Earth Field NMR of Porous Systems

M. Veevaete, V. Hormann, R. Goedecke, H.W. Fischer

Institute of Environmental Physics, University of Bremen, Germany

Earth Field NMR

Earth field NMR uses the globally available, homogeneous Earth magnetic field for detection.

$B_0 \sim 50\ \mu T$ ($\omega_L \sim 2kHz$)

The poor sensitivity arising from the low Larmor frequency is compensated by the large homogeneity that permits the use of large samples and by enhancing the initial magnetisation by means of pre-polarizing [1].

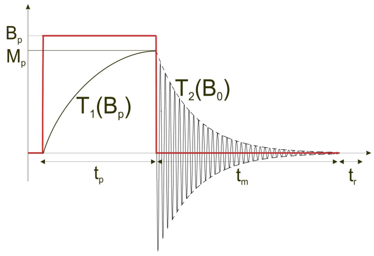
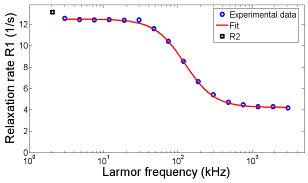


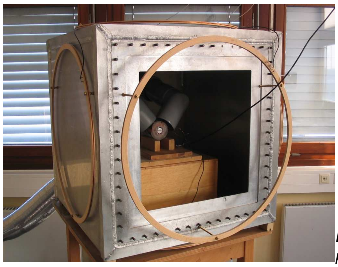
***Figure 1**: Magnetic induction (red) and x-component of the macroscopic magnetic moment (black) in the Earth magnetic field by the method of Packard and Varian 1954 [1]. With: t_p= polarisation time; t_m= measuring time; t_r= repetition time*



By means of varying the polarising current, the apparatus can be used as a field cycling relaxometer. The longitudinal relaxation times can be measured in a range of 3kHz up to 3MHz.

***Figure 2**: Longitudinal relaxation dispersion of a $MnCl_2$ solution (205µmol/l) measured with the Earth field NMR apparatus*

Experimental setup

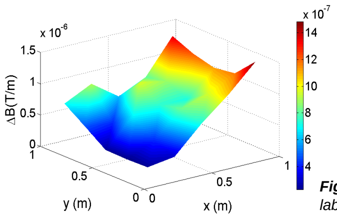


The Earth field NMR device has been developed in-house based on the design presented in [2]. It is built in a way that it can be used in a normal laboratory environment with disturbances from electromagnetic fields and deterioration of the field homogeneity by steel in reinforced concrete or furniture. Self compensation against external alternating fields is achieved by a first order gradiometer construction. The temperature of the sample is kept constant (+/- 1°C) by means of temperated air.

***Figure 3**: Aluminium shielding box with 3 Maxwell pairs and polarisation/detection coil in the center*

The advantages of this measuring method are:

- Low manufacturing and operational costs (magnet is not required)
- Due to the homogeneity of the Earth's field relatively large samples can be used (max. sample volume = 25 ml)
- The magnetization decay can be analysed with resolution of 250 µs
- Accessibility of the sample makes temperature and drying experiments possible
- T_1 dispersion and T_2 can be measured with the same apparatus



In a normal laboratory environment the Earth's magnetic field is disturbed. This disturbance is minimized by an appropriate location of the coil in the laboratory. By adjusting the current through three pairs of Maxwell coils the magnetic field gradient within the sample volume can be almost completely cancelled out and a very homogeneous field is obtained

***Figure 4**: The magnetic field inhomogeneity in the laboratory*

Due to the excellent field homogeneity it is possible to directly derive the transversal relaxation times from the digitised free induction decay (FID) signal with a signal to noise ratio of about 100, without need for pulse sequences as in conventional NMR techniques.

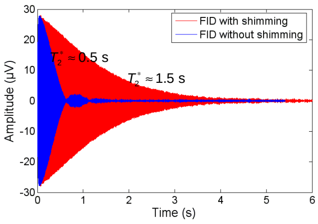


***Figure 5**: FID in the Earth's magnetic field of 25 ml H_2O at 20°C with and without shimming*

Results

Randomly packed glass beads

T_1 and T_2 of cleaned randomly packed glass beads were measured in function of the pore size at 20°C. Pore size, grain size and porosity are related by:

$$d_{pore} = \left(\frac{\phi}{1-\phi}\right)^{1/3} d_{grain} \qquad (1)$$

Usually the FIDs of randomly packed glass beads are considered to be mono-exponential as confirmed by the relaxation time distributions in Figure 6. Therefore we can use a mono-exponential fit to analyse the magnetization decay.

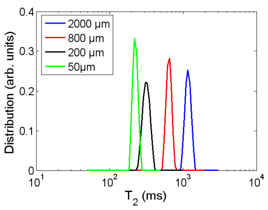


***Figure 6**: Relaxation time distribution of water in randomly packed glass beads*

The general model describing the relaxation of liquids filling pores [3]:

$$\frac{1}{T_{1,2}} = \frac{1}{T_{1,2b}} + \frac{\rho_{1,2}\cdot\alpha}{r}\,\frac{1}{1+\frac{\rho_{1,2}r}{2D}} \qquad (2)$$

gives good results for T_1 and can be simplified to: $\frac{1}{T_{1,2}} = \frac{1}{T_{1,2b}} + \frac{\rho_{1,2}\cdot\alpha}{r}$ (3)

under the condition of surface limited relaxation.

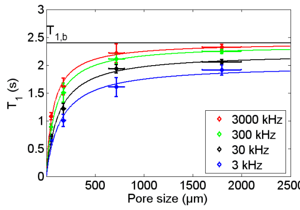


***Figure 7**: T_1 in function of pore size and Larmor frequency. The lines represent the best fit using Eq. (3).*

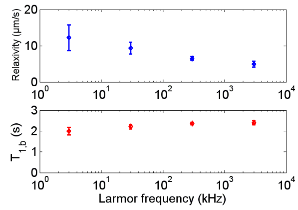


***Figure 8**: Parameters for the surface limited relaxation model (Eq. 3) in function of the Larmor frequency with α=3*

Sintered glass beads

T_1 and T_2 of sintered glass beads were also measured in function of the pore size at 20°C and analysed with a mono-exponential fit. The surface limited relaxation model (Eq. 3) fits very well to both T_1 and T_2 data.

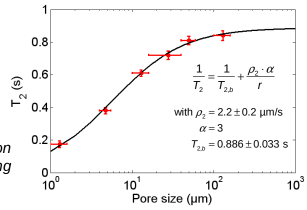


***Figure 9**: Mono-exponential analysis of T_2 in function of the pore size. The line represents the best fit using Eq. (3).*

The values for the relaxivity are comparable with literature values [3, 4]. Although most models attribute the frequency dependence only to the surface contribution, one can see from Figure 10 and 11 that at low fields the bulk value is also frequency dependent:

$$\frac{1}{T_1(\omega_l)} = \frac{1}{T_{1b}(\omega_l)} + \frac{\rho_1(\omega_l)\cdot\alpha}{r} \qquad (4)$$

This was also found by [5].

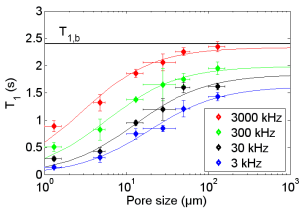


***Figure 10**: Mono-exponential analysis of T_1 in function of the pore size and frequency. The lines represent the best fit using Eq. (3).*

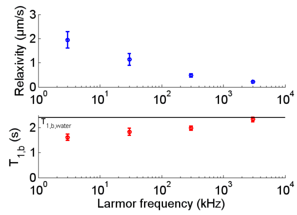
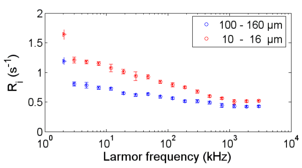


***Figure 11**: Frequency dependence of the relaxivity and $T_{1,b}$ according to Eq. 4 with α=3*



A plot of the longitudinal relaxation dispersion from 3 kHz up to 3 MHz shows that at about 1 MHz the relaxation rates reaches its minimum. At a Larmor frequency of a few kHz R_2 is still significantly larger than R_1.

***Figure 12**: R_1 dispersion (O) and R_2 (▷) in the Earth's magnetic field for sintered glass beads of various pore sizes*

First results from a bimodal porous system

The pore size distribution of a bimodal porous system containing 87 % Al_2O_3 and 13% SiO_2 was analysed by T_2 relaxometry and compared with Hg-porosimetry results.

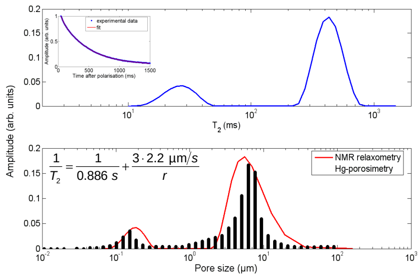


***Figure 13**: Calculation of the pore size distribution of a bimodal porous system with Earth field NMR relaxometry*

References

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