



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 performed.

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 termoporfometrii 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.

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

REFERENCES

- [1] Stępień P., *Relationship of water-ice-water phase transformations to pore characteristics of stone materials*. Doctoral Thesis, Kielce University of Technology, Poland, 2018 – in Polish.
- [2] Padhy G.S., Lemaire C., Amirtharaj E.S., Ioannidis M.A., *Pore size distribution in multiscale porous media as revealed by DDIF-NMR, mercury porosimetry and statistical image analysis*. Colloids and Surfaces: A Physicochemical and Engineering Aspects 2007, Volume 300, pp. 222-234.
- [3] Wardlaw N.C., McKellar M., *Mercury porosimetry and the interpretation of pore geometry in sedimentary rocks and artificial models*, Power Technology 1981, Volume 29, pp. 127-143.
- [4] Compendium of Chemical Terminology Gold Book, 2nd ed.; International Union of Pure and Applied Chemistry, 1997.
- [5] Rusin Z., *Technology of Frost-Resistant Concrete*, 1st ed.; Polish Cement: Warsaw, Poland, 2002 – in Polish.
- [6] Sun Z., Scherer G.W., *Pore size and shape in mortar by thermoporometry*. Cement and Concrete Research 2010, Volume 40, pp. 740-751.
- [7] Mikhail R.S., Copeland L.E., Brunauer S., *Pore Structure and Surface Areas of Hardened Portland Cement Pastes by Nitrogen Adsorption*. Canadian Journal of Chemistry 1964, Volume 42.
- [8] Fagerlund G., *Determination of pore-size distribution from freezing-point depression*. Materiaux et Construction 1973, Volume 6, pp. 215-225.
- [9] Fagerlund G., *The critical spacing factor*. Division of Building Materials, Lund Institute of Technology, Report TVBM-7058 1993.
- [10] Rusin Z., Stelmaszczyk G., *Evaluation of the effect of NaCl on water crystallization in aggregate pores*. In Proceedings of the XLII Scientific Conference of the Committee on Civil Engineering of the Polish Academy of Sciences and the Committee on Science PZiTB, Wisła, Poland, 1996 – in Polish.
- [11] Debbas S., Rumpf H., *Chemistry Engineering Science*. 1966.
- [12] Fatt I., *The network model of porous media I. Capillary pressure characteristics*. Petroleum Transportation AIME 1956, Volume 207, pp. 144-159.
- [13] Fatt I., *The network model of porous media II. Dynamic properties of a single size tube network*. Petroleum Transportation AIME 1956, Volume 207, pp. 160-163.
- [14] Fatt I., *The network model of porous media III. Dynamic properties of networks with tube radius distribution*. Petroleum Transportation AIME 1956, Volume 207, pp. 164-181.
- [15] Hudec P., *Deterioration of aggregates – the underlying causes*. Katharine and Bryant Mather International Conference – Concrete Durability, ACI 1987.
- [16] Torok A., Prikryl R., *Current methods and future trends in testing, durability analyses and provenance studies of natural stones used in historical monuments*. Engineering Geology 2010, Volume 115, pp. 139-142.
- [17] Svoboda J., Slovak M., Prikryl R., Siegl P., *Effect of low and high fluence on experimentally laser-cleaned sandstone and marlstone tablets in dry and wet conditions*. Cultural Heritage 2003, Volume 4, pp. 45-49.
- [18] Bager D.H., Sellevold E.J., *Ice formation in hardened cement paste, part I – room temperature cured pastes with variable moisture content*. Cement and Concrete Research 1986, Volume 16, pp. 709-720.
- [19] Bager D.H., Sellevold E.J., *Ice formation in hardened cement paste, part II – steam-cured pastes with variable moistures content*. Durability of Building Materials and Components 1980, Volume 691, pp. 439-454.
- [20] Kozłowski T., *Some factors affecting supercooling and the equilibrium freezing point in soil-water systems*. Cold Regions Science and Technology 2009, Volume 59, pp. 25-33.
- [21] Usherov-Mashak A.V., Zlatkowski O.A., *Relationship between the structure of cement stone and the parameters of ice formation during stone freezing*. Colloid Journal 2002, Volume 64, pp. 217-223.
- [22] Etris E.L., Brumfield D.S., Ehrlich R., Sterling J., Crabtree Jr., *Relations between pores, throats and permeability: a petrographic/physical analysis of some carbonate grainstones and packstones*. Carbonates and Evaporites 1988, Volume 3, pp. 17-32.
- [23] Ishikiriyama K., Sakamoto A., Todoki M., Tayama T., Tanaka K., Kobayashi T., *Pore size distribution measurements of polymer hydrogel membranes for artificial kidneys differential scanning calorimetry*. Thermochimica Acta 1995, Volume 267, pp. 169-180.
- [24] Powers T.C., *The air requirement of frost-resistant concrete*. American Concrete Institute 1975, pp. 1-11.

- [25] Scanziani A., Singh K., Bultreys T., Bijeljic B., Blunt M.J., *In situ characterization of immiscible three-phase flow at the pore scale for a water-wet carbonate rocks*. Elsevier 2018, Volume 121 pp. 446-455.
- [26] Jahnert S., Vaca Chavez F., Schaumann G.E., Schreiber A., Schonhoff M., Findenegg G.H., *Melting and freezing of water in cylindrical silica nanopores*. Physical Chemistry, Chemical Physics 2008, Volume 10, pp. 6039-6051.
- [27] Morishige K., Denoyel R., Wernert V., *Pore-blocking-controlled freezing of water in cagelike pores of KIT-5*. The Journal of Chemical Physics 2007, Volume 111, pp. 9488-9495.
- [28] Riikonen J., Salonen J., Lehto V.P., *Utilising thermoporometry to obtain new insights into nanostructured materials*. Journal of Thermal Analysis and Calorimetry 2011, Volume 105, pp. 823-830.
- [29] Skowera K., Rusin Z., *Physical properties of Devonian limestones from selected deposits in the context of frost resistance*. Mineral Resources Management 2018, Volume 34, pp. 71-84.
- [30] Skowera K., Rusin Z., *Differential Analysis of Volumetric Strain Method Characterization in the Context of Phase Change of Water in Carbonate Rocks*. Materials 2022, Volume 15.
- [31] Modry S., Svata M., Jindra J., *Bibliography on Mercury Intrusion Porosimetry*. House of Technology 1972.
- [32] Cameron A., Stacy W.O., *Chemical Industries*, 1960, Volume 9.
- [33] Leppard C.J., Spencer D.H.T., *A low pressure mercury porosimeter for measuring macropores*. Journal of Physics E: Scientific Instruments 1968, Volume 1, pp. 553.
- [34] Baker D.J., *A low pressure mercury porosimeter*. Journal of Physics E: Scientific Instruments 1971, Volume 4 pp. 388.
- [35] Ritter H.L., Drake L.C., *Pressure porosimeter and determination of complete macropore-size distributions*. Industrial and Engineering Chemistry, Analytical Edition 1945, Volume 17, pp. 782-786.
- [36] Diamond S., *Mercury porosimetry an inappropriate method for the measurement of pore size distributions in cement-based materials*. Cement and Concrete Research 2000, Volume 30, pp. 1517-1525.
- [37] Villadsen J. *Pore structure in cement based materials*. Technical Report 1992, Volume 227.
- [38] Cnudde V., Cwirzen A., Masschaele B., Jacobs P.J.S., *Porosity and microstructure characterization of building stones and concretes*. Engineering Geology 2009, Volume 103, pp. 76-83.
- [39] Skowera K., *Analysis of the pore structure in carbonate rocks, using the method of differentia analysis of volumetric strain*. Doctoral Thesis, Kielce University of Technology, 2021.