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Determining pore length scales and pore surface relaxivity of rock cores by internal magnetic fields modulation at 2 MHz NMR

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ABSTRACT

Pore length scales and pore surface relaxivities of rock cores with different lithologies were studied on a 2 MHz Rock Core Analyzer. To determine the pore length scales of the rock cores, the high eigenmodes of spin bearing molecules satisfying the diffusion equation were detected with optimized encoding periods in the presence of internal magnetic fields B_{in}. The results were confirmed using a 64 MHz NMR system, which supports the feasibility of high eigenmode detection at fields as low as 2 MHz. Furthermore, this methodology was combined with relaxometry measurements to a two-dimensional experiment, which provides correlation between pore length and relaxation time. This techniques also yields information on the surface relaxivity of the rock cores. The estimated surface relaxivities were then compared to the results using an independent NMR method.

1. Introduction

Rock core samples provide essential data for the exploration, evaluation and production of reservoirs in petroleum, geothermal and hydrological industries. These rock samples allow geoscientists to obtain first-hand information. They offer direct evidence of the presence, distribution and deliverability of geothermal gas, ground water, hydrocarbons and can reveal variations in reservoir traits that might not be detected through down-hole logging measurements alone. One critical petrophysical parameter determined from rock core analysis, the pore length a, characterizes the pore volume in which the reservoir fluid can be held [1]. Another parameter, the surface relaxivity ρ, reflects the boundary properties of pores and depends on the interaction strength between mobile nuclear spins and the solid surfaces. These two parameters are used for permeability estimation, in order to model reservoir behavior and to optimize underground resource exploration [2].

For over half a century, Nuclear Magnetic Resonance (NMR) techniques have been established as an essential method in exploring the interior properties of porous media [3,4]. In particular, ^{1}H low-field NMR has gained extensive acceptance in petrophysical industry for evaluation of reservoir properties, mainly due to the sensitivity to hydrogen rich fluid (such as water and hydrocarbons) [5]. Traditional protocols, such as transverse/longitudinal relaxation time (T_2/T_1) measurements, provide pore size related distributions obtained in lab experiments or in-situ well-logging [6]. To determine the pore size distribution of porous media directly, one technique was developed relying on the internal magnetic fields B_{in} that exists in the pore space, since the inhomogeneity of B_{in} acts dominantly over the pore length [7]. During this experiment, the high eigenmodes of the diffusion equation governing the motion of the spin bearing molecules contribute to the signal attenuation, the eigenvalue of which relates to the pore length directly. Thus the high eigenmodes contribution can be measured and transformed to pore length scales using the numerical inversion method. This technique has been successfully employed to detect pore length scales of rocks [8], concrete [9] and biological tissues [10,11] in high-field NMR systems. However, the contributions from high eigenmodes are mostly "hidden" in low-field NMR because of the relatively weak internal magnetic fields in porous media.

In this paper, we lay out the concepts and theory needed for the context of our work. Then we describe and explain how to measure the high eigenmodes in rock samples at low-field. One-dimensional (1D) results from different types of rock cores proved the feasibility of this technique in fields as low as 2 MHz using the optimized magnetization encoding period. Furthermore, we extend the two-dimensional (2D) NMR method, which is based on the numerical inversion of relaxation time or diffusion data (often referred to as inverse Laplace transform NMR) [12,13]. In the context of this work,

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we correlate the high T_1 mode with ground T_2 mode to further extract rock core parameters. This provides the distribution of pore length, relaxation time, and the information of surface relaxivity of rock samples. The estimated surface relaxivities of the rocks were compared with the results from *Padé* approximant extrapolation in diffusion-relaxation correlation maps, which is a well-established and principle-independent NMR method to estimate surface relaxivity in rock samples [14].

2. Theory

2.1. Review of pore length determination using the first excited mode ($n = 1$)

The magnetization evolution of diffusing molecules is described by the Bloch-Torrey equation [15] and the theory of eigenmodes as a solution to this equation was proposed by Brownstein K. and Tarr C. [16]. When the molecules diffuse in the pore space where the absorption of the spins at the pore surface is characterized by ρ, the evolution of the magnetization density $m(\vec{r},t)$ in the pore volume will satisfy the pore/matrix boundary condition: $(\hat{n}\cdot D\nabla m+\rho m)|_S=0$. Here $\vec{r}$ is the spin position, D is the diffusion coefficient of the saturating fluid and is considered spatially constant, and $\hat{n}$ is the normal unitary vector outward pointing from the pore/matrix interface. The initial condition of the magnetization density evolution is described as:

$$m(\vec{r},0)=\frac{m_0}{V} \tag{1}$$

where m_0 is the initial magnetization in the pore volume, V.

The Bloch-Torrey equation after neglecting the effect from bulk relaxation is the diffusion (or heat) equation and the general solution can be obtained by separating the variables $\vec{r}$ and t. The result is given as:

$$m(\vec{r},t)=\sum_{n=0}^{\infty}A_n\varphi_n(\vec{r})\mathrm{e}^{-\frac{t}{\tau_{1,2}^n}} \tag{2}$$

where φ_n are orthogonal, normalized eigenfunctions of the diffusion equation and $1/\tau_{1,2}^n$ are the corresponding eigenvalues when the magnetization is along the longitudinal axis or in the transverse plane. While the ground eigenfunction φ_0 is approximately constant, the higher eigenfunctions will oscillate in the pore space. The eigenmode amplitude A_n can be calculated using the orthogonal property of eigenfunctions and the initial magnetization:

$$A_n=\frac{1}{V}\int m(\vec{r},0)\varphi_n(\vec{r})dV \tag{3}$$

Considering the behavior of eigenfunctions in the pore space, the ground mode amplitude will be approximately m_0/V but the amplitude of higher modes will be small assuming a uniform magnetization profile.

In order to apply this theory to porous media, the decay times τ_n for spherical pore space are given by [16–18]:

$$\tau_{1,2}^n\approx\begin{cases}\frac{a}{6\rho_{1,2}} & \text{when } n=0\\ \frac{a^2}{4D\zeta_n^2} & \text{when } n\geq 1\end{cases} \tag{4}$$

under the condition of fast diffusion region ($\rho a/D\ll 1$), where the ζ_n are the positive roots for the equation $1-\zeta_n\cot\zeta_n=\rho a/2D$ and a is the characteristic pore length scale which will be defined differently for different pore shapes. In the case of a spherical pore as assumed in Eq. (4) it refers to the diameter of the sphere. Surface relaxivity ρ is affecting longitudinal or transverse magnetization whichever one is involved during the diffusion observation time. The decay time of the ground mode $\tau_{1,2}^0$ will always be larger under this condition, than $\tau_{1,2}^n$ with $n\geq 1$.

Since the detected signal is the integral of the magnetization over the pore space, the result will be a multi-exponential decay weighted by the relative intensity of each mode:

$$m(t)=\int m(\vec{r},t)dV=m_0\cdot\sum_{n=0}^{\infty}I_n\mathrm{e}^{-\frac{t}{\tau_{1,2}^n}} \tag{5}$$

where $I_n=[\int\varphi_n dV]^2$, is the relative intensity of n-th mode of the diffusion equation.

As seen from Eq. (4), the decay time of the ground mode ($n=0$) depends on the pore length a and surface relaxivity ρ, while the high modes ($n\geq 1$) of the diffusion equation are independent of ρ and therefore are more suitable for determining the pore length. However, the relative intensities of the high modes are much weaker compared to the intensity of ground mode [16]. In order to take advantage of the high modes for the detection of pore length scale, the contribution of the high modes to the signal must be enhanced.

One efficient approach to enhance the contributions from the first excited mode ($n=1$) in the presence of spatially distributed internal magnetic field B_{in} was developed for porous media by Song [8,19]. The 1D signal pulse sequence and reference pulse sequences used in this technique are shown in Fig. 1.

In the 1D signal pulse sequence, the first $\pi/2$ rf pulse rotates the longitudinal magnetization in the transverse plane. During the encoding period of t_e, the magnetization in pore space will be modulated with an encoding phase Φ in the presence of the spatially induced magnetic fields B_{in}:

$$m(\vec{r},t_e)=m(\vec{r},0)\mathrm{e}^{-i\Phi}=m(\vec{r},0)\mathrm{e}^{-i\gamma B_{in}(\vec{r})t_e} \tag{6}$$

Here, the nuclei are considered as immobile during the encoding time t_e while the modulation of the magnetization profile takes place. However, if molecules undergo non-negligible diffusion and probe the internal magnetic field during t_e an integral averaging over the positions of the diffusing molecules has to be used instead of $B_{in}(r)$ in the exponential term.

The second $\pi/2$ rf pulse stores the dephased magnetization back to the longitudinal direction. After this, the magnetization evolution during the observation time t_{diff} will undergo spin–lattice relaxation T_1. By choosing the phase of the second $\pi/2$ rf pulse to be incremented by 90° as compared to the first $\pi/2$ rf pulse, one

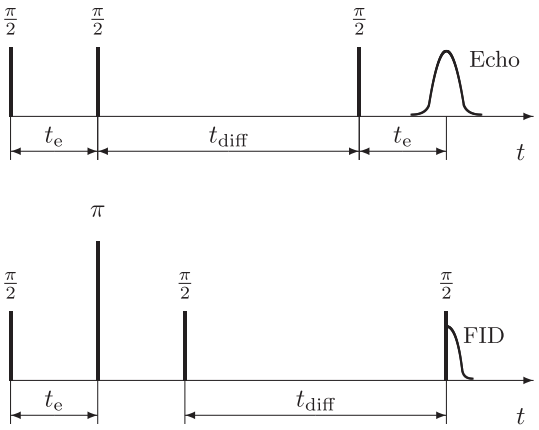

Fig. 1. 1D signal pulse sequence (top) and reference pulse sequence (bottom) are used to detect the first excited mode in porous media [8]. Here t_e is the encoding period and t_{diff} is the observation time of molecular diffusion. The $\pi/2$ rf pulses and the acquisition phases in the signal pulse sequence are +y −y +y −y; +x +x −x −x; +x +x +x +x; +y −y −y +y respectively while the phases for the $\pi/2$ and the π rf pulses as well as the acquisition in the reference pulse sequence are +x −x +x −x +x −x +x −x; +x +x −x −x +x +x −x −x; +x +x +x +x +x +x +x +x; +y +y +y +y −y −y −y −y; +y −y −y +y +y −y −y +y.