

NMR of Liquid ^3He in Pores of a Clay Sample

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Received: 3 November 2009 / Published online: 27 February 2010
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Abstract In the present work a new method for studying porous media by nuclear magnetic resonance of liquid ^3He has been proposed. This method has been demonstrated by an example of a clay mineral sample. For the first time the integral porosity of the clay sample has been measured. For investigated samples the value of the integral porosity is in the range of 10–30%. The inverse Laplace transform of the ^3He longitudinal magnetization recovery curve has been carried out and the distribution of the relaxation times T_1 has been obtained.

1 Introduction

Clay minerals are very important objects for oil mining industry [1, 2]. For a long time clay minerals were assumed to be nonporous systems, nontransparent for gases and liquids.

The study of clay minerals by traditional porometry methods is complicated by the unique properties of clay. The pore sizes are relatively small and probably closed for traditional porometry probes. Consequently, it is necessary to develop new methods for studying such materials.

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The “liquid ^3He –porous media” systems were intensively studied previously [3–7], but mainly for the determination of ^3He properties in contact with porous media and crystal powder samples.

It was found in ref. [8] that the magnetic relaxation of nuclear spins of liquid ^3He in confined geometry substantially acquires new features if compared with the relaxation in bulk liquid, and a new mechanism of magnetic relaxation has been proposed by Naletov et al.

The properties of normal liquid ^3He strongly depend on the size of the volume where ^3He is located. The main reason for that is highly effective spin diffusion, which implies space restriction starting from the size of several millimeters. The nuclear magnetic relaxation of liquid ^3He (both T_1 and T_2) takes place by means of fast spin diffusion from liquid ^3He to adsorbed ^3He , where several effective relaxation mechanisms are active [3, 4, 6, 9]. Thus, the longitudinal relaxation time T_1 , the transverse relaxation time T_2 and the spectral line width strongly depend on the size of the volume filled by liquid ^3He .

In the present study the results of nuclear magnetic resonance (NMR) measurements of liquid ^3He in pores of a clay sample are reported and the integral porosity of the sample is obtained from experimental data.

2 Samples and Methods

The clay sample was cut out of clay mineral in the shape of a tablet with a diameter of 5 mm and a height $\Delta l = 3$ mm. For calibration purposes a hole (diameter of 1.7 mm) was drilled out in the center along the tablet axis (axis l in Fig. 1), forming a calibration cavity. The ratio of the calibration cavity volume to the clay sample

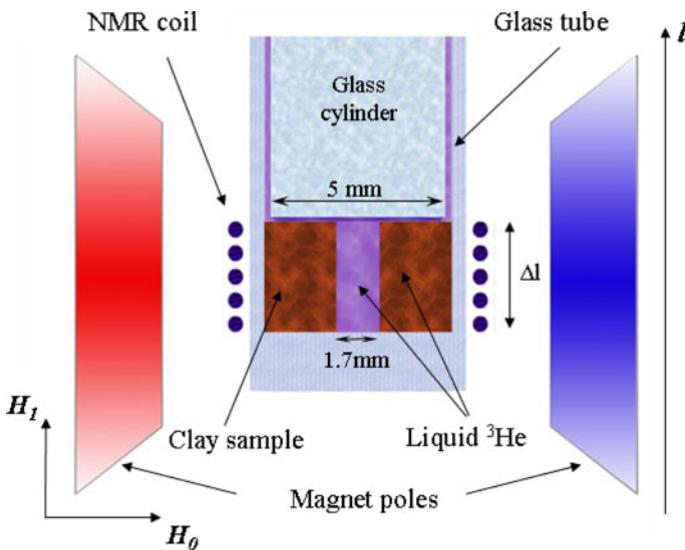


Fig. 1 Clay sample in an NMR probe

volume is 0.13. A priori NMR parameters of liquid ^3He in the calibration cavity significantly differ from those in clay pores (Sect. 1).

The sample was placed in a glass tube which was sealed leak tight to the ^3He gas handling system. On the outer surface of the glass tube an NMR coil was mounted. A homebuilt pulse NMR spectrometer (frequency range of 3–50 MHz) was used. The pulse NMR spectrometer is equipped with a resistive electrical magnet that has a magnetic field strength up to 1 T. The sample was filled by ^3He under the saturation vapor pressure at 1.5 K. Liquid ^3He inside the calibration cavity was used as a reference to estimate the integral porosity of the sample.

The longitudinal magnetization relaxation time T_1 of ^3He was measured by the saturation recovery method using a spin-echo signal. The observation of the spin-echo signal was possible due to the specially induced inhomogeneity of the external magnetic field H_0 . An NMR probe was moved has been decentered in the magnet by lifting along the axis I and, to a first approximation, a linear gradient of an external magnetic field was created in the sample. The spin–spin relaxation time T_2 was measured by the Hahn method.

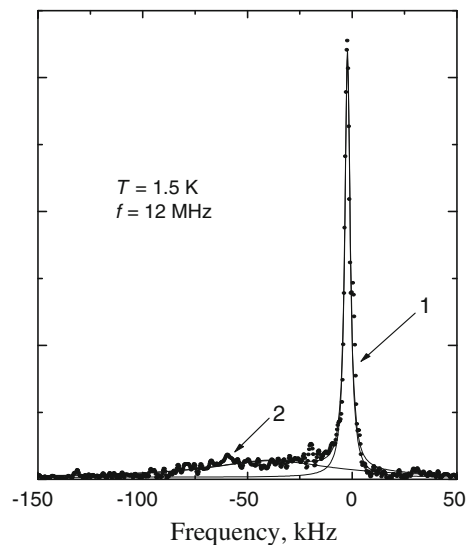
3 Results and Discussion

The “clay sample–liquid ^3He ” system was studied by measuring NMR spectra of liquid ^3He and investigating the nuclear spin kinetics of ^3He at the frequency of 12 MHz and at the temperature of 1.5 K.

In Fig. 2 an example of the liquid ^3He NMR spectrum is presented.

The NMR spectrum in Fig. 2 was obtained by the fast Fourier transformation of spin-echo data from two channels of a quadrature detector. The observed NMR spectrum can be described by two Lorentzian-shape lines with widths of 3 and

Fig. 2 NMR spectrum of liquid ^3He in the clay sample measured at the frequency of 12 MHz and at 1.5 K: 1 liquid ^3He signal from the calibration cavity, 2 liquid ^3He signal from pores



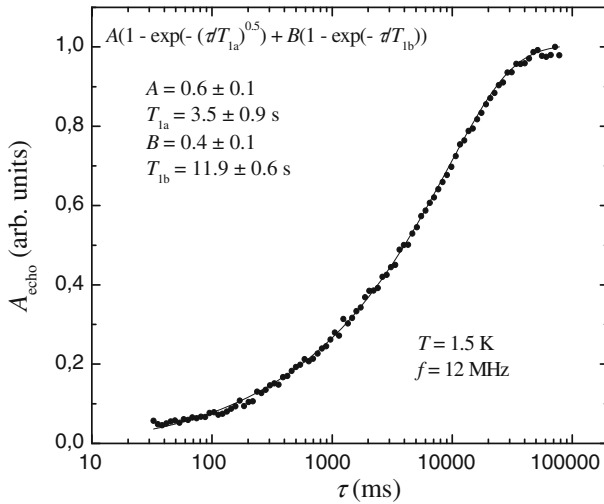


Fig. 3 Longitudinal magnetization recovery of liquid ^3He nuclei in the clay sample measured at the frequency of 12 MHz and at 1.5 K. Equation (1) describes experimental data with the following parameters: $T_{1A} = 3.5$ s, $T_{1B} = 12$ s

91 kHz, and integral intensities $30,200 \pm 300$ and $27,500 \pm 2800$, respectively. As it was mentioned above in Sect. 1, the broad line a priori is the NMR signal of liquid ^3He in pores of the clay sample and the narrow line in the spectrum corresponds to ^3He the calibration cavity because the average pore size in the clay sample is much smaller than the size of the calibration cavity. The frequency shift of the broad line indicates the presence of ferromagnetic impurities in the clay sample. It can be seen that the integral intensities of NMR signals of liquid ^3He in the calibration cavity and in clay pores are almost equal.

Nuclear spin relaxation times T_1 and T_2 of liquid ^3He were measured at a frequency of 12 MHz and at a temperature of 1.5 K. The behavior of the longitudinal magnetization recovery is non-exponential and consists of two processes (see example in Fig. 3).

The longitudinal magnetization recovery curve can be described by the following equation:

$$A_{\text{echo}} = A \left[1 - \exp \left(- \left(\frac{\tau}{T_{1a}} \right)^{0.5} \right) \right] + B \left[1 - \exp \left(- \frac{\tau}{T_{1b}} \right) \right], \quad (1)$$

and parameters are: $T_{1a} = 3.5$ s, $T_{1b} = 12$ s, $A/B \approx 1$.

The first component in Eq. (1) with the shorter T_1 corresponds to the nuclear magnetic relaxation of liquid ^3He in pores of the clay sample. There are several mechanisms of the nuclear magnetic relaxation for liquids in porous media. In the case of liquid ^3He , the main mechanism of the nuclear magnetic relaxation is an energy transfer by means of anomalous fast spin diffusion from liquid ^3He nuclei to the adsorbed ^3He nuclei and further effective surface relaxation in the adsorbed layer of ^3He as a result of quantum exchange in a two-dimensional film [6, 9]. By

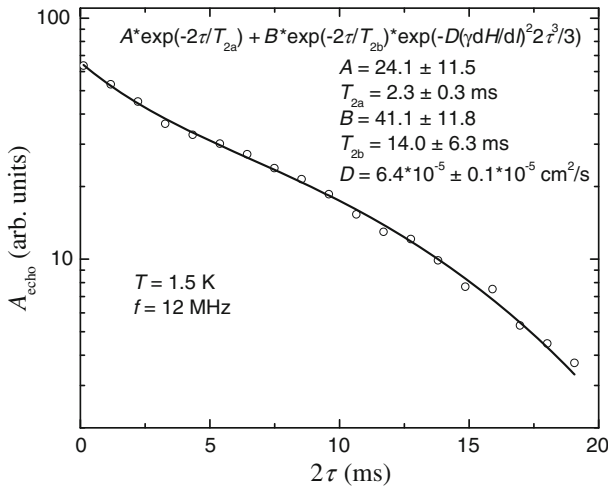


Fig. 4 Transverse magnetization decay of liquid ^3He nuclei in the clay sample measured at the frequency of 12 MHz and at 1.5 K. Equation (2) describes experimental data with the following parameters: $T_{2a} = 2.3$ ms, $T_{2b} = 14$ ms, $D = 6.4 \cdot 10^{-5}$ cm 2 /s

assuming the single-exponential process of the longitudinal relaxation in each pore, the power 0.5 in the first component of Eq. (1) indicates the presence of the pore-size distribution.

The second component in Eq. (1) with the longer T_1 corresponds to the nuclear magnetic relaxation of liquid ^3He in the calibration cavity (see Sect. 1). The observed value of T_{1b} is much smaller than T_1 of bulk liquid ^3He (about 1,000 s [8]) because of fast molecular diffusion of ^3He molecules to the wall of the cavity. According to the estimations, the observed value $T_{1b} = 12$ s corresponds to the 0.6 mm radius of the diffusion, which is comparable with the radius of the calibration cavity.

The behavior of the transverse magnetization decay is nonexponential and consists of two processes as well (Fig. 4).

The fast process of the transverse magnetization decay is the relaxation of liquid ^3He in pores of the clay sample (see Sect. 1). The second process is the relaxation of liquid ^3He in the calibration cavity. One could expect the equality of relaxation parameters T_1 and T_2 for liquid ^3He in the calibration cavity, as for the bulk liquid. But due to the presence of an artificially induced external magnetic field gradient, phase relaxation through diffusion in an inhomogeneous magnetic field should be taken into account [10]. Consequently, the transverse magnetization decay curve is described well by:

$$A_{\text{echo}} = A \exp\left(-\frac{2\tau}{T_{2a}}\right) + B \exp\left(-\frac{2\tau}{T_{2b}}\right) \exp\left[-D \left(\gamma \frac{\partial H}{\partial l}\right)^2 \frac{2\tau^3}{3}\right], \quad (2)$$

and parameters are: $T_{2a} = 2.3$ ms, $T_{2b} = 14$ ms, $D = 6.4 \times 10^{-5}$ cm 2 /s, $A/B \approx 1$. To determine the value $\frac{\partial H}{\partial l}$, a linear approach was applied. So $\frac{\partial H}{\partial l} \approx$

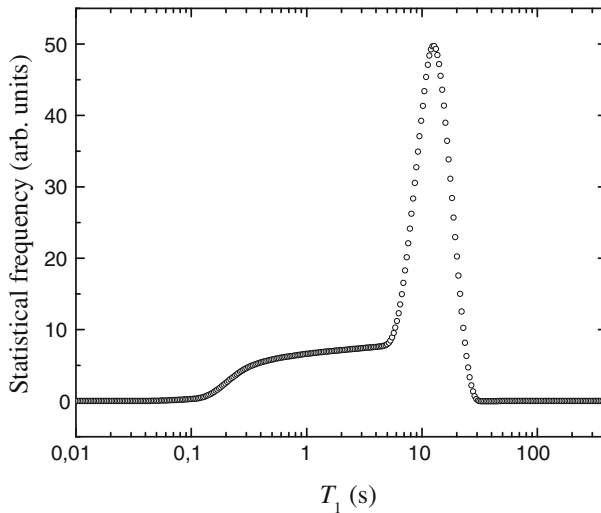


Fig. 5 Distribution of liquid ^3He T_1 relaxation times for the clay sample obtained by the regularized inverse Laplace transformation UPEN algorithm

$\frac{\Delta H}{\Delta l}$, where ΔH is the field inhomogeneity on the sample obtained from the width of the narrow line of the NMR spectrum (Fig. 2) and Δl is the height of the sample (Fig. 1). An excellent agreement of the diffusion coefficient D value, obtained by the approximation experimental data (Fig. 4) to those from ref. [11], proves the applicability of the proposed for the transverse relaxation of liquid ^3He in the investigated system.

The inverse Laplace transform of the longitudinal magnetization recovery curve for the detailed investigation of the ^3He relaxation in clay pores was performed using an algorithm based on a regularized inverse Laplace transform analysis with uniform penalty (UPEN) [12]. The multi-exponential inversion UPEN algorithm employs the negative feedback to a regularization penalty to implement variable smoothing when both the sharp and the broad features appear on a single distribution of relaxation times. The inverse Laplace transform was programmed using this algorithm. For the first time it was applied to the analysis of the magnetic relaxation of liquid ^3He .

The distribution of relaxation times computed by UPEN is shown in Fig. 5, where the narrow peak (in a semi-logarithmic scale) corresponds to the signal of liquid ^3He in the calibration cavity and the wide peak with the shorter T_1 values corresponds to liquid ^3He in pores of the clay sample.

The distribution of relaxation times obtained by the inverse Laplace transform can be converted into the pore-size distribution using specific models of relaxation. For instance, in the case of very small pore sizes, when the ^3He molecular diffusion length during the time of an experiment is longer than the size of pores, the longitudinal relaxation of liquid ^3He is single-exponential in each pore. The T_1 relaxation mechanism in this case is the surface relaxation, and direct knowledge of

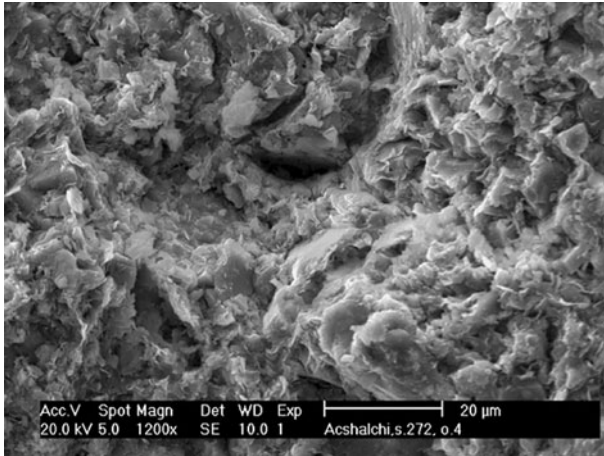


Fig. 6 Image of the clay sample obtained on a scanning electron microscope Philips XL30 ESEM

the surface relaxation time T_{1s} allows obtaining the pore-size distribution. The surface relaxation itself can be induced by different mechanisms, specially complicated for the geological samples in particular, as is the case under investigation.

The image of the clay sample obtained on a scanning electron microscope Philips XL30 ESEM is presented in Fig. 6, where pores with different sizes can also be seen.

In all obtained experimental data (NMR spectra, nuclear spin relaxation processes), the ratio between the signals of liquid ^3He in the calibration cavity and in pores of the clay sample was found to be close to 1. Taking into account the fact that the ratio of the calibration cavity volume to the clay sample volume is about 0.13, the sample porosity was estimated to be about 13%.

4 Conclusion

A new method for studying porous media by NMR of liquid ^3He has been proposed by an example of the clay sample. For the first time the integral porosity of the clay sample has been measured. By combining all experimental results, it can be concluded that the porosity of the sample is 13%. The scanning electron microscopy shows the presence of pores with different sizes in the sample.

It has been also demonstrated that inverse Laplace transform of ^3He relaxation curves in porous media can give information about the distribution of relaxation times. The distribution of relaxation times can be converted into the pore-size distribution using specific models of relaxation.

Acknowledgments We acknowledge A. V. Egorov for enlightening discussions.

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