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Patterns of structure formation in lime composites with additive based on amorphous aluminosilicates

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ABSTRACT: Introduction. One of the reasons for coating destruction enclosing structures is the formation of condensate at the boundary of the fence and the finishing layer. As a result of external impact and freezing of moisture in the pores of the plaster coating, a network of small cracks is formed, and it is also possible to peel off the finishing layer. To test this hypothesis, the facades of three different buildings were examined. It is established that all the studied plaster coatings are made on the basis of cement mortar. It is also known that lime mixture is used less often due to the lack of sufficient resistance to moisture. Therefore, there is a need to increase the resistance of coatings based on lime compositions. This can be achieved by introducing an alumosilicate-based modifying additive into it. **Materials and methods.** Liquid sodium glass, aluminum powder PAP-1 and distilled water were used for the synthesis of the additive. Slaked lime (pushonka) with an activity of 84% was used to prepare test samples. Fritsch particle sizer Analysette 22 was used to analyze the granulometric composition of the additive. Compressive strength was determined on the samples measuring 20×20×20 mm. A testing machine of the type "IR 5057-50" was used for the study of compressive strength of samples. The analysis of rheological properties was determined by the Shvedov-Bingham equation. To study the plastic strength (ultimate shear stress) of the finishing mixture, a conical plastometer KP-3 was used. The plastic viscosity of the composition was determined with a rotary viscometer BCH – 3. **Results and discussions.** The synthesized additive is a light powder of light gray color with a bulk density of 0.55 ± 0.05 g/cm^3. The synthesized additive revealed a high content of oxides Al_2O_3, SiO_2, Na_2O respectively, amounting to 51.03%, 36.36%, 11.89%. The additive consists of particles of 100.0–200.0 microns, which make up more than 20% of the total composition. The influence of an aluminosilicate additive on a lime binder on rheological properties was investigated, a slight increase in static shear stress was revealed, respectively, an increase in the percentage of the additive. The value of the dynamic shear stress increases significantly with an additive content of more than 10%. **Conclusions.** The regularities of hardening of a lime binder with a nanostructured additive based on amorphous aluminosilicates are established, and the optimal content of an aluminosilicate additive in the amount of 10% by weight of lime is determined.

KEYWORDS: modifying additive, aluminosilicates, lime, thermal insulation, dry mixes.

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INTRODUCTION

When using protective and decorative coatings on the external enclosing structures of buildings, these coatings are exposed to moisture caused by rains, high moisture content in the air and the movement of water vapor in the thickness of the fence, due to the difference in partial pressure [1–3]. As a result of the influence of external factors on the coating, partial destruction of the plaster layer is possible, manifested in the form of detachments or small cracks. To protect the enclosing structures from the effects of moisture, various types of protective coatings are used, such as waterproofing materials, paints, varnishes and others. However, the choice of coating depends on many factors, including climatic conditions and design characteristics. In addition, it is important to properly prepare the surface before applying a protective coating to ensure the best adhesion of the coating to the surface and increase its resistance to external factors.

When analyzing the issue of the condition of coatings after prolonged exposure to external factors, the facades of buildings in Penza on Tsiolkovsky St. (Fig. 1), Kalinin St. (Fig. 2), Mozhaisky St. (Fig. 3) were examined.

Plastering works on these streets were carried out using cement-based plasters. After studying the situation, it was revealed that the main problems are peeling and cracking of the coating on the end of the building.

For outdoor work, dry building mixes based on cement binder are most often used, since lime binder has a low resistance of coatings based on it. Cement-based plasters are well suited for outdoor work, as they have high strength and resistance to weather conditions. However, when using such plasters, it must be borne in mind that they may be less flexible than lime-based plasters, which can lead to cracks when temperature and humidity change.

Lime coatings are characterized by greater crack resistance, better perceive tensile forces, have good vapor permeability and resistance to bio-damage [4–6]. At the moment, dry mixtures containing lime as the main binder remain the only finishing compounds that provide connectivity with the finishing materials of historical buildings [7].

Therefore, it is most advisable to use lime binder in decorative plaster compositions.

However, the disadvantage of these compounds is their low strength and water resistance. In addition, lime binders harden very slowly, which makes it difficult to carry out finishing work. To accelerate the curing of lime and increase water resistance, strength and reduce shrinkage deformation, various additives are introduced into the formulation in order to increase the durability of lime coatings. To improve the performance characteristics of binders based on lime compositions, the introduction of active mineral additives into the formulation is proposed [8–12]. Crushed clay that has undergone heat treatment to increase the content of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) is one of the active mineral additives [13, 14]. Its use in the finely ground state ensures the plasticity of the composition and the absence of stickiness, as well as gives them hydraulic properties, which makes it possible to produce high-quality dry mixtures.

Natural materials such as granulated blast furnace slag, fuel ash and silica waste residues containing a large amount of active silicates and aluminates are also used as active mineral additives [15–29]. One of the ways to impart hydraulic properties to the binder is the use of active fine silica. Due to calcium hydrosilicates formed during

Fig. 1. **Covering the facade of the building on Tsiolkovsky Street after 3 years of operation, Penza**

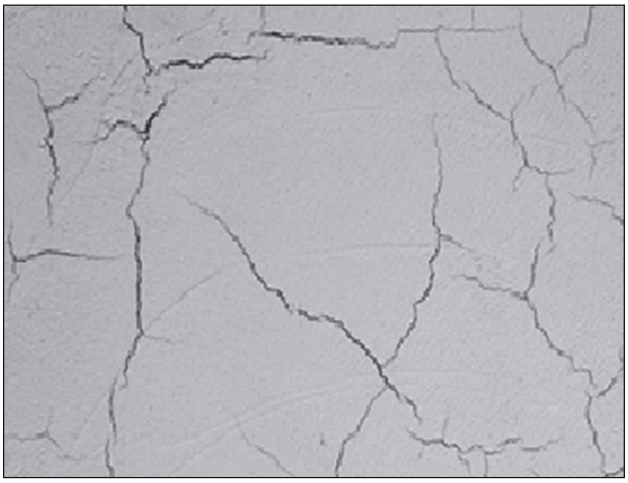

Fig. 2. **Covering the facade of the building on Kalinin Street after 3 years of operation, Penza**

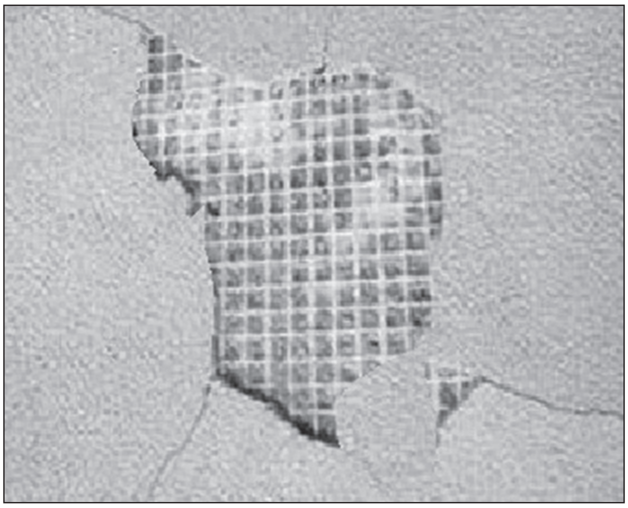

Fig. 3. **Covering the facade of the building along Mozhaiskiy Street after 6 years of operation, Penza**

interaction with lime binder, the composition acquires the ability to harden under the action of moisture after carbonization of lime dough in air, without reducing strength characteristics, as well as leaching resistance [20, 21].

There are both domestic and imported additives based on amorphous aluminum oxides (γAl_2O_3) and aluminum hydroxide Al(OH)3 [28–30].

In [24, 25], it is proposed to introduce additives based on synthesized calcium hydrosilicates (HSC) into the formulation of lime finishing compositions. The use of synthesized calcium hydrosilicates as additives in lime binder accelerates the hardening process and increases strength, which is due to their high activity. When interacting with a lime binder, these additives form a mixture of low-base and high-base hydrosilicates that improve the adhesion of lime to the filler.

Currently, materials containing amorphous aluminosilicates are used as ion exchangers (for example, for water purification), as adsorbents in chromatography, in the purification, drying and separation of gases, as well as in the catalytic cracking of petroleum products [26].

In this regard, it is of interest to study the possibility of using additives containing amorphous aluminosilicates in the formulation of lime mixtures. The interaction of lime binder with aluminosilicates implies an increase in water resistance, acceleration of curing, and improvement of strength characteristics.

METHODS AND MATERIALS

The following materials were used to prepare the additive:

- liquid sodium glass [27];
- distilled water;
- aluminum powder PAP-1 [28] is characterized by the indicators presented in Table 1.

The following materials were used to prepare the dry mix:

- slaked lime (fluff) with an activity of 84%, a true density of 2200 kg/m^3, a bulk density of 280 kg/m^3, with a specific surface area of 13 478 cm^2/g.

In the work, the technology of synthesis of an aluminosilicate additive was used, which consists in adding microdispersed aluminum powders to sodium water glass at a temperature of 60–90^{o}C for 30–120 minutes [29]. The microstructure of the synthesized additive was studied using a scanning electron microscope with a magnification of 20.000 times.

The particle size distribution of the additive was studied using the Fritsch particle sizer Analysette 22.

The compressive strength of the samples was determined according to GOST 5802 [30]. Samples with a size of 20×20×20 mm were tested. As a test equipment for studying the compressive strength of samples, a testing machine of the type "IR 5057-50" was used, the force

Table 1
Physical properties and chemical composition of aluminum powder

Brand mark	PAP-1	PAP-2	PAG-1	PAG-2	PAG-3
Covering capacity on water, cm^2/g, not less	7000	10000	6000	8000	10 000
Floatability, %, not less	80	80	–	–	–
Granulometric composition					
Residue on sieves, %, no more					
+008	1.0	–	1.5	–	–
+0056	–	0.3	-	0.7	–
+0045	–	0.5	–	–	0.5
Chemical composition, %					
Active aluminum, not less than	–	–	90	88	86
Impurities, no more					
iron	0.5	0.5	–	–	–
silicon	0.4	0.4	–	–	–
copper	0.05	0.05	–	–	–
manganese	0.01	0.01	–	–	–
moisture	0.2	0.2	–	–	–
fatty additives	3.8	3.8	2.4	3.0	3.2

measurement range is from 50 to 50,000 N with an accuracy of 1N (0.1 kgf), the load application rate is from 1 to 100 mm /min (according to the displacement). The compressive strength (MPa) of the samples was determined by the formula:

$$R_{comp} = P/F, \qquad (1)$$

where P is the breaking force, N;

F is the cross-sectional area of the sample before testing, m^2.

The influence of the content of additives based on amorphous aluminosilicates in the lime binder on the rheological properties was studied. Since lime compositions are plastic systems, their rheological behavior is described by the Shvedov-Bingham equation.

$$\tau = \tau_0 + \eta\gamma, \qquad (2)$$

where τ_0 – is the ultimate shear stress;

η – plastic viscosity;

γ – shear rate.

The plastic strength (ultimate shear stress) of the finishing mixture was determined using a KP-3 conical plastometer. At the moment the cone reaches equilibrium, the shear stress t in the composition becomes equal to the yield strength τo and is determined by the formula:

$$\eta = \tau = \tau_0 = P/h^2, \qquad (3)$$

where η – is plastic strength;

τ – is the shear stress;

τ_0 – is the yield point;

k – is a coefficient depending on the value of the vertex angle of the cone; for a metal cone with an angle at the top of 30°–k = 1,116;

P – is the weight of the moving part of the device (load);

h – is the depth of immersion of the cone into the mortar mixture.

Tests for the determination of plastic viscosity, dynamic and static shear stress of lime systems were carried out using a rotational viscometer BCH-3.

RESULTS AND DISCUSSIONS

The synthesized additive is a light gray powder with a bulk density of 0.55 ± 0.05 g/cm^3. During the synthesis of the additive, a large amount of gaseous molecular hydrogen is formed, which creates pores of various sizes and shapes in the additive. The output of the finished product is 90%.

The oxide composition is presented in Table 2. It was found that aluminum oxides predominate, making up 51.03%.

Table 2

The content of oxides in the composition of the additive

Oxide	Content, %
Al_2O_3	51.03
SiO_2	36.36
Na_2O	11.89
Fe_2O_3	0.110
CaO	0.107
MgO	0.105
SO_3	0.0290
TiO_2	0.0124
K_2O	0.0112
Other	0.3454
Amount	99.6546

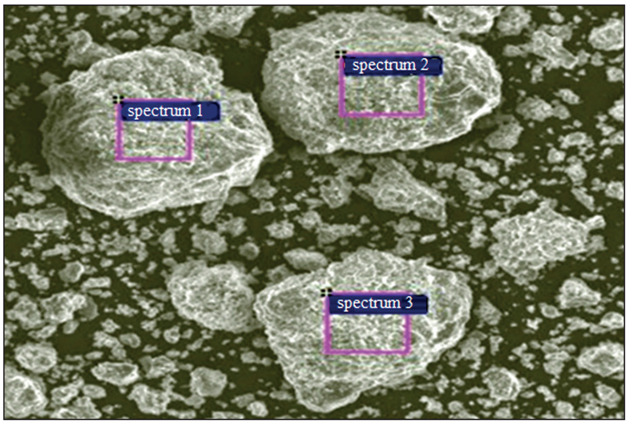

Fig. 4. **Microstructure of synthesized aluminosilicates**

A high content of oxides Al_2O_3, SiO_2, Na_2O was revealed, which is respectively 51.03%, 36.36%, 11.89%.

The microstructure of the additive is shown in Fig. 4.

When evaluating the properties of the additive, the particle size distribution was analyzed using Fritsch particle sizer Analysette 22 (Table 3).

The data obtained show that the additive consists of particles of 100.0–200.0 μm, which make up more than 20% of the total composition.

During operation, repeated temperature changes contribute to the movement of water vapor in the thickness of the building envelope, and can also cause its condensation and freezing on the contact surfaces of the wall structure and the finishing layer. Moisture intensively affects the inner surface of the coatings and exerts a significant force aimed at tearing off the coating from the base. This, in turn, causes the formation of cracks and other damage. To maintain the heat and moisture regime of the building envelope, the materials used for finishing must have a certain vapor permeability.

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Table 3
Granulometric composition of the additive

Fraction, µm	Percentage content, %
0.01–2.0	2.48
2.0-5.0	7.50
5.0–10.0	10.81
10.0–20.0	13.35
20.0–45.0	18.60
45.0–80.0	17.92
80.0–100.0	8.20
100.0–200.0	21.08
200.0–300.0	0.07

When evaluating the porous structure of the studied composite, it was found that an increase in porosity is observed. So, the total porosity of the sample based on lime binder is P = 53.8%, and with the use of an aluminosilicate additive P = 70–74%. Despite the increase in the porosity of the samples based on the developed additive, they are characterized by increased strength, which is apparently due to the chemical interaction of lime with the synthesized aluminosilicates.

Table 4 shows a comparative analysis of the effect of an aluminosilicate additive in an amount of 1–30% on the process of structure formation of samples based on lime with an activity of 84%.

The samples hardened in air-dry conditions at a temperature of 18–20°C and a relative humidity of 60–70%. The test results are shown in Table 4 and Fig. 5.

The compressive strength of the samples with the use of an additive in the amount of 10% by weight of lime after 28 days of air hardening is R_{str} = 2.71 ± 0.108 MPa. The data obtained indicate that the introduction of the additive in an amount of 10% corresponds to the maximum strength index.

After 28 days of hardening, composites prepared on the basis of compositions with a high content of alumi-

Table 4
Strength of lime composite with an additive based on amorphous aluminosilicates

Additive content, % by weight of lime	Compressive strength, MPa, age, days			
	3	7	14	28
Control, water/lime = 1.0	0.33	0.51	0.75	1.00
1%	0.62	1.35	1.58	1.75
5%	0.82	1.56	2.00	2.16
10%	0.90	1.88	2.80	2.71
20%	0.64	1.73	2.23	2.00
30%	0.65	1.82	2.20	2.00

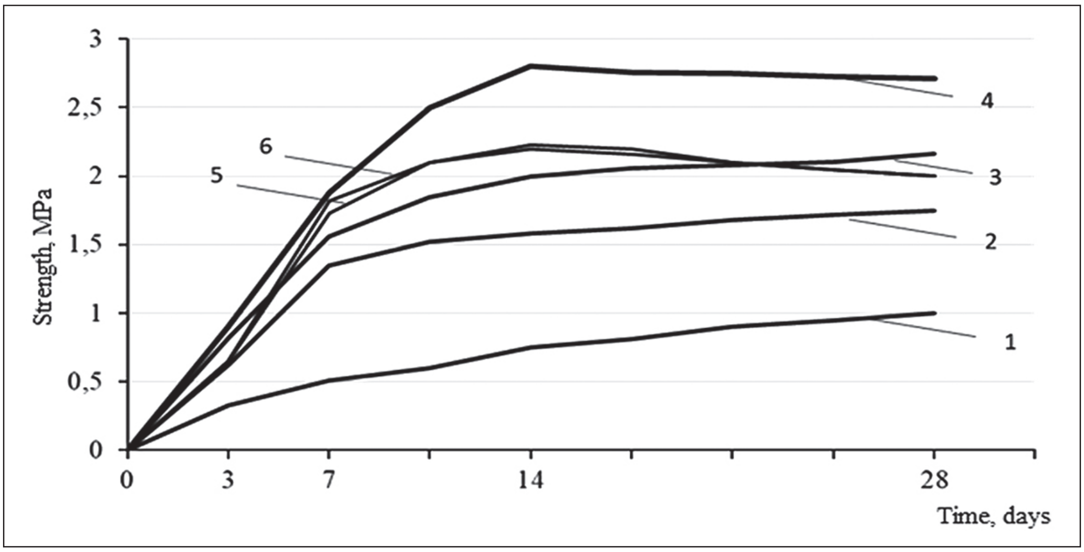

Fig. 5. **Change in compressive strength of lime composite with different content of aluminosilicate additive:** 1 – control sample (W/I = 1); 2 – 1% additives; 3 – 5% additives; 4 – 10% additive; 5 – 20% additives; 6 – 30% additives

Table 5
Dependence of shear stress on additive content

Supplement content		–	1	5	10	20	30
Static shear stress, MPa		**0.0004**	**0.00041**	**0.00042**	**0.00043**	**0.00045**	**0.00046**
Dynamic shear stress, MPa, at rotation speed, RPM	200–400	0.000176	0.000185	0.000194	0.000205	0.000215	0.000217
	300–600	0.000276	0.000285	0.000294	0.000298	0.000312	0.000316
Plastic viscosity, Pas, at rotation speed, RPM	200–400	45.18	45.18	45.18	45.18	49.69	49.69
	300–600	57.23	57.23	57.23	57.23	57.23	66.26

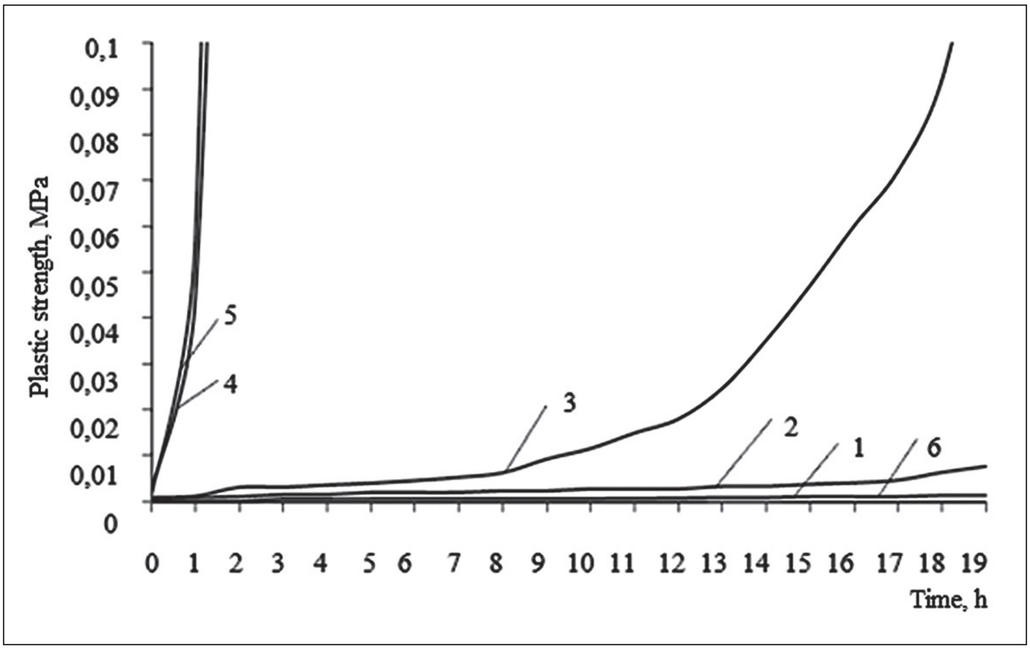

Fig. 6. **Change in plastic strength of lime paste with aluminosilicates:** 1 – the content of the additive is 1% by weight of lime; 2 – the content of the additive is 5% by weight of lime; 3 – the content of the additive is 10% by weight of lime; 4 – additive content of 20% by weight of lime; 5 – additive content of 30% by weight of lime; 6 – control sample (without additive content)

nosilicate additives (20–30% by weight of lime) show a decrease in strength.

The influence of the content of additives based on amorphous aluminosilicates in the lime binder on the rheological properties was studied (Table 5).

An increase in the additive content of more than 10% is characterized by an increase in static shear stress, values of dynamic shear stress, as well as an increase in plastic viscosity. So, the dynamic shear stress of the lime composition at a speed of 200–400 rpm is $\tau = 0.000176$ MPa, and for the composition based on a composite binder with an additive content of 5% – $\tau = 0.000194$ MPa, with an additive content of 20% – $\tau = 0.000215$ MPa.

Also, the use of an additive in a lime mixture leads to an acceleration of the set of plastic strength. The plastic strength of the composition with a content of 10% additive by weight of lime after 8 hours of hardening is $\tau = 0.006217$ MPa (Fig. 6, curve 3), and the control composition (without additive) $\tau = 0.001004$ MPa (Fig. 6, curve 6). At the same time, with an increase in the content of the additive in the composition of the solution, the plastic strength also increases.

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Yulia A. Sokolova – writing an article, scientific editing of the text.

Nikolay I. Shestakov – writing an article, identifying dependencies.

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