Influence of artificial filler made of calcium hydrosilicates of various basicity on the performance characteristics of non-autoclave hardened silicate materials

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Abstract. The work established the nature of the effect of an artificial filler made of calcium hydrosilicates of various basicity on the physical and mechanical properties of non-autoclave silicate composites based on unconventional aluminosilicate raw materials, represented by clay rocks of an unfinished stage of mineral formation. It is determined that the optimal content of an artificial filler of the composition $\text{CaO} : \text{SiO}_2$ is $1:1$ in the raw mixture is in the range of $1–3$ wt.%. The available interval makes it possible to vary the composition of the initial mixture and obtain products with the required properties, which is especially important when the material composition of the feedstock fluctuates, as well as in case of violation of the production technology. The rational content of the artificial filler of the composition $\text{CaO} : \text{SiO}_2 = 2:1$ is $1$ wt. %. It is shown that the addition of an artificial filler promotes the formation of a cementitious substance from neoplasms of a higher degree of crystallization, which contributes to an increase in the strength and water resistance of the material. Mathematical models are proposed for the selection and optimization of the compositions of non-autoclave silicate materials based on unconventional aluminosilicate raw materials and modified with an artificial filler represented by calcium hydrosilicates of various basicity to obtain materials with a compressive strength of 18-23 MPa with an average density of finished products of 1750-2000 kg/m$^3$.

1. Introduction
Currently, an important scientific and technical task is the development and implementation of innovative approaches in the field of energy conservation and resource conservation, as well as the rational use of raw materials. It is necessary to introduce new production of building materials [1–4] with minimal impact on the environment, which will allow the sustainable development of the existing technological base and implement the policy of import substitution in order to increase the competitiveness of the economy of the regions and the country as a whole.

In the construction of buildings and structures, many wall materials are used, including silicate products for various functional purposes [5–9]. In the traditional technology for the production of such materials, the hardening process occurs due to the formation of a crystal structure in the CaO-SiO2-H2O system, which, depending on the conditions of hydrothermal treatment, is represented mainly by calcium hydrosilicates of various basicity [10–12]. There are various ways to modify the crystalline intergrowth of the cementitious substance, one of which is the use of certain components acting as crystallization centers, in particular, the use of natural and artificial calcium hydrosilicates. Research
on improving the properties of building composites with synthetic hydrosilicates of calcium is mainly associated with cement systems and materials based on them [13–15].

To increase the strength characteristics of silicate products, the breakage of this material, as well as a certain kind of crystal seeds, can be used. Using breakage may not have a different effect, because it is a multicomponent system consisting of calcium hydrosilicates with unknown properties. Therefore, calcium hydrosilicates of a certain composition are best obtained synthetically.

Thus, in order to improve the operational characteristics of non-autoclave silicate materials based on unconventional aluminosilicate raw materials, represented by clay rocks of the unfinished stage of mineral formation, the issue of using artificial fillers from calcium hydrosilicates, including those of different basicity, in the technology of their production, is relevant and practically unexplored.

2. Materials and methods

The production of silicate materials of non-autoclave hardening uses unconventional clay rocks of an incomplete stage of mineral formation and characterized by a certain set of properties as an aluminosilicate raw material [16] and calcium oxide (construction quicklime) acts as a binder. In this work, aluminosilicate raw materials from the region of the Kursk Magnetic Anomaly (sandy-clay rock, according to the plasticity number related to sandy loam) were used as the main component.

Artificial calcium hydrosilicates, in these studies, were obtained by hydrothermal synthesis at elevated temperatures and pressures (P = 1 MPa, T = 175 °C). Calcium oxide and quartz sand of the Volsk deposit were used as the initial components. To increase the chemical activity of quartz sand, it was preliminarily crushed ($S_p = 300 \text{ m}^2/\text{kg}$).

The obtained hydrosilicates of calcium were introduced into the raw mixture by dry mixing with a binder component and clay rock in a laboratory mixer. After adding the required amount of water, followed by keeping the mixture for complete quenching of calcium oxide in the mixture, the samples were molded on a hydraulic press at a pressure of 20 MPa. The hardening process of the samples was carried out in a heat-and-moisture treatment chamber (HMC), at a water vapor temperature of 95 °C. The isothermal holding time of the samples was 9 hours.

The study of the phase composition, microstructure of the initial components and forming neoplasms was carried out by appropriate research methods (XRF, DTA, SEM).

3. Results

At present, both in national and international literature, there are many studies in the field of artificially obtaining compounds in the CaO–SiO$_2$–H$_2$O system and their influence on the properties of composites [10–15]. The properties of such a system mainly depend on the molar ratio between CaO:SiO$_2$, the type and properties of SiO$_2$, as well as the parameters at which the synthesis of calcium hydrosilicates occurs. Of the many forms of artificial calcium hydrosilicates in the CaO–SiO$_2$–H$_2$O system, low-base and dibasic hydrosilicates are the most stable.

In the course of research, two types of artificial filler (AF) represented by calcium hydrosilicones were obtained: AF-1 (CaO:SiO$_2$ = 1:1) and AF-2 (CaO:SiO$_2$ = 2:1). The results of X-ray phase and thermographic analysis (Figure 1) of the obtained artificial fillers (AF-1, AF-2) represented by the CaO–SiO$_2$–H$_2$O system indicate the formation of calcium hydrosilicates of CSH(I) and C$_2$SH(A) types.

On the thermogram of AF-2, in comparison with AF-1, there is no exothermic effect in the range of 830–860 °C, which is characteristic of low-basic calcium hydrosilicates CSH(I). The presence of a single endo-effect at 460 °C is noted, which may indicate the presence of C$_2$SH(A) at C/S = 2, while C/S > 2 forms a double endo-effect at 430–480 °C.

In order to determine the influence of CaO content and an artificial filler represented by calcium hydrosilicates of various basicity on the performance characteristics of products, an experiment was carried out using the method of mathematical planning of the experiment. Two experiments were carried out using AF-1 and AF-2.

The data for the experiments are shown in Tables 1 and 2.
Figure 1. Radiographs (a) and thermograms (b) of the obtained artificial filler: 1) AF-1 (CaO:SiO$_2$ = 1:1); 2) AF-2 (CaO:SiO$_2$ = 2:1)

Table 1. Data for the experiment by the method of mathematical planning using AF-1

| Factors                          | Variation levels | Variation interval |
|----------------------------------|------------------|--------------------|
| Natural form                     | Coded form       | -1     | 0   | +1   |
| CaO, wt.%                        | $x_1$            | 4      | 8   | 12   | 4     |
| Artificial filler AF-1, wt.%     | $x_2$            | 0.5    | 3   | 5.5  | 6     |
Table 2. Data for the experiment by the method of mathematical planning using AF-2

| Factors                      | Natural form | Coded form | Variation levels | Variation interval |
|------------------------------|--------------|------------|------------------|-------------------|
| CaO, wt.%                   | x₁           | 4          | 7                | 10                | 3                 |
| Artificial filler AF-2, wt.%| x₂           | 0.5        | 1.5              | 2.5               | 1                 |

After analyzing and processing the initial data, mathematical regression equations were obtained that describe the changes in the compressive strength index (R), as well as the water resistance index (K) and average density (ρ).

The regression equations are (using AF-1):

\[
R_{\text{compr}} = 22.41 - 1.75 \cdot x_2 - 2.42 \cdot x_1^2 - 1.5 \cdot x_2^2
\]

\[
\rho = 1879.43 - 42.51 \cdot x_1 - 45.84 \cdot x_2 - 7.644 \cdot x_1^2 - 7.644 \cdot x_2^2 + 3.75 \cdot x_1 \cdot x_2
\]

\[
K = 0.802 - 4.06 \cdot 10^{-2} \cdot x_1^2 - 5.06 \cdot 10^{-2} \cdot x_2^2
\]

The regression equations are (using AF-2):

\[
R = 23.23 + 0.283 \cdot x_1 - 0.517 \cdot x_2 - 2.33 \cdot x_1^2 - 0.532 \cdot x_2^2
\]

\[
\rho = 1944.72 - 49.34 \cdot x_1 - 11.339 \cdot x_1^2 - 5.6 \cdot x_2^2
\]

\[
K = 0.836 - 3.987 \cdot 10^{-2} \cdot x_1^2 - 1.487 \cdot 10^{-2} \cdot x_2^2
\]

After processing the available regression equations, graphical dependences of the properties of non-autoclave silicate materials on the content of CaO and an artificial filler represented by calcium hydrosilicates of various basicity were built (Figures 2 and 3).

Figure 2. Nomograms of the dependence of the properties of non-autoclave silicate materials on the content of CaO and the artificial filler AF-1: (a) nomogram of the dependence of the ultimate strength in compression; (b) nomogram of the dependence of the average density indicator; (c) nomogram of the dependence of the softening coefficient

Based on the data obtained, it was found that at a CaO content of 4–12 wt.% it is possible to obtain durable non-autoclave silicate materials based on unconventional aluminosilicate raw materials and artificial filler (AF) represented by hydrosilicates of various basicity (Figures 2 and 3).

The rational content of AF-1, which ensures the achievement of maximum strength indicators (22 MPa), is 2 wt.% with a CaO content in the mixture in the amount of 8 wt.%. An increase in the content of AF-1 in the raw mixture to 5.5 wt.% decreases the ultimate strength in compression (Figure 2).
Figure 3. Nomograms of the dependence of the properties of non-autoclave silicate materials on the content of CaO and artificial filler AF-2: (a) nomogram of the dependence of the ultimate strength in compression; (b) nomogram of the dependence of the average density indicator; (c) nomogram of the dependence of the softening coefficient.

The nature of the effect of the AF-2 artificial filler on the strength properties of the samples differs from the AF-1. In this case, the specimens reach their maximum strength (23 MPa) when the content of AF-2 in the mixture is 1 wt. % and that of CaO is 8 wt. % (Figure 3). A further increase in the content of AF-2 to 2.5 wt. % decreases the ultimate strength in compression down to 19.7 MPa.

Figure 4. Effect of the artificial filler on the microstructure of the sample with 8 wt. % of CaO: (a) control composition; (b) content of AF-1 is 3 wt. %.

The least effect of the addition of artificial filler AF-1 and AF-2 has on samples with a mass content of CaO in an amount of 10%.
The indicator of the average density of the material with an increase in the mass content of the binder component (CaO) decreases, and the more, the more the artificial filler is added (Figures 2 and 3). The addition of an artificial filler increases the water resistance of the products. Samples with a CaO content of 8 wt.% and mass content of AF-1 of 2 wt.% and AF-2 of 1 wt.% have good water resistance (softening coefficient is not less than 0.8).

When examining the microstructure of the sample of the control composition, the presence of a crystalline weakly crystallized network of neoplasms was observed (Figure 4a).

In the samples with the addition of an artificial filler, a similar structure of neoplasms has a more crystallized appearance in the total mass of which crystals of an artificial filler are distributed (Figure 4b), which serve as a substrate that intensifies the process of synthesis of neoplasms, including at the early stages of hardening, which contributes to an increase in the operational properties of non-autoclave materials.

4. Conclusion

Thus, based on the data obtained, the nature of the influence of AF-1 and AF-2 on the performance indicators (strength, density, water resistance) of wall silicate materials of non-autoclave hardening based on aluminosilicate raw materials, characterized by the presence of certain clay rocks of an unfinished stage of mineral formation, was established. The optimal content of AF-1 (CaO:SiO$_2$ = 1:1) in the raw mixture is in the range of 1–3 wt.% The available interval makes it possible to vary the composition of the initial mixture and obtain products with the required properties, which is especially important when the material composition of the feedstock fluctuates, as well as in case of violation of the production technology. The rational content of AF-2 (CaO:SiO$_2$ = 2:1) is 1 wt.%, and with an increase in the percentage, the strength characteristics of the finished products decrease.

Mathematical models are proposed for the selection and optimization of the compositions of non-autoclave silicate materials based on unconventional aluminosilicate raw materials and modified with an artificial filler represented by calcium hydroxides of various basicity to obtain materials with a compressive strength of 18-23 MPa with an average density of finished products of 1750-2000 kg/m$^3$.

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References

[1] Lesovik V S and Fomina E V 2019 Vestnik MGSU 14(10) 1241–57
[2] Fomina E V, Lesovik V S, Kozhukhova N I and Chulenyov A S 2019 Mater. Sci. Forum 974 168-174
[3] Mandili B, Taqi M, Bouari A Ei and Errouaiteic M 2019 Construction and Building Materials 228 117097
[4] Nelyubova V V, Babayev V B, Alfimova N I, Usikov S A and Masanin O O 2019 Construction Materials and Products 2(2) 4-9
[5] Fomina E V, Lesovik V S, Kozhukhova M I and Solovyova E B 2019 Mater. Sci. Forum 974 224-230
[6] Volodchenko A N and Strokova V V 2017 Bull. of BSTU named after V.G. Shukhov 1 138-43
[7] Huiwen Wan, Yong Hu, Gang Liu and Yuan Qu 2018 Construction and Building Materials 184 20-26
[8] Yunliang Zhao, Yimin Zhang, Tiejun Chen, Yongliang Chen and Shenxu Bao 2012 Construction and Building Materials 28(1) 450-455
[9] Hamdy El-Didamony, Ahmed A Amer, Mona S Mohammed and Mahmmod Abd El-Hakim 2019 J. of Building Engineering 22 528-538
[10] Liu B, Ray A, Thomas P S, Klimesch D and Guerbois J P 2007 J. of Solid Waste Technology and Management 33(2) 61-66
[11] Nonat A 2010 *Cement, Wapno, Beton* **15(6)** 315-326
[12] Dachowska R and Stepień A 2011 *Procedia Engineering* **21** 1173-78
[13] Kalla P, Misra A, Gupta R C, Csetenyi L, Gahlot V and Arora A 2013 *Construction and Building Materials* **40** 1142-50
[14] Karpikov E G, Lukuttsova N P, Soboleva G N, Golovin S N and Cherenkova Yu S 2019 *Construction Materials and Products* **2(6)** 20-28
[15] Yarusova S B, Gordienko P S, Kozin A V, Zhevtun I G and Perfilev A V 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **347** 012041
[16] Volodchenko A A 2018 *Bull. of BSTU named after V.G. Shukhov* **12** 12-20