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ROCK POROSITY DETERMINATION IN THE HISTORICAL MONUMENTS PRESERVATION

Małgorzata LABUS
Silesian University of Technology

Since ancient times people have used natural stone materials for building purposes. The need of safeguarding historical sites and cultural heritage provoke considering the precise technical characterization of building stones and their changes in weathering processes. In the paper there were listed detailed petrographical analysis used for assessing the quality and durability of the stone material The porosity properties are detected by means of a range of methods, divided into two groups: direct (including thin section microscopy and scanning electron microscopy), which allow direct documentation and measuring of pore space; and indirect (including mercury porosimetry or nitrogen sorption method), which enable calculating the porosity data from the measuring results. Precise knowledge of porosity characteristics, like total porosity, pore sizes, pore size distribution and pore surface is essential for: stone characterization, modeling of transportation processes, assessment of stone durability, interpretation and prediction of the weathering behavior of natural stones, quantification and rating of stone deterioration and evaluation of effectiveness of stone treatments. Basing on the literature digest and own experience, some examples of the stone porosity characteristic application was presented. The variety of natural stones used as construction material, the complicated nature of weathering processes and complex porosity properties determine implication of different analytical methods for stone examination. The most popular method is mercury porosimetry, but it is worth to remember that a reliable characterization of porosity properties can be guaranteed by application of different analytical procedures.

1. INTRODUCTION

Stone elements are used for building purposes more and more frequently, especially in public, monumnetal objects. Stone materials are also needed for the reconstruction of a great number of ancient, historical buildings made of natural materials. During restoration often occurs a need for replacement of stone elements, mainly when dealing with weathering-sensitive historical building stones, eg. calcareous sandstones, soft limestones, etc. The most frequently used as ornamental and dimensional stones are the following lithological types: sandstones, limestones and granites (or other igneous rocks). Because of the various geological origin, all of these types, but sandstones especially, may differ in petrography and mineralogy, which mainly determine their technical properties and wethering resistance [Price, 1996]. Sandstones are the group of the most intensive investigation, what is caused by their lithology variety and the world wide use. A very thoroughful description of research history on sandstone weathering is presented in work by Turkington and Paradise [2005].

All natural stones used as constrution material are affected by natural or anthropogenic weathering processes. This is the reason, there is a need of obtaining precise results on stone properties and their changes due to deterioration.

2. ANALYTICAL METHODS IN NATURAL STONE EXAMINATION

Detailed petrographic analysis (including porosimetry) in needed for assessing the quality and durability of the stone. The specific properties, such as macroscopic characteristic, mineral composition, geochemical composition, microtexture, pore area, hygric properties, mechanical and thermal properties are examined by means of modern analytical procedures (tab.1).

Table 1. The list of laboratory analysis applicable in stone examination [Fitzner, Heinrichs, 2002].

Parameters	Analytical procedures
Visual characteristic Colour, gloss, macrotexture/structure	Hand lens, binocular microscope, colour measuring devices, reflectometer
Mineral composition	Optical microscopy, X-ray diffraction analysis (XDA)
Geochemical composition Chemical compounds, elemental composition, trace elements, soluble salts, pH-value, organic compounds	Wet chemical analysis, scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDX), X-ray fluorescence spectroscopy (XRF), microprobe, atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES), ion chromatography (IC), mass spectroscopy, thermoanalytical procedures
Microtexture Grain shape, grain size, grain contacts, matrix/ground mass/cements, recrystallization, inergrowth/overgrowth, arrangement/orientation of	Optical microscopy with image analysis, scanning electron microscopy (SEM), microtomography, ultrasonic measurements, roughness measuring devices, laser-optical measurements

componenets, inhomogenities, anisotropies interfaces, microcracks, micromorphology, roughness	
Porosity properties Density, porosity, pore size, pore size distribution, pore surface	Pycnometer, optical microscopy with image analysis, scanning electron microscopy (SEM), mercury porosimetry, gas adsorption procedures, X-ray microtomography
Hygric properties Water absorption/desorption, sturation coefficient, water permeability, hygroscopic capacity, isothermal water vapour absorption, water vapour permeability, hygric dilatation – shrinking/swelling	Weighing – mass change (immersion, capillary soaking, sorption/desorption, evaporation), dry cup/wet cup procedure, lenght varaition measurements/dilatometer/extension gauge
Mechanical properties Compressive strenght, tenslie strenght, flexural strenght, elestic modulus, stress-strain-relation, dry-to-wet strenght ratio, static/dynamic hardness, abrasion/wear resistance	Various standardized strenght testing procedures, pull-out test, ultrasonic measurements, scratch/indentation/rebound/impact hradness tests (Schmidt Hammer, sclerometer), drilling resistance measurements, grinding wheel method
Thermal properties Thermal conductivity, heat capacity, thermal resistance, thermal dilatation – shrinking/swelling	Hot plate procedure, hot box procedure, lenght variation measurements/dilatometer/extension gauge

Regarding the aim of this article, the prosimetric measurements should be thoroughly discussed.

3. POROSITY EXAMINATION METHODS

The porosity of a rock, usually given as a percentage, is the ratio of the volume of the pores to the total volume of the rock. Pores in sedimentary rocks are filled with interstitial fluids, e.g. air, water, CO_2, and other gases or hydrocarbons. Size and kind of the pores influence the permeability of the rock. For possible fluid transportion within the rock, pores must be interconnected and of a size rarge enough to exceed capillary forces of the fluids.. Understanding porosity allows one to understand the behaviour of interstitial fluids, i.e. transportation means of soluble salts [Wüst, Schlüchter, 2000].

Experience of the scientists dealing with the rock porosity characteristics has shown that very complex porosity properties cannot be determined satisfactory by only one analytical procedure [Fitzner, Kownatzki, 1991; Fitzner, Heinrichs, 2002; Labus, 2001; Tuğrul, Zarif, 1999]. All of the porosity properties evaluation methods are divided into two groups: direct (including thin section microscopy and scanning electron microscopy), which allow direct documentation and measuring of pore space; and indirect (including mercury porosimetry or nitrogen sorption method) which enable calculating the porosity data from the measuring results.

Microscopic analysis of thin sections is the traditional direct method of porosity investigation. The method enables mineralogial and textural observations, as well as the pore space documentation [Labus, 2000]. The additional use of image analysis has significantly improved statistical evaluation of porosity, pore sizes and pore shapes (fig. 1). Impregnation of the stone material with coloured or UV-fluorescet resin helps the pore determination.

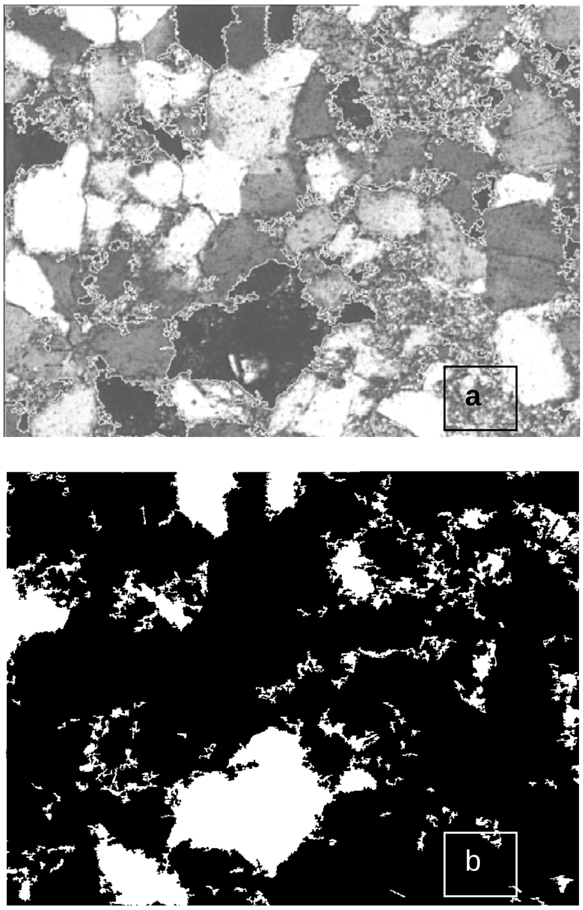

Fig.1. Microphotograph os sandstone sample. Image analsysis helps detecting pores in the sample: a – image transformed into grey colours with contoured pore areas, b – binary map of the previous image

Scanning electron microscopy is a method of resolution up to 0.001 μm, making possible the precise description of geometry and spatial distribution of pores (fig.2). The disadvantage of the method is limited statistical information on porosity (due to high magnification and in consequence the very small sections of the samples) and the need of examination a large number of sections.

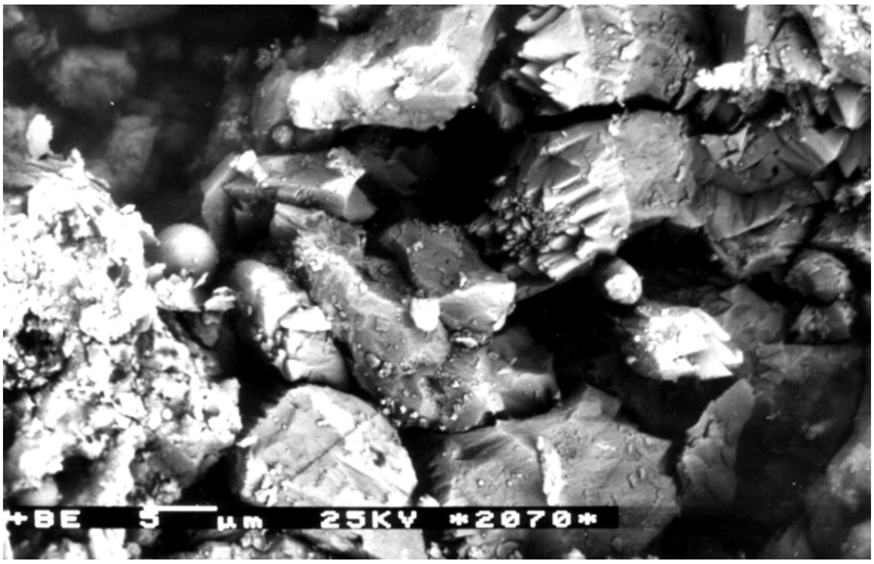

Fig.2. Example of limestone pore space morphology under the scanning electron microscopy (SEM). In central and upper part there are visible secondary calcite crystals; on the left – gypsum crystals and dust spherules.

Mercury porosimetry is the most popular and the most efective measuring method. The advantages of this method are: the small size of the sample and the wide range of pore sizes detected (even from 0.002 μm up to 200 μm). Basing on proportionality between pressure necessary for penetration and the dimension of the pores [Washburn, 1921], the measuring results obtained from mercury porosimetry enable the calculation of total porosity, median pore radius, pore sizes distribution and pore surface.

Nitogen-adsorption method provides the best results for micropores detection, as the measuring range is 0.001 – 0.1 μm. The porosity data are calculated from quantity of gas isothermally adsorbed by the porous material.

Additionally there are used some other complementary methods, such as neutron tomography (detecting water saturation) [Solymar et al., 2003].

The best measuring results are obtained by combining and comparising the results of several methods mentioned above, because the measuring pore ranges partly overlap and partly differs.

Precise knowledge of porosity characteristics like total porosity, pore sizes, pore size distribution and pore surface is essential for [Fitzner, Heinrichs, 2002]:

– Stone characterization,
– Modelling of transportation processes, regarding gaseous and liquid phases,
– Assessment of stone durability,
– Interpretation and prediction of the weathering behaviour of natural stones,
– Quantification and rating of stone deterioration,
– Evaluation of effectiveness of stone treatments.

4. STONE CHARACTERIZATION

The macroscopic appearance of stone material usually allows its rough classification. But in practice more petrographic information is needed. One of the example could be estblishing the origin of stone for the investigation of building history (building process, material transpot, quarries location etc.).

Stone characteristic is frequently needed in quality assessment of replacement stones. Weathered ancient building stones sometimes are replaced by new material, or ruins of the destroyed building have to be rebuilt. The origin of the historic material (variety, quarry) might be not clear and has to be found by comparison with material from existing quarries. If the original material is not available and has to be substituted by a stone from another region, the new material has to be as similar as possible to the original to avoid different weathring behaviour and problems in contact between old and new material [Götze, Siedel, 2004; Jarmontowicz et al., 1994]. The most important factor in such cases is the stone porosity and pore morphology. The thoroughful investigation on stone properties is also conducted when there is a need of appliccation of mineral filling mixture [Smoleńska, Rembiś, 1995].

Replacement is an option that frequently occurs during restoration works when dealing with weathering-sensitive historical building stones, such as calcareous sandstones, soft limestones and weathering-prone sandstones [Dreesen, Dusar, 2004]. The criteria used for replacement of historical building stones are not always based on scientific insight but rather on esthetical and mostly on economic considerations.

All over Europe some scientists and researching groups are trying to prepare petrographical databases of historical building stones and the candidate replacement stones. This could be a useful device, valuable decision-support tool for architects and historians involved in restoration [Dreesen, Dusar, 2004; Fitzner, Heinrichs, 2002; Marszalek, 1994].

5. MODELLING OF TRANSPORTATION PROCESSES

The most critical observations regarding the potential for the stone to take in and hold water, and hence to weather, are given by mercury intrusion porosimetry technique, making possible the evaluation of pore size distribution and relative porosity. Andriani and Walsh [2003] experienced that microporosity or hygroscopic porosity, responsible for atmospheric moisture condesation in the rocks is relevant in the fine and medium calcarenites. For the coarse calcarenites the majority of the pore volume is contributed by macropores that provide rapid fluid transfer into the samples.

Big pores make easier the process of exporting the weathering products, and in the consequence the water soluble salts do not cristallize inside pores and do not crush the stone [Marszalek, 1994].

6. ASSESSMENT OF STONE DURABILITY

The physico-mechanical properties of the rock are essential when assessing their suitability for use as dimension stone, as well as their durability. These data provide appropriate conclusions regarding the propoer use of different materials: tiled floors, indoor or outdoor cladding, etc. [Sousa et. al., 2005]. In case of clastic rocks (eg. sandstones) the main parameter is porosity itself, but in case of limestones (or other carboniferous rocks) and especially granites, the most important problem became microfractures and cracks [Sousa et. al., 2005].

Stone durability is determined not only by each of the porosimeric parameter itself, but by the combination of them. This is the reason for undertaking some attempts to distinguish the weathering-resistnace classes within rocks by means of analysis of capillary pressure curves. The parameterisation of the curves make it possible to distinguish a few groups of the clastic rocks [Labus, 2007]. The identification of the weathering-resistance classes is not dependent on a single feature; such as origin of the samples (lithostratigraphical position), total porosity, grain size distribution or cement content but on a combination of all the mentioned properties.

7. INTERPRETATION AND PREDICTION OF THE WEATHERING BEHAVIOR OF NATURAL STONES

The causes and mechanisms of stone deterioration can only be studied on the basis of good knowledge about the mineral composition and the texture (including pore structure, binding agent, etc) of the building stones [Götze, Seidel, 2004]. The petrographic properties of a stone will influence the weathering processes at least to the same extent as external factors (climate, air pollution). This is the reason a fresh stone from the quarry requires detailed petrographic information, to formulate a prognosis on the expected weathering behavior.

Frost attack is a major cause of building stone decay. Despite considerable progress in understanding frost weathering mechanisms through field observations and experimental work, no one has yet succeeded in reproducing the effects of natural freezing in the laboratory or discriminating between frost-resistant and frost susceptible stones in a way comparable with stone performance in buildings. However Ingham [2005] stated that the combination of total porosity, microporosity, d_{10}, and saturation coefficient data provide an apparently dependable indication of stone performance. It must be explained here that d_{10} is a pore size in µm, where 10% of pores are filled with mercury in porosimetric measurement.

8. QUANTIFICATION AND RATING OF STONE DETERIORATION

There are some properties that are known to change as the stone decays and are helpful in building up an overall picture of the deteriorated stone. These include the porosity and the pore size distribution of the stone and its appearance by visual description [Labus, 1996].

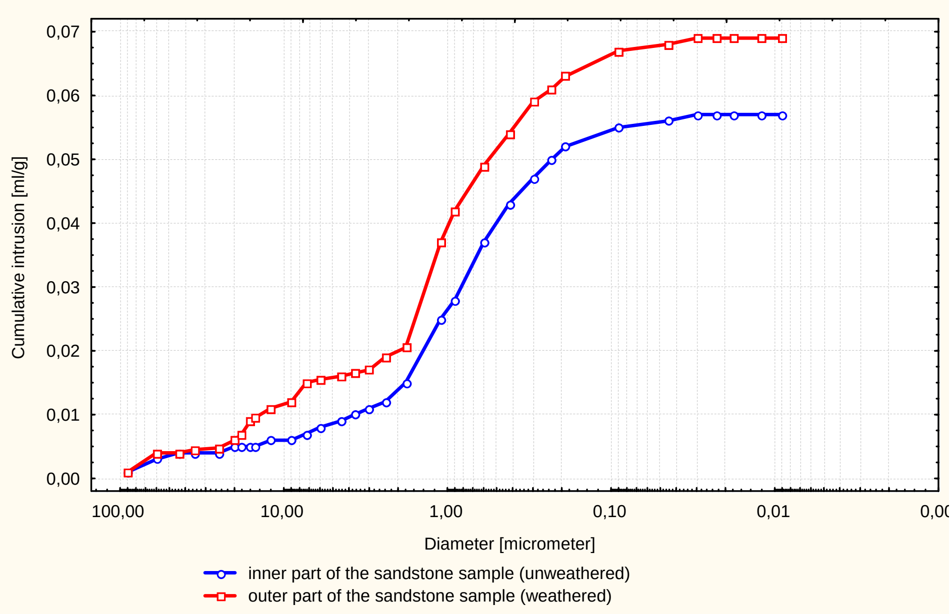

Fig. 3. Capillary pressure saturation curves for sandstone sample from Grodziec castle (Lower Silesia, Poland)

The most effective method is mercury intrusion technique. During the test the mercury fills up large pores under low pressure and small ones under high pressure. The cumulative mercury intrusion per each gram of sample [ml/g] and pore diameter [μm] is shown on the Y and X axes, respectively (fig. 3). Cumulative mercury intrusion is equal to the pore volume. Fig. 3. shows typical curves of cumulative volume plotted versus pore diameter. The effective porosity of weathered samples is generally higher than unweathered samples. There is visible that in the outer (weathered) part of the sandstone block increased the amount of macropores (1,8 – 20 μm). Hence the stone decay may proceed faster, because of the maximum pressure of ice crystallisation in large pores.

9. EVALUATION OF EFFECTIVENESS OF STONE TREATMENTS

The effects of the consolidation of stone elements can be detected using the laser scanner confocal microscopy (LSCM). This method shows 3D distribution of consolidant in the porous network, which is essential for understanding the porosity quantitative data obtained by mercury porosimetry [Zoghlami, Gómez-Gras, 2004].

10. CONCLUSIONS

Combined with the results of the petrographic examination the pore size distribution data become a powerful investigative tool.

The variety of natural stones used as construction material, and the complex nature of weathering processes, determine implication of different analytical methods for stone examination. Precise results on stone properties and their modifications due to weathering processes are essential for effective historical monument preservation measures.

Because of the very complex stone porosity properties, they can not be determined satisfactory by one analytical procedure. A reliable characterization of porosity properties can be guaranteed by application of different analytical procedures.

Porosity characteristic is helpful, or in some cases essential, for: stone durability characterization, rating of stone deterioration or evaluation of stone treatments effectiveness. The weathering-resistivity of the stone could also be detected by means of the porosimetric measurements.

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