Analysis of the Pore Space of the Swietokrzyskie Region’s Jurassic Devonian Limestones Based on Testing with the Use Mercury Intrusion Porosimetry and Differential Scanning Calorimetry

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Abstract. The Świętokrzyskie Region is an important district of exploitation of rocky resources used mainly in construction engineering. The especially valuable limestone deposits are mainly related to two geological periods (Jurassic, Devonian). The region features mines with the highest limestone resource mining output in Poland. The processes that the limestones have undergone were decisive for their technical properties, such as absorptivity, frostproofness, pore size, total volume and the diameter of transitions between them. The size of pores and their connections are crucial for the course of the water-ice phase transition and the material’s absorption of water from its surroundings. The article presents the results of testing the differentiation in the pore space of 10 Jurassic and Devonian limestones. The testing featured determination of the pore size distribution by using the mercury intrusion porosimetry and of the water quantities undergoing phase transition in the pore space. As a result of the conducted testing, it can be ascertained that there is good consistency between the limestone’s origin and its texture, especially porosity. In terms of their porosity, Devonian limestones have good technical parameters, i.e. their porosities were similar and amounted to 1.24-1.77%, whereas the porosities of Jurassic limestones were substantially diverse and amounted to 0.96-9.70%. Based on these results, it can be ascertained that the time and depth of their backlog are not material conditions for the limestone to obtain low porosity. The authors also ascertain that there is consistency in terms of the total volume of pores designated using mercury intrusion porosimetry and low-temperature calorimetry for limestones with porosity higher than 2%. The use of the MIP method for limestones with porosity below 2% does not provide relevant information about the properties of pores which substantially affect the water-ice phase transition.

1. Introduction
The limestone deposits in the Świętokrzyskie Region (Poland) are related mostly to two geological periods. The first period embraced the middle and late Devonian, whereas the second - middle and late Jurassic. It is estimated that the original porosity of the carbonate deposits can reach over 50%. As result of the layering of subsequent sediments, increase in pressure as well as partial or total recrystallization, the sediments became cemented and the original material’s pores became filled with calcium carbonate minerals.
The current technical properties came into being due to such factors as:

- original conditions of sediment formation,
- presence of accompanying sediments,
- impact of live organisms on the accumulated material in the case of carbonate rocks,
- formation of secondary porosity (diagenetic fracturing and dissolution),
- rock backlog depth which affects the pressure and temperature
- limestone backlog time (figure 1b).

The gradual transformation of the Devonian carbonate sediments lasted for at least 350 million years. Throughout this time, the area of the contemporary Świętokrzyskie Voivodship featured numerous marine transgressions and regressions combined with periods of rock weathering and accumulation which directly affected their retention depth. Based on the geological cross-sections of the Świętokrzyskie Mountains region available in literature [4], it can be assessed that the average depth of Devonian limestone layers of the Świętokrzyskie Mountains’ Palaeozoic core did not exceed approx. 1.5 km. As results of geological processes, these layers have undergone upheaval and their backlog depth is sufficiently shallow to allow its exploitation. They are heavily folding with numerous faults, which additionally results in their uneven backlog depth. One the other hand, the Devonian limestones located under the Mesozoic buffer zone of the Świętokrzyskie Mountains are backlogged at the depth of down to 4 km.

The Jurassic era limestones were formed in a much shorter time – 150 to 200 million years and were subject to compaction at shallower depths. According to Peszat’s research [1], the porosities of the Świętokrzyskie Region limestones from the Jurassic era can differ substantially. Their specific porosity amounts from 4 to 8%, but there are also limestones with porosity below 2% and above 20%. The conditions in which limestone sediments changed in terms of structure were locally diversified, which is why there is no standard Devonian or Jurassic limestone. In construction engineering (construction of roads, pavements and substructure layers, concretes industry), Jurassic limestones are deemed as lower quality rocks.

Figure 1. a) Porosity of limestones from the Mississipian Madison Group (upper Carboniferous), [9]. b) The impact of time and backlog depth on the average porosity of selected rocks of the USA region, OR - Ordovician, M(L-C) - “Mississipian” (late Carboniferous), CR- Cretaceous, CE-CR Cenozoic-Cretaceous [9]
The processes that the limestones have undergone were decisive for their technical properties, such as absorptivity, frostproofness, pore size, total volume and the diameter of transitions between them. In the case of limestones intended for elements exposed to periodic freeze-thaw cycles, it is the profile of their pore space that determines the possibility of their application. The size of pores and their connections are crucial for the course of the water-ice phase transition and the material’s ability to absorb water from its surroundings. The purpose of the article was to present the differences in the porosity of Devonian and Jurassic limestones. The testing of the pore space was conducted using the MIP and DSC methods. Using mercury intrusion porosimetry, it was possible to determine the porosity ($P_{MIP}$) and the pore diameter size distribution from 3 nm to 340 μm. The DSC method allowed for measuring the content of ice forming in the pores for typical working temperatures (down to -30 °C) and thereby indirectly assessing the diversification of the pores and their connections.

2. Methodology and subject of testing

The testing included comparison of 10 arbitrarily selected limestones from active rock excavations in the Świętokrzyskie Region. In five cases, these included limestones from the Świętokrzyskie Mountains’ Palaeozoic core, which were formed in the Devonian period, whereas the other 5 originate from the southern and south-western Mesozoic border of the Świętokrzyskie Mountains from the Jurassic era. All of the tested limestones are made of calcite in 95%, with the exception of sample 12(J), which consists of calcite in 90% and iron compounds in 10%. The testing featured determination of the pore size distribution and quantity of ice formed in the pore space during cooling of samples soaked with water. The test samples were cut out of rocky blocks using a drill rig. This way, it was possible to obtain cylindrical samples with the diameter of 14 mm and length of 70 mm, which were used for DSC testing. The samples were then dried to solid mass in the temperature of 105 °C. Then, they were soaked according to the vacuum method [5] by using degassed distilled water. The samples were kept in water for a period of at least 7 days. Then, they were subjected to DSC measurements using the BT 2.15CS differential scanning calorimeter. The calorimeter has two compartments. One compartment featured a water-soaked sample and the other - a standard sample. Prior to inserting them into the calorimeter’s compartments, the samples were weighed and wrapped in teflon film to avoid water vaporisation from their surfaces. The scanning program included cooling the sample from the temperature of +20 °C to -80 °C, then after a half-hour stabilisation at the temperature of -80 °C the sample was reheated to the temperature of +20 °C. The cooling and heating rate amounted to 0.09 °C/min (5.4 °C/h).

The measurements allowed recording a difference in the rate of heat flow $\varphi(t)$ passing through the walls of the container with the water-soaked sample and container with the dry standard sample. In order to determine the amount of energy related to the water-ice phase transition, the heat flow part dependent on the specific heat of water and ice was subtracted from $\varphi(t)$. This was done using the procedure described in paper [5]. The calculated phase transition energy curves were used to estimate the ice mass $m_i$ and the proportion of the ice mass and the initial mass of water included in the samples’ pores ($m_i/m_w$).

After the DSC testing, the samples were divided into smaller parts (length of approx. 2 cm) and dried to solid mass at 105 °C. Then, they were subjected to testing in the AutoPore IV 9500 mercury intrusion porosimeter. The samples were weighed and placed in a low-pressure port prior to testing. The testing included the following: 1) vacuum generation up to 2.6 Pa (20 μm Hg) in the penetrometer with the sample inside; 2) flooding the sample with mercury 3) gradual pressure increase to 414 MPa with simultaneous measurement of the intruded mercury quantity by the apparatus 4) gradual pressure decrease to the ambient value with simultaneous measurement of the outflowing mercury quantity by the apparatus. The calculations featured an adopted contact angle for the mercury $\Theta$ of 130° and a surface tension $\gamma$ of 0.485 N/m. The bulk densities, densities and porosities specified based on the MIP method are presented in table 1.
3. Results and their analysis

Based on the MIP test results available in literature, the total porosity of Devonian limestones in Poland can reach 1.5-6% [2, 8]. Among the examples of limestones collected from boreholes with depths of 3.8-4 km, it is possible to observe a specifically small share of pores with diameters of 16-200 nm. The porosity of the Devonian limestones studied by the authors of this elaboration did not exceed 2% (table no. 1). Also in this case, the share of pores with diameters of 16-200 nm in the entire pore space volume was minor. When referring the obtained porosity results to the results available in worldwide literature, it is visible that the porosities of the studied Devonian limestones of the Świętokrzyskie Mountains are lower in comparison to the average porosities of limestones formed in analogous geological periods (figure 1a and figure 1b) and backlogged at analogous depths (not exceeding 1.5 km). Based on the studies of limestones from the USA region, the expected porosities should amount to approx. 6-8%. This demonstrated that despite the relatively shallow backlog depths, the Świętokrzyskie Mountains’ Palaeozoic core Devonian limestones have good technical parameters in terms of porosity.

On the other hand, the studied Jurassic limestones of the Świętokrzyskie Region featured porosity amounting from 4 to 10%, except for limestone 7(J), the porosity of which did not exceed 1%. The diversification of the porosity of the Świętokrzyskie Region’s Jurassic limestones is substantially higher than in the case of Devonian limestones, which corresponds to other data available in literature [1, 5, 6]. The analysis of the distribution of pores and their volumes (MIP) demonstrates that in the case of the Jurassic limestones, pores with diameters from 16 to 200 nm (figure 2a and figure 2b) have a significant share in their total porosity. The exception is limestone 7(J), for which the pore size distribution is more similar to the distributions of the Devonian limestones than to Jurassic limestones.

Based on the analysis of the geological cross-sections, it can be ascertained that this limestone was not backlogged at a depth that differed substantially from other Oxford limestones. The limestone includes a series of features similar to limestones 10(J), 11(J), e.g. it is made almost entire of calcite. As stated by Peszat [1] and Dżułyński [11], the area of the sea in the Oxford period featured diversified limestone sedimentation environments. The existence of numerous bedded limestone areas usually accompanying rocky limestones demonstrates that the granular material included in them was carried by the Oxford sea currents and derived most probably from the crushing of rocky formations [1, 11].

| Limestone* | Bulk density g/cm³ | Density, g/cm³ | Porosity, P_{MIP} % |
|------------|-------------------|---------------|----------------------|
| 3(D)       | 2.6754            | 2.7117        | 1.34                 |
| 7(J)       | 2.6857            | 2.7117        | 0.96                 |
| 8(D)       | 2.6752            | 2.7088        | 1.24                 |
| 10(J)      | 2.6045            | 2.7095        | 3.87                 |
| 11(J)      | 2.5706            | 2.7060        | 5.00                 |
| 12(J)      | 2.4377            | 2.6994        | 9.70                 |
| 20(D)      | 2.669             | -             | 1.55                 |
| 21(D)      | 2.6804            | 2.7162        | 1.32                 |
| 23(D)      | 2.7915            | 2.8419        | 1.77                 |
| 25(J)      | 2.7408            | 2.8449        | 3.66                 |

Table 1. Average values of the limestones’ density, bulk density and porosity based on the MIP testing.

* (D) - Devonian, (J) - Jurassic.

The above image demonstrated undoubtedly that the impact of (physical compaction) increased pressure, backlog depth, temperature, backlog duration, recrystallization of the Devonian limestones contributed to the decrease in porosity, while in the case of such “young” rocks as the Jurassic limestones, the main factor that affected their porosity was their sedimentation and early diagenesis.
The possibility of existence of Jurassic limestones with porosity below 2% was ascertained. Conditions.

Figure 2. Accumulated volume of Devonian and Jurassic limestones pores: a) Devonian b) Jurassic

The process of water freezing in the limestone’s pore space in the temperature down to -30 °C was also analysed. According to equation (3.1), the temperature -30 °C corresponds to water freezing in pores with the radius of \( r_p = 2.72 \text{ nm} \) [10].

\[
0.647 - 0.57 \Delta T
\]

(1)

where: \( \Delta T = T - T_0 \), T - absolute temperature, \( T_0 = 273.2 \text{ K} \).

In the case of samples 3(D), 8(D) and 21(D), a major share in the limestones’ pore volume included pores that were not filled with water as result of soaking. On the other hand, among the pores that were filled with water to a higher degree, the highest share featured pores with a diameter exceeding 7 nm. The sample 23(D) featured a completely different situation, because among the Devonian limestones it was characterised by the largest quantity of water absorbed per volume unit (in the DSC testing) and the highest porosity \( P_{\text{MIP}} \). In this case, the total volume occupied by water and ice at the temperature of -30 °C is similar to the volume of pores designated using the MIP, which can give evidence of the small number of isolated pores that were not filled with water. Therefore, it is possible to expect a substantially higher quantity of ice in comparison to other Devonian limestones. Despite this fact, most water contained in the pore space of sample 23(D) has not undergone phase transition in temperature down to -30 °C (figure 3a). The water probably occupied pores with a radius lower than 2.7 nm or larger pores connected with others via pores with a radius lower than 2.7 nm.

After using the MIP method for the Devonian limestones, it was not possible to ascertain substantial differences in the size distribution of pores with a radius lower than 2.72 nm (figure 2a and figure 5a), but similar porosities \( P_{\text{MIP}} \) were obtained. During the MIP testing, most pores of Devonian limestones is filled with mercury at the pressure of 88.1 MPa. According to the Washburn-Laplace equation, the pressure corresponds to pressing mercury into pores with the radius of 7 nm. The most probable cause of existence of such large differences between the volume of pores filled with mercury
at the pressure of 88.1 MPa and volume occupied by ice in the samples at the temperature of -10 °C, is the breakdown of the limestones’ shell and penetration of the mercury into the pores that are inaccessible for water during the soaking process.

Figure 3. a) Relative increase in ice mass during the cooling process. b) Increase in ice mass in relation to the sample’s volume during the cooling process.

Figure 4. Volumes of particular phases in the Devonian limestones’ pore spaces for the cooling process with temperature down to -30 °C (based on DSC).

Only in the case of limestone 12(J) nearly 100% of water transitioned into ice in the temperature down to -30 °C. In the case of other limestones, a considerable share of water not subject to phase transition in the temperature down to -30 °C was observed. This water features particles which are strongly absorbed on the surface of pores as well as free water in pores with radius smaller than 2.72 nm, and water in isolated pores [3, 10].
Figure 5. a) Total volume of pores based on MIP. b) Volume of pores based on MIP, where V1 - radius larger than 7 nm, V2 - radius between 2.7 nm and 7 nm, V3 - radius between 1.5 nm and 2.7 nm.

Figure 6. Volumes of particular phases in the Jurassic limestones’ pore spaces for the cooling process with temperature down to -30 °C (based on DSC).

Jurassic limestones, except for 7(J), had a corresponding and similar total volume of pores, designated using the MIP testing method and total volume of water in liquid and solid state in the temperature of -30 °C.
4. Conclusions
The conducted testing confirms substantial differentiation in the pore space of the Świętokrzyskie Region’s Jurassic limestones. Based on the conducted testing, it can be ascertained that there is a general consistency between the limestone’s origin and its texture, especially porosity. Jurassic limestones are more diversified than Devonian limestones. Their porosity is usually much higher. Pores in Jurassic limestones include substantial groups with dimensions of 16-200 nm, which are not observed in Devonian limestones. Adequate depth and time do not constitute essential conditions for the limestone to achieve aptly low porosities, which is clearly visible based on the results of testing for sample 7(J). In limestones with porosity higher than 2%, the total volume of pores possible to be determined using the MIP method is similar to that obtained by using the DSC method, which in turn is impossible for limestones with porosity lower than 2%. It is impossible to obtain information about the material properties of pores which directly affect the water-ice phase transition by using the MIP method for limestones with porosity lower than 2%. Limestones 3(D), 8(D), 20(D), 21(D) and 7(J) feature a substantial volume of pores which are not filled with water during soaking. This results from the substantial share of isolated pores in the shaping of the limestone’s pore space. Limestone 23(D) constitutes an exception, because its pore space consists mostly of a system of connected pores.

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