Results and Conclusions of Laboratory Characteristics of Soft Limestone from Central Poland as a Construction Material

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Abstract. The paper presents the physical and mechanical characteristics of a Cretaceous soft limestone from Poland. For several decades, since the end of the 19th century, this stone had been widespread as a common building material in Koło Basin (Kotlina Kolska) - a lowland region in the central part of the country. The popularity of this material in the mentioned period resulted in the emergence of a unique architecture in the region’s landscape. Despite the decline of its use, as it was replaced by more modern construction materials, over 2000 of these traditional structures exist to this day. The recent years have seen the rising of a vivid discussion over the cultural value they might represent. Likewise debated have been the efforts aimed at the protection and restoration of these structures, as they can be seen as an important element of the region’s cultural heritage. Particularly, it is put under consideration to bring the local limestone once again into popular use, as a trend to return to the use of traditional, natural construction materials develops. In the present situation, the including the soft limestone into the mentioned trend as a raw material or a product would require taking certain steps in its marketing as a viable option for modern use. For this reason, an analysis of its functional characteristics in relation to the modern technical standards would serve as a solid support to the already proven durability of the structures erected decades ago, during the high period of its popularity. A series of tests was conducted, obtaining a petrographic description and determining its mineralogical composition. Furthermore, measures were made of its physical and mechanical properties i.e. bulk density, open porosity, water absorption at atmospheric pressure, frost resistance and compression strength. These tests were based primarily on the methodology recommended by the harmonized EU standards and exceptionally some of the older national standards. The parameters obtained during the laboratory, with the frost resistance in particular, appear not entirely satisfactory. However, the good condition of numerous structures erected using the examined material decades ago indicate that, amongst other conclusions, choosing a proper construction technique, one mastered by practical experience, results in providing these traditional construction materials durability superior to the one determined by laboratory examination.

1. Introduction
Soft limestone is a carbonate and silica rock favoured locally as building material and used for construction purposes in the past centuries. Inter alia, since the end of the 19th century, this stone had been widespread as a common building material, in Koło Basin (Kotlina Kolska) - a lowland region in the central part of Poland. Deposits of Cretaceous limestone in this region is can be found on shallow...
depths, right under the surface soil. This favourable geological condition made the exploitation of that raw material feasible, through the use of outcropping. A number of advantageous properties, including the easy processing, the sufficient insulation and durability, resulted in its use in local construction, especially in the rural areas. In the consequence of the popularity of this material, a unique architecture in the region’s landscape had emerged. Today, more than 2,000 buildings is still being used for residential purposes and as farmhouses [1].

Considering the numerous preserved structures, some of a historical value, the testing and evaluation of durability of soft limestones as a construction material, is still ongoing. Furthermore, there can be observed a developing trend to return to the use of traditional, natural construction materials.

For porous carbonate stone the pore structure plays a critical role in controlling the physical properties and performance of this material [2], [3]. It determines for example the frost resistance and durability of the rocks [4], [5].

The main aim of this paper is to analyse the results of experimental tests conducted on limestone from Central Poland (Koło Basin). The testing involved primarily the use of EN-standardized tests for determining its density and porosity, as well as the examination of pore characteristics from mercury intrusion porosimetry data in combination with frost resistance and compressive strength. The obtained observations were compared in relation to the durability of limestone as a construction material proven already by the good condition of the structures erected decades ago.

2. Material and experimental procedure
Investigated rocks are a sedimentary formation of marine origin, consisting mainly of organogenic silica and calcium carbonate [6], [7]. In the described region (Koło Basin) its deposits reach near the surface as a consequence of tectonic movements, which resulted in an uplift of the Mesozoic substratum and denudation and eroding of younger formations.

2.1. Petrographic and mineralogical evaluation
Electron and optical microscope were used in order to study the petrographic features of the limestone. Observation were made on polished surfaces of a pair of samples.

Mineralogical composition tests were carried out with the use of a thermogravimetric analysis on the Paulik & Paulik Q-1500D apparatus, with a computer-based result acquisition system. The heating time was 100 minutes at a heating temperature ranging from 20 °C to 1000 °C at a heating rate of 10 °C / min.

2.2. Apparent and real density. Open and total porosity.
Tests were set up in accordance with EN 1936:2006 [8]. For determining the apparent density and open porosity twelve prism samples of (30x40x50±5) mm edges were examined using the vacuum water saturation test. Samples were dried to a constant mass at (70±5) °C. After that they were put into the vessel and the pressure was lowered to (2,0±0,7) kPa for two hours in order to eliminate the air contained in the open pores. Demineralized water was introduced into the vessel and samples were completely immersed. After returning to atmospheric pressure samples were left for 24 hours under water. The apparent density and open porosity could be calculated on the basis of the weight, measured under water and the weight of saturated samples. Total porosity was calculated through the relationship between apparent and real densities.

Real density was determined using Le Chatelier volumenometer for the two powdered samples about 50g weighted with accuracy ±0,1 g.

2.3. Porous system characterization
Open porosity was also tested by mercury intrusion porosimetry using Micromeritics AutoPore IV 9500. As the porosimeter pressure ranges are 0,003–200 MPa, porosimetric data for pore sizes between 200µm and 0.005 µm could be obtained under both intrusive and extrusive conditions. The volume of intruded
mercury for each pressure step allows the determination of the connected pore volume, pore size and pore volume distribution [9].

2.4. Water absorption at atmospheric pressure
Tests were performed in accordance with EN 13755:2008 [10]. Twelve cube samples with (50±5) mm edges were dried to a constant mass at (70±5) °C and immersed in stages in tap water. After the constant mass of cubes reached the value of water, absorption was calculated using the mass of water in fully saturated samples.

2.5. Frost resistance
The frost resistance test was set up in accordance with PN-B-04 102:1985 [11]. Twelve cubes with (50±5) mm were subjected to repeated freezing and thawing cycles in a freezer with the temperature recording system capable of measuring temperature with (±0,5) °C margin. Samples were saturated to a constant mass at the start of the experiment and were set in the freezer cooled to -20 °C for 4 hours. After that samples were placed in a bath of water at a room conditions until constant temperature 20 °C were established (min. 4 hours). A minimum of twenty-five cycles was realized for each sample.

After each cycle a visual inspection was performed. Every damages, cracks, holes or detachment of fragments were noted. Mass of samples at the end of cycles was recorded.

2.6. Compressive strength
The uniaxial compressive strength test was set up in accordance with EN 1926:2006 [12]. Nine cube samples with (50±5) mm edges were dried to a constant mass at (70±5) °C and tested on a hydraulic press. Load on samples was applied continuously at a constant stress rate of (1±0,5) MPa/s.

3. Results and discussions
The main component of samples were the silica sponge spicules, which are accompanied by detrital quartz, glauconite, clayey substances and heavy minerals. In the microscopic image, differences could be noticed, depending on the porosity and volume weight of the examined rock. In the more massive sample (A), sponge spicules, primarily silica, were calcite. Calcite was also visible in the pore space. In the more porous one (sample B), silica (chalcedony) and silicified foraminifera were found, with a generally significant proportion of free pore space. There are numerous fossils and imprints of marine fauna: ammonites, including baculites and belemnites, snails and clams, brachiopods, sea urchins, as well as corals, bryozoans and fish.

Petrographic differences of samples A and B see Figure 1 are also visible in the thermogravimetric study. The composition is predominantly calcite representing approximately 70% (sample A) and 60% in the sample with a higher porosity (sample B). Values have been calculated based on the endothermic decomposition of calcite (stoichiometric factor 2,27) in the temperature range 600-900 °C [13]. The characteristic effects for clay minerals as dehydration (at about 180°C) occurring together dehydroxylation (starting depending on mineral at about 500°C-600°C) have not been registered. Only the exothermic effect between 900–1000 °C indicates a transformation into crystalline phases of kaolinite. A few percent weight loss has been presumably caused by a dehydration during structural modification of the aragonite (aragonite changes into calcite at about 455 °C) and dehydration of opal. The effect of the endothermic transformation of quartz (in 575 °C), a mineral component of the samples visible in petrographic studies, has not been registered.
Figure 1. Thermogravimetric (TG), Differential Thermogravimetric (DTG), and Differential Thermal Analysis (DTA) plots for the two samples (A, B)

The results of the physical and mechanical tests, performed in accordance to European harmonized standards [8], [10], [12] collected for all samples are summarized in table 1.

Table 1. Physical and mechanical characteristics of tested soft limestone

| Parameter                                      | Mean value | Min-Max value |
|------------------------------------------------|------------|---------------|
| Apparent density (ρ)                          | 1.42       | 1.28 - 1.55   |
| Real density (ρ_s)                            | 2.57       | 2.52 - 2.62   |
| Open porosity (n_e)                           | 43.9       | 41.4 - 47.3   |
| Total porosity (n_t)                          | 45.3       | -             |
| Water absorption at atmospheric pressure (A_b)| 27.6       | 21.5-30.7     |
| Uniaxial compressive strength (σ_c)           | 16.3       | 13.1-16.9     |

Low values of apparent density and very high average porosity of tested rock have been obtained. Total porosity (n_t) was proximate to the open porosity (n_e). Differences between the open and total porosity (n_e and n_t respectively) indicate a degree of connectivity between pores. It is possible to observe that the tested stone types have a very good connection between the pores, making the whole porous system of the rocks accessible. This characteristic may be also related to the value of connected porosity (n_c), which was determined using mercury intrusion porosity.
Detailed volume of pore distribution, using mercury intrusion method, is presented at the diagram (figure 2).

![Figure 2. Pore size distribution from mercury intrusion porosimetry](image)

**Table 2. Pore properties according to mercury intrusion porosimetry**

| Pore parameters          | Value  |
|--------------------------|--------|
| Porosity \( n_c \)       | %      | 34,23  |
| Median pore diameter \( \phi_M \) | nm     | 1,58   |
| Average pore diameter \( \phi_a \) | nm     | 44,1   |
| Critical radius \( r(V_{10}) \) | \( \mu m \) | 0,013  |
| Microporosity             |        |
| based on % pores <0,1 \( \mu m \), \( V(0.1) \) | %      | 44,92  |

Connected porosity, measured using mercury intrusion, gave a value (\( n_c = 34,23\% \)) which is less than the total porosity (\( n_t \)) and even less than the open porosity \( n_e \) (table 2), set up according to [8]. The most probable cause is the impenetrability of the finest pores to the mercury intrusion (\( \phi < 5 \text{ nm} \)). Large pores could not be measured (\( \phi > 200 \mu m \)).

According to Ordóñez et al. [4] a critical radius, \( r(V_{10}) \), distinguishes materials that are sensitive to freezing/thawing action. The \( r(V_{10}) \) values is obtained from the \( V(r) \) pore size distribution. It is defined as the size of pore for which the pore size distribution curve takes the value of 10% (starting from the smallest values). Samples with \( r(V_{10}) \) less than 2 \( \mu m \) may be considered to be resistant to freezing. The value obtained for the tested soft limestone is 0,013 \( \mu m \). A high proportion of microporosity (\( V(0.1) = 44,92\% \)) was obtained for the tested limestone. Microporosity or hygroscopic porosity \( V(0.1) \) is the porosity mainly responsible for the atmospheric moisture condensation in the rocks. On the other side an ice crystal requires a considerable degree of saturation in order to penetrate into the pore fraction below 0.1 \( \mu m \).

A minimum 25 of freezing-thawing cycles for all samples were made. The freeze–thaw alteration of stones resulted in visually observable deterioration (figure 3) and weight loss in samples (figure 4a). Five samples that showed a weight loss of less than 10% were subjected to an additional 10 cycles.
Figure 3. Weathered samples after 25 freeze-thaw cycles - examples of deterioration.

Figure 4. Weight loss of tested samples in relation to: a) number of freeze-thaw cycles b) apparent density of samples

The weight loss results show no correlation with the apparent density, but for the samples with the lowest density ($\rho < 1.4$ MN/m$^3$) the weight losses are noticeably higher see figure 4b.

Compressive strength values, obtained from the tests, are present in table 1 see figure 5. The average value, although it classifies these rocks into low strength group, is considerably high [2], [14] when taking into account the conspicuous porosity. The studied stone was also characterized by a substantial homogeneity of the properties, giving results in a narrow range of 13,1-16,9 MPa. It is a known phenomenon occurring in soft limestone with silica, noticed also in similar rocks of the same genesis [15].
4. Conclusions

The soft limestone has been used in Koło Basin in Central Poland as the basic construction material since the 19th century and proved to be durable enough for numerous buildings to be preserved in good condition to the present day. In many cases, they do not exhibit a significant external damage. However, the laboratory research of its durability, set up according to modern standards, leads to surprising observations and assessments:

- The tests showed a relatively low frost resistance and significant weight losses during freezing-thawing cycles. These results are not reflected in the condition of the existing walls, as often do not show significant damage. It is obvious that laboratory tests alone cannot be used to predict the effect of weathering processes in the limestone constructions.
- Theoretically, low laboratory frost resistance results correlate with the high open porosity and absorbability values of the tested rock, which may indicate high susceptibility to weathering.
- For the evaluation of durability, the analysis of pore distribution, especially the proportion of micropores ($\varphi<0.1\mu m$), has proven more reliable. The rating indicators obtained from the pore size distribution is a bit more consistent with the actual resistance of limestone used in construction.
- Relatively favourable values of compressive strength of the tested material were obtained, which was sufficient for most applications in rural construction.

These results indicate that durability should be considered with reference to a relevant weathering testing, which consider the behaviour of the rock material in the wall construction. A proper building technique, developed by practice, plays a key role in the accurate assessment of the durability of traditional construction materials.

Acknowledgments

The study was supported by RCI Laboratories: Laboratory of Expansive Soil Research and Laboratory of Materials Construction Research, at the UTP University of Science and Technology in Bydgoszcz, Faculty of Civil and Environmental Engineering and Architecture

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