# SECTION 1. NANOMATERIALS AND NANOTECHNOLOGIES (SYNTHESIS, PROPERTIES AND APPLICATIONS)

## EFFECTIVE SORBENTS BASED ON PLASMA-MODIFIED ALUMINOSILICATE MINERALS

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### I. INTRODUCTION

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 [1]. The development of materials capable of absorbing toxic substances is a promising direction in the construction industry.

Another direction in the development of the construction industry is the use of dry building mixes (DBM). This is an effective way to improve the quality of construction work, while reducing labor costs. To adjust the structure and properties of DBM modifying additives are introduced into the formulation. Research [2] showed that the additive based on synthesized aluminosilicates can be successfully utilized as a structure-forming and water-retaining additive in the formulation of the set cement.

The zeolite rocks containing 50-70% or more of the zeolite mineral are considered to be the most valuable. In turn, the high-silica zeolite – clinoptilolite is the first among zeolites which can be distinguished in terms of practical significance. And this is primarily due to its high sorption properties and selectivity [3-5].

Among aluminosilicates calcium and sodium bentonites stand apart in terms of structural particularities, chemical and mineralogical compositions. Bentonites, as a rule, are seen as fine-dispersed clays consisting of not less than 60-70% of the minerals of the montmorillonite group. Montmorillonite belongs to the mineral group of smectites. The results reported in [6, 7] showed that minerals of this group have a layered structure – a three-layer packet (2:1): two layers of silicon-oxygen tetrahedra cover a layer of alumina hydroxyl octahedra on both sides. This determines special characteristics of bentonite clays – sorption, binding and colloid-chemical 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 existing technologies, which are based on the above mentioned methods, cannot be treated as effective due to their complexity and significant energy costs.

Chemical [13, 14] and thermochemical methods of modifications are considered to be more effective than the thermal one. The authors of [15] showed that the thermochemical modification increases the sorption capacity of zeolites and that 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: an increase of roughness, creation of additional defects or development of the existing ones, partial removal of the surface layer and redistribution of internal stresses. The effect of low-temperature nonequilibrium plasma (LTNP) can serve as an instrument for activating the surfaces of materials at the nanoscale. LTNP treatment is an effective technique for the activation of materials [16, 17].

The objective of this research is to examine the effect of low-temperature nonequilibrium plasma on natural zeolites with the aim of increasing their sorption capacity.

### II. MATERIALS AND METHODS

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.

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.

Determination of the sorption capacity (SC) was carried out by the desiccator method in the sorbent-sorbate equilibrium system [18]. Modified bentonite acts as a sorbent.

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 [19, 20].

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. The installation of the MIPT-MGSU is shown in Fig.1.

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 $15 \cdot 10^{-16}$ V/cm$^2$.

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.

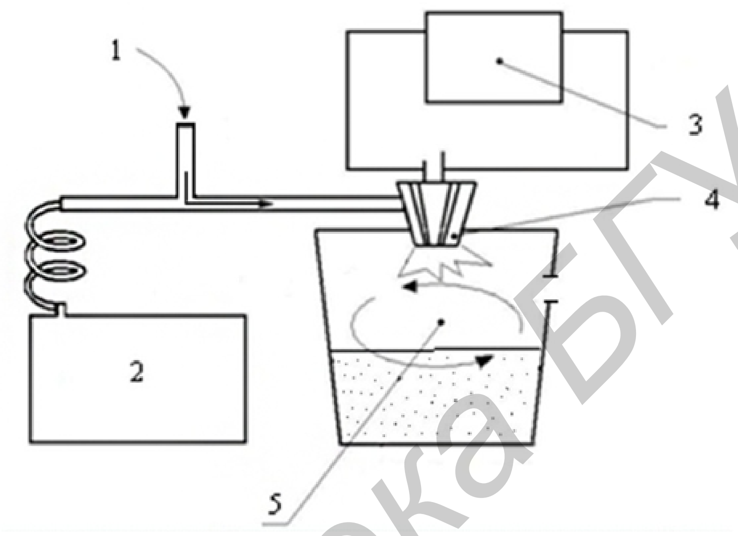

Figure 1 – Scheme of laboratory installation: 1 – feed supply, 2 – piston compressor AWC-3040 – compressed air source with pressure up to 0,8 MPa, 3 – high-voltage source (generator), 4 – plasma chemical reactor (plasmatron), 5 – receiving storage container for Processed raw materials, 5 liters

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.

## III. 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 1, 2).

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 1 – Pore distribution by size of control sample

| Pore diam., A | Pore volume, $10^{-3}$ cm$^3$/кg | Surface area of pores, m$^2$/кg | dV(r), $10^{-9}$ m$^3$/(A·g) | dS(r), $10^{-6}$ m$^3$/(A·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 2 – Pore distribution by the dimensions of the modified sample

| Pore diam., A | Pore volume, $10^{-3}$ cm$^3$/кg | Surface area of pores, m$^2$/кg | dV(r), $10^{-9}$ m$^3$/(A·g) | dS(r), $10^{-6}$ m$^3$/(A·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.

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.

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.

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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# EFFECT OF ELECTROLYTE VISCOSITY ON HEATING OF GROWING ANODIC OXIDE DURING ELECTROCHEMICAL ANODIZING

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## I. INTRODUCTION

Electrochemical anodic oxidation of valve metals has been intensively investigated in recent years, because this process allows to create the nanoscale structures [1]. An important factor affecting the kinetic of electrochemical anodizing is temperature. Growth of metal oxides during anodizing process is caused by the migration of metal cations from an oxide/metal interface to electrolyte and of oxidant anions from an oxide/electrolyte interface toward metal through the oxide barrier layer. As the voltage of an electrochemical cell almost completely drops on the oxide layer, the Joule heating of growing oxide occurs. The heating increases with increasing of energy consumption of the anodizing process and changes the oxide growth rate. Anodizing of aluminum on high power consumption is applied for fabrication of porous alumina with high ordered hexagonal cells [1, 2].

## II. EXPERIMENTAL

We propose an indirect method for temperature measuring of growing oxide during the electrochemical anodizing. This method is based on the property of metals to change their resistance with rising of temperature. To implement this method, a special electrochemical cell has been designed. An anodizing sample in the cell is a tape of aluminum foil with thickness of 10 µm, length of 29 cm and width less than 0.5 mm. An anodic terminal was connected to center of the tape, while ohmmeter terminals to its ends, as shown in Figure 1. Due to the special separation of terminals, the influence of anodic voltage on the measurement chain was minimized. According to the fact that a thin conductive part of aluminum during anodizing is surrounded by growing oxide film, the temperature of aluminum is close to the anodic oxide temperature.

Experiments were carried out at the galvanostatic regime at anodic current density of 200 mA/cm$^2$ in aqueous (low viscous, i.e. less than $10^{-3}$ Pa·s at 20°C) and based on 1:1 (volume) mix of water and glycerin (high viscous, i.e. more than $10^{-3}$ Pa·s at 20°C) solutions of 1% citric acid. Changings in the resistance were interpreted in heating according to the formula:

$$\Delta T = T_i - T_0 = [R(T_i) - R(T_0)]/[\alpha \cdot R(T_0)] \tag{1}$$

where $T_i$ – the conductor temperature during anodization, K; $T_0$ – the conductor temperature at the beginning of anodization, K; $R(T_i)$ – the resistance of the conductor during anodizing, Ohm; $R(T_0)$ – the resistance of