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Original contribution

Characterization of porous media by T_2-T_2 correlation beyond fast diffusion limit

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ABSTRACT

Pore size distribution and surface relaxivity are two important properties of porous media such as rock samples and can be obtained by NMR methods. However, it is difficult to obtain these information beyond the fast diffusion limit. Here we present a new method to directly characterize the averaged pore size of a porous sample with a narrow pore size distribution. This method is based on the parallel plates pore model and the T_2-T_2 correlation sequence. The pore size (a) - surface relaxivity (ρ) correlation maps were obtained using the non-negative least squares method. Three kinds of glass bead samples were measured and the averaged pore size and surface relaxivity were extracted.

1. Introduction

The nuclear magnetic resonance (NMR) method is a powerful tool for studying the structure of porous media and confined fluid. This technique can obtain many important petrophysical parameters such as porosity and pore size distribution, permeability, water saturation, and wettability, etc. [1]. It can be used for core analysis at low field, where there are two key parameters: One parameter is the pore size a, which characterizes the pore volume. Another parameter, the surface relaxivity ρ, reflects the boundary properties of pores and is dependent on the interaction between polarized nuclear spins and paramagnetic impurities at the fluid-solid interface [2]. The fast, intermediate and slow diffusion regime can be defined by pore size, surface relaxivity and diffusion coefficient. Generally, the validity of fast diffusion regime is assumed. Various 1D and 2D Laplace NMR methods were applied to extract pore information under this assumption. For instance, the pore length scale, surface-to-volume ratio (S/V) of porous materials can be obtained by measuring the spin relaxation [3]. Pore connectivity can be acquired by using 2D NMR correlation experiments [4,5]. The appearance of fast 2D inverse Laplace transformation algorithms has greatly accelerated the application of 2D Laplace NMR [6–8]. However, there are also conditions that the intermediate or slow diffusions regimes are applied, such as large pores or strong surface relaxation [3,9,10]. Consequently, the equation based on the fast diffusion assumption cannot be used to obtain pore structure and fluid information in these cases [11]. For example, experimental results of water-saturated glass-bead packs indicated that the best fit between relaxation time and pore size was different from traditional linear relationships [3]. In 2D method, the off-diagonal peaks of the T_1-T_2 spectrum with negative amplitude can be used to explore pore coupling [12]. Then, the time-domain data of T_1-T_2 experiments were analyzed to identify the signature of diffusive coupling between different pores [13]. A similar analysis of the time domain data of T_2-T_2 experiments were performed, which can unambiguously identify the presence of molecule exchange [14]. Furthermore, asymmetry cross peaks were also observed in T_2-T_2 correlation maps when there are three T_2 peaks [15].

In this paper, we used T_2-T_2 correlation sequence to study porous media beyond fast diffusion limit. First, we applied eigenmodes formalism to simulate the T_2-T_2 signals based on the parallel plates pore model and the non-negative least squares method to obtain a-ρ correlation maps. Subsequently, we performed experiments on the glass bead samples saturated with water and extracted the averaged pore size and surface relaxivity information.

2. Method

2.1. Eigenmodes formalism and diffusion regimes

The evolution of magnetization in the presence of diffusion and relaxation phenomena is described by the Bloch-Torrey equation [16,17]. The solution to this equation without applied gradients was provided by Brownstein and Tarr using eigenmodes formalism in

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planar, cylinder and sphere pores [18]. It was assumed that the ρ of the pores was uniform and satisfied the boundary condition $(\hat{n}\bullet D\nabla m + \rho m)|_S = 0$, where $\hat{n}$ is the normal unit vector, D is self-diffusion coefficient, and $m(\vec{r},t)$ is the magnetization density in the pore volume V. Combined with the initial condition $m(\vec{r},0) = m_0/V$, the general solution of $m(\vec{r},t)$ can be written as the sum of eigenmodes,

$$m(\vec{r},t) = \exp(-\mu t)\sum_{n=0}^{\infty} a_n\varphi_n \exp\left(-\frac{t}{\tau_n}\right), \tag{1}$$

where μ is the bulk spin relaxation rate, φ_n and τ_n are the normalized eigenfunctions and eigenvalues. According to the orthogonality of the eigenmodes, the expression of the eigenmode coefficient a_n is

$$a_n = \int m(\vec{r},0)\varphi_n^*(\vec{r})dv. \tag{2}$$

The relaxation of magnetization can be derived by integration,

$$M(t) = M(0)\sum_{n=0}^{\infty} A_n \exp\left(-\frac{t}{\tau_n}\right), \tag{3}$$

where A_n is the relative strength of the different modes. In order to distinguish the multi-exponential relaxation in different regimes, there is a critical parameter $\kappa = \rho a/D$, which is used to define the three diffusion regimes: the fast diffusion regime ($\kappa \ll 1$), the intermediate diffusion regime ($1 < \kappa < 10$), and the slow diffusion regime ($\kappa \gg 10$).

When $\kappa > 1$ is applied, the contribution to the signal from the higher modes increases. Especially in the slow diffusion regime, the magnetization decay is dominated by the lowest mode eigenvalue that is about $a^2/D(\pi/2)^2$, so the signal $M(t)$ is related to a, not to ρ.

2.2. 2D NMR relaxation correlation

Here, we used the T_2-T_2 correlation sequence proposed by Lee et al. [5] as shown in Fig. 1. This sequence consists of two CPMG sequences, where the first encoding period t_1 and the detection period t_2, separated by a mixing time τ_{mix}.

Neglecting the relaxation during rf pulses, the evolution of the magnetization is

$$m(\vec{r},t_1) = \exp(-\mu t_1)\sum_{n=0}^{\infty} a_n\varphi_{2,n}\exp\left(-\frac{t_1}{\tau_{2,n}}\right). \tag{4}$$

After the mixing time, τ_{mix}, where the magnetization relaxes according to the T_1 process, the second train of CPMG pulses in the period of t_2 is used for acquiring data. So the evolution of the CPMG echo signal is

$$m(\vec{r},t_1,t_2) = \exp(-\mu t_2)\sum_{m=0}^{\infty} b_m\varphi_{2,m}\exp\left(-\frac{t_2}{\tau_{2,m}}\right), \tag{5}$$

where $b_m = \int m(\vec{r},t_1,\tau_{mix})\varphi_{2,m}^*(\vec{r})dv$. Using the bra-ket notation ⟨|⟩ of quantum mechanics to define the scalar product as

$$\langle\phi \mid \psi\rangle = \int \varphi^*(\vec{r})\psi(\vec{r})dv, \tag{6}$$

the signal $M(t) = \int m(\vec{r},t)dv$ can be written as $M(t) = \langle 1|m(t)\rangle$, where $|1\rangle$ is the scalar field equal to one everywhere within the pore. Note that when $\tau_{mix} = 0$, the detected signal can be written as

$$M(t_1,t_2) = \sum_n \langle 1 \mid \varphi_{2,n}\rangle^2 \exp(-t_1/\tau_{2,n} - t_2/\tau_{2,n}). \tag{7}$$

To obtain the a-ρ correlation from measured T_2-T_2 data, the following processing procedure was used. Given a pore size and a surface relaxivity, a 2D matrix A(t_1,t_2) (according to Eq. (7)) can be calculated with the parallel plates pore model. The matrix was spliced into a 1D column in units of each row matrix.

$$\begin{bmatrix} A_{11} & \cdots & A_{1n} \\ \vdots & \ddots & \vdots \\ A_{m1} & \cdots & A_{mn} \end{bmatrix} \Longrightarrow \begin{bmatrix} A_{11} \\ \vdots \\ A_{1n} \\ \vdots \\ A_{mn} \end{bmatrix}. \tag{8}$$

Then, changing the pore size and surface relaxivity, the A(t_1,t_2) were calculated in different diffusion regimes with q values. A 2D inversion coefficient matrix A was obtained by combining each column vector data.

$$A = \begin{bmatrix} A_{11,1} & A_{11,2} & \cdots & A_{11,q} \\ \vdots & \vdots & \ddots & \vdots \\ A_{1n,1} & A_{1n,2} & \cdots & A_{1n,q} \\ \vdots & \vdots & \ddots & \vdots \\ A_{mn,1} & A_{mn,2} & & A_{mn,q} \end{bmatrix}. \tag{9}$$

The measured data was converted into a 1D column matrix b $\in \Re^{(m\times n)\times 1}$. The least squares fitting problem was thus established as follows.

$$\begin{bmatrix} A_{11,1} & A_{11,2} & \cdots & A_{11,q} \\ \vdots & \vdots & \ddots & \vdots \\ A_{1n,1} & A_{1n,2} & \cdots & A_{1n,q} \\ \vdots & \vdots & \ddots & \vdots \\ A_{mn,1} & A_{mn,2} & & A_{mn,q} \end{bmatrix} \begin{bmatrix} d_1 \\ d_2 \\ \vdots \\ d_q \end{bmatrix} = \begin{bmatrix} b_{11} \\ \vdots \\ b_{1n} \\ \vdots \\ b_{mn} \end{bmatrix}. \tag{10}$$

Finally, the a-ρ correlation was obtained from the [d_1, d_2, … d_q].

3. Simulation and experiment

Here parallel plates pore model was chosen to study how to use higher modes to characterize simple porous media beyond fast diffusion limit. First, simulations were done according to Eq. (7). When the mixing time is zero, longitudinal surface relaxivity ρ_1 has no influence on the signals. Therefore the relaxation relaxivity ρ was used to represent the transverse relaxation relaxivity ρ_2. To investigate the different diffusion regimes, four pore models are given, where a were 50, 100, 250 and 400 μm, and ρ were 50, 50, 100 and 100 μm/s. In the T_2-T_2 correlation sequence, the number of echoes in the first encoding period was logarithmically changed in 30 steps, and the number of echoes in the detection period was 50. In order to evaluate the effect of

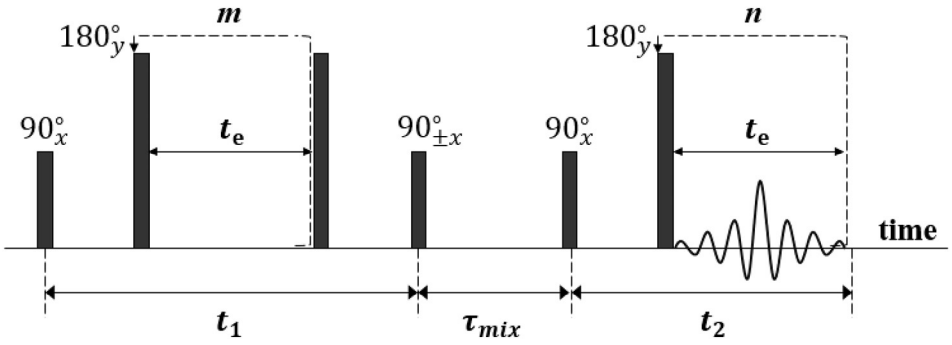

Fig. 1. A schematic of the T_2-T_2 experiment pulse sequence. This sequence consists of two CPMG echo trains separated by a mixing time, τ_{mix}. The number of π pulses of the first CPMG is varied logarithmically from 1 to m. The two durations of T_2 interval are $t_1 = (m + 1)t_e$ and $t_2 = (n + 1/2)t_e$. In this work, τ_{mix} is set to minimum value (100 μs).

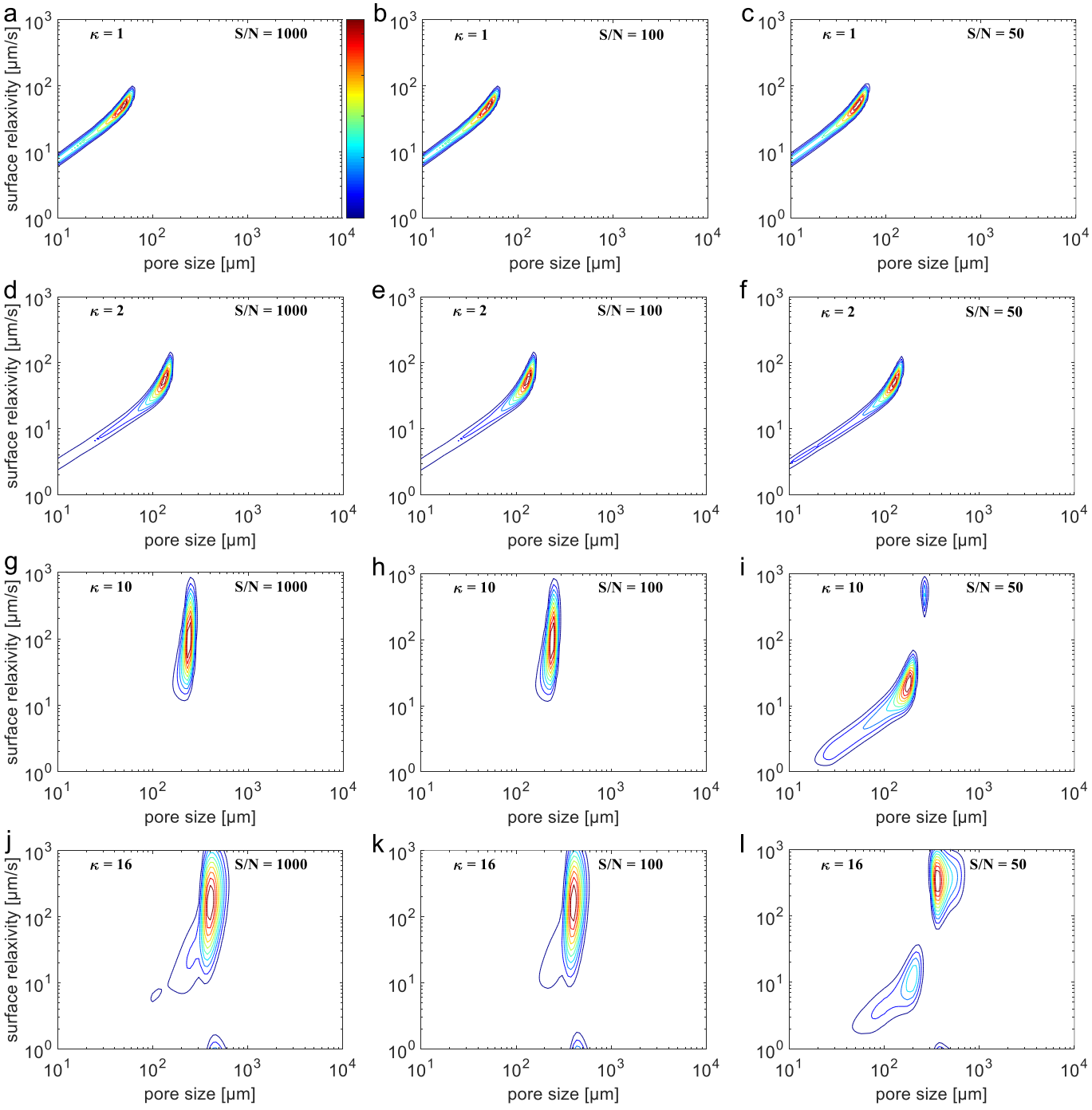

Fig. 2. Two-dimensional a-ρ correlation maps for four models with different S/Ns, which are 1000 (a, d, g, j), 100 (b, e, h, k) and 50 (c, f, i, l), respectively. (a–c) Pore size-surface relaxivity correlation maps for parameter setting $\kappa = 1$, $\rho = 50\,\mu m/s$ and $a = 50\,\mu m$. (d–f) Pore size-surface relaxivity correlation maps for parameter setting $\kappa = 2$, $\rho = 50\,\mu m/s$ and $a = 100\,\mu m$. (g–i) Pore size-surface relaxivity correlation maps for parameter setting $\kappa = 10$, $\rho = 100\,\mu m/s$ and $a = 250\,\mu m$. (j–l) Pore size-surface relaxivity correlation maps for parameter setting $\kappa = 16$, $\rho = 100\,\mu m/s$ and $a = 400\,\mu m$.

noise, three different signal-to-noise ratios (S/Ns) were examined. In all four cases, the self-diffusion coefficient (D = 2.5e–9 m^2/s) and bulk relaxation time (T_B = 3 s) were the same. To inverse the simulated data, the range of the pore size is set from 10 μm to 10^4 μm and surface relaxivity is set from 1 μm/s to 10^3 μm/s.

In order to verify whether this method can be used in the actual samples, we performed experiments on water-saturated glass beads with a narrow pore size distribution, where the average diameter of the three samples were 100 μm, 200 μm and 500 μm, respectively. Before the three samples were measured, in order to obtain an appropriate inversion model, the T_2 relaxation time and diffusion coefficient of the water sample were measured. Then, the T_2-T_2 correlation experiments were performed using the pulse sequence shown in Fig. 1. The echo numbers in the first encoding period varied logarithmically in 50 steps, and the signals were detected in the second CPMG part. The mixing time τ_{mix} was set to 100 us to minimize the T_1 relaxation effect. The experiments were implemented on a 2 MHz Rock analyzer (Oxford Instrument, UK). The pore size-surface relaxivity correlation maps were obtained by the non-negative least square inversion method.

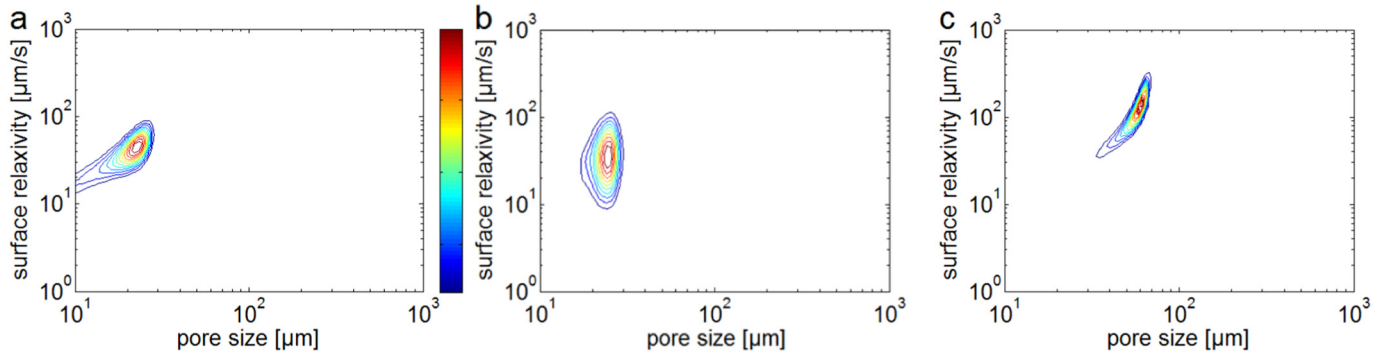

Fig. 3. Pore size-surface relaxivity correlation maps for three samples of glass beads with average diameter of (a) 100 μm, (b) 200 μm and (c) 500 μm.

4. Results and discussion

The simulated results were shown in Fig. 2, where three S/Ns were examined: 1000, 100 and 50. The influence of κ was also explored to examine the validity of this method at different diffusion regime. The averaged pore size and surface relaxivity were obtained from these correlation maps. In Fig. 2a–c, the peaks inversion from the data of $\kappa = 1$ were located at averaged pore size of 30–70 μm and the surface relaxivity 40–60 μm/s, which were consistent with the set value ($\rho = 50$ μm/s, $a = 50$ μm), and the results of different S/Ns were basically the same. It was noted that the position of the correlation peaks were along a slope line. This is because when κ small, the lowest mode dominated and only the value of a/ρ can be determined from the data. The correlation maps of the second model were shown in Fig. 2d–f. The parameters were set to $a = 100$ μm, $\rho = 50$ μm/s and $\kappa = 2$. The peaks were more concentrated and the feature of slope line is weakened. From the position of peaks, the averaged pore size of 90–110 μm and surface relaxivity of 40–80 μm/s were obtained. For the third model with parameter of $\kappa = 10$, $a = 250$ μm, $\rho = 100$ μm/s, the slope characteristic disappeared and the areas of the peak increases (Fig. 2g–i). Although the lowest mode still dominates, the relative intensities of the signals from the higher modes increases, resulting in a weaker correlation between the pore size and surface relaxivity. The peaks position were located at averaged pore size of 210–260 μm and surface relaxivity 50–200 μm/s, which were consistent with the set value ($\rho = 100$ μm/s, $a = 250$ μm). For S/N of 50, it was difficult to get accurate information about the averaged pore size and surface relaxivity. For the fourth model, the parameters were set to: $\kappa = 16$, $a = 400$ μm, $\rho = 100$ μm/s. The areas of the correlation maps became larger in Fig. 2j, k, where the peaks position were 350–420 μm, and surface relaxivity were 50–150 μm/s. In Fig. 2l, the peak is distorted, where S/N was 50. The distribution was broad for ρ and narrow for a with $\kappa = 10$ and $\kappa = 16$.

Based on the results of the simulation, we found that when κ was in the range of 1 and 10, the information of the averaged pore size and surface relaxivity could be effectively obtained. However, when κ was 16, an approximate estimate of the averaged pore size could be obtained, but the distribution of surface relaxivity was abroad and partially at the margins. When the maximum value of the surface relaxivity was increased to 10^4 μm/s, the signal amplitude at the margins still existed. Therefore, this method is applicable to porous media with κ equal to 1 to 10 (intermediate diffusion regime).

Fig. 3 shows the experiment results, The self-diffusion coefficient and bulk relaxation time were first measured to inverse the data properly, where $D = 2.1\text{e}{-9}\ \text{m}^2/\text{s}$ and $T_B = 2.5$ s. The averaged pore size of the three samples were estimated from Fig. 3a–c, which are 16–22 μm, 22–27 μm, and 55–65 μm, respectively. The obtained pore size distributions provide right information for the 100 μm, 200 μm and 500 μm diameter glass bead sample according to [19]. The averaged surface relaxivity of the three samples were obtained for the correlation maps, which are 15–30 μm/s, 20–50 μm/s, and 100–160 μm/s, respectively. The precise value of the surface relaxivity will be determined in the future to check the accuracy of this method of measuring surface relaxivity. Furthermore, the κ values of the samples can also be estimated from the peak center of the correlation maps. For the first two maps, $\kappa < 1$, which means the fast diffusion regime is applied, and for the third map, $1 < \kappa < 10$, which means the intermediate diffusion regime is applied. This offers important information about the diffusion status of molecules.

5. Conclusion

In this work we used two-dimensional T_2-T_2 correlation pulse sequence to record the relaxation information of porous media beyond fast diffusion limit. Based on the eigenmodes formalism, we simulated the signals of T_2-T_2 correlation sequence in the parallel plates pore model. Pore size-surface relaxivity correlation maps were then obtained by non-negative least squares inversion. This method is less sensitive to surface relaxivity than the pore size, where a broad distribution was observed in surface relaxivity direction in the correlation maps. We also measured the T_2-T_2 signals of water-saturated glass samples with a narrow pore size distribution and a uniform surface relaxivity, and directly extract the estimate of the averaged pore size and surface relaxivity. So this method is expected to extract internal pore information at intermediate diffusion regime such as carbonate rock.

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References

[1] Callaghan PT. Translational Dynamics and Magnetic Resonance: Principles of Pulsed Gradient Spin Echo NMR. Oxford University Press; 2011.
[2] Liu H, D'Eurydice MN, Obruchkov S, Galvosas P. Determining pore length scales and pore surface relaxivity of rock cores by internal magnetic fields modulation at 2 MHz NMR. J. Magn. Reson. 2014;246:110–8.
[3] Keating K, Knight R. The effect of spatial variation in surface relaxivity on nuclear magnetic resonance relaxation rates. Geophysics 2012;77(5):E365–77.
[4] English AE, Joy ML, Henkelman RM. Pulsed NMR relaxometry of striated muscle fibers. Magn. Reson. Med. 1991;21(2):264–81.
[5] Lee JH, Labadie C, Springer Jr. CS, Harbison GS. Two-dimensional inverse Laplace transform NMR: altered relaxation times allow detection of exchange correlation. J. Am. Chem. Soc. 1993;115(17):7761–4.
[6] Sun B, Dunn KJ. Probing the internal field gradients of porous media. Phys. Rev. E 2002;65(5):051309.
[7] Hürlimann MD, Venkataramanan L, Flaum C. The diffusion–spin relaxation time distribution function as an experimental probe to characterize fluid mixtures in porous media. J. Chem. Phys. 2002;117(22):10223–32.
[8] Song YQ, Venkataramanan L, Hürlimann MD, Flaum M, Frulla P, Straley C. T1–T2

correlation spectra obtained using a fast two-dimensional Laplace inversion. J. Magn. Reson. 2002;154(2):261–8.
[9] Godefroy S, Korb JP, Fleury M, Bryant RG. Surface nuclear magnetic relaxation and dynamics of water and oil in macroporous media. Phys. Rev. E 2001;64(1):021605.
[10] Valfouskaya A, Adler PM, Thovert JF, Fleury M. Nuclear magnetic resonance diffusion with surface relaxation in porous media. J. Colloid Interface Sci. 2006;295(1):188–201.
[11] Müller-Petke M, Dlugosch R, Lehmann-Horn J, Ronczka M. Nuclear magnetic resonance average pore-size estimations outside the fast-diffusion regime NMR average pore-size estimations. Geophysics 2015;80(3):D195–206.
[12] Song YQ, Zielinski L, Ryu S. Two-dimensional NMR of diffusion systems. Phys. Rev. Lett. 2008;100(24):248002.
[13] Song YQ, Carneiro G, Schwartz LM, Johnson DL. Experimental identification of diffusive coupling using 2D NMR. Phys. Rev. Lett. 2014;113(23):235503.
[14] Song R, Song YQ, Vembusubramanian M, Paulsen JL. The robust identification of exchange from T2–T2 time-domain features. J. Magn. Reson. 2016;265:164–71.
[15] Landeghem MV, Haber A, D'espinose De Lacaillerie JB, Blümich B. Analysis of multisite 2D relaxation exchange NMR. Concept Magn. Reson. A 2010;36(3):153–69.
[16] Bloch Felix. Nuclear induction. Phys. Rev. 1946;70(7–8):460.
[17] Torrey Henry C. Bloch equations with diffusion terms. Phys. Rev. 1956;104(3):563.
[18] Brownstein KR, Tarr CE. Importance of classical diffusion in NMR studies of water in biological cells. Phys. Rev. A 1979;19(6):2446.
[19] Hills BP, Snaar JEM. Water proton relaxation studies of pore microstructure in monodisperse glass bead beds. Mol. Phys. 1995;84:141–57.