High-temperature phase transformations in CaO-SO$_3$-SiO$_2$-H$_2$O system with nanosized component

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The features of transformation of phase composition under thermal effect in gypsum binder and composite nanostructured gypsum binder are studied. It is demonstrated the formation of silicate and sulfo-silicate mineral phases in system CaO-SO$_3$-SiO$_2$-H$_2$O prevents changes in volume of crystal phases under thermal effect leading to growth of destruction resistance at high temperatures. For example, changes in volume of crystal phases when thermal phase transformation of calcium sulfo-silicate binder at $T=1000$ °C is close to zero vs. gypsum binder characterized by four-time decreasing of crystal phases in volume that leads to destruction effect.

Reasoneability of transformation of CaO-SO$_3$-H$_2$O system into CaO-SO$_3$-SiO$_2$-H$_2$O system by introduction of reactive silica for equalization of molar volumes of binders in initial state and after thermal effect when formation of sulfo-silicate and silicate calcium phases is confirmed. It leads to dehydration and desulfation in binder system.

Formation of structurally associated contact zones between mineral new formations and fillers in composite binders is the dominant factor providing a high strength and others performance properties of structural materials. Especially it is applicable to composite sulfo-silicate binders as constituent of hardening mechanism.

Earlier studies [1, 2] demonstrate the interaction of hemihydrate of calcium sulfate and colloid solution of silica (component of NB) when hydration process leads to formation of buffer calcium sulfo-silicate phases such as hydroxylestladite $\text{Ca}_6(\text{SiO}_2)_{4}(\text{SO}_3)_{8}(\text{OH})_2$, providing appearance of structurally associated crystal contacts between units of calcium sulfate hydrate and α-quartz. Formation of $\text{Ca}_6(\text{SiO}_2)_{4}(\text{SO}_3)_{8}(\text{OH})_2$ is confirmed by data of full profile XRD-analysis and IR-spectroscopy.

There is assistant theory the appearance of emergent properties (i.e. unique for components of binding system) in composite nanostructured gypsum binder (CNGB) take place due to formation of optimal structuring matrix taking account realization of two structuring processes jointly: polymerization-polycondensation and hydration.

This work is devoted to study of phase-structural transformations in CNGB under high temperature effect. Gypsum binder is known to be a hydration binder that prevents its application under high temperature or in conditions of high temperature gradient.

Nevertheless, goal of this study is experimental conformation of heat-resistance of CNGB under high thermal treatment up to 1000 °C, associated with crystallization processes involving a silica component of NB used as reactive mineral admixture.

For experiment the samples of 16x4x4 cm obtained with constant «water – gypsum» ratio are prepared. The sample curing is realized at ambient conditions with preliminary drying to constant humidity.

As gypsum binder is heated quite slowly and destructed after 6–8 hours of temperature effect experimental samples were heated up to 1000 °C and cured at constant temperature for 6 hours (Fig. 1).

Analysis of experimental data demonstrates the absence of destruction process in optimal compositions (NB content is 15–20 by wt. %). At the same time in others compositions the strength reducing under temperature effect vs. reference compositions is observed. It can be associated with disordered structure of the obtained samples. Visual analysis of the sample geometry is shown a total shrinkage of reference composition achieves 28,8 % vs. CNGB (9,1 %).

Microstructure of gypsum binder after high temperature treatment (Fig. 2a) is presented by lime crystals those can be phantom of lime crystals in anhydrite.
Microstructure of CNGB (Fig. 2b) is mainly characterized by presence of units with plate-like morphology vs. finely crystalline isometric units placed epitaxially or form globular aggregates. Also units with prismatic-needlelike morphology are observed in small amount that can be associated with silicate new formations.

To obtain the general information about of structuring processes the DTA-method is applied for the studied composite systems in initial state (without temperature treatment).

Comparative analysis of endo- and exo-effects of gypsum binder and CNGB with 15 % and 20 % content of NB is accomplished with the obtained thermogram (Fig. 3).

According to thermogram the first endo-effect is fixed in temperature range of 30–200 °C with double maximum in ranges of 142–145 °C and 158–161 °C that takes place on DTA-curves and associated with removal of crystalhydrate water from gypsum binder and formation of soluble anhydrite III. It should be noted this effect for experimental compositions takes place at lower temperature.

In temperature range of 372–377 °C a dramatic exo-effect connected with transformation of structural crystal lattice with following formation of soluble anhydrite III and soluble anhydrite II is observed.
In high-temperature area of thermogram the thermal effects of sequential polymorphous transformations and structuring process including a crystallization of new phases are observed. Endo-effect appeared only in experimental compositions in thermal range of 574–575 °C is associated with polymorphous transformation α-quartz → β-quartz. It should be noted the variation of particle size significantly influnes on character and intensity of endo- and exo-effect. Also, higher crystallinity degree is found to be lead to intensity of thermal effect in material with fixed particle size [3, 4]. «Wet» mechanochemical synthesis and other forms of mechanical grinding lead to surface degradation of quartz crystal lattice and reactivity enhancement as consequence [5]. For all experimental compositions a temperature growth in range of 650–815 °C the double endo-effect with max peaks at 707 °C, 708 °C and 711 °C takes place. It can be explained by calcium dissociation and leads to mass loss. In range of 650–880 °C exo-effects unusual for gypsum binders (with peak at 875 °C), are appeared. It is, probably, connected with α₄₋₅-Ca₂SiO₄ phase crystallization (Fig. 3). Thus, DTA-analysis of studied binders demonstrates the addition of NB into gypsum binder significantly effect on transformation in systems when thermal treatment.

![Figure 3: Thermograms of gypsum binder and CNGB](image1)

For more deep understanding of thermal phase transformations in CNGB the high-temperature XRD-analysis is realized with diffractometer STOE STADI (STOE & Cie GmbH, Germany) with Cu-cathode irradiation. High-temperature XRD-analysis at T=1000 °C is accomplished with attachment for high-temperature X-ray analysis Stoe for X-ray in temperature range of 25 to 1500 °C. Qualitative XRD-analysis of mineral phases is accomplished with database PDF-2 and Crystallographica SearchMatch v 2.0,2,0 (Oxford Cryosystems) program. Quantitative analysis of crystal mineral formations (without determination of amorphous phase) is realized by full profile XRD-analysis with DDM v.1.95d program in form of the Rietveld algorithm [6]. In this experiment CNGB with NB content of 20 % by wt. and a gypsum binder are studied. X-ray diagrams of hydrated gypsum binder are shown in Fig. 4. One of the features of high-temperature desulfatation of gypsum binder is appearance of reflections associated with calcium sulfide phase – oldhamite (Cas) at T=1000 °C (Fig. 5). Mineral composition of CNGB is in accordance with earlier obtained results [1]. Low concentration of ellestadite vs. earlier data can be explained by low content of colloid silica in NB.

![Figure 4: Quantitative XRD-analysis of gypsum binder before thermal treatment](image2)

![Figure 5: Quantitative XRD-analysis of gypsum binder after thermal treatment at 1000 °C. * is reflections of iridis sample holder](image3)

![Figure 6: Quantitative XRD-analysis of CNGB before thermal treatment](image4)
Using the parameter $a$ – volume variation of crystal components in studied binders under thermal effect:

$$a = \sum_i [C_i^{T=25^\circ C} \cdot V_i^{unitcell} - \sum_j [C_j^{T=1000^\circ C} \cdot V_j^{unitcell}]]$$

where $C_i$ and $C_j$ are concentrations (by wt. %) of mineral phases in binder before (T=25 °C) and after (T=1000 °C) thermal treatment;

$V_i$ is cell volumes of these phases. In this case we have:

- $a_{gypsum} = 3.96$ for gypsum binder;
- $a_{CNG} = 0.88$ for CNGB.

Thus, volume variation of crystal phases when phase transformation of CNGB (parameter $a$) after thermal treatment at T=1000 °C is close to 1 vs. gypsum binder, characterized by four-time reduction in volume of crystal phases initiating a destruction processes.

It allows making conclusion about reasonability of transformation of CaO-SO$_3$H$_2$O system into CaO-SO$_3$-SiO$_2$-H$_2$O system by introduction of reactive silica for equalization of molar volumes of binders in initial state and after thermal treatment when formation of sulfo-silicate and silicate calcium phases. It leads to dehydration and desulfatation processes in binder system.

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