SRSTI 68.05.43 https://doi.org/10.52081/bkaku.2025.v75.i4.287

THERMALLY MODIFIED BENTONITE CLAY AS A WATER-RETAINING MATERIAL FOR SOILS

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Annotation. The impact of thermal treatment on the properties of bentonites from the Kalzhat and Orta Tentek deposits was examined. The samples were analyzed using XRD, XRF, TGA/DSC, and low-temperature nitrogen adsorption (BET) before and after heating at temperatures ranging from 100 to 900°C. Moderate heating at 200–300°C removes physically adsorbed water and part of the interlayer water without affecting the layered structure of montmorillonite, which retains its specific surface area, water-holding capacity, and cation-exchange capacity.

In the 400–600°C range, dehydroxylation and interlayer collapse occur, resulting in a decrease in specific surface area and the loss of exchange sites. At 700–900°C, high-temperature silica and aluminosilicate phases form, and the porosity approaches zero. The comparison of the two deposits reveals that the Orta Tentek bentonites undergo structural degradation earlier than the Kalzhat bentonites, with the latter exhibiting greater resistance to degradation during the initial stages of heating.; However, at elevated temperatures, both materials cease to perform their agronomic functions. To utilize them as soil conditioners, it is recommended to restrict the treatment to a temperature range of 200–300°C, with brief exposure times, followed by granulation. It is crucial to avoid temperatures exceeding 400–600°C and to completely exclude temperatures above 700–900°C. These conditions ensure a sanitary pretreatment without compromising the soil's moisture retention or cation exchange capacity. This approach is particularly suitable for sandy and sandy-loam soils in the arid regions of Kazakhstan.

Keywords: bentonite; thermo treatment; porosity; moisture retention; cation exchange capacity; soil conditioner.

Introduction. A current problem in agriculture is the low water-holding capacity and fertility of light soils (sandy and sandy-loam), especially in degraded agroecosystems. Such soils retain water and nutrients poorly and dry out quickly, which reduces yields and plant drought tolerance. Under a changing climate with frequent droughts, it is important to find effective ways to increase soil water retention and cation-exchange capacity to supply crops with water and nutrients during critical growth periods. One promising approach is the use of natural clay materials as soil "conditioners." In particular, bentonite clays, which are smectites rich in montmorillonite, can markedly improve the hydro-physical properties of light soils due to their high sorption capacity and swelling structure [1–3]. Studies show that adding bentonite to sandy soils increases their water-holding capacity and available water content and reduces percolation losses, leading to better

moisture in the root zone and lower drought stress in plants [4–5,8]. Bentonite also provides additional exchange sites for retaining nutrient cations (K^+, NH^{4+},Ca^{2+}, etc.), thereby enriching the soil with plant-available forms of nutrients and reducing leaching [8–10].

Kazakhstan has significant bentonite reserves, including the Kalzhat and Orta-Tentek deposits [6–7]. These are of interest as local mineral feedstocks for soil amelioration. Using local bentonites as a soil amendment can reduce dependence on imported materials and lower the cost of soil fertility improvement. However, natural bentonites have specific features: they swell strongly upon wetting and can cause over-compaction or soil cracking upon drying [9]. Therefore, methods for preliminary modification of clays are relevant to optimize their properties for use as soil conditioners.

One option for preliminary modification is thermal treatment, that is, heating the clay to defined temperatures to change its structure and properties. Thermal treatment can partially dehydrate and decationate montmorillonite, reduce excessive swelling, and disinfect the material [10]. Excessively high temperatures, however, can destroy the smectite lattice and sharply reduce its cation-exchange capacity and ability to retain water. It is therefore important to select an optimal temperature regime that improves handling properties (flowability, uniformity) without losing the clay's beneficial functions as a soil structure former.

Understanding how temperature affects the structure and functions of bentonite clay is essential for developing effective soil conditioners. Montmorillonite clay has a 2:1 layered structure that contains interlayer water molecules and mobile cations [12–13]. Upon heating, dehydration proceeds stepwise: at about 100 °C, adsorbed interlayer water is removed, which is usually reversible upon rewetting [6–7,10]. Further heating to about 300–400 °C removes more strongly bound water and initiates dehydroxylation, the loss of structural hydroxyls from the octahedral sheets [14]. This process intensifies above 500 °C and is irreversible, involving the breakdown of OH groups and the smectite lattice, which leads to interlayer collapse and loss of swelling and cation retention [15].

According to the literature, heating bentonite to about 600°C causes montmorillonite diffraction reflections to disappear, indicating the loss of an ordered layered structure [16]. Complete smectite destructuring occurs at about 800–900°C. The clay loses crystallinity, becomes amorphous, and nearly completely loses cation-exchange capacity [14]. At the same time, specific surface area and porosity drop sharply because small meso- and micropores sinter during high-temperature treatment [13,19]. By contrast, moderate heating in the 100–300°C range mainly removes moisture and organic impurities and has little effect on specific surface area. Thus there is a temperature threshold below which thermal treatment does not cause irreversible damage to the smectite structure.

Studies [14,16–17] indicate that the critical range for thermal modification is around 500°C. Further temperature increases cause irreversible changes (layer breakdown and loss of interlayer adsorption properties). It is therefore necessary to determine optimal temperatures for thermal modification when bentonites are used as soil conditioners.

The aim of our study is to determine the optimal temperature for thermal modification of bentonites from the Kalzhat and Orta Tentek deposits for application as soil improvers for light soils in Kazakhstan. We focus on how calcination temperature affects key properties that control the conditioning effect, namely water-holding capacity, porosity, swelling, cation exchange, and the associated structural transformations.

Materials and methods. Bentonite clays from the Kalzhat deposit in Almaty Region, Kazakhstan, and the Orta Tentek deposit in the Alakol District of Zhetisu Region, Republic of Kazakhstan, were used in this study [6–7]. Sample preparation included grinding in a ball mill to a particle size of 0.08 mm and pre-drying at 70 °C to remove moisture.

A comprehensive characterization was performed to obtain physicochemical and structural–phase information on the Kalzhat and Orta Tentek bentonites, including their elemental composition, chemical structure, morphology, phase composition, and sorption properties. The

following methods were employed: elemental analysis by improved EDXRF on a Rigaku NEX CG II with polarized X-rays (elemental range Na to U; X-ray tube 50 kV/50 W or 65 kV/100 W); X-ray diffraction (XRD) for crystalline structure using an X'Pert PRO diffractometer with CuKα radiation; porosity by low-temperature nitrogen adsorption (BET); and thermal analysis by thermogravimetry on a synchronous thermal analyzer SKZ1060A at a heating rate of 5 °C min^{-1} in air.

Thermal treatment of clays. Bentonite clays were subjected to thermal treatment at different temperature conditions: 100°C, 200°C, 300°C, 400°C, 500°C, 600°C, 700°C, 800°C and 900°C. For this purpose, the samples were placed in a muffle furnace (SNOL 8.2/1100 LSC 01, Lithuania) and heated at a constant rate (5–10°C/min) to the target temperature. The holding time at each temperature was 2 hours. After heating, the samples were cooled to a temperature of 230°C, under conditions of a slow temperature decrease. The scheme of the thermal treatment of clays is shown in Fig.1.

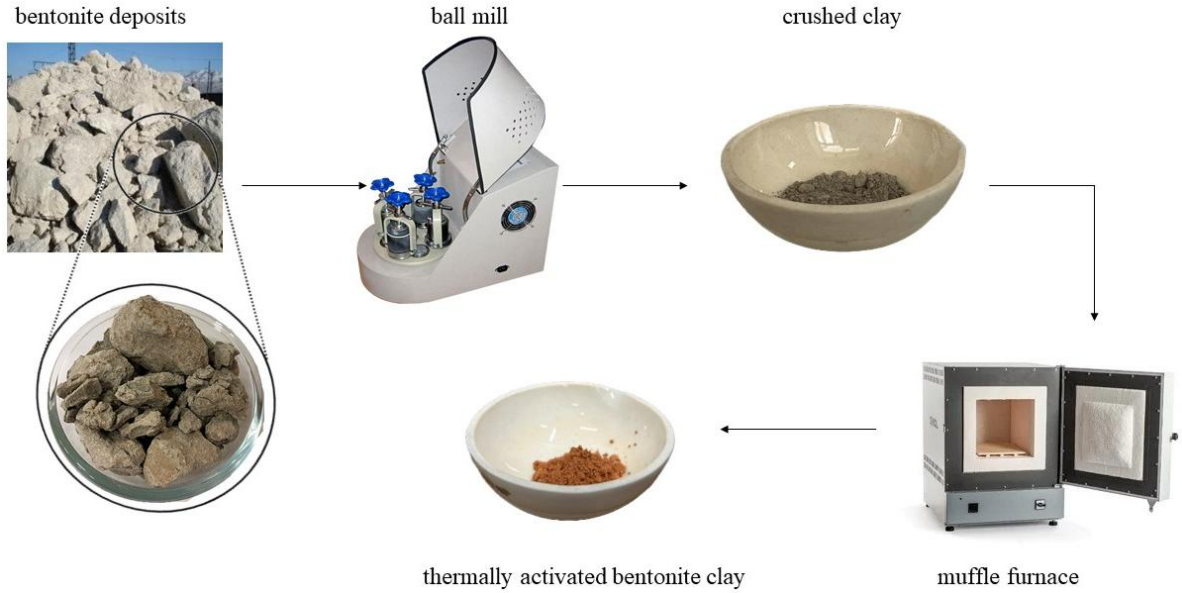

Figure 1 – Scheme of thermal modification of bentonite clays

Results and discussion. The TGA and DSC have allowed to study the thermal behavior of bentonites from the Kalzhat and Orta Tentek deposits. The results obtained revealed key changes in mass and thermal effects caused by dehydration, dehydroxylation and destruction of the montmorillonite structure at different temperatures.

TGA–DSC of Kalzhat bentonites shows (Fig.2) three thermal regions. Below 200°C, a 2–4% mass loss with an endothermic effect corresponds to desorption of physically adsorbed water. Between 200 and 500°C, a further 3–6% loss occurs due to montmorillonite dehydration and removal of organics, accompanied by an exothermic peak near 300–400°C. Above 500°C, an endothermic peak at 500–700°C indicates dehydroxylation with an additional 1–2% loss and the onset of lattice breakdown. The total mass loss decreases with higher heat treatment temperature, and the clay is stable up to about 400°C, with gradual structural degradation at higher temperatures.

For Orta Tentek bentonites, TGA–DSC shows (fig.3) the same three thermal stages as Kalzhat but with stronger mid-temperature responses. Below 200 °C, an endothermic effect corresponds to removal of adsorbed water.

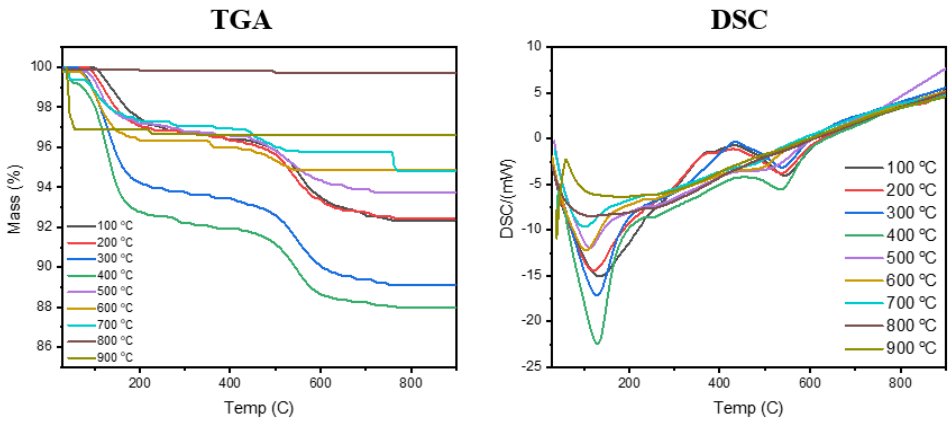

Figure 2 – TGA and DSC curves of thermally modified Kalzhat clay

Between 200 and 500 °C, mass loss reaches 4–7% (higher than Kalzhat), consistent with greater organics and hydrophilicity; this stage features an exothermic peak at 300–400 °C. Above 500 °C, dehydroxylation of montmorillonite dominates, producing an endothermic effect at 500–700 °C and a slower mass decrease. Thermal effects are generally more pronounced than in Kalzhat, indicating higher thermal activity of Orta Tentek clays.

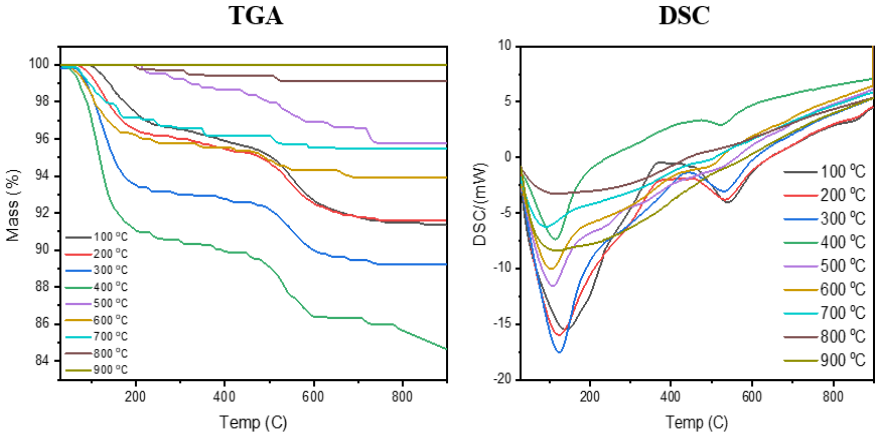

Figure 3 – TGA and DSC curves of thermally modified Orta Tentek clay

A comparative analysis of the thermal behavior of the two deposits showed that the Kalzhat and Orta Tentek bentonites have similar trends in mass changes and thermal effects. However, the Orta Tentek bentonites are characterized by greater mass loss in the medium temperature range (200–500°C) and more intense thermal effects, which is due to the peculiarities of their chemical composition. These differences determine the need to optimize the temperature regimes of thermal treatment for each deposit, which will ensure the preservation of their functional characteristics and increase their suitability for various industrial applications.

From an agrochemical standpoint, the Orta Tentek bentonites exhibit higher hydrophilicity and a greater content of oxidizable organic impurities, which under moderate thermal treatment enhances their ability to retain moisture and nutrient cations. Overheating beyond the dehydroxylation range reduces swelling and the number of active exchange sites, thereby diminishing the retention of ammonium, potassium, and other micronutrients. Accordingly, to preserve functionality, temperatures of 250–350 °C should be used for Orta Tentek, whereas 300–400 °C is sufficient for Kalzhat bentonite. These conditions maintain the montmorillonite structure and the suitability of these clays as soil conditioners.

The Brunauer, Emmett and Teller (BET) method was used to assess changes in the porous structure and adsorption properties of bentonite clays from the Kalzhat deposit as a result of thermal treatment. Nitrogen adsorption-desorption isotherms obtained at treatment temperatures from 100 to

900°C made it possible to determine the specific surface area, volume and pore size distribution.

Figure 4 shows that the original Kalzhat bentonite sample (A) exhibits a high specific surface area of 73.99 m²/g and well-defined hysteresis loops, indicating the presence of an extensive mesoporous structure. These mesopores play a key role in the adsorption of large molecules and capillary retention of moisture, making the starting material ideal for use in processes requiring high adsorption activity, such as water and air purification or catalysis.

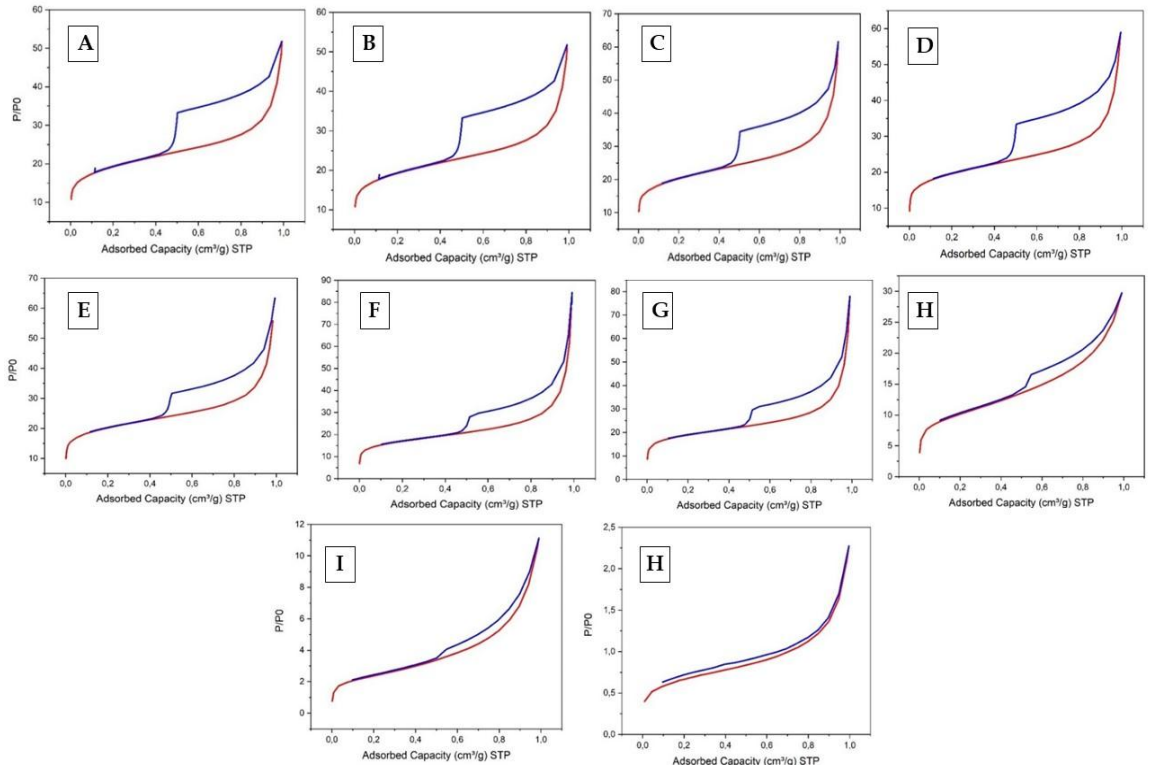

Figure 4 – BET analysis curves of the initial and thermally modified bentonite clay of the Kalzhat deposit: A – initial, B – 100°, C – 200°, D – 300°, E – 400°, F – 500°, G – 600°, H – 700°, I – 800°, J – 900°

However, when the bentonite processing temperature is increased to 900°C (B–J), a significant narrowing and reduction in the severity of the hysteresis loops is observed, indicating a decrease in the number and size of accessible pores. This phenomenon can be interpreted as a compaction of the porous structure due to the destruction of interpore bonds and changes in the chemical structure of the material under the influence of high temperatures. The significant decrease in specific surface area to 2.39 m²/g, as indicated in the data in Table 1, confirms the decrease in adsorption capacity and the loss of functionality of the material. These changes can significantly limit the use of bentonite in applications where high adsorption characteristics are required, such as filtration and catalysis, especially in cases where the efficiency of the process depends on the size and accessibility of the pores.

Table 1 – Parameters of the porous structure of the initial and thermally modified bentonite of the Kalzhat deposit according to the adsorption isotherm data

Name of sample	BET multi-point method, specific surface, m^2/g	Pore size distribution, nm	Volume of pore		Pore surface area	
			cm^3/g	%	$см^3/г$	%
1	**2**	**3**	**4**	**5**	**6**	**7**

1	2	3		4	5	6	7
Initial	73,9857	micro-	0,35-2	0,0204	46,61	46,663	61,54
		meso-	2-10	0,02	44,56	28,2154	37,21
			10-50	0,0042	8.83	0,9486	1,25
Thermally modified 100°C	72.9001	micro -	0,35-2	0,0196	24,40	44,7175	54,92
		meso -	2-10	0,0239	29,64	31,3450	38,49
			10-50	0,0229	17,57	4,5706	5,61
Thermally modified 200°C	72,1023	micro -	0,35-2	0,0198	23,48	45,7186	54,92
		meso -	2-10	0,0241	28,98	31,3457	38,45
			10-50	0,0232	15,58	4,5706	5,61
Thermally modified 300°C	70,9352	micro -	0,35-2	0,0196	21,84	44,9512	54,77
		meso -	2-10	0,0240	26,76	30,8557	37,60
			10-50	0,0238	26,50	4,9360	6,01
Thermally modified 400°C	73,354	micro -	0,35-2	0,0195	20,20	45,5808	55,09
		meso -	2-10	0,0238	24,71	30,3950	36,73
			10-50	0,0303	31,36	5,5554	6,71
Thermally modified 500°C	61,1844	micro -	0,35-2	0,0144	11,58	33,4311	47,55
		meso -	2-10	0,0224	17,99	26,5815	37,81
			10-50	0,0366	29,42	7,5079	10,68
Thermally modified 600°C	68,8874	micro -	0,35-2	0,0181	14,80	42,3284	53,63
		meso -	2-10	0,0221	18,11	27,0792	34,31
			10-50	0,0341	27,94	6,9218	8,77
Thermally modified 700°C	36,3501	micro -	0,35-2	0,0045	9,95	10,6906	27,79
		meso -	2-10	0,0214	47,45	23,9302	62,20
			10-50	0,0188	42,00	3,8495	10,01
Thermally modified 800°C	8,4459	micro -	0,35-2	0,0005	15,84	1,2235	41,59
		meso -	2-10	0,0061	37,38	6,0720	69,92
			10-50	0,0089	54,16	1,8265	21,03
Thermally modified 900°C	2,3901	micro	0,35-2	0,0002	1,52	0,7248	8,55
		meso -	2-10	0,0011	33,36	1,3962	47,46
			10-50	0,0017	50,80	0,3223	10,96

Figure 5 shows a similar trend for bentonites from the Orta Tentek deposit, where the original sample (A) also shows a hysteresis loop, but with a specific surface area of 65.62 m²/g, which is lower than that of Kalzhat. This may indicate a smaller number or smaller size of mesopores in the original initial. With increasing processing temperature, the hysteresis loops decrease and by 900°C they practically disappear, which is accompanied by a decrease in the specific surface area to 6.32 m²/g, as shown in Table 2. This significant reduction in porosity indicates serious structural changes that worsen the adsorption properties of the material. Such a radical reduction in porosity makes these bentonites less suitable for applications requiring high adsorption capacity and porosity, such as sorbents and catalysts in the chemical industry.

Thus, the changes in the adsorption-desorption isotherms and the corresponding changes in the specific surface area for both deposits show that high processing temperatures lead to a significant reduction in porosity.

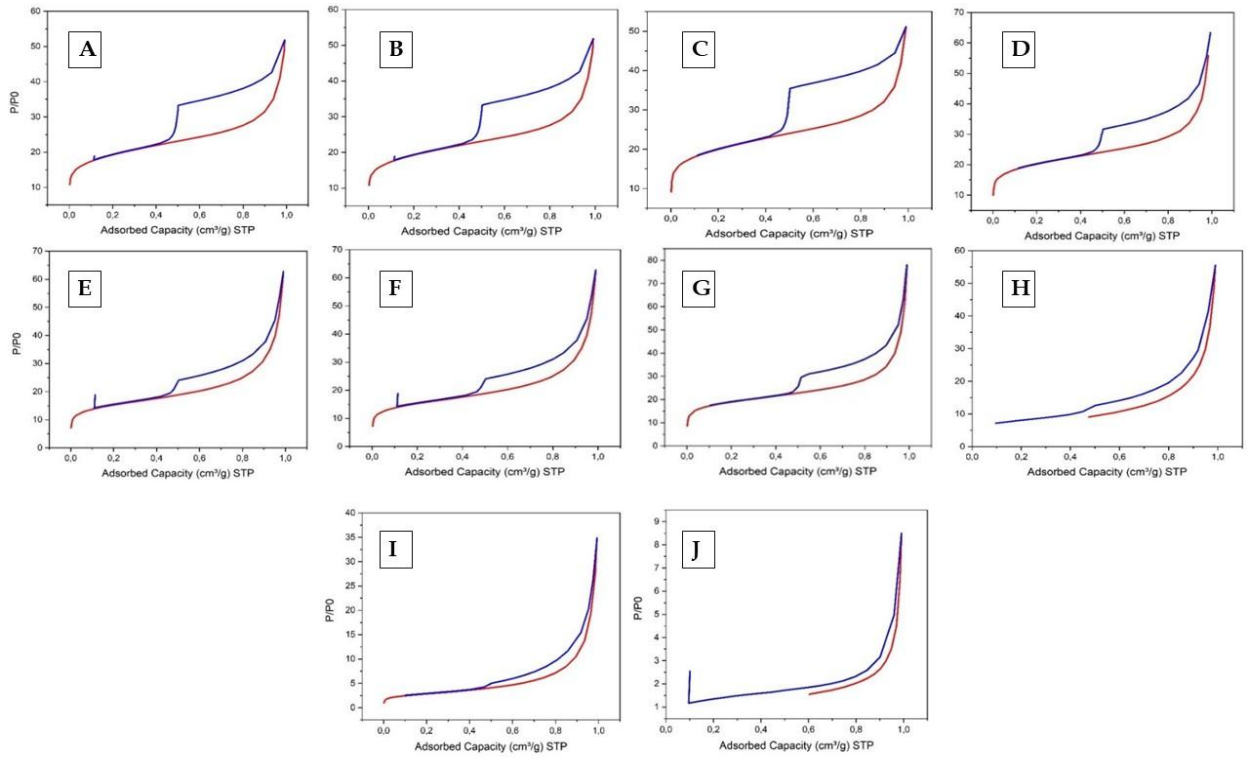

Figure 5 – BET curves of analysis of the initial and thermally modified bentonitonite clay of the Orta Tentek deposit: A – initial, B – 100°, C – 200°, D – 300°, E – 400°, F – 500°, G – 600°, H – 700°, I – 800°, J – 900°

This narrowing and loss of pores affects the functional properties of the material, limiting its use in industrial adsorption and catalytic processes. These data highlight the need for careful control of temperature conditions in bentonite processing processes to optimize their porous and functional properties.

Table 2 – Parameters of the porous structure of the initial and modified bentonite of the Orta Tentek deposit according to the adsorption isotherm data

Name of sample	BET multi-point method, specific surface, m^2/g	Pore size distribution, nm		Volume of pore		Pore surface area	
				cm^3/g	%	cm^3/g	%
1	**2**	**3**		**4**	**5**	**6**	**7**
Initial	65,6156	micro-	0,35-2	0,0204	45,73	46,663	61,54
		meso-	2-10	0,02	44,87	28,2154	37,21
			10-50	0,0042	9,4	0,9486	1,25
Thermally modified 100°C	72.9001	micro -	0,35-2	0,0206	25,04	46,6364	54,83
		meso -	2-10	0,0252	30,68	33,3753	37,21
			10-50	0,0146	17,79	4,2443	1,25
Thermally modified 200°C	72.4589	micro -	0,35-2	0,0204	24,89	46,4624	55,18
		meso -	2-10	0,0245	29,96	32,4267	38,51
			10-50	0,0224	27,34	4,4243	5,25
Thermally modified 300°C	73,1803	micro -	0,35-2	0,0199	19,35	45,3046	46,53
		meso -	2-10	0,0261	46,35	46,7104	47,97
			10-50	0,0265	22,62	4,7246	4,85
Thermally modified 400°C	73,0691	micro -	0,35-2	0,0210	20,52	47,2979	54,86
		meso -	2-10	0,0249	24,34	31,3672	36,38
			10-50	0,0314	30,72	6,2186	7,21

1	2	3		4	5	6	7
Thermally modified 500°C	60,0884	micro -	0,35-2	0,0148	14,87	34,6284	50,38
		meso -	2-10	0,0223	22,35	25,8989	37,68
			10-50	0,0318	31,88	6,5170	9,48
Thermally modified 600°C	55,3211	micro -	0,35-2	0,0127	13,23	29,8919	47,89
		meso -	2-10	0,0211	21,95	23,9306	38,34
			10-50	0,0384	40,0	7,3341	11,75
Thermally modified 700°C	48,256	micro -	0,35-2	0,0096	13,23	28,8989	45,89
		meso -	2-10	0,0208	21,95	24,0306	39,34
			10-50	0,0375	40,0	7,3261	12,55
Thermally modified 800°C	10,1214	micro -	0,35-2	0,0006	1,20	1,4006	11,26
		meso -	2-10	0,0066	13,45	5,6215	45,19
			10-50	0,0207	42,10	4,2057	33,81
Thermally modified 900°C	6,3235	micro -	0,35-2	0,0015	1,20	1,3058	10,33
		meso -	2-10	0,0056	13,45	5,6713	46,18
			10-50	0,0045	42,10	4,3058	35,83

The mesoporous structure enables capillary water retention and reversible ion sorption. Heating at elevated temperatures reduces the specific surface area and narrows the hysteresis loop, weakening these properties. TGA/DSC and BET measurements show that moderate thermal treatment is most effective: unstable oxidizable impurities are removed while the mesopore volume remains essentially unchanged. BET analysis confirms that the temperatures identified as optimal from TGA/DSC for Orta Tentek and Kalzhat bentonites preserve moisture-retention capacity and cation-exchange activity, which substantially improves their performance in soil mixtures.

It has been established that thermally modified clays from the Kalzhat and Orta Tentek deposits have a complex oxide mineral composition, including silicon, aluminum, magnesium, calcium, iron and other elements, data on which are given in Tab.3 and 4. The main components of both clays remain silicon (SiO_2) and aluminum (Al_2O_3) oxides, the content of which varies depending on the processing temperature.

Detailed analysis of the elemental composition of Kalzhat clay (Tab1) reveals significant changes in the chemical composition under the influence of thermal treatment in the range from 100°C to 900°C, which significantly affects the structural and functional properties of the clay. Silicon dioxide, which is the main component, shows resistance to thermal effects, with a slight increase in content from 67.6% to 69.7% at 900°C. This indicates the preservation of the silica matrix, which is critical for maintaining the structural integrity of the clay at the molecular level.

Table 3 - Results of X-ray fluorescence analysis of the initial and thermally modified bentonites of the Kalzhat deposit

Composition % by weight	Initial Kalzhat clay	Thermally modified Kalzhat clay, ^{0}C								
		100°C	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
SiO_2	67,6	69,1	69,4	69,3	69,4	69,6	69,2	69,2	69,6	69,7
Al_2O_3	18,1	18,5	18,0	18,4	18,5	18,6	18,7	18,7	18,9	19,3
Fe_2O_3	7,43	6,26	6,84	6,55	6,69	6,32	6,37	6,60	6,05	5,87
MgO	1,86	2,18	1,48	1,93	1,51	1,73	1,89	1,64	1,70	1,76
S	1,65	0,741	0,820	0,710	0,314	0,715	0,739	0,698	0,683	0,313
CaO	1,46	1,49	1,65	1,43	1,48	1,45	1,43	1,49	1,40	1,39
TiO_2	0,94	0,835	0,879	0,842	0,852	0,835	0,839	0,879	0,819	0,853
K_2O	0,55	0,527	0,546	0,523	0,521	0,516	0,518	0,544	0,513	0,554
P_2O_5	0,132	0,118	0,130	0,121	0,126	0,113	0,116	0,112	0,118	0,112

1	2	3	4	5	6	7	8	9	10	11
Mn	0,0435	0,0295	0,0339	0,0285	0,0398	0,0276	0,0280	0,0299	0,0291	0,0287
V	0,0321	0,0154	0,0202	0,0196	0,0188	0,0166	0,0155	0,0173	0,0154	0,0154
Co	0,0212	0,0170	0,0159	0,0124	0,0176	0,0158	0,0157	0,0163	0,0154	0,0166
Ni	0,0116	0,0061	0,0077	0,0078	0,0084	0,0062	0,0062	0,0072	0,0131	0,0120
Cr	0,0088	0,0065	0,0074	0,0068	0,0076	0,0067	0,0069	0,0087	0,0278	0,0286
Cu	0,0085	0,0051	0,0059	0,0055	0,006	0,0055	0,0054	0,0059	0,0062	0,0058
Cl	0,0084	0,0100	0,0093	0,0102	0,0091	0,0054	0,0052	0,0054	0,0110	0,0027
Zn	0,0061	0,0037	0,0051	0,0037	0,0039	0,0036	0,0034	0,0038	0,0034	0,0033
Ga	0,0045	0,0027	0,0030	0,0029	0,0029	0,0026	0,0026	0,0028	0,0025	0,0022
Y	0,0038	0,0024	0,0025	0,0024	0,0027	0,0019	0,0022	0,0015	0,0017	0,0014
Te	0,0037	0,0031	0,0042	0,0028	0,0027	0,0011	0,0016	0,0017	0,0013	0,0009
As	0,0014	0,0008	0,0009	0,0007	0,0011	0,0008	0,0009	0,0009	0,0009	0,0007
Se	0,0008	0,0005	0,0006	0,0005	0,0004	0,0005	0,0004	0,0003	0,0002	0,0002
Ag	0,0007	0	0,0017	0,0008	0,295	0,0003	0,0004	0,0003	0,0003	0,0002

X-ray fluorescence analysis results of bentonites from the Orta Tentek deposit, subjected to heat treatment in the range from 100°C to 900°C, highlight significant changes in the chemical composition that affect the structural and functional characteristics of the material.

Table 4 – Results of X-ray fluorescence analysis of the initial and thermally modified bentonites of the Orta Tentek deposit

Composition, % by weight	Initial Orta Tentek clay	Thermally modified Orta Tentek clay								
		100°C	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C
SiO_2	67,6	67,3	68,1	69,5	69,5	69,6	68,6	68,9	69,3	67,9
Al_2O_3	18,1	18,0	18,0	17,9	17,9	17,9	17,7	17,8	17,7	17,8
Fe_2O_3	7,43	8,15	7,47	6,60	6,60	6,57	7,23	6,57	6,66	7,45
MgO	1,86	2,06	1,89	1,70	1,86	1,72	1,97	2,09	2,00	2,02
S	1,65	0,0026	0,0015	0,683	0,567	0,670	0,747	0,718	0,749	0,483
CaO	1,46	1,96	1,99	1,99	1,91	1,97	2,06	2,16	1,96	2,67
P_2O_5	0,132	0,154	0,168	0,135	0,128	0,115	0,122	0,117	0,137	0,129
K_2O	0,55	0,574	0,589	0,526	0,519	0,521	0,543	0,584	0,533	0,528
TiO_2	0,94	0,855	0,879	0,780	0,779	0,791	0,802	0,849	0,782	0,806
Mn	0,0435	0,0448	0,0431	0,0383	0,0408	0,0417	0,0425	0,0433	0,0412	0,0492
V	0,0321	0,0198	0,0194	0,0212	0,0223	0,0210	0,0211	0,0222	0,0196	0,0227
Co	0,0212	0,0219	0,0210	0,0133	0,0104	0,0109	0,0128	0,0151	0,0151	0,0164
Ni	0,0116	0,0076	0,0076	0,0077	0,0072	0,0066	0,0075	0,0086	0,0155	0,0130
Cr	0,0088	0,0069	0,0070	0,0063	0,0061	0,0061	0,0064	0,0096	0,0308	0,0221
Cu	0,0085	0,0063	0,0061	0,0048	0,0054	0,0050	0,0055	0,0069	0,0059	0,0058
Cl	0,0084	0,0125	0,0155	0,0087	0,0079	0,0069	0,0079	0,0051	0,0356	0,0052
Zn	0,0061	0,0041	0,0042	0,0036	0,0035	0,0041	0,0038	0,0051	0,0036	0,0040
Ga	0,0045	0,0032	0,0030	0,0027	0,0026	0,0026	0,0026	0,0024	0,0024	0,0025
Y	0,0038	0,0030	0,0030	0,0026	0,0026	0,0026	0,0024	0,0015	0,0017	0,0017
Te	0,0037	0,0010	0,0010	0,0029	0,0025	0,0024	0,0018	0,0008	0	0,0016
As	0,0014	0,0082	0,0080	0,0015	0,0020	0,0016	0,0026	0,0016	0,0019	0,0034
Se	0,0008	0,0012	0,0010	0,0008	0,0008	0,0008	0,0007	0,0005	0,0004	0,0003
Ag	0,0007	0,0008	0,0008	0,0008	0,0006	0,0005	0,0004	0,0002	0,0003	0,0003

The main component, silicon dioxide, shows little fluctuation in concentration, maintaining a level between 67.6% and 67.9% at maximum temperature, indicating its thermal stability. Aluminum oxide remains constant at about 18%, indicating the stability of the aluminosilicate structure. The noticeable increase in calcium oxide, growing from 1.46% to 2.67%, may reflect the

formation of new calcium compounds at high temperatures. At the same time, fluctuations in iron oxide content from 7.43% to 7.45%, with minimum values at medium temperatures, highlight the oxidation-reduction processes occurring in iron-containing minerals. Microelements such as manganese and vanadium show stability in their content, which is important for maintaining certain physical and chemical properties of clay.

Both bentonites have an aluminosilicate composition. In the Orta Tentek bentonite, CaO increases to 2.67 wt% while Fe_2O_3 remains nearly constant at 7.43–7.45 wt%. This matrix configuration under heating supports a pore structure that favors capillary water retention and the reversible sorption of nutrient ions. An increase in CaO after thermal treatment may moderately enhance buffering and cation-exchange properties in soil blends.

The XRD analysis of thermally treated bentonites from the Kalzhat and Orta Tentek deposits allowed to study in detail the changes in their crystal structure at different processing temperatures and to identify key patterns of phase transformations (Figures 5 and 6). The initial composition of both samples is characterized by the dominant presence of montmorillonite, which is confirmed by the presence of intense reflections in the region of $2\theta \approx 6–10°$, corresponding to the basal distance (d001) of this mineral. In addition to montmorillonite, the initial samples show peaks of quartz (SiO_2) at $2\theta \approx 26.6°$, weak signals of feldspars, also impurity phases such as calcite and small amounts of iron-containing compounds, including hematite. XRD records the gradual transformation of bentonites. At 200-300 °C, the basal reflection of montmorillonite weakens and shifts to a higher 2θ angle due to dehydration and densification of the layers. The signals of quartz and feldspar are also enhanced. At 400-600 °C, a degradation peak occurs due to dehydroxylation and the formation of an amorphous component. Above 700 °C, mullite and cristobalite form, and montmorillonite peaks no longer exist, and the structure becomes amorphous.

Orta Tentek begins to lose its layered order earlier and faster than Kalzhat at 400-600 °C. Secondary Fe-containing oxides begin to appear as early as 500 °C for Orta Tentec, while similar phases occur mainly above 600 °C for Kalzhat. These differences in thermal sensitivity are important when choosing the appropriate temperature range for soil applications to avoid impairing moisture retention and ion exchange properties.

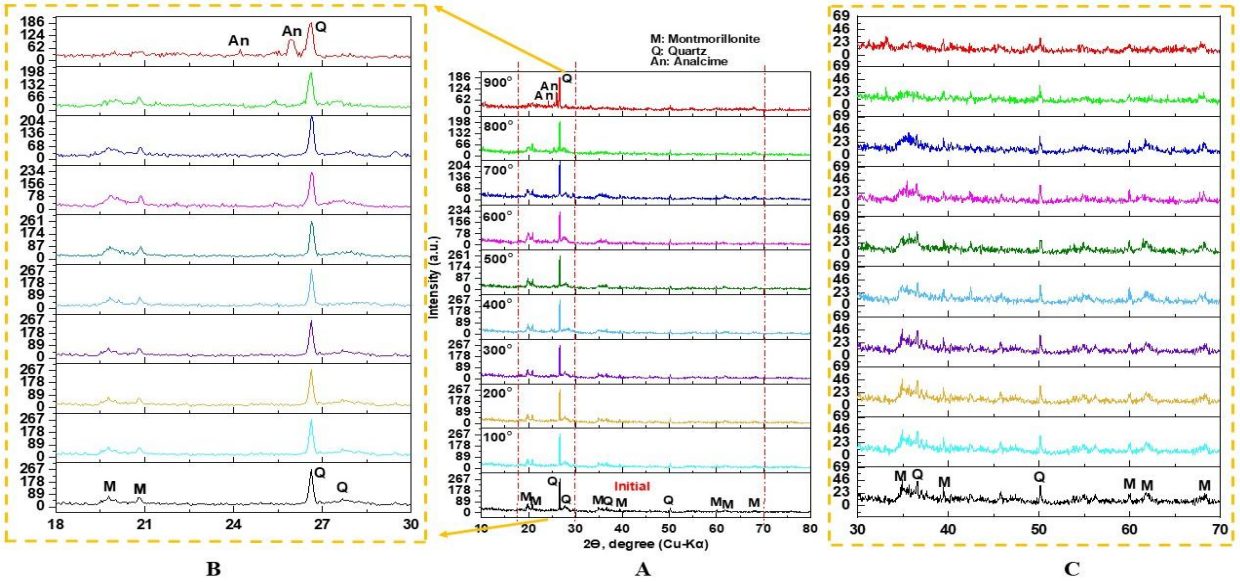

Figure 5 – XRD spectra of thermally treated bentonites from the Kalzhat deposit: A – general 2θ range (10–80°), B – analcime and quartz region (18–30°), C – secondary peak region (30–70°). Temperature increases from bottom to top

X-ray diffraction (XRD) patterns indicate that bentonite from the Orta Tentek deposit dehydrates at lower temperatures than bentonite from the Kalzhat deposit. For application as a soil

conditioner, this implies that the preparation temperature must be limited to preserve swelling, water retention, and the reversible fixation of ions.

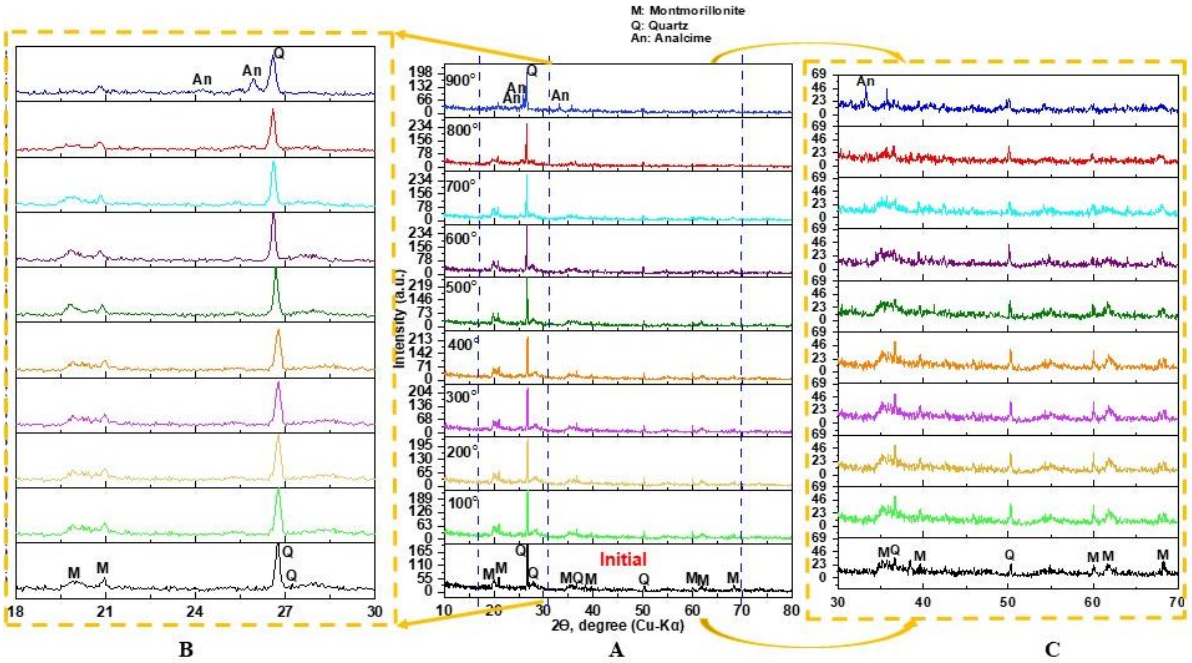

Figure 6 – XRD spectra of thermally treated bentonites from the Orta Tentek deposit: A – general 2θ range (10–80°), B – analcime and quartz region (18–30°), C – secondary peak region (30–70°). Temperature increases from bottom to top

Conclusion. As a result of the conducted studies, structural, phase and textural changes of bentonites of the Kalzhat and Orta Tentek deposits were revealed during their thermal modification in the temperature range of 100–900°C. The use of a set of analytical methods, including X-ray diffraction (XRD), X-ray fluorescence (XRF), thermogravimetric (TGA), differential scanning calorimetry (DSC) and the Brunauer-Emmett-Teller (BET) method, made it possible to establish patterns of change in the chemical composition, phase state, porous structure and sorption characteristics of the studied samples.

The XRD analysis showed that when heated to 400°C, the montmorillonite structure is preserved, but partial dehydration is observed. In the range of 400–600°C, dehydroxylation occurs, accompanied by the destruction of the layered structure and amorphization of the material. In the range of 700–900°C, high-temperature phases such as mullite and cristobalite are formed, indicating a complete restructuring of the structure. These changes are in good agreement with the XRD data, which record a decrease in the content of aluminosilicate components and a relative increase in the proportion of silica.

The TGA analysis revealed three key temperature stages of mass loss: removal of physically adsorbed water at 100–200°C, dehydration of interlayer water and initial dehydroxylation at 200–500°C, and complete destruction of the montmorillonite structure at 500–900°C. The DSC data confirmed the endothermic and exothermic effects associated with these processes, and BET analysis results showed that the most significant decrease in porosity and specific surface area is observed in the range of 400–600°C, which coincides with the phase changes recorded by XRD and TGA.

The optimal temperature mode for thermal treatment of bentonites depends on their targeted use. To maintain maximum adsorption capacity and porous structure, the best range is 300–400°C. In the range of 500–600°C, bentonites acquire increased heat resistance and can be used as catalyst carriers. Complete destruction of the porous structure at 700–900°C makes the material suitable for use in high-temperature processes, such as refractory coatings and special sorbents.

Comparison of Kalzhat and Orta Tentek bentonites showed that Kalzhat samples exhibit

higher thermal stability and can withstand heating up to 500–600°C without significant loss of porosity, while Orta Tentek bentonites begin to lose structural integrity at lower temperatures (300–450°C).

Thus, the obtained results allowed to establish clear interrelations between phase, chemical and textural changes of bentonites during thermal treatment, as well as to determine the optimal modification conditions for their various applications.

The findings can inform the development of effective thermal activation technologies for bentonites aimed at improving soil properties overall, increasing agricultural resilience to drought, enhancing fertilizer efficiency, and improving soil fertility. This is particularly relevant for the arid regions of Kazakhstan.

Acknowledgment. This research is funded by the Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP19175733).

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ТЕРМО-МОДИФИКАЦИЯЛАНҒАН БЕНТОНИТ САЗЫ ТОПЫРАҚ ҮШІН ЫЛҒАЛ САҚТАЙТЫН МАТЕРИАЛ РЕТІНДЕ

Қаржаубаева А.Қ.[1,2], 8D07109 «Инновациялық технологиялар және жаңа бейорганикалық материалдар» білім беру бағдарламасының 2-курс докторанты
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Аңдатпа. Минералдық Калжат және Орта Тентек кен орындарының бентониттерін термиялық модификациялау мен олардың топырақ жақсартқыш ретінде атқаратын функцияларының өзара байланысы зерттелді. Калжат және Орта Тентек кен орындарының бентонит үлгілері термиялық өңдеуге дейін және 100–900°C температура аралығында өңделгеннен кейін XRD, XRF, TGA/DSC және төмен температуралы азот адсорбциясы (BET) әдістерімен талданды.

200–300°C температура шегіндегі орташа термиялық өңдеу монтмориллониттің қабатты құрылымын бұзбай, физикалық адсорбцияланған және қабатаралық судың бір бөлігін жояды, соның нәтижесінде меншікті беткі аудан, ылғал сыйымдылығы және катионалмасу сыйымдылығы сақталады. 400–600°C температура аралығында дегидроксилдену және қабатаралық кеңістіктің коллапсы байқалады, бұл SBET-тің төмендеуімен және алмасу орталықтарының жойылуымен қатар жүреді. 700–900°C температурада жоғары температуралы кремнезем және алюмосиликат фазалары түзіліп, кеуектілік нөлге жуықтайды.

Кен орындарын салыстыру Орта Тентек бентониттерінде құрылымдық деградацияның ертерек басталатынын және бастапқы термоөңдеу сатыларында Калжат бентонитінің тұрақтылығы

жоғары екенін көрсетеді, алайда жоғары температураларда екі материал да агрономиялық функцияларын жоғалтады. Топырақ «кондиционері» ретінде пайдалану үшін температуралық режимді 200–300°C шегінде қысқа уақыт ұстап, кейіннен гранулдау ұсынылады; 400–600°C аймағындағы термиялық өңдеуден және 700–900°C температураларды қолданудан бас тарту қажет. Мұндай режимдер ылғал ұстау қасиеті мен катионалмасу сыйымдылығын жоғалтпай санитарлық өңдеуді қамтамасыз етеді және Қазақстанның қуаң аймақтарындағы құмды және құмдақ топырақтар үшін қолайлы.

Тірек сөздер: бентонит, термо өңдеу, кеуектілік, ылғал ұстау, катион алмасу сыйымдылығы, топырақ кондиционері.

ТЕРМОМОДИФИЦИРОВАННАЯ БЕНТОНИТОВАЯ ГЛИНА КАК ВЛАГОУДЕРЖИВАЮЩИЙ МАТЕРИАЛ ДЛЯ ПОЧВ

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Аннотация. Исследована связь термической модификации бентонитов месторождений Калжат и Орта Тентек с их функциями почвоулучшителей. Образцы бентонитов месторождений калжат и орта тентек до и после термической обработки в диапазоне температур 100–900°C проанализированы методами XRD, XRF, TGA/DSC и низкотемпературной адсорбции азота BET. Умеренная термообработка в пределах температуры 200–300°C удаляет физически адсорбированную и часть межслоевой воды без разрушения слоистой структуры монтмориллонита, что сохраняет удельную поверхность, влагоемкость и катионообменную емкость. В интервале температур 400–600°C фиксируется дегидроксилирование и коллапс межслоев, сопровождающиеся падением S_{BET} и утратой обменных центров. При температуре 700–900°C формируются высокотемпературные фазы кремнезема и алюмосиликатов и пористость стремится к нулю. Сопоставление месторождений показывает более раннюю структурную деградацию бентонитов Орта Тентек и большую стойкость бентонита Калжат на начальных этапах термообработки, однако при высоких температурах оба материала теряют агрономические функции. Для использования в качестве почвенных «кондиционеров» целесообразно ограничить температурный режим в пределах 200–300°C с краткой выдержкой и с последующим гранулированием, избегая температурной обработки в районе 400–600°C и исключая 700–900°C. Такие режимы обеспечивают санитарную подготовку без потери влагоудержания и КОЕ и подходят для песчаных и супесчаных почв засушливых регионов Казахстана.

Ключевые слова: бентонит, термообработка, пористость, влагоудержание, катионообменная емкость, почвенный кондиционер.