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The Proton Nuclear Magnetic Resonance Spin-Lattice Relaxation Rate of Some Hydrated Synthetic and Natural Sands

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Abstract

The proton nuclear magnetic resonance (NMR) spin-lattice relaxation rate (R_1) of hydrated sands is often used to determine porosity characteristics of near-surface aquifers using magnetic resonance sounding. Large variations in R_1 have been reported in laboratory measurements on hydrated sands. To understand these variations, the R_1 values of several fully hydrated sands were studied as a function of grain diameter (d) and magnetic field strength (B_0). We conclude the variations are a consequence of trace paramagnetic metals in the sand grains. R_1 values from magnetic resonance sounding data should not be used to predict void size in aquifers unless the exact chemical composition of the grains is known.

Keywords

hydrated sand, hydrated spheres, NMR spin-lattice relaxation rate, R_1, NMR

1. Introduction

The proton NMR spin-lattice relaxation rate of hydrated sands is important in determining the porosity characteristics of near-surface aquifers using magnetic resonance sounding [1]. Large variations in R_1 have been reported in laboratory measurements on hydrated sands [2]. We believe these variations are attributable to the different B_0 values used for the measurements and paramagnetic impurities in the sand. We measured the R_1 of fully hydrated quartz sands as a function of sand type, particle geometry, d, and B_0 using field cycling NMR. These R_1 values were compared to R_1 values for fully hydrated synthetic sands consisting of glass spheres.

Hydrated sands can be modeled as a network of well-connected pores. In the fast diffusion or surface limiting case of water confined in a pore,

$$R_1 = R_{1B} + \rho\,(S/V)_P \tag{1}$$

where R_{1B} is the bulk water contribution, ρ the surface relaxivity, and $(S/V)_P$ the surface to volume ratio of the pore.

2. Experimental Methods

Three natural quartz sands were investigated: Sea (01B252, City Chemical), Ottawa, IL (F110, US Silica), and Oregon, IL (7020 Granusil, Unimin Corp.). Sand samples were cleaned by repeated rinsing with 18 MΩcm water, dried at 200ºC, and sieved using a mechanical sieve shaker to obtain the mean d values shown in Fig. 1. Eleven synthetic sand samples in the form of monodispersed soda lime glass sphere samples were obtained with $2\ \text{mm} < d < 49\ \mu\text{m}$ from two sources (Quackenbush (Q), Crystal Lake, IL, USA, and Whitehouse Scientific (WS), Chester, UK). Spheres were base cleaned, rinsed multiple times with 18 MΩcm water, and dried at 200°C. Samples were placed in NMR tubes, hydrated with 18 MΩcm water, and sonicated to remove air bubbles.

All samples were characterized using an optical microscope (Eclipse E600PL, Nikon) coupled with image analysis software (analySIS, Olympus). The mean and standard deviation in d were determined from 100 sieved grains, while sphericity and shape factor were determined from 20 sieved grains. Sample porosity was determined using the dry mass, volume, and density. R_1 values were recorded using an inversion recovery sequence [3] and the field cycling technique [4] implemented respectively on a 300 MHz (Bruker DRX-300) NMR spectrometer, and on a fast field cycling NMR spectrometer (Stelar FFC-2000) at $2.3\times10^{-4}\ \text{T} < B_0 < 0.7\ \text{T}$. Chemical analysis was performed by energy dispersive x-ray microanalysis (EDXM) using a scanning electron microscope (JEOL JSM-6400V), and electron spin resonance (ESR) spectroscopy using an x-band (Bruker, ESP-300) spectrometer. The relative concentration of paramagnetic impurities in the sands was determined from the double integration of the first derivative ESR spectra scaled for packing density in the tube.

3. Results & Discussion

Magnetization recovery data for all the sand samples displayed monoexponential behavior. R_1 values increased with decreasing d. The increase became greater as ν decreased. Samples displayed the expected relationship between R_1 and log(ν) [5] for $10\ \text{kHz} < \nu < 30\ \text{MHz}$.

The two smallest d sieved Ottawa sands displayed an order of magnitude faster R_1. EDXM analysis revealed the presence of pyrite grains, probably dislodged by mechanical abrasion during the sieving and stopped by the smallest sieves. In the synthetic sand and the Ottawa 84 and 117 μm samples there is a dispersion between 30 and 300 MHz attributable to proton-electron dipolar and hyperfine interactions associated with the larger amount of paramagnetic material in the synthetic sand and the Ottawa 84 and 117 μm samples.

Fig. 1 presents R_1 values as a function of d for the various sands at $\nu = 10$ kHz. Owing to the relationship between d and $(S/V)_P$, the R_1 dependence on d followed Eqn. 1. The exception is at large d values where the sample tube diameter influenced the packing and $(S/V)_P$. Extrapolation of the relationship between log(ν) and R_1 in the field cycling data, allows prediction of R_1 at $\nu = 2.5$ kHz or $B_0 = B_{\text{Earth}}$. Although predictions based on extrapolations are risky, we are fairly comfortable making this prediction based on knowledge of dispersions and trends in similar systems [6,7]. Measurable R_1 differences were observed between the three natural quartz sands and synthetic glass sands. These differences cannot be attributed to the geometric characteristics of the grains and porosity differences, as these were identical within experimental uncertainty. Ideally, knowledge of the pore surface-to-volume ratio would be useful in comparing sands. In its absence, we infer similar values based on the similarities in the aspect ratio, uniformity, sphericity, shape factor and regularity of the grains. The three quartz sands had different quantities of trace paramagnetic impurities in the grains as determined by ESR, with the highest concentration in the Sea sand and the least in the Ottawa sand. (See Table 1.) Although the exact impurities were not determined, their concentrations explain the ρ values needed to fit the data in Fig. 1.

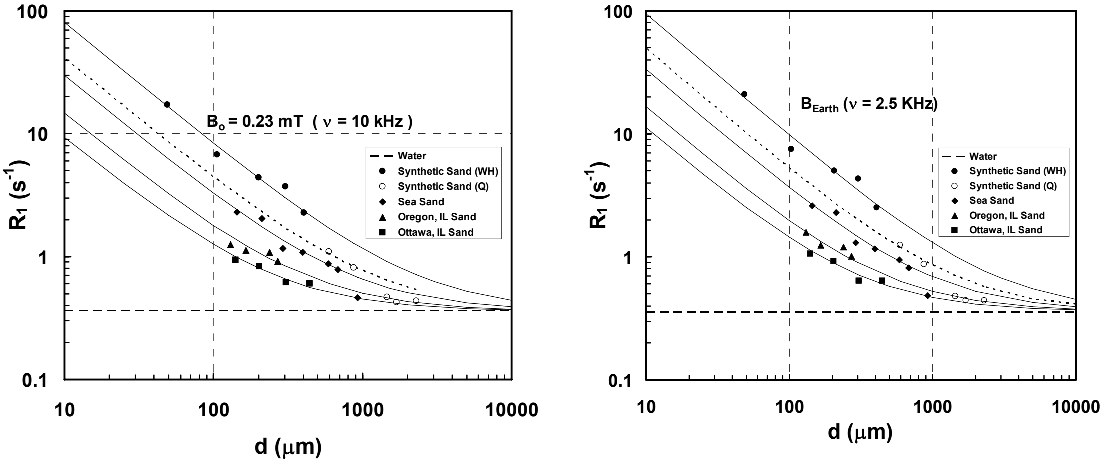

Fig. 1: Proton R_1 as a function of particle diameter a) measured at $\nu = 10$ kHz, and b) predicted at $\nu = 2.5$ kHz or B_{Earth} for fully hydrated, random-packed natural and synthetic sands. Solid and dotted lines are a fit of eqn. 1 to the data using relative ρ values from Table 1. The dashed line represents the R_1 value for bulk water.

Sand Type	ρ^*	ESR Signal**	
		Quartz	Glass
Ottawa	1	1	
Oregon	1.6	1.7	
Sea	3.3	3.6	
Spheres (Q)	4.6		1
Spheres (WS)	8.9		1.5

* Normalized to Ottawa Sand.

** ESR signals may only be compared within a material class.

4 . Conclusion

Hydrated synthetic and natural sands displayed a logarithmic relationship between R_1 and ν. The relationship between R_1 and d followed eqn. 1, except at large d values where the grain packing and $(S/V)_P$ ratio became dependent on the geometry of the sample tube.

Variations in R_1 seen in the geophysical literature are the result of dissimilar B_0 values, grain diameter distributions, and trace paramagnetic metals in the grains. Based on these findings, R_1 values from magnetic resonance sounding data should not be used to predict void size in aquifers unless the exact chemical composition of the grains is known.

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