

Effective sorbents based on plasma-modified aluminosilicate minerals

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Abstract. The construction industry requires the emergence of new promising technologies. This stimulates the creation of modern building materials, which have an expanded set of functional properties. Such materials ensure ecological compatibility of the rooms of constructed buildings and structures. One of the main sources of air pollution is building materials, structures and products. They account for up to 80% of the chemicals found in the air of the rooms in operation. The development of materials capable of absorbing toxic substances is a promising direction in the construction industry. Absorption of toxic products from the air can be achieved by the use of effective, obtainable sorbents. Among such sorbents is a group of natural zeolite-containing minerals. The article presents the results of a study to determine the activity and sorption capacity of modified zeolites of the Hotynets deposit, bentonites of the Tarasovskoye deposit. A comparative evaluation of the ways of sorbent activation is given. The mineralogical and chemical composition of the investigated zeolites, the results of the action of a low-temperature nonequilibrium plasma on the structure of natural aluminosilicates are presented. As a result of the action of a low-temperature nonequilibrium plasma, the sorption capacity of both zeolites and bentonites increased. Modification of low-temperature non-equilibrium plasma maximizes the efficiency of natural zeolite-containing rocks, which makes it possible to expand their functional capabilities. The use of low-temperature nonequilibrium plasma is an economically and environmentally beneficial method.

1. Introduction

The construction industry requires the emergence of new promising technologies. This stimulates the creation of modern building materials, which have an expanded set of functional properties. Such materials ensure ecological compatibility of the premises of the erected buildings and structures.

Ecological condition of the room determines the quality of ambient air. The harmful effect on the quality of the air environment is mainly caused by volatile substances released by various sources. One of the main sources of air pollution are building materials, structures and products. They account for up to 80% of the chemicals found in the air of the premises [1]. The development of materials capable of absorbing toxic substances is a promising direction in the construction industry. Absorption of toxic products from the air environment is possible through the introduction of effective, accessible sorbents. Such sorbents include a group of natural zeolite-containing rocks.

Another direction in the development of the construction industry is the use of dry building mixtures (DBM). This is an effective way to improve the quality of construction work, while reducing



labor costs. Modifying additives are introduced into the formulation to regulate the structure and properties of the CCC. The study showed that the additive based on synthesized aluminosilicates can be successfully used as a structure-forming and water-retaining additive in the cement stone recipe [2].

Natural zeolites are the aqueous framework aluminosilicates of alkali and alkaline-earth metals. The crystal lattice of zeolites is formed by tetrahedra $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$, united by common vertices into a three-dimensional framework, penetrated by cavities and channels. In the cavities and channels are located metal cations (Ca, Na, K, Mg, Ba, Sr, etc.) and molecules of "zeolite" water.

The most valuable are the zeolite rocks containing 50-70% or more of the zeolite mineral. Studies have shown that, for practical purposes, high-silica zeolite-clinoptilolite can be distinguished primarily because of its high sorption properties and selectivity [3-5].

Among aluminosilicates, in view of the structural features, chemical and mineralogical compositions, calcium and sodium bentonites occupy a special place. Bentonite, as a rule, is understood as fine-dispersed clays consisting of not less than 60-70% of the minerals of the montmorillonite group.

Montmorillonite refers to the mineral group of smectites. The studies reported in [6, 7] showed that the minerals of this group possess a layered structure: a three-layer packet (2: 1): two layers of silicon-oxygen tetrahedra, on both sides cover a layer of alumina hydroxyl octahedra, which determines the special properties of bentonite clays - sorption, Astringent, colloid-chemical.

Zeolites and bentonites possess high sorption properties.

The work on increasing the efficiency of the use of natural aluminosilicates as sorbents in the production of building materials is mainly reduced to the basic methods of their modification: chemical [8], mechanochemical [9] and thermal, thermochemical [10-12]. However, to date, technologies based on the above methods can not be attributed to effective, because of their complexity and significant energy costs.

Along with natural zeolite-containing sorbents, new synthetic sorbents appear on the market [13]. The chemical composition and features of the structure of zeolites cause high sorption ability, resistance to acid and thermal effects, catalytic activity. The authors of the study [14] proved that the experimental synthesis conditions (temperature, reaction time and alkali concentration) have a significant effect on the type of zeolite and its content in the reaction products.

The thermal effect was considered in [15, 16]. More effective methods in comparison with the thermal method are chemical [17, 18] and thermochemical modifications. The authors of [19] showed that the thermochemical modification increases the sorption capacity of zeolites, and the degree of removal of heavy metal ions can reach 98-99%.

The solution to the problem of material activation is the development of modification methods that allow changing only surface and near-surface layers at the nanoscale: increase roughness, create additional defects or develop existing defects, remove part of the surface layer, and redistribute internal stresses. As an instrument for activating the surface of materials at the nanoscale, the action of low-temperature nonequilibrium plasma (LTNP) can serve. Processing in LTNP is an effective tool for the activation of materials [20,21].

The objective of the current study was to study the effect of low-temperature nonequilibrium plasma on natural zeolites with the aim of increasing their sorption capacity.

2. Materials and method

In the work, zeolites of the Hotynets deposit of the Oryol region, bentonites of the Tarasovskoye deposit of the Rostov region were used as an object of research for obtaining modified sorbents.

The chemical compositions of the investigated natural zeolites of the Hotynets deposit, bentonites of the Tarasovskoye deposit are presented in Tables 1,2.

In the course of the study, the change in the characteristics of zeolites and bentonites was determined in order to determine the effectiveness of the action of low-temperature plasma to enhance the sorption characteristics of the sorbents on their basis.

As the studied compounds-sorbates used phenol, formalin, kerosene. The choice of sorbates is caused by the negative impact of these substances on the biosphere.

Determination of the sorption capacity (SC) was carried out by the desiccator method in the sorbent-sorbate equilibrium system [22]. Modified bentonite acts as a sorbent.

Table 1. Chemical composition of the Hotinets deposit

Formula	Content, wt. %	Formula	Content, wt. %
Na ₂ O	0.23	S ₀	<0.05
MgO	1.47	SO ₃	<0.05
Al ₂ O ₃	9.68	K ₂ O	3.08
SiO ₂	72.3	CaO	2.95
P ₂ O ₅	0.28	TiO ₂	0.44
MnO	0.02	FeO	0.23
Fe ₂ O ₃	3.98	Fe ₂ O ₃	3.73
C	0.70	H ₂ O	4.98
F	0.089	Loss on ignition	5.14

Table 2. Chemical composition of bentonites of Tarasovskoye deposit

Formula	Content, wt. %	Formula	Content, wt. %
SiO ₂	70.18	CaO	1.45
Al ₂ O ₃	13.04	MgO	1.43
TiO ₂	0.67	MnO	0.02
Fe ₂ O ₃ + FeO	5.40	SO ₃	0.33
Na ₂ O	0.22	H ₂ O	6.09
K ₂ O	1.47	SiO ₂ /Al ₂ O ₃	5.4
		Loss on ignition	5.43

Nitric porosimetry on the NOVA 2200e has been used to determine the influence of LTNP on the variation of the nanoporosity of a natural zeolite. In the calculations, the Barrett-Joyner-Halenda (BJH) method was used [23,24].

To modify the samples, the technology of action of low-temperature nonequilibrium plasma (LTNP) was chosen. Modification of disperse bentonite was carried out on a laboratory unit of the MIPT-MGSU.

In the installation of an AC source with a voltage of up to 8000 V and a frequency of up to 40 kHz between the electrodes, a low-temperature nonequilibrium plasma region is created with an E/N parameter value of 15×10^{-16} V/cm².

Processing time varied from 1 to 4.5 minutes. After processing of the LTNP material in the material, a partial dissipation of energy takes place due to the transition of the ordered processes under the plasma action into disordered processes, including thermal energy.

This process begins immediately at the time of activation and can continue even after the end of the impact of LTNP on the material. At the same time, structural changes in the material take place in surface and near-surface layers with the formation of additional active centers and radicals, which is confirmed by the results of determining the structure change and increasing the sorption capacity of zeolites modified in LTNP.

3. Results and discussion

The study involved control and modified samples. After modification in LTNP for 1.5 minutes of the investigated materials, a qualitative change in the porosity of the modified zeolites is observed (Tables 3, 4).

The observed changes in the structure of zeolites subjected to LTNP treatment are apparently due to both a change in the internal structure and the removal of various forms of water from the surface of the minerals. With a longer exposure (from 3 to 4.5 min), the ordered crystal structure. In addition, a partial reflow of the surface is possible.

Table 3. Pore distribution by size of control sample

Pore diam., A	Pore volume, $\cdot 10^{-3} \text{ cm}^3/\text{kg}$	Surface area of pores, m^2/kg	$dV(r), \cdot 10^{-9}$ $\text{m}^3/(\text{A} \cdot \text{g})$	$dS(r), \cdot 10^{-6}$ $\text{m}^3/(\text{A} \cdot \text{g})$
40.330	6692	6583	1.110	1.092
52.482	10463	9327	0.455	0.316
76.556	14597	11472	0.298	0.155
128.053	21513	13632	0.186	0.582
760.473	48667	15060	0.046	0.023

Table 4. Pore distribution by the dimensions of the modified sample

Pore diam., A	Pore volume, $\cdot 10^{-3} \text{ cm}^3/\text{kg}$	Surface area of pores, m^2/kg	$dV(r), \cdot 10^{-9}$ $\text{m}^3/(\text{A} \cdot \text{g})$	$dS(r), \cdot 10^{-6}$ $\text{m}^3/(\text{A} \cdot \text{g})$
40.628	7017	6904	1.214	1.195
52.726	10350	9391	0.475	0.355
74.898	15168	11941	0.314	0.166
261.184	22635	14221	0.187	0.572
742.414	49255	15655	0.047	0.025

An experimental study of the sorption capacity (SC) of bentonites was carried out in equilibrium systems: phenol-bentonite, formalin-bentonite, kerosene-bentonite. The experimental sample was exposed to LTNP for 1.5 minutes. The determination of SC was carried out for 7 days, respectively, after 1, 2, 4, 6 and 7 days.

Figure-1 shows the results of studies in the formalin-bentonite system. The modified sample (curve 2) has a greater sorption capacity than the control sample. After 1 day, the increase in SC was 70%. Starting from the 4th day, there is a gradual increase in sorption capacity in the next 24 hours, a gradual increase in the sorption capacity within the range of 20-30%.

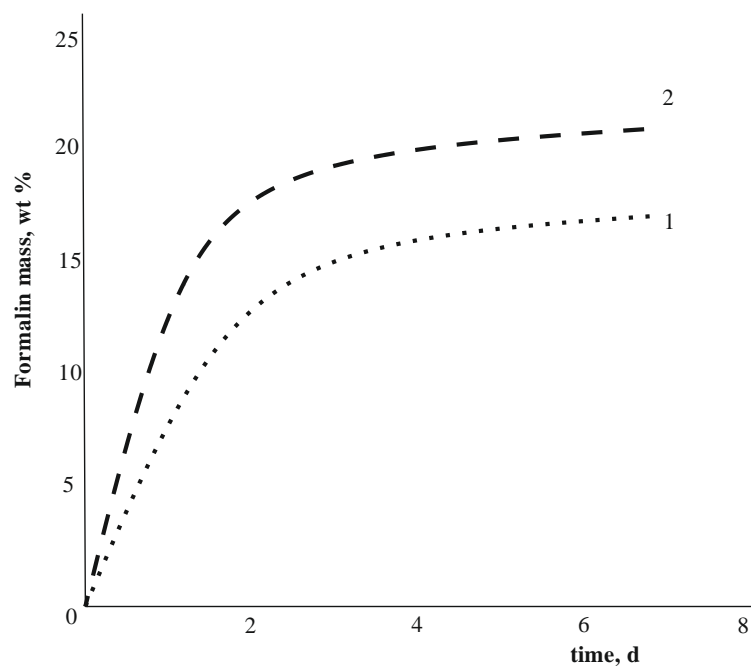


Figure 1. Change in sorption capacity in the formalin-bentonite system:
1 - control sample, 2 - modified sample

The change in sorption capacity in the kerosene-bentonite equilibrium system is shown in Figure 2. Analysis of the curves obtained shows that in this system the greatest increase in sorption capacity occurs in the first day, as in the phenol-bentonite and formalin-bentonite systems.

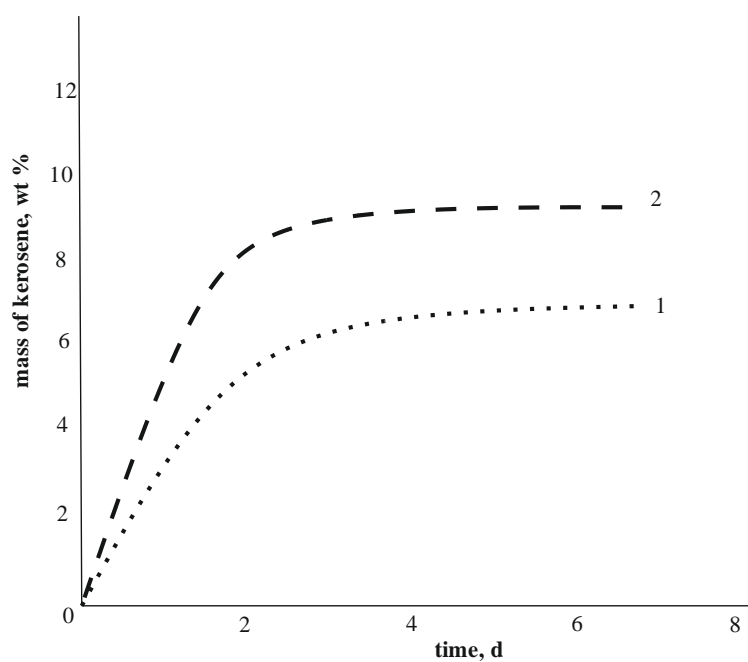


Figure 2. Change in sorption capacity in the kerosene-bentonite system:
1 - control sample, 2 - modified sample

Figure-3 shows the isotherms of the phenol-bentonite system. In the first day the sorption capacity of the modified sample increased by 80%, which exceeds the SC in the formalin-bentonite system over the same period of time.

The observed changes in the structure of zeolites subjected to LTNP treatment are apparently due to both a change in the internal structure and the removal of various forms of water from the surface of the minerals. At longer exposure (from 3 to 4.5 minutes), there is a disruption of the ordered crystal structure, and, probably, partial reflow of the surface.

The nature of the change in the volume of nanopores allows us to conclude that directional influence can be achieved due to a change in the time of action of LTNP to ensure the maximum efficiency of sorption processes with respect to specific sorbates, taking into account their characteristics. Thus, it becomes evident that after the action of LTNP on the zeolite, the pore volume and the area of their surface increase.

A comparative analysis of the curves for control and LTNP dispersed phase dispersions indicates that one of the results of plasma-chemical treatment is an increase in the intensity of luminescence.

Thus, it can be concluded that the surface concentration of functional groups increases with an increased reversal time from the metastable state.

The results obtained make it possible to conclude that the dependence of the increase in the sorption capacity of mineral carriers on the time of exposure to these LTNP is not proportional. The optimum exposure period for achieving maximum sorption capacity and activity is 1.5 minutes.

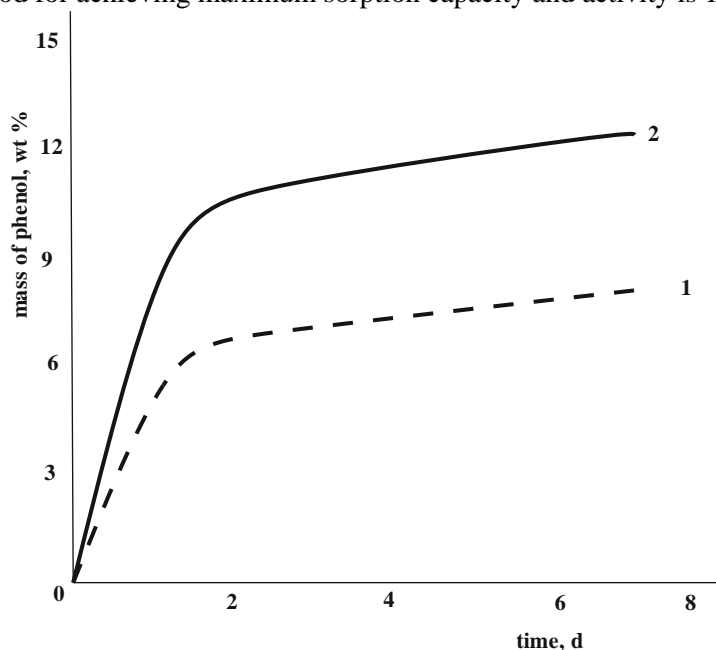


Figure 3. Change in sorption capacity in the formalin-bentonite system:
1 - control sample, 2 - modified sample

Modification of low-temperature nonequilibrium plasma to the greatest extent increases the efficiency of natural zeolite-containing rocks, which makes it possible to expand their functionality, while, unlike other methods of modification, the use of LTNP is economically and environmentally advantageous.

Based on the results of the conducted studies, it can be concluded that the modification in low-temperature nonequilibrium plasma contributes to a significant increase in the sorption capacity of natural bentonites of the Tarasovskoye deposit in relation to the organic sorbates studied.

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