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Compositions for Limestone Restoration

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ABSTRACT

Information about the lime composition used for the restoration of limestone is given. It has been shown that using a polysilicate mortar to formulate a lime composition contributes to an increase in water resistance, adhesion strength of the composition to the base, and acceleration of curing. A primer composition is proposed, including liquid sodium glass and calcium chloride.

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1. Introduction

The problem of preserving historical heritage occupies one of the top places in modern urban planning [1-3]. As a result of the processes of physical weathering aggressive external environment, the destruction of natural stone occurs. Usually, the stone during the operation of the building is covered with layers of pollution from dust, efflorescence, soot, rust, tar, and oil deposits, as well as organic substances emitted by plants. Therefore, natural stone restoration is carried out in three stages. In the first stage, it is cleaned; in the second stage, the cracks are puttied, and the lost fragments are added, after which, in the third stage, measures are taken to preserve the stone [4-7].

The composition of the stone strengthener contains silicic acid ester, which forms a three-dimensional adhesive bridge (a binder in the form of silica gel) in the pore space of the base, which leads to the hardening of the base [8].

Firm Stalker (Russia), for strengthening white stone, marble, sandstone, and products made of natural and artificial stone, offers the composition •AKSIL BeKam-I, which is based on ethyl ether of silicic acid [9]. The composition provides deep processing. During the curing of the material, solid products are formed that do not adsorb dirt. The treated surfaces become weather-resistant, incl. including acid rain, and remain vapor permeable.

The Corporation "Ukrrestavratsiya" (Kyiv, Ukraine) for the conservation of limestone uses structural strengthening with an aqueous solution of amorphous non-porous silica - a bluish-white fluffy powder [10].

Remmers offers various types of fortifications, which differ according to the following criteria:

- according to the content of the binder (the so-called degree of gel settling);
- according to the gel structure (with/without the content of elasticizing structural components); - according to the type of bond with the base [11]

Taking into account the law of structure affinity, it was proposed in [12] to use a dry mix containing white cement, micro filler (ground limestone), and superplasticizer when performing restoration work to imitate limestone.

Previous studies have confirmed the effectiveness of lime compositions for restoring architectural monuments made of limestone [13, 14]. The compositions contain fluffy lime, sand with a fraction of 0.16 ... 0.315 mm, silicic acid sol, stabilizer (polyvinyl alcohol, gelatin, cationic acrylamide copolymer), and aluminum sulfate.

In [15, 16], to intensify the process of lime hardening, it is proposed to add additives based on natural and synthetic zeolites to the formulation of lime compositions. The authors found that with the introduction of an additive based on synthetic zeolite in an amount of 10% by weight of lime, an increase in strength by 94.25% is observed compared to the control sample. The results of thermodynamic calculations and X-ray phase analysis allow us to assert that the most probable mechanism causing the hardening process is the formation of calcite, calcium-sodium hydro silicate, minerals of the zeolite group, and portlandite.

In China, the restoration of historic buildings in the cities of Shanghai and Hangzhou used a system based on hydraulic lime. It is proposed in [17] to restore historical masonry by using lime-metakaolin mixtures. According to the authors, meta kaolinite MK shows high pozzolanic activity, which provides the quick formation of CSH, C_2ASH_8 (stratlingite), and C_4AH_{13} in MK/lime systems. MK with portlandite is considered the primary reaction that results in other dense C-S-H gel. Lime-metakaolin mortars have been used to produce some of the white plasters of Genoa.

To increase the stability of lime compositions, silica-containing additives are introduced into their formulation. The use of polysilicate mortar in lime compositions for restoring and decorating building walls is of practical interest. Polysilicates have a wide range of anion polymerization degrees and are a colloidal silica dispersion in an aqueous solution of alkali metal silicates. The practical use of polysilicates is reflected in the manufacture of sol-silicate paints, where polysilicates are used as a binder. The presence of oligomeric and monomeric forms of

silicon-oxygen anions in the composition of the polysilicate solution ensures its reactivity during interaction with lime.

However, it should be noted that, while remaining relevant, many issues of using a polysilicate mortar to formulate a lime composition intended for the restoration and finishing of building walls have yet to be disclosed.

2. Materials and Methods

In continuation of further research, we have developed and tested the lime composition of the putty to restore limestone. The composition contains, as a polymeric binder, a polysilicate solution obtained by mixing liquid glass and silicic acid sol. To obtain a polysilicate solution, a silicic acid Nanosil 20 and Nanosil 30, produced by PK Promsteklotsentr, and sodium liquid glass with a modulus of M = 2.78 were used.

The initial binder was lime (Atmis-sugar, Russian Federation) with an activity of 75-84%, a natural density of 2205 kg/m^3, a bulk density of 500 kg/m^3, and a specific surface area of 10,000 cm^2/g. KM2 micro calcite was used as a filler, and the Khidetal P-4 additive was used as a plasticizer.

The investigation of finishing layers for strength in compression and bending was researched using a setup developed by the authors on specimens 10 × 10 × 10 mm and 10 × 10 × 50 mm in size, respectively (Fig. **1**).

(a) (b)

Figure 1: Setup for determining the strength in bending (a) and compression (b).

The molybdate method was used to determine the composition of the polysilicate solution [18, 19]. The content of silicon-oxygen anions in the monomeric form α-SiO_2 was determined as follows. 0.5 g of the test solution was weighed and diluted with distilled water to 20 ml, then 1.5 N H_2SO_4 was added. To 40 ml of molybdic acid was added 10 ml of the test solution, stirred, and after 2.5 minutes, the optical density of the solution was measured (at a wavelength of λ=410 nm). Next, the change in optical density over time was recorded for 30 min. The proportion of SiO_2 (P, %) that reacted with molybdic acid at each moment from the total content of SiO_2 in the test solution was calculated by the formula:

$$P = g_x \cdot 100/g_{SiO2}\ , \tag{1}$$

where g_x is the concentration of SiO_2 reacted with molybdic acid at each time point, mg;

g_{SiO2} is the total content of SiO_2 in the sample, mg.

$$g_x = C_{SiO2} \cdot M/100\ , \tag{2}$$

where C_{SiOtot} is the concentration of total SiO_2 in the sample, %;

M is the sample weight, mg.

The total silica content in the binders was evaluated using a UNICO 2100 spectrophotometer. To do this, a sample of the analyzed solution (0.3-0.7 g) was weighed on an analytical balance in a platinum crucible with a lid, then evaporated in a water bath to a dry residue. After cooling, the dry residue was weighed. A fivefold amount of anhydrous sodium carbonate was added to the dried residue and melted in an EKPS-10 muffle furnace at a temperature of 1000 ºC for 20 minutes. The alloy was rapidly cooled by lowering the crucible into distilled water. Then the crucible was transferred to a thermal beaker for 1 l; the alloy was leached in hot distilled water. After leaching, the mixture was cooled to room temperature, and 50 ml of 1.5 N H_2SO_4 was added and made up to the mark with distilled water. A graduated solution was prepared from a standard sample with a silicon mass concentration of 1.00 mg/cm^3. Aliquots of 1, 3, 5, 6, 8, and 10 ml were taken and transferred to a volumetric flask with a capacity of 100 ml, and 10 ml of 1.5 N H_2SO_4 was added to each flask and diluted with water to the mark. The optical density was measured on a UNICO 2100 spectrophotometer at a wavelength of λ=410 nm. As a result of processing the graduated graph, we obtained an equation for calculating the concentration of SiO_2:

$$C_x = (D - 0.0913037)/26.7478 \quad (3)$$

where C_x is the concentration of silica in the test solution, mg/mL;

D is the optical density of the colored solution, rel. units

In a 50 ml flask, 10 ml of the test solution was added to 40 ml of a molybdic acid solution, stirred, and kept until the color was completely yellow. Then, the optical density was determined in rectangular cells made of quartz glass 10 mm thick. Taking into account the dilution, the amount of SiO_2 in the sample was determined by the total content of SiO_2 according to the formula:

$$g_x = C_x \cdot V_x \cdot V_{com}/V_1 \quad (4)$$

where C_x is the concentration of SiO_2, mg/mL;

V_x is the volume of the colored test solution, ml;

V_{tot} is the total volume of the test solution;

V_1 is the volume of an aliquot of the test solution taken to prepare a colored solution, ml.

The formula determined the percentage of silicon dioxide in the test solution:

$$C_{Sio2} = g_x \cdot 100/M, \quad (5)$$

where *M* is the weight of a sample of an alkaline silicate solution, mg.

Static water resistance was determined according to GOST 9.403-80 (method A). The stained samples were vertically placed in a desiccator with water at 2/3 of the height and covered with a lid. The tests were conducted at a water temperature of (20 ± 2) °C for 72 h. After the tests, the samples were removed, and the decorative and protective properties of the coatings were determined by comparison with the control sample using a magnifying glass. Changes in gloss, shade, whitening of the film, and the appearance of bubbles, peeling, and wrinkling were recorded. The paintwork is considered resistant to the static action of liquids if the coating meets the requirements established in the standard or technical specifications for the paintwork material after testing.

3. Results and Discussion

It has been established that polysilicate solutions contain, along with sol particles, a monomer, oligomers, and polymeric varieties of silica [20-22]. It has been established by the molybdate method that in the polysilicate solution, the content of the monomeric form of silica γ-SiO_2 is 15-19.93%, depending on the content of the silicic acid sol [23]. Such a composition of the polysilicate solution contributes to the manifestation of silica's high reactivity in various compositions. The optimal concentration of the polysilicate solution was determined, which is

1% by weight of the lime. The composition of repair composition includes slaked lime and filler. After preparation, the compositions were deposited on a limestone substrate.

A topological analysis of the coating structure's formation was carried out to determine the probable mechanism for the formation of the strength of the "lime-polysilicate mortar" system. It has been established that the most probable mechanism for forming strength is the diffusion transfer of lime ions and the subsequent reaction of their interaction with the polysilicate solution. An increase in lime composites' strength with a polysilicate solution additive is due to the presence of other chemical formations.

X-ray diffraction and differential thermal analysis show that the most probable mechanism causing the hardening process is the formation of calcite, calcium-sodium hydro silicate, portlandite, and hydrate phases similar in chemical composition to C-S-H (I).

This composition of the putty was tested during the restoration of the church of St. John the Theologian in the village of Synkova, Podolsky district, Moscow region (Fig. **2**). When analyzing the state of the object, cracks in the plaster were recorded (Fig. **3**), and in the Znamensky Cathedral (Varvarka St., Moscow), cracks and potholes on the floor tiles made of limestone (Figs. **4**-**5**).

Figure 2: Church of St. John the Evangelist in the village of Synkovo, Podolsky district, Moscow region.

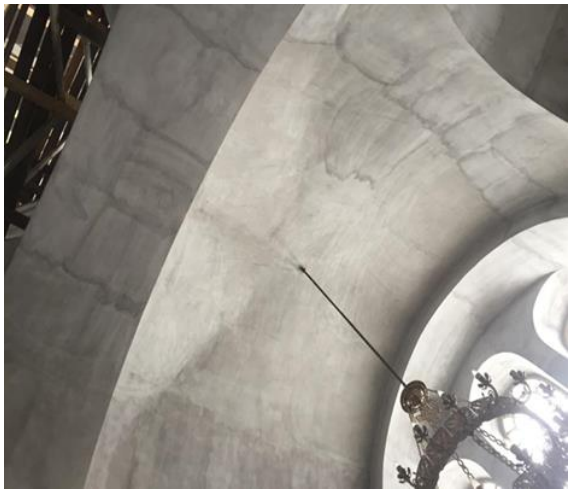

Figure 3: Microcracks in plaster (before repair).

Figure 4: Limestone floor tiles (after renovation).

Figure 5: View after repair and painting.

The technology for carrying out restoration work provides the application of a primer layer - liquid glass, followed by the application of a solution of calcium chloride. When liquid glass interacts with calcium chloride, calcium hydro silicates are formed. In studying the new growth's qualitative composition, it was found that the samples' degree of crystallization is low. The X-ray diffraction pattern (Fig. **6**) of the filler samples contains diffraction lines (Å) of the following compounds: calcium silicate hydrates of the tobermorite group (10.13059; 3.58269; 3.25556; 3.2579; 2.82015; 2.4662; 1.29764; 1.2618); solid solution CSH (B) in the form of slightly

crystallized gel (4.76541; 3.03952; 2.82163) solid solution C–S–H (II): (2.22058; 1.87721; 1.41032); hydrohalites (hydrohalite mineral): (3.85831; 1.99449; 1.62748).

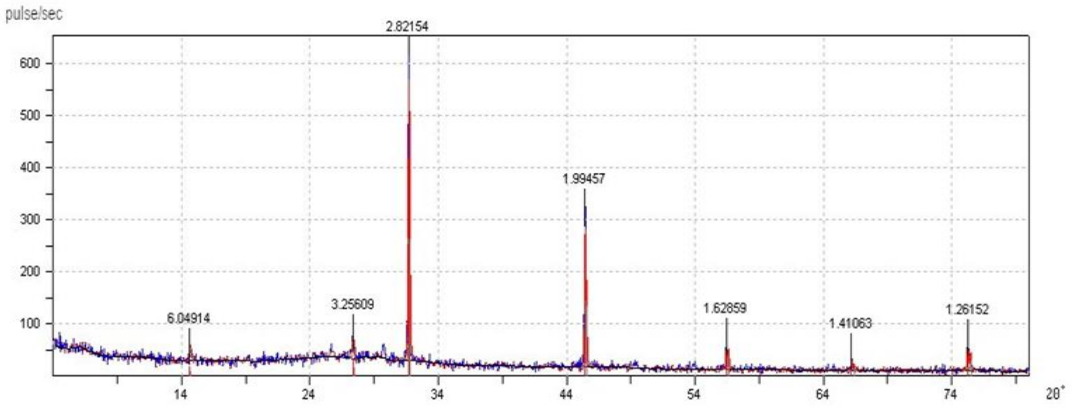

Figure 6: X-ray diffraction pattern of filler samples synthesized with the introduction of $CaCl_2$ additive in 50% of the mass of the water glass with a silicate modulus of 2.9.

Analysis of the IR spectrum of the obtained filler sample was performed for additional assessment. Fig. (**7**) shows distinguished absorption bands in 850–1100 cm^{-1}, 550–750 cm^{-1}, and 400–550 cm^{-1}, confirming the presence of calcium silicate hydrates in the synthesized material.

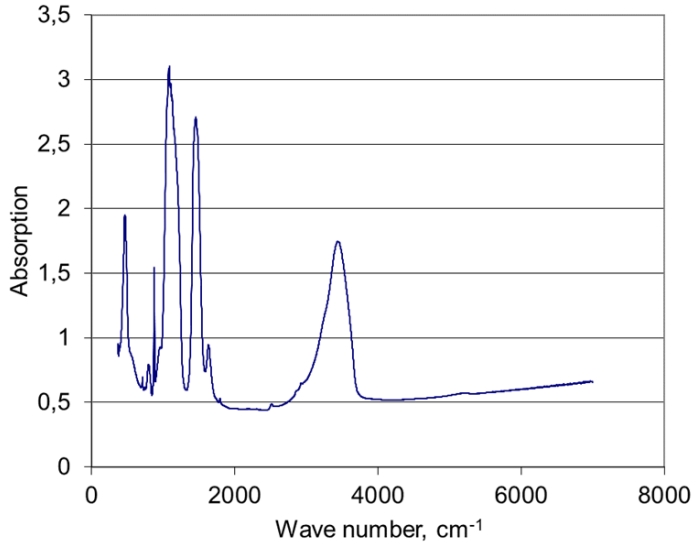

Figure 7: IR spectrum of the synthesized calcium silicate hydrates (CSH) filler sample.

The resulting calcium hydro silicates increase the adhesive interaction between the limestone and the applied finishing layer.

After 20-30 minutes after applying the primer, putty can be applied with a spatula.

The resulting calcium hydro silicates strengthen the limestone surface layer and contribute to a stronger interaction of the applied finishing layer due to the interaction of calcium hydro silicates with lime.

The compositions are characterized by good workability, and the drying time to degree 3 is 10 minutes. The compressive strength at 3 days is 1.75 MPa, and at 28 days - 5.42 MPa. After curing the coatings, tests were carried out for moisture and adhesion strength. At 28 days from the moment of mixing, the compressive strength of the control samples of limestone is 1.2 MPa, and with the use of a polysilicate mortar - 5.42 MPa. In the case of using a

polysilicate solution, a decrease in shrinkage deformations by a factor of 3 is observed. The adhesion strength of the coating to the limestone substrate is more than 1.3 MPa. There is a significant decrease in the water absorption of the composite. Resistance to static action of water by GOST 9.403-80 (method A) is more than 72 hours.

4. Conclusion

The composition of a lime building mixture with a polysilicate solution additive intended to restore and finish building walls, containing fluffy lime, micro calcite, and a polysilicate solution additive, has been developed. It has been established that the introduction of a polysilicate mortar additive into the lime mixture formulation contributes to an increase in the adhesion strength of the finishing layer, compressive strength.

Using liquid glass and calcium chloride as primers enhances the adhesive interaction between the restored object and the finishing material.

References

[1] Fermo P, Cappelletti G, Cozzi N, Padeletti G, Kaciulis S, Brucale M, *et al*. Hydrophobizing coatings for cultural heritage. A detailed study of resin/stone surface interaction. Appl Phys A. 2014; 116: 341-8. https://doi.org/10.1007/s00339-013-8127-z

[2] Khallaf MK, El-Midany AA, El-Mofty SE. Influence of acrylic coatings on stone-based monuments' interfacial, physical, and mechanical properties. Prog Org Coat. 2011; 72(3): 592-8. https://doi.org/10.1016/j.porgcoat.2011.06.021

[3] Cappelletti G, Fermo P. Hydrophobic and superhydrophobic coatings for limestone and marble conservation. In: Montemor MF, Ed. Smart composite coatings and membranes. Elsevier; 2016, p. 421-52. https://doi.org/10.1016/B978-1-78242-283-9.00015-4

[4] Paiva DS, Fernandes L, Trovão J, Tiago I. Uncovering the fungal diversity colonizing limestone walls of a forgotten monument in the central region of Portugal by high-throughput sequencing and culture-based methods. Appl Sci. 2022; 12(20): 10650. https://doi.org/10.3390/app122010650

[5] Loganina V, Zaytseva MV. Compositions for limestone restoration. Key Eng Mater. 2022; 909: 177-83. https://doi.org/10.4028/p-a554k3

[6] Loganina V, Fediuk R. Improving the performance of lime-sand finishing mixes. Constr Build Mater. 2020; 264: 120687. https://doi.org/10.1016/j.conbuildmat.2020.120687

[7] Xiaoli liu, Xunhan D, Jie N, Xu Z, Tao S. Effect of vegetation on species composition and diversity of soil surface arthropod in the limestone mountains in the North of Anhui Province. Acta Ecologica Sinica. 2021; 41(15): 6115-22. https://doi.org/10.5846/stxb202001150117

[8] de Ferri L, Lottici PP, Lorenzi A, Montenero A, Salvioli-Mariani E. Study of silica nanoparticles – polysiloxane hydrophobic treatments for stone-based monument protection. J Cult Herit. 2011; 12(4): 356-63. https://doi.org/10.1016/j.culher.2011.02.006

[9] LLC "Stalker". Available from http://www.aksil.ru/ (Accessed on October 2022).

[10] Ivashko YV. Problems of restoration of architectural monuments and restoration technologies. Available from https://megalektsii.ru/s24010t1.html (Accessed on November 2022).

[11] Ponomarenko MS. The mechanism of action of waterproofing penetrating materials. Exposition 2009; 2: 40-1.

[12] Chulkova IL. The possibility of using dry mixes for the restoration and reconstruction of ancient limestone objects based on the law. Bulletin of the Siberian State Automobile and Road Academy. 2013; 6: 66-9.

[13] Loganina V, Davydova O, Fediuk R, Amran M, Klyuev S, Klyuev A, *et al*. Improving the durability of lime finishing mortars by modifying them with silicic acid sol. Materials. 2022; 15(7): 2360. https://doi.org/10.3390/ma15072360

[14] Loganina VI, Proshina NA. Sol-gel technology for the synthesis of silicon-containing additives for lime finishing compositions. Build Mater. 2009; 7: 48-9.

[15] Loganina V, Zhegera K, Fediuk R, Timokhin R, Zayakhanov M, Liseitsev Y. Amorphous aluminosilicates as a structure-forming additive in cementitious systems. J Mater Civil Eng. 2020; 32(5): 06020004-6. https://doi.org/10.1061/(ASCE)MT.1943-5533.0002995

[16] Simonov EE, Jezierski W, Małaszkiewicz D. Application of activated diatomite for dry lime mixes. Constr Build Mater. 2014; 65: 29-37. https://doi.org/10.1016/j.conbuildmat.2014.04.098

[17] Frías M, Cabrera J. Influence of MK on the reaction kinetics in MK/lime and MK-blended cement systems at 20°C. Cem Concr Res. 2001; 31(4): 519-27. https://doi.org/10.1016/S0008-8846(00)00465-8

[18] RD 52. 24. 433-2005. Mass concentration of silicon in surface waters of the land. (MVI photometric method in the form of a yellow form of molybdosilicic acid. - GU GUI. 2005) pp. 13.

[19] PND F 14. 1:2:4. 215-06. Method of measuring the mass concentration of silicic acid (in terms of silicon) in drinking, surface and waste water photometric method in the form of a yellow silicomolybdenum heteropolyacid. - SPb: Center for Water Research and Control (2006).

[20] Yu G, Frolova M. Obtaining and application of silica hydrosols. 1979 (Proceedings of the Moscow Chemical Technology Institute named after D. I. Mendeleev, v. 107); Ayler R. Silica Chemistry, ch. 1-2, trans. from English, MIR, Moscow, 1982.

[21] Kudryavtsev PG. Alkoxides of chemical elements - promising class of chemical compounds which are raw materials for Hi-Tech industries. J Sci Isr - Technol Adv. 2014; 16(2): 147-70.

[22] Lvovich FO, Alexandrovich BD. Nanostructured silicate polymer concrete. Vestnik MGSU 2014; 2014: 197-204. https://doi.org/10.22227/1997-0935.2014.3.197-204

[23] Loganina VI, Kislitsyna SN, Mazhitov YB. Structure and properties of the modified binding for silicate paints. Mater Sci Forum. 2018; 931: 469-74. https://doi.org/10.4028/www.scientific.net/MSF.931.469