

# STUDY OF ROCK PORE SPACE BY COMBINATION OF DIRECT AND INDIRECT TECHNIQUES

Aleksandr Denisenko, Ivan Yakimchuk, and Boris Sharchilev  
Schlumberger

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## ABSTRACT

During the last few decades, Nuclear Magnetic Resonance (NMR) has become known in the petrophysics community as a convenient and efficient technique for studying pore space structure. NMR is an indirect method of pore size evaluation based on a proportionality between relaxation times and surface-to-volume ratio for each pore. The coefficient of proportionality (surface relaxivity) reflects the ability of mineral pore surfaces to increase the relaxation rates. It is common to use a single value of relaxivity for each core, which assumes that the pore surface properties within a small sample are sufficiently homogeneous [1]. However, in some cases the sample might contain pores with different surface properties that result in a range of relaxivity values characterizing the rock. Induced magnetic susceptibility arising from different sources, for instance metal ions, paramagnetic ( $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) or, in a worst-case scenario, ferromagnetic metallic iron (Fe), leads to interpretation uncertainty of  $T_2$  spectra due to the influence of the internal gradient effects on the transverse relaxation rate. Fortunately, constructed  $T_1$ - $T_2$  2D dependences help to monitor the discrepancies in  $T_1$  and  $T_2$  spectra, which are affected by surface property changes and magnetic susceptibility contrast within the sample structure.

In this study, we implemented several proven techniques designed to evaluate pore structure directly. This approach allows for checking consistency of pore size distribution obtained by NMR  $T_1$  at each pore scale. The results of X-ray microtomography (XmCT) imaging validated the large pore scale or slow  $T_1$ -decays and Scanning Electron Microscopy (SEM) results confirmed the small pores described by the fast NMR responses. The repeatability of all calculated distributions indicates similar abilities of all pore surfaces with the sample to relax the hydrogen nuclei or close relaxivity values responsible for  $T_1$ -relaxation in large and small pores for the observed sandstone rock.

## INTRODUCTION

One of the fundamental pieces of information derived from laboratory core analysis is the pore size distribution. The classical and widespread methods used for pore size distribution are thin-section petrography and mercury intrusion porosimetry. Recently, a number of alternative technically complicated approaches have been proposed by the scientific community, including nuclear magnetic resonance (NMR), X-ray microtomography (XmCT), and scanning electron microscopy (SEM). Each of these

methods, as with any experimental technique, has its advantages and drawbacks. For example, the modern nano-CT devices provide resolution down to 50 nm, but the small field-of-view for such scanners raises concerns whether the imaged volume is representative of the overall sample. In contrast to XmCT, laboratory NMR machines detect hydrogen nuclei of fluid molecules constrained in pores of any geometry. Therefore, NMR is an indirect method for pore size evaluation based on a nearly linear relation between relaxation times and surface-to-volume ratio of a pore NMR distribution covers the broadest range of pore sizes, up to 5 orders of magnitude, far greater than any one direct technique.

Every pore-scale measuring method has its own specific limitation to the size range each can detect. A possible solution that eliminates the limitations of individual method is to perform the study by using a combination of methods instead. The key questions in such a combination of techniques are the analysis accuracy and defining the roles for each method. Research scientists have to understand the interpretation workflow and justify the applicability of each method for the particular case. In other words, the combination of different methods should lead to collaborative and consistent results instead of loosely combined data fragments.

## **METHODS AND APPARATUS**

*NMR* – All of the NMR measurements were carried out using an Oxford Instruments low-field spectrometer, which includes a MARANi-Pharmasence magnet block equipped with a 22×22 mm probe, and DRX-HF electronic control system. The resonance frequency of 20.6 MHz corresponds to hydrogen nuclei spin precession in a ~ 0.5 T magnetic field. The  $T_2$  and  $T_1$  relaxation decays were recorded by ordinary Carr-Purcell-Meiboom-Gill (CPMG) and inversion-recovery with echo detection. We used an echo time of 100  $\mu$ s and numbers of echoes sufficient to complete a decay, 48 logarithmically spaced delay times over the range  $10^{-4}$  to  $10^1$  s, and a relaxation delay of 10 s. The measurement temperature was 34°C. Methodically, all NMR procedures and consequent collation with XmCT data were performed in accordance with our previous work [2].

*XmCT* – We used two laboratory table-top micro-CT scanners in this study [3], [4]. The Using a 100-keV radiation energy for both systems a pixel size of 2.2  $\mu$ m was obtained for the Bruker SkyScan 1172 and 0.5  $\mu$ m for the ZEISS XRadia Versa XRM 500 on studied 8 mm diameter plug without contrast agents. The reconstructed 3D image of a core sample was segmented into two classes of objects: pores and minerals. The most intuitively obvious approach for individual pore analysis consists of separating a whole pore space into a set of individual pores and analyze each pore separately. General algorithms for pore separation are based on watershed techniques [2]. The equivalent spherical diameter is one of the most commonly used quantities for estimating the effective size of the object body. Finally, the histogram of the size values can be constructed.

An alternative method for calculation of the object size distribution is based on sphere fitting inside of the 3D structure [2]. The approach is also applicable for 2D images by using circles instead of spheres. In our opinion, this algorithm more accurately describes the pore space and more correctly fits with the physical phenomena in support of the NMR method, as the magnetic spin relaxation dominated by the nuclei diffusion and subsequent collisions with the grain surfaces. Therefore, the limits of molecules spreads correspond to spherical areas at any time and the sizes of spheres are constrained with the pore body ones.

**SEM** – In comparison with XmCT the SEM method provides much higher image resolution (up to 1 nm per pixel), but only the surface of the sample is investigated. For accurate studying of pore space structure, a special sample preparation procedure should be performed. This special procedure includes epoxy filling, mechanical cutting, multistage polishing and final coating of the surface by a conductive material. Using an image-stitching option makes it possible to cover rather large surfaces limited only by the SEM chamber and the sample holder. For example, scanning an 8×8-mm area with 1-nm resolution is essentially feasible, but would produce an enormous image of 8 million × 8 million pixels (>50 TB). In the work being reported in this paper, a 100-nm resolution was used (image size = ~80,000 × 80,000; file size = ~8 GB).

**Focused Ion Beam coupled with SEM** – The focused ion beam inside SEM (FIB-SEM) allows for obtaining a stack of 2D images of the sample's internal structure of some subsurface volume by ion etching of the surface slice-by-slice [5]. Thus, this method produces 3D images with resolution near that of the SEM. Unfortunately, the field of view is rather small (10 — 20 μm).

**Sample preparation** – The sample for study was cleaned and dried sandstone rock of West Siberia province, 8 mm in diameter and 10 mm long. The plug was saturated with 20 g/l NaCl solution, and placed in hermetically sealed cell for NMR measurements.

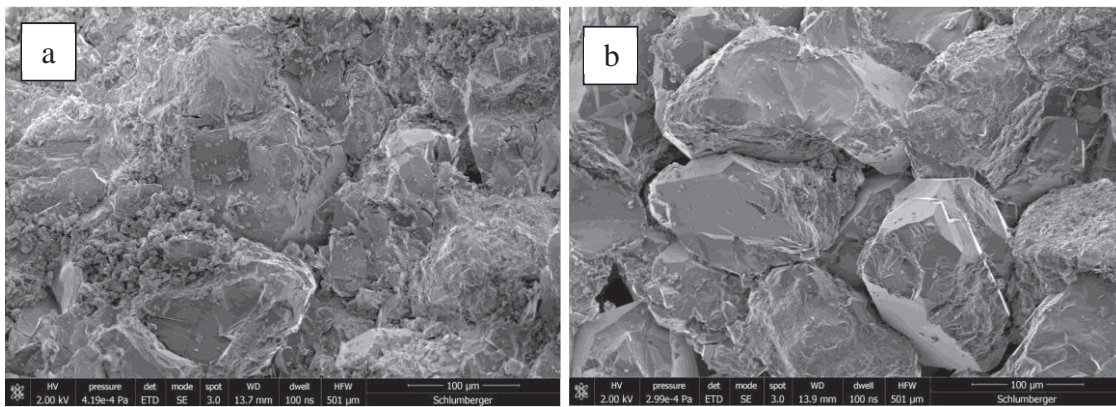
## EXPERIMENTS AND DISCUSSION

Before consolidation the different pore structure evaluation methods, we analyzed the sample size representativeness and the influence of core preparation techniques on rock integrity and invariance. The comparison of NMR evaluation result on 22-mm and 8-mm samples cut from a single core gave rise to this investigation. The dissimilarity in short relaxation times of  $T_1$ - $T_2$  maps for different cylinder diameters indicated alteration of microporosity structure compared with the consistency and stability of large pores. Plugs drilling and especially a cooling fluid could cause the effect as a tap water was used during the coring. The swelling of clay minerals and consequent dispersion of clay particles along with migration of disrupted small solids at the cylinder near-surface area alter rock properties and consequently, pore size distribution. Using the SEM, we analyzed the structure and elemental alteration near the edges and in the central part of the 22-mm diameter sandstone core (Figure 1). As is clearly shown, the internal core structure is complicated, with rough and sharp points protruding from it. Many clay and

mud particles are observed near the edges of core, although rounded and clean grains prevail in the center.

Therefore, many factors determine the representativeness of cores and we had to be confident with our investigation, even with very homogeneous rock. For that reason, we performed all of the experiments on single-core cylinders or their fragments.

As a result, the study of void space structure was performed on 8-mm diameter by 10 mm in length cylindrical samples. This core size allows for performing experiments on the same sample using the NMR, XmCT and 2D SEM techniques. The FIB-SEM as well as Xradia XmCT scans were conducted on a small part of the rock cylinder. The collation of different methods of observing pore structure was studied on well-sorted sandstone rock samples. Initially, we adjusted the  $T_1$  distribution with two XmCT spectra in terms of relaxation activity value, which was a tuning parameter of NMR and XmCT spectra coincidence.



**Figure 1:** SEM images of edge (a) and central parts (b) of granular sandstone core. Note the visible alteration and contamination of pores near the core edges.

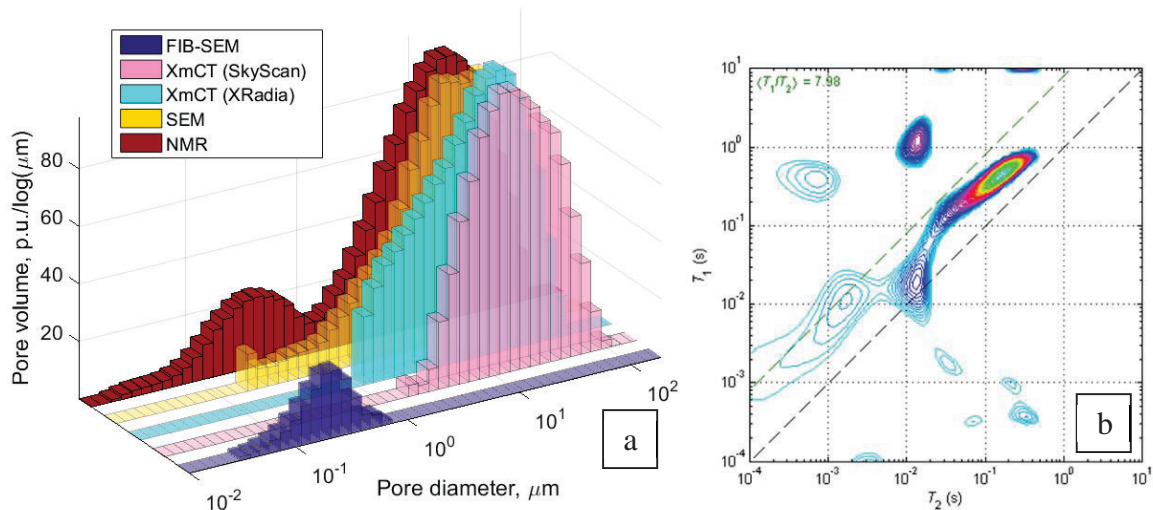
Regardless of the applied model, the relaxation activity value mathematically represents the proportionality coefficient between pore sizes and relaxation times. We adopted the spherical pore model assumption:  $r = 3\rho T_1$ , where  $r$  – is a pore radius,  $\rho$  – a relaxivity; as the inscribed sphere method used to calculate the pore sizes using XmCT data. It is essential that the coefficient of proportionality between relaxation times and pore diameters, a complicated value, be influenced by pore surface magnetism and wettability, as well as pore shape. Therefore, it is more correct to name the coefficient  $\rho$  as being pseudorelaxation activity or cumulative parameter responsible for surface relaxation properties defined by mineralogical composition of rock and a value of specific surface. The fitting of  $T_1$  with XmCT data (Figure 2) provides a value of tuning parameter, relaxivity  $\rho_{T_1} = 7.4\mu\text{m/s}$  and a volume of “invisible” microporosity equal to 29.7% of the total capacity; i.e., 8.2 p.u. The microporosity is the amount of the volume, which is below the XmCT scanner resolution ( $\sim 5\mu\text{m}$ ), i.e., the difference between the NMR and the XmCT porosities.



Combining  $T_2$  spectra with XmCT data leads to a relaxivity value  $\rho_{T_2} = 24 \mu\text{m/s}$ . Higher values of the relaxation activity of the pore surface in the second case were caused by the various physical mechanisms of longitudinal and transverse relaxation. Overestimation of  $\rho_{T_2}$  values is caused by the diffusion relaxation mechanism that originated from significant internal magnetic gradients, as  $T_2$  is strongly influenced by echo time. These gradients exert tremendous influence on NMR studies with high-value of magnetic field (20.6 MHz). Differences in  $T_1$  and  $T_2$  spectra are clearly observed on a 2D  $T_1$ - $T_2$  map (Figure 2). Notice the area with an inflated  $T_1/T_2$  ratio in the upper-center region on the map. This separate region can be associated with the presence of the hydrocarbons remaining after extraction and/or contrasting pore surface areas with high-content paramagnetic centers that enhance local diffusion processes, and hence, drastically reduce  $T_2$ .

The differences of the  $T_1$  and  $T_2$  spectra described previously forced us to use longitudinal relaxation as internal-free gradients; therefore, a more reliable mechanism for observing pore size characteristics of multiminerall rock composition.

The Xradia machine provides enhanced image resolution at the cost of sample size. We use this scanner to verify the consistency of the XmCT results. Both XmCT machines provide similar results; i.e., precisely duplicating large pores (right  $T_1$  mode) in the calculated NMR pore size distribution (Figure 2).

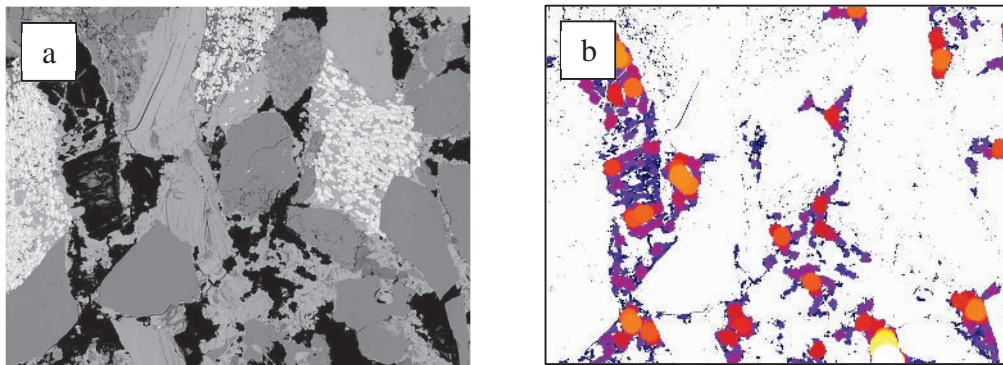


**Figure2:** (a) Pore size distributions measured by different analysis methods (NMR  $T_1$ , XmCT, SEM, and FIB-SEM); (b)  $T_1$ - $T_2$  map for the sandstone rock, West Siberia (Quartz=62%, Feldspar=20%, Clays=18%,  $\Phi$ =27.8%, Permeability=407mD).

After conducting XmCT and NMR measurements on the cylinder, we obtained a small portion of the sample and performed an FIB-SEM study to characterize microporosity, which is invisible to common XmCT machines. Figure 2 also shows the resulting pore size distribution. The reconstructed image of the sample 3D pore geometry structure helped to visualize and detail small grains, their surfaces, internal structure of feldspars,

and clay mineral skeletons. The high-scale resolution of this method allowed for us to construct the distribution of tiny pores with sizes in the range of 50 nm to 1000 nm. The disadvantage of the FIB-SEM technique is its very small field of view ( $15 \times 15 \mu\text{m}$  in our case), which could reduce measurement representativeness of a specimen, making volumetric evaluation difficult. Fortunately, the sample we studied was very homogeneous sandstone rock, and similar to the FIB-SEM field of investigation areas, which could be estimated on the 2D SEM image with a larger scale. The FIB-SEM method was used for an approximate estimation of the volume of rock, which is attributed to microporosity and construct the pore size distribution in porosity units (Figure 3). The sphere fitting technique was also applied during the evaluation of pore size distribution based on SEM data. Suitable repeatability of small pore sizes distributions constructed by NMR and FIB-SEM identified a similarity in the surface abilities to relax the hydrogen nuclei saturating the core. In other words, the pseudorelaxivity value obtained by XmCT and NMR spectra matching is near the small pore region. This result indicates a consistency by combining the input of mineral composition and a specific surface value of the rock matrix.

The SEM image itself contains information about pore scaling. The advantage of the SEM method is the larger field of view compared with the FIB-SEM image, but the data are 2D only.



**Figure3:** (a) SEM slice image examples and resulting pore geometry evaluation technique based on inscribed spheres (b). Each color defines a sphere diameter

This explains why we had to estimate the pore areas instead of volumes and used a circle-fitting technique, which is analogous to previous FIB-SEM technique. Constructed distribution reflects approximate characteristics of pore structure over a wide range of sizes (0.4 — 40  $\mu\text{m}$ ).

## CONCLUSIONS

The results obtained in this study describe the advantages and drawbacks of different methods of pore structure evaluation. These results point out the necessity for using an integrated study of the pore space structure of rocks by the different methods to investigate pore sizes over a wide scale range and resolution. This detailed investigation using

several methods allows for avoiding uncertainties in the interpretation of NMR spectra and consequent evaluation of relaxation activity factors for different pore scales. Sample size as well as core preparation techniques have a strong influence on pore structure and their consistency in different acquisition methods.

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## **REFERENCES**

1. Kleinberg, R., 1994, Pore Size Distribution, Pore Coupling, and Transverse Relaxation Spectra of Porous Rocks, *Mag.Res.Imag.*, 12, 2, 271 - 274.
2. Denisenko, A. and Yakimchuk, I., 2014, X-Ray Microtomography and NMR: complimentary tools for evaluation of pore structure within a core, Society of Core Analysts Symposium, 8–11 September, Avignon, France.
3. High-resolution micro-CT. Bruker Micro-CT. SkyScan 1172, <http://www.skyscan.be/products/1172.html>.
4. High resolution 3D X-ray Microscopes. ZEISS Xradia, [http://microscopy.zeiss.com/microscopy/en\\_de/products/x-ray-microscopy.html](http://microscopy.zeiss.com/microscopy/en_de/products/x-ray-microscopy.html)
5. Lee, E., et al, 2004, 3D Materials Characterization using Dual-Beam FIB-SEM Techniques. *Microscopy and Microanalysis*, 10 (Suppl. 02), 1128-1129.