

NMR SURFACE RELAXIVITY DETERMINATION USING NMR APPARENT DIFFUSION CURVES AND BET MEASUREMENTS

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ABSTRACT

The surface relaxivity is an important parameter in low field NMR T_2 or T_1 relaxation experiments. It can be determined from the apparent diffusion curve at short time. We show in this paper the applicability and limitations of this technique in various situations (grain packs, sandstones, carbonates) and compared the results with BET.

We show first that the V/S ratio is better determined using a fit considering the entire apparent diffusion curve $D(t)$ from short to long diffusion time typically in the range 10 to 1000 ms. The method is validated using a grain pack made of a reference material used in BET measurements with a known specific surface area.

We show various measurements illustrating the proposed procedure. On grain packs made with the same material, the measured V/S ratios are proportional to the grain size. On a suite of Fontainebleau sandstones with different porosity and permeability, we obtained a weak variation of the pore size distribution when scaled by surface relaxivity, as expected for this type of formation. On carbonates, the specific surface is often too high to allow reliable NMR S/V measurements with the actual instrument limitations. In these cases, the BET measurement can be used instead. After calibration, the V/S distributions obtained from T_2 measurements are smaller than mercury injection derived throat size distributions, as expected.

INTRODUCTION

NMR relaxation time distributions called pore size distributions are usually presented in units of milliseconds and not converted into actual length. This calibration step may not be useful when NMR is used only as a porosity partitioning technique to separate clays and intergranular porosity in sandstones, or microporosity and macroporosity in carbonates. However, it is useful to have length scale when comparing NMR to other characterization techniques. The different methods for measuring surface relaxivity are discussed by Kleinberg (1999) and references therein. Essentially, an independent determination of the surface is required and depending on the technique used (from image analysis to BET), a variation up to a factor of 100 is possible. In this work, we revisit the NMR diffusion technique to determine V/S independently of relaxation and

make some comparison with the BET and MICP techniques on simple systems. We focus in this paper on T_2 but the same methodology can be applied to T_1 .

THEORY

Apparent diffusion curve

In the presence of restrictions due to the solid, there is a decrease of the effective diffusivity D depending on the diffusion times. At short time, Mitra et al. [1992] have shown that the effective diffusivity D_{eff} is linked to the total surface to volume ratio S_T/V_T as:

$$D_N(\Delta) = \frac{D(\Delta)}{D_m} = 1 - \frac{4}{9\sqrt{\pi}} \frac{S_T}{V_T} \sqrt{D_m \Delta} + O(D_m \Delta) \quad (1)$$

It means that initially only a small fraction of the diffusive molecules close to the pore walls are influenced by the solid. This relation is mostly independent of surface relaxation when surface relaxivity is low enough. This is the case for emulsions and for most porous media. When measuring the time dependant effective diffusivity at short times, one can in principle determine the ratio S_T/V_T related to the average drop size or the average pore size. At long diffusion times, the molecules may travel over distances larger than one pore length and the diffusivity becomes independent of time. Then, the asymptotic value α of the effective diffusion coefficient depends essentially on the porosity Φ of the porous medium or the continuous phase fraction Φ for emulsions.

In practice, the measurement of diffusivity at very short and very long diffusion times is not an easy task and the asymptotic value α and the slope S_T/V_T must be calculated using all data at intermediate times. This requires an interpolation function described below. Rewriting Eq. 1 using the one dimensional free diffusion length $L_D = \sqrt{2D\Delta}$, we obtain:

$$D_N(L_D) = 1 - C \frac{S_T}{V_T} L_D + O(L_D^2) \quad \text{and} \quad C = \frac{4}{9\sqrt{2\pi}} \cong 0.177 \quad (2)$$

With a given slope at $L_D=0$ and a given asymptotic value α for $L_D \rightarrow \infty$, the general shape of D_N may be of the form:

$$D_N(L_D) = 1 - (1 - \alpha) \frac{f(L_D)}{1 - \alpha + f(L_D)} \quad (3)$$

where f is an arbitrary interpolating function following the conditions:

$$\frac{\partial f}{\partial L_D}(L_D = 0) = C \frac{S_T}{V_T} \quad \text{and} \quad f(L_D = \infty) = \alpha \quad (4)$$

For example, the function f can be a polynomial of order 2:

$$f(L_D) = C \frac{L_D}{L_S} + \left(\frac{L_D}{L_C} \right)^2 \quad L_S = \frac{V}{S} \quad (5)$$

where L_c can be interpreted as a characteristic length scale of the distance between grains. Introducing Eq. 5 in 3 yields:

$$D_N(L_D) = 1 - (1 - \alpha) \frac{C \frac{S_T}{V_T} L_D + \left(\frac{L_D}{L_C}\right)^2}{(1 - \alpha) + C \frac{S_T}{V_T} L_D + \left(\frac{L_D}{L_C}\right)^2} \quad C = \frac{4}{9\sqrt{2\pi}} \quad (6)$$

The above function is close to that proposed by Mitra et al. (1992) by considering a Pade approximation. A plot of D_N vs. L_D is shown in Figure 1 for a given value of α and different values of L_C and V_T/S_T . The curvature is essentially controlled by the parameter L_C but it is clearly seen that the parameters V/S and L_C both influence the D_N curve at small diffusion length.

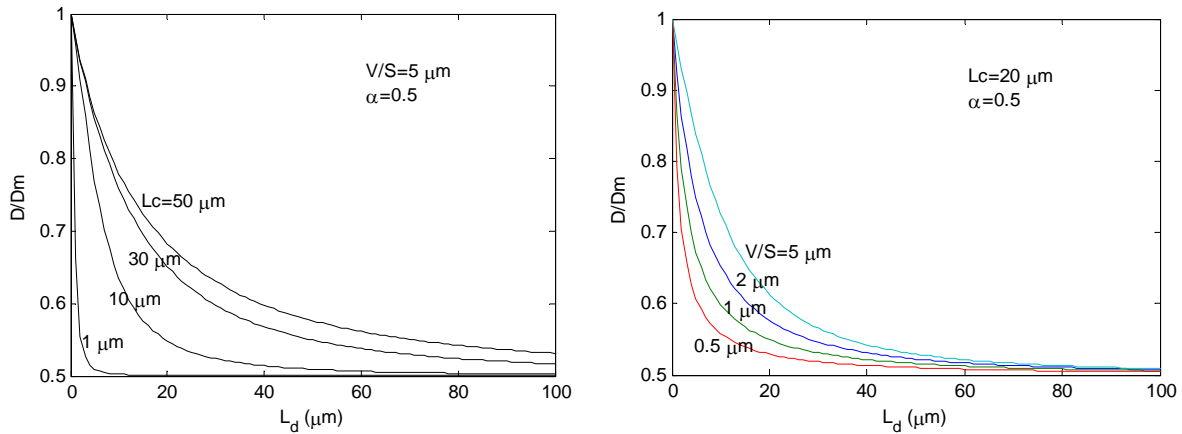


Figure 1: Plot of equation 6 for different values of L_C and V/S .

Surface relaxivity calculation

When the V/S ratio is known, the surface relaxivity ρ_2 can be estimated by the following equation:

$$\frac{1}{T_{2mS}} = \left(-\frac{1}{M} \frac{\partial M}{\partial t} \right)_{t=0} \cong \rho_2 \frac{S_T}{V_T} \quad (7)$$

where T_{2mS} is an average relaxation time representing a “surface weighted” relaxation time in the presence of a T_2 distribution. We estimated T_{2mS} using the first 10 measured points of the magnetization decay $M(t)$ at an echo spacing of 100 μs . Then, ρ_2 can be calculated from the measured V_T/S_T using the apparent diffusion curve or with $S_T = S_{BET}$ and from the NMR pore volume V_T when a BET measurement is available.

NMR derived pore body size and mercury derived throat size

The T_2 distribution is often called pore size distribution but actually reflect a distribution of V/S , a length scale difficult to apprehend in porous media. With this in mind, it is of interest to recall some basic properties of sphere packing in terms of pore entry size and pore body size (Table 1). For these model systems, it is clearly seen that the V/S ratio of a pore is smaller (about a factor of 3) than the pore throat diameter noted

d_{HG} . The latter has been calculated as the largest cylinder fitting into the pore entry and should be close to the value measured by mercury injection. However, as expected, the largest sphere fitting into the pore body is larger than the pore throat (Table 1). For grain packs, we will see that this difference is larger. When rugosity is present the V/S ratio will decrease further. Therefore, we expect in general to find the so-called NMR derived pore size distribution V/S at smaller values than the MICP derived throat size distribution.

EXPERIMENTAL TECHNIQUES AND PROCEDURE

Samples

We analyzed a series of grain packs, each of them obtained with a narrow distribution of grain size ranging from 8 up to 110 μm , in a similar way as in Godefroy et al. [2001] for the study of surface relaxivity. For this set, the porosity is nearly constant and the permeability varies only as a function of the grain size. The different grain packs were packed in glass tubes of inner diameter 3 cm and height 5 cm. After packing, the porous media were flooded with hydrochloric acid in order to remove paramagnetic impurities originating essentially from the grinding process of the SiC grains. The measurements were performed at 2 MHz.

We also measured the apparent diffusion curve on a grain pack made with grain of known specific surface area ($0.1 \text{ m}^2/\text{g}$). The material (BCR170 alpha alumina, LGC Promochem) is commonly used for the calibration of BET measurements. The grains were packed in a small tube of diameter 12 mm and saturated with brine (20 gr/l). The porosity of the pack measured using NMR profiles is 0.42 ± 0.01 and the NMR diffusion measurements were performed at 23 MHz.

On consolidated media, the apparent diffusion curves were measured on a series of Fontainebleau sandstones which are characterized by a well established porosity-permeability relationship. For this set of samples, the grain size is nearly the same and the variable degree of cementation gives different values of porosity and permeability [Jacquin, 1984]. The T_2 characterization (Figure 2) show surprisingly that the mode of the distribution does not vary much (when observed on a log scale) whereas the permeability varies by 4 orders of magnitude (0.3 up to 3000 mD) and the porosity varies by a factor of 3 (from 0.05 up to 0.2). These samples were analyzed as "received" and not specifically cleaned to remove paramagnetic impurities. From visual observation, the presence of iron could be detected from a change of colour of the grain surface which was obvious for the sample with the lowest T_2 mode ($K_w=1164 \text{ mD}$, Figure 2).

Two carbonates samples are presented (CRE and EST). The CRE sample is a microporous bioclastic mudstone-wackestone. The EST sample is a bimodal limestone containing some micritic porosity. They are described in details elsewhere (Fleury et al. 2007). Small cylinders of diameter 10 mm and length 20 mm were analyzed simultaneously with NMR (at 23 MHz) and BET (using krypton).

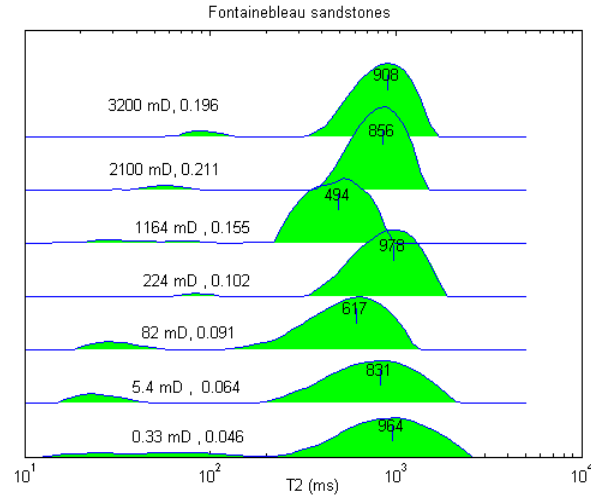


Figure 2: T_2 relaxation time distribution on a suite of 7 Fontainebleau sandstone samples.

NMR diffusion measurements

After many tests of different sequences, we found that the bipolar sequence shown in Figure 3 gave satisfactory results. The gradient pulses are centred around the π pulse in order to better compensate for eddy currents. The time δ_1 can also be set to a large value without increasing too much the total time of the sequence when short diffusion times are needed. Using the method of Cotts et al. (1989), we calculated the echo attenuation as follows:

$$\ln \left[\frac{M(g,t)}{M(0,t)} \right] = -\gamma^2 D \left[g^2 \delta^2 \left(\Delta' + 2\tau - \frac{1}{3} \delta - \delta_2 \right) + \frac{4}{3} g_0^2 \tau^3 \right] \quad (8)$$

where g_0 is a constant gradient present during the entire sequence to mimic either internal gradient or imperfect gradient offset tuning. In addition, we used a 16 step phase cycling to remove potential spurious echoes. The important results are (i) the effect of the perturbing gradient g_0 is limited to a τ^3 term, (ii) there is no $g g_0$ cross-term and (iii) the close bipolar gradients tends to cancel eddy currents. The use of shaped gradients together with a pre-emphasis unit were also critical for the eddy current compensation. Typically, we used $\tau=1.25$ ms, $\delta=1.5$ ms, $\delta_2=0.2$ ms and $g=50$ G/cm for measuring water diffusivity. Therefore, the encoding time is 5 ms and the smallest diffusion time t_d ($t_d = \Delta' + 2\tau - \delta/3 - \delta_2$) accessible is about 8 ms.

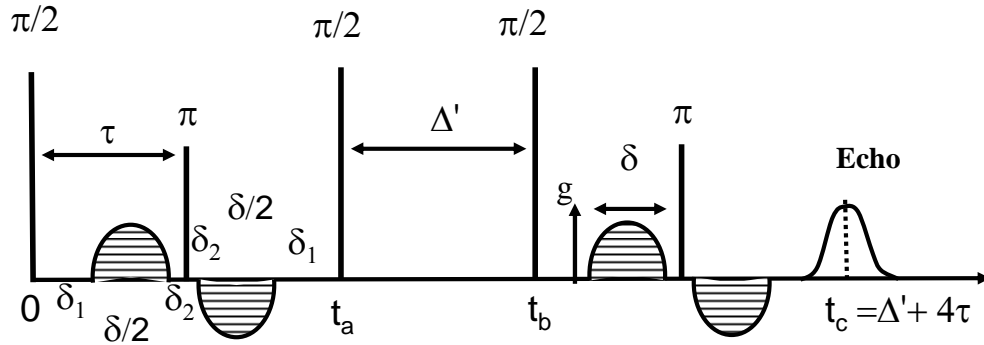


Figure 3: Bipolar sequence used in the diffusion experiments.

The sequence has been tested with different fluids and for different diffusion times. In practice, the experiments are always performed with varying g values. The maximum range of g is used at the shortest diffusion time, then it is decreased according to:

$$g_m(\Delta) = g_{\max} \sqrt{\frac{\Delta_{\min}}{\Delta}} \quad (9)$$

This allows to obtain very stable values for a wide range of diffusion time (Figure 4).

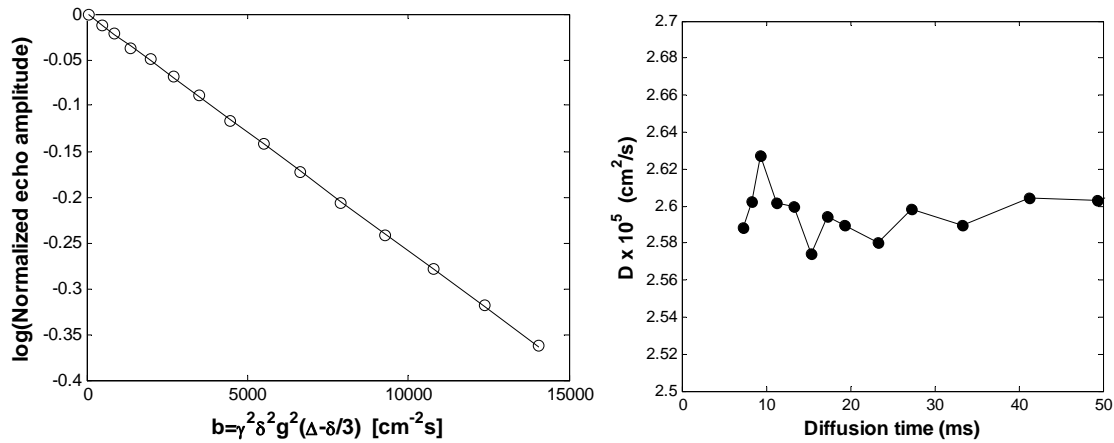


Figure 4: Example of diffusion measurement on water at 30°C. Left: attenuation at the shortest diffusion time $t_d=7.3$ ms. Right: attenuation versus diffusion time. The exact value of the water self diffusivity is $2.6 \cdot 10^{-5}$ cm²/s. Acquisition parameters: g is varied up to 50 G/cm at $t_d=7.3$ ms, $\delta = 0.75$ ms, $\tau=1.25$ ms, $\delta_2=0.2$ ms, minimum value of Δ' : 3 ms, shape: sine. Apparatus: 2 MHz system.

RESULTS

Grain packs

Apparent diffusion curves were measured on each grain pack (Table 2, Figure 5). As expected, the decay of the curve is the fastest for the smallest grain sizes. For the 18 μm grain pack, a second experiment was performed using a mixture of water and glycerol (water:glycerol=36:64 w/w, $D=0.178 \cdot 10^{-5} \text{ cm}^2/\text{s}$) in order to reduce the bulk diffusivity and explore smaller diffusion length (about 3 μm).

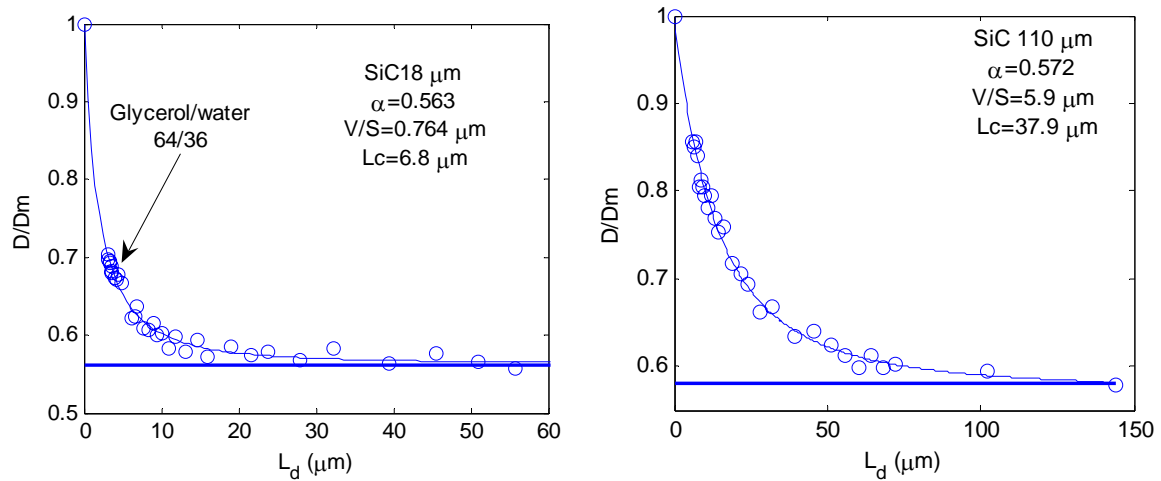


Figure 5: Apparent diffusion curves measured on different grain packs. The line indicates the best fit obtained using equation 6. The thick horizontal line indicates the measured value $1/(FF \Phi)$.

The data points were fitted using Eq. 6 by adjusting the three parameters V_T/S_T , L_c and the asymptotic diffusivity α . We obtained the following relationships (Figure 6):

$$V_T / S_T = 0.053d_g \quad L_C = 0.34d_g \quad (10)$$

As a comparison, the volume to surface ratio for a orthorhombic sphere pack of porosity 0.395 is given by $V/S=0.109d$, where d is the sphere diameter. As expected for grains of irregular shapes, we find a larger surface than for spheres at similar porosity. It is also seen that L_c is proportional to the grain size showing that the diffusion at intermediate times is governed by the pore size. Finally, when comparing the asymptotic diffusivity α obtained from the best fit and the value deduced from the measurement of porosity and formation factor $1/(FF \Phi)$, we obtained a reasonably good agreement (Figure 5).

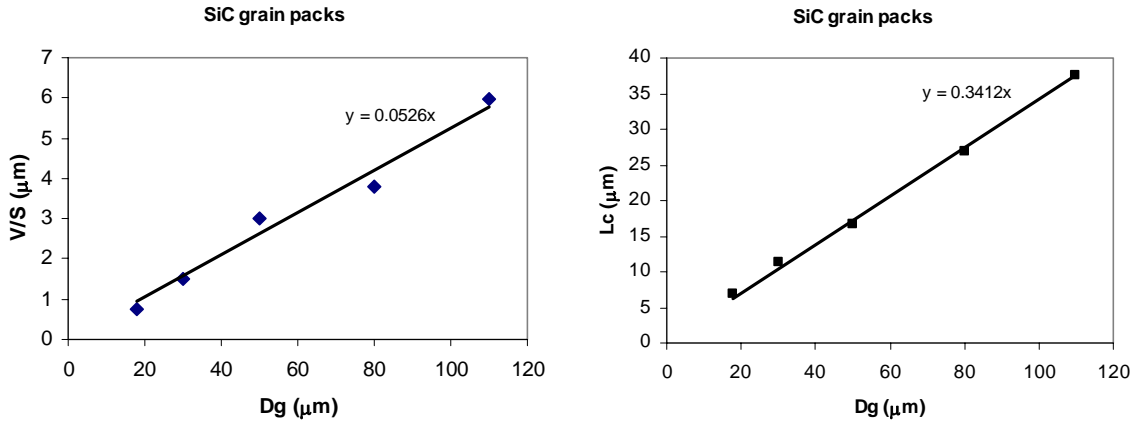


Figure 6: Volume to surface ratio and characteristic spacing between grains Lc obtained from diffusion measurements

For the grain pack of known specific surface area ($0.1 \text{ m}^2/\text{g}$, Figure 7), we found $V/S=2.2\mu\text{m}$. From the specific surface area and with the knowledge of the mass of grains (3.951 gr) and the volume of water wetting the grains (0.780 ml), we deduce $V/S= 2.0 \mu\text{m}$, close to the measured value. For this comparison, we assumed that all the grains are wetted and/or the supernatant water on top of the grain pack has been properly removed. This may be a source of discrepancy between the predicted and measured value. Finally, the calculated surface relaxivity ρ_2 is $5.7 \mu\text{m/s}$ ($T_2=372 \text{ ms}$), a value larger than measured on cleaned SiC grain packs but closer to Fontainebleau sandstones described later.

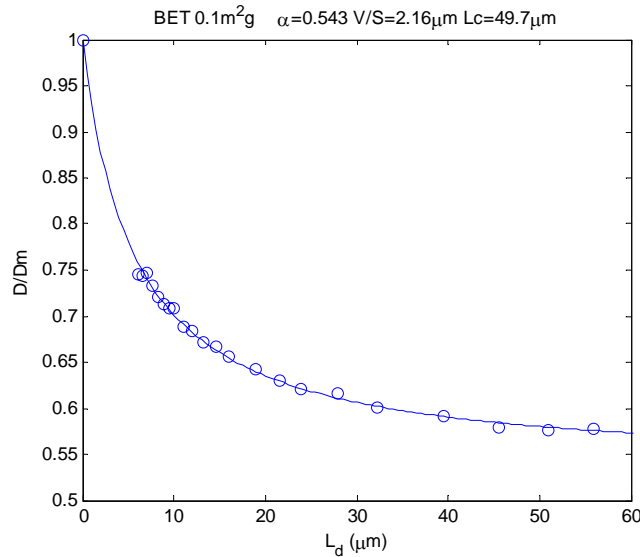


Figure 7: Apparent diffusion curve measured on a reference material of known specific surface area ($0.1 \text{ m}^2/\text{g}$, alpha-alumina grains). Porosity of the grain pack: 0.42. NMR apparatus: 23 MHz, $T_2=372 \text{ ms}$.

Fontainebleau sandstones

This suite of samples is characterized by large values of V/S ratio producing a slow decrease of the apparent diffusion curves (Figure 8). Indeed, at the smallest diffusion time possible, $D_N(L_D)$ is only reduced to 0.9. The drawback is that the asymptotic diffusivity is not reached at the largest diffusion time (about 1 s) and the extrapolated values using Eq. 6 are not in good agreement with the formation factor measurements. Therefore, only the V/S ratios are really meaningful. The calculated V/S ratio (Figure 8) confirm that the water permeability K_w for this system is weakly linked to the pore size determined by T_2 or the ratio V/S. The latter varies only by a factor of two whereas the permeability varies by 4 orders of magnitude. Note that the expected relationship between K_w and the power 4 of the mercury derived throat size was observed (not shown here). The calculated surface relaxivities are in a range 5-10 $\mu\text{m/s}$ (Table 3), the highest value corresponding to the obvious presence of iron indicated by a brown/red colour, as mentioned earlier.

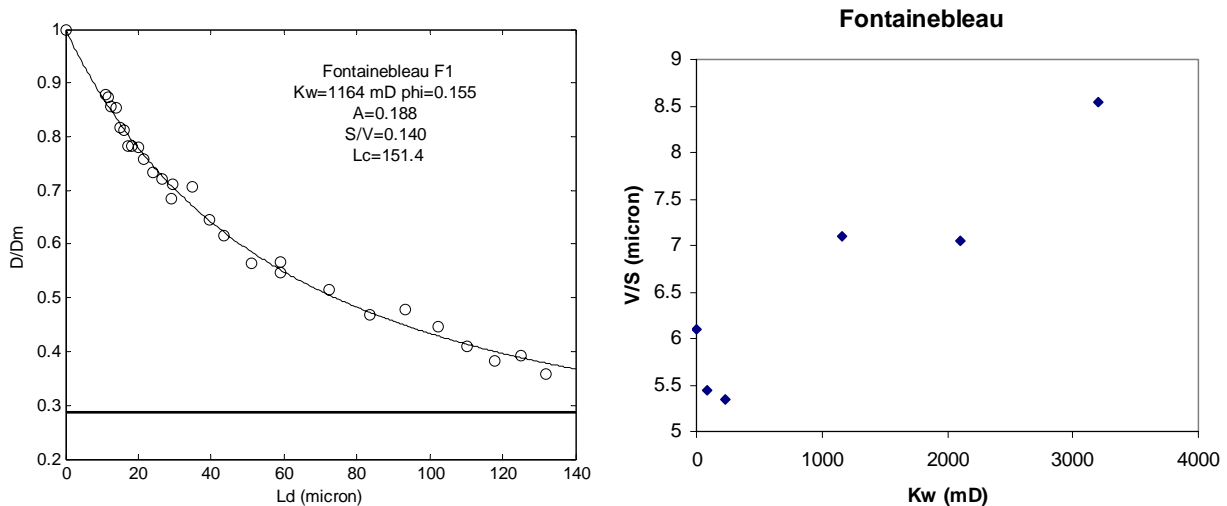


Figure 8: Example of measurement of the apparent diffusion curve on one Fontainebleau sandstone (left). V_T/S_T ratio from diffusion measurements (right).

Carbonate samples

For the two carbonate samples, the diffusion curves could not be used to determine S_T/V_T values due to short time diffusion measurement limitations. We used instead the BET values to deduce surface relaxivities. When plotted on the same graph as MICP derived throat size distributions performed on a companion plug, we find the NMR derived "pore size" curve at smaller values compared to MICP derived throat size. This is not a contradiction and reflects clearly the fact that the NMR measurement includes both a shape and a rugosity factor.

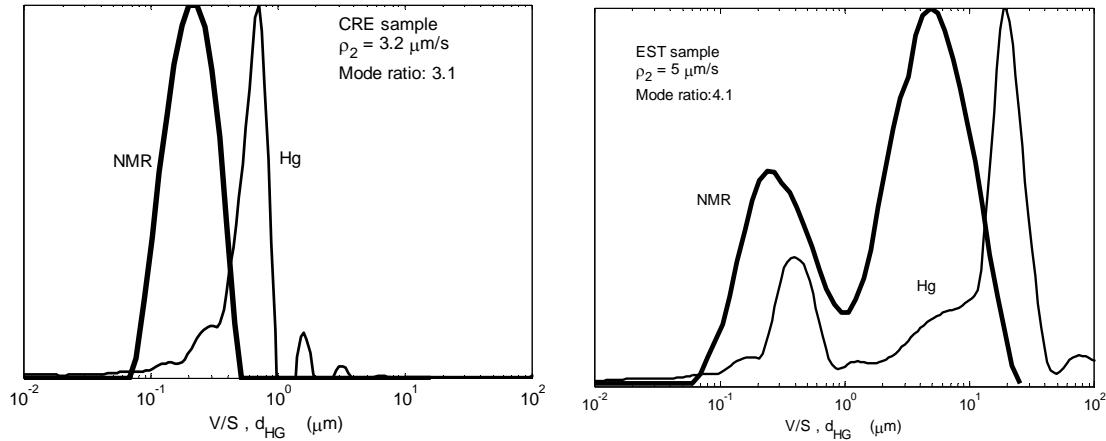


Figure 9: Direct comparison of NMR and MICP data. For the CRE sample, the V/S ratio is smaller than the MICP throat size by a factor of 3, as expected.

DISCUSSION

The apparent diffusion curves allow effectively to deduce the S_T/V_T ratio and surface relaxivities. This is of great help for the detailed interpretation of T_2 distributions, or the comparison between two samples. There are however some limitations; with the present instrumentation, S_T/V_T larger than about $1 \mu\text{m}^{-1}$ are practically not measurable because short diffusion lengths are not accessible. The use of low diffusivity fluids does improve the situation but the decrease of the diffusion length is only proportional to the square root of the diffusivity. Then, with the limitations of gradient amplitudes, the diffusivity becomes rapidly not measurable at short time with commercially available instruments. For the SiC grain packs, no data is available above $D_N=0.7$ in most cases. However, we obtained good estimates of the length V_T/S_T and L_c ; this is because these two length scales are correlated. For complex pore structure containing clays or microporosity (i.e. with large specific surface area), diffusion data closer to 1 are necessary.

The results obtained on the Fontainebleau sandstone suite are intuitively surprising: the characteristic pore length given by the ratio V/S does not vary much whereas the permeability varies 4 orders of magnitude. In this case, there is no specific measurement problem. This can be understood qualitatively using a model of sphere pack in which the porosity and permeability are varied by assuming that a layer of thickness e is deposited at the surface of the spheres, in a similar way as in the grain consolidation model proposed by Roberts et al. [1985] or in the Grain and Pore Throat model proposed by Chauveteau et al. [1996]. This process is thought to reproduce the key natural diagenetic phenomenon occurring in Fontainebleau sandstones. For these systems, we calculated the evolution of porosity, V/S and permeability assuming a simple power law relationship of the form (as observed experimentally):

$$k \propto (r_h - e)^4 \quad (11)$$

where r_h is the initial throat radius of the sphere pack. When $e=0$, we define an initial permeability k_i . We see (Figure 10) that a large variation of permeability is possible with a small variation of the ratio V/S , similarly to the observed behaviour.

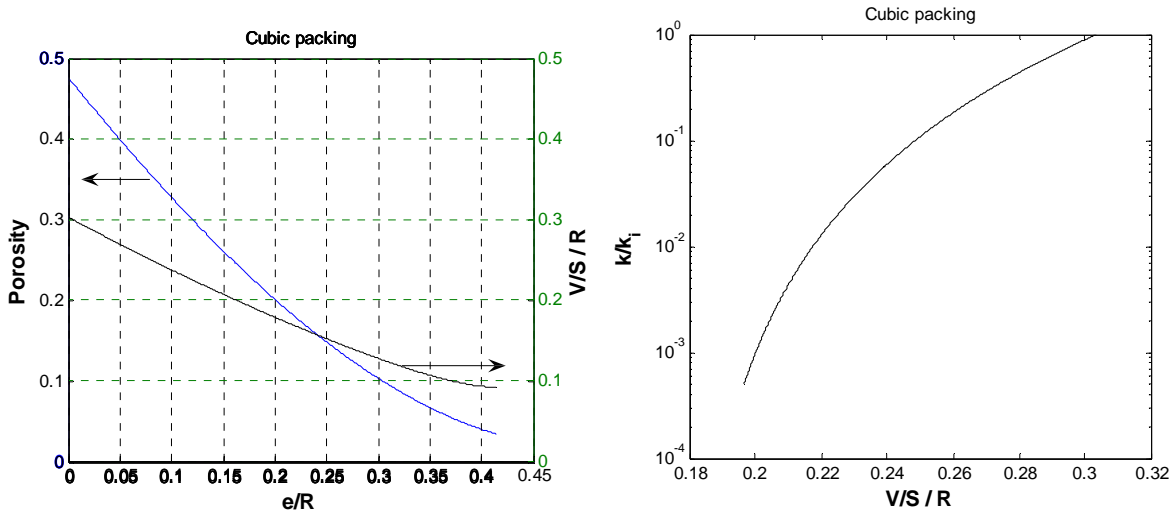


Figure 10: Variation of porosity and V/S (left), and permeability (right) in a sphere pack. A layer of thickness e is deposited on the surface of the spheres of initial radius R . At $e/R=0.414$, the permeability vanishes.

CONCLUSION

The surface relaxivity can be obtained from the analysis of the time dependant apparent diffusion curves for small specific surface area. The lack of data at small diffusion times is a strong experimental limitation. With the present experimental set-up, the specific surface area should be larger than about $0.1 \text{ m}^2/\text{g}$, or equivalently, the volume to surface ratio should be larger than about $1 \text{ }\mu\text{m}$. The measurements on clay free grain packs, sandstones and carbonates suggest that the surface explored by NMR and by the BET technique are the same. Therefore, the BET surface can be used instead for high specific surface area (about $1 \text{ m}^2/\text{g}$).

On grain packs, we found a coherent determination of V/S when the grain size varies. It is also consistent with theoretical values derived from sphere packs. On a suite of Fontainebleau sandstone, we found that V/S is weakly correlated with permeability due to the specific diagenetic process that occurred during the cementation of this sandstone. On two carbonates, we found that NMR calibrated V/S is smaller at least by a factor of 2 than MICP derived throat size. NMR should not be calibrated using a best fit with MICP data.

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Table 1: Geometrical properties of sphere packs of diameter d ; d_p is the pore body size as measured by NMR, d_{HG} the diameter of the largest cylinder fitting into the pore throat.

Sphere pack type	Porosity	Pore entry size d_{HG}	NMR pore size $d_p=V/S$	d_p/d_{HG}	Largest sphere in pore
Cubic	0.476	0.414 d	0.151 d	0.365	0.732 d
Rhombohedral	0.259	0.154 d	0.058 d	0.377	0.224 d

Table 2: Summary of the results obtained for the SiC grain pack series.

Grain size d_g (μm)	Porosity	Permeability K_w (Darcy)	T_2 (ms)	FF	V_T/S_T (μm)	L_c (μm)	α	ρ_2 ($\mu\text{m/s}$)
8	0.494	0.028	164	3.87	-	-		-
18	0.429	0.094	233	4.16	0.76	6.8	0.56	3.0
30	0.401	0.290	558	4.57	1.52	11.4	0.55	2.2
50	0.404	-	864	4.42	3.02	16.7	0.57	2.4
80	0.388	2.37	1226	4.53	3.8	26.8	0.56	1.7
110	0.377	5.40	1740	4.48	5.96	37.6	0.57	1.2

Table 3: Surface relaxivity for the Fontainebleau sandstone suite.

K_w (mD)	Surface relaxivity ($\mu\text{m/s}$)
5.4	5.1
82	6.8
224	3.5
1164	11.7
2100	5.6
3200	6.2