



Simple Method of Rock Pore Structure Determination Presented with the Most Common Rock Types Quarried in Slovakia

Martin Ondrášik^(✉), Jana Frankovská, Miloslav Kopecký,
and Martin Brček

Slovak University of Technology, Bratislava, Slovakia
martin.ondrasik@stuba.sk

Abstract. Porosity is a very important rock property because it controls many other rock properties. However, not only the total or open porosity but also the rock pore structure (RPS) is important because of its relation to some rock properties. The RPS includes characteristics such as the rock pore size and shape, pore size distribution, total and open porosity, active interior pore wall surface, and interconnectivity of pores. Not all the RPS characteristics are easy to identify and express numerically. Porosity is commonly tested in all commercial laboratories of rock mechanics, but the other RPS characteristics are tested in advanced scientific laboratories only, because their determination depends on expensive laboratory devices and highly skilled staff. In the paper we present the practical use of a very simple alternative method of determining RPS. The method is based on an assumption: if water sorption (adsorption and absorption) into rock pores is controlled by RPS, then water sorption under various controlled conditions can determine RPS. The RPS determination is demonstrated on rock samples, from 80 localities, of eight the most common rock types widely used in civil engineering practice in Slovakia. All the results are given as the percentage weight of water in rock pores of four different categories, which are defined by their size and accessibility to water. The results also reveal the average values and ranges of RPS for each tested rock type.

1 Introduction

In engineering practice, the total porosity is routinely tested in laboratories (STN EU 1636 2007). However, to understand the relationship with various rock properties and processes related to the presence and behaviour of water in rock pores, knowing the total porosity is not sufficient. Also, if we want to predict rock resistivity against deterioration, it is important to understand the rock pore structure (RPS) (Prikryl 2013; Moh'd et al. 1996; Benavente et al. 2004; Ruedrich and Siegesmund 2007; Ordóñez et al. 1997; Ondrášik and Kopecký 2014). The rock pore size and geometry, pore size distribution (PSD), and architecture of pore interconnection are characteristics which are not commonly studied in engineering and geological practice but are only investigated in specific research projects focused on the properties of porous material and the consequences resulting from them (Sun and Scherer 2010; Kaneuji et al. 1980). The reason for this is that the most common methods of pore structure determination

(Anovitz and Cole 2015) are tedious, expensive, and time consuming and require special laboratory equipment and skilled operator.

In our researches, focused on identification of the role of RPS in rock deterioration, we identify some of the most important characteristics or features of the RPS by a simple method similar to the one suggested by Kate and Gokhale (2006). Our method is based on water sorption under three different conditions and the assumption that if water sorption (adsorption and absorption) into rock pores is controlled by RPS then water sorption under various controlled conditions can determine (or indicate) RPS. Using this method, we present the indicative RPS of eight rock types quarried in Slovakia for use in civil engineering. The rock samples are from 80 localities.

2 Theoretical Background and Basis

As one of the most important features of the RPS, the PSD is determined by many methods. Anovitz and Cole (2015) summarized 19 methods. Mercury intrusion porosimetry and gas sorption are the most commonly used methods. However, like any of the other methods, they are also limited by assumptions accepted in their theories regarding the final pore size and PSD calculations and by architecture, and geometry of pores (Anovitz and Cole 2015; Thommes et al. 2015). These limits can be crucial for the accuracy of the results, because, as can be seen from the numerous microscopic images of rock pores published in scientific papers (Kate and Gokhale 2006; Labus and Bochen 2012; Benavente et al. 2004) and on the Internet, the pores in rocks have any shape but the ideal cylinder or slot-like shapes with a smooth wall surface.

To avoid the problem of not uniform size and shape of a pore, Brunauer et al. (1967) suggested using the hydraulic radius for calculating the pore size from water vapour adsorption isotherms. Based on this hydraulic radius, Kate and Gokhale (2006) suggested a simple modified water vapour adsorption method to estimate a complete PSD.

According to experiences from our researches concerning the influence of pore water on rock properties, the most important role of the RPS is its influence on the accessibility of pores to water and the quality and quantity of interactions between pore walls and water. The pore accessibility controls the presence of water in pores, that is, the speed of water saturation and degree of saturation. The pore-wall–water interaction controls the water properties, that is, water with interaction is adsorbed water and water without interaction is free water. These two types of water have different thermodynamic properties, which control some of the processes occurring in rock pores, which are especially strong when the temperature passes the freezing point of water (Powers 1955; Hudec 1991, 1993; Ondrášek and Kopecký 2014).

The pore size classification, which takes into account the presence of adsorbed water in pores (physisorption), is the one given by IUPAC (Sing et al. 1985). According to this classification, pores smaller than 2 nm are called micropores, pores with sizes between 2 and 50 nm are mesopores, and pores greater than 50 nm are called macropores. Pores entirely filled with adsorbed water are micropores (micropore filling) and mesopores (monolayer-multilayer adsorption and capillary condensation) (Sing et al. 1985). Free water (also called bulk water) is found in macropores.

The accessibility of pores to water depends on the shapes of the pores, interconnectivity, and pore architecture. Through pores with two ends (openings to external space) or a pore network with three or more ends (Rouquerol et al. 1994) can be filled with water instantly. We call them “easily accessible pores”. One-ended pores (blind pores, ink-bottle pores) or pores with a narrow throat are pores that can only be filled with water under special conditions. We can call such pores “not easily accessible pores”. The last type of rock pore is those which are not accessible to water at all. We call them “closed pores”.

To satisfy our need to understand the basic features of RPS, we have developed a method for the determination of indicative RPS. It is based on the determination of (1) micropores and mesopores by water adsorption, (2) easily accessible macropores by water absorption, and (3) not easily accessible macropores by boiling or vacuum absorption. Also, the content of (4) closed pores can be determined by using the total porosity. The content of the four defined categories of pores is given not as the recalculated PSD in length units but as the percentage weight of water occupying these pores in relation to the dry rock weight.

3 Tested Rock Samples and Test Methods

A new and simple indicative RPS identification is presented here using data from 80 rock samples collected from 80 localities in Slovakia. The samples included rock types quarried for the building industry, either as rock aggregates or as construction or decorative stone: granite, andesite, basalt, rhyolite, tuff, sandstone, travertine, and limestone. All the rock samples were “leftovers” from a project, *The Engineering Geological Atlas of Rocks of Slovakia* (Holzer et al. 2009), in which rocks from 146 localities from Slovakia are described in detail, including 20 physical and mechanical rock properties (basic set of properties required by standards on natural stone). The tested rocks were dimensioned cubes of $50 \times 50 \times 50$ mm or cylinders of 50×50 mm.

The indicative RPS determination presented herein is based on suction tests performed under three different conditions: 59-day water vapour adsorption at 98% RH (relative humidity), 48 h water absorption under atmospheric pressure, and 3 h water absorption by boiling.

The 59-day water vapour adsorption test at 98% RH was performed to identify the content of micropores and mesopores in the rock samples. Usually, a shorter test is sufficient (hours to three days), but a long time was required for the dimensioned $50 \times 50 \times 50$ mm cubes and 50×50 mm cylinders to establish a balance between 98% RH and adsorption; that is, after 59 days there was no gain in the weight of the tested samples. All 80 samples were tested at one time in a climatic chamber with 98% RH controlled by a saturated solution of CaSO_4 and an electrical fan. The rock weight gain was measured.

The 48 h water absorption test, carried out according to STN EN 13755 (2003), was used to identify macropores that were easily accessible to water. The test results were taken from the project *Atlas* (Holzer et al. 2009).

The 3 h water absorption by boiling was performed to identify rock macropores which are not easily accessible to water. The test was performed according to STN EN 13755 (2003).

For identification of the content of closed pores, the rock total porosity determined as part of the *Atlas* project was used. This porosity, determined according to STN EN 1936 (2007) and given as a volume percentage, was converted into a weight percentage of the dry weight of the rock.

To calculate the content of (1) micropores and mesopores (N_{ADS}), (2) easily accessible macropores (N_{BULK}), (3) not easily accessible macropores (N_{VOID}), and (4) closed pores of any size (N_C) from the test results, the following equations were used:

$$N_{ADS} = N_{AD98} \quad [\text{wt.}\%] \quad (1)$$

$$N_{BULK} = N_{48} - N_{AD98} \quad [\text{wt.}\%] \quad (2)$$

$$N_{VOID} = N_V - N_{48} \quad [\text{wt.}\%] \quad (3)$$

$$N_{CLOSE} = n * \frac{\rho_w}{\rho_d} - N_V \quad [\text{wt.}\%] \quad (4)$$

where N_{AD98} is the content of adsorbed water, N_{48} is the content of absorbed water after 48 h saturation, N_V is the content of water saturated in pores by 3 h boiling, n is the total porosity as a volume percentage, ρ_w is the density of water, and ρ_d is the apparent density of dry rock.

The content of the four defined pore types of the indicative RPS is given as a weight percentage (weight of water occupying the space in the pores related to the weight of dry rock). This RPS determination has the advantage that no assumptions are made for the final calculation of the pore size or PSD.

4 Test Results

The indicative RPS of the eight rock types used in civil engineering in Slovakia is given in Table 1 and in the bar graphs in Figs. 1 and 2. Table 1 gives the indicative RPS data for each rock type in two lines. The first line shows the number of samples (n), content of micropores and mesopores (M_{ADS}), easy accessible macropores (N_{BULK}), not easily accessible macropores (N_{VOID}), closed pores of any size (N_{CLOSE}), and total porosity (n). All the data except the total porosity are expressed as weight percentages. The total porosity is given as the volume percentage. The second line shows the same data as the first line but in relation to the total porosity; that is, the contents of (1) micropores and mesopores, (2) easily accessible macropores, (3) not easily accessible macropores, and (4) closed pores of any size are expressed as percentage of the total porosity (recalculated to weight percentage). There are minimal, average, and maximal values. The average values in one line give sum 100%. The last part of the second line shows the maximal and minimal values of total porosity as volume percentages. The average value is in the line above.

Table 1. Indicative RPS of eight rock types from Slovakia (80 rock samples)

Rock type	<i>n</i>	M_{ADS}	N_{BULK}	N_{VOID}	N_{CLOSE}	<i>n</i>
		[wt.%]	[wt.%]	[wt.%]	[wt.%]	[vol.%]
Granite ↓(Ø)↑	4	0.16	0.18	0.04	0.04	0.89
		28.8 (39.1) 46.3	21.5 (42.1) 59.7	4.6 (9.3) 15.7	0.2 (9.6) 35.5	0.17 () 1.41
Rhyolite ↓(Ø)↑	5	1.43	2.81	1.14	2.87	17.44
		11.3 (17.0) 23.9	12.2 (34.5) 50.3	1.9 (12.4) 29.8	14.6 (36.1) 57.3	15.18 () 21.33
Basalt ↓(Ø)↑	3	0.67	0.02	0.05	0.26	2.75
		56.5 (66.9) 74.9	0.0 (0.3) 9.4	2.1 (6.1) 11.9	13.6 (27.3) 38.8	2.07 () 3.40
Tuff ↓(Ø)↑	4	7.28	3.63	2.81	3.64	30.62
		36.3 (42.7) 55.0	18.8 (21.3) 24.9	6.3 (15.6) 22.8	2.3 (20.4) 35.6	21.13 () 41.61
Andesite ↓(Ø)↑	17	1.71	0.0	0.18	0.82	6.31
		20.2 (70.8) 116.1	0.0 (15.0) 32.2	0.0 (5.2) 14.4	0.0 (33.3) 80.0	0.61 () 16.98
Sandstone ↓(Ø)↑	12	0.84	0.46	0.16	0.15	3.61
		3.5 (56.6) 93.0	8.8 (25.4) 105.9	0.0 (7.0) 40.6	0.0 (11.0) 73.2	1.16 () 8.69
Travertine ↓(Ø)↑	2	0.71	2.60	1.37	0.23	9.4
		10.9 (14.8) 18.6	50.8 (53.2) 55.6	19.0 (27.2) 35.3	3.0 (4.9) 6.7	9.23 () 9.65
Limestone ↓(Ø)↑	33	0.13	0.29	0.19	0.46	1.93
		2.4 (24.1) 87.6	0.0 (30.4) 86.7	6.9 (11.6) 43.8	0.0 (33.9) 94.3	0.11 () 19.24

↓(Ø)↑ = minimal (average) maximal values

The graphs present the indicative RPSs of granite (Fig. 1a), rhyolite (Fig. 1b), basalt (Fig. 1c), tuff (Fig. 1d), andesite (Fig. 1e), sandstone (Fig. 2a), travertine (Fig. 2b), and limestone (Fig. 2c). For each rock type, there is one graph with four bar groups. The first bar group represents the content of micropores and mesopores. The second bar group represents the macropores that are easily accessible to water, the third represents macropores that are not easy accessible to water, and the fourth represents closed pores. The content of the pores is expressed as a weight percentage. The bars in each group have the same order and represent the same rock sample. For example, the second rhyolite sample is represented by the second bar in the first group of bars (Fig. 1b), by the second bar in the second group of bars, by the second bar in the third group of bars, and by the second bar in the fourth group of bars. This means of visualization of the results of the indicative RPS was used for better presentation of the RPS of the rock types and not the RPS of the individual rock samples, which are not the priority of this paper.

For a better understanding of the indicative RPS data in relation to the routinely tested total porosity, an extra bar graph is given to each indicative RPS bar graph. The extra graph illustrates the total porosity for each rock sample given as a volume percentage.

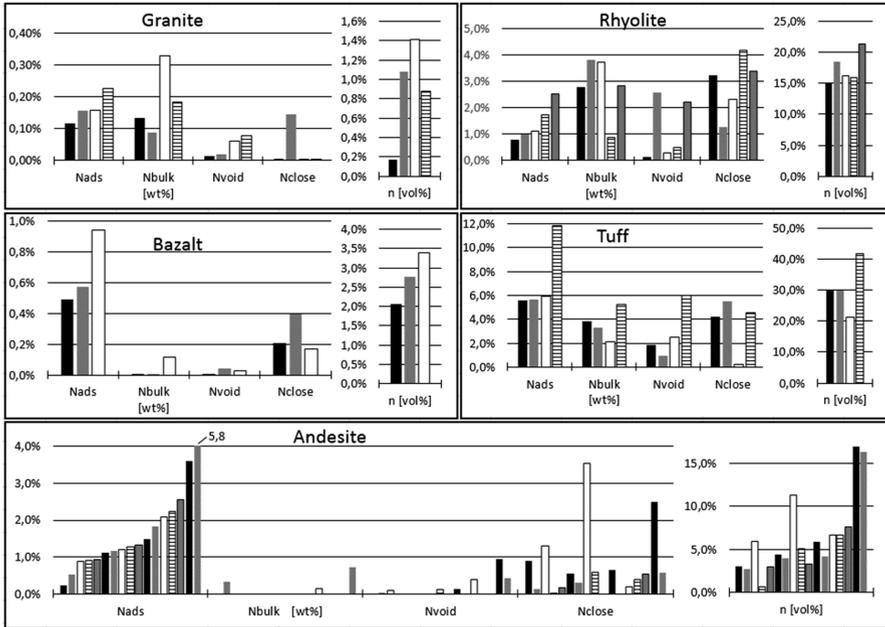


Fig. 1. Indicative RPS of some igneous rocks: (a) granites, (b) rhyolites, (c) basalts, (d) tuffs, and (e) andesites

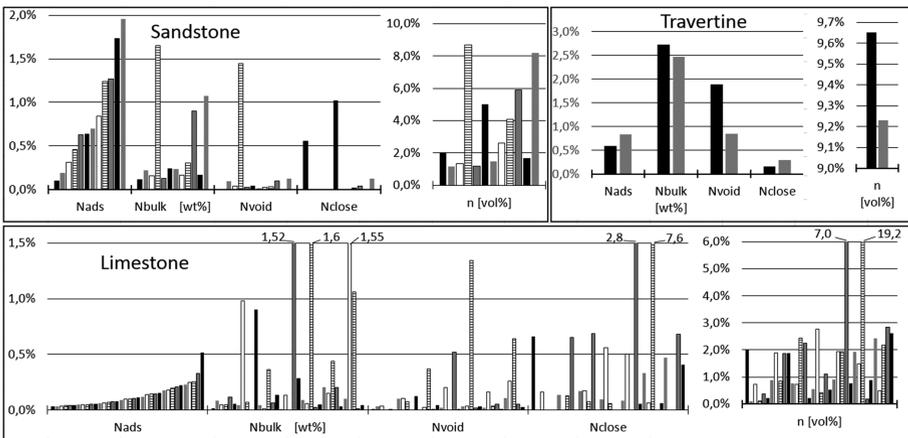


Fig. 2. Indicative RPS of some sedimentary rocks: (a) sandstone, (b) travertine, and (c) limestone

5 Discussion and Conclusions

The results of total porosity (Table 1) for the particular rock types were expected (Matula and Pašek 1986). But the data indicating the RPSs of eight rock types (granite, rhyolite, basalt, tuff, andesite, sandstone, travertine, and limestone) obtained from 80 localities in Slovakia are published for the first time. The data include the average, minimal, and maximal values for each of the four defined pore types of the indicative RPSs of the eight rock types (Table 1) and data for each rock sample from 80 localities (Figs. 1 and 2).

Comparison of the data suggests that each graph shows a unique indicative RPS pattern: unique for each rock type and unique for each rock sample. It can be taken as the rock's "fingerprint", which is characteristic for each rock type and for each locality from which the rock sample was taken. We can also assume that rocks of the same petrological type with similar rock properties which are controlled by RPS also have similar indicative RPSs. This assumption can be used for identification or prediction of the rock properties.

The data from the indicative RPS can be analysed in relation to any other data (permeability, frost resistivity, uniaxial compression strength, tensile strength, and many others) and their possible mutual relationship can be identified.

The advantages of the suggested method are that it is simple (no special sample treatment or laboratory equipment is required), many rock samples can be tested at one time, and the results can be correlated directly with other rock properties.

Acknowledgement. This article was created with the support of the Ministry of Education, Science, Research and Sport of the Slovak Republic through grant VEGA No. 1/0842/18.

References

- Anovitz, L.M., Cole, D.R.: Characterization and analysis of porosity and pore structures. *Rev. Miner. Geochem.* **80**, 61–164 (2015)
- Moh'd, B.K., Howarth, R.J., Bland, C.H.: Rapid prediction of building research establishment limestone durability class from porosity and saturation. *Q. J. Eng. Geol. Hydrogeol.* **29**, 285–297 (1996)
- Benavente, D., García del Cura, M.A., García-Guinea, J., Sánchez-Moral, S., Ordóñez, S.: Role of pore structure in salt crystallization in unsaturated porous stone. *J. Cryst. Growth* **260**, 532–544 (2004)
- Brunauer, S., Mikhail, R., Bodor, E.E.: Pore structure analysis without a pore shape model. *J. Colloid Interface Sci.* **24**, 451–463 (1967)
- Holzer, R., Laho, M., Wagner, P., Bednarik, M.: *Inžinierskogeologický atlas hornín slovenska* (in Slovak, Engineering Geological Atlas of Rocks of Slovakia), ŠGÚDŠ Btislava, 532 p. (2009). ISBN 978-80-89343-29-4
- Hudec, P.P.: Freezing or osmosis as deterioration mechanism of concrete and aggregate? In: *Proceedings of the Second Canadian/Japanese Workshop on Low Temperature Effects on Concrete*, Ottawa, 1–2 August 1991

- Hudec, P.P.: Aggregate and concrete durability as controlled by water and cation adsorption and osmosis. In: *Proceedings Del Seminario International Sobre Tecnologia del Concreto, Concrete Durability*, Monterrey, pp. 32–52 (1993)
- Kaneuji, M., Winslow, D.N., Dolch, W.L.: The relationship between an aggregate pore size distribution and its freeze thaw durability in concrete. *Cem. Concr. Res.* **10**(3), 433–441 (1980)
- Kate, J.M., Gokhale, C.S.: A simple method to estimate complete pore size distribution of rocks. *Eng. Geol.* **84**, 48–69 (2006)
- Labus, M., Bochen, J.: Sandstone degradation: an experimental study of accelerated weathering. *Environ. Earth Sci.* **67**, 2027–2042 (2012)
- Matula, M., Pašek, J.: *Regionálna inžinierska geológia ČSSR* (in Slovak, *Regional Engineering Geology of Českoslovakia*), Alfa Bratislava, 295 p. (1986)
- Ondrášek, M., Kopecký, M.: Rock pore structure as main reason of rock deterioration. *Studia Geotechnica et Mechanica* **36**(1), 79–88 (2014)
- Ordóñez, S., Fort, R., García del Cura, M.A.: Pore size distribution and the durability of a porous limestone. *Q. J. Eng. Geol.* **30**, 221–230 (1997)
- Powers, T.C.: Basic considerations pertaining to freezing and thawing tests. *Proc. Am. Soc. Test. Mater.* **55**, 1132–1155 (1955)
- Prikryl, R.: Durability assessment of natural stone. *Q. J. Eng. Geol. Hydrogeol.* **46**, 377–390 (2013)
- Ruedrich, J., Siegesmund, S.: Salt and ice crystallisation in porous sandstones. *Environ. Geol.* **22**, 225–249 (2007)
- Rouquerol, J., Avnir, D., Fairbridge, C.W., Everett, D.H., Haynes, J.H., Pernicone, N., Ramsay, J.D.F., Sing, K.S.W., Unger, K.K.: Recommendations for the characterization of porous solids (Technical report). *Pure Appl. Chem.* **66**(8), 1739–1758 (1994)
- STN EN 13755: Natural Stone Test Methods. Determination of Water Absorption at Atmospheric Pressure (2003)
- STN EN 1636: Natural Stone Test Methods. Determination of Real Density and Apparent Density, and of Total and Open Porosity (2007)
- Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, A., Rouquerol, J., Siemieniowska, T.: Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.* **57**(4), 603–619 (1985)
- Thommes, M., Kaneko, K., Neimark, A.V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Kenneth, S.W., Sing, K.S.W.: Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical report). *Pure Appl. Chem.* **87**(9–10), 1051–1069 (2015)
- Sun, Z., Scherer, G.W.: Pore size and shape in mortar by thermoporometry. *Cem. Concr. Res.* **40**(5), 740–751 (2010)