Modifying additive for dry building mixtures

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Abstract. It is proposed to use limy finishing compositions with a modifying additive in thermal insulation. Such additives are obtained in two-stage synthesis technology. The mineralogical composition of the additive is represented by a mixture of synthesized hydrosilicates and calcium aluminosilicates. The method of lime absorption from lime solution was used to find out the additive pozzolanic activity. The authors estimate the efficiency of using additives in the composition of calcareous dry mortars. The compressive strength and the content of free lime in lime composites are determined. Further, the paper provide the feasibility of the adopted two-stage synthesis technology. Finally, the authors obtain the crack resistance of coatings based on a heat-insulating calcareous dry mortar intended for finishing aerated concrete.

1. Introduction
To improve the performance of finishing compositions, various modifying additives are introduced into their formulation [1-6]. Various materials of natural origin and industrial wastes containing active silica in amorphous or finely dispersed form are widely used as active mineral additives in lime compositions. Pozzolans, volcanic tuffs, diatomite, clays, etc. can be attributed to mineral additives of natural origin [7,8]. Mineral additives derived from industrial wastes include fuel ashes, granulated slags, silica wastes, etc. [9,10].

In the papers of [11-16], it was proposed to use synthesized calcium aluminosilicates and calcium hydrosilicates as modifying additives. Additives regulate the properties of calcareous dry building mixtures (DBM). It is interesting to study the possibility of using a mixture of hydrosilicates and calcium aluminosilicates as a modifying additive in the DBM formulation.

2. Materials and research methods
The process for preparing the modifying additive includes two steps. In the first stage, the quicklime was quenched with water (heated to 60 °C), and the resulting solution was brought to a boil. Then a solution of liquid sodium glass with temperature to 60 °C was poured into the mixture. The resulting pulp was stirred for 15 minutes, after which it was filtered off. In the second stage, a 10 % solution of aluminum sulfate was added to the precipitate formed, until the pH of the obtained mixture dropped to 6.5. The resulting solution was again filtered off. The precipitates formed (in the first and second stages) were dried at 100-105 °C for 12 hours in a drying cabinet. To assess the feasibility of the two-step synthesis technology of the modifying additive, further studies were carried out in parallel for the additives formed in the first and second stages.
The procedure for determining the pozzolanic activity of the modifying additives is based on the ability of amorphous silica to absorb lime from the lime solution. The order of the experiment is as follows. The test additive was ground in a mortar prior to its passage through a No. 008 sieve. 1 g of the additive was placed in a container, in which 100 ml of a saturated lime solution with a CaO concentration of 0,80-0.85 g/l was then added. During the entire experiment, the container with the test solution was periodically shaken. After every 2 days 50 ml of the titration solution was taken from the tank. Titrated with 0.05 N hydrochloric acid HCl solution with a methylorange indicator. After each titration, 50 ml of a lime solution with a CaO concentration of 0,80-0.85 g/l were poured into the cylinder. The activity of the additives was determined by the amount of Ca(OH)₂, which absorbed 1 g of the additive over 30 days.

The effectiveness of the application of the additives being developed was evaluated by the change in the plastic properties of the lime mixture. The content of additives was 10%.

The crack resistance of coatings was estimated from the values of shrinkage deformations and the value of the limiting extensibility

Shrinkage deformations \( \varepsilon_{\text{def}} \) were determined during the process of coating hardening at a temperature of 20 ± 2 °C and relative humidity of air \( \varphi = 50-55 \% \) with use the optical comparator IZA-2.

Determination of the values of ultimate extensibility and cohesive strength of coating samples was carried out on a tearing machine IR 5057-50. The dimensions of the test samples were 10×10×50 mm, the deformation rate was 1 mm/min. The tests were carried out at an air temperature of 20 ± 2 °C and a relative air humidity of 50-55% after 28 days of air-dry hardening.

To assess the crack resistance of coatings we used the coefficient of fracture toughness \( K_r \), determined by the formula:

\[
K_r = \frac{\varepsilon_{\text{lim}}}{\varepsilon_{\text{def}}}
\]

where \( \varepsilon_{\text{lim}} \) - is the ultimate extensibility, mm/mm; \( \varepsilon_{\text{def}} \) - draft deformations during hardening, mm/mm.

3. Research result

The properties of the modifying additives are shown in Table 1. The oxide composition of the modifying additives is shown in Table 2.

| The stage of synthesis of the additive | Appearance                  | True density, [kg/m³] | Bulk density, [kg/m³] | Specific surface area, [m²/kg] |
|------------------------------------|-----------------------------|-----------------------|-----------------------|--------------------------------|
| 1 stage                            | Powder of white color       | 2100                  | 380                   | 480                            |
| 2 stage                            | Powder of white color       | 2140                  | 240                   | 1380                           |

| The stage of synthesis of the additive | The name of oxides and their content, [%] |
|--------------------------------------|------------------------------------------|
|                                      | SiO₂  | CaO  | Al₂O₃ | Na₂O | MgO  | SO₃ |
| 1 stage                              | 43,76 | 37,61| 0,218 | 16,71| 1,38 | -   |
| 2 stage                              | 37,05 | 31,07| 10,98 | 9,80 | 0,994| 9,84 |
additive obtained at stage 1 was carried out. It is established that its mineralogical composition is mainly represented by minerals of the tobermorite group, portlandite, calcite. In the oxide composition of the additive (are obtained after 2 stages of synthesis) significant proportions of oxides of SiO2, CaO, Na2O remained, but at the same time Al 2O3 and SO 3 oxides were additionally appeared. In the mineralogical composition of the sediments minerals of the tobermorite group, gypsum, semi-aquatic gypsum, solid solution CSH (B) in the form of weakly crystallized gel, X-ray amorphous phase containing aluminosilicates were found.

The activity of additives is presented in Fig. 1.

![Figure 1. Activity of the developed additives: 1 - are obtained after the 1st stage of synthesis; 2 - are obtained after the 2nd stage of synthesis.](image)

It was found, that the activity of the additive (are obtained after the 1st stage of synthesis) is of 238.6 mg/g (curve 1, curve 1). This is caused by a high content of hydrosilicates in its composition. The pozzolanic activity of the additive (are obtained after the 2 stages of synthesis) is 3.2 times higher and amounts to 762.5 mg/g (curve 1, curve 2).

The experiment to determine the activity of the additives was continued until, the amount of calcium hydroxide did not cease to change. The additive (are obtained in the 1st stage) continued to actively absorb Ca (OH)2 up to 40 days, then the absorption rate slowed down and by 90 days the activity reached 285.0 mg/g. The additive (are obtained in the 2 stages) continued to actively absorb Ca (OH)2 significantly longer (up to 90 days), its activity reached 1280.0 mg/g.

The main reasons for the increase in pozzolanic activity of the additive (are obtained after 2 stages of synthesis) is the appearance of an X-ray amorphous phase, containing aluminosilicates in the composition of the additive and an increase in the specific surface area of the additive.

The effectiveness of the application of the additives being developed was evaluated by the change in the plastic properties of the lime mixture. The content of additives was 10%. The growth curves of the plastic strength of the lime mixture are shown in Fig.2.

It is established, that the additive (are obtained after the 2 stage of synthesis) significantly increases the rate of growth of the plastic strength of the lime mixture and after 8 hours the plastic strength is \( \tau = 46.2 \) kPa (Fig. 2, curve 3). The plastic strength of the control composition after 8 hours was \( \tau = 6.39 \) kPa (Fig. 2, curve 1). The additive (are obtained after the 1 stage of synthesis) slightly increases the
The growth rate of the plastic strength of the lime mixture and after 8 hours after mixing the plastic strength is $\tau = 9.85$ kPa (Fig. 2, curve 2).

![Figure 2. A change in the plastic strength of the calcareous mixture: 1 - control composition on a lime, W/L = 1; 2 - composition on a lime with additive (are obtained in the first stage), W/L = 1; 3 - composition on the lime with additive (are obtained in the second stage), W/L = 1.]

To evaluate the hardening kinetics, compressive strength of calcareous composites was measured using the modifying additives obtained respectively after the 1st and 2nd synthesis steps. We also determined the amount of free lime in the studied composites. The results of the studies are presented in Table 3.

| The used modifying additive | Compressive strength $R_{\text{cst}}$, [MPa] | Amount of free lime, [%] |
|----------------------------|--------------------------------------------|--------------------------|
|                            | At the age of 7 days | At the age of 28 days |                                |
| Control (with out additives)| 0.325          | 0.86                | 49.1                           |
| 1 stage                    | 0.425          | 1.33                | 40.2                           |
| 2 stage                    | 1.15           | 2.47                | 28.6                           |

It is established (Table 3) the high efficiency of using the additive, obtained after 2 stages of synthesis. With its use, compressive strength $R_{\text{cst}}$ of calcareous composites at the age of 28 days increased by 2.87 times. When using the additive, obtained after the 1st stage of synthesis, the compressive strength $R_{\text{cst}}$ of composites increased by 1.55 times.

The data presented in the study prove the high efficiency of using a mixture of hydrosilicates and calcium aluminosilicates as a modifying additive in the DBM formulation. The modifying additive, obtained after 2 stages of synthesis technology, has high pozzolanic activity, which makes it possible to significantly improve the performance properties of the lime finish coatings.
To assess the operational properties of coatings based on the lime composition using the developed additive, samples were prepared on the basis of the following composition: lime, modifying additive, white cement, ground waste of aerated concrete, redispersible powder, plasticizing additive, hydrophobizer, light highly porous filler [17-20]. The content of the modifying additive was 10% of the weight of the lime. As fillers, glass hollow microspheres having a bulk density of 130 kg/m\(^3\), a particle diameter of up to 100 \(\mu\)m, a pore wall thickness of 1 ... 3 \(\mu\)m were used.

It is established, that the most intensive growth of shrinkage deformations of samples occurs during the first six days of hardening, after which stabilization is observed. After 90 days the shrinkage is equal to \(\varepsilon_{\text{def}} = 0.615\) mm/m.

The deformative properties of coatings based on the developed composition of DBM are given in Table 4.

| Relative deformations | Elastic deformations \(\varepsilon_{\text{el}}, [\text{mm/mm}]\) | Plastic deformations \(\varepsilon_{\text{pl}}, [\text{mm/mm}]\) | The limiting extensibility \(\varepsilon_{\text{lim}}, [\text{mm/mm}]\) | Elastic modulus at tension \(E_{\text{el}}, [\text{MPa}]\) | Tensile strength \(R_{\text{kog}}, [\text{MPa}]\) | Coefficient of crack resistance |
|-----------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 0.007                 | 0.009                    | 0.016                    | 73.33                    | 0.75                     | 26.1                     |

It is established, that the finish coat has a high crack resistance. The limiting extensibility is \(\varepsilon_{\text{lim}} = 0.016\) mm / mm, and the shrinkage deformation value is \(\varepsilon_{\text{def}} = 0.000615\) mm / mm.

4. Conclusion
Properties of coatings based on the developed composition are given in the Table 5.

| The name of indicators | Values |
|------------------------|--------|
| Compressive strength \(R_{\text{cm}}, [\text{MPa}]\) | 4.00-4.30 |
| Coefficient of thermal conductivity in the dry state \(\lambda, [\text{W/m-K}]\) | Less 0.140 |
| Coefficient of vapor permeability \(\mu, [\text{mg/m-h-Pa}]\) | More 0.150 |
| Adhesive strength \(R_{\text{agl}}, [\text{MPa}]\) | More 0.6 |
| Consumption on 1 m\(^2\) with a layer 10 mm thick, [kg] | 6.5-7.0 |
| Frost resistance | F35 |

The conducted studies prove the expediency of the adopted two-stage technology for the synthesis of the modifying additive. The high pozzolanic activity of the additive makes it possible to effectively use it in the development of thermal insulation DBM for the finishing of aerated concrete.

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