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Optimization of the Process Acid Activation of Bentonite

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ABSTRACT

Montmorillonite is the main component of bentonite clays-natural alum inosilicates. Due to the specific structure of the crystal lattice framework and the developed interfacial surface, montmorillonite clays have excellent adsorption and ion exchange properties. The fields of application of bentonite clays are expanding due to the addition of new properties to them as a result of various types of activation. One of the most effective types of exposure is acid treatment. Acid-activated montmorillonites are used as acid catalysts for various reactions. Acid activation of calcium and sodium montmorillonites of the Navbakhor field with HCl solution was carried out. It is shown that as a result of acid treatment, the porous structure develops due to the removal of both interlayer cations (Na^+, Ca^{2+}) and cations of the octahedral layer (Al^{3+}, Fe^{3+}, Mg^{2+}). The textural characteristics and strength properties of molded composites based on acid-activated montmorillonites are investigated. The nature of changes in the specific surface area, pore volume, and pore volume distribution over the strength dimensions of samples with varying montmorillonite content in the composition is analyzed. It was found that composite materials containing 80% by weight of bentonite have a highly developed monodisperse porous structure in the pore size range of 1.8 nm and a specific surface area of 290-330 m2 / g. At the same time, the strength of the composites reaches 100-115 kg / cm2, which is sufficient for industrial carriers.

The purpose of this study is to identify the optimal conditions for acid activation and to study the textural characteristics of bentonite from the Navbakhor field.

KEYWORDS

bentonite, activation, processing, modification, optimization, texture characteristics.

INTRODUCTION

Bentonite clays are good inexpensive sorbents for various substances, such as heavy metal ions [1], organic dyes [2]. Sorption occurs due to the presence in the composition of clays of layered silicates (phyllosilicates, smectites), such as montmorillonite, palygorskite, illite. Acid activation of bentonite clay is a common method for producing porous sorbents for organic and inorganic substances [5, 6], acid catalysts [4, 7]. In addition, acid activation with the preservation of the layered structure is necessary as an initial stage of chemical modification of phyllosilicates [8]. It should be noted that activation should be cost-effective. Preference is given, if possible, to dilute acid solutions with relatively low activation time temperatures. It is also necessary to take into account that washing clay from excess acid is a rather time-consuming process, so in most cases it is desirable to calculate the optimal concentration of acid in advance, taking into account the chemical composition of natural clay, the presence of impurities. Enough works have been devoted to the study of the physical and chemical parameters of clays of various deposits activated by various acids [9-14]. Much attention in the literature is paid to natural frame aluminosilicates, especially zeolites. These materials have a negatively charged three-dimensional aluminosilicate framework. In the gaps of the framework there are hydrated positive ions of alkali metals, which compensate for the charge of the framework, and water molecules. When the zeolites are heated, water is released from them, and adsorption cavities are formed. The fields of application of bentonite clays will expand due to the addition of new properties to them as a result of various types of activation [7-11]. One of the most effective types of treatment is acid treatment [5, 10-12]. According to the nature and strength of the effect on the crystal structure of

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montmorillonites, the acids can be divided into three groups [13-18]. The first group consists of organic and dilute mineral acids, which extract only exchange cations from the montmorillonite lattice into the solution and do not affect the aluminosilicate layers and the order of their packaging. The porous structure remains practically unchanged: the specific surface area is 60-70 m^2 / g, the maximum specific volume of the sorption space is about 0.1 cm^3/g. The second group – solutions of mineral acids of medium concentrations (2-4 N). Under the influence of these acids, exchange (Na^+, Ca^{2+}) and octahedral cations (Al^{3+}, Fe^{3+}, Mg^{2+}) are extracted into the solution, and the aluminum-silicon packages are ordered in the basal direction, but the structure of the aluminum-silicate layers is not disturbed. As a result, the pore space of montmorillonites develops significantly, $S_{specific}$ increases to 330 m^2 / g, V_{pore} to 0.5 cm^3/g. Concentrated mineral acids (more than 4 n.) belong to the third group, which destroy the crystal structure of montmorillonite, wash out all cations except silicon, resulting in the formation of highly porous silicon oxide [14]. Acid-activated montmorillonites are widely used as acid catalysts for such reactions as cracking, isomerization, alkylation, acetylation, dimerization and polymerization of unsaturated hydrocarbons, hydrogenation and dehydrogenation of hydrocarbons, dehydration of alcohols, hydration of olefins, hydro treatment, formation of esters, etc. [7, 15-19]. In addition, recently, worldwide interest has increased in the use of natural minerals and composites based on them, which can compete with traditional SiO_2, Al_2O_3, and zeolites, both at a lower price and due to higher performance characteristics of the material.

The proposed classifications of porous bodies are based mainly on experimental data on the pore size or their fractional composition. They do not reflect the origin and structure of porous bodies [20-21]. M. M. Dubinin, as is known, divides the pores as follows (according to the effective radius):

- macropores with r ef>100 nm;

- mesopores with 1.5 <r ef<100nm;
- micropores with r ef<1.5 nm.

Of particular interest is the characterization of the microporous structure of adsorbents in the case of activated adsorption [22-25]. It should be recalled that according to the classification of M. M. Dubinin, the effective radius of micropores is within the range of r≤ 1.6...1.8 nm. In a number of studies, micropores are associated with formations with r<0.6...0.7 nm [25-26]. Larger micropores, the so-called supermicropores, are represented by the transition region between the micro and mesopores proper [24].

EXPERIMENTAL PART

The enriched fraction of Navbakhor bentonite [27-32] was used for the work, which was obtained as follows: a suspension of 30 g of native clay in 300 ml of distilled water was prepared with careful mixing; in this case, the particles of all the minerals that make up the clay were divided into fractions. The resulting suspension was left for a day. Further, the enriched clay fraction was separated by centrifugation at 8000 rpm for 5 minutes. The resulting fraction was dried in air for 12 hours, then at a temperature of 65°C - for 12 hours. Activation was carried out with hydrochloric acid concentrations of 0.5 M and 2.0 M at a temperature of 88 °C for two hours. After activation, the clay suspension was immediately cooled by adding 200 ml of distilled water. Then the clay was washed several times with distilled water, centrifuged and dried for 12 hours at room temperature, then for 12 hours at 65°C, ground in a mortar and stored in plastic containers.

Mechanical activation of bentonites during the grinding process makes it possible to increase the overall activity of the particles by reducing their size, increasing the overall surface, achieving a more compact shape, and deep transformations in the crystal structure of the material. To study the parameters of clay activation, a planetary centrifugal mill-activator AGO-2 was used with varying activation time from 10 to 180 seconds, in order to achieve the maximum degree of grinding of bentonite clays at their maximum activity, while preserving the features of the crystal chemical structure and the absence of aggregation.

Mechanical activation (MA) in the AGO–2 planetary-centrifugal mill was carried out at a mass ratio of clay and grinding media of 1:2 (for bentonite clays- 30-180 seconds), at a constant speed of $\upsilon_{об}$=1500 rpm. In the process of clay activation, their quality was evaluated by geometric parameters and technological properties. The technological properties of clays were evaluated according to various indicators according to national standard. The physical and chemical properties of clays as binders are largely determined by the features of their interaction with water, so the effect of the activation time on the swelling, colloidality and water absorption of clays was studied.

The texture characteristics of the synthesized samples were calculated on the basis of nitrogen adsorption and desorption isotherms at a temperature of 77 K, obtained on the Nova 1200 e Quantachrome volumetric unit. The specific surface area ($S_{уд}$) of the samples was calculated by the BET method, the volume and surface of the micropores (V_{mic}, S_{mic}) – by the t – method according to the adsorption curve, the average diameter of the mesopores (D_{me}) – by the Barrett-Joyner-Halenda method according to the desorption curve, the average diameter of the micropores was determined by the equation: $D_{mi} = 2V_{mi}/S_{up}$. Before measuring the adsorption isotherms, the samples were degassed at 300 °C and a residual pressure of 10-3 mm Hg. For 4 hours. The content of zirconium and zinc in the modified bentonite was determined by laser mass spectrometry using the EMAL-2 device.

The chemical composition of the samples was determined by the X-ray fluorescence method on VRA-30 devices (Carl Zeiss, Germany) and Optima X (MRU, Germany). To determine the average particle size, a sieve analysis was performed using a set of sieves (microns): 0.071, 0.100, 0.160, 0.200, 0.250, and 0.315. Fractionation was carried out on Analysette 3 Spartan Fritsch vibration diffusers (Germany) for 15 min. The masses of the fractions that remained on the sieves were determined on the technical scales of the Gosmeter VLTE-1100 (Russia). The average grain size on the screen and the average particle size in the crushed material were calculated according to the method given in [22].

X-ray diffraction patterns of substances were taken on an X-ray diffract meter Bruker D8 ADVANCE (Germany) in CuKα-radiation; The obtained X-ray diffraction patterns were identified using the VA program with a PDF-2 powder data bank. To quantitatively determine the elemental composition of the samples, we used the energy dispersive X-ray fluorescence method using a Shimadzu EDX 800 HS spectrometer (Japan). The analysis was carried out without taking into account light elements. The concentration of the determined elements was calculated by the method of fundamental parameters using the software of the spectrometer. The relative determination error did not exceed ± 2%.

IR absorption spectra of phosphorus-containing samples were recorded in the region of 400-4000 cm–1 in baseline oil using a Shimadzu FTIR Prestige-21 Fourier spectrometer (Japan) at room temperature. The specific surface area of the samples was determined by the method of low-temperature nitrogen adsorption using the device "Sorbtometer-M" (Russia).

RESULTS AND DISCUSSION

The isotherms of nitrogen adsorption on samples of natural and modified bentonite at 88 K are shown in Fig. 1.

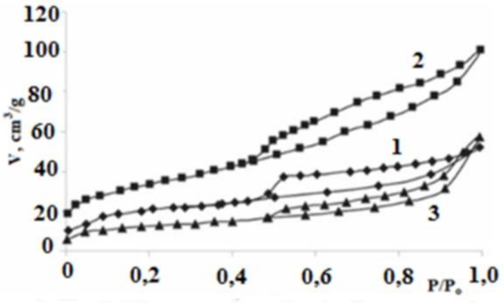

Figure 1. Nitrogen adsorption isotherm on natural (1) and modified (2,3) bentonite at 77 K

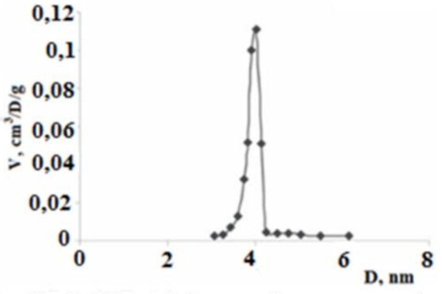

Fig. 2. Differential curve of mesopore volume distribution over the size of natural bentonite

They belong to the type IV isotherms according to the Brunauer classification, which are characterized by a pronounced capillary-condensation hysteresis, indicating the presence of a structure with transition pores. Table 1 shows the experimental results of studying the influence of the nature of the hydrolyzing agent on the texture parameters of the final product. As follows from the table, the volume of micropores in natural clay is approximately 10 % of the total pore volume, the average diameter of mesopores of natural bentonite is 4.02 nm, and the diameter of micropores is 1.0 nm. Figure 2 shows the differential distribution curve of mesopores of natural bentonite by size. From the figure, it can be seen that there is a fairly narrow pore size distribution. It should be noted that, regardless of the nature of the hydrolyzing agent, under experimental conditions, the average mesopore sizes remain almost unchanged, as can be seen from the inflection points on the nitrogen adsorption isotherms in Fig. 1. According to mass spectrometric analysis, the zinc and zirconium content in the obtained samples was 2 and 6 wt. %, respectively. As can be seen from Table 1, during the modification of natural clay with zirconium as a result of hydrolysis with a solution of ammonium hydroxide, the specific surface of the catalyst and the total pore volume increased almost twice, while the volume of micropores and the surface of micropores decreased slightly compared to natural clay, the diameters of micro - and mesopores remained at the same level. When modified with zinc, a similar pattern of changes is observed. Since the modification of the samples in the presence of ammonium hydroxide did not lead to an increase in the volume of micropores, it seems that zirconium and zinc were located in the interlayer space of bentonite in the form of mononuclear ions, and not in the form of polyhydroxocomplexes. In addition, the increase in the total pore volume may be due to the partial destruction of lamellar particles during heat treatment of modified bentonite, while additional formation of mesopores and interparticle voids occurs between disordered fragments of layers due to the removal of adsorbed ammonium ions and water.

Table-1

The chemical composition of the clay samples is shown in the table.

Sample	Native Clay	Enriched clay	Activated 0.5 MHCl clay	Activated 2,0 MHCl clay
Material composition	Content, %			
SiO_2	57,91	60,28	68,79	82,11
Al_2O_3	13,69	12,60	8,41	5.36
Fe_2O_3	10	8,63	7.09	6,38
TiO_2	0,35	1,00	0,73	0,68
Na_2O	1,53	0,40	0,13	0,03
K_2O	1,75	0,89	0,39	0,12
CaO	0,48	0,84	0,28	0,08
MgO	1,84	1,40	0,85	0,21
SO_2	0,75	0,015	0,015	0,04
calcination losses	16,17	12.445	13.345	4.97

Acid activation of bentonite clay with 0.5 M hydrochloric acid solution leads to the removal of calcium and sodium ions by 68.9 and 68.5%, respectively, leaching of magnesium ions occurs by 39.2 %. Activation of bentonite clay with 2.0 M hydrochloric acid solution leads to a decrease in the concentration of calcium ions by 91.8 %, sodium ions by 92.5 %, and magnesium ions are removed by 49 %. Thus, for the almost complete removal of the exchange cations $Ca^{2+}$and Na^{+} from the interlayer space of the bentonite clay under study, it is recommended to activate 2.0 M with hydrochloric acid for 2 hours at a temperature of 88°C. As a result of activation, the layered structure of clay minerals is preserved, which is very important for further modification of the surface of the obtained samples. To obtain a pilling solution, hydrolysis of aluminum and zirconium (zinc) nitrates with solutions of sodium and ammonium carbonates and hydroxides was carried out. For this, a hydrolyzing agent of the same concentration was added to a 0.2 M solution of aluminum and zirconium (zinc) nitrate in a molar ratio Al: Zr (Zn) = 9: 1, the ratio Me: OH was 1: 2. To an aqueous suspension of bentonite with its mass content of 2%, a pilling solution was added in an amount of 10 mol of Me per 1 g of clay with constant stirring. The clay was kept under the mother solution for a day, then centrifuged, dried at 100 °C and calcined at 500 °C.

The resulting oligomeric metal hydroxycations are converted by subsequent heating (modified bentonite was calcined at 400°C, at which the Al2O3 content increased from 14.4 to 18%) into metal oxides, which hold the montmorillonite layers separately from each other, acting like supports in the interlayer space (Fig.1).

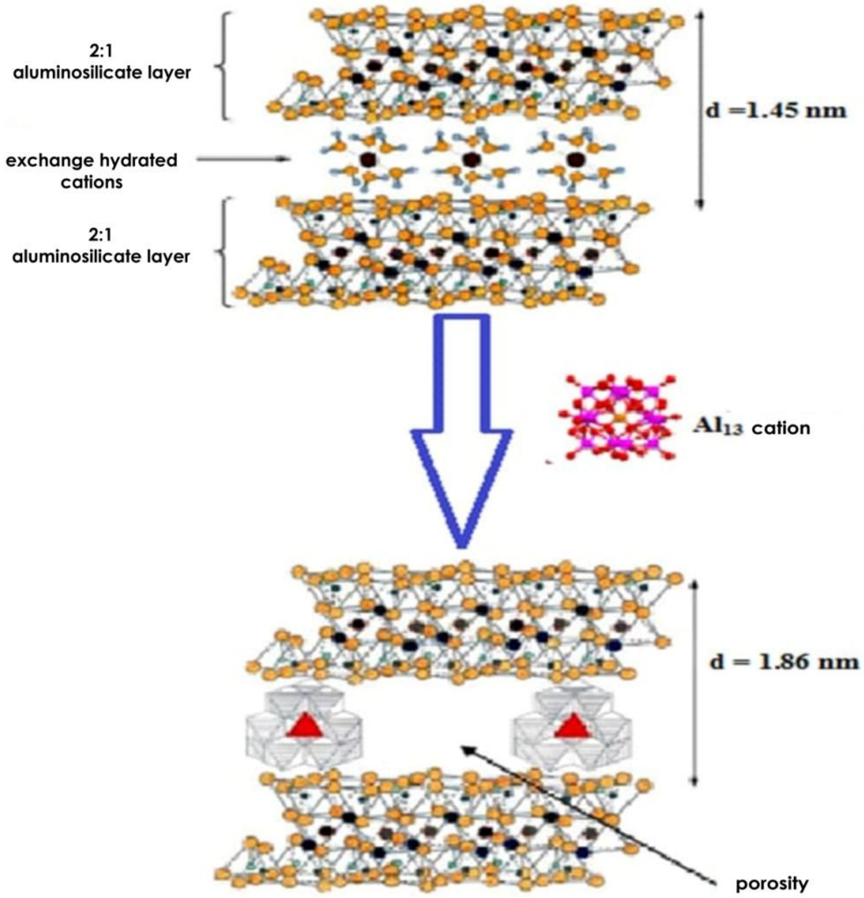

Figure 1. Crystal structure of montmorillonite

The activity of modified bentonite clays depends on the ratio of aluminum and silicon atoms in them. X-rays showed that the modified bentonite clays are a specific chemical compound, such as the mineral montmorillonite, and not a simple mechanical mixture of oxides. The transition of montmorillonite to the H/NH3 form makes it possible to increase the interplane distance of the sample only slightly (up to 1.0 nm) compared to the original bentonite clay. A larger interplane (1.4 nm) was obtained on modified Al^{3+} bentonites, compared to the original ones and converted to the H/NH_3 form. According to X-ray diffraction

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data for the OH form of bentonite, structures resistant to swelling and temperature influence are formed in the interlayer space of montmorillonite with a predominance of interplane distances of 1.8 nm. The specific surface area of the initial and modified bentonite clays was determined by the method of low-temperature nitrogen adsorption (Table.1). Based on the obtained physical and chemical characteristics, it was found that the modification of bentonite with ammonium, aluminum, and aluminum hydroxycation salts allows increasing the interplane distance and the specific surface area of the catalyst (Table 1).

Table 1

Textural characteristics of natural and modified zirconium and zinc bentonite

Specifications Samples	S_{ud}, m^2/g	S_{mi}, m^2/g	S	V_{mi}, cm^3/g	D_{me}, nm	D_{mi}, nm
Natural bentonite	72,6	16,8	0,086	0,008	4,02	1,04
Zr-NaOH- bentonite	68,7	12,6	0,087	0,007	3,95	1,08
Zr-NH_4OH- bentonite	119,8	11,3	0,154	0,006	3,94	0,98
Zr-Na_2CO_3- bentonite	51,0	7,4	0,089	0,005	4,01	0,96
Zr-$(NH_4)_2CO_3$- bentonite	86,4	11,8	0,147	0,006	4,0	1,23
Zn-NaOH- bentonite	67,3	17,2	0,135	0,008	3,90	0,94
Zn-NH_4OH- bentonite	120,8	17,3	0,208	0,008	3,98	0,92
Zn-Na_2CO_3- bentonite	61,6	10,7	0,129	0,006	4,0	0,99
Zn-$(NH_4)_2CO_3$- bentonite	101,5	19,2	0,168	0,008	4,1	0,67

To determine the optimal conditions for acid treatment, the method of planning extreme experiments was used [11]. As a plan, a complete factor experiment was chosen, in which all possible combinations of factors are implemented at all levels selected for the study. The following factors were selected: C-acid concentration, T-activation temperature, and t - time of the clay activation process. As a response function, we used the value of the specific surface area, as well as the average radius of the clay pore. If the specific surface area is used as the response function, the following regression equation can be obtained:

$$\boldsymbol{S = 102 - 4,6\frac{C-8}{2} + \frac{T-80}{10} + 6\frac{t-2}{2} + 7,75\frac{(C-8)(T-80)}{20} - 4,4\frac{(C-8)(t-2)}{4} - 2,6\frac{(T-80)(t-2)}{20} + 2,7\ \frac{(C-8)(T-80)(t-2)}{40}}$$

Equation (1) satisfies the Fisher criterion and is therefore adequate, at least in the range of parameter variation.

Table 2 shows the values of the factors in the full factor experiment for clays I-IV of domestic field. The results on the reproducibility of some characteristics of the porosity of clay I of the *Navbakhor field*, treated at C_{HCl}= 10 N, T= 80 ^{o}C, t = 2 h (conditions of the center of the plan) are shown in Table 3.

Figure, a for clay I shows the response surface for two time values t (1 h lower surface, 3 h upper surface). The figure shows that the response surface is complex. Thus, at low acid concentrations, the specific surface area increases with a decrease in the process temperature, and at high acid concentrations, on the contrary, the surface growth is observed with an increase in temperature. As for the time of acid treatment, the increase in its duration significantly affects the size of the surface.

Table-2

The values of factors in the full factor experiment for clays I-IV of various fields

Experiment number	Factor values for different clay samples								
	Concentration HCl, N			T, ^{o}C			t, h		
	I и II	III	IV	I и II	III	IV	I и II	III	IV
1	6	3	4	70	40	90	1	2	6

2	10	7	7	70	40	90	1	2	6
3	6	3	3*	90	80	90	1	2	6
4	10	7	4**	90	80	90	1	2	6
5	6	3	4***	70	40	90	3	4	6
6	10	7		70	40	-	3	4	-
7	6	3		90	80	-	3	4	-
8	10	7		90	80	-	3	4	-

* Nitric acid HNO_3 is used;** the clay treated in hydrochloric acid was subjected to ion exchange with Al^{3+}; *** hydrochloric acid was reused after experiment № 1.

Table-3

Some characteristics of clay porosity I

№ Sample	**S_{ud}, m^2/g**	**$V_{ep.pore}$, cm^3/g**	**$D_{ep.pore}$, Å**	**$S_{пор}$, m^2/g**	**$V_{micropore}$ cm^3/g**
0	75	0,205	146	56	0,00596
1	93	0,231	140	66	0,0058
2	92	0,216	142	60	0,0082
3	103	0,221	129,7	68,3	0,0084
4	103	0,226	125	72,3	0,0067
5	124	0,23	111	83	0,0076
6	96	0,23	133	68,9	0,0059
7	115	0,237	113	83,8	0,006
8	105	0,228	114,7	79	0,006
9	99	0,21	126,8	66	0,0084
10	103	0,217	126,4	68,6	0,0084
11	104	0,227	125	72	0,0067

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* 0-initial clay sample before acid treatment; 1-8-samples treated under the conditions given in Table 2; 9, 10 and 11-samples (reproducibility test) treated under the conditions of the center of the plan (10NHCl, 80 °C, 2 h).

Only at a low concentration of acid, and with increasing concentration, the influence of the time factor decreases. Extrapolating the response surface beyond the variation intervals probably doesn't make much physical sense, since the resulting surface is essentially non-linear and a different compositional plan, namely, of the 2nd order, should be applied to find the extremum. However, the plan of the 2nd order for three factors involves 27 experiments and does not guarantee finding the extremum, since with an increase in the number of experiments, the probability that the obtained regression equation will be adequate decreases. This is one of the reasons why it is legitimate to focus on the linear plans of a complete factorial experiment.

Additional experiments in the range of factors corresponding to the maximum surface value (C_{HCl}= 2 N, T = 40 °C, t = 4 h) actually allowed us to obtain a surface of less than 100 m^2/g. Thus, we can assume that the extremum is in the range of concentration values from 4 to 6 N, temperature from 70 to 90 °C, and time from 4 to 10 h.

For clay II, Table 4 shows the values of specific surfaces and the average pore diameter, as well as a number of other porosity characteristics. From Table 4, it follows that the tightening of acid treatment, i.e., an increase in the acid concentration, an increase in the temperature and duration of treatment and, entails an increase in the volume of pores, their average diameter and leads to a decrease in the contribution to the total surface of micropores and large-diameter pores. The average pore diameter naturally decreases.

Results of the planned experiment on acid treatment of clay from the Navbakhor deposit.

X-ray phase analysis of bentonite clays of the Navbakhor deposit (clay III) showed that the mineralogical composition of the clays differs in the content of a large amount of montmorillonite. Therefore, the limit values of the factors in the full factor experiment were slightly changed. The changes consisted in softening the acid treatment conditions, i.e. in reducing the acid concentration and the treatment temperature (Table 2).

For clay III, the main porosity characteristics are given in Table. 4. For verification, an extreme experiment was performed at a point with the following values of factors: C_{HCl}= 10 N, T = 90 ^{o}C, t = 10 h, as a result, the characteristics of the porous structure of clay were obtained, shown in Table.4.

Comparison of the data of sample 9 with the data of samples 4,7,8 for clay III shows that the tightening of the acid treatment conditions does not lead to an increase in the specific surface area, but on the contrary, leads to its decrease (up to 105 m^2/g) in comparison with milder treatment conditions. Based on the totality of the obtained data, the optimal acid treatment conditions for bentonite clay IV (Navbakhor deposit) were selected, as shown in Table 2.

For clay IV, in addition to variations in the acid concentration, the effect of the acid type was also studied. Instead of hydrochloric acid, nitric acid was used, and it was also found out how the use of waste acid affects the porosity. Chemical analysis of the spent acid showed that as a result of acid treatment with nitric acid, iron and aluminum ions are washed out of the clay. The results of the study of the porous structure of clay IV are presented in Table 5.

Table 4

Some characteristics of porosity of clays II and III

Number of sample	S_{ud}, m^2/g (BET theory)		$V_{ep.pore}$, cm^3/g		$D_{ep.pore}$, Å		S_{pore}, m^2/g		$V_{micropores}$ cm^3/g	
	II	III	II	III	II	III	II	III	II	III
0	70	61	0,177	0,096	151	125	46,7	31	0,006	0,087
1	96	78	0,172	0,101	115,7	102	59,6	39	0,0089	0,011
2	98	76	0,166	0,095	113	103	58,7	37	0,009	0,012
3	112	109	0,179	0,119	102	78	70,5	61	0,0088	0,01
4	119	124	0,192	0,153	94	67	81,7	91	0,007	0,003
5	112	66	0,19	0,093	106	111	72	34	0,0087	0,0096
6	111	68	0,199	0,096	107,6	120	74	32	0,0077	0,0094
7	136	136	0,224	0,182	92,5	68,7	97	106	0,006	0,004
8	138	146	0,246	0,208	86,3	68	114	122	0,0057	0,003
9	-	105	-	0,226	-	99	-	92	-	0,0048

* 0-initial clay sample before acid treatment; 1-8-samples treated under the conditions given in Table 2; 9-sample (reproducibility test) treated under the conditions: 10 NHCl, 90 ^{0}C, 10 h,

Table 5

Porous characteristics of clay IV

Number of sample	S_{ud}, m^2/g (BET theory)	$V_{ep.pore}$, cm^3/g	$D_{ep.pore}$, Å	S_{pore}, m^2/g	$V_{micropores}$ cm^3/g
0	124	0,164	99	66	0,0146
1	300	0,511	75	272	0,0068
2	266	0,574	90	254	0,004

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3	285	0,480	77	268	0,0052
4	290	0,510	76	270	0,0060
5	290	0,512	76	271	0,0061

* 0initial clay sample IV, 1-5-samples treated under the conditions given in Table 2.

The use of nitric acid in this case (sample 3) and the repeated use of hydrochloric acid (sample 5), as well as the treatment with hydrochloric acid followed by ion exchange with Al^{+3} (sample 4), for the purpose of deep purification of the solution from impurities by removing the ion exchange reaction products from the reaction sphere, resulted in almost the same properties of the porous structure as for sample 1. It should be noted a significant decrease in the specific surface area (sample 2) with an increase in the acid concentration from 4 to 7 N.

Table 6

Optimal conditions for acid treatment of clay I and IV

Clay number	**Sud, m2 / g (according to BET)**	C_{HCl}, N	T^oC	t, h
I	105	4-6	70-90	4-10
II	137	10	90	3
III	266	10	90	10
IV	308	4	90	6

CONCLUSION

Thus, the dependence of the specific surface area of clay on the parameters of acid treatment is nonlinear. The optimal results of acid treatment are given in Table 5. The analysis of the tabular data shows that for all clay samples, the optimal porosity values are achieved at C_{HCl}= 6-10 N, T = 90 ^oC, t = 6-10 h.

The use of spent hydrochloric and nitric acids instead of hydrochloric acid for the treatment of clays practically does not affect their porous characteristics.

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