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Mechanical properties of the Crimean limestone, treated with material based on silicic acids

E.A. Korneeva[a], N.I. Vatin[b], A.E. Dontsova[b]*

[a] St. Petersburg State University of Architecture and Civil Engineering, St. Petersburg, Russia
[b] Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia
** E-mail: anne.dontsoova@gmail.com*

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Abstract. The paper describes shell-limestone treatment with stone strengthener Oxal NK 100. Aging impairs the mechanical characteristics of the stone and reduces its bearing capacity. The purpose of the study was to investigate the efficiency of the stone-strengthening composition Oxal NK 100. The composition is supposed to reduce water absorption and strengthen the stone. Cube samples of the Crimean shell-limestone were used. Several testing operations were made to reveal such specifications as absorption of water, compression capacity, freeze-thaw resistance, and porosity of the material. Tests were done on two kinds of samples: treated and non-treated. The results of the study indicated an improvement of mechanical properties of treated stone, compared to non-treated rock samples. The study proved the efficiency of the use of stone-strengthening materials for construction and restoration with shell-limestone.

1. Introduction

Crimean limestone is a sedimentary rock of organic origin. Extensive range of varieties of Crimean limestone includes stones from yellow porous shells to pink-brown breccias. Generally, limestones are divided into several groups: shells, marble limestones, bryozoan, and nummulite limestones. Nummulite limestone consists of small nummulite shells cemented together, bryozoan is composed of quite long branches of bryozoan colonies. Pieces and whole shells of small marine animals are involved in the formation of shell limestone. Limestones are widely used as building and facing blocks in accordance with Russian State Standards. Crimean limestones are common building materials in the south-western areas of the Russian Federation because of their low cost, ease of processing and high thermal performance. Nevertheless, weakness in load and weather resistance remains to be a major issue, concerned with shell limestones.

The literature survey indicates the relevance of the subject. Research papers related to strength characteristics investigation and improvement are published. Thus, factors that influence limestone durability and quality are reviewed in scientific works [1–6]. To date, wide variety of methods to improve characteristics of the stone material exists. The most common algorithms include appliance of epoxy-silica compositions, calcium or barium hydroxide, ethyl silicates and silicic acids. The ability of these substances to consolidate stone and mortar is examined in papers [7–10]. The comprehensive assessment of effectiveness of epoxy silica and silicone-based treatments as well as acrylic polymers confirmed by laboratory tests results is given in researches [11, 12]. Phosphate-based treatments and bacterial protection are innovative techniques described in studies [13, 14]. Also, the properties of nanomaterials have been comprehensively studied in recent years. The major advantage of such treatments is that nanoparticles penetrate deeper into the material and allow us to achieve the better consolidation effect. For instance, the performance of nanolime that is just a dispersion of lime nanoparticles in a solvent is observed in papers [15–17]. The effectiveness of calcium and barium hydroxide nanoparticles and sulfur-based nanoscale coatings is analysed in studies [18–20].

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Comparative analysis of different treatments is given in article [21]. Consideration of aspects of the theory and practice of stone strengthening is given in the works [22, 23]. Despite the research is based on the investigation of concrete properties similar results can be found showing the efficiency of stone treatment methods in general. Therefore, application of a hydrophobic treatment on shell-limestone in the same way as on concrete to improve the mechanical properties is described in [24].

Need for restoration and conservation of cultural heritage objects is obvious and creates an area for research in the construction industry. Global warming and increase of exhaust gases concentration in the atmosphere accelerates the process of stone aging due to the leaching of mineral compounds from the stone. [2, 3]. The problem of new materials implementation for architectural heritage conservation remains.

In this paper the efficacy of the epoxy-silica consolidant on nummulite Crimean limestone is studied. This type of stone is historically widely used in low-rise construction, moreover, large number of Crimean historical buildings are made of limestone. Silicic acid-based treatment «Oxal NK 100» was used as stone strengthener.

The purpose of this research is to assess the mechanical properties of the limestone treated with Oxal NK 100. For a full and comprehensive assessment, the following tasks should be completed:

1. Literature analysis in the field of the research;
2. Performance characteristics measurement for treated and non-treated samples such as water drop absorption rate, compression capacity, freeze-thaw resistance and porosity;
3. Comparison of the test data and the overall conclusion about stone strengthener effectiveness.

2. Methods

Cubic samples of a nummulite Crimean limestone with dimensions $a = b = c = 50 \pm 2$ mm were used for the tests. Samples were labeled in accordance with the tests (Figure 1).

Stone strengthening material was silicic acid-based treatment «Oxal NK 100». It was applied on several rock samples in accordance with the instructions. Samples were abundantly sprayed with the composition and naturally dried before all the tests.The best operating temperature for the treatment is 10°C to 20°C and optimal relative humidity is ≥ 40 %. Composition is recommended to apply wet in wet until no more material is absorbed from the substrate. The consumption varies between 0.5 and 1.5 l/m^3 and depends on the absorbency of the substrate.

Series of tests was performed in accordance with Russian State Standard GOST 30629-2011 «Facing materials and products made of natural stone. Test methods». Particularly, samples were tested for water absorption, freeze-thaw resistance, compression strength and porosity. The tests were carried out on samples, typical for the rock.

2.1. Equipment

During the tests, the following instruments and equipment were used:

- Dial desktop scales ((Russian State Standard GOST 29329);
- A vessel to saturate samples with water;
- A hydraulic jack with a force 100 to 500 kN with an adjustable speed of load application and deviation ≤ 2 % (Russian State Standard GOST 28840 or GOST 9753);
- A reference square (Russian State Standard GOST 3749);
- A froster achieving and maintaining a temperature of (20 ± 2) °C above zero;
- A vessel maintaining a temperature of 20±2 °C for samples thawing;
- A weighing bottle (Russian State Standard GOST 25336) or a porcelain cup (Russian State Standard GOST 9147);
- Sizing screen (5 mm and 1.25 mm; Russian State Standard GOST 6613).

2.2. Water absorption tests

Water absorption is measured by comparison of dry and wet samples weight. First, samples were put in water for 48h, then they were weighed. After that, limestone cubes were dried in the desiccator until they reached their constant weight and after that they were weighed again.

2.3. Compression strength test

Compression strength tests included measuring of compression resistance and liquostriction. Half of the stone cubes were treated with stone strengthener beforehand. All the samples were weighed in dry and moisturized condition.

During the tests the cubes were put under pressure (Figure 2). The load was increasing uniformly until wrecking.

Figure 1. Limestone sample.

Figure 2. The sample in the compression apparatus.

2.4. Freeze-thaw resistance test

Firstly, the samples were kept in water for at least 48h, then the cubes were put into a froster in a container for 4 hours with temperature (20±2) °C, after that the samples were put in a bath until a complete defrosting. The freeze-thaw cycle was repeated steadily. The cubes passed compression tests after 15, 25, 35, and 50 freeze-thaw cycles. At least 5 samples were compressed in each test.

2.5. Porosity and voids content measurements

Rock density is characterized by average and true specific density.

The samples were dried until fixed-mass, weighed and measured to find the average specific density. The volume of the cubes is taken as product of their sizes, and the average density is the ratio of mass to volume.

The true specific density was measured with a fast-track methodology using the Chatelier apparatus. We used the samples on which the average density had been determined to have an opportunity to compare the results. Generally, the samples were milled until the coarseness was less than 1.25 mm, then dried and cooled to room temperature. Two weighed portions 50g each were used for the tests.

In the start of the test, the Chatelier apparatus was filled with water to the lowest zero mark (the water level was determined with the concave-convex lens). Milled sample was put into the apparatus till the water reached 20 mm mark. The part of the sample that wasn't put into the apparatus, was weighed.

On the basis of true and average density values the rock porosity is determined

3. Results and Discussion

In the description of the results, the term "limestone" refers to untreated stone samples, and the term "limestone NK 100" refers to samples treated with Oxal NK 100 stone strengthening material.

3.1. Water absorption test

Water absorption for each sample is calculated by the formula:

$$W_{ab} = \frac{m_1 - m}{m} \cdot 100\ \%, \qquad (1)$$

where m_1 is the mass of the sample in a water-saturated condition, g

m is the mass of the dry sample, g.

Calculation example for the untreated sample no. 1:

$$W_{ab} = \frac{253.88 - 227.97}{227.97} \cdot 100 = 11.37\ \%.$$

The average water absorption is calculated as the arithmetic average of the results for five rock samples:

$$W_{avg} = \frac{W_1 + W_2 + W_3 + W_4 + W_5}{5}. \quad (2)$$

Calculation example for untreated samples:

$$W_{avg} = \frac{11.37 + 12.23 + 11.59 + 10.67 + 11.61}{5} = 11.49\ \%.$$

The test results are shown in Table 1.

Table 1. The results of the water absorption test.

Sample number	Sample mass, g			Water absorption, %
	Before dehumidifying	After dehumidifying	After water saturation	
Limestone				
1	228.35	227.97	253.88	11.37
2	220.85	220.54	247.52	12.23
3	224.53	224.15	250.12	11.59
4	222.47	222.10	245.80	10.67
5	219.54	221.13	246.80	11.61
			$W_{ab\ avg}$	11.49±0.38
Limestone NK 100				
1	245.02	242.51	250.56	3.32
2	247.76	245.33	254.31	3.66
3	239.38	236.26	241.95	2.41
4	247.24	244.64	250.90	2.56
5	246.54	243.97	252.48	3.49
			$W_{ab\ avg}$	3.09±0.48

A comparative graph of water absorption for treated and untreated samples is shown in Figure 3.

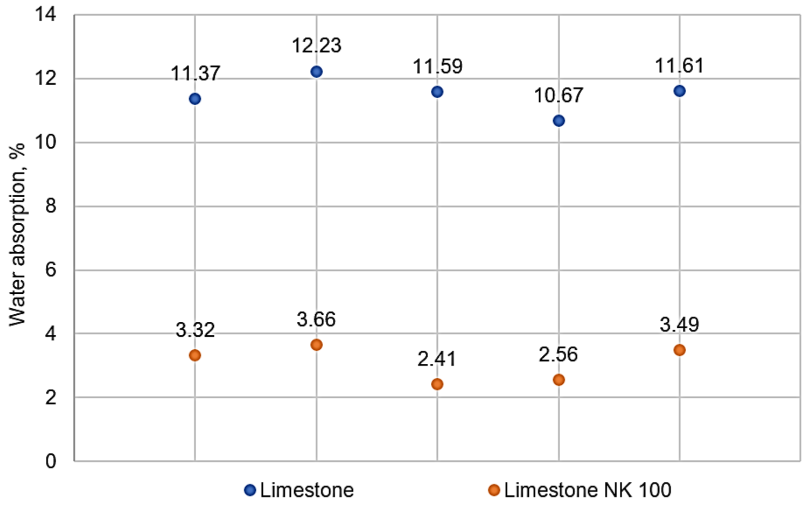

Figure 3. Water absorption of treated and untreated samples.

3.2. Compression strength test

The compressive strength in the dry condition R_{pr}, MPa, is calculated with an accuracy of 1 MPa by the formula:

$$R_{pr} = \frac{P}{F}, \quad (3)$$

where P is breaking strength, N;

F is cross-section area of sample, cm^2.

Average compressive strength is calculated as the arithmetic average of the test results of five samples:

$$R_{pr\ avg} = \frac{R_{pr_1} + R_{pr_2} + R_{pr_3} + R_{pr_4} + R_{pr_5}}{5}. \quad (4)$$

Calculation example for dry untreated samples:

$$R_{pr\ avg} = \frac{23.02+26.13+23.38+17.42+23.95}{5} = 22.78 \text{ MPa}.$$

Liquostriction of the rock ΔR, %, is calculated by the formula:

$$\Delta R = \frac{R_{pr\ avg} - R_{pr}}{R_{pr\ avg}} \cdot 100\ \%, \tag{5}$$

where $R_{pr\ avg}$ is average compressive strength of the samples, dried to fixed-mass, MPa;

R_{pr} is average compressive strength of wet samples, MPa.

Calculation example for untreated samples:

$$\Delta R = \frac{22.78-8.06}{22.78} \cdot 100 = 64.62\%.$$

Compression strength, R_{pr} had been determined automatically by compression apparatus. The test results are shown in Table 2.

Table 2. Compression strength test results.

Sample number	1	2	3	4	5	$R_{pr\ avg}$, MPa	ΔR
Dry samples							
Limestone	23.02	26.13	23.38	17.42	23.95	22.78±2.14	–
Limestone NK 100	21.07	34.93	32.81	26.58	31.82	29.44±4.49	–
Water saturated samples							
Limestone	7.3	8.5	6.9	7.7	9.9	8.06±0.91	64.62
Limestone NK 100	17.3	20.2	26.8	14.2	26.4	20.98±4.50	28.74

In graphical form, the results of compression strength test are shown in Figure 4.

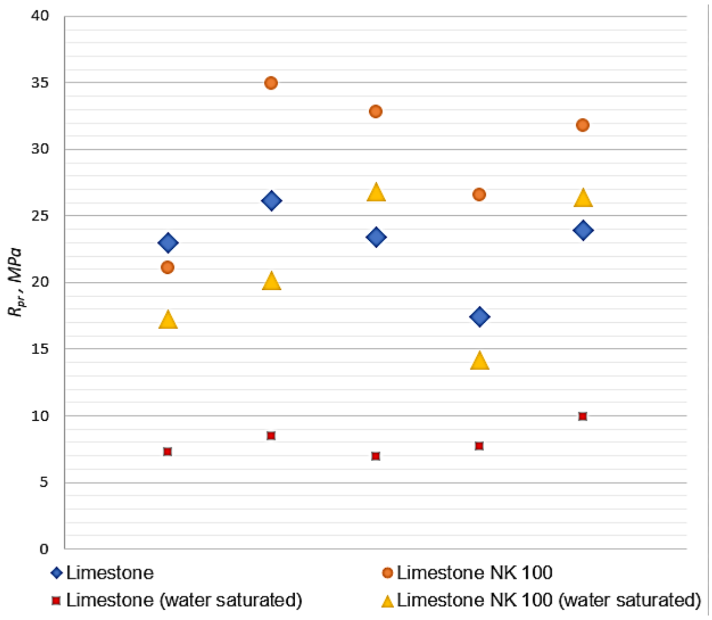

Figure 4. Compressive strength of dry and water-saturated, treated and untreated samples.

3.3. Freeze-thaw resistance test

Strength loss of samples ΔR, %, is determined by the formula:

$$\Delta R = \frac{R_{pr}^{w} - R_{pr}^{f}}{R_{pr}^{w}} \cdot 100\ \%, \tag{6}$$

where R_{pr}^{w} is the arithmetic average of the compressive strength of the samples in a water-saturated condition, MPa,

R_{pr}^{f} is the arithmetic average of the compressive strength of the samples after number of freeze-thaw cycles, MPa.

Average strength loss is calculated as the arithmetic average of the test results for five samples:

$$\Delta R_{avg} = \frac{\Delta R_1 + \Delta R_2 + \Delta R_3 + \Delta R_4 + \Delta R_5}{5}. \quad (7)$$

The freeze-thaw test results are shown in Table 3.

Table 3. Compression strength of the limestone after freeze-thaw cycles.

Sample number	1	2	3	4	5	$R_{pr\ avg}$, MPa	ΔR_{org}, %
15 cycles							
Limestone	8.5	9.7	9.8	11.3	10.1	9.88±0.66	-22.58
Limestone NK 100	19.2	16.5	21.9	18.3	22.5	19.68±2.02	6.20
25 cycles							
Limestone	9.3	7.7	10.2	10.8	11.7	9.94±1.15	-23.33
Limestone NK 100	15.5	18.7	19	17.8	15.8	17.36±1.37	17.25
35 cycles							
Limestone NK 100	6.3	15.3	25.4	19.3	14.5	16.16±4.95	22.97
50 cycles							
Limestone NK 100	10.1	7.2	12.2	13.4	12.8	11.14±1.99	46.90

The untreated samples had shown visible defects after 30 freeze-thaw cycles (Figures 5, 6). This samples were not tested anymore. The reason was their major damage after 30 cycles.

Figure 5. Cracks and delamination on the untreated sample.

Figure 6. Cracks on the untreated sample.

A comparative graph of the change in strength after each stage of freeze-thaw cycles is shown in Figure 7.

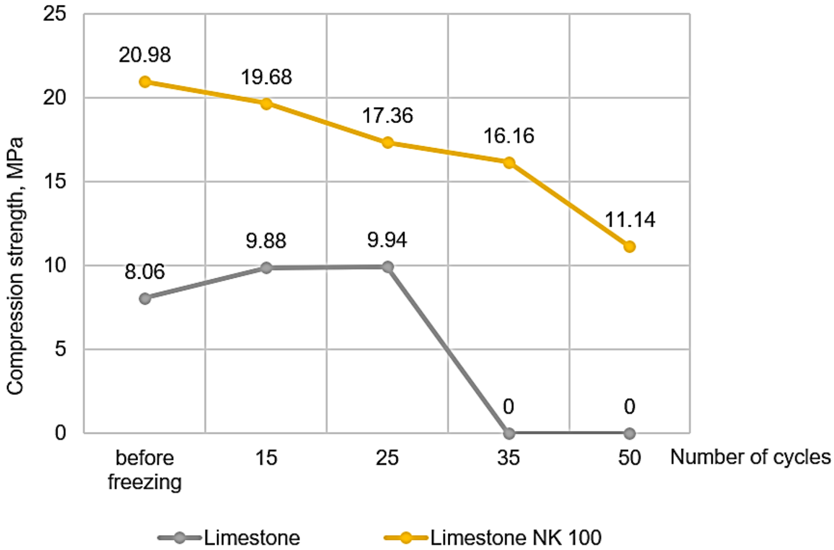

Figure 7. Changes of compression strength after freeze-thaw cycles.

3.4. Porosity and voids content measurements

Average density of the sample ρ_o, g/sm^3, is calculated by the formula:

$$\rho_0 = \frac{m}{V}. \quad (8)$$

Example calculation for the untreated limestone sample no. 1:

$$\rho_0 = \frac{262.077}{128.49} = 2.04 \text{ g/sm}^3.$$

Average density of the rock is calculated as the arithmetic average of the average density of all samples:

$$\rho_{0\,avg} = \frac{\rho_{01} + \rho_{02} + \rho_{03} + \rho_{04} + \rho_{05}}{5}. \quad (9)$$

Example calculation of average density for the untreated samples:

$$\rho_{0\,avg} = \frac{2.04 + 2.49 + 2.19 + 2.18 + 2.08}{5} = 2.20 \text{ g/sm}^3.$$

True special density ρ, g/sm^3, is calculated by the formula:

$$\rho = \frac{m - m_1}{V}, \quad (10)$$

where m is mass of the dried milled sample, 100 g;

m_1 is mass of the part of the sample that wasn't put into the apparatus, g;

V is volume of water displaced by milled sample, 20 sm^3.

Example calculation of true density for the untreated sample no. 1:

$$\rho = \frac{100 - 46.546}{20} = 2.673 \text{ g/sm}^3.$$

Average true density is calculated as the arithmetic average of the true density of all samples:

$$\rho_{avg} = \frac{\rho_1 + \rho_2 + \rho_3 + \rho_4 + \rho_5}{5}. \quad (11)$$

Example calculation of true density for untreated limestones:

$$\rho_{avg} = \frac{2.673 + 2.842 + 2.823 + 2.827 + 2.796}{5} = 2.79 \text{ g/sm}^3.$$

The results of determination of average and true specific density are shown in Table 4.

Table 4. Average and true specific density of the limestone.

Sample number	Fixed mass of a sample, g	A, cm	B, cm	C, cm	V, cm^3	ρ_0	$\rho_{0\,avg}$	m_1	ρ	ρ_{avg}
Limestone										
1	262.077	5.14	5.05	4.95	128.49	2.04	2.20±0.12	46.546	2.673	2.79±0.05
2	319.108	4.99	5.03	5.11	128.26	2.49		43.16	2.842	
3	293.598	5.16	5.06	5.13	133.94	2.19		43.532	2.823	
4	294.258	5.14	5.07	5.18	134.99	2.18		43.462	2.827	
5	270.981	5.01	5.18	5.02	130.28	2.08		44.079	2.796	
Limestone NK 100										
1	284.015	5.15	5.11	5.12	134.74	2.11	2.14±0.09	47.542	2.623	2.70±0.04
2	292.585	4.98	4.96	5.16	127.46	2.30		45.012	2.749	
3	277.966	5.11	5.2	5.14	136.58	2.04		46.034	2.698	
4	276.661	5.15	5.04	5.18	134.45	2.06		45.178	2.741	
5	296.43	5.15	5.19	4.99	133.38	2.22		46.177	2.691	

The values of the average and true density are graphically presented in Figure 8.

Porosity V_{por}, %, is calculated by the formula:

$$V_{por} = \left(1 - \frac{\rho_0}{\rho}\right) \cdot 100\ \%. \quad (12)$$

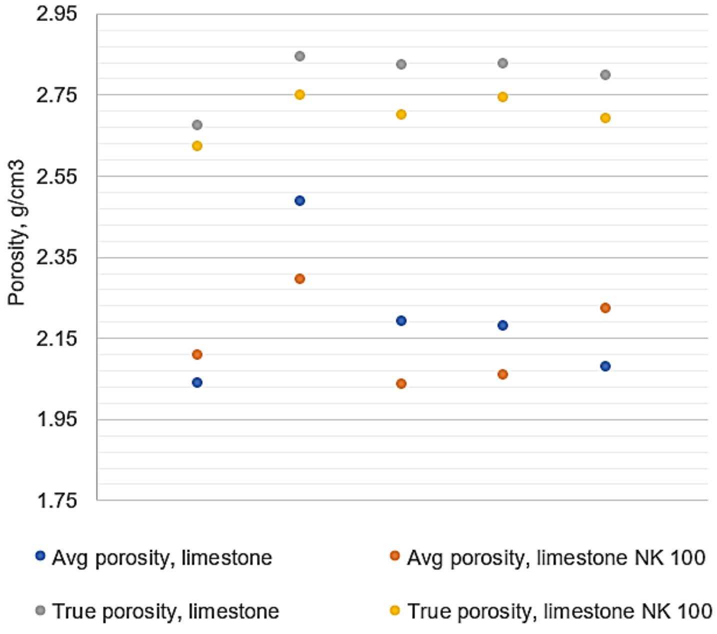

Figure 8. Average and true density of treated and untreated samples.

Porosity of the untreated limestone samples:

$$V_{por} = \left(1 - \frac{2.20}{2.79}\right) \cdot 100 = 21.36\ \%.$$

Porosity of the limestone NK 100 samples:

$$V_{por} = \left(1 - \frac{2.14}{2.70}\right) \cdot 100 = 20.62\ \%.$$

Limestone is a soft rock and is not immune to decay. There is a need for consolidation of limestone buildings and constructions. The works should be corroborated with theoretical studies. Modern methods used for restoration work are often non-effective.

The water absorption of the samples treated with Oxal NK 100 was 3.09 % while the water absorption of untreated stone was 11.49 %. Treatment with stone strengthening material reduced the water absorption of the samples by 4 times. The destruction of limestone because of weather conditions can be represented by the number of wetting and drying cycles, as described in [2]. Many cycles lead to salt weathering that can cause cracking and decay. To combat this phenomenon, swelling inhibitors, phosphate treatment and bacterial communities are used in civil engineering [2, 13, 14]. Reduce in the water absorption rate can slow down the salt weathering and can be an alternative to the described methods.

Dry samples of the limestone treated with Oxal NK 100 shown an increased compressive strength rate (23 % higher than dry untreated samples compressive strength). Liquostriction of treated samples turned out to be significantly (2.3 times) lower than liquostriction of untreated cubes. Generally, after the treatment of the stone, the compressive strength increased from 22.78 MPa to 29.44 MPa in the dry state and from 8.06 MPa to 20.98 MPa in water-saturated condition.

Most of the territory of the Russian Federation is in a subarctic climate area. The highest average January temperature is –5 °C. This means that in absolutely all regions the temperature falls below zero in winter [25]. Therefore, the freeze-thaw resistance of the material is always considered in the conditions of construction in Russia as well as the ways to improve it. The untreated stone had taken only 25 freeze-thaw cycles before cracking, while the treated samples withstood up to 50 cycles with a significant loss of compressive strength after 35 cycles. Limestone compressive strength decreased from 20.98 to 11.14 MPa. Samples treated with Oxal NK 100 stone strengthening material had handled twice as many freeze-thaw cycles as compared to untreated samples.

Porosity of the treated limestone reduced slightly comparing to untreated samples.

Increased compression strength, improved freeze-thaw cycle resistance and reduced water absorption have been noted by many authors in studies of the effectiveness of stone strengthening materials. Thus, the compressive strength of the samples changed from 20 MPa to 25.33 and 34.4 MPa after treatment of limestone with hydroxyapatite and strontium hydroxyapatite, respectively [26]. Based on these data, it is possible to consider silica-based stone consolidation more effective than compositions containing hydroxyapatites. At the same time, strontium stone processing showed a greater increase in the compressive strength of the samples.

The efficiency of treatment with silicic acids depends on the concentration in the solvent, which was studied using the ethyl silicate in [27]. During the study, it was found that the optimal concentration of ethyl silicate in the solvent is 25 %. It is possible that a change in the concentration of silicic acids in the Oxal NK 100 would increase the efficiency of the treatment.

It is also necessary to consider the effect of measurement error on the research results. Since the tests for each of the characteristics were carried out on only five samples, in some cases the relative error reached 30 % and taking the «worst» case into account significantly influenced the results.

Therefore, for the treated samples in the water absorption tests, the relative measurement error was 16 %, and for the untreated ones – 3 %. In the study of the "worst" outcome of events (minimum water absorption rate of untreated samples and maximum absorption rate of processed), the use of a stone-strengthening solution reduces the water absorption of the rock by 3.11 times.

During strength tests, a significant relative error (21 %) exists at the compressive strength of the water-saturated treated samples. The minimum value of the ultimate strength is 16.48 MPa, while the loss of strength ΔR would be 44 %.

The highest relative error in frost resistance tests is 31 % – for the compressive strength of the treated samples after 35 freeze-thaw cycles. The relative error after 50 cycles is 18 %. In the “worst” case, the compression strength of cubes after 35 freeze-thaw cycles would be 11.21 MPa, and after 50 cycles – 9.15 MPa. Loss of compression strength after 50 cycles in such case would be 56 %.

Finally, the errors in measuring the porosity of the material turned out to be small: from 1 % to 5 %.

An analysis of the literature on the chosen topic showed an increase in the number of publications in recent years, which can be explained by the growing interest of the scientific community in the use of stone strengthening materials for restoration and construction [28, 29]. The main methods of stone structures consolidation include treatment with epoxy-silica compositions and silicone-based materials. Stone strengthening material Oxal NK 100 is based on silicic acids and belongs to epoxy-silica compositions. Further research could be aimed to reveal the most effective material to strengthen the Crimean limestone. To reach this objective, it is necessary to compare the mechanical characteristics of the samples treated with different stone strengthening compositions, as was done, for instance, in papers [21, 27].

4. Conclusions

In the study, water absorption, compressive strength, freeze-thaw resistance, and porosity of the samples were tested. The untreated limestone cubes were examined as well as treated to get a comparative characteristic of the studied parameters. Limestone treated with the Oxal NK 100 showed higher strength parameters and freeze-thaw resistance and lower water absorption. The porosity of the treated and untreated samples varied slightly.

The water absorption of the samples treated with Oxal NK 100 was 3.09 % while the water absorption of untreated stone was 11.49 %. Dry samples of the limestone treated with Oxal NK 100 had shown a better result in compressive strength test (23 % stronger than dry untreated samples). Liquostriction of treated samples became 2.3 times lower than this characteristic of untreated cubes. The treated samples withstood up to 50 freeze-thaw cycles while the untreated stone had taken only 25 cycles. It is also possible that a change in the concentration of silicic acids in the Oxal NK 100 would increase the efficiency of the treatment.

During the study, the samples were sprayed with a stone-reinforcing composition, which ensured their uniform impregnation. This technology of application of the composition is recommended by the manufacturer. Changes in technology may lead to reduced improvements in mechanical performance. However, the use of injection treatment, by contrast, can improve test results. This is due to the mechanics of the action of silica-gel, which is a secondary porous material for limestone in this case of processing. Deeper penetration of silicic acid ester into the stone provides better protection, while at the same time it’s a more expensive solution. In any case, this application method must be tested experimentally.

This study is one of the first testing series with the use of stone-strengthening materials. Such solutions seem to become popular soon because of the need to increase reliability and durability of stone materials. The use of the stone-strengthening composition Oxal NK 100 has proven to be an effective method for improving the mechanical characteristics of limestone.

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Contacts:

Elena Korneeva, +79633193218; linka360639020@yandex.ru
Nikolai Vatin, +79219643762; vatin@mail.ru
Anna Dontsova, +79811889300; anne.dontsoova@gmail.com

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Механические характеристики крымского известняка, обработанного камнеукрепителем на основе кремниевых кислот

Е.А. Корнеева[a], Н.И. Ватин[b], А.Е. Донцова[b*]
[a] Санкт-Петербургский государственный архитектурно-строительный университет, Санкт-Петербург, Россия
[b] Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия
** E-mail: anne.dontsoova@gmail.com*

Ключевые слова: известняк; известняк-ракушечник; пропитка; реставрация; долговечность; укрепление.

Аннотация. В настоящее время ведется поиск новых решений для улучшения эксплуатационных характеристик каменного материала. Обработка фасадов и отдельных образцов различными пропитками показала себя эффективной. В статье описаны основные составляющие подобных растворов и исследованы механические характеристики обработанного камня. С камнями крымского известняка-ракушечника был проведен ряд испытаний: на водопоглощение, прочность на сжатие, морозостойкость. Была дана оценка пористости материала после обработки пропиткой. Сравнением характеристик обработанных и необработанных камней была проанализирована эффективность камнеукрепляющего материала Oxal NK 100. В результате было выявлено значительное улучшение параметров обработанных известняков. Водопоглощение обработанных известняков снизилось в 4 раза, предел прочности на сжатие в сухом состоянии увеличился на 23 %, а снижение прочности в водонасыщенном состоянии снизилось в 2,3 раза. Морозостойкость обработанных образцов увеличилась вдвое, а пористость изменилась незначительно (менее, чем на 2 %).

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Контактные данные:

Елена Александровна Корнеева, +79633193218; эл. почта: linka360639020@yandex.ru
Николай Иванович Ватин, +79219643762; эл. почта: vatin@mail.ru
Анна Евгеньевна Донцова, +79811889300; эл. почта: anne.dontsoova@gmail.com