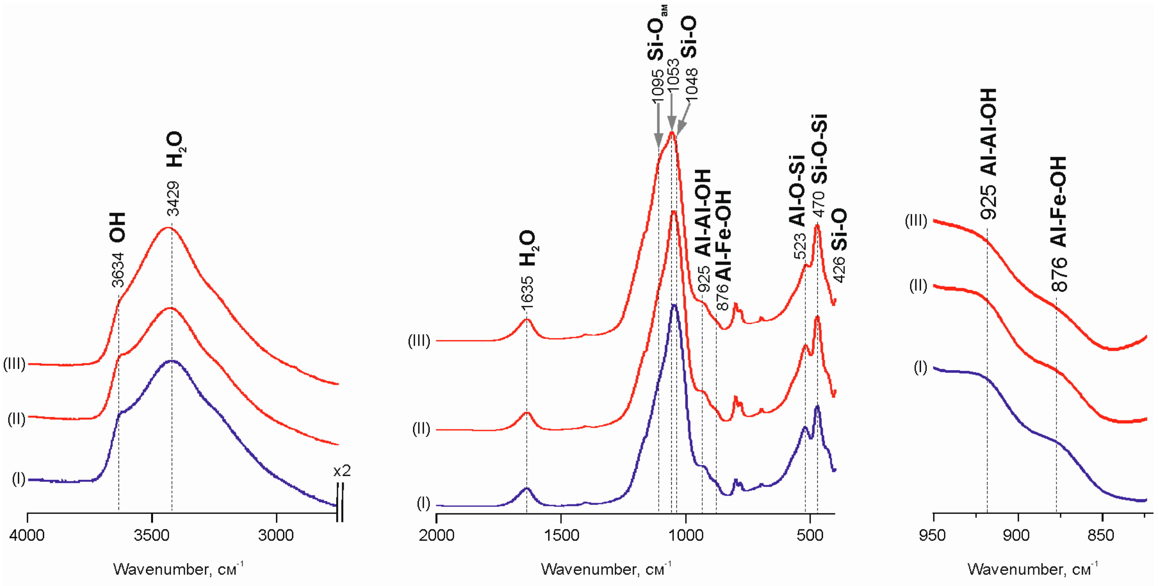
**Table 2.** Chemical composition of natural and acid treated montmorillonites according to energy-dispersive analysis.

| Sample | Particle characteristic | Content. wt. % | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $Na_2O$ | $K_2O$ |
| MM-T2 | Large particles and nano-sized phases | 62.3 | 21.0 | 9.8 | 3.7 | 1.7 | 0.6 | 0.8 |
| | Nano-sized phases | 63.6 | 20.0 | 10.4 | 4.0 | 2.0 | - | - |
| | 12 hours/ $HNO_3$ | 64.1 | 22.7 | 8.1 | 3.4 | 1.7 | - | - |
| | 108 hours/ $HNO_3$ | 75.5 | 15.6 | 4.7 | 2.7 | 1.5 | - | - |
| MM-T1 | Large particles and nano-sized phases | 64.7 | 27.0 | 1.2 | 4.2 | 0.9 | 1.2 | 0.8 |
| | Nano-sized phases | 66.0 | 25.2 | - | 4.4 | 1.4 | 2.3 | 0.7 |
| | 0.25M HCl. 7 days | 67.0 | 26.4 | 2.3 | 3.4 | 0.9 | - | - |
| | 0.5M HCl. 7 days | 69.6 | 24.9 | 1.4 | 3.1 | 1.0 | - | - |
| MM-M | Initial | 65.4 | 25.4 | 3.0 | 2.7 | 1.4 | 0.8 | 1.0 |
| | 3.0M HCl. 7 days | 69.9 | 24.2 | 2.7 | 2.4 | 0.8 | - | - |

Thus, the XRD can provide the information not only about the dissolution of themost defective part of montmorillonite, leaching of interlayer cations and its protonation, but also about leaching of cations from octahedral sites and their further appearances in the interlayer. Moreover, Ca-Mg-montmorillonites are less resistant to the inorganic acid solutions, while the presence of Na+ cations prevents the interlayer protonation.

Also, the changes in the coherent scattering domains (CSD) sizes along the c-axis were calculated in accordance with the Scherrer equation for the 001 reflection of natural and modified montmorillonites (Tab. 1). In general, the size of CSD along the c-axis corresponds with the crystallite thickness [16]. The average crystalite thicknesses of the samples equals 10.7 nm which corresponds to 7 layers (7N), 9.6 nm (7N), 8.2 nm (6N) for natural Mt-M, MtM-T1 and Mt- T2 samples respectively, and to 5.5-5.6 nm (4N) for the acid treated montmorillonites.

The decrease of crystallite size can be tracked by an increase of the adsorbed water bands on IR spectra in the range of 4000-2500 $cm^{-1}$ (Fig. 2a) after the treatment of Mt-T2 sample with $HNO_3$ acid for 108 hours. Previous studies of Mt-M and Mt-T1 samples treated with HCl acid [13] showed the reduction of bands intensity at 841-845 $cm^{-1}$ (Al-Mg-OH), 882 $cm^{-1}$ (Al-Fe-OH) and 914-926 $cm^{-1}$ (Al-Al -OH), which indicates the leaching of $Al^{3+}$, $Mg^{2+}$ and $Fe^{3+}$ cations from the octahedral sites [14, 17, 18, 19, 20]. Reduction of the band intensities at 925 and 876 cm-1 is shown at Fig. 2c. It corresponds to Al-Al-OH and Al-Fe-OH vibrations in the structure of octahedral sheet of montmorillonite (Mt-T2 sample) during the treatment with the nitric acid. It may indicate a leaching of $Fe^{3+}$ and $Al^{3+}$ from the octahedral sites.



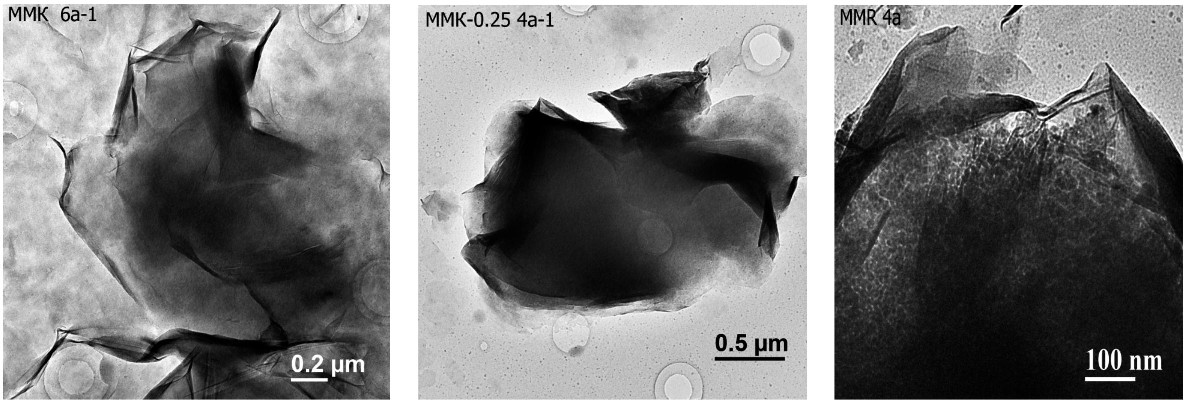
(a) (b) (c)

**Figure 2.** Areas of interest on MM-T IR spectra before and after treatment with 1 M HNO3 during 12 hours (I). 36 hours (II) and 108 hours (III): (**a**) and (**b**) the characteristic part of spectrum; (**c**) a magnified part of the spectra.

Leaching of the octahedral cations leads to modifications of the interaction between the octahedral and tetrahedral sheets in the 2:1 layer and, as a result, to the partial destruction of octahedral sheets. Changes in Si-O-Si band profile within the range of 1100-1050 $cm^{-1}$ (Fig. 2b) indicates the transformation of interaction within the tetrahedral sheet. In particular, a maximum displacement in natural sample from 1050 $cm^{-1}$ to 1095 $cm^{-1}$ after the treating it with 1M $HNO_3$ for 108 hours indicates the increase of amorphous silica content due to partial destruction of the tetrahedral sheet.

Transmission electron microscopy (TEM) allows to obtain data at the level of lattice, and helps to estimate structural transformation of montmorillonite, properties of surface and interactions between the layers during its treatment with inorganic acid solutions, and changes in montmorillonite particles chemical composition [21]. According to TEM analysis, natural Mt-T1 and Mt-T2 montmorillonites are represented by two groups, which differ in particle size: 1) particles with the size of 1-2 microns and 2) nano-particles with a size of 20-80 nm, which are located on the surface of larger particles and fill the space between them (Fig. 3a). Treatment with hydrochloric acid with lower concentrations, as well as the treatment with nitric acid for a shorter periods results in dissolution of nanoparticles of montmorillonite and its disappearance at TEM images (Fig. 3b).

Its important to note that chemical composition of two identified phases of montmorillonite is different. The nanoscale phase of Mt-T2 sample (Tab. 2) is characterized by a higher content of Ca and Na, while the nanoscale phase of Mt-T1 sample have a higher content of Fe, Mg and Ca. So, the major part of Na and Ca cations is attributed to the interlayer, while the most part of Mg and Fe cations is located in the octahedral sheet due to the isomorphic substitution of Al. In general, montmorillonite particles of Mt-M sample are characterized by smoother surface and a lack of nano-sized silica phase (Fig. 3c).



(a) (b) (c)

**Figure 3.** Electron microscopic images: (**a**) natural particles from the sample MM-T; (**b**) treated with 0.25 M HCl; (**c**) natural sample MM-M.

Higher content of Na and K in the in sample is associated with the presence of a small amount of NaCl and KCl phases in natural Mt-M samples, which dissolved during the treatment with hydrochloric acid solutions. Identified by XRD analysis, nano-sized (5-20 nm) opal particles partially or fully coat the surface of lamellar particles of montmorillonite and probably penetrate between the individual layers of packs montmorillonite (Fig. 4c).

Studied samples of the natural montmorillonites are characterized by the peculiar particle morphology, typical for montmorillonites of different genesis, and by a wide spread of welted edges, which can be useful for obtaining pictures of the lattices (Fig. 4). Images obtained from edges of natural montmorillonite (Mt-T2 sample) show the lattice stripes that correspond to the basal planes (Fig. 4a, b). The width of the areas with lattice stripes is about 23-32 nm. The value of the interlayer space for different particles varies within the range from 10.5Å to 11.8 – 12.3Å.

The lattice stripes of different particles can be pulled simultaneously, maintaining a noticeable distance between the adjacent bands or showing some curving of the surface, which indicates only a small change of interlayer space along the layers. Moreover, there are areas of the image with two-dimensional lattice stripes (Fig. 4b). Basal lattice stripes are crossed by lattice stripes with interlayer space of 4.5 Å, corresponding to planes (020) and indicating local manifestations of coherence in stacking of adjacent layers.

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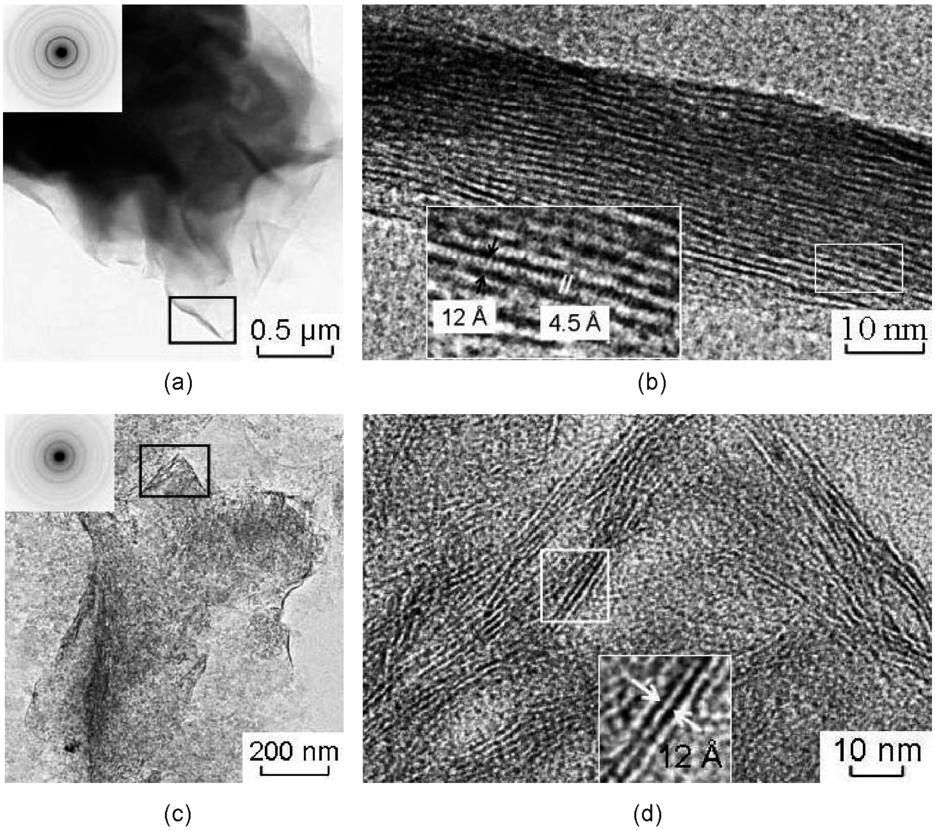
Microaggregate surface of Mt-T2 sample became uneven as a result of the treatment with HNO3 acid for 108 hours. This effect can be seen only at some fragments of the images with folded edges with typical parallel basal lattice stripes from planes (00l). It correlates to the small packs of 2-3 layers (Fig. 4b) less than 25 nm long. The interlayer spacing 12-14 Å, indicates the presence of initial montmorillonite. The observed pattern of distribution of the basal lattice stripes reflects the nano-level changes in the surface morphology of montmorillonite. It implies an existence of a thin packages of layers where the planes (00l) are arranged perpendicular to the surface of the particles. This effect, in particular, leads to an increase of its surface and the occurrence of active sites for the selective sorption of heavy metals and radionuclides.



(a) (b)

(c) (d)

**Figure 4.** Electron microscopic images of natural montmorillonite particles (**a, b**), and treated with 1M HNO3 for 108 hours (**c, d**). Microdiffraction figures are lacated at enlarged areas. b and d - high resolution images from the folded edge of the montmorillonite particles (areas location are shown as black rectangles in Figures **a** and **c**, respectively).

*Transformation of montmorillonite adsorption properties under the acid treatment.*

Specific surface area (BET) and cation exchange capacity (CEC) can be qualified as characteristics of adsorption properties of bentonite clays. Commonly specific surface area (BET) values are in direct relationship with CEC value [22]. Increasing of BET value leads to increasing of CEC value and vice versa. In most cases, the above is true for natural soils with different mineral composition [16]. However, the ratio of these indexes for montmorillonites of different composition may be in a more complex relationship. This dependence can be clearly seen in the Table 1 as an increase of specific surface area and cation exchange capacity decrease due to the acid treatment.

Coherent scattering domain sizes are commonly used to analyze the size of crystallites [16, 23, 24, 25]. There is a cumulative index of physical-chemical activity of the most clay minerals which have correlations with specific surface area and adsorption characteristics. Thus, reduction of crystallite size should lead to an increase of specific surface area, which is shown in the course of the study (Table. 1).

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At the same time, an increase of the specific surface area appears mostly in the samples, which have the greatest structural changes. Thus, in the montmorillonite sample from Taganskoye deposit, treated with $HNO_3$ for a long period, the increase of the specific surface area was 301 $m^2/g$ compared to 67 $m^2/g$ in the natural sample. Also, considerable changes were observed in the sample with montmorillonite from Mukhortala deposit (from 77 to 101 $m^2/g$, respectively).

The average pore size in all samples is approximately 5 nm and is constant during the experiments, while the total pore volume have been changed slightly for Mt-M and Mt-T1 samples and largely for Mt-T2 sample. This fact cannot be related only to the size decrease. In this way, observed increasing of specific surface area, as well as the total pore volume is related to the formation of porous structure during modification of montmorillonites under the acid treatment.

As a result of the treatment, a regular change is observed in chemical composition of montmorillonite (Tab. 2). First of all, the reduction of Ca, Mg, Fe, Al and the increase of Si content is found in all samples after dissolving of the nano-sized phases of montmorillonite from Taganskoye deposit. The most significant changes were found in Mt-T2 sample, treated with $HNO_3$ acid solution for 108 hours. The increase of Si content in montmorillonite samples, subjected to the intensive acid treatment, is connected with subsidence of amorphous silica, formed during the destruction of tetrahedral sheets of 2:1 layers on the particle surface and its accumulation in the micropores.

Protonation of Al bond pairs in octahedron transforms it from 4-coordination to 6-coordination [26], and leads to the modification of octahedral and tetrahedral sheets, and to an appearance of micropores, simultaneously decreasing the number of octahedral cations. Changes in the layer stacking and particles micromorphology results in mesopore formation [15, 27]. Structural transformations are shown simplified in Fig. 5. Thus, there is an increase of specific surface area and pore space, capable of large cations sorption, e.g., Cs.

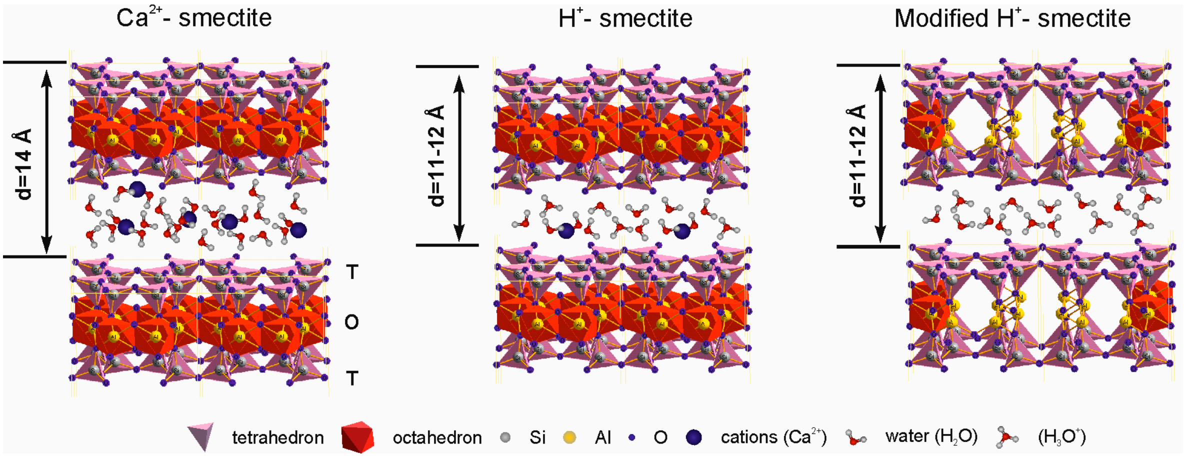

**Figure 5.** Schematic picture representing the structural changes in natural montmorillonite during the treatment with inorganic acid solutions: (**a**) natural Ca-montmorillonite; (**b**) partial protonation of interlayer space; (**c**) full protonation of interlayer space (H-smectite), and protonation of the OH-groups of the octahedral sheet and Al coordination change.

Critical values for describing the concept of "micropores", "mesopores" and "macropores" vary in classifications developed for different science approaches. In engineering geology, for example, mesopore sizes are in the range of 10 to 1000 μm and micropores are from 0.1 to 10 μm [28]. V. Osipov and V. Sokolov in their morphometric investigations of soil microstructures with different composition [22] detailed the previously proposed classification of pore sizes. They divided micropores into thin (0.1-10 μm), small (1-10 μm) and large (10-100 μm) ones, suggesting the lower limit for macropores as 100 μm.

There are other classifications to consider, for example, the International Union for Pure and Applied Chemistry (the IUPAC) recommended to distinguish pores size into macropores (50 nm), mesopores (2 to 50 nm) and micropores (up to 2 nm) [29, 30, 31]. The micropores are conventionally divided into thin ultramicropores (less than 0.7 nm) and supermicropores, having an intermediate size between ultramicropore and mesopores.

In fact, all the pores in montmorillonite, referred above and predominantly involved in the adsorption, and have the size not larger than 6-9 nm for mesopores and 1-3 nm for micropores [32]. The average pore size measured in natural and modified montmorillonites is about 5 nm, which corresponds to interparticle pores, according to Osipov and Sokolov [22]. At the same time, acid treatment, as shown above, leads to appearance of pores in the structure of the layer (micropores) by partial leaching of octahedral cations, protonation of OH-groups and changes in coordination of Al3+. The above process does not lead to an increase of an average pore size, however it results in increasing of the total pore volume (Table 1).

Thus, the measured cation exchange capacity value (CEC) decreases from 86 meq/100 g in natural bentonite clay, to 40 meq/100 g in bentonite samples with the longest time of the treatment by $HNO_3$ solutions during 108 hours (Table 1). Such a decrease of CEC under the treatment with inorganic acid solutions (e.g, HCl and $H_2SO_4$) was described by other researchers [33]. Cation exchange capacity of bentonite clays is connected not only with montmorillonite content, but also with the particularities of its structure. As a result, treatment with inorganic acid solutions leads to a layer charge reduction due to leaching of the octahedral cations, and destruction of the structure. All of which leads to a decrease in the cation exchange capacity. In addition, amorphous silica, appeared in result of the destruction of tetrahedral sheets, can settle on the surface of montmorillonite particles and reduce its exchange capacity.

A lot of attention in the works devoted to the acid treatment of natural bentonite clay was paid to the issues of activation – improving the properties of modified clays in comparison with natural clays [33, 34, 35]. An increase of specific surface area and pore volume is observed in the course of conducted experiments (Table 1). Leaching of the cations from interlayer space and octahedral positions results in a modification of a layer charge and particles in general, this in turn affects the interaction of the individual particles between each other. As a result, the destruction of large aggregates, the restructuring of smaller ones, the appearance of uneven surface, the appearance of micropores on the site of octahedral grid, takes place. All the processes described above result in the increasing of the total pore size and surface area. However, opportunities for cation exchange and its value are reduced, due to a layer charge modification and protonation of interlayer space (Table 1).

## 5. Conclusions

The study concludes that an interlayer modification occurs even at early stages of the treatment with HCl and $HNO_3$ solutions. This modification involves partial substitution of interlayer cations, especially Ca and Mg, and its partial protonation. Natural nano-sized smectites and the most defective phase are completely dissolved in natural montmorillonite samples after acidic treatment as the least stable components.

Further treatment of montmorillonite structure with inorganic acid solutions (with increasing concentration and exposure period) leads to further modification of its structure, accompanied by intense leaching of cations from the octahedral positions and partial penetration of leached octahedral cations to interlayer space. These transformations lead to partial protonation of OH-groups, partial destruction of the octahedral sheets, and modification of the interaction between tetrahedral and octahedral sheets, changing a layer charge and the nature of interaction between adjacent layers, and partial amorphization of tetrahedral sheets.

As a result of the changes described above, specific surface area and total pore volume increase significantly, while the cation exchange capacity decreases. However, adsorption capacity of the bentonite clays, treated with acids solutions, still remains high due to considerable increase in specific surface area and the micropores appearance.

Modification of structural and adsorption characteristics with the acid treatment can be used to simulate behavior of the engineering barrier properties for depositaries of radioactive and industrial wastes.

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**Author Contributions:**

Victoria V. Krupskaya prepared material, conceived and designed the experiments, wrote the paper, Sergey V. Zakusin performed the experiments by HNO3 treatment, measured samples by x-ray diffraction, CEC, Ekaterina A. Tyupina analyzed specific surface area and porosity, Olga V. Dorzhieva collected daya by infrared spectroscopy, Anatoliy P. Zhukhlistov studied samples by electron microscopy, Maria N. Timofeeva performed the experiments by HCl treatment acid treatment and Petr E. Belousov prepared <1 μm fractions, measured CEC

**Conflicts of Interest:**

The authors declare no conflict of interest.

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