Sorption-desorption properties of saponite-containing material

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Abstract. The sorption mechanism of the mineral additive showed that self-saturation of the saponite-containing material with water vapors has a long-term nature (12 days). The nature of desorption differs from adsorption isotherm, i.e. the adsorption/desorption hysteresis is observed. Saponite-containing material samples studied after moisture desorption using infrared spectroscopy demonstrated that chemical compounds in the material have the ability to form calcium silicate hydrates when saturated with water. This fact along with the additive capability to control the water-cement ratio during concrete curing contributes to significantly better physical and chemical properties (strength, frost resistance) of the concrete composite.

1. Introduction
The efficiency of concrete curing is determined by the hydration of cement minerals forming a new colloidal dispersion phase (condensation reaction) of different basicity calcium silicate hydrates. However, condensation producing colloidal sized particles is only possible under certain conditions. Thus, the system must be oversaturated with the substance to enable its condensation. Nuclei of a new phase form at a certain degree of solution oversaturation. Therefore, formation of colloidal systems is controlled by the rate of nuclei formation and growing. In turn, the rate of new phase nuclei (calcium silicate hydrates) formation is proportional to the solution oversaturation degree. Consequently, water-cement (W/C) ratio regulation during cement curing by means of physisorption of water by the mineral additive can stabilize the degree of system oversaturation relative to new formation of hydrosilicates [1, 2]. This leads to the uniform distribution of cement mineral hydration products throughout the sample. The basic process, which enables W/C ratio regulation during concrete composite curing, is the water physisorption by the modifier.

It is known that bentonite clays are natural hydroalumosilicates and exhibit a number of properties typical of common clays (hydration swelling, dense gel formation to prevent moisture penetration, non-toxicity, chemical stability). A typical representative of such systems is a saponite-containing material (SCM) extracted from recycled water at mining plants [3-5]. Our preliminary studies conducted to investigate hydrophysical properties of this material identified the water-absorbing ability of the SCM. Moreover, the paper [6] demonstrates the possibility to use the saponite-containing material as a binder.

Therefore, the objective of research described in this paper is to characterize sorption-desorption properties of the saponite-containing material with respect to water and identify potential products of superfine mineral additive hydration.
2. Materials and methods

2.1. Materials
The tests used a composite sample of recycle water suspension with the saponite-containing material sampled at different heights of the tailing dump.

The SCM was extracted from the suspension 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\textsubscript{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, the Lab Center XRF-1800 unit was used for X-ray phase analysis at the Arktika CUC to determine mineral composition of the saponite-containing material by measuring the intensity of characteristic X-Rays (fluorescence) when exposing solid samples.

Sorption process was studied by placing a weight portion (100 g) of the SCM taken on the counterbalance to a desiccator above the distilled water layer at the constant ambient temperature 25±1 °C. Water absorption was characterized by changes in sample mass determined at specified time intervals. Measurement results were based on two parallel experiments.

For desorption the moisture-saturated test sample was placed in the desiccator above the calcium oxide layer, while the temperature remained constant (25±1 °C).

After sample desorption tests the SCM was placed in a drying box and brought to the constant mass at 105 °C, 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\textsuperscript{-1}, resolution 4 cm\textsuperscript{-1}.

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

Table 1. Grinding time and characteristics of fractions of SCM samples.

| Fraction, \(N_e\) | Samples dispersion time, min | Average particle size, nm | Specific surface area, \(S_{sp}\) m\textsuperscript{2}/kg |
|------------------|-----------------------------|---------------------------|---------------------------------|
| 1                | 5                           | 1113±23                   | 18610±10                        |
| 2                | 10                          | 827±52                    | 19810±10                        |
| 3                | 30                          | 764±43                    | 21210±20                        |
| 4                | 60                          | 591±28                    | 35280±30                        |
| 5                | 90                          | 445±40                    | 50670±20                        |
| 6                | 110                         | 447±34                    | 50672±20                        |
| 7                | 120                         | 517±22                    | 30359±30                        |
Relation between the SCM specific surface and dispersion time demonstrated that dispersion within over 90 min causes no $S_{sp}$ increase. Therefore, the modifier of Size Fraction No. 5 ($S_{sp} = 50670 \, \text{m}^2/\text{kg}$) was used for further studies.

Figure 1 shows Size Fraction No. 5 indicating the uniformity of size distribution by their size in this range. Test data regarding particle sizes obtained using photon correlation spectroscopy are in good agreement with electron microscopy results (Figure 2). Moreover, electron microscopy showed that the saponite-containing material has a flaky structure with numerous voids able to be filled with water.

![Figure 1. Dimensional distribution of particles in pre-production SCM sample of Size Fraction No. 5, obtained on Delsa Nano analyzer.](image1)

![Figure 2. The microphoto of pre-production SCM sample (Size Fraction No. 5), obtained on raster electronic microscope Sigma VP.](image2)

The chemical analysis of the SCM sample showed that the major elements of the test sample (calculated as oxides) are $\text{SiO}_2$, $\text{MgO}$, $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{CaO}$ and $\text{K}_2\text{O}$. The content of the above oxides is - 97.4% (Table 2)
Table 2. The composition of the SCM samples calculated as oxides.

| Selected component | SCM content, % | Selected component | SCM content, % |
|--------------------|----------------|--------------------|----------------|
| SiO$_2$            | 51.746         | SO$_3$             | 0.318          |
| MgO                | 19.405         | P$_2$O$_5$         | 0.660          |
| Al$_2$O$_3$        | 9.971          | Cr$_2$O$_3$        | 0.112          |
| Fe$_2$O$_3$        | 10.406         | ZnO                | 0.031          |
| CaO                | 4.199          | BaO                | 0.197          |
| TiO$_2$            | 1.017          | MnO                | 0.156          |
| K$_2$O             | 1.693          | SrO                | 0.044          |
| CuO                | 0.045          | other              | 0.001          |

Figure 3 demonstrates test results regarding sorption properties of the saponite-containing material (Size Fraction No. 5) indicating that the process of solid phase saturation with water vapors has a long-term nature. The weight portion of the test material is fully saturated within 12 days from the test beginning. The sample mass is increased by 11% (saturation of the sample surface layer). The process of water desorption with the test sample has a nature other than the adsorption isotherm (Figure 3, Curve 2). Therefore, the test showed the presence of adsorption/desorption hysteresis in the SCM/water vapor system. It should be noted that the SCM weight after desorption differed from the initial sample weight by 8%.

Marked adsorptive hysteresis is characteristic of process of the polymolecular adsorption which is followed in parallel by the proceeding condensation of vapors of an adsorbтив (water) in small pores of adsorbent (SCM). Therefore, it is necessary to consider two various mechanisms: polymolecular adsorption in direct and capillary evaporation in the return processes. Thus, different mechanisms in direct and return processes define the nature of the adsorptive hysteresis.

Figure 3. The dependence of SCM moisture absorption ($S_{sp} = 50670 \pm 20 \, \text{m}^2/\text{kg}$) on time: 1 - adsorption process; 2 - desorption process.

IR spectroscopy results (Figure 4) obtained after desorption and residual moisture removal from the SCM demonstrated the presence of new formations in the material – silicate groups (975 cm$^{-1}$).
The analysis of the peak form having a complex nature (with “shoulders”) allows us to conclude that there are also hydrosilicates of different basicity. The lines of O-H groups are present in the 3600-3200 cm\(^{-1}\) and 1635 cm\(^{-1}\) areas that also indicates the presence of hydrosilicates.

4. Conclusion
Summarizing the obtained test results, we can conclude the following:

1. The process of water sorption with the superfine additive of the saponite-containing material proceeds spontaneously, while saturation of samples with water takes place within 12 days. Removal of moisture accumulated in the material is accompanied with adsorption/desorption hysteresis.

2. The study of saponite-containing material samples after moisture desorption by infrared spectroscopy demonstrated that chemical compounds in the material can form calcium silicate hydrates under test conditions.

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

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