INACCESSIBLE POROSITY – INSIGHT TO PORE DEVELOPMENT AND SOLUTIONS TO MICP DATA INTERPRETATION

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ABSTRACT
Shale is the most abundant sedimentary rock, which under certain conditions might be both source and reservoir rock. A Micrometer to nanometer scale pore system has been found in organic matter and inorganic matrix of shale reservoirs, which can have significant influence on storage and fluid transport. Peculiar MICP results are observed in 5-15% of the investigated Silurian shales from the Central European formations. These samples have calculated porosity that is greater than total porosity measured with the use of helium pycnometry on powdered samples. This effect is visible only for pores of diameters smaller than 10 nm and produces a characteristic shape of cumulative pore size distribution curves. The combination of helium pycnometry, MICP and adsorption investigations as well as a set of mineralogical measurements (XRD, thin section microscopic investigations, SEM analyses) were performed in order to describe pore space. The results show that inaccessible porosity is created by a large number of isolated pores, which collapse under great pressure of mercury exerted during measurements. The results show that isolated nanopores can create up to 4% of MICP porosity.

INTRODUCTION
A problem of inaccessible porosity was mentioned by several authors. Clarkson at.al. [1] estimated the volume of this part of pore space in the range of 15-30%.Typical situation is presented in Figure 1A and 1B. During laboratory investigations of the Polish shale rocks about 5% of investigated samples show the effect presented in Figure 1C For pore diameters smaller than 10 nm cumulative curve sharply goes up and reaches the volume of porosity greater than open porosity calculated with the use of helium pycnometry, or even greater than total porosity (which is performed using powdered sample). The hypothesis is that this effect is caused by closed porosity which collapsed under very high pressure applied during MICP measurements.

INVESTIGATIONS
More than 2000 samples from the Polish shale basin were investigated. A workflow consisted of density measurements, total and connected porosity investigations as well as nitrogen adsorption [5] and high pressure MICP analyses and petrographical analyses with the use of thin sections and SEM [2,3,8]. This set of analyses was done for all samples.

Special attention was paid to prepare homogeneous samples to all analyses. Total porosity was performed with the use of powder sample while connected porosity, MICP and adsorption low pressure analyses were done using granulated samples (0.5-1 mm) [4,8]. Such granulation conserves porosity and specific surface of investigated rocks (correctness and reliability was checked during independent investigations). Total porosity was measured with the use of powdered sample and this analysis shows some volume of closed pores in great part of investigated samples. These both analyses were done with the use of helium and mercury pycnometry. During MICP analysis full intrusion and drainage curve are completed. In the figures only part of intrusion curve is presented. From 40 m of core analyzed during petrophysical investigations 6 samples were chosen to cover a broad range of properties (Table 1). Additionally, for all selected samples a thin section was prepared and for 3 of them SEM analyses were performed. One can see from Table 1 that sample 2 shows an extreme value of MICP porosity in comparison with total and open. To a lesser degree this phenomenon is also present in sample 5 (helium porosity is almost equal to MICP porosity). Sample 1, 3, 4 and 6 were used in order to prepare reliable pore space characteristics of over 80 % of shale rock matrix. The mineral composition of all samples is very similar. The main minerals are quartz (29-45%), minerals from group muscovite/illite (33-45%), chlorite (6-17%), carbonates (calcite, dolomite, ankerite) (2-6%), feldspar (2-5%), minerals from illite/smectite group (2- 8%) and pyrite and marcasite (3-8%). Generally the analyzed rocks can be described as silty clays (clays with a large admixture of thicker detrital material).

These samples contain from 1 to 7% of TOC. A degree of thermal transformation of organic matter reached the level of gas window. SEM analyses were performed for samples number 2, 3 and 5. These samples were chosen because of their extreme MICP and porosity analyses (total and open porosity). In these samples a mixed pore network is dominant with the presence of interparticle pores (interP), intraparticle pores (intraP) and pores in organic matter (OM) [6,7].

DISCUSSION

MICP measurements show generally low calculated porosity. All factors present during analyses decreased it. These are compressibility of rocks and bad penetrability of mercury. The effect is that 60-70% of the investigated samples show calculated porosity lower than 2,5%. For the rest this parameter could reach 5%.

The results presented for sample 2 from Table 1 show, that in shale rocks there must exist closed porosity, not penetrable even to helium (even for powdered sample). Of course there are no isolated pores in geological time because of molecular diffusion but we are interested in exploitation time. In this time these pore can be treated as isolated (eventually the volume of transport is negligible. Typical shape of such cumulative curve shows inflexion point for diameter lower than 10 nm – it means it is connected with the pressures greater than 1000 at and covers one or two points of cumulative curve (it mean that time is 1-3 min). These parameters indicate that the observed phenomena must depend only on invades of mercury into closed objects.

After reaching inflexion point, cumulative volume occupied by mercury rapidly grows. The key word to this situation is high pressure. When the pressure produced by porosimeter becomes greater than 50 000 psi and still increases, the closed pores start to squeeze and break providing additional volume of pore space. Such great pressure is necessary to displace mercury through nanopore space and additionally break the pore in organic matter. For those types of rocks MICP shows in fact rather total than dynamic porosity.

In order to confirm above stated hypothesis three questions must be answered:

- Is really such part of pore space closed/inaccessible?
- Why do such pores occur only in 5-8% of investigated samples?
- Which element of shale rock is responsible for closed pore space (residual matter or some kinds of minerals)?

Answers to above mentioned questions might be found analysing MICP data and SEM images. For discussed samples (sample 2 and 5) MICP data do not show distribution of diameters (below 10 nm) but only the pressure of collapse. The results show that the only restriction for inaccessible pores is diameter of powdered grains (too big to open that pore space). All surface effects were precisely removed from MICP curves. Figure 2 shows cumulative curves of selected investigated samples. Collapse of sample 2 and 5 started near pore diameter equal to 10 nm. Figure 3 shows incremental curves for the same set of samples. Open part of its pore space is built with pores of diameter 1 – 0.1 μm. The interpretation is that the dominant peak in samples 2 and 5 consists of inaccessible pores, closed accessible pores (open by powdered sample) and even part of open pores. The significance of this effect is even greater because porosity built with pores greater than 10 nm is less than 2% for these samples so the rest of pore space (over 8 and 6%, respectively) is included in great peak below 10 nm. More precise and direct answer to the stated questions is given by SEM images analysis which indicates main differences between pore space in analyzed shale rocks (resolution of instrument equal to 5 nm). Figure 4 shows SEM images of pore space of investigated samples (sample 2 - A, B, sample 3 - C, D and sample 5 - E, F). In sample 2 all OM pores, interP pores and intraP pores were found, which suggests mixed pore network [7]. Pores observed in organic matter (1.9%), which is highly dispersed in a rock sample, achieve the size of 300 nm and are mainly in the center part of the OM grains. Arrangement of pores inside the grains of OM, with no contact with the grains of mineral framework (Figure 4 A), allows for a statement that the pores occurring in OM, in the majority of cases, are isolated. Organic matter is pressed into ductile clay mineral packages, which provide also isolation of OM from interparticle pore space. Moreover, in pyrite framboids interparticle pores between crystals of pyrite were found and pores in OM, which fill and surround framboid structures. A part of pores in framboids might be also isolated by OM. Sample 2 shows also a number of intraparticle pores located in the plaques of clay minerals and detrital grains and interparticle pores (intrerP) between detrital grains. Presented SEM images suggest that differences between MICP and helium pycnometry might be associated with isolated pores in OM and framboidal pyrites. Pore space of sample 5 (Figure 4 – E, F), in which similar effect like in sample 2 is observed, can also be described as mixed pore network. Both pores in OM, interP and intraP pores were distinguished. Differences from the sample 2 are associated with the location of the pores in the OM. Most of these pores adhere to the detrital grain boundaries and clay minerals, and probably creates the system connected to the system of interparticle pores. These pores are larger than the pores observed in sample 2 (the size reaches 800nm). OM (3.66%) is also highly dispersed in the rock matrix. Differences are also observed in the pores of the pyrite framboids, which are filled with less OM resulting in fewer pores isolated. Such structure of the pore space results in lower number of isolated pores what consequently leads to slight difference between MICP (8.25%) and helium porosity (6.12%). In sample 3 inerP and intraP pores are two main types of pores observed. Although most of the OM do not contain pores, very few pores in OM might be distinguished. The size of such pores is in the range of several nm. The position of OM (7.16%) in the rock matrix indicates strong compression of OM between detrital grains and ductile clay minerals. Often thin laminas of OM are observed. No pores in OM indicates a different type of OM, requiring a greater activation energy for the generation of hydrocarbons. Rock-Eval studies showed that very high content of residual carbon (RC) indicating a very low transformation of OM in discussed sample.

Analyzing such samples another question arises: is existence of such isolated pores possible? In geological time it is not. Molecular diffusion is fast enough to connect all empty spaces in rocks. But this scale is not interesting for us. Our problem is: are such pores accessible during exploitation of shale well (up to three years). The first visible effect is difference of porosity between granulated and powdered sample. Difference between total and connect porosity shows volume of pores opened in powdering process. Empty spaces opened during collapse of pore space were also inaccessible by helium even for powdered sample. Dimensions of these closed pores are restricted only by dimensions of powder grains not by Washbourne formula. Taking into consideration very short path of migration in powdered sample and helium penetrability we can conclude that possible influence of this part of pores space on total flux will be negligible.

CONCLUSION

1. In part of examined samples there exists closed porosity, inaccessible even to helium. These pores can be opened only by collapse of rock due to high pressure. It manifests during high pressure MICP on the cumulative curve as a great peak of pores below 10 nm range of diameter. However, interpretation of MICP data needs to be performed very carefully, because as the results show, the pore sizes reflected by that peak are much higher than 10 nm. That is why, in order to depict pore size distribution, additional investigations are needed.
2. Inaccessible porosity is found in dispersed organic matter and in framboidal pyrite. Single pores can reach diameters of several hundreds of nanometers.
3. Higher value of MICP porosity than of open porosity might be considered as a parameter that indicates the occurrence of dispersed organic matter (highly thermally transformed) in the rock sample.
4. A lower value of MICP porosity than open porosity in the shale samples suggests the presence of OM that is considered as a low thermal maturity OM (another type of OM) or in this sample pores are filled with asphaltenes (as a result of bitumen migration).

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REFERENCES

1. Clarkson C.R., Solano N., Bustin R.M., Bustin A.M.M., Chalmers G.R.L., He L., Melnichenko Y.B., Radlinski A.P., Blach T.P., "Pore structure characterization of North American shale gas reservoirs using USANS/SANS, gas adsorption, and mercury intrusion" *FUEL*, (2013) 103, 606-616

2. Clarkson C.R., Wood J., Burgis S., Aquino S., Freeman M. "Nanopore-Structure Analysis and Permeability Predictions for a Tight Gas Siltstone by Use of Low-Pressure Adsorption and Mercury –Intrusion Techniques." *SPE* (2012) -155537

3. Curtis M.E., Cardott B.J., Sondergeld C.H., Rai Ch., S., "Development of organic porosity in the Woodford Shale with increasing thermal maturity." *International Journal of Coal Geology, (*2012), no 103, 23-31

4. Howard J.J., "Porosimetry Measurement of Shale Fabric and Its Relationship to Illite/Smectite Diagenesis." *Clays and Clay Minerals*, (1991) v.39, no.4, 355 – 361

5.Kuila U., Prasad M. 2011: Surface area and pore size distribution in clays and shales, SPE-146869

6. Loucks R. G., Reed R. M., Ruppel S. C., Jarvie D. M., "Morphology, genesis, and distribution of nanometer-scale pores in siliceous Mudstones of the Mississippian Barnett shale." *Journal of Sedimentary Research* (2009), v. 79, 848-861

7. Loucks R.G., Reed R. M., Ruppel S. C, Hammes U., "Spectrum of pore types and networks in mudrocks and a descriptive classification for matrix-related mudrock pores." *AAPG Bull*. (2012), v.96 no 6, 1071-1098

8. Such P., "Porosity: what does it mean in shale gas reservoirs." *Nafta-Gaz*, (2014) no7, 411-415

Table1. Porosity data

Sample ID	MICP porosity (%)	Total porosity (%)	Open porosity (%)
1	4.98	5.49	2.56
2	10.22	4.62	0.70
3	1.76	8.57	3.29
4	2.88	8.41	8.40
5	8.25	8.53	6.12
6	4.19	8.00	1.85

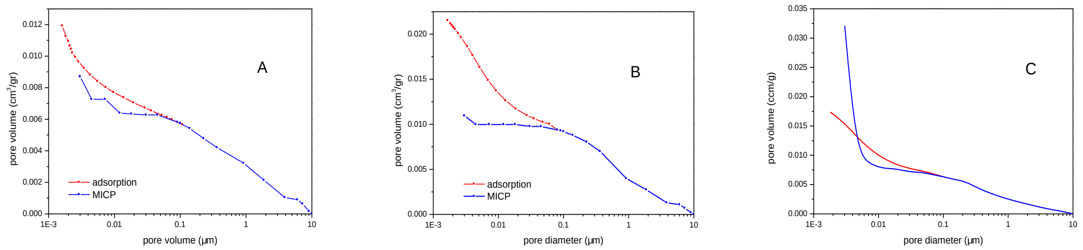

Figure 1. Comparison of MICP and adsorption pore size distributions cumulative curves calculated using BHJ and Halsey theory. MICP – blue curve, Nitrogen adsorption – red curve. Merging procedures was applied to combine both cumulative curves. Of course MICP curves shows volume of porosity in a function of pore throats while adsorption shows pore bodies. Obtained results are similar to results obtained by Clarkson at al. Typical curves are presented in Fig A and B. Adsorption curve in fig A could be shifted during greater values of diameter but because of plateau or near plateau part of MICP curve total volume of penetrated pores can be reliably estimated. Fig B shows the same run of both curves in some range of diameters and it also give us opportunity to calculate pore volume. Figure 1C – calculated total volume is lower than calculated MICP porosity

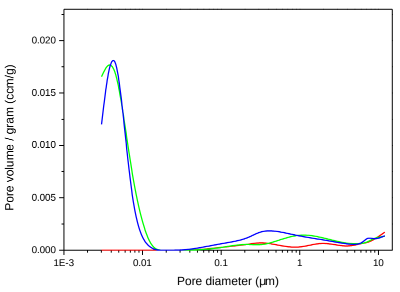

Figure 3. Incremental curves
(sample 2 – green, sample 3 – red sample 5 – blue)

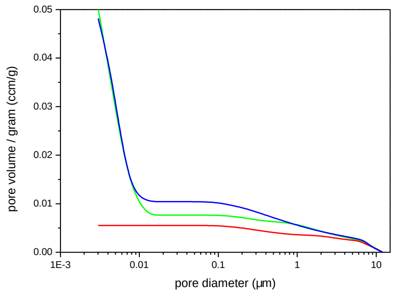

Figure 2. Cumulative curves for 3 investigated samples
(sample 2 – green, sample 3 – red sample 5 – blue)

Figure 4 Types of pore space in analyzed samples. A, B – sample 2, B, C sample 3, E, F – sample 5.