Phase-structural irregularity of the mechanically activated saponite-containing material surface

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Abstract. The purpose of the studies was to evaluate the possibility of using mechanically activated saponite-containing material (SCM) as an additional binder in cementitious binders of hydration type of hardening. According to the working hypothesis, the activated SCM is able to show the binding properties. To confirm this fact, the phase-structural heterogeneity investigation of the material was made. As a result, after mechanical dispersion the content of the amorphous phase increases by 2 times. Investigations of the microstructure of the binder samples with and without saponite showed that: in the first case, there are two types of crystals: spongy and needle. The SEM and IR spectroscopy data showed that when the additive is introduced, the formation of hydroxides of the tobermorite group is observed, which play the role of an additional binder in the cement hardening process.

1. Introduction

The papers [1, 2] show that the saponite-containing material (SCM) extracted from recycled water suspension in the diamond industry can exhibit sorbent properties through the extended surface. Moreover, the paper [3] establishes that SCM samples with a specific surface value over 35000 m²/kg demonstrate the optimal water absorption.

The additive based on this material can stabilize system oversaturation with water relative to the solid phase in concrete compositions [4, 5]. This provides for evenly distributed products of clinker mineral hydration reaction throughout the composite.

An imbalance in original sample weights was noted when studying water sorption and desorption by the highly dispersed mineral additive. In our opinion, it is associated with additional calcium silicate hydrates formed through activation of chemical compounds in the saponite-containing material (elemental composition equivalent to oxides: silicon - 56%, magnesium - 22%, aluminum - 7%, iron - 8%, calcium - 5% [3]). As mentioned above, intensive mechanical activation of the SCM promotes its moisture sorption [7 – 8]; besides, this process is accompanied by active amorphous phase formation in the material that consequently improves its binding properties. This is due to structural features of the saponite-containing material. Therefore, according to [6] this mineral has a three-layer structure with two layers of silicon–oxygen tetrahedron and aluminium-oxygen, octahedral, dioctahedral and trioctahedral layers between them. The layered structure is destroyed and silicon dioxide is released during the mechanical activation of raw materials.
The selected object of research was evaluating the possibility to use the mechanically activated saponite-containing material as an additional binder in hydration-type hardening binding compositions.

2. Materials and methods

2.1. Materials
The saponite-containing material was extracted from the suspension circulating water in the process of kimberlite ore enrichment during industrial diamond mining at the M.V. Lomonosov deposit located in the Archangelsk region by electrolytic coagulation based on transforming superfine particles to the state close to an isoelectric one.

2.2. Methods
The saponite-containing material extracted from recycle water was brought to the constant mass at 105 °C.

Dry milling at the Retsch PM100 planetary ball mill was used to reduce the material to the required particle size. Optimal dispersion parameters were selected for each test sample to ensure minimum particle sizes in samples and high reproducibility (at least three parallel tests). Rotor speed was 420 rpm. Dispersion was performed using tungsten carbide grinding balls (20 pcs).

Particle sizes were determined at the Delsa Nano zeta potential and submicron particle size analyzer by measuring dynamic and electrophoretic light scattering.

A superfine sample obtained was characterized by nitrogen sorption at the Autosorb-iQ-MP analyzer using the \( S_{\text{sp}} \) specific surface value.

The Zeiss Sigma VP scanning electronic microscope was used to take photographs of the superfine SCM (at 20,000X magnification with a resolution up to 1.3 nm) at the Arktika Common Use Center (Arktika CUC).

In addition, phase structural heterogeneity of saponite-containing material samples before and after SCM mechanical activation was studied by X-ray diffraction using the XRD-7000S X-ray diffractometer at the Arktika CUC.

Then infrared spectra of samples were recorded using the Vertex 70v FT-IR spectrometer. Spectra were recorded under the following conditions: range 4000-600 cm\(^{-1}\), resolution 4 cm\(^{-1}\).

3. Results and discussion
Dispersion produced the saponit-containing material samples with a particle size range of 1 \( \mu \)m to 400 nm and specific surface of 18610±10 m\(^2\)/kg to 50670±20 m\(^2\)/kg respectively.

Correlation between the SCM specific surface and dispersion time have shown that the increase in grinding time over 90 min. does not lead to higher \( S_{\text{sp}} \), and the increase in machining time over 100 min. demonstrates conglomeration of particles in the system. Therefore, the fraction with \( S_{\text{sp}} = 50670 \) m\(^2\)/kg and an average particle size of 445±40 obtained within 90 min was chosen for further research.

The material is found to have a flaky nature with numerous voids that can be filled by water (Figure 1).
Figure 1. The microphoto of pre-production SCM sample, obtained on raster electronic microscope Sigma VP: a – the original (porosity – 0.088 cm$^3$/g); b – crushed (porosity – 0.001 cm$^3$/g).

The phase-structural heterogeneity of saponite-containing material samples studied before and after SCM mechanical activation demonstrated that the amorphous phase content in comparison with initial raw materials is doubled (Figure 2).

Figure 2. Diffractogram of the sample SCM: a – the original; b – sample after mechanoactivation; 1 – crystal part; 2 – amorphous part (a.p.).

Further studies focused on making samples with the reference (original) and mechanically activated saponite-containing material having the following composition: sand – 55%, SCM – 30%, water – 15%. Electron micrographs of test objects were made after 28-day aging (time of clinker mineral hydration reaction) (Figure 3).
Figure 3. The microphoto of SCM sample: a – control (average size of particles SCM – 1 mm); b – prototype (average size of particles SCM – 445 nm).

The results of SEM have shown that the sample microstructure is presented as spongy crystals. However, numerous voids (Figure 3a) predominate in reference samples, while the surface of test samples (with activated SCM) is denser and more uniform (Figure 3b).

Therefore, based on the data obtained the saponite-containing material can be considered not only as a sorbent that optimizes structure formation by aqueous phase sorption, but also as an active mineral component in hydration-type hardening binding compositions.

The binder samples (portland cement) with and without addition of the saponite-containing material (20%) were produced in order to confirm binding properties of mineral additives. The IR spectra of compositions under test were recorded after mixing with water and aging for 28 days (Figure 4).

Figure 4. IR spectrums of cement examples of structure: 1 – skilled with SCM additive; 2 – control without SCM additive.

Spectroscopic data show the presence of new formations in the form of silicate groups (oscillations at 975 cm\(^{-1}\)). However, the intensity of oscillations for the initial saponite-containing material under the same wave numbers (975 cm\(^{-1}\)) is several times higher than for control samples without SCM.

The electron micrographs of samples confirmed changes in the cement structure when introducing a mineral additive. According to SEM data, the formed hydrosilicates are conglomerates of particles
with grain sizes ranging from 2 to 20 µm. Particles have different shapes, but basically two types of particles can be distinguished: spongy particles (Figure 5a) with a developed microporous surface sized from 5 to 10 µm; needle-shaped particles (Figure 5b) with a length of 0.5 to 5 µm (needle diameters are about 0.5 µm).

**Figure 5.** Microstructure of a cement example of structure: a – control; b – prototype.

By comparing the results of scanning electron microscopy and IR spectroscopy of cement samples (Figure 4), the following conclusion can be drawn. The presence of absorption maxima in the IR range at 1400-1600 cm\(^{-1}\) and of a broad band at 3300-3500 cm\(^{-1}\), as well as the formation of needle-shaped crystals in the sample with the saponite-containing material added, confirms the presence of tobermorite group hydrosilicate submicrocrystals additional generation.

Synthesis of these crystals (alite and belite) from clinker minerals can occur according to the following pattern:

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\begin{align*}
\text{alite} & : \quad 2(3\text{CaO} \cdot \text{SiO}_2) + 6\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{Ca(OH)}_2 \\
\text{belite} & : \quad 2(2\text{CaO} \cdot \text{SiO}_2) + 4\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + \text{Ca(OH)}_2 \\
\text{tobermorite} & : \quad 5\text{Ca(OH)}_2 + 6\text{SiO}_2 \rightarrow 5\text{CaO} \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}
\end{align*}
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The result of the chemical reaction (3) is the synthesis of tobermorite crystals through the interreaction of cement clinker hydration products and saponite-containing material minerals.

Tobermorite crystals growing in all directions act as an additional binder during cement hardening. The obtained findings about shapes and sizes of particles and spectral features of hydrosilicates are in line with literature sources.

Therefore, based on the data obtained the saponite-containing material can be considered not only as a sorbent that optimizes structure formation by aqueous phase sorption, but also as an active mineral component in hydration-type hardening binding compositions.

**4. Conclusion**

Summarizing the experimental results we can draw the following conclusions:

1. It has been proved that chemical compounds in saponite-containing material can form calcium hydrosilicates after the mechanical activation of raw materials.
2. Surface amorphization (up to 40%) after the SCM mechanical dispersion and new growth of silicate groups with different basicity may indicate a potential for using raw materials to improve binding properties in hydration-type hardening compositions.

5. Acknowledgements
The research was carried out on the unique scientific equipment “Physical Chemistry of Surfaces of Nano-Dispersed Systems”.

References
[1] Morozova M V, Frolova M A and Mahova T A 2016 Abstracts of the international youth conference "Physicist. SPb" p 118
[2] Morozova M V, Ayzenshtadt A M and Tutyigin A S 2013 J. Industrial and civil construction 11 29-31
[3] Morozova M V, Ayzenshtadt A M, Mahova T A and Frolova M A 2015 15th International Multidisciplinary Scientific GeoConference & EXPO SGEM 2015, Nano, bio and green — technologies for a sustainable future 1 135-142
[4] Strokova V V, Cherevatova A V, Zhernovskiy I V and Voytovich E V 2012 J. Construction Materials 7 9-12
[5] Izotov V S and Ibragimov R A 2010 J. News of the KazSACU 2 229-233
[6] Ovcharenko F D 1961 Hydrophilicity of clay and clay minerals (Kiev: National Academy of Sciences of Ukraine) p 292
[7] Harhardin A N, Strokova V V and Kozhuhova M I 2012 J. Higher Education News (Construction) 10 109-115
[8] Andrievskiy R A and Glezer A M 2009 J. Successes of physical sciences 4 337-358
[9] Glezer A M 2002 J. Russian chemical magazine 5 57–63