Porosity of source rocks eligible for interaction with gases and liquids

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ABSTRACT: The extent of the porosity of different source rocks may vary with their composition, weathering of the bedrock etc. To determine the further use of source rocks, it is necessary to understand and describe their physicochemical properties. Complex textural analyses of source rocks with variable amounts of organic matter were carried out using N_2 and CO_2 sorption, scanning electron microscopy and mercury intrusion porosimetry. The total adsorption of CO_2 ranged from 0.03 to 1.5 mmol/g. The porosity and the pore size distribution varied according to the origin of the studied samples. The porosity ranged from 0.2% to 21%. Lower porosity values indicated a connection with gas capturing. Higher porosity values can be explained by the presence of macropores and larger pores, serving mainly for the migration of gases and liquids. Monitoring of sorption properties can provide a scientific basis for the safe utilization of reservoirs and rock layers.

Keywords: Rocks, porosity, gas adsorption, textural parameters.

1 INTRODUCTION

The genesis of rocks, geological processes and the degree of stress over time, and also chemical composition of rocks, affect the pore network. Precise high-tech instruments and technology are currently available, so it is possible to study the structural and textural parameters of solid porous materials in detail. Knowledge of the interconnections between all factors and the pore network helps us to understand the upcoming physical processes in rock massifs (Guével et al. 2022, Ishola et al. 2022). The network of pores in rocks is variable, and the different pore sizes, shapes and types have a diverse influence on their permeability and on the formation/adsorption/motion of gases and liquids in the pore space (Liu et al. 2020). Even a seemingly non-porous material can have some pores, which are classified to size classes as micropores (< 2 nm), mesopores (2 – 50 nm), and macropores (> 50 nm) (Everett 1972, Thommes et al. 2015).

Molecules migrating from the injection site through macropores and coarse pores can be captured in micropores and in low-dimensional mesopores. Physical adsorption is the most probable mechanism where micropores play a key role (Choma et al. 2021). Conversely, macropores and coarse pores influence permeability, and serve as transport pathways for liquids and macromolecular compounds (Saurabh et al. 2022). Differences between the sorption of organic and inorganic substances are evident in the adsorption process. These are mainly differences in molecular structure. The number of adsorbed molecules depends on the size and shape of the pores in relation to the shape and size of the trapped molecule.

To characterize the surface properties of materials and the migration of molecules over the pores, it is important to determine the maximum possible quantity of adsorbed molecules. Some studies have been focused on investigations of the CH_4 adsorption capacity of coal or shale reservoirs (Weniger et al.2012, Gasparik et al. 2014, Gu et al. 2017, Weishauptová et al. 2017). The adsorption capacity of CO_2 for various rocks has been studied less frequently in the context of prospecting sites suitable for gas sequestration (Řimnáčová et al. 2020, Liu and Liu 2022). Nowadays, the issues of thermogenic gases (CO_2, CH_4) are often discussed, due to their high level of production leading to global changes in the environment. The possibility of capturing these gases in rocks is an innovative trend that is gradually gaining in popularity.

The goal is to understand the relationship between the texture and the permeability of rocks and their adsorption capacity. The possibility of capturing gases, together with gas-tightness, are the most important parameters for the use of various rocks for storing or insulating gases below the surface of the Earth. Sufficiently permeable rock allows the movement of molecules, and microporous materials capture them, while an insulating layer (mostly clay rocks or igneous rocks), will prevent the gases being released from the repository.

2 SAMPLES AND EXPERIMENT

2.1 Studied materials

Rocks of various origin, composition and texture were compared, and their ability to capture gases was determined. A basic description of the materials demonstrates the main differences between them.

- A hard coal sample containing C^d > 80 wt% was collected from a coal seam in the Upper Silesian Coal Basin (USCB).
- Coal-bearing rock consisting mainly of siltstones with variable coaly matter, C^d up to 40 wt%, was collected from a drill hole in the USCB.
- A siltstone sample containing up to 25 wt% grains of silicate fraction, a calcareous, feldspar, and a sandstone sample with a quartz content of above 50 wt%, clays and carbonate cement were both collected from outcrops in the Bohemian Cretaceous basin.
- A granite sample as a relatively homogeneous non-altered igneous rock containing quartz (24 w%), orthoclase (24 w%), plagioclase (43 w%), biotite (5 w%) and other silicates was obtained from a quarry on Rhode Island, USA.

A shale sample containing a low organic carbon content C^d <2.5 wt% and with a high content of clay minerals >60 wt% and plagioclase >15 wt% was collected from an outcrop in the Prague Basin.

2.2 Measurements

The micropore and mesopore parameters of the solid materials were determined by adsorption of gases. The gas molecules were adsorbed onto the surface of the pores by physisorption.

The Hiden Isochema *IGA-100* gravimetric sorption analyser was used for gauging micropore (< 2 nm) parameters by low-pressure CO_2 adsorption at 25 °C and pressure up 0.1 MPa (Medek1977, Dubinin 1967). The CO_2 adsorption capacities and isotherms were also investigated. The approximated Langmuir adsorption capacity was evaluated using the Langmuir equation, the most commonly used model for CO_2 adsorption based on adsorption in a monolayer on a homogeneous surface (Liu, 2006).

The important textural parameter for solid materials is the specific surface area (S_{BET}) measured by low-pressure physisorption of N_2 at -196 °C and up to 100 kPa, using the *SURFER* volumetric sorption device, Thermo Fisher Scientific (Brunauer et al. 1938).

The crucial textural analysis applied for rocks of various origin is mercury intrusion porosimetry, which determines the porosity and the pore size distribution of pores in the size range from 6 nm to 120 μm in diameter. The parameters were measured with a set of two *Pascal EVO 140* and *440* mercury intrusion porosimeters, Thermo Fisher Scientific, with work pressures of mercury up to 200 kPa and 400 MPa, respectively (Washburn 1921).

The method is based on mercury as a non-wetting intrusion fluid. The pores from largest to smallest are gradually filled with the increasing pressure of the mercury. The wide pore size distribution (Figure 1) is calculated from the displaced volume at a given pressure according to Washburn's equation (Washburn 1921).

The network of cracks and the effect of the weathering process of the samples were studied by optical microscopy and by scanning electron microscopy. The character of the cracks material structure can be observed in detail. A *Keyence VHX-6000* digital microscope was used for visualizing the cracks and pores in different light systems (full ring light, mix ring and coaxial light). The *Apreo S LoVac* scanning electron microscope, Thermo Fisher Scientific, was used to identify the composition, pore sizes, mineral particles, etc.

3 RESULTS AND DISCUSSION

The textural analyses and the CO_2 adsorption tests revealed clear differences between various natural materials (e.g. the main parameters in Table 1). The micropores made a minimal contribution to the total porosity. The value was dependent on the presence of larger pores.

Table 1. The textural parameters and the CO_2 adsorption capacity. S_{mic} / V_{mic} – surface / volume of micropores, S_{BET} – specific surface area, S_{Hg} / V_{Hg} – surface / volume of mesopores and macropores by mercury porosimetry, P – total porosity, n – CO_2 adsorption experimental, n_L – CO_2 adsorption approximated by Langmuir equation.

Sample	S_{mic}	S_{BET}	S_{Hg}	V_{mic}	V_{Hg}	P	n	n_L
	(m^2/g)			(cm^3/g)		(%)	(mmol/g)	
Coal	119.86	12.0	4.5	0.0501	35.47	4.6	0.239	1.841
Coal-bearing rock	3.85	4.3	0.6	0.0014	17.11	4.3	0.028	0.036
Shale	24.44	12.9	6.2	0.0086	53.11	12.2	0.129	0.174
Siltstone	3.89	9.6	2.8	0.0013	23.05	5.7	0.033	0.035
Sandstone	0.54	< 0.001	18.2	0.0002	103.48	21.0	0.006	0.006
Granite	< 0.0005	< 0.001	0.2	0.00005	0.9	0.2	0.0011	0.0008

The pore size distributions obtained by mercury porosimetry were different (Figure 1a), and other size classes prevailed in similar types of materials (Figure 1b). In the pore size distribution for rocks with organic carbon content, coal and coal-bearing rocks, the obvious differences lie in the pore volume. Coal has a four times higher volume of pores (up to 3 nm) than coal-bearing rock. Coal also contains the largest proportion (58%) of micropores among all of the samples (Figure 1b). Granite is almost non-porous, and has the lowest values of all parameters.

The volume of micropores is similar in coal-bearing rock 0.0014 cm^3/g and in siltstone 0.0013 cm^3/g, as is the CO_2 adsorption capacity. However, the representation of mesopores is different for these two samples, due to the larger volume of macropores in coal-bearing rock. Shale, in this case carbon-depleted, is a promising material with a pore content sufficient for potential gas storage. There is a relatively high volume of micropores and mesopores, and also a number of large pores suitable for the migration of molecules. The applicability depends on the orientation of the shale layers deposited directly in the environment (Bai et al. 2021). Lower total porosity was observed (<5%) in carbon-rich samples and in compacted rocks such as siltstone (5.7%), which predominantly contains mesopores (Figure 1b, 2a). The sandstone sample was tested as a possible permeable material for water and gases. It has the highest porosity with mainly coarse intergranular pores (Figure 1b, 2b), which is typical for a rock-type material.

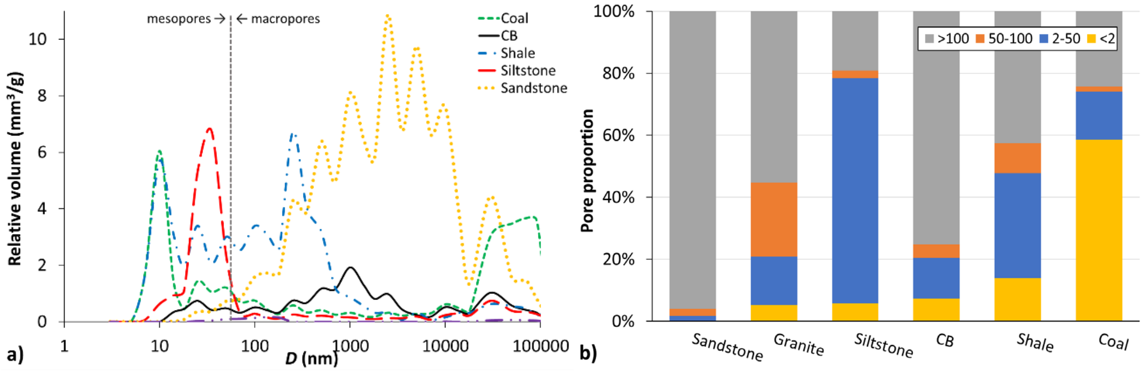

Figure 1. a) Pore size distribution of samples measured by mercury intrusion porosimetry. The volume of pores in the granite sample is close to zero. b) Proportion of pore volume in defined size classes in diameter of the pores (nm), obtained by mercury porosimetry. CB is a coal-bearing rock sample.

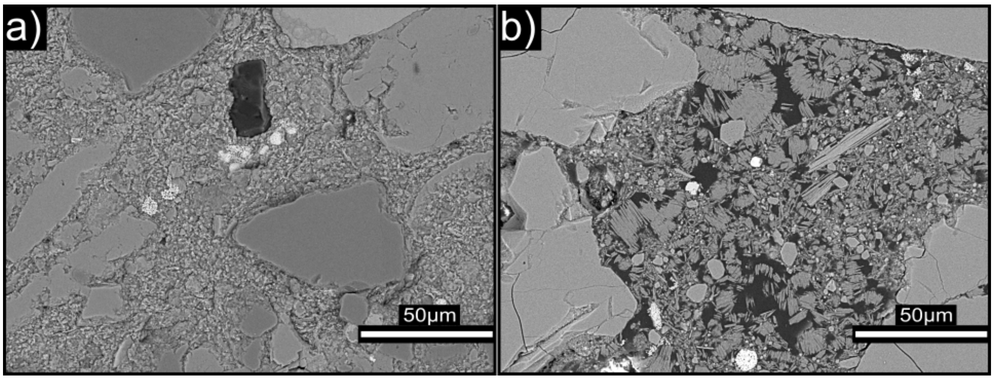

Figure 2. The pore space and a detailed view on the pores between the grains of minerals a) in siltstone and b) in sandstone, obtained by a scanning electron microscope.

The view from a digital microscope shows an example of an almost non-porous rock granite (Figure 3). The main observed minerals are plagioclase and orthoclase (yellow and silk grains). The light grains are quartz, some of which are cracked, as can be seen clearly in image b). The dark and weathered grains are biotite.

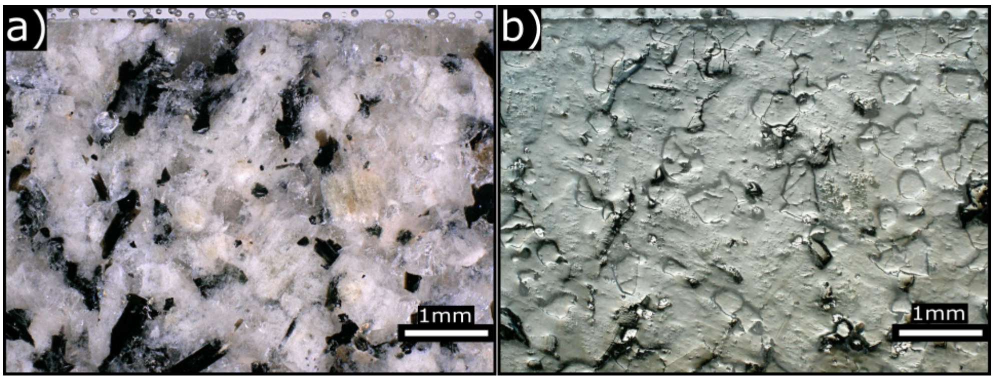

Figure 3. Sample of granite observed in a Keyence VHX-6000 digital microscope. The same part of granite observed under different light conditions, a) full ring light; b) mix ring and coaxial light.

The experimental data on CO_2 adsorption and Langmuir approximation with increasing pressure, are shown in Figure 4. The CO_2 adsorption isotherms fluctuated, with the exception of granite. The most commonly used Langmuir model for CO_2 adsorption is based on adsorption in a monolayer on a homogeneous surface. This means that agreement between the model and the experimental data also indicates homogeneity of the material. The siltstone sample was the most homogeneous material. There was a relationship between micropore volume and Langmuir CO_2 adsorption capacity (R^2=0.9885), while no relationship was observed for other pore classes ($R^2 < 0.3$).

On the basis of pore content, capture of gases with smaller molecules can occur more easily in the pores of coal and shale due to their textural properties, with a high proportion of micropore volume. The adsorption capacity of coal and shale were about 10 times higher than in coal-bearing rock and siltstone. Siltstone can be used for capturing of gases and compounds with larger molecules due to the high proportion of mesopores (75%). Sandstone is a permeable material due to the presence of macropores and coarse pores which serve as transport corridors for gas and water molecules and fluids (Guo et al. 2019). This kind of sandstone can be used for drainage. The granite sample contained the fewest pores and almost no micropores. The representation of other pore sizes is almost proportionally balanced, and the total pore volume is close to zero. This allows granite to be used as an insulating material in reservoirs or as a barrier for water penetration.

The shale sample can be transformed to a greater or lesser extent by environmental conditions such as pressure and temperature, and the application depends on the orientation of the layers directly in the environment. It has sufficient adsorption capacity (> 0.1 mmol/g) for capturing CO_2 and can act as an isolating underlay material for reservoirs for ground water or liquids, or as a top cover for gas reservoirs.

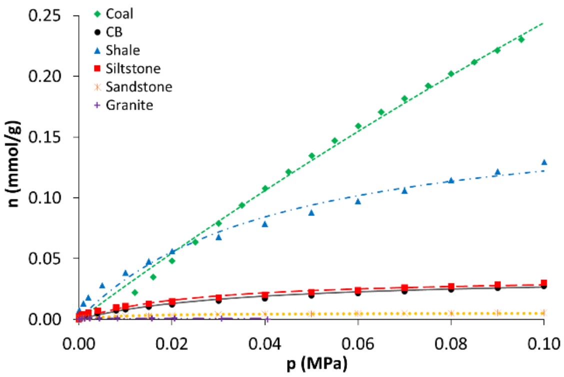

Figure 4. Experimental CO_2 adsorption isotherms (dots) and Langmuir approximation (lines) for samples obtained by gravimetric sorption. CB is coal-bearing rock. The isotherm of granite is close to zero.

4 CONCLUSION

- The total porosity of the studied samples ranged from 0.2 wt% for granites up to 21 wt% related to the presence of different size classes of pores. This can be considered as the typical porosity of the studied materials.
- The sandstone sample has the highest porosity, because it contains macropores and coarse pores, but the content of micropores was close to zero. Due to this fact, the sandstone sample may be used as a drainage material for liquids, whereas materials such as shale and coal are suitable for capturing gases and compounds with small molecules.
- Metamorphic rocks such as granite had low porosity, and are preferably used as an insulating material in gas and water deposits.
- Materials such as coal, shale, coal-bearing rock and compacted siltstone are potentially suitable for capturing CO_2 or for other gas deposition.

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