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# Effect of Goethite Coating on the Nuclear Magnetic Resonance Relaxation Signal in Sand

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## Abstract

Nuclear magnetic resonance relaxation is a fast and well-known method to get a measure of pore size distributions. To obtain reliable results, one needs to get information about influences like internal gradients evoked by paramagnetic impurities on the NMR relaxation signal. Therefore, we did a series of longitudinal and transverse relaxation experiments of samples with variable paramagnetic content. Missing echo time and magnetic field strength dependence leads us to the conclusion that we have no significant influence of internal gradients in our measurements.

## Keywords

Relaxation, Porous media, Internal magnetic field gradients, Paramagnetic impurities

## 1. Introduction

Nuclear magnetic resonance (NMR) relaxation is a fast and furthermore non-invasive method of measuring water content and relaxation time distributions of porous media like soil. Relaxation times are related to pore size distributions [1] but one has to take into account that different processes may contribute to the relaxation rate. These are changes in the surface relaxivities $\rho_1$ and $\rho_2$ due to different materials on the surface of pores [2], and molecular diffusion of water molecules through local field gradients, often called internal gradients. Magnetic susceptibility differences between solid and liquid phases create these field gradients which depend on the magnetic field strength [3-5]. But also paramagnetic impurities may evoke local field gradients [6]. Diffusion through these local gradients, independent of their cause, accelerates the transverse relaxation rate of the NMR signal dependent on the echo time, but not the longitudinal relaxation rate.

The aim of this work is to separate the relative contributions of the different processes to the NMR relaxation signal and to determine the effect of paramagnetic impurities. Already in [6] theoretical work on relaxation in porous media with paramagnetic content was shown together with studies of sands with variable magnetite content. Taking a step forward, in this work we measured the longitudinal and transverse relaxation time distribution functions at increasing echo times for a series of sand samples which are covered with various amounts of goethite (FeO(OH)) in two magnetic field strengths.

## 2. Methods and Materials

The NMR relaxation experiments were conducted at two different magnetic field strengths, at 0.15 T and at 7 T. The low field system consists of a home built Halbach magnet with solenoid RF coil as resonator which was operated by a STELAR spectrometer (Stelar, Mede, Italy). In high field, the experiments were performed in a vertical wide bore super-conducting magnet (Oxford Instruments, UK) with a birdcage resonator connected to a Varian console. To determine the transverse relaxation time $T_2$, the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was employed using different echo times $t_E$. The longitudinal relaxation time $T_1$ was determined using the Inversion Recovery pulse sequence. The relaxation time distributions were calculated using the 1D Inverse Laplace Transformation of Magritek (Wellington, NZ).

All relaxation experiments were performed for water saturated samples in glass tubes with an inner diameter of 18 mm and a height of 40 mm.

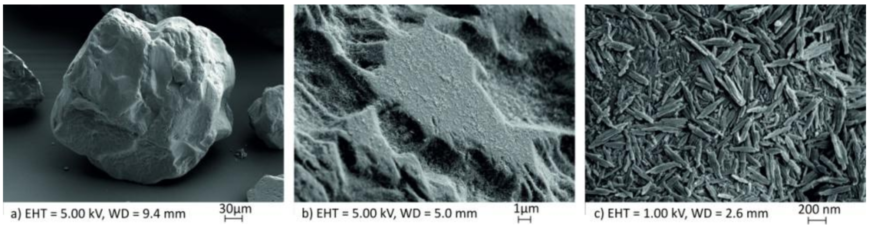

**Fig. 1:** SEM images of the coated sand sample with highest coating density in various scales. The goethite coating is non-uniformly distributed over the grain.

We measured a series of quartz sand samples with different coating densities of goethite (α-FeOOH, Sigma Aldrich Chemie GmbH, Steinheim, Germany) at the surface of the grains. Thus, $Fe^{3+}$ is the paramagnetic ion. We started with an acid washed $SiO_2$ sand (Sigma Aldrich Chemie GmbH, Steinheim, Germany) without any impurities at the surface of the sand grains and a medium grain size of 0.22 mm. We produced two different surface densities of goethite by preparing a suspension of goethite at a fixed pH value (2.5 and 4.0) and shaking the sand in this suspension for 24 hours at 80° C. After cooling to room temperature, the sand-goethite-mixture was washed with 1 M $NaNO_3$ and DI water to remove all particles not attached to the sand surface until a clear, colorless solution and a constant pH was reached. Due to strong electrostatic bonding between adsorbed goethite particles and the sand surface, detachment of goethite particles into water was negligible. An SEM image of the coating is shown in Figure 1. We created further surface densities by washing the coated sand for 20 minutes with various acids (0.01 M $C_6H_8O_7$ and 2 M HCl). The different mass fractions are summarized in Table 1.

| sample | preparation | mass fraction [µg Fe / g sand] |
|---|---|---|
| SG1 | $SiO_2$/goethite suspension with pH of 2.5 | 980 |
| SG2 | SG1 in 0.01M $C_6H_8O_7$ washed | 770 |
| SG3 | $SiO_2$/goethite suspension with pH of 4.0 | 540 |
| SG4 | SG1 in 2M HCl washed | 440 |
| SG5 | SG3 in 0.01M $C_6H_8O_7$ washed | 320 |
| SG6 | SG3 in 2M HCl washed | 220 |
| F32 | natural quartz sand | 300 |
| $SiO_2$ | acid washed $SiO_2$ sand | 0 |

**Tab. 1:** Investigated sand samples with varied preparation technique and variable fractions of goethite on the surface.

As reference samples without additional paramagnetic impurities served the original acid washed $SiO_2$ sand and the natural quartz sand F32 (Quarzwerke GmbH, Frechen, Germany) with a medium grain size of 0.24 mm and a natural iron oxide content of 0.03 % w/w. It should be noted that for this sand, both the distribution of Fe between surface and interior and the oxidation number are unknown. The effective pore size for all samples was less than 100 µm considering the grain size of the parent $SiO_2$ material. That makes the surface relaxation term more than a factor three higher than the bulk water relaxation term and thus the surface relaxation played the dominant role in our measurements.

## 3. Results and Discussion

$T_2$ relaxation time distributions of all samples were measured in low ($B_0$ = 0.15 T) and high ($B_0$ = 7 T) magnetic field (Figure 2).

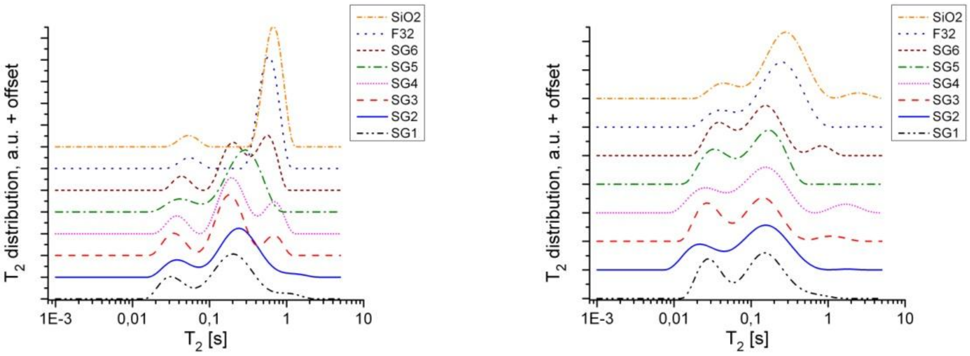

**Fig. 2:** Transverse relaxation time distributions of all samples at low (left) and high (right) magnetic field strength, echo time $t_E$ = 0.5 ms. The goethite fraction increases from top to bottom. The repetition time was $t_R$ = 7 s, the number of echoes $n_E$ = 6000. The number of scans was $n_S$ = 128 at $B_0$ = 0.15T, and $n_S$ = 4 at $B_0$ = 7T.

Generally, bimodal distributions are observed with some non-systematic exceptions. At high field some minor modes at $T_2$ > 1s are observed which are most probably due to bulk water. All samples measured at 0.15 T show a fast mode which shifts slightly from 60 ms to 30 ms with increasing Fe content. At 7 T the corresponding mode shifts from 40 ms to 20 ms. The slower mode is broader and in some cases resolved into two modes or a shoulder. For these modes no change of the average $T_2$ time is observed for the coated samples and we find values of $T_{2,\ slow} \cong 200$ ms at both field strengths. With decreasing Fe content an additional very slow mode develops at around 600ms for 0.15 T. This is also the only slow mode for the untreated samples. For 7 T the situation is not so clear. The slow mode occurs at about 150ms for all coated samples, but the very slow mode of the reference samples is now at about 300 ms. This is too close that any occurrence of such mode at the coated samples could be distinguished beneath the 150 ms mode.

To check if some of the modes are controlled by diffusion in internal gradients, we also performed measurements with various echo times (an example is shown in Figure 3, but the other samples showed comparable effects at both high and low field strengths). Minimum echo time common for both field strengths was 0.3 ms due to technical limitations at high field, the maximum echo time was 3.0 ms. Experiments with smaller echo times possible at low field only did not show different effects. For increasing values of $t_E$ we observed a relative increase of the average amplitude of the fast mode at the expense of that of the slow mode. However, we observed no shift of the slow mode and only insignificant shift of the fast mode depending on the echo time. It should be noted that only if one would plot the average $T_2$ of both modes an apparent decrease of this $T_2$ with increasing echo time would result, as it was reported earlier [7]. Anyway, this detailed analysis proves that diffusion in internal gradients plays no significant role in our measurements.

Additionally, one can compare the measurements in low and in high magnetic field (Figure 2) because internal gradients evoked by susceptibility differences are expected to be field strength dependent [4]. We observed only relatively small decreases of $T_2$ of about a factor two when increasing the field strength from 0.15 T to 7 T. Taking both effects into account, the independence of the $T_2$ relaxation modes from $t_E$ and the minor influence of $B_0$ indicate the negligible influence of diffusion in internal gradients.

In contrast to the transverse relaxation time distributions the longitudinal relaxation time distributions (Figure 4) show only one mode also with no significant shift with coating density. Only the reference sample peaks are shifted to longer relaxation times.

## 4. Conclusion

We investigated the effect of different goethite coating densities on the surface of sand grains on the longitudinal and transverse relaxation times as a function of echo time at low and high magnetic field strengths. Both longitudinal and transverse relaxation time distributions show no dependence on the coating density. There is only a difference if there is goethite on the sand surface or not. This indicates that all coated samples have enough paramagnetic centers at the pore walls that each water molecule reaching the pore wall actually relaxes at a goethite particle. Thus, we would expect a transition between the reference samples and the coated samples for much smaller coating densities.

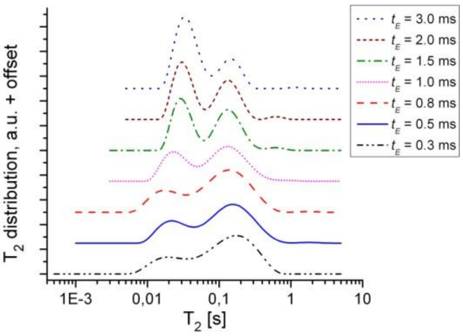

**Fig. 3:** $T_2$ relaxation time distributions of measurements with various echo times of one example (sample SG2) at $B_0$ = 7 T. The echo times are $t_E$ = 0.3 ms, 0.5 ms, 0.8 ms, 1.0 ms, 1.5 ms, 2.0 ms, and 3.0 ms.

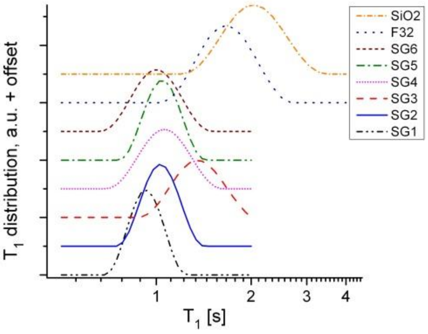

**Fig. 4:** Longitudinal $T_1$ relaxation time distribution of all samples at $B_0$ = 7 T. The repetition time was $t_R$ = 7 s with 32 logarithmically spaced waiting times between 10 ms and 2 s.

Furthermore, there are only insignificant shifts of the relaxation time distribution modes with the echo time and only small shifts depending on the magnetic field strength. Both indicate negligible influences of diffusion in internal gradients in our experiments. These findings are partly contradictory to the results of [6] where the authors report echo time dependent $T_2$ relaxation times at high surface particle densities of magnetite but with shorter relaxation times. Moreover, in our study the longitudinal relaxation time distributions are monomodal while the transverse distributions show a bimodal behavior. The amplitudes of the fast modes increase with $t_E$ while the amplitudes of the slow mode decrease. We have no conclusive explanation for this. One possibility would be that due to the high surface relaxivity the $T_2$ processes are not in the fast diffusion limit, another explanation is a parallel surface relaxation mechanism independent of internal gradients. Further clarification requires additional experiments.

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