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FUSION OF DIFFERENTIAL ANALYSIS OF VOLUMETRIC STRAIN METHOD (DILATOMETRIC THERMOPOROMETRY) AND MERCURY INTRUSION POROSIMETRY METHOD FOR PORE SPACE CHARACTERIZATION IN CARBONATE ROCKS

POŁĄCZENIE METODY RÓŻNICOWEJ ANALIZY ODKSZTAŁCEŃ ORAZ METODY POROZYMETRII RTĘCIOWEJ DO OKREŚLENIA CHARAKTERYSTYKI PRZESTRZENI POROWEJ W SKAŁACH WĘGLANOWYCH

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Abstract

Many characteristics of capillary-porous materials, including limestones and dolomites, depend on the structure of the pore space of a given material, so the article attempts to accurately determine the geometric characteristics of pores and their ability to transport water. Much information on the pore structure of carbonate rocks can be obtained from literature studies. There is a lack of information on the use of full hysteresis dilatometric thermoporometry methods for this purpose, as well as the fusion of differential analysis of volumetric strain (DAVS) results with mercury intrusion porosimetry (MIP) results.

The subject of the research presented in this article is the analysis of pore structure in carbonate rocks using the method of differential analysis of volumetric strain and mercury intrusion porosimetry. Based on the measurements made, the pore size, pore volume, content of empty pores and pores containing water incapable of phase transformation were analyzed. The geometry of mesopores of rock samples examined by differential analysis of volumetric strain and mercury intrusion porosimetry was compared. A fusion of the distribution of mesopores from the DAVS study with a part of the distribution of meso- and macropores obtained by the MIP study was performer.

Keywords: differential analysis of volumetric strain method, mercury intrusion porosimetry, carbonate rocks, pore space

Streszczenie

Wiele cech materiałów kapilarno-porowatych, w tym wapieni i dolomitów, zależy od struktury przestrzeni porowej danego materiału, dlatego w artykule podjęto próbę dokładnego określenia cech geometrycznych porów i ich zdolności do transportu wody. Wiele informacji na temat struktury porów skał węglanowych można uzyskać ze studiów literaturowych. Brakuje informacji na temat wykorzystania w tym celu metod termoporometrii dylatometrycznej z pełną histerezą, a także połączenia wyników różnicowej analizy odkształceń (DAVS) z wynikami porozymetrii rtęciowej (MIP).

Przedmiotem badań przedstawionych w niniejszym artykule jest analiza struktury porów w skałach węglanowych z wykorzystaniem metody różnicowej analizy odkształceń i porozymetrii rtęciowej. Na podstawie przeprowadzonych pomiarów przeanalizowano wielkość porów, objętość porów, zawartość porów pustych oraz porów zawierających wodę niezdolną do

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przemiany fazowej. Porównano geometrię mezoporów próbek skalnych badanych metodą różnicowej analizy odkształceń i porozymetrii rtęciowej. Wykonano fuzję rozkładu mezoporów z badania DAVS z częścią rozkładu mezo- i makroporów uzyskanych w badaniu MIP.

Słowa kluczowe: różnicowa analiza odkształceń, porozymetria rtęciowa, skały węglanowe, przestrzeń porowa

1. INTRODUCTION

The structure of the pore space of rocks decisively affects their durability and other performance characteristics. Precise determination of the geometric characteristics of pores and their connections is a difficult task. There is no single consistent method for this purpose. Only the combination of several dedicated testing techniques allows a more realistic depiction of the complete pore structure of a specific material [1-3]. Of particular interest is the imaging of mesopores (2÷50 nm – according to IUPAC [4]), which determine the material's essential properties in the context of the movement of gases and liquids in its interior [1, 5-9].

The paper analyzes the possibility of using tests performed by DAVS analysis and MIP tests for qualitative and quantitative assessment of pores. An important goal was also to develop DAVS testing methodologies, enabling analysis of „bottle" pores and geometric features of their connections to the overall pore system. The study was limited to carbonate rocks that are among the most diverse in terms of pore structure, and are commonly exploited and used in the construction industry.

Pores are responsible for the flow and retention of liquids in rock materials. They are characterized by a wide range of diameters. The largest of them are possible to see even with the eye. The total volume of pores, in the main, depends on the type of rock. In magmatic rocks, they mostly occur as microcracks between individual crystals and their size depends on the formation process of the rock. In sedimentary rocks, pores are formed as undensified free spaces between individual components of the rock. In both cases, the vast majority of these pores are accessible to water [10].

How do we properly define the object that is a „pore" or perhaps more precisely a „pore space"? A completely general definition of pore is probably not possible. However, it can be said that a pore is defined as a part of pore space that is bounded by solid surfaces and planes, in which the hydraulic radius of the pore space is minimal.

Many different definitions of pores and their dimensions have been used over the years. One of the more well-known concept of so-called „air voids", was first used by Rumpf [11]. Pioneering studies of pore and pore space connections, Fatt's research, realized in 1950, and his 1956 publications [12-14], are considered to be the first.

Without familiarity with the subject matter in question, the depiction of pores in the material can give an illusory picture of them. The shape of pores in a material is influenced by many factors. These include, for example, the origin of the rock, the genesis of its formation, as well as its mineral composition. However, given the nature of water freezing processes in the rock material, the shape of the pores is not as important as their smallest dimension. In addition, the smaller the dimensions of the pores, the more important adhesion forces become. They cause at least an increase in resistance to water flow. This phenomenon is caused by the ordering of dipoles near the walls of the micropores [15].

Accurately determining the geometric characteristics of pores is not a simple task. In addition, wishing to analyze also the connections of pores in the material, there is no single method that will allow one hundred percent certainty of the measurement results. According to [16], the physical properties of elements made of rock materials that directly or indirectly affect the durability of such an element do not depend only on the material itself, but also on the conditions in which it is located. By combining research methods sometimes taken from other scientific fields, such as medicine or aerospace, it is possible to better understand the phenomena occurring inside rock materials [17]. Comparative studies were also conducted by Padhy and his team [2]. Evaluating the geometric structure of the pore space with a single method requires in some cases to make sure that the results of studies conducted by other methods are correct and convergent and the conclusions drawn are valid [18-21].

An additional problem in the analysis of porosity and pore space is posed by pores „bottle pores". The name refers to pores that are connected to the rest of the system by narrow constrictions. At the same time, more than one constriction can lead to a larger pore. Their presence in the material can lead to a distortion of the actual picture of the geometrical characteristics of the pores toward smaller pores [22, 23].

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Due to the acting pressures inside the material, the tensile strength, mineral composition and (above all) – the geometric characteristics of the pores – have an impact on its durability in addition to the amount of absorbed water. This is particularly important when rock materials are used as exterior cladding. In rock materials, in which the predominant group is large pores in which most of the water freezes as soon as the temperature passes below 0°C, no relationship has been observed between the internal surface of the pores and the material's resistance to cyclic freezing and thawing. The situation is different for pore-containing materials in which water does not freeze immediately after passing below 0°C. In this type of material, a correlation between frost resistance and internal surface area has been observed [24]. In addition, studies have shown that the ratio of the amount of water in the smallest pores to its total content in the material determines how the destruction inside the material will occur [25] – whether it will be caused by the occurrence of hydraulic or osmotic pressures.

There are many papers in the literature on the problem of the hysteresis of the water-ice phase transition during the cooling and heating of a material. However, there is no single clear answer as to how the various factors affect the on the formation of ice in capillary-porous material and also what exactly happens during the cooling process of the material and during its heating [1, 6, 26, 27]. It is also suggested that the course of the ice melting process is influenced not only by the diameter of the pores but also by their shape [28]. However, it is assumed that one of the reasons for the differences in the course of the exo- and endothermic phases may be the mechanism controlling the formation of ice in large pores via smaller pores [1, 6, 27].

2. METHODOLOGY

Rocks and products made from them are widely used in many areas of everyday life and science. It's not just construction and related fields in the broadest sense, but also agriculture or even everyday items. With such extensive use of rock materials, the requirements for their performance characteristics are also increasing. Nevertheless, the porosity of rocks is generally low compared to other building materials such as bricks or concrete.

Using studies of the technical properties of rocks, the aim is to obtain results that are reproducible and comparable, which are necessary to characterize the suitability of the studied rock for practical purposes. Rocks have certain properties that determine their usability. These properties, fluctuate within wide limits and even within a single deposit. The mere determination of the type of rock tells us little about its usable characteristics and technical suitability. Therefore, it seems necessary to determine their variability. In almost every deposit it is possible to distinguish varieties characterized by optimal properties and right next to them varieties with inferior properties [29].

Without a single, proven and scientifically recognized method to accurately determine the distribution of pore sizes, their connections, dimensions – we cannot perform this type of research, without any doubt about the result achieved. Therefore, the author focused on combining two methods – DAVS and MIP to fully determine the pore size distribution in carbonate rocks. The use of two methods also made it possible to cross-check the correctness of the data obtained.

The first method described, which allows indirect determination of pore size distribution in capillary-porous material, is differential analysis of volumetric strain DAVS (dilatometric thermoporometry). The upgraded methodology makes it possible to determine the dimensions of the pore entrances during the cooling process of the sample and the internal dimensions of the pores based on the heating of the sample. The method of differential strain analysis with various modifications has been used in pore space studies for many years [26, 93, 137]. Its main task is to qualitatively and quantitatively evaluate the pores in a material for its ability to absorb water that is or is not capable of freezing under operating conditions [10]. Over the years, the method of differential strain analysis has significantly evolved and been upgraded. Nowadays, differential strain analysis tests are performed using metal measuring dilatometers equipped with conical lids with a spigot for graduated tubes. This method, was widely described in the article [30].

The mercury intrusion porosimetry (MIP) method makes it possible to measure the volume as well as the size of pores in a material. One of the main advantages of this method is the ability to study a wide range of pore sizes. As a result, not only the total porosity value but also the pore size distribution is obtained. The test is based on one of the characteristics of mercury which is the lack of wettability of the surface of most solids. Thus, mercury under reduced pressure does not spontaneously penetrate the interior of the pores. The penetration of mercury into the pores is caused by increasing the pressure during the measurement. As a result of carrying out the

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measurement, knowing the final amount of injected mercury, it is possible to determine the porosity of the material under study and then using appropriate calculation algorithms – to determine the geometric characteristics of the material taking into account the internal size of the pores. Despite the sophistication of this method, one must be aware that mercury is not able to enter all curves or corners of pores. Mercury porosimetry is a method extensively reported in the literature – for example, Modry et al. [31]; Cameron and Stacey [32]; Leppard and Spencer [33]; Baker [34]. The initial principles of the methodology were presented by Ritter and Drake [35] as early as 1945. Since then, the method has evolved considerably. The basic assumption of this method is that the pores in the material are cylindrical in shape. According to [36], there are actually different types of pores and their connections in capillary-porous materials. The occurrence of pores with narrow entrances, so-called bottle-shaped pores, can cause a shift in the signal obtained from mercury injection toward smaller pores, which may not fully correspond to the actual geometry of the pore space [2, 3, 37, 38].

3. MEASUREMENTS AND RESULTS

More than a dozen samples of carbonate rocks (limestone and dolomite), from domestic deposits, were examined using the differential strain analysis method. Porosimetric tests were also performed on fragments of the same rocks. While more than a dozen samples were used in the study, only selected results are presented in the article. The entire study is presented and described in detail in author doctoral thesis [39].

Cylindrical samples, 50 mm in diameter and 150 mm in length, cut directly from a block of rock taken at the mine, were used for DAVS tests. The rock sample for the DAVS test is shown in Figure 1.

Figure 1. DAVS test specimens with dimensions $\phi50$ and h = 150 mm [own elaboration]

The porosimetry (MIP) test used small pieces of rock samples that were placed as tightly as possible in a penetrometer. The rock crumbs for the MIP test are shown in Figure 2.

Figure 2. Samples prepared for MIP testing [own elaboration]

The rock samples for testing had a total mass in the range of 5 to 12 grams. The samples were cleaned before testing, then dried at 105°C to constant weight and cooled in a desiccator.

The comparison of the results obtained by the DAVS method and the MIP method began with a general look at the question of the volume of pores occupied by water in vacuum soaking (in DAVS) and mercury (in the MIP method). These data are presented in Table 1.

In addition, it should be noted that the samples selected and presented in this article were from different deposits and geological periods. Sample A2 is a Devonian limestone. Sample C2 is Devonian dolomite. Sample F2 is dolomite from the Jurassic period. Meanwhile, the sample labeled G2 is Jurassic limestone.

Table 1. Total pore volume occupied by mercury in the MIP test in relation to porosity and volumetric absorbability

Sample number	Volumetric absorbability (vacuum met.) [%]	Total porosity [%]	Total pore volume occupied by mercury (MIP) [%]
A2	0.40	4.27	4.10
C2	0.45	6.04	3.55
F2	2.05	5.48	5.35
G2	4.23	9.27	9.03

The porosity of samples A2, C2, F2 and G2 is higher than the total pore volume occupied by mercury. This means, that the destruction of the pore space of the material caused by the high pressures generated during the MIP test did not apply in this

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case. Such destruction in the structure of the smallest pores can be observed when conducting tests using the MIP method. Particularly large differences in the geometric structure of the pore space are obtained in the part of the pores of small pores (the radius limit of less than 0.02 μm is assumed in the work), where the pressures acting on the pore walls are very large [1-3, 39].

Table 2. Pore volume occupied by ice (DAVS) and mercury (MIP), in radii >0.02

Sample number	Pore volume occupied by ice in the range of radii >0.02 μm (DAVS) [%]	Pore volume occupied by mercury in the range of radii >0.02 μm (MIP) [%]
A2	0.22	0.23
C2	0.20	0.25
F2	0.38	0.44
G2	0.57	0.62

The data presented in Tables 1 and 2 indicate that mercury filled the pores of the sample in the MIP test in a much larger volume than water in the DAVS test. This is true both for the total pore volume in the material and (on a much smaller scale) for the pore volume in the range of radii >0.02 μm. It is clear that one of the reasons for the differences occurring is the failure of all pores in the material to fill with water in soaking by the vacuum method. In the MIP study, very high pressures for mercury injection (up to about 420 MPa) can cause damage in the pore space of the rock, especially in the smaller pores, where the largest differences in water and mercury volumes were observed. The cause is probably local crushing of pore walls, widening of passages, unblocking access to previously separated pores, etc. We don't know this exactly, but results from the world literature indicate that damage in the pore space of the material under study may be created as a result of the application of high pressure during measurement. The effect of this is precisely the differences in the total pore volume determined by the DAVS method compared to MIP.

Based on analysis of the DAVS method results, we are currently unable to define pore sizes with radii greater than 0.02 μm. In this range of pore sizes, the MIP method is very useful because the pressures of mercury forced to move it in the rock sample are not yet very high, and it can be assumed arbitrarily that there is still little or no damage in the pore space of the rock. Determination of geometric pore dimensions

is not yet contaminated by possible damage, which is certainly the case at pressures much higher when mercury is forced into pores with small and very small cross sections. These conclusions were supported by the results of DAVS and MIP tests at radii of >0.02 μm. The graphs below clearly show that the total values of the volume occupied by the pores for both methods are similar. The smallest differences were recorded for sample A2. The pore volume occupied by ice in the DAVS study in the range of radii >0.02 μm was 0.22%. In the MIP study, the pore volume occupied by mercury in the same range was 0.23%. On the other hand, we have the F2 sample, for which the difference was 0.06%. This may indicate, for example, the greater „fragility" of the F2 rock. Mercury, even under not much pressure, could damage the pore walls and penetrate those that were not accessible to water during soaking by the vacuum method. The differences could also have resulted directly from the heterogeneity of the material under study. Locally, there may be more numerous voids/pores in the rocks, the effect of which, in comparing the results, are visible differences in the values of, for example, just the volume of pores.

Thus, an opportunity arises to use part of the distribution of pore dimensions and volumes determined by the MIP method to estimate the actual geometric structure of the pore space in rocks. This part of the MIP chart will be used to supplement the quantitative evaluation of pore volumes and dimensions determined by the DAVS method.

Below are selected graphs of the results of pore size distribution determined from the DAVS study (left) based on heating phase analysis, and (on the right) data from MIP analysis. The portion of the pore size distribution that depicts pores with radii >0.02 μm as a single value in the DAVS study was decomposed into smaller subsections based on the MIP study.

Based on the analysis of DAVS results, we are currently unable to define pore sizes with radii above 0.02 μm. In this range of pore sizes, the MIP method is very useful. Thus, this part of the MIP chart was used to supplement the quantitative evaluation of pore volumes and dimensions determined by the DAVS method.

In order to be able to determine the pore space characteristics in more detail, a description of the distribution of pore size and volume occupied by ice was also added to the analysis in individual samples, determined by the exothermic phase in the DAVS study.
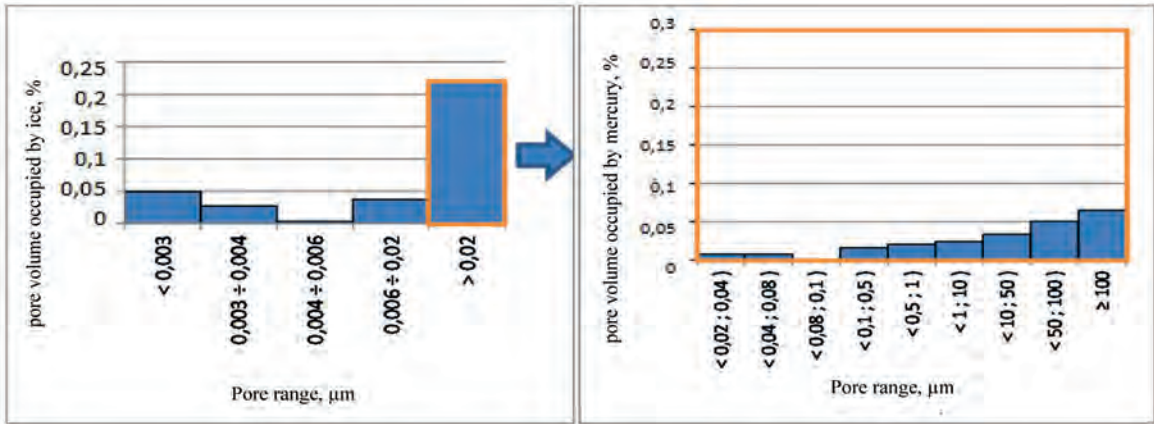
Figure 3. Idea for presentation of pore size distribution according to MIP, referring to pores with radii >0.02 µm in sample A2
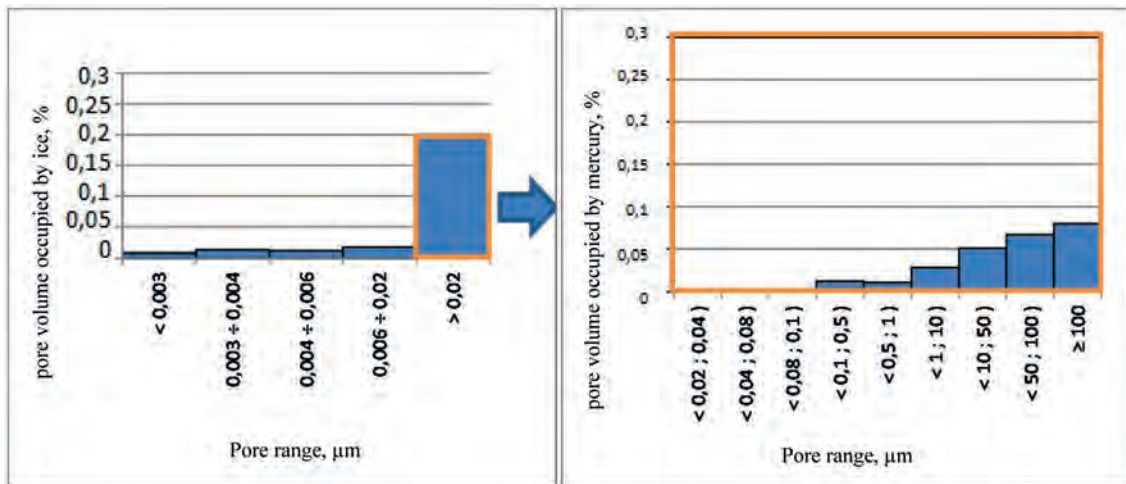

Figure 4. Idea for presentation of pore size distribution according to MIP, referring to pores with radii >0.02 µm in sample C2

The pore size distributions shown in Figure 3 give a wide range of geometric characteristics of the pore space in sample A2. Pores with radii >0.02 µm revealed by the DAVS test are essentially large pores, with radii greater than 0.1 µm. The smaller pores determined by DAVS analysis represent a significant portion of the total porosity. They mainly represent a portion of the volume, which corresponds to connecting pores and small capillaries. The large pores shown on the basis of the MIP study are to some extent connected to other pores by much smaller transitions. The pore size distribution of the A2 sample lacks pores in the 0.08÷0.1 µm range.

The volume of pores with radii >0.02 µm occupied by ice in the DAVS test, represents about 0.22% of the sample volume while in the MIP test it is about 0.23%.

In the case of sample C2, one can notice the complete absence of pores from the range of 0.02÷0.1 µm radius. The distribution characteristics of the remaining pores determined by MIP analysis are similar to those shown in the previous case. Based on the analysis of the results obtained by the MIP method, it can be assumed that the dimensions of the pores with radii above 0.02 µm refer to the internal dimensions of the pores and not their smaller connections. In contrast to sample A2, significantly fewer ice-filled pores were recorded in the range of radius dimension below 0.02 µm. Thus, the pore size distribution illustrates some presence of large pores in the pore space of the material, which are connected by significantly smaller passages. In addition, the pore size distribution of the C2 sample lacks pores in the range of 0.02÷0.1 µm.

The volume of pores with radii >0.02 µm occupied by ice in the DAVS test, represents about 0.20% of the sample volume while in the MIP test it is about 0.25%.
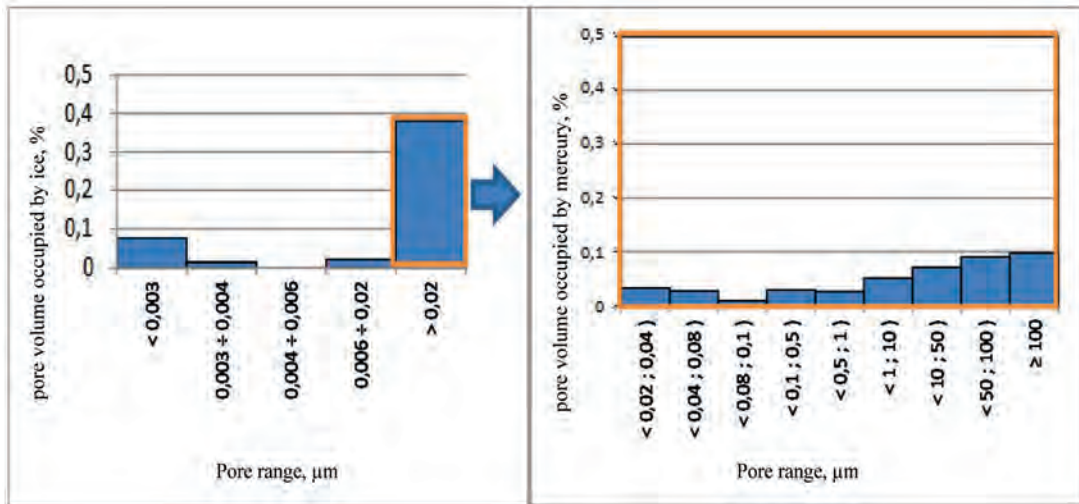
Figure 5. Idea for presentation of pore size distribution according to MIP, referring to pores with radii >0.02 μm in sample F2
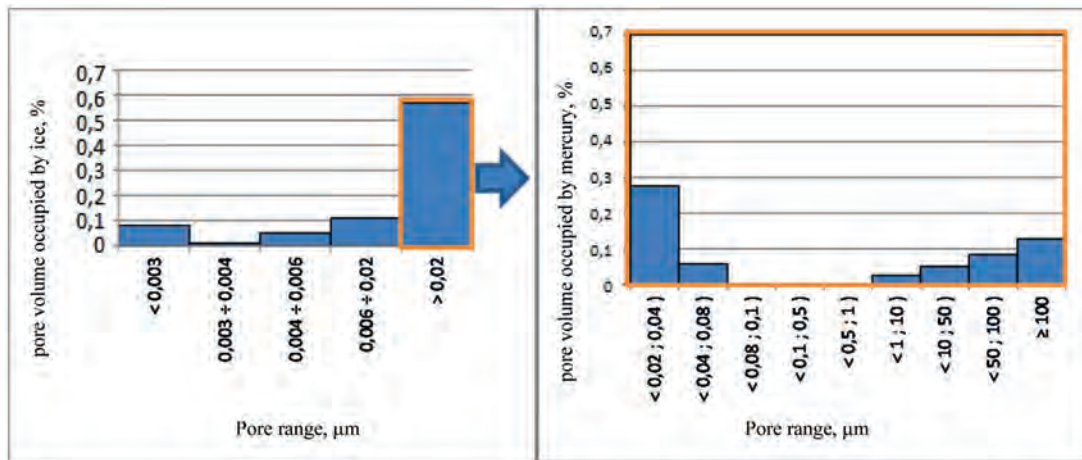

Figure 6. Idea for presentation of pore size distribution according to MIP, referring to pores with radii >0.02 μm in sample G2

The graph from sample F2 shows a relatively numerous group of the smallest pores filled with ice, with radii <0.003 μm, when cooling samples down to –25°C (Figure 5). The second largest pore group in the sample in terms of volume is made up of pores with radii >0.02 μm. Of all the rock samples discussed so far, F2 is characterized by the presence of pores in every defined range of their size. Such a material can fill with water fairly quickly under atmospheric conditions, but there is a sizable volume of pores that will only become active under conditions of water soaking at reduced pressure, or over a longer period of soaking [1, 8, 9, 39]. The volume of pores with radii >0.02 μm occupied by ice in the DAVS test is about 0.39% of the sample volume, and in the MIP test about 0.43% of the sample volume.

The pore size distribution of the G2 sample differs from the previous ones (Figure 6). The pores with radii >0.02 μm, visible on the DAVS graph, are primarily pores with radii in the range of 0.02÷0.04 μm, visible on the MIP chart. This is the range of pores dominant in the studied rock material. Next in terms of total volume are the largest pores with radii >50 μm. The pore size distribution of the G2 sample lacks pores in the 0.08÷1 μm range. Large and small capillary pores predominate. The volume of pores in the G2 sample with radii >0.02 μm occupied by ice in the DAVS test is about 0.59% of the sample volume, and about 0.62% in the MIP test.

4. CONCLUSIONS

The differences in the total volume of pores with radius dimensions above 0.02 μm occupied by freezing water and mercury in the samples tested are small. On the basis of the MIP test alone, we are unable to determine the actual dimensions of pores

with radii <0.02 μm. Injection of mercury into such pores is carried out at very high pressures, which can cause damage to the pore walls. It can be assumed that the pressures generated when injecting mercury into pores with radii above 0.02 μm are not large enough to significantly distort the image of the imaged pores, with the result that the pore size distribution in this range is real or close to real. It seems that in order to obtain information about the size and volume of macropores in rocks, the MIP method is appropriate. The DAVS method helps to better visualize the geometric characteristics of pores and their connections in the material at radius dimensions below 0.02 μm. The combination of the two methods makes it possible to present a more complete picture of the size distribution, volume and nature of pore connections in the material.

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