Improving the Efficiency of Non-Autoclaved Silicate Materials Based on Aluminosilicate Feedstock through the Use of a Synthetic Crystalline Filler

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Abstract. Currently, there are various ways to improve the performance specifications of building composites of various functional purposes. Thus, one of the possible ways to improve the performance specifications of building materials is to control and modify the composite structuring processes at the microlevel by using of various crystal seeds. The studies have established the possibility of improving the performance specifications of non-autoclaved silicate materials based on non-conventional aluminosilicate feedstock, which consists in the crystallochemical modification of the CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O system with a synthetic crystalline filler C-S-H mainly represented by low-basic calcium hydrosilicates of variable composition. The optimal CaO and crystalline filler C-S-H contents at which the maximum strength characteristics are ensured are 8 and 2.5 %, respectively. The use of the synthetic crystalline filler in the technology of non-autoclaved silicate materials based on non-conventional aluminosilicate feedstock allows increasing the softening coefficient by 15-20 %, which may expand the scope of this material.

1. Introduction
Currently, the production of conventional building materials and the technologies applied have reached their limits. Materials meeting the construction industry requirements just a few years ago, do not comply with today’s world ones, including those related to saving energy and resources.

From the second half of the 20th century to the present day, many researchers improve the building composite quality by optimizing compositions, introducing functional modifiers, and using various engineering techniques [1-5]. To date, with the development and emergence of fundamentally new research equipment, research techniques, and software systems in recent years, it seems possible to not only fully unlock the potential of conventional raw materials but also find new types of feedstock that have previously been considered unsuitable but are more prepared for the production of one or another building material by geological and man-made processes [5-10]. This will fundamentally change the approach to the design of building materials and, as a result, radically modify their properties [11-12].

From this point of view, clayey rocks related to layered and layer-ribbon silicates that have been widely distributed and used in construction for many centuries are of interest. The interlayer clay stacks are nanosized, have a highly developed active surface, and can serve as a ‘base matrix’ for the controlled structuring of the entire system. The use of clayey rocks composed of mixed-layer and X-ray amorphous formations is of particular interest.
The data previously obtained in the experimental research has shown the possibility of synthesizing newgrowths in the CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O system represented by lime and non-conventional clayey rocks. The formation of newgrowths represented by mainly low-basic calcium hydrosilicates in this system provides the material with the performance specifications required [13-14, 21].

Currently, there are various ways to improve the performance specifications of building composites of various functional purposes. Thus, one of the possible ways to improve the performance specifications of building materials is to control and modify the composite structuring processes at the microlevel by using of various crystal seeds. [15-20].

In this regard, the issue of improving the performance specifications of non-autoclaved silicate materials based on aluminosilicate feedstock through the crystallochemical regulation of the structuring processes is relevant.

2. Materials and methods

To obtain non-autoclaved silicate materials based on aluminosilicate feedstock, quicklime meeting the European standard EN 459-1:2010 was used as a binder. For the development of non-autoclaved silicates, unconventional aluminosilicate raw materials were used. The synthesis of the crystalline filler C-S-H was performed under elevated pressure and temperature from a mixture of Ca(OH)$_2$ and silica. Fractionated quartz sand of the Volsk deposit was used as silica.

The study of the material composition of the feedstock and the samples of the newgrowths obtained was performed using the X-ray diffraction and differential thermal analyzes. The sample microstructure was studied using scanning electron microscopy.

To obtain samples, the raw materials were prepared by mixing dry components in predetermined proportions. The resulting mixture was moistened with the required amount of water and kept in a hermetically sealed cup until the full lime hydration. Samples were molded from the mixture obtained at a specific pressing pressure of 20 MPa. After molding, the sample cylinders were placed into a steaming chamber for steam curing at atmospheric pressure under the conditions of temperature within 90–95 °C and the curing duration of 9 hours.

3. Main part

When obtaining the non-autoclaved wall products, as a result of the interaction of the source components, newgrowths of a certain composition are synthesized with definite properties and morphological features mainly depending on the material composition of their components, which determines the final properties of the resulting composites. In this regard, the research objective was studying the possibility of improving the performance specifications of non-autoclaved silicate composites by the crystallochemical modification of the CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O system based on non-conventional aluminosilicate raw materials using a synthetic crystalline filler C-S-H.

Based on the analysis of the material composition of non-conventional aluminosilicate raw materials used herein, it has been found that this feedstock is characterized by the presence of highly dispersed components, i.e. clayey minerals (kaolinite and montmorillonite) and mixed-layer compounds based on them, as well as finely dispersed quartz, which is characterized by surface and crystal lattice defects.

The synthetic crystalline filler represented by the CaO-SiO$_2$-H$_2$O system was synthesized at steam curing in an autoclave at a pressure of 1 MPa and a temperature of 175 °C from a mixture of Ca(OH)$_2$ and crystalline silica at a ratio of C/S=1. The synthetic calcium hydrosilicates are long crystalline fibers with a diameter of 30-40 nm (Figure 1).
Figure 1. The Microstructure of the Synthesized Crystalline Filler C-S-H.

The X-ray diffraction pattern of the synthetic calcium hydrosilicates is shown in Fig. 2. Reflexes in the regions of 5.3, 2.8, 3.07, and 2.1 Å probably indicate the presence of dyscrystalline low-basic calcium hydrosilicates C-S-H (I).

Figure 2. X-ray Diffraction Pattern of the Synthetic Crystalline Modifier.

It should be noted that according to the literature sources, due to the gradual temperature rise during the steam curing, the solubility of the components (SiO$_2$ and Ca(OH)$_2$) changes, as a result of which the composition of the liquid phase and, accordingly, the newgrowths formed in the CaO-SiO$_2$-H$_2$O system continuously modifies.

Thus, at the first Ca(OH)$_2$ and crystalline silica mixture steam curing stage, dibasic calcium hydrosilicates C$_2$SH are formed, and with an increase in temperature and the steam curing duration, mainly low-basic calcium hydrosilicates of the CSH group are formed. Thus, based on the initial ratio C/S = 1 and the presence of reflexes in the regions of 3.9, 3.548, 3.28, 2.8, 27, and 2.0-2.2 Å on the X-ray diffraction pattern (Figure 3), dibasic calcium hydrosilicates C$_2$SH are probably present in a small amount in the synthetic crystalline filler.

Based on the differential thermal analysis results, by the endothermic effect at 120 °C and the exothermic effect at 863 °C on the DTA curves, a conclusion can be drawn that the CaO-SiO$_2$-H$_2$O system synthesized consists of mainly low-basic calcium hydrosilicates of variable composition (Figure 3).
Figure 3. Thermogram of the Synthetic Crystalline Modifier.

In this experiment, the amount of quicklime in the raw mixture was 6, 8, and 10 % wt. The synthetic crystalline modifier was introduced in an amount of 1, 3, and 6 % wt. The raw material mixture moisture content was 10 % wt.

After the steam curing at atmospheric pressure, the samples were stored in natural conditions, upon which their performance specifications were determined (Figure 5, Table 2).

With the increase in the synthetic crystalline filler C-S-H content in the raw mixture (Fig. 5) up to 2.5 % wt. the compressive strength of samples (CaO content - 6 % wt.) increases from 17.9 to 21 MPa; it is worth noting that with an increase in the crystalline filler content in the raw mixture from 3 to 6 %, the strength indicators of products decrease from 21 MPa to 19.2 MPa. In samples with a CaO content of 8 % wt., the compressive strength increases from 18.6 to 22.5 MPa with an increase in the crystalline filler content up to 3 % wt.; with a further increase in the crystalline filler C-S-H content, the strength indicators also decrease. For samples with a CaO content of 10 % wt., the strength increment turned out to be the smallest and amounted to 6 % at a crystalline filler C-S-H content of 1 % wt. Thus, a crystalline filler C-S-H content of 1 to 3 % wt. gives an increase in strength indicators of non-autoclave silicate materials based on aluminosilicate feedstock up to 18 %, thereat, the optimal CaO content in the raw mixture is 8 % wt.

The average sample density (Table 1) decreases with increasing CaO content from 1,960 to 1,890 kg/m³. The inclusion of synthetic crystalline filler C-S-H in the raw mixture reduces this indicator to 1,850 kg/m³.

Figure 4. The Crystalline Filler Effect on the Properties of the Samples Obtained:
1 – the CaO content is 6 % wt.; 2 – the CaO content is 8 % wt.; 3 – the CaO content is 10 % wt.
The use of synthetic crystalline filler in the technology of non-autoclaved silicate materials based on non-conventional aluminosilicate feedstock may increase the softening coefficient from 0.7 to 0.85 (Table 1), which can expand the scope of this material.

Table 1. Physical and Mechanical Characteristics of the Samples.

| Physical and Mechanical Characteristics | Crystalline Filler C-S-H Content, % wt. |
|----------------------------------------|----------------------------------------|
|                                        | 0 | 1 | 3 | 6 |
| Compressive strength, MPa              | 17.9 | 21.3 | 20.8 | 19.2 |
| Average density, kg/m³                 | 1,960 | 1,950 | 1,920 | 1,850 |
| Softening coefficient                  | 0.65 | 0.78 | 0.85 | 0.75 |

| Compressive strength, MPa              | 18.6 | 22.1 | 22.65 | 18.1 |
| Average density, kg/m³                 | 1,950 | 1,945 | 1,880 | 1,850 |
| Softening coefficient                  | 0.7 | 0.74 | 0.8 | 0.7 |

| Compressive strength, MPa              | 19.7 | 21 | 19.2 | 17.6 |
| Average density, kg/m³                 | 1,890 | 1,890 | 1,850 | 1,810 |
| Softening coefficient                  | 0.71 | 0.7 | 0.73 | 0.7 |

A decrease in the strength indicators of non-autoclaved silicate materials when a synthetic crystalline filler is introduced into the raw mixture in an amount of more than 3 % wt. and a slight increase in strength at a CaO content of 10 % wt. can be explained by the irrational microstructure of the resulting composites. Thus, from the composite macrostructure point of view, the synthesis of newgrowths represented by mainly low-basic calcium hydrosilicates is optimal. The introduction of the synthetic crystalline filler C-S-H into the raw mixture, including at an increased CaO content, contributes to an increase in the crystalline phase in the material microstructure, including that probably represented by high-basic calcium hydrosilicates. The formation of newgrowths with an irrational ratio between low-basic and high-basic calcium hydrosilicates probably contributes to a decrease in the strength indicators of products.

4. Conclusion

Thus, the use of synthetic crystalline filler C-S-H synthesized at steam curing from a mixture of Ca(OH)₂ and crystalline silica at a ratio of C/S=1 in the technology of non-autoclaved silicate materials based on non-conventional aluminosilicate feedstock allows improving the performance specifications of the resulting products up to 18 % and more.

The optimal CaO and crystalline filler C-S-H contents at which the maximum strength characteristics are ensured is 8 and 2.5 %, respectively. The increase in strength indicators is ensured by the crystallochemical modification of the CaO-SiO₂-Al₂O₃-H₂O system based on non-conventional aluminosilicate feedstock with a synthetic crystalline filler C-S-H, which is mainly represented by synthetic low-basic calcium hydrosilicates of variable composition.

5. References

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