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EVALUATION OF LIMESTONE STRENGTH AFTER LONG-TERM WEATHERING IN NATURAL CONDITIONS

J. A. GONZÁLEZ SÁNCHEZ [1], *O. L. BILYY* [1], *R. Ya. YUKHYM* [2]

[1] *Centre for Corrosion Research, Autonomous University of Campeche, Mexico;*

[2] *Karpenko Physico-Mechanical Institute of the National Academy of Science in Ukraine, Lviv*

The sorption properties, porosity and density of the limestone rocks of the state of Yucatan in Mexico (Campeche) are studied. Studies are needed for saving historical heritage, namely the optimization technology of polymer materials injection in order to restore strength and integrity of the colonial and pre-Spanish buildings made from limestone.

Keywords: *porosity, density, sorption properties, calcareous stone.*

In previous publications positive conclusions of the use of mortars based on epoxy and polyester resins as injecting materials to restore the strength of damaged building structures from limestone under long-term operation were obtained. This is a widespread practice and not only the continuity of building elements can be restored, but their workability on a level no lower with the starting one. During investigations of limestone from Yucatan region it was established that the adhesive properties of epoxy and polyester resins caused cracks formed outside the lines of pasting materials during repeated application of destructive stress. This means that the use of such injection materials is a fast and effective method of recovery of bearing strength and integrity of the structures. In Yucatan a great heritage of historical buildings belonging to the culture of the Maya, Inca, Aztec (many churches and defensive walls of pre-Spanish period) is saved. They are built of limestone – material that is most common in the region. Under the influence of high humidity, sea air, biological activity and hot tropical climate, superficial elements of historical buildings degraded, changed their mechanical properties, porosity. At the same time frequent precipitation, as rain, washes away the joints between limestone from which all, with no exception, cultural monuments (the Maya pyramids, citadels, walls, forts, buildings) are composed.

To evaluate the strength characteristics of limestone the models, that take into account the porous material and directly connect it with compressive strength of porous material, are used. Therefore the reported research, apart from specifying density and porosity of local species, allows us to determine how to relate the strength of limestone and its porosity.

Mathematical model of a solid body with a porous structure. Consider the deformation of a rock subjected to a uniaxial stress. The simulation can be carried out with a two-dimensional model of a body. Cracks and pores with a crack are randomly oriented in the material with respect to the direction of the applied stress. Since the crack propagation occurs along trajectories where the resistance to fracture (energy) takes a minimum value, the series of the collinear cracks only is considered. In that way the lower level of the material strength is attained due to collinear crack orientation which is more dangerous in terms of strength diminution. Defects available in parallel planes will have a negative effect on the estimated strength. Thus, consider the location of defects and uniaxial stress action in a body of infinite width, as shown in Fig. 1.

Corresponding author: O. L. BILYY, e-mail: bilorestl@gmail.com

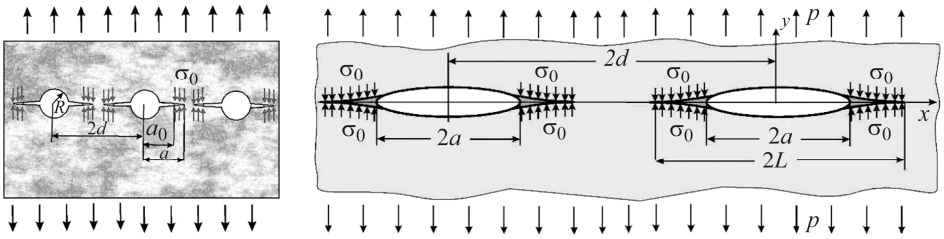

Fig. 1. Scheme of fracture of a body with cracks under tension.

Assuming a small size of cracks [1, 2] and applying the concept of stress intensity factors, it is possible to use the known problem solution for the system of collinear cracks as shown in Fig. 1 according to the Dugdale–Leonov–Panasyuk model. These authors obtained the correlation between the intensity of the external load with the size of the pre-fracture zone:

$$p = \frac{2}{\pi}\sigma_0 \cdot \arccos\left(\frac{\sin\left(\frac{\pi}{2}\frac{a}{d}\right)}{\sin\left(\frac{\pi}{2}\frac{L}{d}\right)}\right). \quad (1)$$

Here σ_0 is the ultimate strength of the defect-free stone between pores and cracks. Taking the condition of merging the pre-fracture zones with the neighboring cracks as a criterion for the material destruction, a formula for estimating the ultimate tensile strength of porous material under tension is obtained as [3, 4]:

$$\sigma_b = \sigma_0\left(1 - a/d\right). \quad (2)$$

Note that this equation presents the relation between the crack size and the distance between the cracks (a/d), and displays the content of defects in the material and its damage. A lot of works for stochastically distributed pores in the material gives the following relationship, which allows us to find the distance between the pores by their size and porosity:

$$d = a(2 + V_p)/3V_p. \quad (3)$$

It should be noted that the dominant effect on fracture has the open porosity, or to be more precise, the accumulation of larger pores in homogeneous structures is dangerous. In view of the previous equation, the strength of the material under tension can be determined by using the matrix strength as follows [3]:

$$\sigma_b = \sigma_0\left(1 - \frac{3V_p}{2 + V_p}\right). \quad (4)$$

From the last equation it is possible to note the critical influence of pores on the material strength. Matrix material (limestone) depends on its mineralogical composition and nature in terms of the phase stratification and mixture. More precise models that better simulate the absorption properties of limestone are described in [5, 6].

Thus, to evaluate the effectiveness of strength recovery of the cracked stones by application of polymer injection it is necessary to carry out researches on the adhesion characteristics of injection materials. Determination of porosity allows characterizing the nature of the stone and its strength properties.

Experimental methodology. ***Determination of real density and apparent density, total and open porosity.*** The density and porosity of rocks can be determined in several ways, including the guidelines of British Standard EN 1936:1999, European Standard EN 14617-1:2005 or Ukrainian Standard GOST 26450.1-85. In general, the final formula does not differ, with the exception of tolerance for the size of samples.

Open porosity and apparent density. The specimens should be dried in a stove at (70±5)°C until the difference between 2 successive weightings at intervals of 24±2 h is less than 0.1% of the sample mass. The specimens shall be kept in a desiccators until room temperature (20±5)°C is attained. After that determine the sample mass M_0 (kg) weighed in air after drying. The next step involves the slow pouring of deionized water into a container until the specimens are completely immersed and covered by 2 cm. After about 1; 8 and 24 h from the beginning of the tests, and later at regular 24 h intervals, take the specimens out of water, wipe with a damp cloth and weigh them. Continue to immerse the specimens in water and repeat the tests until the weight variation of water saturated specimens (M_2) differs by less than 0.01%. Immediately after the final weighing of each sample, determine the apparent mass (M_1) by weighing the sample in water using a hydrostatic balance. The apparent density ρ_V is calculated by:

$$\rho_V = \frac{M_0 \cdot \rho_{H_2O}}{M_2 - M_1}, \tag{5}$$

where ρ_{H_2O} is the true density of water at the measuring temperature, kg/m^3.

Water absorption (%) can be determined as:

$$C = \frac{M_0}{M_2 - M_0} \cdot 100\%. \tag{6}$$

The open porosity describes the volume of open capillaries which can be interconnected. This characteristic is evaluated also (%) by:

$$K_p = \frac{M_2 - M_0}{M_2 - M_1} \cdot 100\%. \tag{7}$$

During determination of the open porosity the intensity of water absorption can be found simultaneously. This parameter is determined by the amount of water absorbed for time *t*, area of 1.0 dm^2 of the sample partially immersed in 0.5 cm thick layer of water.

To do this, dip the sample in water to a depth of 0.5 cm at t = 1; 5; 15; 60 min to determine the weight of the sample. Before weighing wipe with a damp cloth the surface of the sample in contact with water. Then determine the difference between the current weight and the weight in the initial time and build a graph of g/dm vs. time (min) axes.

The relationship between the intensity of water absorption W_A of stone vs. time can be expressed by the following formula:

$$W_A = W_1 + A(t-1)^B, \tag{8}$$

where A, B are parameters determined approximately from the diagram, using analytical methods, for example measuring at two points (15; 60 min). The intensity of water absorption varies depending on the direction of layers and is always greater in the case of perpendicular placing of the stone layers to the water surface.

Real density and porosity (British Standard EN 1936:1999) [7]. In case of working with dense, low-porosity stones, the differences between real and apparent density, as well as between open porosity and total porosity, is very small. For these stones it is sufficient to determine the apparent density and the open porosity. In case of calcareous stone the open porosity can be 20% or greater, thus it is necessary to determinate the full porosity, which can be even twice the value of the open porosity. Two methods for the determination of the real density can be applied, using the pycnometer (Method 1) and Le Chatelier volumenometer (Method 2).

The first method involves the grinding of each specimen separately until the particles pass through a sieve with 0.063 mm mesh. After that dry the ground specimen to a constant mass and set a mass m_e of approximately 25 g weighed with an accuracy of

±0.01 g. Then fill the deionized water about half full of the pycnometer, add the weighed mass m_e of the ground specimen into the pycnometer and agitate the liquid to disperse the solid matter. Expose the pycnometer to a vacuum of (2±0.7) kPa until no further air bubbles rise, then fill it with deionized water almost to the top and leave the solid matter to settle down until the water above the residue is clear.

Next, carefully top up the pycnometer with deionized water, fit the ground stopper and gently wipe off any overflow. Finally weigh the pycnometer to an accuracy of ±0.01 g (m_1). Empty and wash the pycnometer, fill it with deionized water only and weigh to an accuracy of ±0.01 g (m_2).

The real density (kg/m^3) after test can be calculated by applying formula:

$$\rho_r = \frac{m_e}{m_2 + m_e - m_1}\rho_{H_2O}. \quad (9)$$

Results and discussion. ***Determination of porosity and absorption properties.*** To determine intensity of water absorption the samples were placed in a container with water 0.5 cm height. After 1; 5; 15; 30 and 60 min samples were wiped with a damp cloth and their weight was determined. Then samples were covered with water 2 cm above the height. Several times a day they were returned to another facet and the bubbles from grain were removed until fully saturation with water. When the weight between the two neighboring inspections stabilized, the hydrostatic weight and weight in air were determined. To determine the intensity of water absorption, Eq. (8) was applied to obtain results (Table 1). Parameters *A*, *B* can be determined using different approximation methods, for example a simple way by two points – as a rule, the volume of adsorbed water for time 15 and 60 min.

Table 1. Adsorption properties of stones, depending on their porosity (K_p)

№	K_p, %	W_1, g	*A*	*B*
1	14.41	21.56	8.42	0.33
2	21.04	8.42	1.95	0.91
3	24.34	15.27	15.51	0.44
4	3.89	1.04	0.27	0.5
5	4.44	8.97	0.29	0.5
6	18.28	38.31	8.14	0.66
7	9.73	7.02	2.28	0.57
9	4.37	2.56	0.67	0.54
10	7.51	–	–	–
11	9.56	8.78	2.38	0.55
12	31.8	39.07	10.8	0.56
13	19.65	12.27	2.57	0.57
14	20.63	11.38	1.33	0.56
15	30.25	19.0	4.28	0.58
17	15.91	17.89	7.8	0.48

As a result we received a plot with experimental points and the simulation (solid line) (Fig. 2). The analysis of all these experimental data is presented in Table 1. It should be noted that for most materials water penetration law is similar to the root law depending on whether parameter *B* is in the range from 0.5 to 0.55.

According to Table 1 the results of approximation of the intensity of water absorption are illustrated graphically in Fig. 3. All lines are noted in accordance to the porosity.

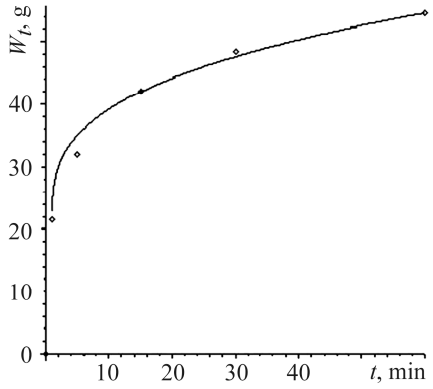

Fig. 2.

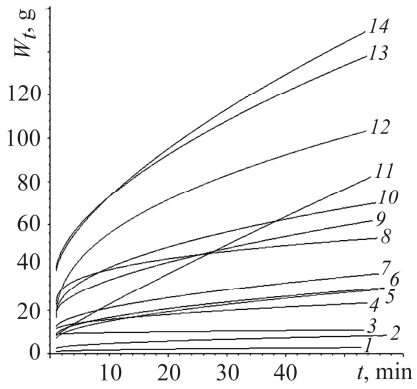

Fig. 3.

Fig. 2. Water penetration curve.

Fig. 3. Dynamics of water penetration for 1 h: *1* – 3.89; *2* – 4.37; *3* – 4.44; *4* – 20.63; *5* – 9.73; *6* – 9.56; *7* – 19.65; *8* – 14.41; *9* – 30.25; *10* – 15.91; *11* – 21.04; *12* – 24.34; *13* – 31.8; *14* – 18.28.

Cubic specimens of calcareous stone were cut out for studies of the open porosity and the apparent density. It was found that mineralogical density of the investigated limestone lies within 2.66 and 2.7 g/cm^3. This in turn helped to determine the closed porosity of the material. The results of these studies gave the values of these parameters which we-re obtained by following the methodology of EN 1936-1999 and are presented in Table 2.

Table 2. Test result

Number of sample	Open porosity	Closed porosity	Apparent density, g/cm^3
	%		
1.2	19.1	7.9	1.94
1.3	17.6	8.9	1.95
1.4	17.6	8.5	1.97
1.5	16.6	8.0	2.00
2.2	8.9	5.3	2.28
2.3	9.7	5.6	2.25
2.4	9.9	5.7	2.25
2.6	8.6	4.3	2.31
3.1	7.4	3.1	2.38
3.2	24.8	1	1.97
5.1	4.7	2.2	2.48
5.2	4.9	1	2.5
5.3	6.1	2.3	2.43
6.1	9.5	5.7	2.26
6.2	5.7	1.6	2.46
6.3	17	8	2.0
6.4	16.2	7	2.03
7.1	20.7	1.5	2.07
7.3	19.3	1.7	2.1
7.4	25.3	1.9	1.93

Continuation of Table 2

8.1	4.2	0.7	2.53
8.2	7	6.1	2.31
8.3	6.5	7.1	2.3
8.5	5.2	1	2.49
12.1	31	0.7	1.8
12.2	25.9	8	1.76
12.3	33.7	1.8	1.72
12.4	33.3	0.2	1.77
13.2	22.1	4	1.97
13.5	23.5	2.9	1.95
14.1	14	5.1	2.15
15.1	29.8	4.2	1.75
15.2	33.7	2.2	1.7
16.1	15.2	4.4	2.14
16.3	17.1	4.4	2.14
17.1	8	4.3	2.33
17.2	14.6	5.9	2.1
17.3	12.1	5.9	2.1
17.4	21.2	6.1	1.93
18.1	23.6	3.6	1.93
18.2	26	4.7	1.84
21.1	5.4	2.8	2.44
21.2	6.5	3.9	2.38
21.3	5.3	3.5	2.43
22.1	6.7	1.3	2.44
22.2	3.7	1	2.53
22.3	3.4	0.8	2.55
22.4	8.6	5.6	2.28
23.1	21.7	2.5	2.02
23.2	19.6	2.7	2.07
23.3	20.7	2.8	2.03
1	19.7	2.9	2.05

Results indicate that the samples with high mechanical characteristics have higher density 2.3…2.6 g/cm^3 and low open porosity (3…10%). Closed porosity changes in the range 1…9% and does not indicate a good correlation with apparent density and open porosity. For example stone samples of series 1; 7 and 23 have similar open porosity and apparent density, but closed porosity is equal to 8.3; 1.7 and 2.7%, respectively. This scatter of experimentally obtained parameters could be due to the different crystal structure, strength and deformation properties.

Porosity varies within a very wide range and for samples of series 7; 12; 13; 15; 18; 23 this property reaches values of 20…33%. Unexpected results were those for calcareous stone samples of series 7 and 23 which showed the porosity of about 20% and high mechanical strength and fracture toughness. Investigation of mineralogical composition and crystalline structure is needed in order to explain this behaviour. At the end of the present research work it is only possible to establish that the studied calcareous stone material has a very low level of closed porosity. To establish a correla-

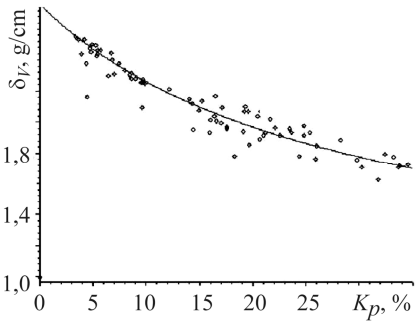

Fig. 4. Relationship between the open porosity and the apparent density.

tion between the open porosity and the apparent density the values listed in Table 2 were plotted as shown in Fig. 4. From data in Fig. 4 it can be suggested that the experimental points have a good convergence with the open porosity in the range from 4 to 10%. The second group of materials with porosity values from 15 to 35% present more variation in density. The relationship between the density and the porosity is not linear and can be described by:

$$\delta_V = \frac{2,75}{\ln(e + 0.063K_p)}. \qquad (10)$$

This formula is correct only when the open porosity of calcareous stone is less than 35%. This ratio may be suitable for the tasks solved.

CONCLUSIONS

Studied calcareous stones have heterogeneous mineralogical origin and nonuniorm structure. The performed analysis only superficially describes the characterristics of calcareous stones that are deposited on the territory of Campeche. During experiments the strength and deformation characteristics, the open porosity and the apparent density of natural stones were established. Based on experimental data the analytical pendence for predicting the limestone density, in dependence of its porosity, was built.

РЕЗЮМЕ. Вивчено сорбційні властивості пористості та густини вапнякових каменів із штату Юкатан в Мексиці. Дослідження необхідні для збереження історичної спадщини, а саме оптимізації технології ін'єктування полімерних матеріалів з метою відновлення міцності та цілісності колоніальних та доіспанських будівель з вапняку.

РЕЗЮМЕ. Изучены сорбционные свойства пористости и плотности известняковых камней из штата Юкатан в Мексике. Исследования необходимы для сохранения исторического наследия, а именно оптимизации технологии инъектирования полимерных материалов с целью восстановления прочности и целостности колониальных и доиспанских зданий из известняка.

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