Colloid chemical aspects accelerated artificial petrification of wood

V E Danilov, A M Ayzenshtadt, N V Kilyusheva, T A Makhova, A O Belyaev
Northern (Arctic) Federal University named after M.V. Lomonosov, Severnaya Dvina Emb. 17, Arkhangelsk, 163002 Russia

E-mail: v.danilov@narfu.ru

Abstract. The paper describes various approaches to increasing the processing efficiency of coniferous wood with a partially soluble organo-mineral suspension for the manufacture of artificially petrified wood. The suspension was prepared by grinding the polymineral river sand from the Krasnoflotsky West deposit (Arkhangelsk region) and then mixing it with a solution of arabinogalactan. Standard samples (20x20x30 mm) of wood were immersed in the suspensions for 24 hours, after which they were taken out, dried and weighed. The processing efficiency was evaluated by increasing the density of the samples due to the filling of the wood matrix with silica (excluding arabinogalactan). The influences of the concentration of components, size characteristics and zeta-potential of the surface of silica particles on the increase in the density of samples were studied. It was confirmed that arabinogalactan promotes deeper penetration of silica particles into wood, which leads to a greater increase in density (up to 9% per treatment). It was also found that a decrease in the size of silica particles from 243 nm to 163 nm, as well as increasing the zeta potential from -30 mV to -45 mV, do not lead to a significant increase in the density of the samples.

1. Introduction
It is known that some polysaccharides are able to form complex compounds with insoluble substances and easily penetrate the cell membrane of a plant cell. Such a chemical compound is arabinogalactan (AG), isolated from larch wood [1]. This compound has surface-active properties [2] and can form water-soluble complexes with insoluble metal molecules and oxides [3], as well as with quartz-containing rocks in a finely dispersed state in a diluted buffer solution. The organomineral complex consisting of 10 parts of arabinogalactan and 1 part of mineral sand is applicable for the impregnation of plant cell walls and the accelerated production of artificially petrified wood [4].

However, according to [5], the petrification of wood should be considered as two joint processes - replacing the original organic components of the cell walls with mineral ones and filling the free space of the wood matrix with different minerals. Therefore, the study of the colloid chemical aspects of filling the capillary-porous structure of the wood matrix with organic-mineral dispersions, in our opinion, is an important step in optimizing the process of accelerated wood petrification. Thus, the task of the study outlined in this work was to study the effect of wood processing with a suspension containing soluble organic-mineral complex and fine silica particles on its density and surface tension.
2. Materials and methods

2.1. Materials
Scots pine wood was chosen as object of study. Arabinogalactan and polymineral sand from the Krasnoflotsky Zapad deposit (Arkhangelsk region) were used for partially soluble organo-mineral suspension synthesis.

2.2. Methods
The mineral composition of sand was determined using X-ray fluorescence spectroscopy using the Shimadzu EDX-800 HS spectrometer.

The sand was mechanically activated by mechanical dry grinding for 20 minutes at a rotor speed of 420 rpm by 2 cm large grinding balls in the Retsch PM100 planetary ball mill. Silica particle size was measured by dynamic light scattering (DLS) using a DelsaNano C. NaOH aqueous solutions were added to vary protolytic properties of the dispersion medium in the obtained silica suspension. The Expert-001-3 fluid analyzer was used for pH control. Zeta potential of silica particles in water was determined by electrophoretic velocity measurement using a DelsaNano C.

Partially soluble organo-mineral suspensions were prepared by mixing arabinogalactan water solutions (2, 5 and 10% by weight) with silica powder (1, 2, 5, 10, 20, 30, 40 and 50% by weight).

In order to study the wood density increase as a result of processing, standard (20x20x30 mm) wood samples were made, dried to constant weight, weighed and then left for 24 hours in suspension containing soluble organic-mineral complex and fine silica particles.

The surface tension at the “solid-solution” phase interface was calculated by the Owens, Wendt, Rabel and Kaelble method (OWRK) using experimentally determined wetting angles of the wood surface with polar and non-polar solvents. Contact angle measurements were conducted using a Drop Shape Analyzer EasyDrop DSA20E (Kruss).

3. Results and discussions
Table 1 shows the mineral composition of sand from the Krasnoflotsky Zapad deposit expressed as oxides.

| The content of oxides, Wt.% | SiO₂ | Al₂O₃ | Na₂O | Fe₂O₃ | K₂O | CaO | TiO₂ | SO₃ | other oxides |
|-----------------------------|------|-------|------|-------|-----|-----|------|-----|-------------|
|                             | 91.35 | 5.06  | 1.37 | 0.647 | 0.356 | 0.255 | 0.045 | 0.019 | 0.898       |

Table 2. Details of silica dispersions used for partially soluble organo-mineral suspension synthesis.

| Type of grinding mill, grinding time (min) | Particle size, D(50) (nm) | Polydispersity Index | Standard deviation in size | pH | Zeta potential (mV) |
|-------------------------------------------|---------------------------|----------------------|----------------------------|----|---------------------|
| planetary ball mill, dry, 20             | 243                       | 0.446                | 51.2                       | 7  | -30                 |
| colloid mill, wet, 10                     | 163                       | 0.287                | 52.6                       | 7  | -30                 |
| planetary ball mill, dry, 20             | 199                       | 0.911                | 55.0                       | 12 | -45                 |

*D(50) is the median average particle size by number distribution.

As is seen from the Table 1, the SiO₂ content in sand is more than 90%, which indicates a high raw material quality. For the preparation of suspensions, a sand dispersion with a particle size of 243 nm was used. Dispersions with a smaller particle size and a large zeta potential were used only for the comparison experiment.

The dependences of the increase in the density of wood samples Δρ on the concentration of silica suspension and arabinogalactan solution is shown in the Figure 1.
Discussing the results presented in Figure 1, we can conclude that the increase in the density of wood will depend more on the concentration of arabinogalactan, since its penetrating power is much greater. Arabinogalactan penetrates into all the pore and cellular space, while silica particles spontaneously are able to penetrate into wood only to a depth of 1.8-2.7 mm (along the tracheids).

The dependence of the increase in the density of wood samples on the concentration of partially soluble organo-mineral suspensions components is shown in the Figure 2.

Discussing the results presented in Figure 2, we can conclude that increase in the density of the wood from the concentration of the suspension components is well described by the plane of the equation 1:

$$\Delta \rho = 0.59 \times C_{AG} + 8.31 \times 10^{-2} \times C_{SiO_2} + 8.66 \times 10^{-3} \times C_{AG} \times C_{SiO_2}$$  \hspace{0.3cm} (1)$$

The slope of the lines on the plane shows that arabinogalactan and silica together give greater increase in the density than individually.

The increase in wood density for this situation can be expressed by the equation 2:
\[ \Delta \rho = \Delta \rho_1 + \Delta \rho_2 + \Delta \rho_3 + \Delta \rho_4 \]

where \( \Delta \rho_1 \) – increase in the density due to arabinogalactan (curve 1 from figure 1);

\( \Delta \rho_2 \) – increase in the density due to insoluble silica particles (curve 2 from figure 1);

\( \Delta \rho_3 \) – increase in the density due to additional amount of insoluble silica particles penetrated the wood (due to the action of arabinogalactan as surfactant);

\( \Delta \rho_4 \) – increase in the density due to soluble silica (part of soluble complex).

The dependencies of increase in the density of the samples due to the filling of the wood matrix with silica \( \Delta \rho_{2,4} \) on the concentration of partially soluble organo-mineral suspensions components are shown in the Figure 3.

\[ \text{Figure 3. Dependencies of increase in the density of the samples due to the filling of the wood matrix with silica on the concentration of partially soluble organo-mineral suspensions components.} \]

The data presented in Figure 3 show that with an increase in the content of arabinogalactan in the suspension, the penetrating ability of silica into the pore and cellular space of wood increases, which is confirmed by large values of increase in the density. Wood density increases (up to 9\% per treatment) due to spontaneous filling of capillaries with fine silica particles and impregnation of cell walls with arabinogalactan-silica complex. However the concentration of silica must be limited, since after treating the wood with highly concentrated suspensions (more than 10\% by weight) its tracheids becomes clogged and repeated processing no longer leads to a significant increase in density.

The use of smaller particles (163 nm), as well as the use of particles with a high value of zeta potential (-45 mV) for the preparation of an impregnating suspension (concentration of 10\%) did not lead to a significant increase in results. However, in our opinion, a more pronounced effect of these parameters will be important when wood is impregnated with less concentrated suspensions.

During the experiments, the following data obtained wetting angle of the wood samples with working fluids (Table 3). The functional dependencies of the OWRK method are presented in Figure 4.

\[ \text{Table 3. Wetting angle of wood samples before and after treatment} \]

| Sample        | Working fluid | Water | Ethylene glycol | Ethanol | Decane |
|---------------|---------------|-------|-----------------|---------|--------|
| No. 1 – Control | 101           | 97    | 20              | 10      |
| No. 2 – After processing | 83           | 86    | 16              | 15      |
Figure 4. Ounce-Wend charts for samples No. 1 (a) and No. 2 (b):

\[ x = \frac{\sigma_D}{\sigma_L}; \quad y = \frac{\sigma_L (\cos \theta + 1)}{2\sqrt{\sigma_D}}. \]

The obtained dependences, which have a satisfactory approximation confidence coefficient (0.80 for sample No. 1 and 0.77 for sample No. 2), made it possible to calculate the values of the surface tensions of the control and experimental samples. So the dispersion component of the surface tension of the material under study is equal for the 1st sample - 15.3 mN/m, for the 2nd sample - 15.8 mN/m. The polarization component of the surface tension of the material under study is equal for the 1st sample - 9.4 mN/m, for the 2nd sample - 7.3 mN/m. The total surface tension for the first sample \( \sigma_S = 24.7 \) mN/m, for the second - 23.1 mN/m. The obtained experimental results of determining the surface tension showed that the process of processing experimental samples of pine wood does not lead to a significant change in the total surface energy. At the same time, there is a redistribution of components of this magnitude associated with the dispersion \( \sigma_{SD} \) (van der Waals force) and polarization \( \sigma_{SP} \) (chemical structure) parts. Thus, an increase in the value of \( \sigma_{SD} \) and a decrease in the value of \( \sigma_{SP} \) characterize the presence of an active chemical interaction of the components of coniferous wood and the AG-silica complex.

4. Conclusions

Thus, we have found that the concentration of the components of the suspension has the main impact on the process of spontaneous filling of wood with mineral particles, while the size and zeta potential of particles (in the studied ranges of 243–163 nm and -30 – -45 mV, respectively) do not have significant influence. In order to accelerate the process of mineralization of wood, it is necessary to use its vacuum impregnation.

5. Acknowledgements

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