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A laboratory study of the effect of magnetite on NMR relaxation rates

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Abstract

We conducted a laboratory study to measure the effect of magnetite concentration and grain size on proton nuclear magnetic resonance (NMR) relaxation rates of sand mixtures and to determine the dominant mechanism by which relaxation occurs. We measured mixtures of quartz and three different forms of magnetite: a powdered synthetic magnetite; a small-grained, natural magnetite; and a large-grained, natural magnetite. The powdered synthetic magnetite was mixed with quartz in five concentrations ranging from 0.14 to 1.4% magnetite by weight; both sizes of natural magnetite were mixed with quartz in concentrations of 1 and 2% magnetite by weight. The NMR response of the water-saturated samples was measured and used to calculate four averaged relaxation rates for each magnetite concentration: the total mean log, bulk fluid, surface, and diffusion relaxation rates. The results of this study show that: 1) surface relaxation was the dominant relaxation mechanism for all samples except the powdered synthetic magnetite sample containing 1.4% magnetite; 2) the surface relaxivity is a function of the fraction of the surface area in the sample composed of magnetite; 3) there is no clear dependence of the diffusion relaxation rate on the concentration of magnetite.

Keywords: NMR; Magnetite; Transverse relaxation; Grain size

1. Introduction

Proton nuclear magnetic resonance (NMR) is a technique that can be used to detect the presence of hydrogen nuclei and to obtain information about their physiochemical environments. In a water-saturated geologic material the NMR relaxation measurement involves monitoring the relaxation, or return to equilibrium, of the bulk nuclear magnetization of the hydrogen nuclei in the pore water after the sample has been perturbed with a radio-frequency pulse. NMR relaxation measurements can be made in the laboratory or in the field using a well-logging device or a system deployed at Earth's surface. The well-logging system has been used for a number of years in the petroleum industry to determine reservoir permeability (e.g. Seevers, 1966; Timur, 1969; Korb et al., 2003) and has recently been used for hydrogeophysical applications (Clayton, 2006). The surface-based system, referred to as MRS (magnetic resonance sounding), has been used to estimate hydraulic conductivity in the top ~ 100m of Earth (e.g. Shushakov, 1996; Legchenko et al., 2002).

Of interest in our research is the effect of magnetite (Fe_3O_4), a commonly occurring oxide, on the NMR relaxation measurement for geological materials. It is well known that the NMR relaxation rate of a material can be affected by the presence of paramagnetic ions such as Fe(III), and by contrasts in magnetic susceptibility between the pore water and the solid phase. Magnetite contains Fe (III) and has a large magnetic susceptibility, so it is not surprising that, in a study by Keating and Knight (2007), the addition of magnetite to quartz sand was found to have a significant effect on the relaxation rate. This previous study compared the relaxation behavior of five iron-oxide minerals including magnetite and found that the presence of magnetite had a much stronger effect on the relaxation rate than the presence of the other iron-oxides. The objective of this study was to extend the previous by determining the specific mechanism/s by which magnetite impacts the NMR relaxation rate.

We conducted laboratory experiments using quartz sand mixed with known concentrations of magnetite. We limited our measurements to magnetite concentrations of less than 2%

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which is representative of the magnetite concentrations found in natural environments (Thompson and Oldfield, 1986). Because magnetite can be present in soils as small crystals formed by biogeochemical processes (Oldfield, 1999; Evans and Heller, 2003) or as large grains from anthropogenic sources or physical weathering, we tested three grain sizes by using a powdered synthetic magnetite, a small-grained natural magnetite and a large-grained natural magnetite. These measurements advanced our understanding of the effect of magnetite on NMR relaxation data; knowledge that is essential if we are to obtain accurate information from NMR data in many geologic environments.

2. Background and theory

2.1. NMR relaxation theory

Proton NMR detects the presence of hydrogen nuclei; for hydrogeophysical applications the ability to detect hydrogen nuclei is of interest due to the presence of hydrogen in water. Each hydrogen nucleus, composed of a single proton, possesses a nuclear spin angular momentum. When in a static magnetic field, B_0, the nuclear spins in water precess about the static field. The nuclear spins precess at the Larmor frequency, f_0, which is related to B_0 by

$$f_0 = \gamma|B_0|/(2\pi) \tag{1}$$

where γ is the gyromagnetic ratio for hydrogen protons in water molecules ($\gamma = 0.267$rad/[nT·s]). For MRS instruments f_0 ranges from 0.8 to 2.8kHz; for NMR well-logging instruments f_0 ranges from 0.5 to 2MHz; for most laboratory instruments f_0 ranges from 0.01 to 900MHz. If a weak magnetic field oscillating at f_0 is applied the nuclear spins will tilt away from their equilibrium position. Once the oscillating field is removed the nuclear spins will return, or relax, to their equilibrium position. The return to equilibrium results in a measurable signal from the bulk nuclear magnetization, which can be described in terms of the transverse magnetization, M_{xy}.

For a bulk fluid the return to equilibrium behaves as an exponential decay:

$$M_{xy}(t) = M_0 \exp(-t/T_{2B}) \tag{2}$$

where M_0 is the initial magnetization, t is time and T_{2B} is the bulk fluid relaxation time; the inverse, T_{2B}^{-1}, is referred to as the bulk fluid relaxation rate. M_0 is proportional to the total number of hydrogen nuclei in the bulk water. The magnitude of T_{2B}^{-1} for a fluid is controlled by dipole–dipole molecular interactions and depends on the viscosity of the fluid, the concentration of dissolved paramagnetic species (such as dissolved oxygen, Mn (II) ions or Fe(III) ions) and pH (Bloembergen et al., 1948).

For water confined in a pore, the measured relaxation rate is generally found to be greater than the bulk fluid relaxation rate due to two mechanisms that can enhance relaxation: surface relaxation and diffusion relaxation. In a single pore, the relaxation rate of water, T_2^{-1}, is described as a sum of relaxation rates (Brownstein and Tarr, 1979):

$$T_2^{-1} = T_{2B}^{-1} + T_{2S}^{-1} + T_{2D}^{-1} \tag{3}$$

where T_{2S}^{-1} represents the surface relaxation rate and T_{2D}^{-1} represents the diffusion relaxation rate. Eq. (3) is valid for samples in the fast diffusion regime, which assumes that all protons travel to and interact with the solid surface within the time interval of the NMR experiment. For water in a porous geological material with a range of pore sizes, a multiexponential decay is observed,

$$M_{xy}(t) = \sum_i m_i \exp(-t/T_{2i}). \tag{4}$$

Here m_i is proportional to the number of moles of hydrogen relaxing with rate T_{2i}^{-1}. The total number of moles of hydrogen is proportional to $M_{xy}(0) = \Sigma m_i$. The values of m_i versus T_{2i} are often plotted to show the distribution of relaxation times. In studies of the NMR response of porous materials, the arithmetic mean of log T_{2i}, T_{2ML}, is typically calculated from the distribution of relaxation times and used to represent the relaxation behavior. Eq. (3) then becomes:

$$T_{2ML}^{-1} = T_{2B}^{-1} + T_{2S}^{-1} + T_{2D}^{-1} \tag{5}$$

where rates are now taken to be average values for the entire pore space of the sample material instead of a single pore. While the magnitude of T_{2B}^{-1} is determined by the properties of the pore fluid, the magnitudes of T_{2S}^{-1} and T_{2D}^{-1} are strongly affected by the properties of the solid phase and controlled by very different relaxation mechanisms, referred to as the surface and diffusion relaxation mechanisms. Central to our research is the question of how the presence of magnetite influences these mechanisms. In the next sections we briefly review the way in which the properties of a geological material determine surface and diffusion relaxation rates.

2.2. Surface relaxation

The surface relaxation rate is determined by interactions that occur between the hydrogen nuclei in water and the solid surface of the geologic material. In the case of fast diffusion the surface relaxation rate is given by (Senturia and Robinson, 1970; Brownstein and Tarr, 1979),

$$T_{2S}^{-1} = \rho_2 S/V \tag{6}$$

where S/V is the surface-area-to-volume ratio of the water-filled pore-space and ρ_2 is the surface relaxivity. For the fast diffusion assumption to be valid, the following relationship must be satisfied: $\rho_2 V/S \ll D$, where D is the self-diffusion coefficient of water ($D = 2.5 \times 10^{-5}$ for water at 30°C). The relationship between the surface relaxation time and the surface-area-to-volume ratio shown in Eq. (6) is the basis for the use of NMR relaxation times to estimate permeability (e.g. Seevers, 1966; Timur, 1969) and hydraulic conductivity (e.g. Legchenko et al., 2002).

Current NMR theory associates ρ_2 with the presence of paramagnetic species (i.e. unpaired electrons) on the surfaces of the pore-space (Brownstein and Tarr, 1979; Godefroy et al., 2001). Laboratory studies of samples with known concentrations of paramagnetic ions, both in solid grains and adsorbed to