PROBING THE CONNECTIVITY BETWEEN PORES IN ROCK CORE SAMPLES

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ABSTRACT

By Nuclear Magnetic Resonance (NMR) measurements of relaxation and diffusion at a predefined observation time in 100 % brine saturated rock core samples it is possible to probe the connectivity between the pores within the sample. By plotting the observation time dependent diffusion coefficients as a function of the surface-to-volume ratio characteristic for each sample, it is possible to compare the connectivity between rock core samples.

INTRODUCTION

When working with NMR special core analysis (SCAL) methods at laboratory conditions, rock core samples may be saturated with brine and the surface-to-volume ratio and pore size distribution may be measured by dynamic NMR (Mitra et al (1993), Sørland et al (2006)). The diffusional displacement of water molecules in a system of isolated pores is restricted by the surrounding pore walls. Introducing some degree of connectivity in the system increases the possibilities of diffusion between pores during a given observation time and the apparent diffusion coefficient, as measured by NMR, increases.

From diffusion measurements at short observation times an average surface-to-volume ratio \( \langle S/V \rangle \) can be found. Having found this value, one may choose an observation time for the measurement of the diffusion coefficient such that the mean square displacement at bulk diffusion is, for example, \( 3\langle V/S \rangle \). With a connected pore space one would then expect to measure a diffusion coefficient which lies between the two extreme cases; bulk diffusion and diffusion within spheres of radius \( 3\langle V/S \rangle \), in the case of spherical pores. Previous attempts to measure connectivity, which in turn may be related to permeability using NMR, has failed because the life time of the NMR signal is not long enough for the diffusing molecules to probe the heterogeneity of the porous rock. Usually the NMR signal has decayed substantially before the tortuosity limit is reached, \( i.e. D(\text{observation time})/D(\text{bulk}) = \text{constant} \). Our approach is different as we are aiming at measuring the diffusion coefficient at an observation time that is predefined or scaled to the measured \( V/S \) for the specific rock core sample. Thus we measure a diffusion coefficient that can be compared against the extreme cases, zero connectivity and no restrictions.
THEORY

By the means of various NMR measurement techniques, it is possible to reveal information on the porous structure of a brine saturated rock core sample. The apparent diffusivity, or time-dependent diffusion coefficient, is defined in terms of the mean-square displacement of the molecules during a time \( t \) by Einstein’s diffusion mobility relation

\[
D(t) = \frac{\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle}{6t}
\]  

where \( \mathbf{r}(t) \) is the position of the spin polarized molecule at time \( t \) and the average is over the entire ensemble of such molecules in the pore. According to Mitra et al (1993) this can be approximated as

\[
\frac{D(t)}{D_0} \approx 1 - \frac{4}{9\sqrt{\pi}} \sqrt{D_0 t S/V}
\]

where \( D_0 \) is the unrestricted diffusion coefficient, in bulk fluid, and \( t \) is the observation time. Equation (2) is the first term of a perturbation expansion of the time-dependent diffusion coefficient. The implied approximation is valid at short observation times, i.e. when only a small amount of the fluid is probing the restrictions (pore walls). Then the deviation from bulk diffusion is dependent on the surface-to-volume ratio alone and not on the surface relaxivity. Thus by conducting diffusion experiments at short observation times, a linear fit to the attenuation will give the surface-to-volume ratio \( S/V \). This can be combined with relaxation time measurements to give a pore size distribution of the rock core sample (Sørland et al 2006) Knowing the surface-to-volume ratio, one may also transform the observation time dependent diffusion by using the Einstein relation for the root of the means squared displacement

\[
\sqrt{D_0 t} = n \left( \frac{S}{V} \right)^{-1}
\]

where \( n \) is an arbitrary number. Substitution of Equation (3) into Equation (2) yields

\[
\frac{D(t)}{D_0} = 1 - \frac{4}{9\sqrt{\pi}} n
\]

Thus by plotting the observation time dependent diffusion coefficient as a function of \( n \), i.e. in units of \( (S/V)^{-1} \), we shall get a slope of the initial attenuation that is independent of the sample being investigated, i.e. a universal slope equal to \(-4/(9\sqrt{\pi})\) (Valfouskaya et al (2005)). However, using the same scaling at longer observation times, the attenuations may deviate from the universal slope to a degree depending on the porous structure of the sample. Assuming that the observation time dependent diffusion coefficient is determined by the pore space geometry only, we expect that the given scaling would give overlapping curves only for identical structures. With this scaling the molecules in two identical structures of different dimensions will probe identical pore spaces at the same value of \( n \). Thus their curves should overlap at all numbers of \( n \). This situation is equivalent to measuring diffusion in the same system but at different temperatures (Hurlimann et al 1994, Seland et al 2000). Then a plot of the \( D(t)/D_0 \) as a
function of the mean squared displacement is independent of temperature, as shown elsewhere. In figure 1 we recapture the results on compact polystyrene spheres of diameter 45 and 98 µm, plotted as a function of the root of the mean squared displacement and normalized against \((S/V)^{-1}\). The initial decay coincides with the universal slope \(-4/(9\sqrt{\pi})\), while at higher values it approaches a tortuosity limit of approximately 0.7. When scaling the x-axis with the inverse of the surface-to-volume ratio, the two curves tend to overlap. This is to be expected when the packing of the spheres is similar. Then the pore space should have the same characteristic features, such as connectivity between pores, and one should therefore expect to identical systems of different scale to overlap when the scale is normalized out along the abscissa. A deviation from the universal slope will be a measure of the connectivity between the pores. The larger the deviation, the better are the pores connected. The upper limit is of course bulk diffusion, while the lower limit could be diffusion within closed cavities of infinite surface relaxivity.

Figure 1: Observation time dependent diffusion coefficients of compact mono-sized spheres of diameter 48 and 98 µm, plotted in units of the inverse of the surface-to-volume ratio.
EXPERIMENTAL
The method for determining pore size distributions and plotting the time dependent diffusion coefficient in units of the inverse of the surface-to-volume ratio were applied to two brine saturated carbonate core samples using a 12 MHz Maran DRX from Oxford Instruments. The permeability of the two rock core samples were different, 7.2 mD (sample ID O30) and 37.8 mD (sample ID F48). The operating temperature was 35 °C and the bulk diffusion coefficient of the brine was $D_0=2.9 \times 10^{-9}$ m$^2$/s. Due to finite rise time on the gradient amplifier, the shortest duration of the applied gradient pulse was set to $\delta = 0.5$ ms. The eddy current settling time was set to $\delta_1 + \delta_2 = 0.4$ ms, thus yielding an inter echo spacing of $\tau = 0.9$ ms. $G_i$ is the internal magnetic field gradient while $g$ is the applied magnetic field gradient. The pulse sequences used are the CPMG (Meiboom and Gill (1958)), the 11-interval PFGSE (Sørland et al (1991)), and the 13 interval PFGSTE (Cotts et al (1989)). The compact mono sized spheres of 45 and 98 $\mu$m were polystyrene spheres (ID) delivered from Duke Scientific.

RESULTS AND DISCUSSION
In figure 2 we see the two pore size distributions as determined from the NMR measurements. O30 clearly has a broader distribution of pore sizes and its peak position is also at a smaller pore size. Peak positions are 2.1 $\mu$m for O30 and 3.7 $\mu$m for F48. The broader distribution and smaller average pore size for O30 is in agreement with the lower permeability as measured by water injection.

Figure 2: Absolute pore size distributions from rock core samples F48 and O30
In figure 3 we show the time dependent diffusion coefficients for the two rock core samples, plotted as a function of the root of the mean squared displacement and divided by the inverse of the surface-to-volume ratio. The solid line indicates the universal slope \(-4/(9\sqrt{\pi})\) which all brine saturated rock core samples should follow at the shortest observation times. Both samples seem to follow this line up to \((S/V)^{-1}\approx 1\). At larger distances the two samples depart, and sample F48 remains at a higher diffusion coefficient than O30 when having probed the same lengths of \((S/V)^{-1}\). This is in agreement with the higher permeability of F48 compared to O30. The higher diffusion values for F48 implies that it is easier for the water molecules to travel distances larger than the typical size of the cavity of the rock core sample. Thus the connectivity between the pores is better for sample F48 than O30. Figure 3 demonstrates that with a plot of the observation time dependent diffusion coefficients as a function of the individual surface-to-volume ratios, one may compare the connectivity from sample to sample. With a plot
of the diffusion coefficient with respect to observation time only, this would not have been feasible.

CONCLUSION

We have shown that by scaling the time dependent diffusion in units of the inverse of the surface-to-volume ratio, a universal slope is expected at short observation times. At longer observation times, the curves overlap for identical porous structures, as water between random closed sphere packs of different dimensions. With respect to rock core samples it deviates due to difference in connectivity between the pores. The method probes the root mean squared displacement of brine at 35 °C up to approximately 100 µm.

REFERENCES


