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Features of the study of the pore space of the core by the method of nuclear magnetic resonance

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Introduction

Many processes of interest to industry and society are associated with the presence of liquids in a porous medium. Biopolymers, catalysts, native and artificially created membranes – most of the materials that surround us are porous. One of the areas in the study of porous materials is rocks – cores. Today, there is an extensive list of classical methods [1] that can be used to characterize the porous space of a core, however, in most cases, their use is associated with the need to violate the integrity of the sample. In this regard, the non-invasive method of nuclear magnetic resonance (NMR) has been widely used in oil field geology and geophysics in recent decades [2]. In this paper, we will demonstrate some features that need to be paid attention to when conducting studies of the porous space of a core using the NMR method.

Materials and methods

Atlantic sal NMR studies were performed on a dolomite core sample. To determine the open porosity, the core sample, previously dried to a constant mass, was saturated with a proton-containing fluid - water. According to the results of preliminary tests, the open porosity of the core is ~ 5%. For a number of tests, the core sample was saturated with an aqueous solution of copper sulfate.

To study the pore space of the core, a comprehensive approach was used based on the analysis of experimental data from a number of NMR techniques:

1. Spin-spin relaxation. Relaxation attenuation was recorded using a CPMG pulse sequence;

2. NMR cryoporometry. Based on the data obtained by the Solid-echo pulse technique, the dependence of the fraction of the solid-state component of the NMR signal (p_s) on temperature is constructed;

3. DDIF. Using internal magnetic field gradients for spatial localization of diffusing molecules.

Results

Well The non-exponential relaxation decays obtained by the KPMG method were presented in the form of a spectrum (Figure 1a) of relaxation times using the original program "Spectrum of spin-spin relaxation times" developed at the Department of Physics of Molecular Systems of the Institute of Physics of Kazan Federal University. According to [3], the obtained spectrum of spin-spin relaxation times can be formally presented as a pore size distribution (Figure 1b) by applying the following relationship:

$$\frac{3}{r} = \frac{1}{T_2 \rho}$$

where ρ is the relaxivity value, which essentially determines the degree of interaction of liquid molecules with the pore surface and can depend on many, a priori unknown, factors. Based on literary sources, for example [4,5], devoted to the study of dolomite cores, ρ≈1 μm/ms was adopted as a trial value for the relaxation characteristic.

Figure 1 shows the spectrum of spin-spin relaxation times, as well as the pore size distribution.

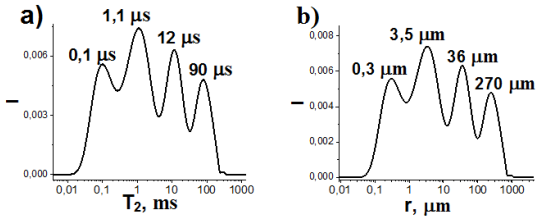

Figure 1. a) Differential spectrum of spin-spin relaxation times for a core sample saturated with water; b) Pore size distribution. Each peak is labeled with the average spin-spin relaxation time (a) and the average pore size (b)

Thus, within the framework of the accepted assumptions, at least four pore size regions with a minimum of ~ 0.3 μm and a maximum of ~ 270 μm were recorded in the core sample under study. Usually, in most studies based only on the analysis of relaxation time spectra, the study is completed at this stage.

Nevertheless, simple calculations indicate some inconsistencies in the obtained results. For example, the estimate of the pore size of 270 μm, made for $T_{2max} \approx 90$ ms at $\rho = 1$ μm/ms, seems implausible, since the time required to reach the corresponding boundaries of a pore with such dimensions by the diffusion method is about 4.5 sec, which is significantly more than 90 ms.

In this regard, let us consider the results of additional studies. One of the factors that significantly influences the values of relaxation times, and, consequently, the values of the calculated pore sizes, may be associated with the influence of paramagnetic impurities, which may be located not only on the pore surface, but also dissolved in the fluid itself. Therefore, let us consider the influence of the copper sulphate concentration in the saturating fluid on the recorded NMR characteristics of the fluid in the pore space, namely, on the maximum value of the relaxation time in the T_2 time spectrum (Fig. 2).

As can be seen from Figure 2, an increase in the copper sulphate concentration to 1% has virtually no effect on the T_{2max} times, although for free water in the same concentration range the T_2 time decreases by about 30 times. Thus, the presented results give reason to believe that the maximum value of $T_{2max} \approx 90$ ms found above is indeed associated with the characteristics of the porous structure and, therefore, characterizes a certain pore size. As a reasonable estimate, we can take the value of the diffusion range of water molecules with a self-diffusion coefficient equal to $2.7*10^{-9}$ m^2/s for a time of $T_{2max} \approx 90$ m. The calculated value of the maximum pore size in the core obtained in this way turns out to be approximately equal to only 36 μm. Interestingly, approximately the same value (38 μm) was recorded by us experimentally using the DDIF technique [6], which is by definition sensitive to the maximum values in the pore size distribution. Such discrepancy between the results obtained from the analysis of the relaxation time spectra and the data of other NMR techniques may be due to the fact that the accepted value of $\rho = 1$ μm/ms, taken from the literature as typical for dolomites, does not correspond to the sample we studied. In order to match the value of the maximum pore size determined from the relaxation time spectrum with the calculation data and experimental results of the DDIF technique, it was necessary to take $\rho = 0.14$ μm/ms, which is almost an order of magnitude less than the value recommended for dolomites in the literature. Then, the pore sizes determined from the relaxation time spectrum data (Fig. 1) at $\rho = 0.14$ μm/ms will take the following values, respectively: 0.04; 0.49; 5 and 38 μm. Note that the pore size value of 0.04 μm in this case is in good agreement with the results obtained by the NMR cryoporometry method (Fig. 3).

The differential spectrum shown in Figure 3 demonstrates the presence of two regions of different sizes: 2 and 33 nm. The size of the 2 nm limits is classified as micropores.

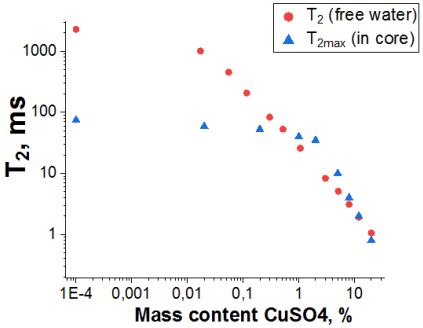

Figure 2. Dependence of spin-spin relaxation times on the concentration of copper sulfate. The behavior of the relaxation time of water with copper sulfate in the volume (T_2) is indicated by round symbols, and the value of the longest transverse relaxation time for water molecules in the core (T_{2max}) is indicated by triangular symbols

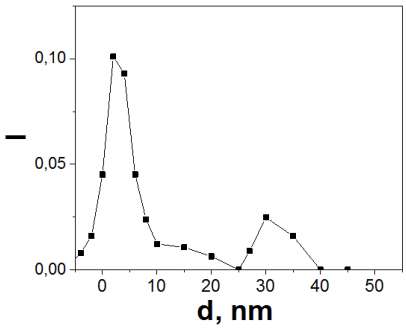

Figure 3. Pore size distribution spectrum obtained from NMR cryoporometry data

Thus, the minimum size of 0.04 μm obtained from NMR relaxometry is close to one of the sizes (33 nm) obtained in NMR cryoporometry, and the maximum size of 38 μm practically coincided with the estimate of 36 μm in the DDif method.

Thus, this work demonstrates the importance of the simultaneous use of complementary NMR methods for the correct analysis of the characteristics of the porous structure of the core. At the same time, it is shown that based on the comparison of the results, such an important characteristic of the porous material as relaxivity can be determined for each studied sample independently.

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