Effect of thermal modification of saponite-containing material on energy properties of its surface

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Abstract. Preliminary experimental studies have shown the fundamental possibility and feasibility of using saponite-containing material (SCM), extracted from the pulp of the tailings dump of industrial enrichment of ores of the diamond deposit named after M.V. Lomonosov, as a mineral binder for mineral wool insulation. The technology of the production of mineral wool composite was based on the effect of high temperatures (up to 1200 °C) on the raw mix consisting of SCM as a binder and basalt fibers as a fibrous aggregate. However, the new properties of the saponite-containing material after thermal modification have not been investigated. Therefore, in this study, we studied the effect of the temperature of modification of the saponite-containing material on the criterion for evaluating the energy properties of the surface (the Hamaker constant). The experiments have shown that the maximum value of the Hamaker constant is observed in the modification temperature range from 100 to 200 °C, then a decrease in the value of this criterion to a temperature of 600 °C is observed, and, there is a stabilization of the Hamaker constant in the range of temperatures from 700 °C to 1000 °C, the average value of which was 1.23·10^-20 J.

1. Introduction
At present, phenol-formaldehyde resins are mainly used as a binder component for mineral wool insulation [1]. But among alternative binders tested in different years and in different countries, one can note bitumen-containing compounds, silicate dispersions, compositions based on liquid glass and cement, aqueous solutions of bentonite clay, alum-chromophosphate bonds [2-4]. Preliminary experimental studies have shown the fundamental possibility and feasibility of using saponite-containing material (SCM) (saponite content is 65%), extracted from the pulp of the tailings dump of industrial enrichment of ores of the diamond deposit named after M.V. Lomonosov, as a mineral binder [5,6]. The chemical composition of SCM (in terms of oxides) is represented by SiO2 (52%), MgO (19%), Al2O3 (10%), CaO (4%) and other oxides in small quantities. Saponite has a three-layer structure with a swelling crystal lattice (Figure 1). The layering of saponite is represented by two layers of silicon–oxygen tetrahedron with aluminum-oxygenous octahedral layers located between them.
The destruction of the layered structure of the mineral occurs in the process of its mechanical activation. Amorphous silica released during this process is able to interact with calcium hydroxide (which is formed as a result of the contact of SCM with water due to the presence of calcium oxides in the chemical composition of SCM) [7].

The technology of the production of mineral wool composite was based on the effect of high temperatures (up to 1200 °C) on the raw mix consisting of mechanically activated SCM as a binder and basalt fibers as a fibrous aggregate [8]. Thus, a thermal insulating material with a thermal conductivity coefficient of 0.12 W/(m·K) and compressive strength of 3.0 MPa (3 times higher in comparison with a specimen not subjected to thermal modification) was obtained. At the same time, the physicomechanical properties of the mineral wool composite depend on the adhesional strength of the binder (SCM) with the surface of the aggregate. Therefore, the most important factor defining strength of contact in the system "SCM-basalt fibers", hence the composite as a whole is the surface energy in the area of the contact surfaces [9]. This energy potential must be associated with structural or chemical transformations of the components of the system under study during its heat treatment. According to the classical ideas of the theory of molecular interaction [10-12], the Hamaker constant is a measure of the force of attraction acting between the surfaces of solids. For example, for flat surfaces, the force acting on a surface unit is (1):

\[ f = \frac{A}{6\pi h^3} \]  

where \( h \) – the shortest distance between surfaces and \( A \) – the Hamaker constant.

At the same time, we have developed a method [13] for determining the value of \( A \) by the value of the wetting angle of a solid surface (\( \theta \)) using the Deryagin equation (2):

\[ \cos \theta = 1 + \frac{A}{12\pi h^2 \sigma_{\text{liq}}} \]  

where \( \sigma_{\text{liq}} \) – surface tension of wetting liquids.

The purpose of this research is to study the effect of heat treatment on the structural or chemical modification of highly dispersed saponite-containing material, estimated by the value of the Hamaker constant.
2. Methods
Saponite-containing material (SCM) was recovered by electrolytic coagulation from recycle water suspension obtained during the enrichment of kimberlite ores from the diamond deposit named after M.V. Lomonosov.

SCM was preliminarily made to its constant weight under the temperature of 100 °C. Then SCM was ground in the planetary ball mill Retsch PM100 using the dry mechanical dispersion method. Optimal dispersion parameters were selected experimentally to achieve finely dispersed state (grinding jar with volume 500 ml; 18 grinding balls from stainless steel alloy with diameter of 20 mm; sun wheel speed – 420 rpm; grinding time – 45 minutes). The particle size of saponite-containing material was determined by photon correlation spectroscopy using the Delsa Nano Series Zeta Potential and Submicron Particle Size Analyzers.

Differential thermal analysis of a highly dispersed sample of SCM was researched on a differential scanning microcalorimeter DSK-500. Scanning was carried out by heating the sample in the temperature range from 22 °C to 500 °C at a rate of 10 °C/min. Temperature measurement accuracy was ± 1 °C.

The Zisman method was used for experimental determination of energy characteristics.

To implement the Zisman method, ethanol solutions with different water contents, the concentration of which in the mixture did not exceed 50 %, were used. The surface tension of aqueous solutions of ethanol and the wetting angle of the surface of disperse systems were measured at a temperature of 20 ± 2 °C using a KRUSS Easy Drop unit.

To determine the surface wetting angle with water-ethanol solutions, samples were made by compacting highly dispersed SCM under a load of 5 kPa into a metal mold with a diameter of 30 mm. Then samples were exposed to thermal treatment in laboratory muffle furnace at a temperature range of 100 °C to 1000 °C in increments of 100 °C. Thus, 10 samples modified at different temperatures were obtained. A sample not exposed to thermal modification was used as a control.

Then, the contact angle of the surface of each sample was determined using solutions with different ethanol contents (from 4 to 50%). Then, dependency graphs of the form \( \cos \theta - 1 = f\left(\frac{1}{\sigma_{\text{liq}}}\right) \) were constructed and, using expression 2, the Hamaker constant was calculated.

3. Results
The measured values of the surface tension of water-ethanol solutions are given in table 1.

Particle size distribution of the saponite containing material is shown in Figure 2. The average particle size of the SCM was 1270 ± 314 nm.

| No | Volume fraction of water, % | \( (\sigma_{\text{liq}}=0.02) \cdot 10^3 \), N/m |
|----|-----------------------------|---------------------------------------------|
| 1  | 4                           | 24.74                                       |
| 2  | 10                          | 26.61                                       |
| 3  | 20                          | 27.34                                       |
| 4  | 30                          | 28.11                                       |
| 5  | 40                          | 28.42                                       |
| 6  | 50                          | 31.31                                       |
Figure 2. SCM particle size distribution.

Figure 3 shows a photograph of a water-ethanol solution on the surface of highly dispersed SCM. Figures 4 and 5 show photographs of SCM control sample and SCM sample thermomodified at 500 °C, respectively.

Figure 3. Water-ethanol solution on the surface of highly dispersed SCM.
Figure 4. SCM control sample.
Figure 5. SCM sample thermomodified at 500 °C.

The differential thermal analysis (DTA) of highly dispersed SCM showed the presence of endo-effect (figure 6) in the temperature range of 80 ... 220 °C, which indicates the removal of free and bound water.

Figure 6. DTA of SCM.

Table 2 shows the values of the coefficients "a" and "b" of the linear equations of the dependence \( \cos \theta - 1 = f(1/\sigma_{liq}) \) with an acceptable value of the approximation coefficient \( R^2 \) for the control sample and the samples thermally modified at different temperatures and the calculated Hamaker constant.
Table 2. The values of the coefficients in the equation $\cos \theta - 1 = a \left(1/\sigma_{liq}\right) + b$.

| Temperature of modification of SCM sample, °C | Coefficient | $R^2$ | $A \cdot 10^{20}$, J |
|---------------------------------------------|-------------|-------|---------------------|
| SCM control sample                          | $a \cdot 10^2$ | 0.91  | 2.28                |
|                                            | $-b$         |       |                     |
| 100                                        | 1.05        |       | 2.78                |
| 200                                        | 1.28        | 0.58  | 2.61                |
| 300                                        | 1.20        | 0.55  | 2.28                |
| 400                                        | 0.85        | 0.49  | 1.85                |
| 500                                        | 0.42        | 0.23  | 0.91                |
| 600                                        | 0.31        | 0.18  | 0.67                |
| 700                                        | 0.59        | 0.29  | 1.28                |
| 800                                        | 0.59        | 0.28  | 1.28                |
| 900                                        | 0.56        | 0.28  | 1.22                |
| 1000                                       | 0.54        | 0.26  | 1.20                |

The experiments have shown that the maximum value ($2.78 \cdot 10^{20}$ J) of the Hamaker constant is observed in the modification temperature range from 100 °C to 200 °C, then a decrease in the value of this criterion to a temperature of 600 °C is observed, and, there is a stabilization of the Hamaker constant in the range of temperatures from 700 °C to 1000 °C, the average value of which was $1.23 \cdot 10^{20}$ J. The absence in the scientific literature of information about the value of $A$ for other binders (in particular for phenol-formaldehyde resins) does not allow at this stage to conduct a comparative assessment of binders for this characteristic. Figure 7 shows the functional dependence of the relative change ($A_i$) of the value of the Hamaker constant with a change in the processing temperature. In this case $A_i = A_i/A_c$ ($A_i$ - Hamaker constant values for samples depending on temperature modification; $A_c$ - Hamaker constant value for control sample). This dependence has a pronounced maximum at a temperature ranging from 100 °C to 300 °C. In addition, it should be noted that at $t > 500$ °C the value of $A_i$ practically stabilizes.

![Figure 7](image_url)
4. Discussions
The maximum values of the above criteria for samples thermally modified at temperatures from 100 °C to 200 °C may indicate the presence of X-ray amorphous silica in the mechanically activated SCM, which provides interparticle interaction due to bound and free water. The stabilization of the Hamaker constant to a value of 1.23·10^{-20} J suggests that the structural changes in the SCM during thermal treatment to 1000 °C end when the temperature reaches 500 °C. Comparison of the results of differential thermal analysis with calculated $A_s$ values showed good convergence of experimental data. Thus, the positive extremum of the functional dependence $A_s = f (t)$ in the temperature range of 100…300 °C coincides well with the temperature regime at which the endo effect on the DTA curves appears, associated with the removal of residual free and bound water. At the same time, further stabilization of $A_s$ and $dT$ values with increasing temperature up to 1000 °C may indicate the absence of transformational transformations of mechanically activated prototypes of SCM in this temperature range.

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