Compounding and technological methods for increasing the efficiency of wood matrix mineralization

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Abstract. This paper presents the results of a study of the efficiency of mineralization of the plant matrix of pine wood samples by immersion of experimental samples in an organo-mineral water suspension (dispersion medium) and holding for 24 hours under natural conditions, as well as under autoclave impregnation at an excess pressure of up to 1.5 MPa. To create the necessary working pressure in the autoclave, an inert gas (argon) was used. As working fluids, we used an aqueous solution of arabinogalactan, aqueous suspension containing polymineral sand, pre-dispersed to a fine state and a soluble complex obtained by mechanical mixing of the above components. Prototypes were made from ordinary pine wood. The effectiveness of impregnation was evaluated by increasing the density of samples. In addition, data on changes in Brinell hardness, compressive strength of samples along the fibers, and water absorption of impregnated wood were obtained. It was found that autoclaving in the studied mode leads to an increase in the density of samples by more than two times, reduces their water absorption, and increases strength by 84%.

1. Introduction
To increase the resistance to rotting of wooden building materials and their destruction under the influence of biological organisms, there are many ways to modify it, including treatment with various antiseptics [1]. However, these techniques have a number of significant disadvantages, among which, first of all, we can note the duration of treatment, a large number of components used, and the toxicity of reagents. One of the ways to increase the durability and reliability of materials from plant raw materials is artificial petrification, the technology of which consists in processing wood materials with a soluble complex [2, 3] obtained from the natural polysaccharide arabinogalactan and nanoscale quartz-containing rocks of various genesis. This was demonstrated by us in preliminary studies [4], where an organo-mineral complex of 10 parts of arabinogalactan per 1 part of polymineral sand was effectively used as the main reagent. It was found that the processing of plant raw materials is associated with the transfer of a soluble complex compound through the surface of experimental samples due to their capillary-porous structure and subsequent replacement of the cell wall material with a mineral component, filling the free space of the wood matrix with various minerals [5, 6]. According to [7] for effective and long-term protection of wood from biodegradation, it is preferable to use an autoclave processing method. Almost all systems for protecting wood from biodegradation must be introduced into the pore space of wood and the structure of cell walls [8]. Impregnation can occur under the action of capillary forces, external overpressure, as well as due to the diffusive movement of molecules or ions of impregnating substances through the capillaries of wood filled with...
water [9-14]. However, the problem faced by researchers [15] engaged in wood protection is related to the different penetration capacity of the bulk phase of plant raw materials (for example, pine sapwood). This fact has not allowed us to identify general patterns of changes in the main performance characteristics of the material when processing it with the water composition used. Therefore, the purpose of these studies was to determine the influence of the main compounding and technological factors (composition, processing conditions) on the water-physical and mechanical characteristics of wood treated with organo-mineral suspension.

2. Materials and methods

2.1 Materials

The wood of ordinary pine was chosen as the object of research (Pinus Sylvestris L.).

To obtain an aqueous suspension containing an organo-mineral complex, the following components were used: polymineral river sand (S) of the Krasnoflotsky-Zapad deposit in the Arkhangelsk region, the main rock-forming minerals of which are quartz (74%) and albite (17%); natural polysaccharide arabinogalactan (AG), isolated from an aqueous extract of Siberian larch wood; distilled water.

2.2 Methods

The mineral composition of the sand was determined using x-ray fluorescence spectroscopy using a Shimadzu EDX-800 HS spectrometer. The sand was mechanically activated by dry grinding for 20 and 40 minutes at a rotor speed of 420 rpm in a Retsch PM100 planetary ball mill. The dimensional characteristics were determined by the method of dynamic light scattering on a particle analyzer DelsaNano.

To determine the time of stable state of the organo-mineral complex in an aqueous dispersion medium, electronic absorption spectra of aqueous solutions of AG, suspension of raw S and AG (after 15 minutes of settling) and samples of sand with AG after mechanical grinding were recorded on a spectrophotometer SF-2000 in the visible spectral range (400÷700 nm). The spectral characteristics were recorded for 24 hours with a time interval of 2 hours.

Water solutions and suspensions for processing experimental samples of wood were prepared by adding to the dispersion medium (water): 5% AG; 2.5% S and 5% AG-2.5% S. for quantitative calculation of the content of components, the mass percentage was used. The total volume of the working fluid was 2 liters.

For research, samples of wood of standard sizes (20x20x30 mm) were produced without visible defects. Processing of wood with working solutions and suspensions was carried out in two ways. Brought to a constant mass in the drying cabinet, wood samples for the first option were immersed in a suspension (load was used) and kept at a temperature of 25°C for 24 hours.

In the second variant, impregnation was performed using the same time and temperature parameters with similar working fluids using autoclaving at an excess pressure of 1.5 MPa. To create the necessary working pressure in the autoclave, an inert gas (argon) was used. In addition, experiments on the autoclave variant were supplemented with experiments in which the working suspension was heated to 80°C before use.

A photo of a specially manufactured laboratory autoclave is shown in Figure 1.

After a specified period of time, the samples were extracted from the impregnating liquids, dried in a drying cabinet at a temperature of 40°C (brought to a constant mass).

To conduct a comparative assessment of changes in performance characteristics, control samples of wood were produced that were not subjected to the above treatment.
The density of wood before and after processing was determined taking into account the corresponding mass of samples (m₀ - before and m₁ - after processing) and their volume (calculated by geometric dimensions). The relative density change (Δρ) of wood was calculated using the expression (1):

\[ \Delta \rho = \frac{\rho_1 - \rho_0}{\rho_0} \cdot 100\%, \]  

where \( \rho_0, \rho_1 \) – the density of the prototype before and after modification, g/sm³.

The compressive strength along the fibers (\( R_c \), MPa) and Brinell hardness (\( HBW \), MPa) were calculated based on the following expressions:

\[ R_c = \frac{R_{\text{max}}}{S}, \]  

where \( R_{\text{max}} \) – maximum breaking load, H; \( S \) – the cross-sectional area of the sample, mm.

\[ HBW = \frac{0.102 \cdot F}{0.5 \pi D(D - \sqrt{D^2 - d^2})} \]  

where \( F \) – applied load, H; \( D \) – ball diameter, mm; \( d \) – the diameter of the imprint, mm.

Determination of mechanical characteristics (strength, hardness) of wood before and after modification was carried out on the test press TP-1-100 and the test machine Shimadzu AGS-5kNX.

Water absorption of wood was determined by the amount of water absorbed after 30 days with periodic weighing of samples. The maximum moisture content of wood held until water absorption was stopped was taken as the water absorption index. To do this, the samples were placed in a
desiccator under the insert, filled with distilled water so that one of the planes of the cross section remained dry, closed with a lid and kept at a temperature of (20±2) °C.

All series of experiments were performed on three samples. As the final result, the average value of the indicator was used.

3. Results and discussions
The elemental composition of the mineral component (river sand) in terms of oxides is shown in Table 1. The quartz-containing rock used is a high-quality sand (more than 90% silicon oxide content).

| Table 1. Mineral composition of sand expressed as oxides. |
|----------------------------------------------------------|
| The content of oxides, Wt. %                             |
| SiO₂          | Al₂O₃       | Na₂O       | Fe₂O₃       | CaO         | K₂O         | LOI         |
| 91.35         | 5.06        | 1.37       | 0.65        | 0.26        | 0.36        | 0.95        |

The average size distribution of sand particles after mechanical activation showed that this parameter had a value of 426±20 nm when grinding for 20 min, and 360±10 nm when grinding for 40 min. For Figure 2 for example, the size distribution of polymineral sand particles of 20-minute grinding is presented. It should be noted that the used modes of mechanical dispersion allow to obtain fairly narrowly dispersed fractions of the mineral component. The grinding time does not significantly affect the particle size characteristics.

![Figure 2. – Number based sand particle size distribution](image)

The results of spectral studies have shown that when mixing the mineral and organic components of the impregnation solution, the formation of a complex occurs in the case of using mechano-activated sand. At the same time, the holding time of the reaction system before its use should be at least two hours. So, a graph of the dependence of the relative change in the absorbance \( \frac{A_{700}}{A_{700}} \) at 700 nm over time for organomineral suspensions prepared using the initial sand and sand after mechanical grinding in relation to the optical density of arabinogalactan is presented in Figure 3. These dependencies show that complexation is characterized by compositions with mechano-activated sand. For further research, we used samples of polymineral sand with particle size characteristics equal to 420 nm.

The results of experiments on the influence of the composition of the impregnation solution and suspension on the change of the studied physical and mechanical properties of wood samples under spontaneous and autoclave impregnation methods are presented in Table 2.
Figure 3. Change in the relative absorbance $A_{700}$ over time for compositions: 1 – AG; 2 – $S_0$+AG; 3 – $S_{420}$+AG; 4 – $S_{360}$+AG ($S_0$ – source polyn mineral sand, $S_{420}$ and $S_{360}$ – sand with an average particle size of 420 and 360 nm, respectively).

Table 2. Changes in the physical and mechanical properties of wood samples with different methods of impregnation

| Composition | $\Delta \rho$,% | HBW, MPa | $R_c$, MPa |
| ----------- | -------------- | ---------- | ----------- |
|            | $*25$ °C | Autoclave | $*25$ °C | Autoclave | $*25$ °C | Autoclave |
| AG         | 0.1 | 2.8 | 3.3 | 1.74 | 1.88 | 1.89 | 68.3 | 71.0 | 74.4 |
| S          | 0.9 | 1.6 | 2.1 | 1.02 | 1.43 | 1.63 | 53.4 | 63.5 | 65.2 |
| AG-S       | 3.2 | 17.5 | 21.0 | 1.47 | 1.54 | 2.49 | 40.1 | 53.4 | 77.2 |
| Control    | - | - | - | 1.12 | - | - | - | 42.0 |

* - spontaneous impregnation process

Experiments have shown that when impregnated with the AG-S complex, the density increase is significantly higher than when impregnated with its individual components. In the process of wood impregnation with both the AG-S complex and its individual components, the density of samples increases, but a significant increase (up to 21%) is achieved only with the second version of autoclave impregnation with an increase in the suspension temperature, which is seven times higher than the results obtained with spontaneous impregnation in natural conditions at normal (25 °C) temperature. This effect is due, in our opinion, to the fact that the autoclaving mode leads to a more complete saturation of the pore and cell space of wood with mineral components, which causes a sharp increase in its density. The hardness of samples impregnated with the AG-S complex in the same way increased by 123%. The compressive strength along the fibers when processed under natural conditions by individual components in comparison with the control sample increases, and in the case of a solution of AG increases by 70%, while the organo-mineral complex reduces the strength. At the same time, after autoclave impregnation by the second method with an increase in the temperature of the suspension containing the AG-S complex, the strength of the samples increases by 84% in comparison with the control one. This can be explained as follows. Since the mechanical properties of wood are determined by the inter-fiber bonds that occur as a result of the formation of hydrogen bonds between macromolecules on the fiber surfaces, the decrease in strength is due to the weakening of
these bonds, due to their elongation and even rupture due to the introduction of a mineral component (quartz) into the structure of crystals. Therefore, a decrease in the maximum load that a sample of wood can withstand indicates that there is an impregnation with solutions, in which particles of quartz sand penetrate the wood and partially destroy and weaken its structure. When impregnated with a solution of AG (without adding sand), the binding component is replaced with this polysaccharide and, accordingly, the formation of new intermolecular bonds. Experiments have shown that in order to increase the efficiency of capillary impregnation, it is advisable to use heated liquids, since their viscosity decreases with increasing temperature and the rate of penetration into the wood increases, which gives an increase in strength and hardness.

Experiments conducted to determine the water absorption of experimental samples showed that after 30 days of exposure in distilled water, autoclave-treated wood at a temperature of 25°C reduces this indicator by 17% compared to samples modified in spontaneous mode. A 28% decrease in water absorption is observed in wood samples that are autoclave modified at elevated temperatures.

4. Conclusions
It was found that the modification process of the wood matrix by an organo-mineral complex based on an aqueous suspension of arabinogalactan and mechano-activated polymineral sand associated with mineralization of the pore and cell space of a plant object can occur in a spontaneous mode. Autoclave modification mode at an excess pressure of 1.5 MPa allows for deeper saturation of the mineral component of wood samples. At the same time, it is noted that an increase in the autoclaving temperature intensifies this process. As a result of modification transformations, the maximum increase in the density of the prototypes was 21%, the compressive strength was 84%, and the hardness was 123%. These indicators of prototypes provide a reduction in their water absorption by 28%.

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