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FID NMR Studies of Suspensions and Porous Media:

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Abstract

Nuclear Magnetic Resonance is used for the determination of the properties of porous media in Geophysics and oil exploration. As it stands, there is a challenge in understanding the connection between the times measured in Free Induction Decay Nuclear Magnetic Resonance experiments and the shape of samples. In this work, suspensions and water-saturated densely-packed porous media with the volume fraction of the glass solid phase in the range from 10^{-4} to $\sim$1 are found to exhibit FID decay rates proportional to the square root of the volume fraction of the solid phase of the samples. A model of spheres in liquid is proposed for the description of such behavior.

Keywords

Nuclear Magnetic Resonance, Free Induction Decay, porous media, suspensions, dense packing

1. Introduction

Free Induction Decay (FID) experiments are used for the determination of the quantity of the liquid phase in porous samples [1], [2], [3], [4]. In comparison to other TD-NMR experiments the relaxation rate in the FID experiment is strongly affected by the inhomogeneity of the magnetic field due to the lack of refocusing pulses. The sample is irradiated by an RF-pulse at the Larmor frequency. As a result the magnetization of the sample is transformed. The shape of the sample and the difference in the magnetic susceptibilities of the solid and the liquid phases of the sample increase the inhomogeneity of the constant magnetic field in the sample. The coherence of the transverse magnetization of the sample is assumed to be lost mostly due to the inhomogeneity of the magnetic field in the sample. The connection between the FID decay rate $1/T_2^*$ of the sample and the inhomogeneity ΔB of the magnetic field in the sample is the following [3], [5]:

$$\frac{1}{T_2^*} = \gamma \frac{\Delta B}{2}, \quad (1)$$

where γ is the gyromagnetic ratio of protons.

The width of the NMR spectral line is proportional to the FID decay rate of the sample:

$$\Delta\nu = \frac{1}{\pi T_2^*}. \quad (2)$$

The results of simulations and numerical studies exhibit proportionality between the inhomogeneity ΔB of the constant magnetic field and the product of the constant magnetic field B_0 and the difference $\Delta\chi$ between the magnetic susceptibilities of the solid and the liquid phase of the sample [5], [6], [7]:

$$\Delta B \propto \Delta\chi B_0. \quad (3)$$

Although studies of the connection between the pore size heterogeneity of densely packed porous media and the transverse relaxation rate exist [8], the connection between FID decay rate $1/T_2^*$ and the shape of samples is poorly described [3]. The aim of this work is to study the connection of the volume fraction of the solid phase of model suspensions and water-saturated densely packed particles and the FID decay rate $1/T_2^*$ of the liquid phase of the samples.

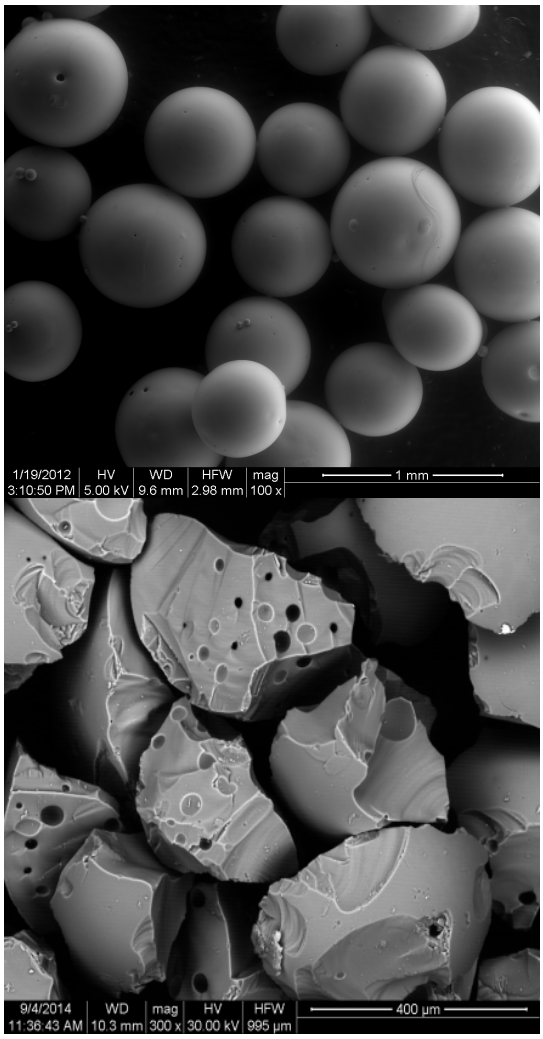

Fig. 1: Glass spheres and glass particles with irregular shape constitute the solid phase of the samples

2. Materials and Methods

2.1. Samples

Water suspensions and water-saturated densely packed particles are chosen as samples in this work (Fig. 1). The solid phase of the suspensions is glass spheres with the diameter form 0 to 2 μm, the square root of the volume fraction of the solid phase of the suspensions is in the range from 0.06 to 0.02. The material of the densely packed particles is glass, the shape of the particles is spherical and irregular, the size of the particles is in the range from 60 to 440 μm. The square root of the volume fraction of the solid phase of the particles is in the range from 0.73 to 0.80. The samples are prepared by placing the known mass of the solid phase into an NMR sample tube with the known volume of water.

2.2 Instrumentation

The FID decay rates of the samples are measured with the utilization of a Varian Inova 500 NMR spectrometer. The magnetic field of the spectrometer is 11.74T, the inhomogeneity of the magnetic field is 2.4×10^{-7}T. The inhomogeneity of the magnetic field is determined with the use of the spectral line width of 10.2Hz of a pure water sample as well as the formulas (1) and (2). The images of the samples are acquired with the utilization of a Quanta FEI apparatus.

3. Results

3.1 Measurements

The widths of the NMR spectral lines of twelve samples are measured. The shape of the NMR spectral lines is close to Lorenzian. The FID decay rates of the samples are acquired with the utilization of the NMR spectral line widths and the formula (2) (Table 1). The outlier $\Delta\nu$=12.6Hz, which breaks the monotonicity of the experimental dependence, is accounted by the inhomogeneity of the constant magnetic field of the instrument. The values of true transverse relaxation rate are found to be in the range from 0.2 to 2 s^{-1}. It supports the validity of the assumption that the FID decay occurs due to the susceptibility differences between the solid and the liquid phase of the samples in this work.

Table 1 Particle sizes, NMR spectral line width $\Delta\nu$, volume fraction of the solid phase ξ, square root of the volume fraction of the solid phase $\xi^{0.5}$, FID decay rates $1/T_2^*$, FID times T_2^* of water suspensions and water-saturated porous media

	Avg size [μm]	$\Delta\nu$ [Hz]	ξ†	$\xi^{0.5}$	$1/T_2^*$ [s^{-1}]	T_2^* [ms]
Water suspensions of glass beads	1.5	12.6	0.03%	0.02	40	25.2
	1.5	12.1	0.06%	0.03	38	26.3
	1.5	17.9	0.11%	0.03	56	17.8
	1.5	25.6	0.17%	0.04	80	12.5
	1.5	27.3	0.24%	0.05	86	11.7
	1.5	35.3	0.32%	0.06	111	9.0
Water-saturated densely packed glass spheres	60	603	62%	0.78	1620	0.62
	390	393	56%	0.75	1320	0.76
	440	367	63%	0.79	1140	0.88
Water-saturated densely packed glass particles with irregular shape	95	517	64%	0.80	1890	0.53
	175	420	62%	0.79	1240	0.81
	275	362	53%	0.73	1150	0.87

3.2 Approximation

The experimental dependence is processed with the utilization of the method of least squares [9] and the analytical dependence $y=ax+b$ (Table 2). The experimental data acquired as a result of the measurements of the FID decay rate $1/T_2^*$ as well as the results of the approximation are plotted in a graph (Fig. 2). The proportionality constant of the dependence between the FID decay rate $1/T_2^*$ and the square root of the volume fraction of the solid phase $\xi^{0.5}$ of the samples is introduced to be equal to the coefficient a of the performed approximation:

$$a_{\text{Experiment}} = (1.83\pm0.25)\times10^3 s^{-1}. \qquad (4)$$

Table 2 The coefficients acquired as a result of the application of the method of least squares to the data acquired as a result of the measurement of the FID decay rates with a model function $y=ax+b$, r^2 is the coefficient of determination

	Value	Standard Deviation
a	1830	250
b	0.28	9.8
r^2	0.931	N/A

† For an ideal packing structure (i. e. either f. c. c. or h. c. p.) of solid spheres the volume fraction of the solid phase is equal to 74% [10], [11].

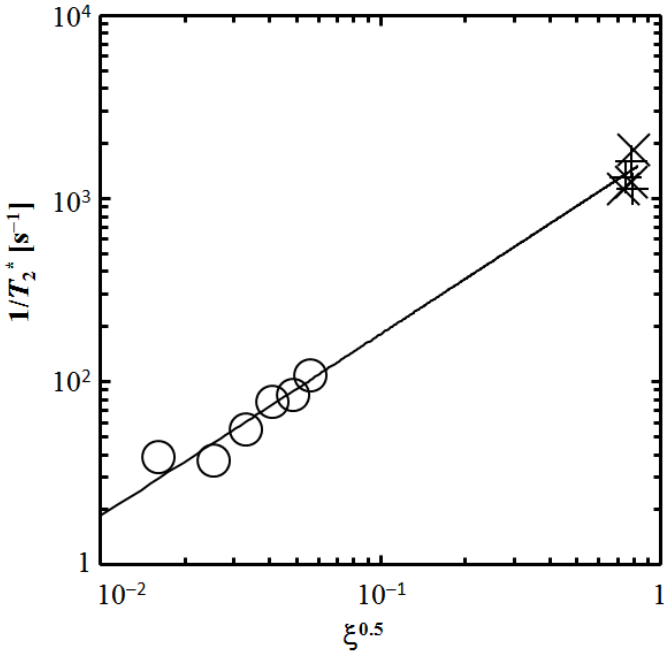

Fig. 2: The dependence of the FID decay rate $1/T_2^*$ on the square root of the volume fraction of the solid phase of suspensions (○) and water-saturated densely packed glass particles with spherical (+) and irregular (×) shape is linear

3.3 Model

A model of the decoherence of transverse magnetization is proposed. The model contains identical spheres in liquid and a constant external magnetic field. The magnetic susceptibility of the spheres and the magnetic susceptibility of the liquid are distinct. The following notations are utilized: $\Delta\chi$ — the difference between the magnetic susceptibility of the spheres and the magnetic susceptibility of the liquid; V_i — the volume of the i-th sphere; V — the volume of the sample; B_0 —the external constant magnetic field; $\nu_0=\omega_0/2\pi$ — Larmor frequency; B_i — the magnetic field in the volume equal to V_1 above the surface of the sphere; ξ — the volume fraction of the spheres; $1/T_2^*$ — the transverse magnetization decoherence rate.

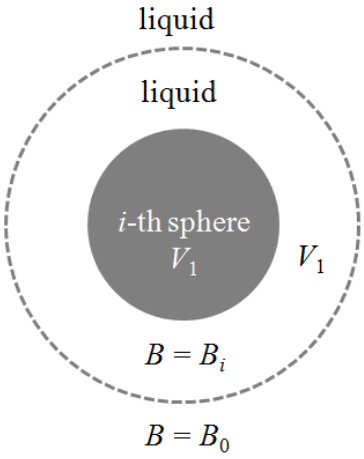

Fig. 3: It is assumed in the model an individual sphere creates an additional magnetic field exceptionally in the volume V_1 above the surface of the sphere.

Since the external magnetic field affects the sample and the magnetic susceptibilities of the spheres and the liquid are distinct an individual sphere creates an additional magnetic field. It is assumed the additional magnetic field is created exceptionally in the volume V_1, which is equal to the volume of the sphere, above the surface of the sphere (Fig. 3) and the displacement of an individual molecule during the time of the experiment exceeds the width of the layer above the sphere. The mean magnetic field in the sample is equal to the external magnetic field. The FID decay rate is proportional to the standard deviation of the magnetic field.

$$\frac{1}{T_2^*} \propto \Delta B_0 \equiv \sqrt{\frac{1}{V}\sum_i (B_i - B_0)^2 V_i} \equiv \sqrt{\xi \sum_i (B_1 - B_0)^2}\ , \tag{5}$$

$$\xi = \frac{1}{V}\sum_i V_i\ . \tag{6}$$

The totalization is performed with respect to all the spheres.

An analytical calculation of the proportionality constant a between the square root of the volume fraction of the solid phase $\xi^{0.5}$ of the sample and the FID decay rate $1/T_2^*$ of the sample is performed with the utilization of a similar model, in which different sphere sizes are allowed and the additional magnetic field, which is created by an individual sphere, is not limited by the layer above its surface. The following result is acquired:

$$\frac{1}{T_2^*} = \frac{8\pi^2}{3}\sqrt{\frac{2}{5}}|\Delta\chi|\nu_0\sqrt{\xi} = a\sqrt{\xi}\,,\ a = \frac{8\pi^2}{3}\sqrt{\frac{2}{5}}|\Delta\chi|\nu_0 = 16,6|\Delta\chi|\nu_0\,. \qquad (7)$$

A calculation of the constant a is performed for samples with the solid phase constituted by glass and the liquid phase constituted by water. The volume magnetic susceptibilities of water and glass are considered to be 0.79×10^{-6} and 1.0×10^{-6} CGS units respectively. The following result is acquired:

$$a_{\text{Model}} = 2.33\times10^{3}\text{s}^{-1}. \qquad (8)$$

3.4 Collation

A collation of the proportionality constants between the square root of the volume fraction of the solid phase $\xi^{0.5}$ of the sample and the FID decay rate $1/T_2^*$ of the sample acquired with the utilization of the measured FID decay rates (4) and with the utilization of the proposed model of the decoherence of transverse magnetization (8) is performed. Although the model proportionality constant is out of the range allowed by the experimental proportionality constant the two proportionality constants agree within a 50% error.

4. Conclusions

To conclude, this work contains evidence that allows to state that the Free Induction Decay rate of the liquid phase of suspensions of 1.5 μm glass particles in water and water-saturated densely packed particles with the size from 60 to 440 μm is proportional to the square root of the volume fraction of the solid phase of the sample for the volume fractions of the solid phase in the range from 10^{-4} to $\sim$1. Additionally, the proposed model of spheres in liquid is suitable for the description of the results of the measurements of the Free Induction Decay rates of such two-phase media. The magnetic susceptibility differences of samples are considered the dominant factor to FID decay in this work. The authors point out in certain in-situ locations other factors to the FID such as external constant magnetic field inhomogeneity might be substantial. The authors also point out that in this work the two-phase media with the volume fraction of the solid phase of the order of 10^{-4} and of the order of 1 are assumed to demonstrate identical dependence of the FID decay rate on the volume fraction of the solid phase. The behavior of such media with the volume fraction of the solid phase in the range from 10^{-3} to 10^{-1} should be studied in the future. Finally, the relatively large error of the model in comparison to the experiments is accounted by the fact that the model considers suspensions of spheres and does not consider particles with irregular shape or densely packed particles.

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